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GEOCHEMICAL NATURAL ANALOGS LITERATURE REVIEW

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ABSTRACT

The Geochemical Natural Analogs Project is designed to provide knowledge of the state of the art in natural analog studies applied to contaminant transport. Task 1 of the project, "Literature Review and Workshop," has been completed and the results are presented herein. The high-level waste literature has been reviewed for applications of natural analog studies. From these studies, the usefulness and the limitations of natural analogs have been ascertained and are considered in light of the regulatory interest in natural analog investigations in support of the siting of a high-level waste repository. Processes and events likely to control contaminant transport at Yucca Mountain are identified in this report and those processes which are amenable to natural analog study are discussed. A set of criteria for the selection and successful use of natural analog studies is presented. Based on this information, candidate sites for a natural analog study relevant to Yucca Mountain are proposed. These sites are the Peña Blanca, Mexico, uranium deposits and the Santorini, Greece, archaeologic sites. Descriptions of these sites and discussions of their potential usefulness are included.

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EXECUTIVE SUMMARY

This paper is a review of the state of the art in natural analog studies applied to geologic disposal of high-level radioactive waste. The high-level waste (HLW) literature has been reviewed for applications of natural analog studies. Processes and events likely to control contaminant transport at Yucca Mountain are identified herein and those processes which are amenable to natural analog study are discussed. A set of criteria for the selection and successful use of natural analog studies is presented. Descriptions of candidate natural analog sites relevant to the proposed HLW repository at Yucca Mountain and discussions of their potential usefulness are included.

Natural analogs are occurrences of materials or processes in nature that may be viewed as comparable to some aspect of a system of interest. Natural analog studies are particularly applicable to systems for geologic disposal of high-level nuclear waste because of the long time and large space scales required. Natural materials that approximate components of a repository may be studied to gain a better understanding of the behavior to be expected from the repository materials. Similarly, a process which occurs (or has occurred) in nature and which may be significant to the performance of a repository may be investigated to learn of possible effects on a repository system.

The Environmental Protection Agency (EPA) rule 40 CFR Part 191 (section 191.13(a)) specifies that HLW must be isolated from the accessible environment (as

defined in the regulations) for the first 10,000 years following closure of the repository. The Nuclear Regulatory Commission (NRC) rule 10 CFR Part 60 (sections 60.21(c)(1)(ii)(F) and 60.101(a)(2)) calls for use of natural analog studies to support analyses and models that will be used to predict future conditions and changes in the geologic setting at a repository site over the period of regulatory interest. A geologic nuclear waste repository will constitute a system much larger than can be accommodated by laboratory facilities and must operate over a time scale exceeding that of prior human civilization. By studying natural systems which have operated for time spans comparable to radionuclide isolation requirements and which are of similar scale to a repository, the uncertainty inherent in projecting such large scale processes so far into the future can be reduced.

Though natural analog studies extend the sort of investigations possible in the laboratory, they have a variety of inherent limitations. Chief among these is the incompleteness of the geologic record, at any geologic analog site, of all processes and events important (or potentially important) to the development of the analog. Consequently, it is generally difficult to adequately constrain the initial and boundary conditions for specific processes within natural geologic systems. Quantification of effects to the degree desired is often difficult. Further, there are no natural analogs of an entire repository system; a given site will only be analogous to some portion of a repository or to a subset of the processes which will occur in a repository. Finally, the elements and materials involved in an analog study are, by definition, approximations of the materials and elements which will be placed in a repository.

The above limitations notwithstanding, there are critical contributions to be made by natural analog studies. It is only through the use of natural analogs that one may identify and confirm that a process occurs in nature as well as in a laboratory or in theory. Natural analogs allow testing of the pertinence of individual processes over geologic time; the assessment of the relative importance of various processes; and the effects of the coupling

of processes. Through analog investigations we may determine the conditions under which the processes occur and the effects of the processes as well as the magnitude and duration of the phenomena.

Direct validation of long-term predictions of models is impossible using only laboratory or field data; and given the uncertainties in analog studies, it may be that a given model cannot be validated (in a strict sense) through the use of natural analogs. However, natural analogs provide the only means of testing models of long term processes for pertinence. The results of short-term, small-scale laboratory experiments, and the long-term predictions of models based on the laboratory experiments, may be compared to observations of natural systems which have operated for long periods at large scales (i.e. natural analogs). Models of natural phenomena can be developed and validated through a process of iterative and simultaneous evaluation of numerical models, natural analogs, and laboratory and field experiments. However, the limitations of validation by comparison must be clearly understood. It is not to be expected that the comparisons will be exact; in fact, performance assessment models are typically conservative in their predictions and therefore deliberately differ from reality. Therefore, comparison of model predictions with the results of natural analog investigations will in general only permit confirmation that the model takes into account the appropriate processes in appropriate ways. Validation of a predictive model by such comparison provides a measure of assurance that the model accurately reflects future behaviors.

This report contains examples of natural analog studies relevant to contaminant transport at the candidate HLW repository at Yucca Mountain, Nevada. This compilation is not exhaustive, but it gives an overview of the range of analogs which have been considered. Several sites are discussed as candidates for future natural analog studies relevant to Yucca Mountain.

Processes and events that are likely to control contaminant transport at Yucca Mountain fall into two groups: (1) those processes and events which are likely to be

important at any geologic HLW repository and (2) those processes and events which are peculiar to Yucca Mountain. These processes are identified and the importance of those processes peculiar to Yucca Mountain are discussed. These include processes which result from 1) the occurrence of the proposed repository at Yucca Mountain in tuffaceous host rock, 2) the chemically oxidizing environment of the site, and 3) the partial hydrologic saturation of the proposed repository horizon.

The uranium ore deposit at Peña Blanca, Mexico, and the archaeologic site at Santorini, Greece, have been identified as potential sites for a natural analog study by Murphy et al. (1990) and uranium deposits at the McDermitt Caldera, Nevada-Oregon, have been proposed by Alexander and Van Luik (1990). A brief description of relevant aspects of the proposed repository site at Yucca Mountain is followed by descriptions of the Peña Blanca site, the McDermitt site, and the Santorini site with comparisons to Yucca Mountain and some general conclusions with regard to the usefulness of these potential analogs with respect to contaminant transport at Yucca Mountain.

1. Introduction

Natural analogs are occurrences of materials or processes in nature that may be viewed as comparable to some aspect of a system of interest. Natural analog studies are particularly applicable to systems for geologic disposal of high-level nuclear waste because of the long time and large space scales required. Natural materials that approximate components of a repository may be studied to gain a better understanding of the behavior to be expected from the repository materials. Similarly, a process which occurs (or has occurred) in nature and which may be significant to the performance of a repository may be investigated to learn of possible effects on a repository system. Furthermore, demonstration of the capacity to describe analogous natural phenomena, both qualitatively and quantitatively, can help to validate predictions of repository performance.

Natural analog studies have been used for many years. Geologists have always been limited in their investigative approaches by the physical and temporal scales of many aspects of their subject. Mountains do not fit into a laboratory and the time and forces involved in building them are not available for experiments. Therefore, in many cases the only test of a geologic hypothesis is how well it fits with observations of nature. Consequently, it is often difficult to prove a geologic hypothesis in the same sense that hypotheses in other disciplines can be proven through rigorous duplication of experiments by many investigators. Instead, geologists routinely rely on generalizations inferred from numerous observations of similar rocks to test their ideas, that is, they use natural analogs.

The object of this paper is to review the state of the art in natural analog studies applied to geologic disposal of high-level radioactive waste. The high-level waste (HLW) literature has been reviewed for applications of natural analog studies, with special attention to geochemical analogs. Processes and events likely to control contaminant transport at the repository proposed for Yucca Mountain, Nevada, are identified and those processes which are amenable to natural analog study

are discussed. A set of criteria for the selection and successful use of natural analog studies is presented. Descriptions of candidate natural analog sites relevant to the proposed HLW repository at Yucca Mountain and discussions of their potential usefulness are included.

1.1 Uses of natural analogs for high-level waste repository planning

The Environmental Protection Agency (EPA) rule 40 CFR Part 191 (section 191.13(a)) specifies that HLW must be isolated from the accessible environment (as defined in the regulations) for the first 10,000 years following closure of the repository. The Nuclear Regulatory Commission (NRC) rule 10 CFR Part 60 (sections 60.21(c)(1)(ii)(F) and 60.101(a)(2)) calls for use of natural analog studies to support analyses and models that will be used to predict future conditions and changes in the geologic setting at a repository site over the period of regulatory interest. A geologic nuclear waste repository will constitute a system much larger than can be accommodated by laboratory facilities and must operate over a time scale exceeding that of prior human civilization. By studying natural systems that have operated for times comparable to radionuclide isolation requirements and that are of similar scale to a repository, the uncertainty inherent in projecting such large scale processes so far into the future can be reduced.

Public perception is a difficult problem associated with nuclear waste disposal. It has been suggested (e.g. Winograd, 1986; Papp, 1987; Vovk, 1988; Chapman and McKinley, 1990) that natural analogs may be useful in conveying to the public a sense of the long-term stability possible in a geologic environment. For example, many studies consider uranium ore deposits as natural analogs of HLW repositories. The ability of these sites to contain substantial quantities of radioactive material for periods much longer than required for HLW isolation is an appealing intuitive argument for the possibility of safe nuclear waste disposal. Indeed, these deposits, as well as other natural formations, prove the immense stability of some geologic environments. This stability is the fundamental rationale for disposal of nuclear waste in geologic sites. However, these same ore deposits may be used to make arguments for massive transport of radioactive materials over large distances by natural processes (Sargent, 1990; Apted, 1990). The substantial

quantity of uranium contained in these deposits was originally dispersed throughout some larger volume. Natural processes mobilized, transported, and concentrated the uranium at the site of the present deposit. Therefore, uranium ore deposits also provide implicit evidence of the element's considerable potential mobility in the natural environment.

1.2 Limitations of natural analog studies

Though natural analog studies extend the sort of investigations possible in the laboratory, they have a variety of inherent limitations. Chief among these is the incompleteness of the geologic record, at any geologic analog site, of all processes and events important (or potentially important) to the development of the analog. Further, the record that exists may be uninterpretable. Erosion, metamorphism, hydrothermal or meteoric alteration, and structural disruption are all processes commonly responsible for erasing portions of the geologic record. Even if a given portion of the geologic record is not erased by a later event, the overlapping effects of sequential phenomena may make it difficult or impossible to sort out the geologic history of the area in detail. It is also possible that there may be no unique interpretation to the development of the analog; more than one combination of processes and events may be consistent with the present state of the system. Consequently, it is generally difficult to adequately constrain the initial and boundary conditions for specific processes within natural geologic systems. Temperatures, pressures, fluid compositions, timing of process onset and duration, are all examples of factors which may only be indirectly estimable. Of course, limits may always be placed, but they may be broad. Quantification of effects to the degree desired is often difficult.

There are no natural analogs of an entire repository system. A given site will only be analogous to some portion of a repository or to a subset of the processes which will occur in a repository. Furthermore, additional processes will have occurred that are not characteristic of the repository. Therefore, choices must be made as to the processes of greatest relevance and the ability to isolate them for study.

The elements and materials involved in an analog study are, by definition, approximations of the materials and elements which will be placed in a repository. The approximations may be quite close, for example: uraninite is a good analog to the bulk composition and crystal form of spent fuel (Finch and Ewing, 1989); basaltic and rhyolitic glasses hydrate similarly to vitrified HLW (Arai et al., 1988). However, there is almost always some deviation, for example: natural uraninite does not contain the internal phase segregations present in spent fuel or a substantial transuranic component; borosilicate nuclear waste forms have compositions substantially different from basaltic or rhyolitic glass. Some technological materials (e.g. Zircaloy) are particularly difficult to approximate with natural materials (Apted, 1990).

The 10,000 year period of interest for evaluating HLW isolation is a difficult period to approximate with natural analogs. Most ore deposits are much older (10^6 to 10^9 years) and most anthropogenic sites are much younger (0 to 10^3 years). To make the best use of an analog study, the process(es) studied should have occurred over an interval of 10^3 to 10^4 years.

1.3 What can natural analog studies provide?

The above limitations notwithstanding, there are critical contributions to be made by natural analog studies. These contributions have been summarized notably by Petit (1990 a and b) from which much of the following discussion is taken. It is only through the use of natural analogs that we may identify and confirm that a process occurs in nature as well as in a laboratory or in theory. Natural analogs allow testing of the pertinence of individual processes over geologic time and space scales; the assessment of the relative importance of various processes; and the effects of the coupling of processes. Through analog investigations we may determine the conditions under which the processes occur and the effects of the processes as well as the magnitude and duration of the phenomena.

Data from natural analogs can provide the basis for evaluation of the assumptions on which proposed models of repository or other systems are based. Development of mathematical models generally requires qualitative information to establish the scope and components to be incorporated.

Quantitative data are introduced to allow calculations only after those choices are made and a conceptual model is developed. For example, performance assessment model results are typically extremely quantitative, however, the choices of what processes and components to include in the model and the point in the model at which to insert individual processes are all qualitative, and those qualitative determinations control the model predictions. Natural analog studies can provide the information required to place legitimate constraints on system characteristics, namely the identity of significant processes and composition of the system.

Direct validation of long-term predictions of models is impossible using only laboratory or field data; and given the uncertainties in analog studies, it may be that a given model cannot be validated (in a strict sense) through the use of natural analogs. However, natural analogs may provide the only means of testing models of long-term processes for pertinence. The International Atomic Energy Agency (IAEA) definition of validation of a model is:

> A conceptual model and the computer code derived from it are 'validated' when it is confirmed that the conceptual model and the derived computer code provide a good representation of the actual processes occurring in the real system. Validation is thus carried out by comparison of calculations with field observations and experimental measurements. (IAEA, 1982)

Models of natural phenomena can be developed and validated through a process of iterative and simultaneous evaluation of numerical models, natural analogs, and laboratory and field experiments.

The results of short-term, small-scale laboratory experiments, and the long-term predictions of models based on the laboratory experiments, may be compared to observations of natural systems which have operated for long periods at large scales (i.e. natural analogs). This process of testing by comparison can contribute to validation of the model. However, the limitations of

validation by comparison must be clearly understood. Comparisons will be inexact; in fact, performance assessment models are typically designed to be conservative in their predictions and consequently they are intended to differ from reality. Therefore, comparison of model predictions with the results of natural analog investigations will in general only permit confirmation that the model takes into account the appropriate processes in appropriate ways. Validation of a predictive model by such comparison can result in reasonable assurance that the model reasonably reflects future behaviors. This is the level of confidence required by 10 CFR Part 60 section 60.101(a)(2) which reads in part:

> Proof of the future performance of [a HLW repository] over time periods of many hundreds or many thousands of years is not to be had in the ordinary sense of the word. For such long-term objectives and criteria, what is required is reasonable assurance...

10 CFR Part 60 does not use the word "validation" or "validate" except in section 60.131(b)(7) which refers to "experiments used to validate the method of calculation" to ensure nuclear "criticality control" in handling HLW.

2. Natural analog studies

This section contains examples of natural analog studies relevant to contaminant transport at the candidate HLW repository at Yucca Mountain, Nevada. This compilation is not exhaustive but it gives an overview of the range of analogs which have been considered. The studies are organized according to the type of site at which the study was conducted.

2.1 Ore deposit studies

2.1.1 Oklo, Gabon

The uranium ore deposit at Oklo, Gabon, is the best known natural analog to geologic nuclear waste systems. The deposit is the site of the only known natural nuclear reactors and as such has been subject to intensive study. In 1972, an analyst (H. Bouzigues) at the French Atomic Energy Commission noticed that the abundance of ^{235}U in an ore sample was 0.7171 atomic percent rather than the normal 0.7207. This discrepancy was small, but significant, and led to an investigation which turned up other samples with depletions down to 0.296%; all of the samples came from the same source: the Oklo uranium deposit (De Laeter, 1985). There were only a few possible explanations for such depletions and the occurrence of ancient nuclear chain reactions was confirmed when substantial quantities of fission products were found in the depleted ores (Naudet, 1976).

Today ^{235}U constitutes only 0.72% of natural uranium, however, in the past the proportion was higher because ^{235}U has a shorter half-life (700 Ma) than ^{238}U (4500 Ma). Therefore about 2 Ga ago, ^{235}U constituted 3% of natural uranium, a concentration similar to that used in modern nuclear reactors (Cowan, 1976). This concentration and the presence of an appropriate moderator (probably groundwater) allowed the formation of a self sustaining nuclear reaction (Cowan, 1976). Current estimates are that the ores formed about two billion years ago and that nuclear fission was sustained for a period of a few hundred thousand years (Curtis et al., 1989). It is unlikely that Oklo is the only place where natural nuclear chain reactions have occurred, but searches have turned up no other sites (De Laeter, 1985). It is likely that other sites are buried, were removed long ago by erosion, or were mined without recognition.

Uranium at Oklo is contained in deltaic sediments overlying fluvial deposits of coarse sandstone and conglomerates which are the source rocks for the uranium (Gauthier-Lafaye and Weber, 1989). The uranium was originally concentrated in the conglomerates as a placer, a process possible in the more reducing surface conditions present on Earth more than 2 Ga ago.

The increase in atmospheric oxygen about 2 Ga ago allowed the oxidation, dissolution, and remobilization of the uranium into the reducing delta sediments where precipitation occurred (Cowan, 1976). Uranium mineralization probably took place during an uplift stage in relatively high levels of the basin which were also good hydrocarbon traps, so that uranium was precipitated as oxidizing transport fluids were reduced by mixing with fluids carrying hydrocarbons (Gauthier-Lafaye and Weber, 1989). Host rocks consist of organic-rich, impure shales with high carbonate contents (Brookins, 1976b). The reactor zones range from 10 to 20 m in length and are about 1 m thick (De Laeter, 1985). Mineralogy of the reactors consists of uraninite, chlorite, illite, and carbonates; there is little organic carbon or quartz in the reactor zones (Brookins, 1976b). Most of the ore at Oklo is relatively low grade, on the order of 0.2 - 0.5 % U; the highest grades range up to 75% U (Brookins, 1976a).

Natural analog investigations at Oklo have concentrated on the mobility of the fission product elements during the two billion years since their production; these fission products are identical to the radioelements which are to be placed in HLW repositories and so constitute excellent analogs. The fission products originally collected in the crystalline uraninite of the reactor zones as the nuclear reaction proceeded. Radiometric dating and modeling of the nuclear reaction permit estimates of the production and decay of fission products at the site (Curtis et al., 1981). Although there has been little mechanical alteration of the uraninite subsequent to its formation, some of the fission products have escaped from the uraninite, probably by solid state diffusion (Curtis et al., 1981), and there has been some redistribution of radionuclides subsequent to their release from the uraninite.

In 1980 De Laeter et al. reported that Pd and Te appear to have been retained in the reactor zones, whereas Ag, Sn, and Cd were lost, and Ag and Sn may have been retained in the surrounding host rock. Gancarz, et al. (1980) inferred that Ru and Tc may have been preferentially removed from rocks beneath the reactor zones and deposited in rocks above the reactors. This result is consistent with findings of Curtis et al. (1981) that Ru, Tc, and Nd were dispersed into the rocks surrounding the reactor zones, but appear to have been contained within a

few tens of meters of their source. Loss et al. (1984) confirmed earlier reports that Pd and Te were retained in the reactor zones and that Ag and Cd appear to have been lost (data for Ag were not conclusive). Curtis (1986) noted the deficiency of Tc in the reactor zones and the Tc excesses in the surrounding rocks and postulated that increased temperatures and greater oxidizing conditions in the reactors led to dissolution of Tc in hydrothermal fluids and migration to the surrounding rocks where it precipitated in response to a drop in temperature and more reducing conditions. Most recently, Curtis et al. (1989) suggested that a portion of the fission-produced Te, Ru, Pd, Tc, Cd and Mo was retained essentially at the site of production and that the portion that escaped the uraninite crystals of origin was completely removed from the reactor zone. Further, Curtis et al. (1989) presented evidence that Nd and Sn were removed from the site of their production, but have been retained within the reactor zone.

2.1.2 Alligator Rivers, Australia

The Alligator Rivers Analog Project (ARAP) began in 1987 as a cooperative venture under the auspices of the Organization for Economic Cooperation and Development's Nuclear Energy Agency. The project involves research by six organizations from five countries: the Australian Nuclear Science and Technology Organisation, the Japan Atomic Energy Research Institute, the Japan Power Reactor and Nuclear Fuel Development Corporation, the Swedish Nuclear Power Inspectorate, the UK Department of the Environment, and the US Nuclear Regulatory Commission (Hardy and Duerden, 1988). Prior to ARAP (1981-1986), the Australian Atomic Energy Commission (AAEC) conducted research at Alligator Rivers with funding from the US Nuclear Regulatory Commission (NRC). Studies are continuing at present and the ARAP has recently been extended until 1992 (Nuclear Waste News, June 21, 1990).

Investigations at Alligator Rivers have been designed to study the migration of radionuclides away from a uranium deposit as an analog to migration from a waste repository. A description of the area is found in Airey et al. (1987). The Alligator Rivers deposits are located in the Pine Creek geosyncline (14 km of interlayered tuffs and sediments resting on Archean granite).

The host sediments were regionally metamorphosed about 1.8 Ga ago and were subsequently covered by proterozoic and younger rocks. The deposits occur in chloritized zones juxtaposed with lenses of massive dolomite and/or magnetite. ARAP has focused on the Koongarra deposit because it contains high uranium concentrations, its hydrology has been undisturbed by mining, and elemental migration has occurred on a time scale comparable to that of regulatory interest for high level waste isolation. The study area has a monsoonal climate with most of the rainfall coming between November and March, consequently the water table rises and falls significantly (AAEC, 1986). The Koongarra deposit consists of two distinct ore bodies of uranium veins in quartz-chlorite schists; secondary mineralization extends to depths of 25 to 30 m and forms a fan in the weathered schist extending some 80 m downslope from the deposit (AAEC, 1986).

Transport of uranium from sites of primary mineralization is an ongoing process at Alligator Rivers. Uranium at Koongarra is being leached from the rocks in the unsaturated zone and deposited just below the top of the water table in the weathered, oxidized zone (Airey, 1986). No correlation has been found between Ra and U distributions in the secondary deposit; which is attributed to differences in chemical and adsorption properties of the two elements (Airey, 1986). Most of the uranium and thorium is associated with iron phases, whereas radium tends to accumulate in the clay and quartz rich phases (Airey, 1986). In addition to this vertical redistribution, uranium is also being remobilized into a roll front type deposit from the areas of primary mineralization in the direction of the presumed regional flow (Airey et al., 1987). This remobilization allows estimation of uranium transit times by two independent methods: groundwater travel times calculated from a hydraulic model and transit times derived from sorption coefficients calculated from the ratio of uranium concentration in groundwater to that in neighboring drill core (Airey et al., 1987). Preliminary results show an agreement between the two methods to within an order of magnitude.

Sverjensky (1988) used measured water compositions, temperatures, pressures, oxidation states, and pH values to calculate the speciation and saturation states of the groundwaters in the phosphate zone at Koongarra. He reported that the redox state of the groundwaters is not well

constrained at present, that the Fe and Al in the water analyses may be due to particulate matter rather than dissolved species, that uranium is complexed by HPO_4 or CO_3 depending on the concentrations of those agents and the pH, and that waters from the weathered zone are undersaturated with respect to chlorite, illite, carbonate minerals, uraninite, uranophane, saleeite, torbernite, and carnotite, consistent with the idea that the present groundwaters may actually be dissolving and dispersing the uranium of the deposit. Sverjensky noted that the complicated geologic history of the Koongarra deposit obscures understanding of the present day processes.

Samples of groundwater taken from drill holes at Koongarra have been studied with respect to their colloidal contents (Airey, 1986; Ivanovich et al., 1987; Edghill, 1988). Drill holes closest to faults were found to have the greatest variety of colloids (Ivanovich et al., 1987). Colloids identified include: iron particles, clays (kaolinite and chlorite), silica, lead, uranium, and titanium particles. All colloid samples were dominated by Fe-rich particles and, for all particle sizes, uranium was only found in Fe-rich species (Ivanovich et al., 1987). Radionuclides were found to be associated with the colloids only near the center of the ore body (Edghill, 1988). Colloids were observed to carry between 0.01% and 2% of the ^{238}U and between 0.3% and 39% of ^{230}Th in groundwater samples (Airey, 1986). Isotopic disequilibrium is observed between the colloids and the solutions for both U and Th (Airey, 1986). Low colloid concentrations (about 10^6 particles/l or less), and the absence of radionuclides in colloids outside the ore body, indicate that colloidal transport of radionuclides is minor at Koongarra (Edghill, 1988).

A variety of other investigations are under way at Alligator Rivers. Studies of alteration mechanisms of chlorite and uranium adsorption/desorption on chlorite and other clays have been reported by Sekine et al. (1988). Curtis and Perrin (1988) have studied plutonium geochemistry by measuring ^{239}Pu abundances in uranium-rich rocks; samples with uranium concentrations between 14% and 40% contain between $1.7x10^{-12}$ and $2.6x10^{-12}$ $^{239}Pu/U$. Edghill and Davey (1988) used alpha autoradiography to determine which mineral phases exhibit alpha activity, and how those associations varied with differing degrees of weathering; a strong connection between alpha activity and iron and manganese minerals was noted.

2.1.3 Poços de Caldas, Brazil

The Poços de Caldas natural analog project began in June 1986 and officially ended in December 1989. The project was jointly sponsored by SKB (Sweden), NAGRA (Switzerland), the Department of the Environment (UK) and the Department of Energy (US). There was also participation by Nuclebras (Brazil). A summary report on the project is to be generated by N.A. Chapman. The study area was the Poços de Caldas caldera, Minas Gerais, Brazil. The caldera contains two sites of interest: the Osamu Utsumi uranium mine and the Morro do Ferro thorium and rare earth element (REE) deposit. Osamu Utsumi is known for its well developed redox fronts within the uranium ore; Morro do Ferro was of interest as one of the most radioactive locations on the surface of the Earth. At Osamu Utsumi, research was directed toward the behavior of natural decay series nuclides at the redox fronts whereas at Morro do Ferro, attempts were made to relate the distributions of Th, U, and light REE to the groundwater flow patterns to evaluate the extent of mobilization of these elements (MacKenzie et al., 1990).

The Poços de Caldas caldera is the largest alkaline igneous complex in South America (about 33 km average diameter) (Schorscher and Shea, 1990). The two study areas are located near the center of the caldera, about 5 km apart (Smellie, 1985). Early volcanism at Poços de Caldas was followed by caldera subsidence and nepheline syenite intrusions along ring dikes (Schorscher and Shea, 1990). Local magmatic brecciation occurred in association with intense hydrothermal potassium- and sulfur-rich alteration (Schorscher and Shea, 1990). These processes caused the formation of a Th-REE concentration at Morro do Ferro and a U-Zr-REE deposit at Osamu Utsumi. Late stage events included intrusion of lamprophyre dikes followed by strong weathering which has developed redox fronts of enriched uranium mineralization. The mineralizing events ended about 76 Ma ago (Ar/Ar date on an unmineralized lamprophyre dike) (Schorscher and Shea, 1990).

Morro do Ferro is a 140 m high hill (Lei et al., 1986), the highest point in the Poços de Caldas caldera, evidence of the relative resistance of the deposit to erosion (Waber, 1990). The

deposit is about 150 m by 320 m in area and about 100 m deep (Lei et al., 1986). At Morro do Ferro, a carbonatite intrusion resulted in the formation of stockwork magnetite veins (Schorscher and Shea, 1990). Later hydrothermal alteration and weathering caused *in situ* concentration of Th - Zr - Ce - La - Nd - rich resistates (Barretto and Fujimori, 1986). The ore occurs as elongated argillized lenses of mineralization which run down the hill slope (Waber, 1990). Major ore minerals include: bastnaesite, monazite, cheralite, goyazite, thorianite and thorite (Waber, 1990).

The Osamu Utsumi uranium mine is an open pit about 100 m deep, 1 km long and 0.5 km wide and is located at the bottom of a valley (Cross et al., 1989). Subvolcanic porphyritic phonolites are the main rock type and these have been intruded by later nepheline syenites (Cross et al., 1989; Waber et al., 1990). Early hydrothermal alteration probably occurred at temperatures well below 200°C since kaolinite was stable (Waber et al., 1990). During the later potassic alteration, fluid inclusions recorded temperatures of 210-260°C (Waber et al., 1990). Maximum temperatures occurred at the end of the potassic stage and were probably in the range of 260 to 360°C as indicated by fluid inclusions and illite crystallinity data (Waber et al., 1990). The lower portions of the deposit contain about 2% pyrite and are reducing whereas the upper portions have been oxidized by infiltration of rainwater with subsequent alteration of the pyrite to ferric oxyhydroxides (Cross et al., 1989); a sharp redox front separates the two regions (Cross et al., 1989).

Groundwaters in the Poços de Caldas area typically have low concentrations (<1 mg/l) of colloids (1-450 nm) (Miekely et al., 1988; Miekely et al., 1990a). Most of the colloids present are composed of iron and organic species. Only minor amounts of U are associated with colloids but greater amounts of Th and REE's are transported by colloid-sized particles. The tendency to form colloidal species is: U < Ce < Th. Suspended particles >450 nm show the same elemental associations as the colloids, but the elemental concentrations are higher (about 1000x). The suspended particle concentration is 5 - 10 times greater at Morro do Ferro than at Osamu Utsumi; however, there appears to be very little thorium transport at Morro do Ferro, either by colloids or true solution.

The groundwaters at Osamu Utsumi have high concentrations of uranium (up to 10 mg/l) whereas those from Morro do Ferro are much lower [unspecified] (Miekely et al., 1990b). ^{232}Th concentrations are low in groundwaters from both sites (<0.1μg/l) but are occasionally higher (up to 100x) in surficial waters with abundant humic compounds or sulfate. Substantial radioactive disequilibria was noted between ^{234}U and ^{238}U in the groundwaters. $^{230}Th/^{234}U$ ratios are low due to the low solubility of Th and its strong tendency to sorb on suspended particles.

The groundwaters in the Poços de Caldas area have an unusual K-Fe-SO_4 composition because of the weathering of the altered mineralized rocks in the area (Nordstrom et al., 1990). Seasonal compositional variability was noted only in the shallowest groundwaters (Nordstrom et al., 1990) even though the area is wet from November to April and dry the rest of the year (Holmes et al., 1990). All of the groundwaters appear to be of meteoric origin as indicated by tritium and stable isotope measurements (Nordstrom et al., 1990). Shallow groundwaters are less than 40 years old, but deeper waters may be a mixture of younger and older fluids producing an apparent age of 40-60 years (Nordstrom et al., 1990).

The effects of microbial activity on geochemical processes in the Poços de Caldas area have also been studied (West et al., 1988; West et al., 1990). Both rock cores and groundwaters were sampled for microbes; microbes were found in all samples with no depth correspondence. It is estimated that the nutrients available at Osamu Utsumi from the rock and groundwater would support about 0.1 g/m^3 of biomass. The rate of movement of the redox front depends on the rate of supply of oxidants; West et al. (1988) reported that microbes are present and are currently enhancing the supply of oxidants and hence the rate of advance of the front. These inferences are compatible with the observation that the redox front is moving faster than would be expected on the basis of simple dissolved oxygen concentration. West et al. (1990) suggested that the local sulfur geochemistry may be largely microbially catalysed and that such processes could be responsible for the formation of the pitchblende concretions observed in the ore and the presence of secondary pyrite.

Mobilization rates of elements considered to be chemical analogs of HLW components have been studied at Poços de Caldas. The transuranic actinides occur in nature only in vanishingly small concentrations, therefore it is necessary to choose elements of greater abundance, which have similar chemical characteristics in order to predict the chemical behavior of transuranic actinides (Krauskopf, 1986). Thorium was used as analog for Pu and La as an analog for Cm and Am (Eisenbud et al., 1984; Barretto and Fujimori, 1986). Mobilization rates have been estimated considering both surface erosion and dissolution by groundwater (Eisenbud et al., 1984). Eisenbud et al. (1984) determined that, at Morro do Ferro, about 27.2 kg of Th is transported as particulates each year and only 0.015 kg in "soluble" form; the numbers for La were similar to those for Th. These mobilization rates are considered by Eisenbud et al. (1984) to be so low that despite the long half-lives of some actinide isotopes, essentially complete decay should occur *in situ*.

2.1.4 Cigar Lake, Canada

Atomic Energy of Canada Limited (AECL) has carried out natural analog studies at the Cigar Lake uranium deposit, Saskatchewan, Canada, since 1982 (Cramer et al., 1987). Uranium ore at Cigar Lake occurs as an E-W trending lens 2 km long and 25 - 100 m wide at a depth of 400 m (Vilks et al., 1988) at the unconformable contact between the Athabasca Sandstone and the basement rock (Goodwin et al., 1988). There are no direct surface indications (radiologic, thermal, geophysical, or geochemical) of the existence of the deposit (Cramer, 1986); the deposit was discovered by indirect geophysical means coupled with a knowledge of the genetic processes which can form such a deposit (Goodwin et al., 1988). Dominant uranium minerals are uraninite and coffinite; the average grade is about 12% uranium with maximum concentrations as high as 55% (Goodwin et al., 1988). This primary mineralization has been dated at about 1.3 Ga (Sunder et al., 1987). The deposit is surrounded by a 5 to 30 m thick alteration zone consisting of illite, kaolinite, quartz, and minor rutile all of which is covered by a quartz-cemented cap (Goodwin et al., 1988).

Goodwin et al. (1988) suggest this list of analog aspects of the Cigar Lake deposit: (1) uraninite (the main ore mineral) is a good analog to uranium dioxide (the main waste component); (2) the Canadians anticipate a titanium container which would alter to have a rutile coating in an aqueous environment, the accessory rutile in the alteration zone at the deposit is a good analog; (3) a planned bentonite and sand buffer is approximated by the illite-rich alteration zone around the ore; and (4) rather than the large granitic pluton envisioned for Canadian waste, the Cigar Lake deposit is hosted by a porous sandstone; water circulation in the sandstone is much greater than would be expected for a granite, so the deposit provides a conservative estimate of the effects of circulating groundwaters.

Migration of radionuclides from the deposit into the surrounding rocks has been limited at Cigar Lake by a combination of hydrogeologic, geochemical, and mineralogical factors (Cramer, 1986). The deposit is in a basal sandstone unit which is the main local aquifer; this unit has a much higher groundwater flux than the ore deposit itself (Cramer, 1986). The present fluids are chemically reducing (Eh is estimated at about -0.2 to +0.2 volts, Sunder et al., 1987), therefore there is little dissolution of uraninite or the daughter radionuclides contained within the uraninite (Cramer, 1986). The uranium concentrations in the groundwater are similar to those expected for uraninite equilibrium; measured values are $10^{-7.5}$ to 10^{-9} mol/dm^{-3} (Sunder et al., 1987). Any radionuclides that dissolve and migrate out of the ore zone encounter a naturally sorptive mineralogical barrier in the form of the clay alteration zone consisting of illite, chlorite, kaolinite, and iron oxides (Cramer, 1986).

The concentration, size distribution, and composition of colloidal material (<500 nm) in groundwater near the deposit have been investigated (Vilks et al., 1988). Concentrations ranged from 0.6 - 261 mg/l; most particles were in the 5000 - 10000 nm range, with an additional peak in colloid size between 50 and 100 nm (Vilks et al., 1988). Particles consisted of clays (mostly illite), Fe-Si precipitates, organics, rock particles, and drilling impurities (Vilks et al., 1988). Both concentration and composition appear to have been determined by local alteration mineralogy and Fe oxidation (Vilks et al., 1988). The proportions of uranium and thorium in groundwater

samples associated with colloidal particles vary from 5 to near 100%, whereas the fraction of total radium present as colloids ranges from 0 to 70% (Cramer et al., 1987).

2.1.5 Other ore deposit analog studies

2.1.5.1 Palmottu, Finland

At Palmottu, Finland, a small uranium deposit consisting of uraninite in microcline granite dikes has been the subject of analog studies (Valkiainen, 1988; Ruskeeniemi et al., 1989). Uranium at Palmottu occurs mainly as extensively corroded uraninite (average grade is about 0.1% U) (Ruskeeniemi et al., 1989). Shallow groundwaters at the deposit are more oxidizing and have a lower pH than deeper fluids (Valkiainen, 1988; Ruskeeniemi et al., 1989). The shallow waters are rich in Ca, Na, and HCO_3, whereas the deeper waters are dominated by Na-Cl-SO_4-HCO_3 (Ruskeeniemi et al., 1989). Uranium concentration is higher in the oxidizing upper waters than in the lower, more reducing, waters, even though the uranium concentration in the rock is greatest at depth (Valkiainen, 1988). About one third of the uranium in the deep water is bound to a particulate (>0.45 μm) fraction, whereas only about 3% of the uranium is bound to particulates in shallower fluids (Valkiainen, 1988).

2.1.5.2 Portage Lake volcanic copper deposits, Michigan

Native copper which occurs in the basalts of the Keweenaw Peninsula was studied as an analog of copper waste containers in the proposed HLW basalt site at Hanford, Washington, by Crisman and Jacobs (1982). Similarities between the two sites include: basalt host rocks, comparable groundwater compositions, and the occurrence of elevated temperatures after emplacement of the copper in the basalt (metamorphism at Keweenaw). The copper has been stable in the geohydrologic environment of the Keweenawan basalts since deposition, having survived contact with both a near surface fresh water (Na-HCO_3-Cl) and a deep brine water (Ca-Na-Cl). Only copper in samples exposed to the atmosphere and water in the adits or open surfaces

showed alteration. Crisman and Jacobs (1982) concluded that a basalt-water geohydrologic system (i.e. low total dissolved solids, low Cl, moderate pH, low Eh) could be favorable for the preservation of copper HLW cannisters.

2.1.5.3 Krunkelbach, Germany

At Krunkelbach, Germany, uranium-bearing quartz-barite-fluorite veins several centimeters to a few meters wide occur in a highly differentiated two-mica granite, near the contact of the granite and juxtaposed gneisses and metasediments (Hofmann, 1988). The veins were formed about 310 Ma ago and were subject to hydrothermal alteration in the Tertiary, and to low temperature oxidation since uplift in the Quaternary (Hofmann, 1988). The ore body lies parallel to, and only a few meters away from, a fracture zone which acts as a major groundwater channel; the ore is oxidized down to a depth of at least 240 m (Hofmann, 1988). At present, uranium migration is retarded by sorption on iron oxyhydroxides, gorceixite [$BaAl_3(PO_4)(PO_3OH)(OH)_6$], and clays; radium is fixed in barite (Hofmann, 1988). Suspended material composed of clays (illite > kaolinite > smectites), quartz, gorceixite, and amorphous iron oxyhydroxides, with diameters >0.22 μm constitutes 0.006 to 5.9 ppm of the groundwater; these particles appear to have been transported 1 to 2 km (Hofmann, 1988). As much as 10% of the uranium and all of the thorium in the groundwaters may be transported by colloidal iron oxyhydroxide phases under the ambient oxidizing, near neutral pH conditions (Jeremy et al., 1988). Dissolved uranium occurs in concentrations of 1 - 4 ppm (Jeremy et al., 1988). Over a distance of a few meters, the concentration of dissolved uranium drops some two orders of magnitude, the major uranium species changes from carbonate to phosphate, secondary uranium sulfates precipitate, and uranium is accumulated by gorceixite and smectite and chlorite clays (Jeremy et al., 1988).

2.1.5.4 Shinkolobwe, Zaire

The Shinkolobwe uranium deposit is about 1.8 Ga old and is hosted by dolomitic shales, siliceous dolostones and chloritic siltstones (Finch and Ewing, 1989). The deposit has been

exposed to surface weathering for the last 60 Ma and has suffered highly oxidizing alteration. In response to this oxidation, the uraninite crystals form alteration zones on the order of a few centimeters in width. The alteration paragenesis of the ore has been studied as an analog to the weathering of spent fuel. Bequerelite [$Ca(UO_2)_6O_4(OH)_6 \cdot 8H_2O$], vandendriesscheite [$PbU_7O_{22} \cdot 12H_2O$], fourmarierite [$PbU_4O_{13} \cdot 4H_2O$], schoepite [$UO_3 \cdot 2H_2O$], billietite [$Ba(UO_2)_6O_4(OH)_6 \cdot 8H_2O$] and compriegnacite [$K_2(UO_2)_6O_4(OH)_6 \cdot 8H_2O$] are formed relatively early in the alteration sequence, whereas curite [$Pb_2U_5O_{17} \cdot 4H_2O$], clarkeite [$(Na,Ca,Pb)_2U_2(O,OH)_7$], and masuyite [$Pb_3U_8O_{27} \cdot 10H_2O$] tend to be formed later. The uranyl silicates uranophane [$(H_3O)_2Ca(UO_2)_2(SiO_4)_2 \cdot 3H_2O$] and cuprosklodowskite [$(H_3O)_2Cu(UO_2)_2(SiO_4)_2 \cdot 2H_2O$] appear to be the last phases to be formed. There is a general decrease in grain size as alteration proceeds.

2.1.5.5 Tono, Japan

The Tono uranium mine is the largest uranium reserve in Japan (Ochiai et al., 1988). Uranium is concentrated in paleochannels in a Tertiary sediment package composed of arkosic sandstone, tuffaceous sandstone, carbonaceous mudstone, and conglomerate. The deposit is less than 150 m deep and the local groundwater is stagnant and bicarbonate-rich. The uranium is characteristically associated with zeolites, clay minerals, and organic material; only seldom are primary uranium minerals such as coffinite and uraninite observed. A 1 cubic meter block of ore from the Tono mine was subdivided into 64 blocks 25 cm on a side and the mineralogy, chemistry and isotopic compositions of the blocks determined to study the distribution and migration of uranium and related elements. It was found that equilibrium among ^{238}U, ^{234}U, and ^{230}Th had been maintained and that ^{226}Ra had been leached.

2.1.5.6 Stripa, Sweden

An inactive iron mine at Stripa, Sweden, has been the site of a variety of field tests related to geologic disposal of HLW. In addition to these tests, geologic and geochemical studies have

been conducted at Stripa which constitute analog studies of radionuclide migration (Wollenberg and Flexser, 1986). The host rock at Stripa is a quartz monzonite which is intruded into metamorphics; the monzonite has relatively high concentrations of uranium in comparison to local granites and to the adjacent metamorphic rocks. Uranium and thorium in granitic rocks usually occur in accessory minerals such as sphene, allanite, and zircon; at Stripa there are very few of these accessory minerals, but uranium and thorium are abundant, occurring largely with chlorite as fracture fillings. Although surface rocks are depleted in uranium relative to rocks at depth, groundwater uranium concentrations increase from the surface to about 175 m and then decrease steadily with depth. It appears that uranium is being dissolved from near surface rocks, transported to deeper zones and redeposited in the fractures along with chlorite.

2.2 Igneous contact zones

2.2.1 Eldora Stock, Colorado

The Eldora Stock is a 60 Ma old quartz monzonite which intruded Precambrian schists, gneisses and pegmatites (Brookins, 1986). Elemental migration across the contact zones (0 to 2 m) has been investigated as an analog to elemental transfer in a repository during heating by the waste cannisters (Brookins, 1986; Wollenberg and Flexser, 1986). Oxygen isotopic data show a distinct contrast between the stock and the country rock, which has been interpreted to indicate a lack of hydrothermal convective cooling (Wollenberg and Flexser, 1986). Samples taken across the contact zone show that uranium occurs in primary accessory minerals in both the stock and the country rock; secondary uranium minerals only occur within a few meters of the contact (Wollenberg and Flexser, 1986). There is no systematic uranium enrichment or depletion in the rocks related to distance from the contact (Wollenberg and Flexser, 1986). Brookins (1984) reports that there is no evidence for movement of Th, Cr, Co, Sc, Rb, Sr, or Fe from the stock into the intruded rocks (in addition to no U mobilization). The light REE's appear to have been reorganized in and near the contact zone, but with no additions from the stock (Brookins, 1984).

2.2.2 Alamosa River Stock, Colorado

The Alamosa River stock is a monzonite body which intruded tuffaceous and andesitic volcanic rocks about 30 Ma ago (Brookins, 1984). In contrast to the Eldora stock discussed above, intrusion of the Alamosa stock set up a large scale convecting hydrothermal system (Brookins, 1986). Alteration of the tuffs is observable 60 m from the contact with the occurrence of calcite intergrown with the rock matrix; chlorite and sericite appear within 40 m of the contact along with quartz overgrowths; and epidote is a common alteration mineral within about 12 m of the contact (Wollenberg and Flexser, 1986). The contact itself contains a dense intergrowth of epidote with some sphene along with fine hematite-filled fractures; uranium occurs in the sphene but is otherwise absent from the contact (Wollenberg and Flexser, 1986). Abundances of Cs, Rb, Sc, V, Fe, Th, U, and Co are much higher in the monzonite than in the tuff (Wollenberg and Flexser, 1986). There are gradients of Cs, Th and Co in the tuff, with concentrations increasing toward the contact; the other elements show no indication of migration between the stock and the tuff (Wollenberg and Flexser, 1986).

2.2.3 Mafics intruding evaporites

Tertiary lamprophyre dikes intruded the evaporite sequence near the Waste Isolation Pilot Plant (WIPP) site about 32 to 35 Ma ago at depths close to those proposed for the pilot storage of radioactive waste (Brookins, 1980, 1986). Brookins (1980) suggests that the contact effects of the lamprophyre emplacement constitute a good analog for a HLW cannister at an elevated temperature. Lamprophyres are enriched in U and Th and the emplacement temperature of these dikes was about 600 - 800°C (Brookins, 1980). The strongest effects at the evaporite-dike contact are melting, partial melting, and recrystallization of the evaporites (Brookins, 1980). The REE patterns of the lamprophyre at the contact are typical of lamprophyres and show no evidence of elemental gain or loss (Brookins, 1980). It appears that there has been little if any chemical exchange between the dikes and the evaporites (Brookins, 1980, 1986).

Sidle et al. (1985) studied contact metamorphism resulting from intrusion of mafic dikes into salt formations at sites in New Mexico, Utah, and Germany. They found aureoles ranging from <1 m up to 7 m developed as a result of intrusions with temperatures of about 600-800°C. Phase changes in the salt were mainly the recrystallization of halite and the incongruent melting of polyhalite and sylvite. No changes in Y, REE, Th or U concentrations were observed around the intrusives. Sidle et al. (1985) conclude that there would likely be little disturbance to a salt host from the lower temperatures expected from HLW containers.

2.2.4 Valles Caldera, New Mexico

Krumhansl and Stockman (1988) reported on elemental migration and secondary mineral development at the boundary of the Banco Bonito obsidian flow and the underlying tuffaceous rocks in Valles Caldera, New Mexico. Criteria for choosing the site included: accessibility; a young age and simple geologic history; decades of heating at 150 - 350°C; and unsaturated hydrologic conditions. Contact effects include a reddish "baked" zone extending some tens of feet into the tuffs. Cs and Rb showed little variation with distance from the contact whereas Th, Ta, Hf, Co, and REE had slight concentration trends; it is possible that these trends may have predated the obsidian flow. The Cs/Rb ratio does not vary with distance from the contact. Water and chlorine are depleted adjacent to the contact.

Most recently Stockman et al. (1990) have extended the earlier work by examining trace element concentrations, water content, and isotopic compositions across the contact between the tuff and the overlying obsidian. No trends in trace element abundance were found. The only changes observed were for water, F, and Cl; water and Cl are depleted near the contact whereas F is slightly enriched toward the contact. A relatively constant D/H ratio (-95 to -110 ‰) extends from the contact for at least 29 m into the tuff. No evidence of hydrothermal alteration was noted. At present, trace element measurements extend only 7.2 m from the contact. Future work is planned to lengthen these trace element profiles.

2.2.5 Oriciatico intrusion, Italy

The Oriciatico volcanic body was emplaced into clays at about 800°C "many thousands" of years ago and is considered to be an analog of a "worst case scenario with regards to a radioactive waste repository" (Brondi, 1985). The intrusion caused recrystallization of the clay (the illitic clays changed to a to K-feldspar - plagioclase - pyroxene - biotite assemblage), with strong hardening and abundant micro-crack formation within a 0.5 to 1.5 m contact zone. Hydrothermal circulation caused by the intrusion resulted in the mobilization of Na, K, Rb, Ca, Ba, and Sr for distances up to 15 m.

2.3 Glass alteration

More detailed reviews of the use of natural glasses as analogs to nuclear waste forms are available in McKenzie (1990) and Petit (1990). A brief review is provided here.

2.3.1 Basaltic glass

Of the natural glasses, basalt glasses are compositionally the most similar to HLW glasses (Lutze and Grambow, 1987). There are a number of similarities between basaltic glasses and waste form glass: silica contents, alteration products, alteration layer morphologies, and alteration rates in laboratory experiments (Arai et al., 1988). A variety of environments have been investigated, including: ocean floor, subglacial, hydrothermal, and surficial weathering (Arai et al., 1988). Inferred alteration rates range from 0.001μm/1000 years - 30μm/1000 years (Arai et al., 1988).

Byers et al. (1987) reported the results of a wide ranging study of natural basalt glasses. Samples were collected from British Columbia, Hawaii, New Mexico, Washington, Iceland, West Germany, the Galapagos Islands, the Mariana Islands, and the deep ocean. Ages of the samples range from a few years to 350 Ma. All of the samples were found to have altered to palagonite and to exhibit dissolution textures. Alteration products are mainly smectite clays, zeolites (chabazite, phillipsite, and analcime), and calcite. Paragenesis and composition of the alteration minerals is

largely a function of the composition of the altering fluid. Byers et al. found no simple correlation between the thickness of the alteration rinds and age or general alteration environment.

Cowan and Ewing (1988) collected samples from a cliff over Hanauma Bay, Oahu, Hawaii, where the basaltic glass has weathered for the last 12,000 to 28,000 years. All of the samples were altered at least partially to palagonite and zeolites; zeolites were formed in the order: analcime to phillipsite to chabazite. The rate of alteration was less than that predicted by experiments; the authors infer that the difference was due to the episodic presence of the groundwater over the years.

Arai et al. (1988) studied basaltic glasses from the Fuji volcano, Japan. Two sets of samples were taken, one set 280 years old and one set 2800 years old; both sets were altered by rainwater. Comparing average thicknesses of altered layers, they estimated alteration rates of several μm/1000 years.

2.3.2 Rhyolitic glass

Ericson (1980) used 14 samples of rhyolitic obsidian from California and Oregon and associated archeological data (for duration of weathering) to determine hydration rates. This natural alteration was then compared with laboratory alteration experiments on the same obsidians. The laboratory alteration rates were found to be much less than the rates for natural hydration. Ericson inferred that the laboratory experiments omitted some significant processes [not specified] and that the rhyolitic obsidian is much more unstable than indicated by the laboratory results.

Malow and Ewing (1980) compared the thermal and chemical stabilities of 2 borosilicate glasses and 1 glass ceramic to those of 3 rhyolite glasses using a variety of laboratory tests and observations of natural weathering. They concluded that natural glasses are more stable than the waste form glasses as a result of the greater silica contents of the natural glasses (74% vs 28-50%). Though the natural glasses ranged in age from 500 years to 670,000 years, they noticed no difference in natural weathering among the samples, but they noted that these samples were chosen in the first place because they were "fresh and unweathered." At elevated temperatures, the waste

glasses tended to form new phases and to recrystallize, whereas the natural glasses showed no such tendency. They noted that most volcanic glasses are less than 2 Ma old and that this suggests a long term stability at ambient, weathering conditions of not more than 1 Ma.

2.3.3 Tektites

Tektites range in age from hundreds of thousands of years to 35 Ma, however, it is rare that any alteration, hydration, or devitrification effects are noted (Lutze and Grambow, 1987). This great durability may be due to their high silica and alumina contents (usually at least 30 weight %) and to their low alkali contents (generally < 4 weight %) (Lutze and Grambow, 1987).

2.3.4 Archaeologic glass

Glass was first manufactured about 1500 B.C. in what is now Egypt and Iraq (Kaplan, 1980). This early glass was rich in soda and lime; about 1000 A.D. potassium-lime glass began to be manufactured (Kaplan, 1980). Lead glass was not made until about 200 B.C. and has been only rarely produced (Kaplan, 1980). Kaplan and Mendel (1982) noted that some of this glass has survived for 3500 years even though much of it has high alkali concentrations; they suggest that we could expect much better performance from borosilicate glass under similar conditions. Many ancient glasses may already have survived more destructive environments (e.g. changing temperatures and humidity) than those that will be faced by HLW glass (Kaplan and Mendel, 1982). Kaplan and Mendel (1982) identify five main types of decomposition observed in ancient glasses: 1) weeping - the sweating of droplets of water when excavated glasses come into contact with moisture in the air, 2) crizzling - the formation of networks of tiny cracks all over an object's surface, 3) pitting - formation of pit-like scars by abrasive action or chemical dissolution leaving holes filled with weathering products, 4) layering - development of a filmy iridescent surface formed of multiple layers of mica-like minerals, and 5) crusting - development of powdery, amorphous and opaque residues by the leaching of chemicals out of the glass in a way that alters

the object's structural stability. These alteration styles may be indicative of the sort of alteration to be expected in HLW glass forms (Kaplan, 1979).

2.4 Miscellaneous natural analogs

2.4.1 Nuclear explosion sites

Radionuclide migration associated with underground nuclear tests at the NTS has been studied in the field since 1974 (Thompson, 1984; Buddemeier and Hunt, 1988). The Radionuclide Migration Project was begun "to determine the potential for movement, both on and off the NTS, of radioactivity from underground nuclear explosions" (Thompson, 1984). Work has been reported for the Cheshire Site, the Cambric Site, and the Nash Site.

The Cheshire event occurred on 14 February, 1976 (Buddemeier and Hunt, 1988). The site is on Pahute Mesa where the detonation occurred at a depth of 1167 m in fractured rhyolitic lavas. Water samples were taken during 1983, 1984, and 1985 from within the detonation cavity and from about 300 m outside the cavity. All of the Mn, Co, Ce, and Eu was associated with colloids in samples from both locations. Colloid sizes ranged from 0.003 μm to 0.45 μm; concentrations ranged from 63 mg/l to 4.3 mg/l. Colloid concentrations were about an order of magnitude greater in samples from within the cavity. Buddemeier and Hunt (1988) maintain that the presence of colloidal radionuclides outside the cavity indicates radionuclide transport as colloids.

The Cambric test was detonated in tuffaceous alluvium at the NTS in 1965 and subsequent nuclide migration has been reported by Coles and Ramspott (1982). The explosion point was 294 m deep; the water table was 220 m deep. Fifteen years after the explosion, water was sampled from a well that intersected the explosion cavity; only ^{3}H and ^{90}Sr were found in concentrations above the maximum permissible concentration (MPC). In 1974 a well was drilled 91 m south of the explosion point and a pump placed at 294 m depth for water sampling. Coles and Ramspott (1982) assume that ^{3}H is not retarded and compare radionuclide movement to ^{3}H to determine a

retardation factor. They observe that ^{106}Ru migrates at the same velocity as ^{3}H, a finding which contradicts earlier laboratory studies which indicated that Ru would migrate much more slowly than ^{3}H.

At the Nash site (where the detonation occurred in alluvium above the water table) water samples have been restricted to fluids from the carbonate aquifer beneath the alluvium, in order to test the migration of radionuclides from the unsaturated zone into the saturated zone (Thompson, 1984). However, it is not clear whether the nuclides measured in the waters originated in the explosion cavity or whether they represent "material driven by the explosion into fractures in the carbonate rocks" (Thompson, 1984).

2.4.2 Uraniferous nodules

The Permo-Triassic redbeds of the Littleham Mudstone Formation in Devon, UK, contain dark colored radioactive nodules frequently larger than 10 cm diameter which are interpreted as areas of reduction (Hooker et al., 1986). These nodules contain high concentrations of S, Cu, Pb, Ag, Co, As, Ni, Cr, and V as well as the uranium minerals pitchblende, coffinite, and metatyuyamunite. Diffusion of uranium decay series isotopes from these well defined reduction centers into the enclosing clays is considered as an analog to HLW radionuclide migration (Hooker et al., 1986; Hooker and Chapman. 1987).

2.4.3 Sediment studies

2.4.3.1 Boom Clay, Belgium

The Boom Clay formation, Belgium, has been studied as a potential host for HLW disposal since 1974 (Patyn et al., 1987). Hydrologic study wells installed in the area to define local water flow paths showed a regional aquifer system consisting of three main aquifers, two below the Boom clay and one above. Models of this groundwater flow were developed, and ^{14}C measurements were made in an attempt to validate these models. The ^{14}C contents of

groundwaters above and below the clay horizon were compared with data from the hydrologic studies with ambiguous results; it appears that simple horizontal flow cannot explain the observations, raising the possibility that there is a component of vertical groundwater movement in the Boom Clay. It is hoped that investigations of the compositions of the interstitial clay waters will help resolve the questions.

2.4.3.2 Loch Lomond, UK

At Loch Lomond, UK, a 1 m thick layer of marine sediments (about 8000 years old, Hooker, 1988) is bounded above and below by fresh water sediments and occurs about 4 m below the bed of the lake (Chapman, 1985). The marine sediment and its pore waters constitute a geochemical discontinuity when juxtaposed with the fresh water sediments and act as a source for elemental migration (I and Br, Hooker et al., 1986; Hooker, 1988) into the surrounding sediments (Chapman, 1985). Although the physicochemical conditions and the age profile are well known, the initial and boundary conditions are difficult to constrain and have required many assumptions for interpretation (Chapman, 1985). The largest uncertainty lies in the initial form and concentration of the source term elements; consequently, it is unknown whether the estimated diffusivities are maxima or minima (Chapman, 1985).

2.4.3.3 Redbeds, Switzerland

Cores from Permian redbeds in Northern Switzerland often intersect reduction haloes of 1 to 100 mm diameter (Hofmann et al., 1987; McKinley and Frick, 1988). The cores of the haloes are enriched in U, Th, Se, REE and Pd and may contain organic material (Hofmann et al., 1987). The spherical shape of the haloes suggests formation by diffusion controlled migration of the elements which may be analogous to elemental migration in a HLW repository (Hofmann et al., 1987). Uranium concentrations in the cores range from 35 wt% U to 6 ppm U over a distance of 10 to 15 mm (Hofmann et al., 1987). Profiles characterizing variations in the elemental and natural decay series concentrations have been measured on a millimeter scale across the reduction haloes to

evaluate the redox-controlled diffusion processes responsible for the profiles (McKinley and Frick, 1988). Interpretation of the results has been complicated by a "recent perturbation of the system" [unspecified] (McKinley and Frick, 1988).

2.4.3.4 Madeira Abyssal Plain, UK

At the Madeira Abyssal Plain, field observations indicate the presence of a redox front migrating down through the turbidite sediments (Duffield et al., 1988). The turbidites are compositionally homogeneous vertically (except for uranium) and consist mainly of calcite (63%); the oxidized front penetrates some 18 cm into the sediments. Uranium concentration is about 1.5 ppm in the oxidized sediments, has a maximum just beneath the redox front of about 7 ppm, and is slightly enriched deeper in the reduced sediments with a concentration of about 2.5 ppm. Modeling of the chemical controls and processes affecting uranium distribution has been conducted; the modelling generally fits the field observations, given a variety of assumptions, including ignoring organic complexing, sorption, and colloid formation.

2.4.3.5 Gorleben Aquifer, Germany

The Gorleben aquifer system consists of porous sands with some clay and has been the subject of colloid transport investigations (Kim et al., 1987, 1988). Kim et al. (1988) point out that "all natural colloids" contain many trace heavy metals and REE which are chemically similar to some fission products and actinides and which may therefore serve as analogs of colloidal transport of HLW species. Colloid concentrations at Gorleben are on the order of 10^{12} particles/L and consist of both organic and inorganic particles. Waters with high concentrations of humic substances tend to have higher colloid concentrations than those with low humic concentrations. Kim et al. (1987) reported that concentrations of trivalent and tetravalent heavy metal ions are linearly correlated with the organic carbon (largely humic colloids) concentrations of the waters. It is noted that the formation of such colloids may enhance or inhibit the migration of radionuclides depending on the filtration properties of the system (Kim et al., 1988).

2.4.4. Hydrothermal analogs

2.4.4.1 Salton Sea, California

Elders (1987) studied the Salton Sea Geothermal Field, California, system as a chemical analog to a HLW repository in salt. A goal of the project was "to produce data to validate geochemical computer codes" (specifically EQ3/6, e.g. Wolery 1979, 1983). Elders and his associates attempted to develop a 3-dimensional model of the geothermal system (temperature, fluid composition, lithology, mineralogy). To test the model, they analyzed brines and assemblages of minerals "apparently in equilibrium with them." They found brine compositions considered to be similar to those expected at a salt repository site (7 - 25 wt % total dissolved solids). The brines are enriched in Na, Mn, Zn, Sr, Ra, Po and depleted in U and Th relative to the local sedimentary country rocks. Significant radioactive disequilibria exists between the brines and the solid phases in the system. Elders (1987) found the models capable of predicting mineral assemblages "similar" to those observed. However, this similarity was "in general not true for ... dissolved species."

2.4.4.2 Newberry, Oregon

Wollenberg and Flexser (1986) noted that active hydrothermal systems constitute good analogs to the convective flow that might be established around a HLW package during the period of high heat generation because the temperatures are comparable, and the lifetimes are similar. As an example, Wollenberg and Flexser (1986) suggested Newberry, Oregon, where an active hydrothermal system exists in andesitic basalt flows. A 950 m deep core hole drilled by the US Geological Survey provided much of the information on the Newberry system. Temperatures range from 150 - 265°C, with a generally linear increase over the deepest 200 m. This linear increase was interpreted to indicate conductive thermal conditions resulting from the low vertical permeability of the basalt flows. A general decrease in uranium and thorium concentrations with

depth was found. This decrease is independent of the degree of hydrothermal alteration, suggesting the presence of more oxidizing conditions at depth.

2.4.4.3 Empire Creek Stock, Montana

Tammemagi et al. (1986) considered the Empire Creek Stock, Montana, as an analog to a nuclear waste repository, for the following reasons: "(a) temperatures in the ground are approximately the same as those anticipated in a repository (95°C maximum); and (b) the anomaly is associated with a granitic pluton." The system is unusual in that it had no surface manifestation such as hot springs or fumaroles. In 1972-1974 the site was explored for geothermal resources, part of which involved the drilling of a 2.1 km well. This well showed that the thermal anomaly was related to a granite pluton (the Empire Creek Stock) which had intruded metamorphosed Precambrian sediments. Tammemagi et al. (1986) conducted extensive petrographic investigations of the system characterizing the mineralogy, phase relations, alteration, fracturing and veining of the rocks. They found significant fracture permeability extending to 2 km depth with no indication of decrease in permeability with depth. They conclude that it is not clear whether or not the Empire Creek Stock is a valid natural analog for a spent fuel repository, inasmuch as the present conditions of the pluton appear to be largely due to the original emplacement of the stock rather than to subsequent hydrothermal effects.

2.4.4.4 Icelandic geothermal fields

Ulmer et al. (1986) conducted a series of experiments reacting Columbia River basalt with synthetic groundwater in autoclaves and compared the results with parallel experiments using Icelandic basalt and with data from Icelandic geothermal fields to establish the ability of short term experiments to approach long term results. Rock compositions, temperatures, hydrologic residence times, glass compositions, and groundwater compositions of the Hanford site and the Icelandic geothermal fields are comparable. Experimental results for cation/proton ratios, neutral species concentrations, redox, and alteration phases are similar, indicating that short term

experiments do approach long term conditions. However, there are differences (e.g. CO_2) which may reflect additions from volcanic gasses in the geothermal fields not present at Hanford.

2.4.5 Mine tailings

2.4.5.1 South Terras, UK

At South Terras, Cornwall , UK, a uranium mine has been idle since 1929; mine dumps act as sources of uranium and thorium which migrate into adjacent soils and streams (Hooker et al., 1987). Soil profiles were collected from alluvial sediments between the dump piles and a stream. The top 15 cm of the soil was enriched in uranium as well as organic matter and iron oxides (Hooker and Chapman, 1987). Water samples from the stream were found to have high $^{230}Th/^{234}U$ activity ratios and a ^{228}Th excess (Hooker and Chapman, 1987). The uranium speciation in these fluids was modeled with good agreement to the field data (especially when organic complexing is assumed to be relatively simple) (Duffield et al., 1988).

2.4.5.2 Kennecott copper leaching

Cathles (1988) suggested that industrial processes make reasonable "natural" analogs to waste disposal processes because the scale is large relative to laboratory work but small enough to be carefully monitored, and the commercial value of the work has funded extensive testing and model development. He presented an example of copper leaching from low grade sulfide waste dumps. This low grade ore is formed into huge piles sometimes filling entire canyons, then water is applied. The water oxidizes and dissolves the copper which can then be economically recovered. Cathles found that the dumps heat to 55 - 65°C due to the exothermic sulfide oxidation reactions and that this heat produces a coherent pattern of air circulation in the dump. Oxygen content of the air at the base of the dump was near normal, whereas the air at the top was 50 to 100% oxygen depleted. Based on the field data, models of the processes involved were

developed. After extensive testing, measurement and model development, however, Cathles admitted that "the accurate, a priori prediction of the behavior of a new dump remains elusive."

2.4.6 Rock alteration

2.4.6.1 Granite wave breaks, Falmouth, UK

In 1956, freshly blasted granite blocks were placed in the sea at Falmouth, UK, to act as wave breaks; the blocks remained totally immersed in the sea water (except at Spring low tides when the upper surfaces were exposed) until 1987, when two blocks (about 1.5 x 1.0 x 0.5 m) were retrieved for study (Hooker and Chapman, 1987). Concentration profiles of Cl, Br, F, and SO_4 were measured in the blocks (Jefferies, 1987). Profiles of Cl and Br were flat, indicating equilibrium between the blocks and the sea water with respect to those elements; profiles of F and SO_4 were interpreted as a result of outward diffusion of these elements (Jefferies, 1987). Estimated diffusion rates ($\geq 10^{-13} m^2 s^{-1}$) are much higher than diffusion rates estimated by laboratory studies (Hooker and Chapman, 1987).

2.4.6.2 Grimsel, Switzerland

Alexander et al. (1987) measured the distribution of natural decay series radionuclides and REE's in core sections of granite from the Swiss Radioactive Waste Cooperative (NAGRA) underground test facility at Grimsel, Switzerland. Two cores were studied, one from an area of active deposition of secondary uranium mineralization on the tunnel walls and one from an unmineralized area 1-2 m away. The ongoing remobilization of uranium was attributed to the introduction of oxygen into the rocks by the construction of the tunnels for the laboratory. The observed depth of redox disturbance was found to be about 2 cm rather that the <1mm predicted by theory. They found that both hydrothermal alteration and mechanical damage apparently enhance radionuclide retardation by increasing the rate and depth of penetration of a redox front, which forms iron oxides with strong radionuclide sorption capacities.

2.4.6.3 Eye-Dashwa Lakes Pluton, Canada

Kamineni (1986) evaluated the alteration and fracture fillings in the 2.7 Ga Eye-Dashwa Lakes Pluton, Ontario, Canada, in order to infer the mobility and redistribution of elements which are chemically similar to HLW radionuclides. The distribution of U, Th, and REE's were examined in unaltered granite, altered granite, and highly altered granite adjacent to open fractures, and fracture filling minerals. Th is concentrated in highly altered granite adjacent to open fractures and in fracture filling minerals. Kamineni concludes that remobilization of U, Th, and REE's is possible due to alteration along fractures, but that mobilization is limited by sorption onto "clays" (kaolinite, chlorite, and goethite), inclusion in structural site of minerals (epidote, sphene, calcite, and gypsum), and by precipitation of minerals such as bastnaesite, uraninite, and thorogummite.

2.4.7 Archaeologic analogs (other than glasses)

2.4.7.1 Bronze cannon, Baltic Sea

A bronze cannon submerged in the Baltic Sea and embedded in clay since 1676 was recovered in 1985 and investigated as an analog to copper HLW cannister stability (Hallberg et al., 1987). The cannon is 96.3 wt % Cu and was buried in a vertical position for 300 years in dense clays of a similar composition to the clays used in the Swedish repositories (illite, montmorillonite, and kaolinite). Corrosion products were mainly cuprite with lesser malachite. The corrosion products were evenly distributed on all parts of the cannon, suggesting that redox reactions other than those involving oxygen controlled the formation of the corrosion products. The clay pore waters had a measured pH of 7.0 and Eh of +450 mV, and so may be characterized as neutral and oxidizing. Migration of Cu into the clays was found to be only 4 cm; minimum rates of corrosion were estimated to be 1.5 - 7.5 mm per 100,000 yrs.

32.4.7.2 Gallo-roman cements, France

Gallo-roman baths constructed about 1800 years ago in western France are composed of concrete which has been considered as an analog to modern hydraulic binders (Petit, 1988). This concrete is mostly calcium carbonate, but also contains calcium aluminosilicates, hydrated calcium silicates, and ettringite deposits in fissures and voids. This composition is similar to modern binders, which suggests that the modern materials might also survive 1800 years in active alteration conditions.

2.4.8 Uraniferous veins

2.4.8.1 Marysvale, Utah

A natural analog study at Marysvale, Utah, was funded by the U.S. Department of Energy through the Office of Crystalline Repository Development. The site is an inactive hydrothermal uranium/molybdenum vein ore deposit hosted by granitic rocks (Shea, 1985). This fossil hydrothermal system was considered as an analog to a HLW repository at some time after the cannisters had been breached and interactions between groundwater, rock, and the waste had occurred (initially at elevated temperatures) (Shea, 1985). Fluid flow at Marysvale was controlled by faults and fractures (Shea, 1988). The mineralizing fluids are inferred to have had low pH and f_{O2} and to have had temperatures of about 200°C, and it is likely that precipitation of the uranium minerals occurred in response to increased pH after reaction with wall rocks (Rasmussen et al., 1985). At the deepest levels exposed, alteration of the wall rocks was to kaolinite and sericite, with deposition of uraninite, coffinite, jordisite, fluorite, molybdenite, quartz and pyrite; higher in the system, the fluids were increasingly oxidized (wall rocks are altered to hematite with deposition of "sooty" uraninite and umohoite) (Rasmussen et al., 1985).

2.4.8.2 Needle's Eye, Dalbeattie, UK

At Needle's Eye, pitchblende veins occur beneath coastal sediments and outcrop in a cliff of Silurian hornfelses (Ledoux et al., 1990). These veins have been dated at about 185 Ma (Hooker et al., 1987). At present, uranium is remobilized from the vein exposures in the cliff and is efficiently concentrated in the organic-rich sediments (a peat bog) at the base of the cliff (Hooker et al., 1987). The top 40 cm of the organic-rich sediments had uranium concentrations of up to 659 dpm g^{-1}, with decreasing uranium concentrations below 40 cm; groundwater from the top 40 cm has uranium concentrations of about 45 dpm g^{-1} whereas water in a stream 20 m away has only about 2 dpm g^{-1} (Hooker et al., 1987). Uranium fixation is controlled by humic substances in the upper silt layers and by sorption onto iron and manganese oxyhydroxides deeper in the silts (Roberts et al., 1988).

2.4.8.3 Broubster, UK

At Broubster, UK, uranium and hydrocarbon mineralization in sandstone provides a source of uranium, thorium and REE's to local groundwater which carries the elements to a peat bog about 100 m away (Read and Hooker, 1988). The migration of uranium and thorium were found to be quite different: after leaching, uranium is oxidized and transported in "true solution" as carbonate or phosphate species; thorium appears to be carried as a colloidal oxy-hydroxide phase. The mechanism of uranium accumulation in the peat is unknown but is not believed to be simple reduction. Thorium tends to co-precipitate with ferric flocs and may accumulate in the peat as a result of "pore-clogging" as the thorium colloids become trapped in the peat.

3. Criteria for selection and successful use of natural analogs

Chapman et al. (1984) presented the following criteria for selecting analogs:

1) The process involved should be clear-cut. Other processes which may have been involved in the geochemical system should be identifiable and amenable to quantitative assessment as well, so that their effects can be 'subtracted.'

2) The chemical analogy should be good. It is not always possible to study the behavior of a mineral system, chemical element or isotope identical to that whose behavior requires assessing. The limitations of this should be fully understood.

3) The magnitude of the various physico-chemical parameters involved (P, T, pH, Eh, concentrations, etc.) should be determinable, preferably by independent means and should not differ greatly from those envisaged in the disposal system.

4) The boundaries of the system should be identifiable (whether it is open or closed, and consequently how much material has been involved in the process being studied).

5) The time scale of the process must be measurable, since this factor is of the greatest significance (the *raison d'etre*) for a natural analog.

Airey and Ivanovich (1985) added a requirement for transport analogs:

6) A contaminant transport analog requires a spatial discontinuity across which to observe transport.

In addition to the above criteria, the following should be considered:

7) It is important that the source term (e.g. the original distribution of the elements of interest) be well constrained.

8) It is important that the environmental analog be close. The argument that an analog has suffered more extreme conditions than the system of comparison and therefore provides a conservative example is inappropriate. More extreme conditions are different conditions than those present in the system of comparison; such different conditions may include different processes or different combinations of processes than at the site of interest.

These criteria address the limitations of natural analog studies discussed in Section 1.2. It must be understood that it is highly unlikely that any one site can fully meet all of these desirable conditions. Realistically, these criteria will be approached at a site rather than achieved. It is important, therefore, to identify the analog aspects of greatest interest when evaluating a site for possible study.

4. Processes and events likely to control contaminant transport at Yucca Mountain

Processes and events that are likely to control contaminant transport at Yucca Mountain fall into two groups: (1) those processes and events which are likely to be important at any geologic HLW repository and (2) those processes and events which are peculiar to Yucca Mountain. Each of these is discussed in turn in the following sections.

4.1 Processes important to contaminant transport at any geologic HLW repository

Processes likely to be important in general to contaminant transport at geologic HLW repositories include:

- mineral/container/waste form dissolution and/or precipitation
- aqueous speciation of repository fluids (including organic complexing and radioelement speciation)
- colloid transport and/or retardation of waste elements
- microbial activity (redox controls, mineral precipitation/dissolution, and formation of organic colloids)
- matrix and intra-crystalline diffusion of elements
- fracture flow of fluids and gases
- matrix flow of fluids and gases
- changes in permeability due to thermal, chemical, or physical effects
- redox equilibration (kinetics) and redox front migration
- chemical species and mineral phase stability, solubility and metastability
- radiolysis

- thermally driven elemental diffusion
- convective (buoyancy driven) fluid movement
- alpha recoil effects
- adsorption
- ion exchange
- coprecipitation
- dispersion

4.2 Processes and events which are peculiar to contaminant transport at Yucca Mountain

A number of processes important to contaminant transport result from 1) the occurrence of the proposed repository at Yucca Mountain in tuffaceous host rock, 2) the chemically oxidizing environment of the site, and 3) the partial hydrologic saturation of the proposed repository horizon. The host tuffs contain large amounts of glass fragments which interact readily with groundwater. This interaction may take the form of elemental exchange, dissolution of the glass, or alteration of the glass or its components to new minerals. Large volumes of the tuffs which underlie the repository horizon have been altered so that they contain abundant zeolites; sorption onto these zeolites is likely to impede radionuclide transport. The response of these tuffs to thermal and hydrothermal alteration may change their sorptive capacity. Mineralogic alteration of the tuffaceous host rocks may also result in volume change which in turn could open fractures enhancing fluid flow and contaminant transport. The oxidizing environment at the site will increase the potential for the waste forms and the waste containers to degrade by oxidation, will determine the oxidation state of the radioelements and the phases that control their solubilities and concentrations, and will increase mobility of contaminant species that are more soluble in an oxidized state. The lack of hydrologic saturation at the repository level means that unsaturated fluid flow will control contaminant transport (as long as under-saturation is maintained), including vapor phase ^{14}C transport. Undersaturation also means that the hydrostatic pressure will be low, increasing the tendency for water vaporization in the presence of a thermal pulse from the waste.

4.3 Geochemical processes amenable to natural analog study

All of the processes listed above are potentially amenable to analog study. Choices among them therefore depend on which processes are considered to be the most important to contaminant transport at the proposed repository at Yucca Mountain, and which are well exhibited at identified natural analog sites.

5. Potential sites for a natural analog study

The Yucca Mountain site differs from those currently under investigation in other countries for permanent disposal of HLW in that the proposed repository horizon is in the hydrologically unsaturated, chemically oxidizing zone of a volcanic tuff. Sites under consideration elsewhere occur in a variety of host rocks, but they are generally in hydrologically saturated rocks in chemically reducing environments (IGC, 1989). These characteristics, and the processes which result from them (as discussed above), necessitate consideration of analog sites different from those reported in part two of this paper.

The uranium ore deposit at Peña Blanca, Mexico, and the archaeologic site at Santorini, Greece, have been identified as potential sites for a natural analog study appropriate to Yucca Mountain by Murphy et al. (1990) and uranium deposits at the McDermitt Caldera, Nevada-Oregon, have been proposed by Alexander and Van Luik (1990). A brief description of relevant aspects of the proposed repository site at Yucca Mountain is followed by descriptions of the Peña Blanca site, the McDermitt site, and the Santorini site with comparisons to Yucca Mountain and some general conclusions abstracted from Murphy et al. (1990).

5.1 Yucca Mountain, Nevada

Yucca Mountain is 150 km northwest of Las Vegas, Nevada, on federal land including part of the Nevada Test Site (NTS). Geologic investigations at Yucca Mountain were initially directed toward mineral and energy resource exploration; more recently, studies have been connected with

government activities at the NTS. Since 1977, the DOE has gathered considerable information on Yucca Mountain, and the information presented below is drawn largely from that collection (e.g. DOE, 1988).

Yucca Mountain is in the southern part of the Great Basin physiographic province, which is bounded to the east by the Colorado Plateau and to the west by the Sierra Nevada Range. The Great Basin is a product of continental extension over the last 20 Ma and is characterized by north-south trending horsts and grabens which are offset in southern Nevada by widely spaced regional strike slip faults. The southern part of the basin is composed of heavily eroded tilted-block ranges and sediment filled valleys. Tectonic features near Yucca Mountain are dominated by normal faults and other extensional structures. Yucca Mountain consists of a series of north-trending structural blocks which have been tilted eastward by west-dipping, high-angle normal faults related to Basin and Range tectonism over the last 7 Ma.

At Yucca Mountain a series of silicic volcanic units with a thickness ranging from 1 to 3 km rests on Silurian dolomite. Erupted from calderas north of Yucca Mountain, these volcanic rocks are variably welded, devitrified and altered ash flow and air fall tuffs with minor volcanic flows and breccias. The oldest of the silicic volcanic units at Yucca Mountain was deposited about 14 Ma ago and the youngest is about 12 Ma old. Subsequent small scale basaltic volcanism has occurred near Yucca Mountain episodically into the Pleistocene Epoch.

The proposed repository horizon is in a devitrified rhyolite ash-flow tuff unit in the Topopah Spring Member of the Paintbrush Tuff, which was deposited 12 - 13 Ma ago and is about 300 m thick at Yucca Mountain. The basal welded vitrophyre of the Topopah Spring Member grades upward into a densely welded, devitrified, nonlithophysal zone from 27 to 56 m thick which is the proposed location of the repository. This zone is phenocryst poor (2 - 22%); the phenocrysts include sanidine, plagioclase (andesine to oligoclase), and minor quartz, biotite, amphibole, iron-titanium oxides, allanite, and zircon. The primary groundmass of the Topopah Spring Member is glass and/or devitrification products comprised of alkali feldspar and silica minerals. Smectite and the silica-rich zeolite minerals clinoptilolite and mordenite are dominant

alteration products. In some areas primary glass is completely converted to zeolites. Overall, the Topopah Spring Member averages about 70-80% SiO_2, 10-15% Al_2O_3, and 5-8% K_2O (Byers, 1985). Approximately 10 m beneath the Topopah Spring Member is a layer 30 - 300 m thick which is locally rich in zeolites (60 - 80 % clinoptilolite and mordenite).

The saturated zone groundwaters from tuffaceous aquifers at Yucca Mountain are dilute ($<10^{-2}$ m), oxidizing, sodium bicarbonate solutions, rich in silica, with lesser calcium, potassium, magnesium, chloride, sulfate, nitrate, and fluoride (Kerrisk, 1987). Information about the pore waters in the unsaturated zone is limited at this time. The proposed repository horizon is about 200 m above the water table in rocks thought to be 40 to 70% saturated with water. At these saturation levels, it is believed that the fluid pressure would be low enough to allow the water to readily vaporize as temperatures increase in the near field. Water movement in the unsaturated zone is thought to be slow (e.g. 0.5 mm/yr) if it is dominated by matrix flow. The chemistry, distribution and behavior of water in unsaturated, fractured tuffs is incompletely understood, particularly under conditions of thermal perturbations, and is currently a subject of investigation.

Yucca Mountain is in a mid-latitude desert climate with average annual precipitation less than 15 cm and average temperature of about 13°C. Only about 0.3% of the local precipitation is thought to penetrate to the deeper portions of the unsaturated zone. A variety of evidence (e.g. pack rat middens, palynology, stable isotopes) suggests that the climate has been arid to semi arid for the last 2 Ma. The aridity of the region results in little groundwater recharge and hence a low rate of groundwater movement. The groundwater in southern Nevada does not discharge into rivers or large bodies of surface water; rather, it discharges by evapotranspiration (e.g. at Alkali Flats, California) and at springs (e.g. at Death Valley, California).

5.2 Peña Blanca, Mexico

The Peña Blanca district is in northern Mexico about 50 km north of Chihuahua City and is part of the Chihuahua City uranium province. Uranium deposits in the district have been drilled and/or developed by underground or open pit mining over a period of 20 years (Goodell, 1981);

however, there has been no mining activity at Peña Blanca since 1983, except in the extreme northwest of the area where an exploration adit was completed in 1987 (J. Altamirano, personal communication). Combined, these deposits include more than 2000 metric tons of U_3O_8 and constitute the bulk of Mexican uranium resources.

Peña Blanca is part of the northern Mexico basin and range system and lies near the boundary between a stable craton to the west and a more mobile belt to the east (Goodell, 1985). The regional structural province is bounded to the east by the Trans-Pecos Range and to the west by the Sierra Madre Occidental (George-Aniel et al., 1985). The Sierra Peña Blanca is a west-dipping horst block with a superimposed set of parallel northwest-striking normal (extensional) faults.

Peña Blanca stratigraphy consists of a sequence of Cretaceous limestones and mudstones on which a series of Tertiary silicic volcanics has been deposited (Cardenas-Flores, 1985). Host rocks for most of the uranium deposits are the Escuadra and Nopal Formations which are composed of variably welded tuffs with air-fall, ignimbrite, vitrophyre, lahar, and water-worked units. The preserved total thickness of the volcanic units varies over the Sierra Peña Blanca area from 106 to 538 m, and rock ages range from 44 Ma to 35 Ma (Goodell, 1981).

The Peña Blanca tuffs are rhyolitic ignimbrites consisting largely of glass devitrified to cristobalite and feldspar with quartz, sanidine and minor biotite phenocrysts (Cardenas-Flores, 1985). These tuffs have SiO_2 contents between 63 and 78%, Al_2O_3 at 11 to 14%, and K_2O at 4 to 7% (Goodell, 1981). Background uranium concentrations of the tuffs range from about 4 to 10 ppm (George-Aniel et al., 1985). Uranium in the ores was likely derived from the alteration of volcanic glass in the tuffs by convective hydrothermal groundwater systems. Uranium deposits, tentatively dated at 3.5 Ma, are commonly associated with minor hydrothermal alteration at faults, fractures, and breccias. Fluid inclusion evidence suggests mineralization by low salinity (0 - 4.94 wt % NaCl equiv.), moderate temperature (150 - 250°C) fluids (George-Aniel et al., 1985). The present uranium mineralization is predominantly uranyl silicates (mostly uranophane, nominally $Ca(UO_2)_2Si_2O_7 \cdot 6H_2O$), however, small quantities of uraninite (UO_{2+x}) occur at the Nopal I

deposit. The uraninite occurs as irregularly shaped masses of fine-grained crystals and is best described as pitchblende. It appears that pitchblende was the original form of the uranium mineralization and that it has been oxidized and altered to form the uranium silicates.

The distribution of uranium indicates that mineralizing hydrothermal fluids circulated primarily in faults and fractures, with brecciated zones, and small fissures controlling detailed ore distribution. Matrix flow may have been important locally; some samples show pervasive penetration of mineralizing fluids through the matrix of the tuffs (e.g. samples from the Puerto I mine in which feldspar phenocrysts are replaced by weeksite, $K_2(UO_2)_2Si_6O_{15}\cdot 4H_2O$). There is general agreement that the ores were emplaced by a geothermal, convecting groundwater system (Goodell, 1981; Goodell, 1985; Cardenas-Flores, 1985) which may have had significant inputs of volcanic fluids (George-Aniel et al., 1985) in addition to dominant meteoric waters (Goodell, 1985).

All of the Peña Blanca uranium deposits are presently above the water table in the unsaturated zone. At present, uranium is being remobilized by oxidizing meteoric groundwaters which episodically penetrate the deposits through fractures in the unsaturated tuffs. The climate in the Peña Blanca area is arid, with annual precipitation of about 24 cm and average annual temperature of 19° C.

The Nopal I deposit at Peña Blanca has been the subject of earlier research (e.g. Goodell, 1981; Cardenas-Flores, 1985; George-Aniel et al., 1985; Leroy et al., 1987; Ildefonse et al., 1990a, b, c; George-Aniel et al., 1991). The deposit consists of a near vertical breccia pipe about 20 by 40 m in horizontal dimension which extends across the boundary of the Nopal and Coloradas formations, and is known to cover a vertical interval of at least 100 m. The host formations are silicic tuffs and are separated by a basal vitrophyre. The breccia pipe contains high grade uranium mineralization in the form of pitchblende and uranyl silicates. The lowest level of the deposit is significantly above the water table (perhaps 100 to 200 m), as indicated by water levels in nearby wells.

Uraninite at Nopal I is interpreted to have been precipitated along with pyrite and kaolinite (Ildefonse et al., 1990a; George-Aniel et al., 1991). Fluid inclusion studies suggest that this uraninite-pyrite-kaolinite assemblage formed at about 190 to 250°C from solutions with a median salinity of 2.5 equivalent wt. % NaCl (George-Aniel et al., 1991). Subsequent oxidizing hydrothermal alteration has produced rims of soddyite $(UO_2)_2SiO_4 \cdot 2H_2O$, uranophane $Ca(UO_2)_2Si_2O_7 \cdot 6H_2O$), and bequerellite-group minerals, $(UO_2)_7 \cdot 11H_2O$, around the uraninite (Ildefonse et al., 1990a). There may also have been supergene alteration of the mineralization (George-Aniel et al., 1991). There is some spatial zoning within the breccia pipe, with K-phases (e.g. weeksite $K_2(UO_2)_2Si_6O_{15} \cdot 4H_2O$, boltwoodite $K(UO_2)(SiO_4)(H_3O)$, carnotite $K_2(UO_2)_2V_2O_8 \cdot 3H_2O$) concentrated in the center of the pipe and Ca-phases (e.g. uranophane $Ca(UO_2)_2Si_2O_7 \cdot 6H_2O$) toward the margins of the pipe (Ildefonse et al., 1990a). Paragenetically, uraniferous opal was deposited after the uranophane, which was itself deposited upon the earlier uranium mineralization (Ildefonse et al., 1990a).

Release and transport of radionuclides in a Yucca Mountain HLW repository will be affected by the gas, groundwater and mineral chemistry and by the hydrologic properties of the medium. The exceptional geologic, hydrologic, and geochemical similarities between the sites suggest that mass transfer and transport processes at Peña Blanca are likely to be comparable to those which would occur at Yucca Mountain. Specifically, alteration of the uranium ores at Peña Blanca by hydrothermal and supergene processes resulted in elemental remobilization and development of phase assemblages analogous to those that would also characterize the Yucca Mountain repository. The geologic record at Peña Blanca permits recognition and detailed evaluation of these processes. Furthermore, it offers the opportunity to test models that will be used to predict the evolution of geologic nuclear waste disposal systems.

Uraninite (UO_{2+x}) is structurally and compositionally similar to spent nuclear fuel (largely UO_2; Johnson and Shoesmith, 1988), which is the predominant waste form proposed for Yucca Mountain. Therefore, the geochemical processes which controlled elemental redistribution during alteration of the primary uraninite mineralization at Nopal I may be considered to be analogous to

alteration of spent fuel in a HLW repository and the resulting radionuclide mobilization. The primary and secondary ore and host rock minerals can provide information on the composition and evolution of the remobilizing fluids. Detailed studies of the secondary mineral assemblages and the paragenetic relations among the phases may indicate the relative stabilities and sequence of alteration minerals to expect during hydrothermal degradation of spent nuclear fuel. The distributions and compositions of these secondary minerals may indicate the relative mobilities of elemental species. Such secondary uranium minerals may effectively control the release of spent fuel radionuclides to the broader environment. Analysis of uranium-series radionuclides may allow absolute time constraints to be placed on the remobilization of the ore components at Peña Blanca under varying conditions, and hence provide information on the rate and controls of elemental transport. Secondary localization of uranium, thorium, and other trace elements in or on specific minerals may reveal which phases are important to retardation of radionuclide migration.

Among the several uranium deposits in the Peña Blanca district, the Nopal I deposit has been identified as the most promising site for a geochemical analog study relevant to a HLW repository at Yucca Mountain. The suite of uranium minerals of varying oxidation states, including pitchblende and the assemblage of uranyl silicate minerals, is a good analog of the alteration of spent nuclear fuel in a silicic oxidizing environment. Mining operations at Nopal I have left excellent exposure for field research and sampling, and several recent and detailed petrographic studies of this deposit provide valuable background information.

5.3 McDermitt Caldera, Nevada and Oregon

The McDermitt Caldera, located on the Nevada-Oregon border, contains "the most significant" volcanogenic uranium deposits in the northern Basin and Range (Dayvault et al., 1985). The National Uranium Resource Evaluation study conducted by the Department of Energy identified approximately 36,000 short tons of U_3O_8 at McDermitt.

The McDermitt Caldera forms an ellipse about 40 km north-south and about 30 km east-west. Large-scale silicic volcanism occurred at McDermitt between 18.5 and 15.8 Ma ago

(Dayvault et al., 1985). This activity was followed by the eruption of iron-rich andesite and icelandite flows within the caldera and finally by resurgence of the central dome of the caldera and the deposition of lacustrine sediments (mudstones, tuffaceous sandstones, and air fall tuffs) in the caldera moat. Uranium mineralization at McDermitt occurs in the ring fracture zone of the caldera, the moat and the outer part of the resurgent dome.

Hydrothermal uranium deposits at the McDermitt Caldera can be separated into five distinct types: 1) uranium associated with pyrite and titanium minerals hosted by icelandite lavas, 2) uranium with fluorite, pyrite, and a zirconium-bearing clay in steeply dipping veins in commendite lava flows, 3) hot spring mercury deposits developed in volcanic sediments with anomalous uranium contents, 4) uranium in silicified and argillized rhyolites, and 5) stratabound uranium hosted by caldera moat sediments.

The Moonlight mine is the only area at McDermitt with recorded uranium production (approximately 700 kg of U_3O_8 with an average grade of about 0.13% U_3O_8). Host rocks at the Moonlight are dacite flows and rhyolite ash flow tuffs in the footwall and biotite rhyolite breccias in the hanging wall; the ore occurs mainly in the rhyolite breccias. Uraninite has been noted at the mine, but Dayvault et al. (1985) were unable to identify any uranium minerals during their investigation of the site due to the small grain size of the ore minerals. The ore at Moonlight is exposed by an inclined adit some 80 m deep which is presently flooded at a depth of about 50 m.

The McDermitt Caldera uranium deposits have been mentioned as possible analogs to the proposed repository at Yucca Mountain (Alexander and Van Luik, 1990). It is possible that some of the uranium mineralization at McDermitt may constitute good analogs to aspects of contaminant transport at Yucca Mountain, however, it is not clear that such is the case. Of the many uranium occurrences at McDermitt only one has been exposed by mining. Most of the uranium at McDermitt is hosted by rocks which are quite different from the repository horizon at Yucca Mountain (e.g. icelandite lavas, lacustrine sediments, and rhyolite breccias); and the nature of the uranium mineralization at the one mine with recorded production is presently uncertain and is in any event very fine grained.

5.4 Santorini, Greece

The eruption at Stronghyle volcano in approximately 1645 B.C. (Hammer et al., 1987) buried a Minoan city under volcanic debris on what is now the Akrotiri peninsula on the island of Thera, Santorini. This event was one of the largest explosive eruptions in post-glacial time; a caldera with an area of 83 km^2 and a depth of 600-800 m was formed (Watkins et al., 1978). Since archaeological excavations began in 1967, much information has been unearthed regarding the archaeology and geology of the area. Investigations at the site are ongoing.

Santorini comprises a complex of volcanos located about 100 km north of Crete. Prior to the 1645 B.C. eruption, the single large island of Stronghyle occupied the area of the Santorini group. The great eruption destroyed Stronghyle and left the islands of Thera, Therasia, and Aspronisi as remnants. During the past 1800 years, the islands of Palea and Nea Kameni have formed in the caldera by submarine and subaerial volcanism (Pichler and Kussmaul, 1980). All of the eruptions have been confined to a 3-4 km wide, northeast trending graben which formed as a result of extension in the eastern Mediterranean over the past 10 Ma (Heiken and McCoy, 1984).

The oldest subaerial volcanic activity at Santorini deposited ash and pumice on Lower Tertiary phyllite basement approximately 1 Ma ago. Volcanic activity continued intermittently, depositing 30 to 90 m of pumice, ash, and lava flows on the island. The Minoan eruption buried settlements under 30 m of volcanic sediment (Pichler and Friedrich, 1980). Four phases of this eruption have been identified (Heiken and McCoy, 1984): 1) plinian eruption with massive pumice fall; 2) phreatomagmatic base surge of fine ash and pumice lapilli; 3) phreatomagmatic eruption of pumice bombs, lithic fragments, ash, and including distal mudflows; and 4) ignimbritic eruption deposited at temperatures greater than 500°C (Wright, 1978). All of the Minoan eruption phases deposited pyroclasts of rhyodacitic composition (Heiken and McCoy, 1984). Paleosols are preserved in several places below the Minoan tuff and locally reach thicknesses of 3-4 m. These paleosols developed on the series of welded tuffs and ignimbrites upon which the buildings of

Akrotiri (the largest of the known Minoan towns buried by the eruptions) were founded (Pichler and Friedrich, 1976).

The vitric portions of the silicic tuff near Akrotiri has been altered to a mixture of K and K-Ca rich clinoptilolite, opal-CT, and clays (Tsolis-Katagas and Katagas, 1989). In addition to clinoptilolite, some mordenite occurs, but no analcime was found. Zeolite volumes vary from trace amounts to about 60% of the rock. The alteration of the original dacites to the zeolite-rich rocks was accompanied by an increase in H_2O and MgO and a decrease in SiO_2, Na_2O, K_2O, Al_2O_3, and CaO.

The anthropological horizon at Akrotiri is located in the unsaturated zone above the groundwater table. In the semi-arid climate the mean annual precipitation is essentially equivalent to the estimated annual evapotranspiration loss (approximately 35 cm/year, mean air temperature is 17° C) (Marinos and Marinos, 1978). The hygroscopic character of the upper soil layers generally prevents deep infiltration of rain water even though the deeper soils appear to be permeable (Marinos and Marinos, 1978). In the Akrotiri area, steep-sided gullies have been cut into the tephra sequence by runoff after exceptionally heavy rains. Paleoclimatological data indicate that the climate on Santorini at the time of its eruption did not differ strongly from the present climate; air temperatures were slightly warmer and the climate was slightly more arid (McCoy, 1980).

Elemental migration at the Akrotiri site, analogous to that which would occur at the Yucca Mountain repository, could possibly be well constrained chemically, temporally, and spatially using artifacts as analogs for contaminant sources. For example, numerous lead balance weights discovered at this site have distinct chemical compositions (Gale and Stos-Gale, 1981). Oxidation rinds developed on the lead weights (Petruso, 1978) suggest that some components have been released during alteration. Artifacts may therefore constitute well constrained point sources for dispersion of trace species analogous to migration of waste elements at Yucca Mountain. The known period of 3600 years between the eruption of Santorini and the present corresponds well to the time frame of interest in the evaluation of the HLW repositories. The rock types (including

alteration mineralogies) enclosing the archaeological site are similar to those at Yucca Mountain, and the climates and hydrological relations are comparable.

Information required for a detailed study of the Santorini analog site includes compositions of lead weights or other artifacts (major and trace elements). Mineralogy and composition of the alteration products of the artifacts (e.g. oxide coatings), and more detailed knowledge of the primary and alteration mineralogy of the rocks surrounding the artifacts is required. Bulk chemical compositions of the rocks surrounding the weights must be measured as a function of location, with particular emphasis on concentration gradients of (trace) elements derived from the artifacts. Present and former hydrological relations in the area of the contaminant analogs and groundwater compositions (including local variations) are also of importance.

5.5 Conclusions

This review shows that a wide variety of material occurrences and processes have been studied as natural analogs. Broadly speaking, many sites could be considered as comparable to some aspect of a high level waste repository. It is necessary, though, to select sites for analog study which most closely match the important characteristics of the system of interest while bearing in mind the limitations inherent in analog studies. These limitations include the incompleteness of the geologic record, the difficulty of quantifying important effects, the presence at a given site of only a subset of the processes which will occur in a repository, and the existence at natural sites of materials which are only approximations of the materials to be used in a repository. These limitations notwithstanding, it is only through the use of natural analogs that one may identify and confirm that a process occurs in nature as well as in a laboratory or in theory. Natural analogs allow testing of the pertinence of individual processes over geologic time; the assessment of the relative importance of various processes; and the effects of the coupling of processes. Through analog investigations we may determine the conditions under which the processes occur and the effects of the processes as well as the magnitude and duration of the phenomena.

Validation of numerical models is the reason most often cited for conducting natural analog investigations. However, the likelihood that a study will produce results useful for validation and the nature of the validation which may reasonably be expected from analog studies must be clearly understood. Because of the uncertainties involved in analog studies, it may be that a given model cannot be validated (in a strict sense) through the use of natural analogs. Nevertheless, natural analogs provide the only means of testing models of long-term processes for pertinence. The results of short-term, small-scale laboratory experiments, and the long-term predictions of models based on the laboratory experiments, may be compared to observations of natural systems which have operated for long periods at large scales (i.e. natural analogs). This process of testing by comparison constitutes validation of the model. Validation of a predictive model by such comparison provides a measure of assurance that the model accurately reflects future behaviors.

Uranium deposits at Peña Blanca, Mexico and archaeological sites at Santorini, Greece offer good analogs of processes that would be expected to occur in the geologic setting of the proposed HLW repository at Yucca Mountain, Nevada. Some areas of uranium mineralization at the McDermitt Caldera may be good analogs to aspects of a repository at Yucca Mountain, but the limited exposure, differences in host rocks, and lack of knowledge as to the ore mineral compositions make the possibility of a McDermitt analog uncertain.

The sites at both Peña Blanca and Santorini are in the hydrologically unsaturated zone of siliceous tuff sequences, and both sites occur in climates similar to that of southern Nevada. The past and present oxidation of uraninite at Peña Blanca constitutes an analog for the alteration of spent nuclear fuel. Processes governing the oxidation of Peña Blanca uraninite, the resulting dispersion of uranium from the sites of original mineralization, and the formation of secondary uranyl silicates are analogous to processes that may affect spent nuclear fuel and elemental migration at the proposed repository. Studies using buried artifacts at the Santorini archaeological site as analogs of contaminant sources would permit analyses of the rates and mechanisms of trace elemental migration in a geologic setting analogous to Yucca Mountain. The initial and boundary

conditions at Santorini could be especially closely constrained, and the time period since burial of the artifacts (3600 years) is comparable to the period of interest in radioactive waste management.

Though Peña Blanca and Santorini provide good analogs to some processes important to high level waste containment, there are no perfect analogs. The source term and boundary conditions at Peña Blanca may be difficult to constrain closely because of the complexity of the original hydrothermal systems and subsequent alteration. Conversely, at Santorini (where the source term and boundary conditions are relatively well known) the material and elemental sources are not necessarily close analogs to spent fuel or vitrified waste forms. Nevertheless, the physical similarities between these sites and Yucca Mountain could permit identification and characterization of relevant waste form degradation and contaminant migration phenomena, and could aid in the development and validation of predictive models for performance assessments.

6. References

This bibliography contains only the references cited in the foregoing text.

AAEC. 1986. The Alligator Rivers analogue project - proposed international project on analogues of radioactive waste repositories. Australian Atomic Energy Commission. Technical Brief.

Airey, P. L. 1986. Radionuclide migration around uranium ore bodies in the Alligator Rivers region of the Northern Territory of Australia: analogue of radioactive waste repositories - a review. *Chemical Geology* 55:255-268.

Airey, P. L., P. Duerden, D. Roman, C. Golian, T. Nightingale, T. Payne, B. G. Davey, D. Gray, A. Snelling and D. Lever. 1987a. The prediction of the long-term migration of radionuclides in the far field of high level waste repositories; results from the Alligator Rivers natural analogue study. *The Geological Disposal of High Level Radioactive Wastes*. Greece: Theophrastus: 507-524.

Airey, P. L., P. Duerden, D. Roman, G. Golian, T. Nightingale, T. Payne, B. G. Davey, D. Gray, J. Fabryka-Martin, D. B. Curtis, A. Snelling, D. A. Lever and P. J. Shirvington. 1987b. Radionuclide migration around uranium ore bodies - analogue of radioactive waste repositories - Annual Report for 1984-1985. (manuscript completed 1986, published 1987) Australian Atomic Energy Commission for U.S. NRC. NUREG/CR-5040, AAEC/C55.

Airey, P. L. and M. Ivanovich. 1985. Geochemical analogs of high level radioactive waste repositories. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analog Working Group, First Meeting*. Brussels: CEC.

Alexander, D. H. and A. E. Van Luik. 1990. Natural analogue studies useful in validating regulatory compliance analyses. *Proceedings GEOVAL*, Stockholm, Sweden. In press.

Alexander, W. R., R. D. Scott, A. B. MacKenzie and I. G. McKinley. 1987. Natural analog studies at Grimsel, southern Switzerland. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium*. Brussels: CEC:473-484.

Apted, M. J. 1990. Natural analogues for the predictive reliability of the engineered barrier system for high-level waste. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print*. Brussels: Commission of the European Communities: n° EUR 13014 EN.

Arai, T., Y. Yusa, N. Sasaki, N. Tsunoda and H. Takano. 1988. Natural analogue study of volcanic glass - a case study of basaltic glasses in pyroclastic fall deposits of Fuji Volcano, Japan. *Scientific Basis for Nuclear Waste Management XII - Materials Research Society Symposium Proceedings*. Pittsburgh: Materials Research Society: 73-80.

Barretto, P. M. and K. Fujimori. 1986. Natural analogue studies: geology and mineralogy of Morro do Ferro, Brazil. *Chemical Geology* 55:297-312.

Brondi, A. 1985. Italian activity in the field of natural analogues and natural evidence. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, First Meeting*. Brussels: CEC:112-128.

Brookins, D. G. 1976a. Oklo phenomenon: geological and nuclear aspects. *American Association of Petroleum Geologists Bulletin* 60:1391.

Brookins, D. G. 1976b. Shale as a repository for radioactive waste: the evidence from Oklo. *Environmental Geology* 1:255-259.

Brookins, D. G. 1980. Geochemical study of a lamprophyre dike near the WIPP site. *Scientific Basis for Nuclear Waste Management III - Materials Research Society Symposium Proceedings*. New York: Plenum Press: 307-313.

Brookins, D. G. 1984. Natural analogs. *Geochemical Aspects of Radioactive Waste Disposal*. New York: Springer-Verlag: 197-231.

Brookins, D. G. 1986. Natural analogues for radwaste disposal: elemental migration in igneous contact zones. *Chemical Geology* 55:337-344.

Buddemeier, R. W. and J. R. Hunt. 1988. Transport of colloidal contaminants in groundwater: radionuclide migration at the Nevada Test Site. *Applied Geochemistry* 3:535-548.

Byers, C. D., M. J. Jercinovic and R. C. Ewing. 1987. A study of natural glass analogues as applied to alteration of nuclear waste glass. Argonne National Laboratory for the U.S.NRC. ANL-86-46, NUREG/CR-4842.

Cardenas-Flores, D. 1985. Volcanic stratigraphy and U-Mo mineralization of the Sierra de Peña Blanca District, Chihuahua, Mexico. *Uranium Deposits in Volcanic Rocks*. Austria: International Atomic Energy Agency, proceedings of a technical committee meeting, El Paso, TX April 1984. IAEA-TC-490: 125-136.

Cathles, L. M. 1988. Perspectives from industrial scale natural analogues. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting*. Snowbird, Utah: CEC:220-226.

Chapman, N. 1985. Analogue of elemental diffusion over 5000 years in sediments: close but not close enough? B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, First Meeting*. Brussels: CEC:157-159.

Chapman, N. A., I. G. McKinley and J. A. T. Smellie. 1984. The potential of natural analogues in assessing systems for deep disposal of high-level radioactive waste. Swedish Nuclear Fuel and Waste Management Co. (SKB) and the Swiss Radioactive Waste Cooperative (NAGRA). NTB 84-41. KBS 84-16. Eir Ber 545.

Chapman, N. and I. McKinley. 1990. Radioactive waste: back to the future? *New Scientist* 54-58.

Coles, D. G. and L. D. Ranspott. 1982. ^{106}Ru migration in a deep tuffaceous alluvium aquifer, Nevada Test Site. *Science* 215:1235-1237.

Cowan, G. A. 1976. A natural fission reactor. *Scientific American* 235:36-47.

Cowan, R. and R. C. Ewing. 1988. Freshwater alteration of basaltic glass, Hanauma Bay, Oahu, Hawaii: a natural analogue for the alteration of borosilicate glass in fresh water. *Scientific Basis for Nuclear Waste Management XII - Materials Research Society Symposium Proceedings*. Pittsburgh: Materials Research Society: 49-56.

Cramer, J. J. 1986. Sandstone-hosted uranium deposits in northern Saskatchewan as natural analogs to nuclear fuel waste disposal vaults. *Chemical Geology* 55:269-279.

Cramer, J. J., P. Vilks and J. P. A. Larocque. 1987. Near-field analog features from the Cigar Lake uranium deposit. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium.* Brussels: CEC:59-72.

Crisman, D. P. and G. K. Jacobs. after 1982. Native copper deposits of the Portage Lake Volcanics, Michigan: Their implications with respect to canister stability for nuclear waste isolation in the Columbia River Basalts beneath the Hanford Site, Washington. Department of Energy. RHO-BW-ST-26 P, Contract DE-AMO6-76-RLO2225.

Cross, J. E., A. Haworth, I. Neretnieks, S. M. Sharland and C. J. Tweed. 1989. Modelling of redox front and uranium movement in a uranium mine at Poços de Caldas. Migration '89. Monterey, CA.

Curtis, D., T. Benjamin, A. Gancarz, R. Loss, K. Rosman, J. De Laeter, J. E. Delmore and W. J. Maeck. 1989. Fission product retention in the Oklo natural fission reactors. *Applied Geochemistry* 4:49-62.

Curtis, D. B. 1986. Geochemical controls on ^{99}Tc transport and retention. *Chemical Geology* 55:227-231.

Curtis, D. B., T. M. Benjamin and A. J. Gancarz. 1981. The Oklo reactors: natural analogs to nuclear waste repositories. *The technology of high-level nuclear waste disposal DOE/TIC-4621.* DOE: 255-283.

Curtis, D. B. and R. E. Perrin. 1988. Plutonium Geochemistry. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting.* Snowbird, Utah: CEC:

Dayvault, R. D., S. B. Castor and M. R. Berry. 1985. Uranium associated with volcanic rocks of the McDermitt Caldera, Nevada and Oregon. *Uranium Deposits in Volcanic Rocks.* Austria: International Atomic Energy Agency, proceedings of a technical committee meeting, El Paso, TX April 1984. IAEA-TC-490: 379-409.

De Laeter, J. R., K. J. R. Rosman and C. L. Smith. 1980. The Oklo natural reactor: cumulative fission yields and retentivity of the symmetric mass region fission products. *Earth and Planetary Science Letters* 50:238-246.

De Laeter, J. R. 1985. The Oklo reactors: natural analogues to nuclear waste repositories. *Search* 16:193-196.

DOE. 1988. "Site characterization plan - Yucca Mountain site, Nevada Research and Development Area, Nevada." U.S. Department of Energy. DOE/RW-0199.

Duffield, J. R., L. Xu and D. R. Williams. 1988. Chemical speciation modelling of the South Terras and Madeira Abyssal Plain natural analogue sites. Department of the Environment. DOE-RW-87.128; APCM-56.

Edghill, R. 1988. Colloids in Koongarra groundwater. Australian Nuclear Science and Technology Organisation. ANSTO Alligator Rivers Analogue Project - Progress Report, May 1988 - August 1988 :245-252.

Edghill, R. and B. G. Davey. 1988. Alpha activity and mineralogy associations. Australian Nuclear Science and Technology Organisation. ANSTO Alligator Rivers Analogue Project - Progress Report, May 1988 - August 1988 :147-156.

Eisenbud, M., K. Krauskopf, E. P. Franca, W. Lei, R. Ballad and P. Linsalata. 1984. Natural analogs for the transuranic actinide elements: an investigation in Minas Gerais, Brazil. *Environmental Geology and Water Science* 6:1-9.

Elders, W. A. 1987. A natural analog for near-field behaviour in a high level radioactive waste repository in salt: the Salton Sea geothermal field, California, USA. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium.* Brussels: CEC:

Ericson, J. E. 1980. Durability of rhyolitic obsidian glass inferred from hydration dating research. *Scientific Basis for Nuclear Waste Management III - Materials Research Society Symposium Proceedings.* New York: Plenum Press: 283-289.

Finch, R. J. and R. C. Ewing. 1989. Alteration of natural UO2 under oxidizing conditions from Shinkolobwe, Katanga, Zaire: a natural analogue for the corrosion of spent fuel. Swedish Nuclear Fuel and Waste Management Company (SKB). Technical Report 89-37.

Gale, N. H. and Z. Stos-Gale. 1981. Lead and silver in the ancient Aegean. *Scientific American* 244:176-192.

Gancarz, A., G. Cowan, D. Curtis and W. Maeck. 1980. 99Tc, Pb and Ru migration around the Oklo natural fission reactors. *Scientific Basis for Nuclear Waste Management.* New York: Plenum Press: 601-608.

Gauthier-Lafaye, F. and H. Ohmoto. 1989. Natural fission reactors of Oklo. *Economic Geology* 84:2286-2295.

George-Aniel, B. G., J. Leroy and B. Poty. 1985. Uranium deposits of the Sierra Peña Blanca. *Uranium Deposits in Volcanic Rocks.* Austria: International Atomic Energy Agency, proceedings of a technical committee meeting, El Paso, TX April 1984. IAEA-TC-490: 175-186.

George-Aniel, B., J. L. Leroy and B. Poty. 1991. Volcanogenic uranium mineralization in the Sierra Peña Blanca District, Chihuahua, Mexico: three genetic models. *Economic Geology* 86:233-248.

Goodell, P. C. 1981. Geology of the Pena Blanca uranium deposits, Chihuahua, Mexico. *Uranium in Volcanic and Volcaniclastic Rocks- AAPG Studies in Geology No. 13.* El Paso, TX: American Association of Petroleum Geologists: 275-291.

Goodell, P. C. 1985. Chihuahua City uranium province, Chihuahua, Mexico. *Uranium Deposits in Volcanic Rocks.* Austria: International Atomic Energy Agency, proceedings of a technical committee meeting, El Paso, TX April 1984. IAEA-TC-490: 97-124.

Goodwin, B. W., J. J. Cramer and D. B. McConnell. 1988. The Cigar Lake uranium deposit: an analogue for nuclear fuel waste disposal. B. Come and N. Chapman, eds. *Commission of*

the European Communities Natural Analogue Working Group, Third Meeting. Snowbird, Utah: CEC:180-189.

Hallberg, R. O., P. Ostlund and T. Wadsten. 1987. A 17th century bronze cannon as analogue for radioactive waste disposal. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium*. Brussels: CEC:

Hammer, C. U., H. B. Clausen, W. L. Friedrich and H. Tauber. 1987. The Minoan eruption of Santorini in Greece dated to 1645 BC? *Nature* 328:517-519.

Hardy, C. J. and P. Duerden. 1988. Progress in the Alligator Rivers analogue project. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting*. Snowbird, Utah: CEC:43-49.

Heiken, G. and F. McCoy Jr. 1984. Caldera development during the Minoan eruption, Thira, Cyclades, Greece. *Journal of Geophysical Research* 89:8441-8462.

Hofmann, B. 1988. Geochemical analogue study in the Krunkelbach mine, Mezenschwand, Southern Germany: Geology and water - rock interaction. *Scientific Basis for Nuclear Waste Management XII - Materials Research Society Symposium Proceedings*. Pittsburgh: Materials Research Society: 921-926.

Hofmann, B., J. P. Dearlove, M. Ivanovich, D. A. Lever, D. C. Green, P. Baertschi and T. Peters. 1987. Evidence of fossil and recent diffusive element migration in reduction haloes from Permian red-beds of northern Switzerland. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium*. Brussels: CEC:217-238.

Holmes, D. C., A. E. Pitty and D. J. Noy. 1990. Geomorphological and hydrogeological features of the Poços de Caldas caldera and the Osamu Utsumi mine and Morro do Ferro analogue study sites. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print*. Brussels: Commission of the European Communities: n° EUR 13014 EN.

Hooker, P. J. 1988. The U.K. natural analogues programme. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting*. Snowbird, Utah: CEC:88-95.

Hooker, P. J. and N. A. Chapman. 1987. UK (United Kingdom) natural analogue co-ordinating group: first annual report. Department of the Environment. DOE-RW-88.036.

Hooker, P. J., N. A. Chapman, A. B. MacKenzie, R. D. Scott and M. Ivanovich. 1987. Natural analogues of radionuclide migration in sediments in Britain. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium*. Brussels: CEC:

Hooker, P. J., A. B. MacKenzie, R. D. Scott, M. Ivanovich, T. K. Ball, I. R. Basham, A. J. Bloodworth and P. D. Roberts. 1986. Natural analogues of radionuclide migration: reconnaissance study of sites. British Geological Survey. FLPU 86-6.

IAEA, 1982. Radioactive waste management glossary. IAEA Report IAEA-TECDOC-264.

IGC, 1989. Geological problems in radioactive waste isolation - a world wide review, Workshop W3B. P. A. Witherspoon and G. de Marsily, conveners. 28th International Geological Congress, Washington, D.C. Lawrence Berkeley Laboratory. LBL-27333.

Ildefonse, P., J.-P. Muller, B. Clozel and G. Calas. 1990a. Study of two alteration systems as natural analogues for radionuclide release and migration. *Engineering Geology* 29:413-439.

Ildefonse, P., J.-P. Muller and G. Calas. 1990b. Assessment of radionuclide migration in natural analogues by radiation-induced centers in kaolinites. *Scientific Basis for Nuclear Waste Management XIV*. Boston: Materials Research Society Symposium Proceedings Series Vol. 212:474.

Ildefonse, P., P. Agrinier and J.-P. Muller. 1990c. Crystal chemistry and isotope geochemistry of alteration associated with the uranium Nopal 1 deposit, Chihuahua, Mexico. *Geochemistry of the Earth's Surface and of Mineral Formation*. Aix en Provence, France: 371-372.

Ivanovich, M., P. Duerden, T. Payne, T. Nightingale, G. Longworth, M. A. Wilkins, R. B. Edghill, D. J. Cockayne and B. G. Davey. 1987. Natural analog study of the distribution of uranium series radionuclides between the colloid and solute phases in the hydrogeological system of the Koongarra uranium deposit N.T., Australia. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium*. Brussels: CEC:300-313.

Jefferies, N. L. 1987. Long-term solute diffusion in granitic blocks immersed in sea water. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium*. Brussels: CEC:

Jeremy, P. L. D., D. C. Green and M. Ivanovich. 1988. Uranium transport and the partitioning of U, Th, and Ra isotopes between solid and aqueous phases in the Krunkelbach mine, Federal Republic of Germany. *Scientific Basis for Nuclear Waste Management XII - Materials Research Society Symposium Proceedings*. Pittsburgh: Materials Research Society: 927-932.

Kamineni, D. C. 1986. Distribution of uranium, thorium and rare-earth elements in the Eye-Dashwa Lakes Pluton: a study of some analogue elements. *Chemical Geology* 55:361-373.

Kaplan, M. F. 1979. Ancient materials data as a basis for waste form integrity projections. prepared for DOE by The Analytic Sciences Corporation. TR-1746-1.

Kaplan, M. F. 1980. Characterization of weathered glass by analyzing ancient artifacts. *Scientific Basis for Nuclear Waste Management 2*. New York: Plenum Press: 85-92.

Kaplan, M. F. and J. E. Mendel. 1982. Ancient glass and the safe disposal of nuclear waste. *Archaeology* July/August:22-29.

Kerrisk, J. F. 1987. Groundwater chemistry at Yucca Mountain, Nevada, and vicinity. Los Alamos National Laboratory Report LA-10929-MS, 118 p.

Kim, J. I., G. Buckau and R. Klenze. 1987. Natural colloids and generation of actinide pseudocolloids in groundwater. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium*. Brussels: CEC:

Kim, J. I., G. Buckau, H. Rommel and B. Sohnius. 1988. The migration behavior of transuranium elements in Gorleben aquifer systems: colloid generation and retention process. *Scientific Basis for Nuclear Waste Management XII - Materials Research Society Symposium Proceedings*. Pittsburgh: Materials Research Society: 849-854.

Krauskopf, K. B. 1986. Thorium and rare-earth metals as analogs for actinide elements. *Chemical Geology* 55:323-335.

Krumhansl, J. L. and H. W. Stockman. 1988. Site selection criteria and preliminary results from the Valles Caldera natural analog study. D. Evans, eds. *Proceedings of Workshop IV on Flow and Transport Through Unsaturated Fractured Rock - Related to High-Level Radioactive Waste Disposal*. University of Arizona: 249-276.

Ledoux, E., P. J. Hooker, P. Jamet and P. Escalier des Orres. 1990. Hydrogeochemical modelling of the Needle's Eye natural analogue (Scotland). *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print*. Brussels: Commission of the European Communities: n° EUR 13014 EN.

Lei, W., P. Linsalata, E. Penna Franca and M. Eisenbud. 1986. Distribution and mobilization of cerium, lanthanum and neodymium in the Morro do Ferro Basin, Brazil. *Chemical Geology* 55:313-322.

Leroy, J. L., B. Aniel and B. Poty. 1987. The Sierra Pena Blanca (Mexico) and the Meseta Los Frailes (Bolivia); the uranium concentration mechanisms in volcanic environment during hydrothermal processes. B. Poty and M. Pagel, eds. *International Colloquium on Concentration mechanisms of uranium in geological environments, Oct. 2-5, 1985*. Nancy, France: 211-234.

Loss, R. D., K. J. R. Rosman and J. R. De Laeter. 1984. Transport of symmetric mass region fission products at the Oklo natural reactors. *Earth and Planetary Science Letters* 68:240-248.

Lutze, W. and B. Grambow. 1987. The use of natural analogs in the long-term extrapolation of glass corrosion processes. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium*. Brussels: CEC:

MacKenzie, A. B., R. D. Scott, P. Linsalata, N. Miekeley, J. K. Osmond and D. B. Curtis. 1990. Natural radionuclide and stable element studies of rock samples from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print*. Brussels: Commission of the European Communities: n° EUR 13014 EN.

Malow, G. and R. C. Ewing. 1980. Nuclear waste glasses and volcanic glasses: a comparison of their stabilities. *Scientific Basis for Nuclear Waste Management III - Materials Research Society Symposium Proceedings*. New York: Plenum Press: 315-322.

Marinos, G. P. and P. G. Marinos. 1978. The groundwater potential of Santorini Island. *Thera and the Aegean World*. C. Doumas, ed. London: Thera and the Aegean World, Inc.: 297-305.

McCoy, F. W. 1980. Climatic change in the eastern Mediterranean area during the past 240,000 years. *Thera and the Aegean World*. C. Doumas, ed. London: Thera and the Aegean World, Inc.: 79-100.

McKenzie, W. F. 1990. Natural glass analogues to alteration of nuclear waste glass: a review and recommendations for further study. Lawrence Livermore National Laboratory. UCID - 21871.

McKinley, I. G. and U. Frick. 1988. Swiss natural analogue research. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting*. Snowbird, Utah: CEC:104-109.

Miekely, N., H. Coutinho de Jesus, C. L. Porto da Silveira and C. Degueldre. 1990a. Chemical and physical characterisation of suspended particles and colloids in waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print*. Brussels: Commission of the European Communities: n° EUR 13014 EN.

Miekely, N., H. Coutinho de Jesus, C. L. Porto da Silveira, P. Linsalata, R. Morse, K. Osmond and J. N. Andrews. 1990b. Natural series nuclide and rare-earth element geochemistry of waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print*. Brussels: Commission of the European Communities: n° EUR 13014 EN.

Miekely, N., H. C. Jesus, C. L. P. Silveira and I. L. Kuechler. 1988. Colloid investigations in the 'Pocos de Caldas' natural analogue project. *Scientific Basis for Nuclear Waste Management XII - Materials Research Society Symposium Proceedings*. Pittsburgh: Materials Research Society: 831-842.

Murphy, W.M., E.C. Pearcy and P.C. Goodell. 1990. Possible analog research sites for the proposed high-level nuclear waste repository in hydrologically unsaturated tuff at Yucca Mountain, Nevada. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report* . Brussels: Commission of the European Communities: n° EUR 13014 EN.

Naudet, R. 1976. The Oklo nuclear reactors: 1800 million years ago. *Interdisciplinary Science Reviews* 1:72-84.

Nordstrom, D. K., J. A. T. Smellie and M. Wolf. 1990. Chemical and isotopic composition of groundwaters and their seasonal variability at the Osamu Utsumi and Morro do Ferro analogue study sites, Poços de Caldas, Brazil. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print*. Brussels: Commission of the European Communities: n° EUR 13014 EN.

Ochiai, Y., M. Yamakawa, S. Takeda and F. Harashima. 1988. Natural analogue study on Tono Uranium Deposit in Japan. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting*. Snowbird, Utah: CEC:126-139.

Papp, T. 1987. The role of natural analogues in safety assessment and acceptability. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium*. Brussels: CEC:

Patyn, J., P. Del Marmol and M. Monsecour. 1987. Environmental tracers for validating predictive models. B. Come and N. Chapman, eds. *Commission of the European*

Communities Natural Analogues in Radioactive Waste Disposal - A Symposium. Brussels: CEC:444-448.

Petit, J.-C. 1990a. Design and performance assessment of radioactive waste forms: what can we learn from natural analogues? *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print.* Brussels: Commission of the European Communities: n° EUR 13014 EN.

Petit, J.-C. 1990b. Migration of radionuclides in the geosphere: what can we learn from natural analogues? *Radiochimica Acta,* in press.

Petit, J. C. 1988. Analogue studies at the French Atomic Energy Commission during the period 1986-1988. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting.* Snowbird, Utah: CEC:75-87.

Petruso, K. M. 1978. Lead weights from Akrotiri: preliminary observations. *Thera and the Aegean World.* C. Doumas, ed. London: Thera and the Aegean World, Inc.: 547-553.

Pichler, H. and W. Friedrich. 1976. Radiocarbon dates of Santorini volcanics. *Nature* 262:373-374.

Pichler, H. and W. L. Friedrich. 1980. Mechanism of the Minoan eruption of Santorini. *Thera and the Aegean World.* C. Doumas, ed. London: Thera and the Aegean World, Inc.: 15-30.

Pichler, H. and S. Kussmaul. 1980. Comments of the geological map of the Santorini Islands. *Thera and the Aegean World.* C. Doumas, ed. London: Thera and the Aegean World, Inc.: 413-427.

Rasmussen, J. D., C. G. Cunningham, T. A. Steven, R. O. Rye and S. B. Romberger. 1985. Origin of hydrothermal uranium vein deposits in the Marysvale volcanic field, Utah. *Uranium Deposits in Volcanic Rocks.* Austria: International Atomic Energy Agency, proceedings of a technical committee meeting, El Paso, TX April 1984. IAEA-TC-490: 317.

Read, D. and P. J. Hooker. 1988. The speciation of uranium and thorium at the Broubster natural analogue site, Caithness, Scotland. *Scientific Basis for Nuclear Waste Management XII - Materials Research Society Symposium Proceedings.* Pittsburgh: Materials Research Society: 763-770.

Roberts, P. D., T. K. Ball, P. J. Hooker and A. E. Milodowski. 1988. A uranium geochemical study at the natural analogue site of Needle's Eye, S.W. Scotland. *Scientific Basis for Nuclear Waste Management XII - Materials Research Society Symposium Proceedings.* Pittsburgh: Materials Research Society: 933-940.

Ruskeeniemi, T., H. Niini, B. Sodernolm and M. Versterinen. 1989. The Palmottu U-Th deposit in SW Finland as a natural analogue to the behaviour of spent nuclear fuel in bedrock: a preliminary report. *Water-Rock Interaction.* Rotterdam: Balkema: 601-604.

Sargent, F. P. 1990. Natural analogues and performance assessment of the geological disposal of nuclear waste: a review. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print.* Brussels: Commission of the European Communities: n° EUR 13014 EN.

Schorscher, H. D. and M. E. Shea. 1990. The regional geology, mineralogy and geochemistry of the Poços de Caldas alkaline caldera complex, Minas Gerais, Brazil. *Fourth Natural*

Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print. Brussels: Commission of the European Communities: n° EUR 13014 EN.

Sekine, K., T. Murakami, N. Yanase, T. Ohnuki, H. Isobe and A. Kasai. 1988. Migration behaviour of uranium and thorium series nuclides: relevant to alteration. Australian Nuclear Science and Technology Organisation. ANSTO Alligator Rivers Analogue Project - Progress Report, May 1988 - August 1988 :157-186.

Shea, M. 1985. Performance assessment input: Marysvale natural analog study. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, First Meeting.* Brussels: CEC:160-163.

Shea, M. 1988. Marysvale fracture controlled mass transport study. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting.* Snowbird, Utah: CEC:11-25.

Sidle, W. C., D. Sayala and T. Steinborn. 1985. Natural analogues in evaporites for the interpretation of mineralogic and geochemical variations in a nuclear waste repository system. *EOS, Transactions, American Geophysical Union* 66:1153.

Smellie, J. 1985. Proposed programme of investigation at Pocos de Caldas, Minas Gerais, Brazil. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, First Meeting.* Brussels: CEC:171-174.

Stockman, H.W., J.L. Krumhansl, C.L. Stein, V.S. McConnell, K.M. Kimball. 1990. NRC - Sandia natural analog program - report for the third and fourth quarters, FY90. December 10, 1990.

Sunder, S., P. Taylor and J. J. Cramer. 1987. XPS and XRD studies of uranium rich minerals from Cigar Lake, Saskatchewan. *Scientific Basis for Nuclear Waste Management XI - Materials Research Society Symposium Proceedings.* Pittsburgh: Materials Research Society: 465-472.

Sverjensky, D. A. 1988. Geochemical modelling of the Koongarra uranium deposit. Australian Nuclear Science and Technology Organisation. ANSTO Alligator Rivers Analogue Project - Progress Report, May 1988 - August 1988 : 21-64.

Tammemagi, H. Y., B. Haverslew and N. C. Sturchio. 1986. Investigations of the Empire Creek Stock, Montana, as an analogue to a nuclear waste repository. *Chemical Geology* 55:375-385.

Thompson, J. L. 1984. Laboratory and field studies related to the radionuclide migration project. Los Alamos National Laboratory. LA-10372-PR.

Tsolis-Katagas, P. and C. Katagas. 1989. Zeolites in pre-caldera pyroclastic rocks of the Santorini volcano, Aegaen Sea, Greece. *Clays and Clay Minerals* 37:497-510.

Ulmer, G. C., G. H. Kacandes and D. E. Grandstaff. 1986. Icelandic geothermal fields as an analog for nuclear waste disposal in basalt. *Advances in Ceramics* 20:755-764.

Valkiainen, M. 1988. Finnish natural analogue research. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting.* Snowbird, Utah: CEC:110-118.

Vilks, P., J. J. Cramer, T. A. Shewchuk and J. P. A. Larocque. 1988. Colloid and particulate matter studies in the Cigar Lake natural analog program. *Radiochimica Acta* 44-45:305-310.

Vovk, I. F. 1988. The IAEA report of the role of natural analogues in performance assessment. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting*. Snowbird, Utah: CEC:140-144.

Waber, N. 1990. Mineralogy, petrology and geochemistry of the Poços de Caldas analogue study sites, Minas Gerais, Brazil. II Morro do Ferro. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print.* Brussels: Commission of the European Communities: n° EUR 13014 EN.

Waber, N., H. D. Schorscher, A. B. MacKenzie and T. Peters. 1990. Mineralogy, petrology and geochemistry of the Poços de Caldas analogue study sites, Minas Gerais, Brazil. I Osamu Utsumi uranium mine. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print.* Brussels: Commission of the European Communities: n° EUR 13014 EN.

Watkins, N. D., R. S. J. Sparks, H. Sigurdsson, T. C. Huang, A. Federman, S. Carey and D. Ninkovich. 1978. Volume and extent of the Minoan tephra from Santorini volcano: new evidence from deep-sea cores. *Nature* 271:122-126.

Wenrich, K. J., P. J. Modreski, R. A. Zielinski and J. L. Seeley. 1982. Margaritasite: a new mineral of hydrothermal origin from the Sierra de Peña Blanca uranium district, Mexico. *American Mineralogist* 67:1273-1289.

West, J. M., I. G. McKinley and A. Vialta. 1988. The influence of microbial activity on the movement of uranium at Osamu Utsumi mine, Pocos de Caldas, Brazil. *Scientific Basis for Nuclear Waste Management XII - Materials Research Society Symposium Proceedings.* Pittsburgh: Materials Research Society: 771-777.

West, J. M., A. Vialta and I. G. McKinley. 1990. Microbiological analysis at the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print.* Brussels: Commission of the European Communities: n° EUR 13014 EN.

Winograd, I. J. 1986. Archaeology and public perception of a trans-scientific problem: disposal of toxic wastes in the unsaturated zone. U.S. Geological Survey. Open-file Report 86-136.

Wollenberg, H. A. and S. Flexser. 1986. Contact zones and hydrothermal systems as analogues to repository conditions. *Chemical Geology* 55:345-359.

Wolery, T. J. 1979. Calculation of Chemical Equilibrium Between Aqueous Solution and Minerals: the EQ3/6 Software Package. *Lawrence Livermore Laboratory Report* UCRL-52658.

Wolery, T. J. 1983. *EQ3NR, A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations, User's Guide and Documentation.* Lawrence Livermore Laboratory (UCRL-53414).

Wright, J., 1978. Remnant magnetism of poorly sorted deposits from the Minoan eruption of Santorini. *Bulletin of Volcanology* 41:1-5.

7. Annotated bibliography

This bibliography includes all of the papers reviewed for this project. Each reference is followed by a short summary of the pertinent information contained in the paper.

AAEC. 1986. The Alligator Rivers analogue project - proposed international project on analogues of radioactive waste repositories. Australian Atomic Energy Commission. Technical Brief.

This proposal describes the ARAP project as envisioned in 1986. The project was designed to study the migration of radionuclides away from a uranium deposit as an analog to migration from a waste repository. Prior to ARAP, the AAEC did work at Alligator Rivers with funding from the USNRC (1981-1986). This paper includes some of the findings from those studies. The ARAP project began in July, 1987; a parallel project to study colloids in groundwater was begun in 1986 with funding from the UKDOE. The work to date (1981-1986) at Alligator Rivers has shown that most of the uranium and thorium is associated with iron phases whereas radium tends to accumulate in the clay and quartz rich phases. Only a few percent of the uranium appears to be carried by colloids but as much as 38% of the thorium is accounted for by colloids. Migration of ^{129}I has been studied and attempts are underway [in 1986] to measure ^{239}Pu concentrations. The ARAP project will focus on the Koongarra uranium deposit because it is rich and its hydrology has been undisturbed by mining. The study area has a monsoonal climate with virtually all of the rainfall coming between November and March. Consequently the water table rises and falls steeply. The Koongarra deposit consists of two distinct ore bodies of uranium veins in quartz-chlorite schists. Secondary mineralization extends to depths of 25 to 30 m and there is a fan of secondary mineralization in the weathered schist extending some 80 m downslope from the deposit.

Aiken, C. L. V., D. L. Garvey, G. R. Keller, P. C. Goodell and M. de la Fuente Duch. 1981. A regional geophysical study of the Chihuahua City Area, Mexico. *Uranium in Volcanic and Volcaniclastic Rocks- AAPG Studies in Geology No. 13*. El Paso, TX: American Association of Petroleum Geologists: 311-328.

Volcanic rocks have highly variable densities and magnetic susceptibilities which result in complicated geophysical signatures. This paper presents the results of interpretation of reconnaissance gravity and aeromagnetic surveys in the Chihuahua City Area. By removing the geophysical effects of the Basin and Range Structures, it is shown that the Pena Blanca Area lies at the margin of a regional gravity low associated with the Sierras del Nido and Majalca. The authors suggest that this relationship may be a "definitive feature" of this type of deposit. They were unable to identify any corresponding characteristic magnetic feature.

Airey, P. L. 1985. The role of natural analogs in modelling for field transport of radionuclides. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analog Working Group, First Meeting*. Brussels: CEC.

This paper discusses approaches to modelling and summarizes some of the difficulties with formulating mathematical models of real systems. It is suggested that one use of natural analog studies will be to place upper limits on parameters important to modelling. The arguments depend heavily on observations from the Koongarra uranium deposit, Australia.

Airey, P. L. 1986. Radionuclide migration around uranium ore bodies in the Alligator Rivers region of the Northern Territory of Australia: analogue of radioactive waste repositories - a review. *Chemical Geology* 55:255-268.

A mathematical model has been developed to satisfy the observed U-series fractionation, the rate of advance of the weathering front, and assumed boundary conditions for the redistribution of U in the upper parts of the ore bodies. Colloids were observed to carry between 0.01% and 2% of the ^{238}U and between 0.3% and 39% of ^{230}Th. For neither U nor Th is there isotopic equilibrium between the colloids and the solutions. By comparing results from a number of deposits in the area they hope to arrive at generally applicable solutions to nuclide mobility. In general, it was observed that U was leached from "zone I" (the unsaturated zone) and U was deposited in "zone II" (just below the top of the water table in the weathered, oxidized zone). No correlation was found between Ra and U distributions; the differences are attributed to differences in chemical and adsorption properties of the two elements. U and Th tend to concentrate in Fe phases whereas Ra accumulates in the "clay/quartz" fraction.

Airey, P. L., P. Duerden, D. Roman, C. Golian, T. Nightingale, T. Payne, B. Davey and D. Gray. 1986. The Koongarra ore body: a natural analogue of radionuclide migration in the far field of HLW repositories. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium.* Brussels: CEC:175-215.

The authors review the use of uranium ore bodies as analogs of HLW repositories with respect to radionuclide migration, giving particular attention to Koongarra. The validity of transport codes is assessed with regard to time dependent sorption coefficients, colloid transport and a-recoil effects. They discuss using separable mineral phases as an approach to modelling the distribution of uranium series nuclides and suggest a method for applying the results of natural analog studies to HLW site assessment.

Airey, P. L., P. Duerden, D. Roman, C. Golian, T. Nightingale, T. Payne, B. G. Davey, D. Gray, A. Snelling and D. Lever. 1987. The prediction of the long-term migration of radionuclides in the far field of high level waste repositories; results from the Alligator Rivers natural analogue study. *The Geological Disposal of High Level Radioactive Wastes.* Greece: Theophrastus: 507-524.

The authors note that natural analogue studies at uranium deposits have a number of advantages: 1) they contain a wide variety of radionuclides and heavy metals including low but measurable quantities of ^{239}Pu, ^{237}Np, ^{99}Tc, and ^{129}I 2) accessible timescales range from <1 year to about 500000 years. The Alligator Rivers U deposits are located in the Pine Creek geosyncline (14 km of interlayered tuffs and sediments resting on Archean granite). The host sediments were regionally metamorphosed about 1.8 Ga ago and were subsequently covered by proterozoic and younger rocks. The deposits occur in chloritized zones juxtaposed with lenses of massive dolomite and/or magnetite. The results in this paper are from the Koongarra deposit. The authors emphasize the potential importance of colloid transport of radionuclides. Evidence is presented which suggests that U is transported mainly in solution whereas Th is transported partly in solution and partly by colloids. The U from Koongarra is being remobilized into a roll front type deposit down the hydrologic gradient from the primary mineralization allowing the estimation of U transit times by two independent methods: water travel times calculated from a hydraulic model and by measured or calculated sorption coefficients from the ratio of U concentration in groundwater to

that in neighboring drill core. Preliminary results show an agreement between the two methods to within an order of magnitude.

Airey, P. L., P. Duerden, D. Roman, G. Golian, T. Nightingale, T. Payne, B. G. Davey, D. Gray, J. Fabryka-Martin, D. B. Curtis, A. Snelling, D. A. Lever and P. J. Shirvington. 1987. Radionuclide migration around uranium ore bodies - analogue of radioactive waste repositories - Annual Report for 1984-1985. (manuscript completed 1986, published 1987) Australian Atomic Energy Commission for U.S. NRC. NUREG/CR-5040, AAEC/C55.

This is one of a series of reports and as such reflects the evolving nature of the project. The "current aims" of the project are given as: 1) to assess the validity of transport codes for long-term prediction of radionuclide transport 2) to include fission products and transuranic elements in the study 3) to extend the analogue to fractured rock studies. They are making detailed analyses of isotope fractionation within secondary mineralization in an attempt to validate transport equations. Attempts are being made to obtain geochemical evidence for proposed chemical analogues of transuranic elements. Thorium transport as colloids is an area of ongoing research (validity of separation procedures, size ranges, residence times, retardation factors, effects of groundwater mixing, and exchange between stationary and mobile phases). They plan to consider matrix diffusion in the future to respond to the importance of crystalline rock in many HLW repository concepts. [Note that this "Annual Report" was published 2 years after the end of the reporting period.]

Airey, P. L. and M. Ivanovich. 1985. Geochemical analogs of high level radioactive waste repositories. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analog Working Group, First Meeting*. Brussels: CEC:Airey and Ivanovich discuss the values of natural analogs with regard to repository siting and the difficulties with the application of analogs in general. They define some characteristics of geochemical analogs. Examples of natural analog approaches are given. This paper includes methods of relating findings from a geochemical analog to a proposed repository site and emphasizes the necessity of considering "nonclassical" effects in radionuclide transport (e.g. colloids and long term phase changes).

Alexander, W. R., R. D. Scott, A. B. MacKenzie and I. G. McKinley. 1987. Natural analog studies at Grimsel, southern Switzerland. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium*. Brussels: CEC:473-484.

Alexander et al. have measured the distribution of natural decay series radionuclides and REE's in core sections from NAGRA's underground test facility. They found that both hydrothermal alteration and mechanical damage can enhance radionuclide retardation. The observed depth of redox disturbance was found to be about 2 cm rather that the <1mm predicted by theory.

Alexander, W. R., U. Frick and I. G. McKinley. 1990. Natural analogue studies in the radioactive waste research programme of Switzerland (status 1990 and bibliography). *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print*. B. Come and N. A. Chapman, eds. Brussels: Commission of the European Communities: n° EUR 13014 EN.

Uses of natural analogs in Switzerland have included identification of potential problem areas for inclusion in conceptual safety models, verification and validation of models or assumptions for

safety assessment. There has "always" been close communication between modellers and those conducting natural analog studies. This paper includes a bibliography of Swiss natural analog studies which range from work at a deep borehole in Bottstein, a granite in southern Sweden, and an alkaline spring in Oman.

Alexander, W. R. and I. G. McKinley. 1990. Natural analogues in performance assessment: improving models of radionuclide transport in groundwaters by studying the natural environment. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print.* B. Come and N. A. Chapman, eds. Brussels: Commission of the European Communities: n° EUR 13014 EN.

This paper is a review of groundwater solute transport studies applied to performance modelling for HLW repositories. They authors note that though the natural analog literature is extensive, much of what goes by that name is actually work in which the link to radionuclide transport models is "tenuous or, indeed, incorrect." They further observe that when good studies have been done, little note is usually taken by persons involved in performance assessment.

Alterescu, S. 1987. Leaching of natural and nuclear waste glasses in sea water: progress report, CY 85, 86 and 87. NASA Goddard Space Flight Center/ Dept. of Energy. DOE/ET/47927-T2.

Microtektites found in sea bed sediments were studied as natural analogs of nuclear waste glass durability. Experiments showed that the microtektites have relatively high leach rates in deionized water, but that the leach rates in seawater are about 2 orders of magnitude lower This difference is attributed to the presence of high levels of Mg in the seawater. Tests show a similar 2 order of magnitude difference in the leach rates of borosilicate glass in deionized water and in seawater.

Andersson, K. 1988. The INTRAVAL Project. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting.* Snowbird, Utah: CEC:171-172.

The INTRAVAL Project began in October 1987; twenty organizations from twelve countries participate in the project. INTRAVAL will integrate information from laboratory, field and natural analog studies in an effort towards validation of flow and transport models in geologic media. The author notes some of the uncertainties associated with natural analog studies: conditions prevailing during the evolution of the site may be poorly known; the "initial extent, occurrence and duration of a geochemical anomaly" will not be as well constrained as a lab or field experiment; the local hydrology may have changed over time at the site. INTRAVAL includes two analog studies: Pocos de Caldas, Brazil, and Koongarra, Australia.

Apted, M. J. 1990. Natural analogues for the predictive reliability of the engineered barrier system for high-level waste. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print.* Brussels: Commission of the European Communities: n° EUR 13014 EN.

Apted describes analogs to engineered barrier materials and to processes which affect such materials. Among the analog materials discussed is the native copper which occurs in the Portage Lake volcanics, Michigan. Apted notes that the alteration of this material can serve as an analog to the alteration of copper cannister materials. He also points out that the formation of the deposits in

the first place demonstrates the relative mobility of copper in the environment and as such can be considered as a negative analog.

Arai, T., Y. Yusa, N. Sasaki, N. Tsunoda and H. Takano. 1988. Natural analogue study of volcanic glass - a case study of basaltic glasses in pyroclastic fall deposits of Fuji Volcano, Japan. *Scientific Basis for Nuclear Waste Management XII - Materials Research Society Symposium Proceedings*. Pittsburgh: Materials Research Society: 73-80.

Many alteration studies of natural glasses as analogs of waste form glass have been conducted. There are a number of similarities between basaltic glasses and waste form glass: silica contents, alteration products, alteration layer morphologies, and alteration rates in laboratory experiments. Several different environments have been considered: ocean floor, subglacial, hydrothermal, and surficial weathering. Inferred alteration rates varied from 0.001μm/1000 years - 30μm/1000 years. Arai et al. report here the results of their study of glasses 280 and 2800 years old which were altered by rainwater. The authors have taken pains to characterize the weathering environment in terms of water flow rate and water chemistry. They found alteration rates of several μm/1000 years.

Astudillo, J. 1988. Spanish activities in the field of natural analogues. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting*. Snowbird, Utah: CEC:119-125.

Astudillo describes a plan for a recently begun natural analog project which involves laboratory and field characterization of actinide complexes and colloid migration in the Berrocal granite (site of a former uranium mine). The author lists the information to be gathered and the activities to be undertaken. No preliminary results are provided.

Barretto, P. M. and K. Fujimori. 1986. Natural analogue studies: geology and mineralogy of Morro do Ferro, Brazil. *Chemical Geology* 55:297-312.

Morro do Ferro is located in southeastern Brazil, 270 km from São Paulo and 15 km south of Pocos de Caldas. The deposit is located if the center of an alkaline caldera. The ore forms elongate clay lenses resulting from in situ concentration after the original host rock (54 Ma) was hydrothermally altered and weathered. Ore minerals are Th - Zr - Ce - La - Nd - rich resistates. Most of the Th is present as amorphous complexes adsorbed onto clays and Al and Fe oxyhydroxides. The deposit has a complex geologic history which frustrates efforts to understand the processes involved. Th^{4+} is analogous in its chemical behavior to Pu^{4+} and Np^{3+}, Am^{3+}, and Cm^{3+}. A detailed description of the deposit is given. The authors emphasize the difficulties of adequately resolving the very fine grained Th mineralogy. Th and REE's were introduced to the area as primary minerals. Later hydrothermal activity resulted in intensive seritization and kaolinitization of the host rock. Silica, alkaline elements and U were removed by the leaching solutions; Th, REE's, and the refractory minerals were left behind in concentrated form.

Birchard, G. F. and D. H. Alexander. 1984. Natural analogues: a way to increase confidence in predictions of long-term performance of radioactive waste disposal. D. G. Brookins, ed. *Scientific Basis for Nuclear Waste Management VI*. Boston, MA: Elsevier:323-329.

The authors note that no analog to a waste repository *per se* exists. The NRC's interest in natural analogs derives from a need to identify any important parameters which might be missed in

laboratory and theoretical studies because of the long time and large physical scales involved. They recommend "uncomplicated" natural systems to serve as analogs because they can be described by simple models with only a few, well understood variables. Several NRC-sponsored research projects are briefly described including: low level waste sites, a reactor site at Hanford, weapons test fallout, a monzonite-tuff contact, and the integrated radionuclide migration project at Alligator Rivers, Australia.

Bockoven, N. T. 1981. Tertiary stratigraphy of the Sierra Del Gallego Area of Chihuahua with comparisons to the Pena Blanca Uranium District. *Uranium in Volcanic and Volcaniclastic Rocks- AAPG Studies in Geology No. 13*. El Paso, TX: American Association of Petroleum Geologists: 181-187.

Sierra del Gallego is about 30 km north of Pena Blanca. (Pena Blanca is about 230 km south of El Paso, 145 mi.) At both locations, the volcanics unconformably overlie carbonate rocks. Basal units at Sierra del Gallego are quite similar to those at Pena Blanca but the correlations toward the top of the sections are poor. The Mesa Formation at Pena Blanca may have no parallel at all at Sierra del Gallego.

Brondi, A. 1985. Italian activity in the field of natural analogues and natural evidence. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, First Meeting*. Brussels: CEC:112-128.

The authors briefly describe several natural analog projects, including: a volcanic body emplaced into clay at about 800°C many thousands of years ago which has resulted in recrystallization of the clay and in the mobilization of Na, K, Rb, Ca, Ba, and Sr for distances up to 15 m due to hydrothermal circulation; clay permeability studies at a central Italy geothermal field; and clay fracture permeability studies in deep tunnels.

Brookins, D. G. 1976. Oklo phenomenon: geological and nuclear aspects. *American Association of Petroleum Geologists Bulletin* 60:1391.

Most of the ore at Oklo is relatively low grade, on the order of 0.2 - 0.5 % U; the highest grades range up to 75% U. The geologic setting of the Oklo deposits is similar to the sandstone deposits of the Colorado Plateau. Consequently, Brookins proposes exploration for sedimentary, sandstone-type uranium deposits in Precambrian basins in Gabon, and worldwide, in addition to the more common quartz - pebble conglomerate type Precambrian uranium deposits.

Brookins, D. G. 1976. Shale as a repository for radioactive waste: the evidence from Oklo. *Environmental Geology* 1:255-259.

Host rocks at Oklo (part of the Francevillian Series) consist of organic - rich, impure shales with high carbonate contents. The reactor zones consist of chlorite, illite, and carbonates in addition to uraninite; there is little organic carbon or quartz in the reactor zones. Between the reactor zones the fractured rocks are coarse, brecciated quartz with mechanically deposited chlorite and illite; dolomite and siderite are also noted but evidence for other authigenic 1.8 b.y. old minerals is missing. U, Th, and Pu have experienced only minor migration. Rb and Sr appear to have migrated out of the uraninite but to have been trapped in nearby host rocks.

Brookins, D. G. 1978. In Paris, Oklo reactor re-analysed. *Geotimes* 23:27-28.

This paper is essentially a report of Oklo II, the second international meeting devoted to research on the Oklo deposits. The mechanism of concentration of the high grade uranium ore remains uncertain; though the location of the high grade ores is clearly tectonically controlled, the chemistry of transport and deposition is not known. All of the identified reactor zones at Oklo have been removed by mining except part of reactor zone 2 which is at this time about 50 feet above the mine floor and is protected by a cover. Ore which appears to have undergone chain reactions has been identified at the Okelobondo deposit, about 1 km south of Oklo. Research at Okelobondo is proceeding as mining allows.

Brookins, D. G. 1980. Alkali and alkaline earth element studies at Oklo. *Scientific Basis for Nuclear Waste Management III - Materials Research Society Symposium Proceedings*. New York: Plenum Press: 275-282.

The Oklo natural reactors were recognized by French scientists in 1970. Brookins reports here on the distributions of rubidium, strontium, cesium, and barium as inferred from 25 samples taken from reactor zones I(2), II(8), III(8), IV(3), V(3), and VI(1). These samples are organized as: samples from high grade reactor ore, samples from the edges of the reactor zones, and samples from the edges of and from between reactor zones. Ba is present in relatively large quantities [not specified]. Brookins interprets the data to indicate that fissiogenic Rb and Sr have been lost from the reactor ore and at least some fissiogenic Rb and Sr have been fixed at the reactor margins. The background Ba concentrations are too high to assess Ba migration or retention. An alkali/alkaline earth mass balance is not possible due to the lack of adequate samples.

Brookins, D. G. 1980. Geochemical study of a lamprophyre dike near the WIPP site. *Scientific Basis for Nuclear Waste Management III - Materials Research Society Symposium Proceedings*. New York: Plenum Press: 307-313.

Tertiary lamprophyre dikes intruded the evaporite sequence near the WIPP site about 32 to 35 Ma ago at depths close to those proposed for the pilot storage of radioactive waste. Emplacement temperatures were about 600 - 800°C. Brookins suggests that the contact effects of the lamprophyre emplacement make a good analog for a HLW cannister at an elevated temperature. Lamprophyres are enriched in U, Th "and other key elements." The strongest contact effects are melting, partial melting, and recrystallization of the evaporites. The REE patterns of the lamprophyre at the contact are typical of lamprophyres and show no evidence of elemental gain or loss. Brookins infers that there has been little if any chemical exchange between the dikes and the evaporites.

Brookins, D. G. 1983. Migration and retention of elements at the Oklo natural reactor. *Environmental Geology* 4:201-208.

This paper is reproduced almost verbatim as the last half of Brookins (1984). See that reference for a summary of this paper.

Brookins, D. G. 1984. Natural analogs. *Geochemical Aspects of Radioactive Waste Disposal*. New York: Springer-Verlag: 197-231.

Brookins includes a lengthy section on the use of Eh-pH diagrams for evaluating radionuclide mobility. He discusses diagrams for uranium, americium, curium, neptunium, and plutonium.

Most of the rest of the paper is a synthesis of the work to date at Oklo. Brookins suggests that the Oklo ores are similar to the sandstone deposits of the Colorado Plateau [the atmospheric chemistry 2Ga ago would have been quite different - more reducing - however]. The reactor ores consist of pitchblende with chlorite, illite, and rare quartz (in the reactor zones). The presence of both pyrite and hematite leads Brookins to suggest that the redox potential was along that mineralogic boundary [it may be that the two were not in equilibrium at all but that one was altered to the other]. The behavior of specific elements at Oklo is discussed, including: selenium, bromine, rubidium, strontium, yttrium, zirconium, niobium, molybdenum, technetium, ruthenium, rhodium, palladium, silver, cadmium, indium, tin, antimony, tellurium, iodine, xenon, cesium, barium, REE, lead, bismuth, thorium, uranium, and transuranics. Brookins points out that the Oklo site is not especially favorable for the retention of radionuclides compared to sites under consideration for HLW disposal, nevertheless, the fission products experienced very little mobility over a very long period. Brookins briefly describes work at the Eldora Stock, Idaho, the Alamosa River Stock, Colorado, and a lamprophyre dike intruding into the evaporite rocks of the WIPP area. He further notes that active and paleogeothermal systems may serve as analogs of portions of some disposal scenarios.

Brookins, D. G. 1986. Natural analogues for radwaste disposal: elemental migration in igneous contact zones. *Chemical Geology* 55:337-344.

Many studies have been conducted to examine elemental transfer across igneous contact zones. Some of the systems which have been investigated are: granite intrusive into shale and siltstone; basalt intrusive into granodiorite, diorite, rhyolite and dolomite; diabase intrusive into rhyolite and extrusive over arkose; rhyolite extrusive over basalt; lamprophyre intrusive into evaporites; monzonite intrusive into tuff and andesite; and quartz monzonite intrusive into metasedimentary rocks. Elemental migration is attributed to both diffusion and chemical reaction. In general, data from the above indicate that elemental migration is often restricted to within 0.5 - 1.0 m of the contact. Complications involved in using igneous contacts as analogs for HLW packages include: igneous temperatures are higher than those postulated for waste packages; dikes will have cooled more quickly than the waste; differences in permeability of the intrusive and intruded rocks which affect the cooling rates (presence of convective vs. conductive cooling). A number of representative examples of such studies are discussed.

Brookins, D. G. 1987. Natural and archeological analogs: a review. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium.* Brussels: CEC.

Brookins describes various sorts of natural analogs (e.g. radio-geochronology, intrusive contact zones, "special" mineral and rock occurrences, anthropogenic analogs). Many examples of igneous contact zone studies are provided. This paper includes a good discussion of some uncertainties associated with igneous analogs. There is a brief summary of work at Oklo. Among "special" minerals, Brookins suggests: corundum, native Cu and Fe and natural glasses.

Brookins, D. G. 1987. Sandstone uranium deposits: analogs for SURF disposal in some sedimentary rocks. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium.* Brussels: CEC.

This paper gives a brief summary of the formation of sandstone U deposits and compares them to spent unreprocessed fuel (SURF). Most of the paper is devoted to descriptions of the differing behaviors of the various groups of elements present in sandstone U deposits. Arguments are

developed for the use of more common elements as analogs for the behaviors of less common elements. Brookins emphasizes that argillaceous rocks appear to be effective radionuclide barriers.

Brookins, D. G. 1987. Igneous contact zones; natural analogs for high level radwaste disposal. *The Geological Disposal of High Level Radioactive Wastes*. D. G. Brookins, ed. Greece: Theophrastus: 545-553.

Brookins asserts that igneous contact zones are good analogs for high level waste disposal because actinide and actinide daughter elements are present in most igneous rocks (Cs, Rb, REE, Ba, U, Th, Sr, Mo, Pb) and chemical and thermal gradients exist at contact zones so that there is the potential for elemental migration. He notes that there are some problems with igneous contact zones as analogs of high level waste systems: thermal loads in a repository are expected to be about 250° C whereas igneous contact temperatures are several hundred degrees higher; the dimensions of typical waste canisters are many orders of magnitude smaller than those of even modestly sized igneous intrusions; and igneous intrusions cool much more rapidly than high level waste packages. Brookins emphasizes that igneous contact zone studies may nevertheless provide information on HLW elemental behavior in natural rock systems. Systems which have been studied include granite intrusive into shale and siltstone; basalt intrusive into granodiorite, diorite, rhyolite, and dolomite; diabase intrusive into rhyolite and extrusive over arkose; rhyolite extrusive over basalt; lamprophyre intrusive into evaporite; monzonite intrusive into tuff and andesite; and quartz monzonite intrusive into metasedimentary rocks.

Buddemeier, R. W. and J. R. Hunt. 1988. Transport of colloidal contaminants in groundwater: radionuclide migration at the Nevada Test Site. *Applied Geochemistry* 3:535-548.

Radionuclide migration associated with underground nuclear tests at the NTS has been studied in the field since 1974. This project focussed on the Cheshire event which occurred on 14 February, 1976. The site is on Pahute Mesa in the Silent Canyon Caldera. The detonation occurred at a depth of 1167 m in fractured rhyolitic lavas. Water samples were taken during 1983, 1984, and 1985 from within the detonation cavity and from about 300 m outside the cavity. All of the Mn, Co, Ce, and Eu were associated with colloids in samples from both locations. The authors suggest that the presence of colloidal radionuclides outside the cavity indicates transport as colloids. Colloid sizes ranged from 0.003 μm to 0.45 μm. Concentrations ranged from 63 mg/l to 4.3 mg/l. Colloid concentrations were about an order of magnitude greater in samples from within the cavity.

Byers, C. D., M. J. Jercinovic and R. C. Ewing. 1987. A study of natural glass analogues as applied to alteration of nuclear waste glass. Argonne National Laboratory for the U.S.NRC. ANL-86-46, NUREG/CR-4842.

This report has two parts: the results of investigations of natural basaltic glasses from a variety of locations; the results of laboratory experiments intended to simulate natural glass alteration processes. The first part describes the process of natural glass alteration to palagonite, clays and zeolites. The second part reports that the alteration of natural and synthetic glasses is similar. The authors conclude that both natural alteration of basaltic glass and laboratory tests can be used to evaluate the anticipated performance of nuclear waste glass in a repository.

Cardenas-Flores, D. 1985. Volcanic stratigraphy and U-Mo mineralization of the Sierra de Peña Blanca District, Chihuahua, Mexico. *Uranium Deposits in Volcanic Rocks*. Austria: International Atomic Energy Agency, proceedings of a technical committee meeting, El Paso, TX April 1984. IAEA-TC-490: 125-136.

There are three economic deposits at Peña Blanca: Nopal I, Margaritas, and Puerto III. In all cases, the structural characteristics of the deposits, the epithermal "essence" of the mineralization, and the lack of known intrusive rocks suggest that the origin of the mineralization was a geothermal convective groundwater system rather than a magmatic - hydrothermal source. The authors include an excellent summary of local stratigraphic relations. Nopal I is a small, high grade deposit, located in a breccia pipe at the intersection of two step faults. U mineralization is confined to the Nopal and Coloradas formations. The Margaritas deposit is a stockwork ore with a mean grade of 0.1% U_3O_8 and 0.09% Mo. Margaritas has some vertical zoning with Mo increasing upwards and U increasing downwards. Puerto III is a stratabound manto deposit.

Cathles, L. M. 1988. Modeling the fluid flow responsible for primary mineralization at Pocos de Caldas, Osamu Utsumi uranium mine, Brazil. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting*. Snowbird, Utah: CEC:190-192.

Cathles has estimated the fluid circulation at the deposit by assuming an intrusive heat source and permeability distribution. Mineralization is localized in relatively permeable breccia dikes about 0.5 km in diameter. The amount of fluid which circulated through the dikes depends most critically on the size and geometry of the intrusive(s) driving the hydrothermal circulation and the permeability contrast between the breccia zones and the surrounding country rocks. Cathles says "We have only the sketchiest idea of these geologic variables." Based on his calculations, Cathles suggests that about 800 kg of water passed through each square cm of exposed mineralized surface area.

Cathles, L. M. 1988. Perspectives from industrial scale natural analogues. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting*. Snowbird, Utah: CEC:220-226.

Cathles suggests that industrial processes make reasonable "natural" analogs to waste disposal processes because the scale is large relative to laboratory work but small enough to be carefully monitored and the commercial value of the work has funded extensive testing and model development. He discusses the example of copper leaching from low grade sulfide waste dumps. After extensive testing, measurement and model development, however, Cathles admits that "the accurate, a priori prediction of the behavior of a new dump remains elusive."

Cathles, L. M. and M. E. Shea. 1990. Near-field high temperature transport: evidence from the genesis of the Osamu Utsumi uranium mine, Poços de Caldas alkaline complex, Brazil. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print*. Brussels: Commission of the European Communities: n° EUR 13014 EN.

Cathles and Shea have studied the hydrothermal ore forming processes at Osamu Utsumi as an analog to near-field radionuclide migration. They infer that $>10^5$ kg/cm^2 of boiling hydrothermal fluid must have circulated through the breccia pipe with uranium concentrations much higher (2.5 orders of magnitude) than those indicated in the most recent experiments.

Chapman, N. 1985. Analogue of elemental diffusion over 5000 years in sediments: close but not close enough? B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, First Meeting*. Brussels: CEC:157-159.

At Loch Lomond, a 1 m thick layer of marine sediments (about 5000 years old) is bounded above and below by fresh water sediments and occurs about 4 m below the bed of the loch. The marine sediment and its pore waters constitute a geochemical discontinuity when juxtaposed with the fresh water sediments and act as a source for elemental migration into the surrounding sediments. Although the physicochemical conditions and the age profile are well known, the boundary conditions are difficult to constrain and have required many assumptions for interpretation. The largest uncertainty lies in the initial form and concentration of the source term elements. Consequently, it is not known whether the estimated diffusivities are maxima or minima. These problems exist even in this analog which is by most standards a well defined, "single process" example.

Chapman, N. and I. McKinley. 1990. Radioactive waste: back to the future? *New Scientist* 54-58.

This is a general overview article for the layman describing the usefulness of natural analogs in building confidence in HLW repositories. The authors note that even James Hutton, one of the "founding fathers" of geology, tossed out the idea of lab experiments to simulate geologic processes on account of "the immensity of the natural agents" which he felt worked in ways beyond our understanding. A series of natural analog studies are summarized and related to repository conditions, including: Oklo (Gabon), Cigar Lake (Saskatchewan), Lock Lomond (Scotland), springs in Jordan, Pocos de Caldas (Brazil), Morro do Ferro (Brazil, which has the highest natural radioactivity on the surface of the earth), Roman iron nails, and Swedish bronze canon. All examples given indicate the extreme stability of geologic settings and their abilities to impound radioisotopes for long periods. The authors encourage the use of "simple comparisons with natural examples."

Chapman, N. A. 1988. Natural analogue studies in the CEC MIRAGE-2 programme (1985-1989). A review of progress to January 1988. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting*. Snowbird, Utah: CEC:26-42.

This paper is Chapman's progress report on phase 2 of the MIRAGE program which includes nine analog studies. Five of the projects concern diffusion and advection processes in sediments (clays); the others are applied to matrix diffusion or elevated temperature elemental migration in granitic rocks. These studies are designed to gather qualitative information with regard to important natural processes rather than quantitative, transferable parameter values. It is expected that the qualitative information will be useful for model validation.

Chapman, N. A., I. G. McKinley and J. A. T. Smellie. 1984. The potential of natural analogues in assessing systems for deep disposal of high-level radioactive waste. Swedish Nuclear Fuel and Waste Management Co. (SKB) and the Swiss Radioactive Waste Cooperative (NAGRA). NTB 84-41. KBS 84-16. Eir Ber 545.

This report identifies nine processes which may lead to the breakdown of containment in a HLW repository in crystalline rock. These nine are: thermal/chemical breakdown of buffers and seals, waste package corrosion, waste form dissolution and breakdown, solubility and speciation of radionuclides, mineralogical fixation at elevated temperatures, radiolysis, redox equilibration,

retardation during transport, and matrix diffusion. The authors discuss the important unknowns for each of these processes and the types of natural analogues which are appropriate for each. The authors emphasize the importance of "linking analogues to well defined processes." A list of "essentials" for selecting analogues is presented: 1) The process involved should be clear-cut. 2) The chemical analogy should be good. 3) The magnitude of the various physico-chemical parameters involved should be determinable. 4) The boundaries of the system should be identifiable. 5) The timescale of the process must be measurable (for more detail see page 12).

Chapman, N. A. and J. A. T. Smellie. 1986. Natural analogues to the conditions around a final repository for high-level radioactive waste. *Chemical Geology* 55:167-173.

The main performance assessment issue with regard to a high-level waste repository is the ability to predict with confidence the nature and effects of geologic processes far into the future. There are no analogs of a complete disposal system. The role of a natural analog study should be to confirm: 1) that a process can and will occur in nature; 2) where, when and the conditions under which the process can occur; 3) that the effects of the process are the same as those in the model; 4) the magnitude and time scale of the effects. A good analog should include these factors: 1) a clearcut process or processes; 2) a reasonable chemical analogy; 3) ability to determine physico-chemical parameters such as T, P, Eh, pH, concentration ...; 4) system boundaries (open? closed?) how much material is involved?; 5) time - scale. Process oriented studies are generally more practical because adequate sites are easier to find for 1 or 2 processes than for many or all processes of interest. Processes of interest include: retardation of radionuclides, matrix diffusion, radiolysis, redox equilibration, thermal/chemical breakdown of buffer and seal materials (bentonite), waste package corrosion, waste form dissolution and breakdown. Table 1 is a list of possible chemical analogs for the long-lived radionuclides present in HLW. For some processes archaeological analogs are better than geological analogs.

Coles, D. G. and L. D. Ranspott. 1982. ^{106}Ru migration in a deep tuffaceous alluvium aquifer, Nevada Test Site. *Science* 215:1235-1237.

The Cambric test was detonated in tuffaceous alluvium at the NTS in 1965 (0.75 kt yield). The explosion point was 294 m deep; the water table was 220 m deep. Fifteen years after the explosion, water was sampled from a well that intersected the explosion cavity; only 3H and 90Sr were found in concentrations above the maximum permissible concentrations (MPC). In 1974 a well was drilled 91 m south of the explosion point and a pump placed at 294 m depth for water sampling. The authors assume that 3H is not retarded and compare radionuclide movement to 3H to determine a retardation factor. They observe that Ru-106 migrates at the same velocity as 3H, a finding which contradicts earlier laboratory studies which indicated that Ru would migrate much more slowly than 3H.

Come, B. 1985. The CEC's actions in the field of natural analogues: an overview. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, First Meeting*. Brussels: CEC:167-170.

The CEC has participated for a number of years in natural analog-related studies within the MIRAGE (Migration of Radionuclides in the Geosphere) program. Some of the projects have included: REE migration in a hydrothermally altered granite at Vosges and in silicic volcanic rocks in Brittany; elemental migration (17 elements) in the Loch Lomond sedimentary horizon (6900 - 5400 years B.P.) and at the Orte site (volcanics overlying sand overlying clay) at which uranium, thorium, radium and REE's leach from the volcanics and are retarded at the clay.

Cowan, G. A. 1976. A natural fission reactor. *Scientific American* 235:36-47.

This paper is an excellent summary of the radiochemistry of the Oklo reactors. The collection of fission products preserved at Oklo makes it unmistakable that a chain reaction occurred. Formation of a natural reactor requires unusual circumstances. The most likely scenario calls for a mass of relatively pure uranium oxide to have formed by hydrothermal remobilization of an earlier placer enrichment of uranium. The size of the uranium oxide mass must have been large with respect to the distance a neutron travels before capture. Some appropriate moderator to slow down the neutrons would also be required, groundwater is the most likely candidate. It is likely that other natural reactors of the Oklo type formed in the past and that they have been mined out without recognition or that they were subsequently dispersed by weathering and/or oxidizing groundwaters or that they have not yet been found. In addition to the Oklo type natural reactor, it is possible that a breeder reactor could have formed which would have left behind ores enriched in ^{235}U rather than depleted as at Oklo.

Cowan, R. and R. C. Ewing. 1988. Freshwater alteration of basaltic glass, Hanauma Bay, Oahu, Hawaii: a natural analogue for the alteration of borosilicate glass in fresh water. *Scientific Basis for Nuclear Waste Management XII - Materials Research Society Symposium Proceedings*. Pittsburgh: Materials Research Society: 49-56.

Ten samples were collected from a cliff over the bay where the basaltic glass has weathered for the last 12,000 to 28,000 years. All of the samples were altered at least partially to palagonite and zeolites. Zeolites were formed in the order: analcime to philipsite to chabazite. The rate of alteration was less than that predicted by experiments; the authors infer that the difference was due to the episodic presence of the groundwater over the years.

Cramer, J. J. 1985. Cigar Lake project: a U-deposit natural analog. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analog Working Group, First Meeting*. Brussels: CEC.

Cramer includes detailed justification for natural analog studies of unweathered sandstone-hosted U-deposits. Similarities to the Oklo deposit are noted. A brief description of the Cigar Lake deposit is given. The scope of their project and the future possibility of international involvement is described.

Cramer, J. J. 1986. Sandstone-hosted uranium deposits in northern Saskatchewan as natural analogs to nuclear fuel waste disposal vaults. *Chemical Geology* 55:269-279.

This paper discusses unconformity-type U deposits as they relate to HLW disposal. Secondary dispersal of U by ground waters is very limited (often only about 5 m from the ore body, even though the ores were formed on the order of 1 Ga. ago; only radiogenic Pb has been significantly dispersed. These deposits are not detectable from the surface by geophysical techniques dependent on radioactivity (even relatively shallow deposits) due to the immobility of the U; they are found by exposure due to erosion or geophysical conductivity techniques. Ore formation probably occurred due to the mixing of two fluids: an oxidizing U-rich solution and a reduced solution. Redox conditions and the low carbonate composition of the groundwaters are indicated as the important factors in fixing U both at high temperatures in the past and at the low temperatures at present.

Cramer, J. J. 1988. Natural analogue studies on the Cigar Lake uranium deposit: an update. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting*. Snowbird, Utah: CEC:50-56.

Investigations of the Cigar Lake U deposit have continued since 1984. This paper summarizes work in late 1987 - early 1988, covering ore mineralogy, clay mineralogy, radionuclide migration, hydrogeochemistry, and hydrogeology. Mine development began in August 1988. The next phase of analog studies will monitor the effects of mining disturbance on the deposit (especially the role of the clay zone with respect to radionuclide migration).

Cramer, J. J., P. Vilks and J. P. A. Larocque. 1987. Near-field analog features from the Cigar Lake uranium deposit. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium*. Brussels: CEC:59-72.

This paper is an excellent summary of the geology and state of research at Cigar Lake. Cramer et al. describe features of the deposit which make it a good analog to some repository features. Included are discussions of U mineralogy, clay mineralogy, host rock alteration, radionuclide migration/retardation, groundwater composition, colloids and radiolysis. There is also a general description of field methods of groundwater sampling and analysis (methods are elaborate and well thought-out). This paper emphasizes the importance of Fe compounds (both amorphous and crystalline) in radionuclide retardation.

Crisman, D. P. and G. K. Jacobs. after 1982. Native copper deposits of the Portage Lake Volcanics, Michigan: Their implications with respect to canister stability for nuclear waste isolation in the Columbia River Basalts beneath the Hanford Site, Washington. Department of Energy. RHO-BW-ST-26 P, Contract DE-AMO6-76-RLO2225.

Native copper which occurs in basalt of the Keweenaw Peninsula was chosen as an analog of copper waste containers in the proposed HLW basalt site at Hanford. Similarities between the two sites include: basalt chemistry, water chemistry, controls on water chemistry, and the occurrence of elevated temperatures after emplacement of the copper in the basalt (metamorphism at Keweenaw). The authors report that the copper has been stable in the geohydrologic environment of the Keweenawan basalts since deposition having survived contact with both a near surface fresh water ($Na\text{-}HCO_3\text{-}Cl$) and a deep brine water (Ca-Na-Cl). Only the samples exposed the atmosphere and water in the adits or open surfaces showed alteration. The authors conclude that a basalt-water geohydrologic system (i.e. low total dissolved solids low Cl, moderate pH, low Eh) may be favorable for the preservation of copper HLW cannisters.

Cross, J. E., A. Haworth, P. C. Lichtner, A. B. MacKenzie, L. Moreno, I. Neretnieks, D. K. Nordstrom, D. Read, L. Romero, R. D. Scott, S. M. Sharland and C. J. Tweed. 1990. Testing models of redox front migration and geochemistry at the Osamu Utsumi mine and Morro do Ferro analogue sites, Poços de Caldas, Brazil. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print.* Brussels: Commission of the European Communities: n° EUR 13014 EN.

The authors note that redox fronts are an anticipated phenomenon in HLW repository environments and that models of such fronts may be tested against field evidence. They conclude that: current coupled transport/chemistry models do a poor job of predicting redox front movement (the models

tend to predict more rapid front movement than is observed and so may be considered conservative), trace element removal by co-precipitation is not simulated by current models, microbial effects are important to elemental migration chemistry (especially sulfur chemistry) and are not modelled at present.

Cross, J. E., A. Haworth, I. Neretnieks, S. M. Sharland and C. J. Tweed. 1989. Modelling of redox front and uranium movement in a uranium mine at Poços de Caldas. Migration '89. Monterey, CA.

At Pocos de Caldas, an open pit uranium mine has been operated since 1975. The pit is up to 100 m deep (with accessible walls) and is about 1 km long and 0.5 km wide and is located at the bottom of a valley. Host rocks are phonolites and nepheline-syenites. the lower portions of the rock contain about 2% pyrite and are reducing whereas the upper portions have been oxidized by infiltration of rainwater with subsequent alteration of the pyrite to ferric oxyhydroxides. A sharp redox front separates the two regions. Groundwater was sampled from both the reducing and the oxidizing horizons using well samples. Advection of groundwater and diffusion in static pore waters are both thought to be important to the advance of the redox front. The CHEQMATE computer code was used to model the redox system with one result being a predicted rate of advance of the front of 21 m/Ma. Some aspects of the modelling did not give good agreement with field data resulting in some suggested modifications: changing the solubility limiting mineral phases in the model, mineral precipitation reactions not being at equilibrium, and possible contamination of water samples.

Curtis, D. B., T. M. Benjamin and A. J. Gancarz. 1981. The Oklo reactors: natural analogs to nuclear waste repositories. *The technology of high-level nuclear waste disposal DOE/TIC-4621*. DOE: 255-283.

This paper is a comprehensive summary of the Oklo work to date. The arguments are developed explicitly in terms of HLW repository performance. The fission products of the Oklo reactors were originally contained in crystalline uraninite. Loss of some of the fission products (Ru, Tc, and Nd) from the uraninite was by solid state diffusion. Fission products that were released from the uraninite were retained within a few meters of their source as a result of temperature-dependent aqueous deposition. The rate of movement of the nuclides was on the order of 10-5 m/y even though the convecting fluids may have moved as fast as 5 m/y. This paper includes an extensive discussion of Tc and Ru systematics.

Curtis, D., T. Benjamin, A. Gancarz, R. Loss, K. Rosman, J. De Laeter, J. E. Delmore and W. J. Maeck. 1989. Fission product retention in the Oklo natural fission reactors. *Applied Geochemistry* 4:49-62.

Eight samples from reactor zone 9 (total zone volume approximately = 45 cubic meters) were analyzed to determine the abundances and isotopic compositions of uranium, molybdenum, ruthenium, paladium, silver, cadmium, tin, tellurium, and neodymium. The authors here challenge the generally accepted idea that the uraninite in the reactor zones at Oklo has been stable since the occurrence of nuclear criticality about 2 Ga ago. They assert that it is "unambiguous" that Te, ^{99}Ru, Ru, Pd and Mo have been lost or gained in the reactor zones. Nd and Sn are enriched in some samples and depleted in some samples, relative to Te. At least some fissiogenic Ag has been lost from the reactor zone and Cd has been almost entirely removed.

Curtis, D. B. 1986. Geochemical controls on ^{99}Tc transport and retention. *Chemical Geology* 55:227-231.

^{99}Tc is important to HLW considerations because it is a high yield fission product and because of its long half-life (2.13×10^5 yr) it will be a significant component of the waste for more than 1 m.y. Examination of the Oklo ores finds the reactor zones to be Tc deficient and the rocks surrounding the reactor zones to be enriched in Tc. It appears likely that increased T and oxidation by radiolysis in the reactor zones mobilized the Tc which was moved out of the reactor zones and then precipitated further away under ambient geologic conditions of lower T and more reducing Eh. The study was conducted by inferring paleo Tc concentrations from present day Ru ratios.

Curtis, D. B. and R. E. Perrin. 1988. Plutonium Geochemistry. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting*. Snowbird, Utah: CEC.

The authors are studying Pu geochemistry by measuring ^{239}Pu abundances in uranium-rich rocks. Samples with uranium concentrations between 14% and 40% contain between 1.7e-12 and 2.6e-12 $^{239}Pu/U$. The uranium ores at Koongarra, Australia, are being weathered and the ore constituents dispersed by oxidizing groundwater. The solubility of uranophosphate minerals, coprecipitation with ferric hydroxides, and adsorption onto secondary mineral surfaces appear to be the limiting factors for the rate of dispersion.

Davidson, D. A. 1978. Aegean soils during the second millennium B.C. with reference to Thera. *Thera and the Aegean World.* C. Doumas, ed. London: Thera and the Aegean World, Inc.:725-739.

Attempts to identify soils underlying the Minoan eruption indicate that soils were not well preserved, probably due to extensive and vigorous erosion at the time of the eruption (as is ongoing today). There is little organic matter, low clay content, low ion exchange capacity, and low moisture content. Erosion is indicated by the irregular nature of the unconformity at the base of the pumice exposed in quarries.

Dayvault, R. D., S. B. Castor and M. R. Berry. 1985. Uranium associated with volcanic rocks of the McDermitt Caldera, Nevada and Oregon. *Uranium Deposits in Volcanic Rocks*. Austria: International Atomic Energy Agency, proceedings of a technical committee meeting, El Paso, TX April 1984. IAEA-TC-490: 379-409.

Hydrothermal uranium deposits at the McDermitt Caldera can be separated into 5 distinct types: 1) uranium associated with pyrite and titanium minerals hosted by icelandic lavas (ex. Aurora) 2) uranium with fluorite, pyrite, and a "clayey zirconium phase" in steeply dipping veins (ex. Moonlight, Granite Pass, Horse Creek) 3) hot spring mercury deposits developed in volcanic sediments with low uranium contents (ex. Bretz, Opalite, McDermitt) 4) uranium in silicified and argillized rhyolites (Thacker Pass) and 5) stratabound uranium hosted by volcanic sediments. The Moonlight mine is the only area at McDermitt with recorded uranium production (about 1500 lbs of U_3O_8 with an average grade of about 0.13% U_3O_8). Host rocks at the Moonlight are rhyolite ash flow tuffs and dacite flows in the footwall and biotite rhyolite breccias in the hanging wall.

De Laeter, J. R. 1985. The Oklo reactors: natural analogues to nuclear waste repositories. *Search* 16:193-196.

This paper provides a brief summary of the geology and investigations at Oklo. The author reports that the 2 Ga old reactors operated intermittently for about 500 Ka producing about 6 tons of fission products, the majority of which have been retained within the Oklo site. The uranium mineralization is located in a clay gangue within a conglomerate lens; each reactor zone is a single compact volume of rich ore, flattened parallel to the strata, ranging from 10 - 20 m in length and with a thickness of about 1 m. The author notes that the remarkable thing about Oklo is "not so much that a nuclear reactor occurred some time in the past, but in the fact that it still exists today. He attributes this existence to the formation of the deposit on old, stable basement rocks, and to the addition of sediment on top of the deposits, which had the effect of protecting it for 2 Ga. Other natural reactors have been sought, but none have been found. Oklo may be the only one.

De Laeter, J. R., K. J. R. Rosman and C. L. Smith. 1980. The Oklo natural reactor: cumulative fission yields and retentivity of the symmetric mass region fission products. *Earth and Planetary Science Letters* 50:238-246.

The isotopic composition and concentrations of palladium, silver, cadmium, tin, and tellurium were measured on three samples from the reactor zones at Oklo. Pd and Te appear to have been retained in the reactor zones. Ag and Sn were lost from the reactor zones, but may have been retained in the surrounding host rock. Sn appears to have migrated during the operation of the reactors. Almost all the fission product Cd appears to have been lost.

de Marsily, G. 1985. A modeller's viewpoint on the possible use of analogues for flow and transport. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, First Meeting*. Brussels: CEC.

The author is concerned that present techniques may not be able to recognize "short circuits" in flow paths and suggests that natural analogs may provide an opportunity to observe such "short circuits" directly and to show whether they could have been detected with present surveying techniques. de Marsily raises the question of whether or not there exists some group of elements which do not behave as predicted by current speciation and sorption studies; he suggests that validation of predictions is a role for natural analogs. He points out that mass balance will be very difficult to constrain in natural analogs because of poor knowledge of the source term; retention of some elements is not a proof that some part of those elements has not migrated.

Doumas, C., ed., 1978. *Thera and the Aegean World*. London: Thera and the Aegean World, Inc.:823.

This book is a comprehensive collection of archeological, geological, and hydrological studies of the island of Thera. Individual chapters are referenced separately in this bibliography.

Doumas, C. and L. Papazoglou. 1980. Santorini tephra from Rhodes. *Nature* 287:322-324.

Tephra from the Santorini eruption has been found on Crete. This paper confirms that northwesterly winds prevailed during the eruption and that Rhodes and the south coast of Turkey received significant tephra fall.

Doumas, C. G. 1983. *Thera.* London: Thames and Hudson.

Many Minoan "discoid" lead weights of various sizes have been found on Thera. K. Petruso has inferred a unit of some 61 grams from the mass multiples present in the weights. Akrotiri and Ayia Irini have produced about two thirds of the total number of Minoan balance weights known, suggesting the importance of the area as an Aegean center of commerce.

Duerden, P., ed., 1988. *Alligator Rivers Analogue Project - Progress Report: May 1988 - August 1988.* Australian Nuclear Science and Technology Organisation (ANSTO):270.

The results of the February 1981 modelling workshop are presented. Five modelling tasks are recommended: 1) weathering history of Koongarra 2) migration of radionuclides in the weathered zone 3) open system modelling 4) preliminary geochemical modelling to identify controlling reactions 5) preliminary hydrogeological modelling. Aquifer tests and drilling are proceeding. Radionuclide disequilibrium studies are continuing including: U adsorption onto chlorite, distribution between fresh rocks and groundwaters, distribution of U(IV) and U(VI). See individual papers within this report for more detail.

Duerden, P., ed., 1990. *Alligator Rivers Analogue Project - Progress Report: June 1990 - August 1990.* Australian Nuclear Science and Technology Organisation (ANSTO):227.

The cooperative investigation of the Koongarra uranium deposit is divided into a series of subprojects. Subproject 1 - Modelling of radionuclide migration: The geochemical portion of this subproject involves EQ6 runs aimed at assessing which processes are "quantitatively" controlling uranium mobility in the weathered zone. Subproject 2 - Hydrogeology: three dimensional modelling results indicate that regional groundwater flow is probably topographically controlled; three cells have been identified in the modelled region. Tracer tests are being considered. Subproject 3 - Uranium - thorium series disequilibria: Characterization of secondary uranium phases is underway as are experiments on uranium adsorption onto smectite, kaolinite, chlorite, vermiculite, and ferrihydrite. Colloid sampling shows two types, flaky and spherical; both types are much more abundant in the weathered zones than in the unweathered zones. Subprojects 5 and 6 - Fission products and transuranics: ^{239}Pu analyses showed concentrations in Koongarra samples to be barely above the detection limit. Much of the work in this report was published for the Materials Research Society meeting in December 1990 and can be referenced under those papers.

Duffield, J. R., L. Xu and D. R. Williams. 1988. Chemical speciation modelling of the South Terras and Madeira Abyssal Plain natural analogue sites. Department of the Environment. DOE-RW-87.128; APCM-56.

This work has been carried out by the Speciation Research Group of the University of Wales College of Cardiff. Their aims are summarized as: 1) to validate predictive models 2) to identify areas requiring further research and 3) to clarify areas of uncertainty and to test the reliability of assumptions made. South Terras is a defunct U mine in Cornwall where U concentrations in streamwaters flowing near dumps have been measured. The U speciation in these fluids was modeled with good agreement to the field data (especially when organic complexing is assumed to be relatively simple). At the Madeira Abyssal Plain, field observations indicate the presence of a redox front migrating down through the turbidite sediments. Modeling of the chemical controls and processes affecting U distribution within the sediments has been conducted with reasonable

results, given a variety of assumptions, including ignoring organic complexing, sorption, and colloid formation.

Dunn, C. 1980. The biogeochemical expression of deeply buried uranium mineralization in Saskatchewan, Canada. *Developments in Economic Geology - Geochemical Exploration 1980*. 437-452.

A uranium deposit [geologically similar to the Cigar Lake deposit] 150 m deep, at the boundary between the Athabasca Sandstone and the basement, is being leached of uranium which is concentrated in the plants above. Uranium concentrations in the ash from several species of plants are on the order of 100 ppm. The highest concentrations occur in plants laterally displaced from the uranium mineralization at depth. The author infers that uranium ions are moving upward along inclined fractures. The soils in which the plants are growing have only background concentrations of uranium. Other sites nearby have limonite coatings on fractures suggesting oxidizing solutions and at one site 14 km west, oxidized uranium mineralization occurs at the surface 200 m above the main uranium ore body.

Eargle, D. H., G. W. Hinds and A. M. D. Weeks. 1971. Uranium Geology and Mines, South Texas. Texas Bureau of Economic Geology, Guidebook No. 12.

Early uranium mining in South Texas was of oxidized ores from shallow pits (about 40 feet in depth). These ores occurred in pods and were out of radiometric equilibrium. Ore minerals in order of decreasing abundance were: uranyl phosphates, uranyl silicates, uranium vanadates, and uranium oxides. More recent mining has concentrated on unweathered, unoxidized ores.

Edghill, R. 1988. Colloids in Koongarra groundwater. Australian Nuclear Science and Technology Organisation. ANSTO Alligator Rivers Analogue Project - Progress Report, May 1988 - August 1988 :245-252.

The goal of the colloid project is to identify the colloidal components at Koongarra in terms of chemical composition, size, shape, crystallinity, mineralogy, and concentrations. A description of the sampling procedures is given. Colloids identified include: iron particles, clays (kaolinite and chlorite), silica, lead, uranium, and titanium particles. Colloid concentrations are low (about 10^6 particles/l or less), so the amount of colloidal material is small compared to the amounts of elements actually dissolved in the groundwater. Radionuclides were found to be associated with the colloids only near the center of the ore body. The authors conclude that it appears that colloidal transport is minor at Koongarra.

Edghill, R. 1990. The redistribution of uranium series radionuclides at Koongarra. eds. *Scientific Basis for Nuclear Waste Management XIV*. Boston: Materials Research Society Symposium Proceedings Series Vol. 212:473.

The $^{234}U/^{238}U$, $^{230}Th/^{234}U$, and $^{226}Ra/^{230}Th$ ratios in the "accessible" and "inaccessible" U-bearing phases were measured. The accessible (i.e. extractable) phases had ratios below unity whereas the inaccessible (i.e.. non-extractable) phases had ratios above unity. U was found to accumulate most rapidly at the base of the weathering zone. U was found to be most highly concentrated on iron oxides (goethite and ferrihydrite) and manganese oxides.

Edghill, R. and B. G. Davey. 1988. Alpha activity and mineralogy associations. Australian Nuclear Science and Technology Organisation. ANSTO Alligator Rivers Analogue Project - Progress Report, May 1988 - August 1988 :147-156.

Goals of this project were to determine which mineral phases exhibit alpha activity, and how those associations varied with differing degrees of weathering. Alpha autoradiography was the main technique used. The authors found a strong connection between alpha activity and iron minerals (both iron "nodules" and fine iron coatings). Alpha activity associated with clay minerals is limited to the surfaces of the minerals. Manganese minerals also had a high concentration of alpha activity, but the abundance of manganese minerals in the samples examined was low.

Eisenberg, N. A. 1986. Natural analogues and validation of performance assessment models. *Chemical Geology* 55:189-201.

So far (1986), natural analog studies have not been used to validate performance assessment models in a decisive fashion. The biggest problem with performance assessment is the long time scales involved (10^2 - 10^6 years). Natural analogs are essentially unplanned experiments which run for very long times and so are potentially useful for performance assessment. A review of previous uses of natural analog studies is given. Recommendations for future analog studies include: study simpler systems, use analogous elements rather than insisting on those actually in HLW, emphasize determination of the "environmental conditions" during the period of studies ("thermal, chemical, hydraulic, etc.").

Eisenbud, M., K. Krauskopf, E. P. Franca, W. Lei, R. Ballad and P. Linsalata. 1984. Natural analogs for the transuranic actinide elements: an investigation in Minas Gerais, Brazil. *Environmental Geology and Water Science* 6:1-9.

Morro do Ferro is a deposit of thorium and REE's located near the summit of a hill near the center of the Poços de Caldas Plateau, in the state of Minas Gerais, Brazil, about 300 km north of São Paulo. The Poços de Caldas Plateau is roughly circular (about 35 km in diameter) and is thought to be a deeply eroded caldera. The ore body was discovered in the early 1950's. The ore deposit is highly weathered; host rock was originally nepheline syenite (tinguaite). Mobilization rates of elements considered to be chemical analogs of HLW components have been studied. Thorium was used as analogue for Pu+4, and La+3 as and analogue for Cm+3 and Am+3. Mobilization rates were estimated considering both surface erosion and solubilization by groundwater. The authors found the mobilization rates to be so low that despite the long half-lives of some HLW isotopes, essentially complete decay should occur *in situ*. They note that this finding is consistent with the results of investigations at Oklo, Gabon.

Elders, W. A. 1987. A natural analog for near-field behaviour in a high level radioactive waste repository in salt: the Salton Sea geothermal field, California, USA. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium.* Brussels: CEC.

Elders is studying the SSGF system "to produce data to validate geochemical computer codes" (specifically EQ3/6). He emphasizes that the data used to "develop a computer model must be kept distinct from data used to validate it." Elders and his associates are using a variety of mineralogical and geochemical methods to develop a 3-dimensional picture of the system (temperature, fluid composition, lithology, mineralogy). With regard to code verification, they analyzed brines and assemblages of minerals "apparently in equilibrium with them." They have found the codes capable

of predicting mineral assemblages "similar" to those observed. However, this similarity "is in general not true for ... dissolved species." They plan to continue validation efforts.

Ericson, J. E. 1980. Durability of rhyolitic obsidian glass inferred from hydration dating research. *Scientific Basis for Nuclear Waste Management III - Materials Research Society Symposium Proceedings*. New York: Plenum Press: 283-289.

The author used 14 samples of obsidian from California and Oregon and associated archeological data to determine source-specific hydration rates. This natural alteration was then compared with laboratory alteration experiments on the same obsidians. The laboratory alteration rates were found to be much less than the rates for natural hydration. The author infers that the laboratory experiments omit some significant processes and that the rhyolitic obsidian is much more unstable than indicated by the laboratory results.

Escalier, P. 1988. French radioactive wastes performance assessment and the natural analogues approach: an overview. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting*. Snowbird, Utah: CEC:193-202.

Escalier reports that the main French interests in natural analogs derive from increased confidence in: long term behavior of materials, thoroughness and correctness of choices of processes considered in performance assessment, confining properties of various geologic settings, modelling of coupled processes and overall systems. He notes that "complete validation of models and complete analogy with waste disposal repositories are pure nonsense."

Ewing, R. C. and M. J. Jercinovic. 1987. Natural analogues: their application to the prediction of the long-term behavior of nuclear waste forms. *Materials Research Society Symposia Proceedings* 84:67-83.

This paper is divided into two parts. The first part is a discussion of the inherent limitations of arguments based on analogy; the second part is a summary of the work done to date using natural glasses as analogs for borosilicate glasses. "Analogy" refers to the logical inference that partial similarity implies further similarity. "Proof" of the long term performance of any aspect of a HLW repository can only be approached, never arrived at. There is no way to actually test a geologic hypothesis regarding long term phenomena. The "test" of a geologic hypothesis is its compatibility with a large body of independent observations. Lord Kelvin's attempt to calculate the age of the earth is an example of a mathematical model which failed to take into account important phenomena. Darwin came closer in his estimate of the earth's age based on deposition and erosion rates - long before Kelvin's attempt. There are many problems with natural analogs (they are seldom analogous in detail) but they are the only means by which long term behavior of a geologic repository may be assessed. There is no method by which the long term behavior of a repository can be proved. The authors discuss a variety of natural glass analogs including: tektites, rhyolitic glass, and basaltic glass.

Finch, R. J. and R. C. Ewing. 1989. Alteration of natural UO2 under oxidizing conditions from Shinkolobwe, Katanga, Zaire: a natural analogue for the corrosion of spent fuel. Swedish Nuclear Fuel and Waste Management Company (SKB). Technical Report 89-37.

Alteration of natural uraninite in an oxidizing environment "always" produces more than one secondary phase. Uraninite crystals weather in zones on the order of a few centimeters in width.

The authors maintain that altered uraninite is the best analog to spent fuel after thousands of years of storage. The Shinkolobwe deposit is about 1.8 Ga old and is hosted by dolomitic shales, siliceous dolostones and chloritic siltstones. The deposit has been exposed to surface weathering for the last 60 Ma and has suffered highly oxidizing alteration. This paper is essentially a detailed petrographic description of the present state of the uraninite. Inferences are made as to the alteration paragenesis: bequerelite, vandendriesscheite, fourmarierite, schoepite, billietite and compriegnacite are formed relatively early in the alteration sequence whereas curite, clarkeite, and masuyite tend to be formed later. The uranyl silicates uranophane and cuprosklodowskite appear to be the last phases to be formed. There is a general decrease in grain size as alteration proceeds.

Gabelman, J. W. 1981. Microscopic distribution of thorium and uranium in volcanic rock textures and minerals. *Uranium in Volcanic and Volcaniclastic Rocks- AAPG Studies in Geology No. 13*. El Paso, TX: American Association of Petroleum Geologists: 23-36.

Gabelman used EDS and SEM along with petrography and autoradiography to map the positions of radiogenic elements in a variety of volcanic rocks. He believes the distributions to be largely controlled by the volatility of U and Th: "Th/U may be more prone to volatilization than the more abundant elements." He did not often find much U or Th in glass samples; much is made of the possibility of abundant organic components in the glass. Differences were found in the distribution of radiogenic components between extrusive and intrusive rocks: plutonic rocks were found to have numerous "spot" concentrations of a and b sources whereas shallower samples had fewer such areas.

Gale, N. H. 1978. Lead isotopes and Aegean metallurgy. *Thera and the Aegean World.* C. Doumas, ed. London: Thera and the Aegean World, Inc.:529-545.

Lead isotope analysis of two samples from Thera indicates that the lead was derived from the Laurion field. One sample was arsenical copper from a jug and the other a sample of lead.

Gale, N. H. 1980. Some aspects of lead and silver mining in the Aegean. *Thera and the Aegean World.* C. Doumas, ed. London: Thera and the Aegean World, Inc.:161-195.

Isotopic data for Laurion lead is provided along with a discussion of Bronze Age trade routes and mining practices. Lead isotope compositions from Laurion are compared to those of other lead sources in the Aegean. Sources of gold and silver are also discussed.

Gale, N. H. and Z. Stos-Gale. 1981. Lead and silver in the ancient Aegean. *Scientific American* 244:176-192.

The authors analyzed 24 lead artifacts from Akrotiri. These artifacts include 21 lead weights, pottery rivets, fishnet sinkers, and doorpost sockets, and 3 samples of "litharge" (lead oxide from smelting). They believe that lead and silver may both have been mined on Thera (p. 186). They report having made both "chemical and isotopic" measurements on the artifacts, but only the isotopic analyses are reported. There is not even a qualitative description of the chemical compositions of the artifacts. Based on the isotopic determinations, the authors believe that the metal for 23 of the artifacts originated on Laurion and 1 in Siphonos.

Galloway, W. E., R. J. Finley and C. D. Henry. 1979. South Texas uranium province: geologic perspective. Texas Bureau of Economic Geology, Guidebook 18.

Common accessory phases in the uranium ores include: organic material, marcasite, pyrite, clinoptilolite, clay minerals, and calcite. Reworked, interbedded volcanic ash was the source of the uranium. Ore distributions generally follow the coarsest and initially most permeable horizons. Regional uranium content is not well correlated with a single factor such as sand distribution, faults, underlying hydrocarbons etc. After ore deposition, low sea levels during the Pleistocene exposed the shallow portions of the ores to the oxidizing environment above the water table and to oxidizing meteoric waters. This oxidation did not result in large scale remobilization of the uranium, but did cause reactions in which uranium formed more stable minerals such as autunite.

Galloway, W. E. and C. G. Groat. 1976. South Texas uranium province: geology and extraction. Texas Bureau of Economic Geology, Research Note 6.

Uranium was discovered in the South Texas coastal plain in 1954; mining began in 1960. In general, the water table is shallow (50 - 100 feet deep). Volcanic ash interbedded with the Tertiary sediments (especially the Catahoula) was the source of the uranium. Typical ore grades are only 0.X percent to 0.0X percent U3O8. Radioactive disequilibrium due to late uranium remobilization is common. Ore thicknesses range from a few feet up to 10 to 20 feet.

Gancarz, A., G. Cowan, D. Curtis and W. Maeck. 1980. 99Tc, Pb and Ru migration around the Oklo natural fission reactors. *Scientific Basis for Nuclear Waste Management.* New York: Plenum Press: 601-608.

The authors analyzed 10 samples peripheral to the reactor zones at Oklo. Samples which were originally below the reactors have lost ruthenium and ^{99}Tc relative to uranium and have either lost ^{99}Tc relative to ruthenium or have no fractionation of the two. Samples which were originally above the reactors have been enriched in ruthenium and ^{99}Tc relative to uranium and ^{99}Tc relative to ruthenium. It appears that ruthenium and ^{99}Tc were removed from below the reactors and deposited above the reactors (assuming that uranium has been quantitatively retained). These regions are about 10 m apart.

Gascoyne, M. 1987. The use of uranium-series disequilibrium for site characterization and as an analog for actinide migration. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium.* Brussels: CEC.

Uranium-series disequilibrium in a rock or mineral phase may be used to determine how recently alteration occurred and the prevailing chemical conditions at that location. This technique may be applied to a proposed repository site itself (all rocks contain trace U and Th) thereby avoiding the site specific difficulties encountered in using other natural analogs. Gascoyne describes decay-series disequilibrium and its uses. A summary of relevant alteration processes and their effects on isotopic ratios is included. The suggested ratios record evidence of disequilibrium for widely varying time ranges (234U/238U: 1.5 Ma, 230Th/234U: 350 ka, 226Ra/230Th: 8 ka).

Gauthier-Lafaye, F. and H. Ohmoto. 1989. Natural fission reactors of Oklo. *Economic Geology* 84:2286-2295.

The fission reactors at Oklo are surrounded by clay whereas the rest of the deposit consists of sandstones. The authors argue that the clays are the result of hydrothermal alteration of the host rocks by hot convecting fluids driven by the heat of the reactors. The reactor zones have 20-60 wt % uranium content. This high concentration (the normal ore is on the order of 1 to several tenths of a percent uranium) may have been produced by the hydrothermal leaching of silica from the reactor zones as well as by the addition of uranium to the zones. This ongoing enrichment may have maintained criticality for the continuation of the reactions. Fractures appear to have been the main fluid pathways and therefor to have controlled the geometry of the reactor zones.

Gauthier-Lafaye, F. and F. Weber. 1989. The Francevillian (Lower Proterozoic) uranium ore deposits of Gabon. *Economic Geology* 84:2267-2285.

The authors have reconstructed the geologic conditions under which uranium was concentrated at Oklo. The uranium is contained in deltaic sediments which overlie fluvial deposits of coarse sandstone and conglomerates which are the source rocks for the uranium. The deltaic sediments are overlain by marine black shales. The deposits are in tectonic structures which served as traps for both uranium and petroleum. The authors suggest that uranium mineralization took place during an uplift stage in relatively high levels of the basin which were also good hydrocarbon traps. The relation between uranium and petroleum occurrence is believed to be direct - uranium was precipitated as the oxidizing transport fluids were reduced by mixing with reduced fluids carrying hydrocarbons.

George-Aniel, B. G., J. Leroy and B. Poty. 1985. Uranium deposits of the Sierra Peña Blanca. *Uranium Deposits in Volcanic Rocks*. Austria: International Atomic Energy Agency, proceedings of a technical committee meeting, El Paso, TX April 1984. IAEA-TC-490: 175-186.

Using mineralogic, petrographic, geochemical and fluid inclusion data, the authors have divided the ores of Peña Blanca into three groups. First, hydrothermal ores (e.g. Nopal I) which are linked to faults or breccia pipes. Second, stratiform deposits (e.g. Puerto III) of oxidized mineralization which occur in the upper part of the Nopal Formation. Third, mixed ore deposits (e.g. Las Margaritas) formed by the interaction of hydrothermal fluids and supergene groundwaters. At Nopal I the main alteration is kaolinization of the upper Nopal tuffs (well formed hexagonal plates imply hydrothermal origin). Some fluid inclusions at Nopal I "in the vapor phase of quartz" are reported to contain CO_2 and N_2 as well as H_2O and to have high homogenization temperatures (400°C). Other inclusions have low salinity (0 to 4.94 wt % equiv. NaCl) and lower temperatures (150 - 250°C). Background U concentrations in the Nopal tuff are given as 6 - 10 ppm and in the Escuadra tuff: 3.93 ppm U.

Girardi, F. and M. D'Alessandro. 1988. Applicability and perspectives of natural analogues as "demonstration" of Pagis models. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting*. Snowbird, Utah: CEC:145-158.

This paper presents a preliminary set of tables which show lists of phenomena associated with a variety of HLW disposal options (clay, granite, seabed, and salt) and possible natural and archaeologic analogs to the associated phenomena. Granite - related analogs are the most

abundant. This information was prepared for the PAGIS Project (the European Community Project on Performance Assessment of Geological Isolation Systems).

Glasbergen, P. and G. C. Wijland. 1990. A Netherlands natural analogue - uranium enriched nodules in a brackish sandy aquifer. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print*. B. Come and N. A. Chapman, eds. Brussels: Commission of the European Communities: n° EUR 13014 EN.

Three layers of phosphorite nodules (0.5-10 cm) occur in porous, unconsolidated sediments under brackish groundwater conditions. The nodules contain uranium which is bound to apatite; apatite constitutes 30-40% of the nodules. The authors plan a study of uranium migration from these nodules to provide information for model validation. Specifically, they hope that such a study will "contribute to the understanding of the influence of variable salt concentrations" on migration processes, and will "provide confidence in our understanding of the processes" involved. They plan to validate their models by "comparing the present-day concentration profiles with the predicted ones."

Golian, C., M. Ivanovich, D. A. Lever and G. Longworth. 1988. Modelling radionuclide migration in the Koongarra ore deposit. Australian Nuclear Science and Technology Organisation. ANSTO Alligator Rivers Analogue Project - Progress Report, May 1988 - August 1988 : 65-68.

In the past two one-dimensional models have been used, these authors are using a two dimensional model which incorporates sorption onto two solid phases: one which comes to equilibrium rapidly and one more slowly. They have tested the model against data from one region of the Koongarra ore deposit with poor results. They conclude that a more sophisticated model involving a recoil mechanism between the two phases is required.

Goodell, P. C. 1981. Geology of the Pena Blanca uranium deposits, Chihuahua, Mexico. *Uranium in Volcanic and Volcaniclastic Rocks- AAPG Studies in Geology No. 13*. El Paso, TX: American Association of Petroleum Geologists: 275-291.

Limestone bedrock underlies the Pena Blanca District. Above this limestone is a limestone conglomerate (Pozos Formation) followed by a partially welded crystal-lithic to lithic crystal tuff (Nopal Formation) which is overlain by a sequence of air-fall and water worked tuffs, a thick lahar and a single cooling unit (Escuadra Formation). The clastic and air-fall tuffs of the Pena Blanca Formation are next, followed by a single cooling unit comprised of a thin volcanic arenite, a vitrophyre and a densely welded zone (Mesa Formation). At the Nopal 1 deposit, uranium mineralization occurs in a breccia zone and extends a short distance into the welded tuff. Uranium mineralogy at Nopal 1 consists mostly of U-silicates with only minor U-oxides. At the Margaritas deposit, uranium occurs in tuff, altered vitrophyre and pumice zones, structurally dislocated zones and in the bedrock limestone; uranium mineralogy consists solely of U-silicates. Geochemical zoning at the deposits is similar to that of uranium roll front deposits. The uranium was likely derived from the alteration of volcanic glass by convective hydrothermal groundwater systems. Rock facies and structures probably controlled fluid paths. These deposits appear to be chemically zoned; the uranium is associated with selenium, arsenic, lead, molybdenum, and mercury.

Goodell, P. C. 1985. Chihuahua City uranium province, Chihuahua, Mexico. *Uranium Deposits in Volcanic Rocks*. Austria: International Atomic Energy Agency, proceedings of a technical committee meeting, El Paso, TX April 1984. IAEA-TC-490: 97-124.

Goodell briefly mentions two alternative hypotheses as to the origin of the Peña Blanca uranium deposits, then presents his ideas. First, it is possible that an alkalic magma at some depth beneath the Pena Blanca Block has given off magmatic-hydrothermal fluids which are the source of the mineralization. Second, a vague process of "degassing and recrystallization" of the ignimbrite units operating at "lower temperatures" and drawing on a "near-source origin" for the uranium is postulated. Goodell proposes that the ores formed by infiltration of meteoric water into a geothermal system driven by the high heat flow at a rift boundary. These fluids may have leached uranium from the peralkaline, uranium-rich rocks (20-60 ppm U) and deposited it in response to cooling, passing into a reducing environment, and/or a siliceous environment. These possible mechanisms of deposition are not further described.

Goodwin, B. W., J. J. Cramer and D. B. McConnell. 1988. The Cigar Lake uranium deposit: an analogue for nuclear fuel waste disposal. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting*. Snowbird, Utah: CEC:180-189.

This paper is an excellent summary of the analog characteristics of the Cigar Lake deposit. The deposit occurs at a depth of 430 m at the unconformable contact between the Athabasca Sandstone and the basement rock. There are no direct surface indications of the existence of the deposit (radiologic, thermal, geophysical, or geochemical); the deposit was discovered by indirect geophysical means coupled with a knowledge of the genetic processes which can form such a deposit. Primary uranium minerals are uraninite and coffinite. The average grade is about 12% uranium with maximum concentrations as high as 55%. The deposit is surrounded by a 5 to 30 m thick alteration zone consisting of illite, kaolinite, quartz, and minor rutile. The ore is also covered by a quartz-cemented cap. A list of analog aspects includes: (1) waste form - uraninite (the main ore mineral) is a good analog to uranium dioxide (the main waste component) (2) container - the Canadians anticipate a titanium container which would alter to have a rutile coating in an aqueous environment, the accessory rutile in the alteration zone at the deposit is a good analog (3) buffer - a planned bentonite and sand buffer is approximated by the illite-rich alteration zone around the ore; bentonite would alter to illite at the conditions (150 - 200°C and solution compositions) anticipated for the site (4) geosphere - rather than a large granitic pluton, the Cigar Lake deposit is hosted by a porous sandstone; water circulation in the sandstone is much greater than would be expected for a granite, so the deposit provides a conservative estimate of the effects of circulating groundwaters.

Grambow, B., M. J. Jercinovic, R. C. Ewing and C. D. Byers. 1985. Weathered basalt glass: a natural analogue for the effects of reaction progress on nuclear waste glass alteration. *Materials Research Society Symposia Proceedings* 50:263-272.

This paper compares observations of alteration of natural basaltic glasses with the predictions of a computer model developed to describe the alteration of nuclear waste form glasses. Glass samples include: nine from subglacial volcanoes in British Columbia, three from pillow basalts in Iceland, and four from drill core of the Deep Sea Drilling Project. The calculated alteration sequence is: nontronite - saponite - phillipsite - chabazite. This agrees well with the observed sequence: palagonite - smectite (saponite) - phillipsite - gyrolite - chabazite - analcime, with some discrepancies. In both experiments and in nature, it was observed that saponite forms and persists even though calculations show it to be metastable with respect to celadonite, emphasizing the possibility of solution composition control by metastable phases. The environment of weathering can vary the alteration rate by as much as five orders of magnitude; long term survivability of the glass is enhanced by low temperatures and low water circulation. The surfaces of even the smallest cracks in the glass are as altered as the open surfaces, an important observation for the cracks in waste glasses.

Grauch, R. I., A. R. Kirk, K. Hon, K. R. Ludwig, H. H. Mehnert, J. A. Zamudio and L. M. Bithell. 1985. Episodic uranium mineralization in the western San Juan Caldera complex, Colorado. *Uranium Deposits in Volcanic Rocks*. Austria: International Atomic Energy Agency, proceedings of a technical committee meeting, El Paso, TX April 1984. IAEA-TC-490: 315.

This paper describes several uranium occurrences in the Lake City and Uncompahgre calderas of the western San Juans. The host rocks range from early calc-alkaline andesites to younger high silica alkali rhyolites and alkalic basalts. Specifically, 27.5 Ma uraninite is noted at the Golden Fleece vein and other mines, usually in association with gold and silver, and often with tellurides. U concentrations are quite low, on the order of 10 - 50 ppm.

Guthrie, V. 1991. Determination of recent ^{238}U, ^{234}U and ^{230}Th mobility in granitic rocks: application of a natural analogue to the high-level waste repository environment. *Applied Geochemistry* 6:63-74.

This paper presents interesting results of a study of differential U and Th mobility in Australian granitic rocks. The "application of a natural analogue to the high-level waste repository environment" promised in the title occurs as a few sentences in the final paragraph where it is observed that the measured disequilibrium "provides a qualitative identification of the migration processes" likely to operate in a repository environment. In all three sites examined, it appears that significant mobilization of radionuclides occurred within the past 1 Ma, probably as a result of groundwater migration. The author says that the association of U with highly sorptive phases implies that sorption is the mechanism for U fixation rather than coprecipitation incorporating U into the crystal lattice of the Fe and Ti oxyhydroxides.

Haaker, R. F. and R. C. Ewing. 1980. Natural analogues for crystalline radioactive waste forms, part II: non-actinide phases. *Scientific Basis for Nuclear Waste Management III - Materials Research Society Symposium Proceedings*. New York: Plenum Press: 299-305.

This paper summarizes data on mineral analogues to components of the proposed waste forms "synroc" and "supercalcine." Nepheline, scheelite, pollucite, sodalite, and priderite (hollandite) are discussed. The authors recommend that nepheline syenites would be the most stable hosts for high-Na supercalcine, that granites would be the most stable hosts for low-Na supercalcine, and that low silica, feldspar-free rocks would be the most stable hosts for synroc.

Hallberg, R. O., P. Ostlund and T. Wadsten. 1987. A 17th century bronze cannon as analogue for radioactive waste disposal. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium*. Brussels: CEC.

A bronze cannon (96.3 wt % Cu) was investigated as an analog of Swedish copper HLW canisters. The cannon was buried for 300 years in dense clays of a similar composition to the clays used in the Swedish repositories. Migration of Cu into the clays was found to be only 4 cm. Minimum rates of corrosion were estimated to be 1.5 - 7.5 mm per 100,000 yrs.

Hammer, C. U., H. B. Clausen, W. L. Friedrich and H. Tauber. 1987. The Minoan eruption of Santorini in Greece dated to 1645 BC? *Nature* 328:517-519.

Hammer et al. report a new date for the Santorini eruption of 1645 ± 20 BC based on acid fallout preserved in ice layers in a core from South Greenland. The village of Akrotiri is presently being excavated (1987).

Hardy, C. J. and P. Duerden. 1988. Progress in the Alligator Rivers analogue project. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting*. Snowbird, Utah: CEC:43-49.

Much of this paper is a history of the organizational evolution of the Alligator Rivers - Koongarra project. The authors also provide a summary of research progress to date, including modelling, hydrogeology, radionuclide disequilibria and other chemistry. There is a brief discussion of extraction and analytical techniques for 239Pu and 99Tc. Sampling methods for water and colloids are also described.

Heiken, G. and F. McCoy Jr. 1984. Caldera development during the Minoan eruption, Thira, Cyclades, Greece. *Journal of Geophysical Research* 89:8441-8462.

The Santorini eruptions of about 1400 BC may be divided into four distinct phases: 1) Plinian eruptions from subaerial vents; 2) large-scale base surge deposits formed by phreatomagmatic activity; 3) poorly bedded tuff formed by phreatomagmatic eruptions which deposited about 60% of the volume of Minoan tuff; 4) ignimbrite flows. All eruption phases deposited pyroclasts of rhyodacitic composition. Akrotiri was the largest and best known of the Minoan villages destroyed by the eruptions. No human skeletons have been found indicating that most of the inhabitants had left in advance of the eruption.

Henry, C. D. and R. R. Kapadia. 1980. Trace elements in soils of the South Texas uranium district: concentrations, origin, and environmental significance. Texas Bureau of Economic Geology, Report of Investigations No. 101.

Molybdenum, arsenic, and selenium are concentrated with uranium in the ores of the South Texas uranium deposits. Background levels of these elements in unmineralized areas are similar to published average concentrations in soils worldwide. High soil concentrations of Mo, As, and Se correspond well with shallow U mineralization. There is no evidence that windblown dust from mining operations has affected the concentrations of these elements in the soils.

Hodgkinson, D. and D. Lever. 1985. Natural analogues for radioactive waste burial: a modelling perspective. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, First Meeting*. Brussels: CEC:15-31.

The authors stress that given the likelihood of substantial uncertainty in the interpretation of natural analogs, it is their general features that should be emphasized and models with appropriate levels of sophistication should be used. Modelers should also remember that there is no requirement to model the future with certainty, but only within the limits specified by regulatory authorities. Laboratory experiments are relatively well constrained and the results can be modelled in some detail whereas field experiments are less well characterized necessitating less detailed models and natural analogs are even less well defined experiments requiring yet more general models. "To date, even the most carefully performed and analysed field migration experiments have not yielded

unambiguous interpretations." Nevertheless, natural analogs have many uses, including: general confirmation of radionuclide migration; the relative migration of different species; evidence that the migration mechanisms under consideration are important over the relevant time scales; evidence of important mechanisms which may have been overlooked in the models. The highest dose rates may arise from ^{129}I, ^{99}Tc, and ^{237}Np, so they have high priority in natural analog studies. Some questions to bear in mind when modelling natural analogs are: 1) Which phenomena need to be included in the model? 2) Which parameters can be measured and how accurately are they known? 3) How much have these parameters varied over the time scale of the analog? 4) What are the initial conditions from which the analog developed and when did they occur? 5) What complexity of mathematical model is appropriate to the available data?

Hofmann, B. 1988. Geochemical analogue study in the Krunkelbach mine, Mezenschwand, Southern Germany: Geology and water - rock interaction. *Scientific Basis for Nuclear Waste Management XII - Materials Research Society Symposium Proceedings*. Pittsburgh: Materials Research Society: 921-926.

The uranium ore body at Krunkelbach lies parallel to and only a few meters away from a fracture zone which acts as a major groundwater channel. The ore is oxidized down to a depth of at least 240 m. At present, uranium migration is retarded by sorption onto iron oxyhydroxides, gorceixite, and clays; radium is fixed in barite. At an earlier stage, when pyrite was actively altering, radium was probably more mobile due to the formation of sulfur complexes. Suspended material composed of clays (illite>kaolinite>smectites), quartz, gorceixite, and amorphous iron oxyhydroxides, with diameters >0.22μm constitutes 0.006 to 5.9 ppm of the groundwater; these particles appear to have been transported 1 to 2 km. [No information is given as to the radionuclide composition of these colloids.]

Hofmann, B., J. P. Dearlove, M. Ivanovich, D. A. Lever, D. C. Green, P. Baertschi and T. Peters. 1987. Evidence of fossil and recent diffusive element migration in reduction haloes from Permian red-beds of northern Switzerland. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium*. Brussels: CEC:217-238.

Cores from Permian redbeds in Northern Switzerland often intersect reduction haloes of 1 to 100 mm diameter. The cores of the haloes are enriched in U, Th, Se, REE and Pd and may contain organic material. The spherical shape of the haloes suggests formation by diffusion controlled migration of the elements which may be analogous to elemental migration in a HLW repository. Uranium concentrations in the cores range from 35 wt% U to 6 ppm U over a distance of 10 to 15 mm. Modelling is being undertaken to try to quantify the diffusion rates.

Holmes, D. C., A. E. Pitty and D. J. Noy. 1990. Geomorphological and hydrogeological features of the Poços de Caldas caldera and the Osamu Utsumi mine and Morro do Ferro analogue study sites. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print*. Brussels: Commission of the European Communities: n° EUR 13014 EN.

The sites are located in water shed areas near small streams in the center of the Poços de Caldas plateau. The climate of the area varies from quite wet from November to April to dry the rest of the year. Natural slopes tend to be steep. The caldera is relatively stable with an erosion rate of about 12 m per million years over the last 50 Ma.

Hooker, P. J. 1988. The U.K. natural analogues programme. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting*. Snowbird, Utah: CEC:88-95.

Four natural analog sites are being studied by the British Geological Survey: Loch Lomond, Scotland; Needle's Eye, Scotland; South Terras, Cornwall; and Broubster, Scotland. At Loch Lomond, 8000 year old sediments have been cored and the halogen speciation in the pore waters studied. At Needle's Eye, pitchblende veins occur beneath coastal sediments and outcrop in a cliff of Paleozoic rocks. The chemical compositions of local groundwaters have been measured and the fluid speciations modeled. A comment indicates they have had difficulties with inadequate descriptions of the source terms and redox conditions affecting elemental mobilization. At South Terras, they have taken samples from soil profiles between dump piles of a uranium mine. Distributions of uranium decay series elements were found to correlate with the amounts of organic matter, iron oxyhydroxides and sorbing clays in the soils. Water samples from a river next to the dumps indicate leaching of uranium from the dumps. At Broubster, uranium and hydrocarbon mineralization in sandstone has provided a source of uranium and associated elements to local groundwater which has tended to carry the elements to a peat bog about 100 m away. U was found to be associated with organics whereas Th tended to accumulate with Fe/Al oxyhydroxides and colloids.

Hooker, P. J. and N. A. Chapman. 1987. UK (United Kingdom) natural analogue co-ordinating group: first annual report. Department of the Environment. DOE-RW-88.036.

This report contains only very general descriptions of sites and research programs underway in the UK and in Brazil (Poços de Caldas) and Australia (Alligator Rivers). Sites in the UK include: Needle's Eye, South Terras, Lundin Castle, Loch Lomond, Permo-Triassic radioactive nodules (at Littleham and Knowle), and granite blocks submerged at Falmouth Docks from 1956 - 1987.

Hooker, P. J., N. A. Chapman, A. B. MacKenzie, R. D. Scott and M. Ivanovich. 1987. Natural analogues of radionuclide migration in sediments in Britain. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium*. Brussels: CEC.

Hooker et al. have studied 2 locations in Britain where pitchblende veins are associated with sediments and occur in shallow, low temperature weathering environments. They report highly efficient removal of mobilized U from solution upon contact with anoxic soils. Concentrations of mobilized U and Th isotopes were found to be a function of organic contents, presence of secondary Fe oxyhydroxides and permeability.

Hooker, P. J., A. B. MacKenzie, R. D. Scott, M. Ivanovich, T. K. Ball, I. R. Basham, A. J. Bloodworth and P. D. Roberts. 1986. Natural analogues of radionuclide migration: reconnaissance study of sites. British Geological Survey. FLPU 86-6.

This is a progress report to the UK's Department of the Environment (DOE) describing attempts to "define locations within the UK and abroad worthy of detailed investigation" as natural analogues of radionuclide migration. Sites identified include: Needle's Eye (diffusion of decay series elements from a pitchblende vein into overlying clay-rich silt over the last 10 ka), South Terras (transport of decay series elements from U mine tailings in surface waters), Lundin Castle (diffusion of U, Th, REE, Br ... in sediments), Loch Lomond (mobilization of I and Br from an organic origin from marine sediments into the overlying freshwater deposits), Permo-Triassic

radioactive nodules (diffusion of decay series isotopes from reduction centers into the enclosing clays), Broubster, Caithness (speciation and transport of U/Th in peat groundwaters).

Ildefonse, P., P. Agrinier and J.-P. Muller. 1990. Crystal chemistry and isotope geochemistry of alteration associated with the uranium Nopal 1 deposit, Chihuahua, Mexico. *Geochemistry of the Earth's Surface and of Mineral Formation.* Aix en Provence, France: 371-372.

The authors assert that "crystal-chemical properties and isotopic compositions of" clay minerals "can be used to [establish] precise physico-chemical parameters of alteration." They say they have applied this idea to the Nopal I deposit. They recognize two major alteration types: 1) kaolinization/silicification in the mineralized zone and 2) smectitization of the glassy matrix and weak argillization of feldspars in the underlying tuffs. The authors find that kaolinites in the mineralized area have a greater concentration of "defect centers" than those away from the mineralized area. The authors assume formation of the ores from local meteoric water, and then calculate formation temperatures from O and H isotope data on kaolinite, smectite and opal. Temperatures are believed to have been about 60°C (kaolinite) to 25 - 50°C (smectite) to 35°C (opal). They mention a "thermal gradient" within the deposit which is in accordance with mineralogical variations which they do not describe.

Ildefonse, P., J.-P. Muller and G. Calas. 1990. Assessment of radionuclide migration in natural analogues by radiation-induced centers in kaolinites. *Scientific Basis for Nuclear Waste Management XIV.* Boston: Materials Research Society Symposium Proceedings Series Vol. 212:474.

The authors have used kaolinite as an "in situ dosimeter" to infer a history of past irradiation. They used electron paramagnetic resonance to measure the abundance and types of paramagnetic defect centers (PDC) present in kaolinite from various locations within ore deposits. By comparing observations of naturally irradiated kaolinites to kaolinite irradiated in the lab (X-rays, g-rays, He^+ and $Pb2^+$ ion beam implantation), several types of defect centers have been resolved. This is essentially a technique report. They have tried it at Peña Blanca, Mexico, and other ore deposits and they propose that "PDC dosimetry" could be used in natural analog sites.

Ildefonse, P., J.-P. Muller, B. Clozel and G. Calas. 1990. Study of two alteration systems as natural analogues for radionuclide release and migration. *Engineering Geology* 29:413-439.

The authors report on the Nopal I deposit at Peña Blanca, Mexico and some weathering profiles from Cameroon with regard to paragenesis of secondary minerals and radionuclide behavior. They found that the concentration of paramagnetic defect centers in kaolinite at the Peña Blanca site varied with location (highest in the breccia pipe/ore body) and were always "more than ten times" more abundant than those in the weathering profiles. Ildefonse et al. conclude that such defect centers could be useful to determine paleoradiation exposure in HLW natural analogs. Primary and secondary uranium mineralization at Peña Blanca is described briefly. [a reference is made to an as yet unpublished paper giving the details].

Ivanovich, M. 1985. Evidence for field measurements of retardation factors for U/Th/Ra radionuclides. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, First Meeting*. Brussels: CEC:129-132.

Ivanovich notes that there have been only a few studies in which retardation factors have been measured or relevant data obtained for the calculation of retardation factors. He further observes that different workers have measured retardation factors for the same elements which differ by orders of magnitude, results partly deriving from differing assumptions and partly from differing geochemical and geological conditions. He is, however, encouraged that the values for uranium and thorium are "sufficiently large" that natural retardation does appear to occur.

Ivanovich, M., P. Duerden, T. Payne, T. Nightingale, G. Longworth, M. A. Wilkins, R. B. Edghill, D. J. Cockayne and B. G. Davey. 1987. Natural analog study of the distribution of uranium series radionuclides between the colloid and solute phases in the hydrogeological system of the Koongarra uranium deposit N.T., Australia. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium*. Brussels: CEC:300-313.

Samples of groundwater from 5 drill holes at the Koongarra uranium deposit at Alligator Rivers, Australia, were sampled for study of their colloidal content. This paper includes brief descriptions of the sampling and analytical procedures. Very little particulate material was found in the "colloid" size range (<1 micron). Drill holes closest to faults were found to have the greatest variety of colloids. All colloid samples were dominated by Fe-rich particles and for all particle sizes, uranium was only found in Fe-rich species. Only Th, Ac, Fe, U, and possibly Al were found to be carried as colloids.

Jakubick, A. T. and W. Church. 1986. *Oklo natural reactors: geological and geochemical conditions-a review*. Ottawa: Atomic Energy Control Board (Canada) Research Report.

This paper reviews published and unpublished information about Oklo with regard to the long-term aspects of radioactive waste disposal. Topics include: Pu retention, metamictization, fission product release, hydrogeochemical stability, and migration of fission products. The authors believe that quantitative reconstruction of the coupled thermo - hydrologic - chemical processes at Oklo can be achieved by studying the deviations in the 2H/1H and 18O/16O ratios of minerals.

Jantzen, C. M. 1986. Prediction of nuclear waste glass durability from natural analogs. *Advances in Ceramics* 20:703-712.

Jantzen compared the durability of HLW glasses to that of natural glasses with respect to their relative thermodynamic stabilities with the intention to extrapolate the results to "geologic time." He found that the durability of natural glasses and ancient man-made glasses bracket the durability of nuclear waste glasses. He proposes that the lifetime of waste glass may be expected to fall between 10^6 and 10^3 years. Durability is directly related to glass composition.

Jefferies, N. L. 1987. Long-term solute diffusion in granitic blocks immersed in sea water. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium.* Brussels: CEC.

Elemental profiles of Cl^-, Br^-, F^-, and $SO_4^=$ have been measured in a block of granite which has been submerged in seawater for 30 years at Falmouth, Cornwall, England. Profiles for Cl and Br were flat, indicating equilibrium between the pore water and the seawater. F and SO_4 have high concentrations at the margins of the block which is interpreted as indicating that they are diffusing out of the block into the seawater.

Jercinovic, M. J., R. C. Ewing and N. S. Criepi. 1987. Basaltic glasses from Iceland and the deep sea: natural analogues to borosilicate nuclear waste-form glass. Svensk Kaernbraenslefoersoerjning A.B., Stockholm. SKB-JSSP-TR-88-01.

The authors studied the alteration processes and products of basaltic glasses from submarine deposits near Iceland and from sub-glacial volcanic deposits. Leached layers were found to consist mainly of smectite-type clays. Channels through the altered layers were observed which provide access for solutions to reach fresh glass so that the glass is not protected from the solutions by the formation of an alteration layer. Corrosion rates were difficult to establish because contact time of the solution with the glass was not well known. Two rates were apparent, however: an initial rate in silica undersaturated environments and a long-term rate in silica-saturated environments. Long-term alteration is estimated to proceed at a rate of at least 0.01 μm/1000 years. The palagonite formed in seawater is rich in alkalis and iron relative to the palagonite formed in fresh water. The rind thickness of the palagonite does not correlate with age of a sample because of differences in solution contact time, as well as solution composition differences (e.g. pH and silica concentration).

Jeremy, P. L. D., D. C. Green and M. Ivanovich. 1988. Uranium transport and the partitioning of U, Th, and Ra isotopes between solid and aqueous phases in the Krunkelbach mine, Federal Republic of Germany. *Scientific Basis for Nuclear Waste Management XII - Materials Research Society Symposium Proceedings.* Pittsburgh: Materials Research Society: 927-932.

At the Krunkelbach mine, uranium is dissolved by carbonate rich waters and carried in concentrations of 1 - 4 ppm. Over a distance of a few meters, the concentration drops about 2 orders of magnitude, the major uranium species changes from carbonate to phosphate, secondary uranium sulphates precipitate, and uranium is accumulated by gorceixite $[BaAl_3(PO_4)(PO_3OH)(OH)_6]$ and smectite and chlorite clays. These observations are in good agreement with modelling with PHREEQE. As much as 10% of the uranium and all of the thorium may be transported by colloidal iron oxyhydroxide phases under oxidizing, near neutral pH conditions.

Johnson, A. B., Jr. 1988. Metal durability from the ancient metals. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting.* Snowbird, Utah: CEC:227-230.

The ancient metals include metal meteorites, native metals (most commonly copper, gold, silver, Ni-Fe alloys, platinum and some iron), and archaeological metals (gold, silver, copper, iron, lead, tin, and mercury). The ancient metals do not constitute close analogs to nuclear waste containers. Their compositions are different; they have not experienced high temperatures (in general); and they have not been exposed to radiation. Johnson points out that: coppers and bronzes are

generally more durable than iron-based metals; oxides formed on the surfaces of metal meteorites contain bits of metal which are more durable that the bulk metal; oxides and oxide coatings may contribute to metal preservation; even iron-based metals can survive well in dry or even periodically moist environments; galvanic coupling effects have been observed in ancient metals.

Kamineni, D. C. 1986. Distribution of uranium, thorium and rare-earth elements in the Eye-Dashwa Lakes Pluton: a study of some analogue elements. *Chemical Geology* 55:361-373.

The distribution of U, Th, and REE's were examined in unaltered granite, altered granite, highly altered granite adjacent to open fractures, and fracture filling minerals. Th is concentrated in highly altered granite adjacent to open fractures, and fracture filling minerals. Mobilization of these elements is limited by sorption onto "clays" (kaolinite, chlorite, and goethite), inclusion in structural site of minerals (epidote, sphene, calcite, and gypsum), and by precipitation of minerals such as bastnaesite, uraninite, and thorogummite.

Kaplan, M. F. 1979. Ancient materials data as a basis for waste form integrity projections. prepared for DOE by The Analytic Sciences Corporation. TR-1746-1.

Kaplan summarizes the available data on long-term durability of glass and glass-like materials. She provides descriptions of the objects, chronological relations, and chemical compositions where available. The chemical compositions are usually only major oxides though some trace elements are given. One section discusses the environment of preservation; Kaplan notes that the arid, near constant (temperature and humidity) conditions of Egypt are clearly the best for preserving glass, but no sites or specific examples are given. Glass corrosion products are discussed in some detail (composition and mineralogy and form). No geologic relations are included in this paper.

Kaplan, M. F. 1980. An archaeological perspective on a modern issue: nuclear waste disposal. *Journal of Field Archaeology* 7:265-267.

Glass has been suggested as a HLW form because it is relatively unreactive chemically and its lack of crystalline structure reduces the possibility of radiation damage. Mankind has been making glass for about 3500 years and some of these objects have survived to the present. Mankind has, therefore, already manufactured materials which have survived under actual burial conditions for time periods comparable to those proposed for HLW repositories. The HLW forms would have to endure radiation and heat which were not present for the archaeologic glass, but the HLW glass will also be designed to last for thousands of years and to accommodate the heat and radiation whereas the archaeologic glass was intended only for a relatively brief useful life.

Kaplan, M. F. 1980. Characterization of weathered glass by analyzing ancient artifacts. *Scientific Basis for Nuclear Waste Management 2*. New York: Plenum Press: 85-92.

Glass was first manufactured about 1500 B.C. in what is now Egypt and Iraq. Early glass was soda-lime; in about 1000 A.D. potassium-lime glass began to be manufactured. Lead glass was not made until about 200 B.C. and has been only rarely produced. The author makes a case for use of ancient glass as an analog for HLW glass. Major oxide compositions are given and the types of weathering are described.

Kaplan, M. F. 1982. Marking a nuclear waste repository: an archaeologist's perspective. *Transaction of the American Nuclear Society* 41:96-97.

Kaplan emphasizes the difference between "durable" materials and "survivable" materials; many metals are quite durable but will not survive due to the inherent value of metallic materials. She suggests that rock is the most survivable material and recommends basalt and granite for marker materials because of their fine grained texture, low permeability and porosity, hardness (but not brittleness) and homogeneity.

Kaplan, M. F. 1986. Mankind's future: using the past to protect the future - Archaeology and the disposal of highly radioactive wastes. *Interdisciplinary Science Reviews* 11:257-268.

Kaplan discusses the archaeological background for designing a marking system for a HLW repository. "Archaeology is concerned with man-made monuments and information which have survived for long periods of time." Archaeological examples include the 4th Dynasty Pyramids at Giza, Egypt; Stonehenge, England; the Acropolis, Greece; the Great Wall of China; and Serpent Mound, Ohio. These examples provide a record which spans nearly 5000 years. She emphasizes that the materials which have survived the best are natural ones (earthworks and stone); the inherent value of metals has led to the destruction of monuments and parts of monuments constructed of metals.

Kaplan, M. F. and J. E. Mendel. 1982. Ancient glass and the safe disposal of nuclear waste. *Archaeology* July/August:22-29.

Glass objects have been identified which are as old as 3500 years; these artifacts were not designed to last this long and are made of soda-lime glasses rather than the borosilicate glasses proposed for HLW. There are five main types of glass decomposition: 1)weeping - the sweating of droplets of water when excavated glasses come into contact with moisture in the air, 2)crizzling - the formation of networks of tiny cracks all over an object's surface, 3)pitting - formation of pit-like scars by abrasive action or chemical dissolution leaving holes filled with weathering products, 4)layering - development of a filmy iridescent surface formed of multiple layers of mica-like minerals, and 5)crusting - development of powdery, amorphous and opaque residues by the leaching of chemicals out of the glass in a way that alters the object's structural stability. The authors include a ternary diagram showing the range of archaeologic glass compositions. The authors suggest that many ancient glasses may already have survived more destructive environments (changing temperatures and humidity) than those that will be faced by HLW glass.

Kent, D. V., D. Ninkovich, T. Pescatore and S. R. J. Sparks. 1981. Palaeomagnetic determination of emplacement temperature of Vesuvius AD 79 pyroclastic deposits. *Nature* 290:393-396.

Based on the variation of remnant magnetism with temperature, the authors conclude that the maximum temperature of the deposits was about 400°C. Earlier work (Maury, 1976) using incinerated wood from the site, indicated a minimum temperature of about 400°C. Kent et al. conclude that the actual temperature must therefore have been quite close to 400°C.

Kim, J. I., G. Buckau and R. Klenze. 1987. Natural colloids and generation of actinide pseudocolloids in groundwater. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium.* Brussels: CEC.

Kim et al. point out that "all natural colloids" contain many trace heavy metals, REE's and etc. which are chemically similar to some fission products and actinides and which may therefore serve as analogs of colloidal transport of HLW species. Groundwater samples were taken at the Gorleben aquifer and the colloids studied (chemical composition, abundance, size distribution). Americium was added to form "pseudocolloids" to study speciation and behavior. A method is suggested for distinguishing between humic colloids and humate complexes in solution.

Kim, J. I., G. Buckau, H. Rommel and B. Sohnius. 1988. The migration behavior of transuranium elements in Gorleben aquifer systems: colloid generation and retention process. *Scientific Basis for Nuclear Waste Management XII - Materials Research Society Symposium Proceedings*. Pittsburgh: Materials Research Society: 849-854.

The Gorleben aquifer system consists of porous sands with some clay. Colloid concentrations are on the order of 1012 particles/L and may be both organic and inorganic. Waters with high concentrations of humic substances tend to have higher colloid concentrations than those with low humic concentrations. The formation of colloids may enhance or inhibit the migration of radionuclides depending on the filtration properties of the system.

Koss, V. 1988. Modeling of nickel sorption and speciation in a natural sediment-groundwater system. *Scientific Basis for Nuclear Waste Management XII - Materials Research Society Symposium Proceedings*. Pittsburgh: Materials Research Society: 843-848.

Using samples and data from 15 Gorleben groundwater systems, the author has modelled the sorption behavior of nickel. He reports that the main factors controlling nickel sorption are the cation exchange capacity of the sediment, and the ionic strength and the pH of the groundwater. Results of the calculations indicate that carbonate complexes are the important nickel species in Gorleben groundwaters and that a simple surface complexation model describes sorption correctly in systems too complex to be modelled with available data.

Krauskopf, K. B. 1986. Thorium and rare-earth metals as analogs for actinide elements. *Chemical Geology* 55:323-335.

The transuranic actinides occur in nature only in vanishingly small concentrations, therefore it is necessary to choose elements of greater abundance, which have similar chemical characteristics in order to predict the chemical behavior of transuranic actinides. Th is a good analog for Pu (IV) because over a wide range of Eh and pH conditions, Pu remains as Pu (IV). For both Th and Pu, the stable form under most conditions is the dioxide; the main dissolved species is the undissociated hydroxide. Complexes with common ligands have similar stability constants. There are some differences: Pu has stable oxidation states above and below (IV). Especially important are carbonate complexes of Pu (III) (V) and (VI) which are particularly stable (enough to make Pu dioxide more soluble than Th dioxide under low Eh and pH, and of high Eh and pH. But without high carbonate concentrations, the two compare well. REE's make good analogs for Am and Cm which exist only as (III) under repository conditions and which have very similar stability constants for compounds and complexes to the REE's. The low groundwater concentrations of Th at Morro do Ferro are good assurance that Pu would also stay put. The difference in oxidizing conditions between the ore deposit and a repository is not important since Th is not affected by oxidation and reduction. Similarly, the low concentrations of La and Nd in groundwater at Morro do Ferro indicate that Am and Cm will not tend to migrate far. Th also makes a reasonable analog for Np, thought the range of oxidizing conditions over which the comparison is valid is smaller than for Pu.

Krumhansl, J. L. and H. W. Stockman. 1988. Site selection criteria and preliminary results from the Valles Caldera natural analog study. D. Evans, ed. *Proceedings of Workshop IV on Flow and Transport Through Unsaturated Fractured Rock - Related to High-Level Radioactive Waste Disposal.* University of Arizona: 249-276.

The site is located in the Jemez mountains of Northern New Mexico. The objective of the study is to investigate elemental migration and secondary mineral development at the boundary of the Banco Bonito obsidian flow and the underlying tuffaceous rocks. There is a reddish "baked" zone extending some tens of feet into the tuffs. Criteria for choosing the site included 1) accessibility 2) young age and simple geologic history 3) decades of heating at 150 - 350°C 4) unsaturated hydrologic conditions. Cs and Rb (relatively mobile elements) showed little variation with distance from the contact whereas Th, Ta, Hf, Co, and REE (relatively immobile elements) had slight compositional trends (which may have predated the obsidian flow). The Cs/Rb ratio (which is usually a good indicator of hydrothermal alteration) does not vary with distance from the contact. The only evidence of elemental transport so far is H_2O and chlorine which are depleted adjacent to the contact.

Ledoux, E., P. J. Hooker, P. Jamet and P. Escalier des Orres. 1990. Hydrogeochemical modelling of the Needle's Eye natural analogue (Scotland). *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print.* Brussels: Commission of the European Communities: n° EUR 13014 EN.

This project was jointly conducted by the British Geological Survey, the Scottish Universities Research and Reactor Center, and the Ecole des Mines de Paris. Local host rocks include Silurian hornfelses which are intruded by Devonian granodiorites which are in fault contact with carboniferous limestones. Pitchblende veins occur in the hornfelses and are exposed in a cliff. Hydrogeochemical modelling was able to account "reasonably" for the observed uranium distributions in the sediments at the base of the cliff. However, the model may be overly simplistic in that it ignores competing geochemical mechanisms.

Lei, W., P. Linsalata, E. Penna Franca and M. Eisenbud. 1986. Distribution and mobilization of cerium, lanthanum and neodymium in the Morro do Ferro Basin, Brazil. *Chemical Geology* 55:313-322.

The REE's are chemically similar to the actinides and therefore may serve as analogs to their behavior. Morro do Ferro is a hill which rises some 140 m above its base. The deposit is about 150 m by 320 m in area and about 100 m deep (maximum dimensions). REE's tend to be precipitated as carbonates and hydroxides in neutral to alkaline soils and tend to be adsorbed by clays and oxides in acid soils. The authors have been unable to identify the original minerals which contained the REE's and Th and are therefore unable to account for the weathering sequence responsible for the present distribution of the elements. Nd and La have almost identical distribution patterns, however, Ce is different. Ce is concentrated in the top 50 cm of soil. The difference between Ce and La-Nd may be due to the ability of Ce to coexist as Ce(III) and Ce(IV) whereas La and Nd only occur in the (III) valence. The Ce/Th ratio is stable both at the surface and at depth, suggesting that Ce oxidation is occurring at depth. La has very low mobility even under tropical weathering conditions. The majority of La being transported out of the deposit is by erosion.

Lemire, R. J. and F. Garisto. 1989. *The solubility of U, Np, Pu, Th, and Tc in a geological disposal vault used for nuclear fuel.* Pinawa, Manitoba, Canada: Atomic Energy of Canada Limited (AECL).

Lemire and Garisto describe a solubility model used to calculate the concentrations of uranium, thorium, technetium, neptunium, and plutonium in solutions associated with a geologic HLW repository. This paper is most useful for the collection of thermodynamic data which has been compiled in support of these calculations. Data suitable for equilibrium calculations over the range 25 - 150°C is provided for all of the above elements and recent updates to the data (since 1980) are discussed. Lists of pertinent reactions are also given.

Leroy, J. L., B. Aniel and B. Poty. 1987. The Sierra Pena Blanca (Mexico) and the Meseta Los Frailes (Bolivia); the uranium concentration mechanisms in volcanic environment during hydrothermal processes. B. Poty and M. Pagel, eds. *International Colloquium on Concentration mechanisms of uranium in geological environments, Oct. 2-5, 1985.* Nancy, France: 211-234.

This paper compares uranium mineralization at Peña Blanca to that at Meseta Los Frailes, Bolivia. Uranium has been mined at three deposits at Peña Blanca: Nopal I (333 tons U_3O_8), Las Margaritas (350 tons U_3O_8), and Puerto III (498 tons U_3O_8). The Nopal Formation is dated at 44 Ma and is characterized as a potassic alkaline rhyolite with low phenocryst content. Uranium was originally disseminated in the glassy matrix of the host rock. They note that "vapour phase" crystallization is well developed at Peña Blanca in the upper parts of the Nopal and Escuadra rhyolites and was responsible for mobilizing some of this U and concentrating it in the weakly welded parts of the Nopal rhyolite. This period of vapor phase crystallization was related to H2O, CO2, and N2 - rich fluids and temperatures of about 400°C (Aniel, 1983). Subsequent hydrothermal alteration (kaolinization) has been "intense" at Peña Blanca and leached U from the earlier vapor deposition reprecipitating it as pitchblende along with pyrite in the main structures at Nopal. After this period, there has been lower temperature hydrothermal alteration: montmorillonite-heulandite (about 100°C) then opal-Fe oxides (less than 150°C). Most recently there has been supergene remobilization.

Lever, D. A. 1987. Natural analogues and radionuclide transport model validation. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium.* Brussels: CEC.

Lever emphasizes the likelihood of uncertainty associated with natural analog studies and the necessity of using models with an appropriate level of sophistication when interpreting the data. Comparisons are drawn among the 3 methods of model validation: 1) lab experiments 2) field experiments 3) natural analogs. A summary of work at Alligator Rivers is included.

Lever, D. A. 1988. Some comments on the application of natural analogues in support of performance assessments in the U.K. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting.* Snowbird, Utah: CEC:203-208.

Lever notes some disadvantages to natural analog studies, including: the impossibility of matching all chemical conditions, poorly characterized initial and boundary conditions, unknown variations in conditions over the intervening time, lack of unique interpretations to the data. He points out that anomalies are often chosen for natural analog studies and that therefore we are looking at

elemental concentrations which have not dispersed rather than those that have. Lever notes that there have been few if any explicit applications of natural analog results to performance assessments to date.

Longworth, G., M. A. Wilkins and M. Ivanovich. 1988. Characterisation of natural colloids in a shallow glacial aquifer and their radionuclide loading. *Scientific Basis for Nuclear Waste Management XII - Materials Research Society Symposium Proceedings*. Pittsburgh: Materials Research Society: 755-761.

The groundwaters in a shallow sand aquifer are characterized physically, chemically, and radiometrically. Colloid concentrations were determined to be 10^8-10^{10} particles/L; activity fractions were 0.1 -0.5% for uranium and 1-5% for thorium. Size ranges were from 0.05 to 1 μm.

Loss, R. D., K. J. R. Rosman and J. R. De Laeter. 1984. Transport of symmetric mass region fission products at the Oklo natural reactors. *Earth and Planetary Science Letters* 68:240-248.

The isotopic composition and concentrations of palladium, silver, cadmium and tellurium were measured in four samples from reactor zones at Oklo and in four samples outside the reactor zones. After correcting for terrestrial components, cumulative fission yields of these elements have been calculated. Pd and Te have been retained almost entirely in the reactor zone whereas much Ag and Cd have migrated out of the reactor zones. Cd was retained in the surrounding host rocks. The present data do not allow a clear assessment of the retention of Ag by the surrounding host rocks, however, it appears that Ag has migrated out of the host rocks as well as the reactor zones.

Lutze, W. and B. Grambow. 1987. The use of natural analogs in the long-term extrapolation of glass corrosion processes. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium*. Brussels: CEC.

This paper reviews much of the work done on natural glass analogs of borosilicate HLW glass. Considerable space is devoted to consideration of the extent to which natural analogs should be used to verify HLW scenarios. Descriptions of tektites, rhyolitic glass and basaltic glass are given. Lab experiments, natural alteration and modelling results are briefly summarized. Lutze et al. conclude that natural glasses are useful as analogs. Alteration effects were characterized by experimental, empirical, and theoretical studies with good agreement. Basalt glasses are compositionally the most similar to HLW glasses. The authors conclude that basalt glass and borosilicate glass have similar alteration products and comparable chemical durabilities.

Maas, R. 1989. Nd-Sr isotope constraints on the age and origin of unconformity-type uranium deposits in the Alligator Rivers Uranium Field, Northern Territory, Australia. *Economic Geology* 84:64-90.

Sm-Nd ages of from 1600-1650 Ma are reported for the Nabarlek, Jabiluka II, and Koongarra deposits. These ages are older than published U-Pb ages (900-1437 Ma). The narrow range of the Sm-Nd ages is interpreted to indicate that mineralization occurred "soon" after deposition of unconformably overlying sediments. Maas suggests that the highly altered Kombolgie volcanics are likely the source of the U in the deposits. Mineralization at the Ranger deposits appears to have

involved different processes than those at the above listed deposits. Ranger processes are not well resolved at present.

Maas, R. and M. T. McCulloch. 1990. A search for fossil nuclear reactors in the Alligator River uranium field, Australia: constraints from Sm, Gd and Nd isotopic studies. *Chemical Geology* 88:301-315.

The Nabarlek deposit at Alligator Rivers, Australia, was considered a good bet as a fossil reactor because of its age (1600-1700 Ma), and its generally high grade (about 2%, with some sections of tens of centimeters of solid uraninite). All of the measured isotopic ratios are close to normal, however, small but systematic deviations were detected. The largest deviation between a sample and the normal composition is in the $^{150}Sm/^{149}Sm$ ratio and amounts to 0.26%. This and other deviations are considered to indicate the presence of fossil reactors at the Nabarlek deposit. Thermal neutron fluences at Nabarlek were only on the order of 10^{16} n cm^{-2} whereas those at Oklo were on the order of 10^{20} n cm^{-2}. This is believed to represent a real difference in the amount of U burnup. This difference is probably due to the higher concentration of HREE present at Nabarlek relative to Oklo.

MacKenzie, A. B., R. D. Scott, P. Linsalata, N. Miekeley, J. K. Osmond and D. B. Curtis. 1990. Natural radionuclide and stable element studies of rock samples from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print.* Brussels: Commission of the European Communities: n° EUR 13014 EN.

At Osamu Utsumi the work was on the behavior of natural decay series nuclides at the redox fronts whereas at Morro do Ferro, attempts were made to relate the distributions of Th, U, and LREE to the groundwater flow patterns to evaluate the extent of mobilization of these elements. The natural decay series work at Osamu Utsumi confirmed that the relative mobility of U^{6+} and Ra is greater than that of U^{4+}, Th and Pa in the groundwater. Uranium and other elements are dissolved at the redox fronts and uranium is deposited in the reduced rock by reduction from U^{6+} to U^{4+} and by uptake onto iron oxides. One of the redox fronts at Osamu Utsumi appears to have been stable for about 7×10^5 years whereas others indicate movement of about 2-20 m per million years, rates comparable to regional erosion rates.

Malow, G. and R. C. Ewing. 1980. Nuclear waste glasses and volcanic glasses: a comparison of their stabilities. *Scientific Basis for Nuclear Waste Management III - Materials Research Society Symposium Proceedings.* New York: Plenum Press: 315-322.

The authors compare the thermal and chemical stabilities of 2 borosilicate glasses and 1 glass ceramic to those of 3 rhyolite glasses using a variety of laboratory tests and observations of natural weathering. They conclude that natural glasses are more stable than the waste form glasses as a result of the greater silica contents of the natural glasses (74% vs 28-50%). Though the natural glasses ranged in age from 500 years to 670,000 years, they noticed no difference in natural weathering among the samples, but they note that these samples were chosen in the first place because they were "fresh and unweathered." At elevated temperatures, the waste glasses tended to form new phases and to recrystallize whereas the natural glasses showed no such tendency. They note that most volcanic glasses are less than 2 Ma old and that this suggests a long term stability at ambient, weathering conditions of not more than 1 Ma.

Marinos, G. P. and P. G. Marinos. 1978. The groundwater potential of Santorini Island. *Thera and the Aegean World.* C. Doumas, ed. London: Thera and the Aegean World, Inc.: 297-305.

Mean annual precipitation is 355 mm/yr. Estimated evapotranspiration is 333 to 368 mm/yr. Maximum recharge is estimated at 20 mm/yr. 70% of rainfall is in November to February. The summer is dry, but relative humidity is 60%. Mean air temperature is 17°C. Torrential materials on the pumice in the Akrotiri area indicate surface runoff in the past.

McConnell, D. B. and J. J. Cramer. 1987. Simulating the movement of radium and lead away from the Cigar Lake uranium deposit. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium.* Brussels: CEC.

The authors have created a mathematical description of the distribution of secondary lead above the Cigar Lake ore body. Their model is dependent upon "reasonable" values of transport parameters. Base codes included SYVAC3 and GEONET.

McConnell, V. S., J. L. Krumhansl, K. M. Kimball, C. L. Stein, H. W. Stockman and M. M. Cheatham. 1990. Geochemistry of the Battleship Rock tuff: a natural analog study. *EOS Transactions of the American Geophysical Union* 71:1713.

The authors report on elemental migration in the tuff in response to a thermal gradient of "an appropriate magnitude." A vertical profile from the contact between the tuff and the overlying Banco Bonito obsidian was sampled for about 30 m into the tuff. Analyses were made for major, minor and rare-earth elements, glass content, volatiles, D/H, mineralogy and texture. Apparently, few changes attributable to the contact heating were found: "variations in the data appear to be related to changes in the primary tuff mineralogy ... the analytical results indicate little evidence of migration as a consequence of the thermal environment."

McCoy, F. W. 1980. Climatic change in the eastern Mediterranean area during the past 240,000 years. *Thera and the Aegean World.* C. Doumas, ed. London: Thera and the Aegean World, Inc.:79-100.

Using deep sea sediment cores and terrestrial sediment data, the authors have inferred climatic variability in the eastern Mediterranean area during the past 240,000 years. Paleoclimatological data indicate that the climate on Santorini at the time of its eruption did not differ strongly from the present climate. Air temperatures were slightly warmer and the climate was slightly more arid.

McKenzie, W. F. 1990. Natural glass analogues to alteration of nuclear waste glass: a review and recommendations for further study. Lawrence Livermore National Laboratory. UCID-21871.

This paper is a review of work on the weathering of natural glasses. McKenzie also makes recommendations for future work regarding glass alteration. Studies have considered basaltic glasses, rhyolitic glasses, lunar glasses, meteoritic glasses and tektites. Lunar glasses are of particular interest due to their stability over some 4 Ga indicating the stability of glass over very long periods in an anhydrous environment at relatively low temperatures. The main alteration form of glasses is the development of palagonite. Palagonite may form as a result of solution

precipitation, hydrogen ion metasomatism, hydration, or solid state diffusion accompanied by hydration. Composition of palagonite varies from one occurrence to another and is a function of glass composition, solution composition, temperature, flow rate and et cetera. McKenzie includes summaries of the work of Jercinovic and Ewing (1987) and of Byers et al. (1987).

McKinley, I. G. 1985. Applications of analogs in near-field geochemistry. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analog Working Group, First Meeting*. Brussels: CEC.

This paper presents a brief discussion of the range of information required for a natural analog of the near field environment of various waste containment scenarios. Emphasis is given to various backfill materials. Possible near-field environments are described.

McKinley, I. G. and U. Frick. 1988. Swiss natural analogue research. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting*. Snowbird, Utah: CEC:104-109.

The authors summarize some recent and ongoing Swiss natural analog studies. (1) At Böttstein, researchers are measuring elemental profiles across water - carrying fissures in a granite to study matrix diffusion. No results are given. (2) At the Krunkelbach uranium mine (Menzenschwand), uranium leaching and retardation processes were studied by measuring the compositions and abundances of alteration minerals. Comparisons with predictions of alteration mineralogy by PHREEQE showed general agreement, but some important discrepancies were found - uranium arsenite complexes were identified at the site for which no thermodynamic data exist. (3) In Oman, natural high pH (>10), reducing groundwaters have been examined as an analog to pore waters in cement backfill.

McKinley, I. G., C. McCombie and P. Zuidema. 1988. Applications of natural analogues in Swiss safety analysis. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting*. Snowbird, Utah: CEC:173-179.

The authors review some of the thinking behind the use of natural analogs in the Swiss HLW program. Most of the paper discusses the applicability of natural analog work done elsewhere to the Swiss program. Matrix diffusion studies are highlighted as a major part of natural analog studies in Switzerland. These studies have concluded that connected porosity extends at least some centimeters into the host rock around water-carrying fissures; no other details are provided here. Research into matrix diffusion in consolidated sediments is planned for the future.

McVay, G. L., D. J. Bradley and J. F. Kircher. 1981. Elemental release from glass and spent fuel. *The technology of high-level nuclear waste disposal DOE/TIC-4621(Vol.1)*. Technical Information Center of the U.S. Department of Energy: 171-202.

This chapter is a good summary of the state of the art in 1981 with respect to leaching studies of glass and spent fuel. Previous work is listed, results generalized, and deficiencies described. For spent fuel, the authors observe that leaching is initially incongruent (Cs and Sr are preferentially leached) but approaches congruency with time. Most fuel leaching data have been interpreted in terms of simple UO_2 leaching. Temperature effects on spent fuel leaching are small. Oxygen content is probably important, but there are only limited data to support that probability. The

authors mention that "it is not clear whether [spent fuel] will react with aqueous solutions in a manner similar to UO_2" because of the significant differences between the two. Among other conclusions, the authors report that elemental release from spent fuel is generally higher than leach rates from borosilicate glass except in fluids with significant sodium bicarbonate, in which case the release rates are similar.

Miekely, N., H. Coutinho de Jesus, C. L. Porto da Silveira and C. Degueldre. 1990. Chemical and physical characterisation of suspended particles and colloids in waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print.* Brussels: Commission of the European Communities: n° EUR 13014 EN.

Groundwaters in the Poços de Caldas area typically have low concentrations (<1 mg/l) of colloids (1-450 nm). Most of the colloids present are composed of iron and organic species. Only minor amounts of U are associated with colloids but greater amounts of Th and REE's are transported by colloid-sized particles. Particles >450 nm show the same elemental associations as the colloids but the elemental concentrations are higher (about 1000x). The suspended particle concentration is 5 - 10 times greater at Morro do Ferro than at Osamu Utsumi.

Miekely, N., H. Coutinho de Jesus, C. L. Porto da Silveira, P. Linsalata, R. Morse, K. Osmond and J. N. Andrews. 1990. Natural series nuclide and rare-earth element geochemistry of waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print.* Brussels: Commission of the European Communities: n° EUR 13014 EN.

The groundwaters at Osamu Utsumi have high concentrations of uranium (up to 10 mg/l) whereas those from Morro do Ferro are much lower [unspecified]. ^{232}Th concentrations are low in groundwaters from both sites (<0.1μg/l) but are occasionally higher (up to 100x) in surficial waters with abundant humic compounds or sulfate. Substantial radioactive disequilibria was noted between ^{234}U and ^{238}U in the groundwaters. $^{230}Th/^{234}U$ ratios are low due to the low solubility of Th and its strong tendency to sorb onto suspended particles.

Miekely, N., H. C. Jesus, C. L. P. Silveira and I. L. Kuechler. 1988. Colloid investigations in the 'Pocos de Caldas' natural analogue project. *Scientific Basis for Nuclear Waste Management XII - Materials Research Society Symposium Proceedings.* Pittsburgh: Materials Research Society: 831-842.

Concentrations of colloidal particles (450 nm to <1 nm) are <1 ppm in Morro do Ferro groundwaters. Colloids here are mainly composed of iron and organic species. A significant amount of thorium and REE is concentrated on colloids but relatively little uranium is involved. The tendency to form colloidal species is as: U < Ce < Th. Humic acids appear to be especially important in the formation of colloids. There appears to have been very little thorium transport at Morro do Ferro, either by colloids or true solution.

Mitchell, S. M., P. C. Goodell, D. V. LeMone and N. E. Pingitore. 1981. Uranium mineralization of Sierra Gomez, Chihuahua, Mexico. *Uranium in Volcanic and Volcaniclastic Rocks-*

AAPG Studies in Geology No. 13. El Paso, TX: American Association of Petroleum Geologists: 293-310.

At Sierra Gomez, uranium deposits occur in limestone. The authors infer that these deposits formed by the leaching of uranium from overlying volcanics (probably the Mesa Formation) by low temperature groundwaters, transport of the uranium as carbonate and fluoride complexes, and precipitation in fractures, faults and collapse breccias of the host limestones. There are no known magmatic-hydrothermal uranium sources in the area. The lack of host rock alteration is evidence of the low temperatures of the mineralizing solutions. The authors note that the Mesa Formation contains anomalously high concentrations of uranium and would make a viable source for the ores.

Murakami, T., H. Isobe and R. Edghill. 1990. Effects of chlorite alteration on uranium redistribution in Koongarra, Australia. *Scientific Basis for Nuclear Waste Management XIV*. Boston: Materials Research Society Symposium Proceedings Series Vol. 212:483.

The authors have studied the alteration of chlorite relative the distribution of U at Alligator Rivers. Altered chlorite tends to have higher U contents than unaltered chlorite (on a mm scale). On a meter scale, areas with abundant chlorite have low U abundance, vermiculite dominant areas have intermediate levels of U, and areas with abundant kaolinite have the highest U concentrations.

Nash, J. T., H. C. Granger and S. S. Adams. 1981. Geology and concepts of genesis of important types of uranium deposits. *Economic Geology 75th Anniversary Volume*. New Haven: Economic Geology Publishing Co.: 63-116.

This paper reviews chemical processes important to uranium transport and deposition. The authors describe the distribution of uranium in the crust through time and relate it to crustal evolution. They also review various types of uranium deposits and generalize as to the factors important to deposit formation. Examples of each type are given (with references). This paper is especially good at identifying minerals and chemical species previously identified as important (i.e. common) in natural settings.

Naudet, R. 1976. The Oklo nuclear reactors: 1800 million years ago. *Interdisciplinary Science Reviews* 1:72-84.

Naudet recounts the early history of the discovery of the Oklo reactors and the first investigations; he also summarizes the state of knowledge at the end of a major international conference in 1975 convened to discuss the Oklo work. Ore at Oklo is in a sedimentary horizon some 5-8 m thick and is inclined at 45°. Uranium in the most enriched zones at Oklo occurs in concentrations typically between 25 and 40% and up to 60%. Uranium occurs as uraninite rather than pitchblende which implies temperatures of 300 - 350° C. The reactor sites lie near the surface, "in a zone of alteration where oxidizing waters circulate." Naudet lists the elements which have been mobilized and those which have remained stationary. It appears that the reactors operated under deep overburden (several thousand meters) and that only relatively recently have the sites of the reactors been uplifted to their present near-surface positions such that oxidizing fluids can now remobilize the uranium.

Neretnieks, I. 1985. The need for geologic evidence for radionuclide migration in the geosphere. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analog Working Group, First Meeting*. Brussels: CEC.

Neretnieks emphasizes the need for natural analog studies to evaluate the importance of matrix diffusion and oxidation due to radiolysis of water infiltrating the spent fuel. This paper summarizes a study (Curtis and Gancarz, 1983) at Oklo which found the 10% of U in the natural reactor was mobilized by oxidation attributed to radiolysis and a complimentary 10% reduction of Fe minerals (to Fe++) in the reactor core itself.

Neretnieks, I. 1986. Some uses for natural analogues in assessing the function of a HLW repository. *Chemical Geology* 55:175-188.

Neretnieks discusses model needs which might be addressed by natural analog studies. The author's comments are all with reference to the proposed Swedish HLW repository deep in granitic rocks. Some information is of general applicability. Matrix diffusion will expose fluids to much greater surface areas than will fracture flow, greatly enhancing the retardation of elemental migration by sorption. The author considers matrix diffusion to include mobility along microfractures of 10 micron width or less in which elemental migration would proceed by diffusion only.

Nordstrom, D. K., I. Puigdomenech and R. H. McNutt. 1990. Geochemical modelling of water-rock interactions at the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print.* Brussels: Commission of the European Communities: n° EUR 13014 EN.

Modelling of geochemical processes was based on groundwater compositions and mineralogical data for the two sites. The models "were validated by predicting the masses of minerals precipitated and the pH of the final water" [no other explanation is given here]. It is reported that the major processes are CO2 production in the soil zone by organic decay; dissolution of fluorite, calcite, K-feldspar, albite, manganese oxides; the oxidation of pyrite and sphalerite; and precipitation of ferric oxides, silica and kaolinite.

Nordstrom, D. K., J. A. T. Smellie and M. Wolf. 1990. Chemical and isotopic composition of groundwaters and their seasonal variability at the Osamu Utsumi and Morro do Ferro analogue study sites, Poços de Caldas, Brazil. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print.* Brussels: Commission of the European Communities: n° EUR 13014 EN.

Samples of ground and surface waters were collected over 3 years. The groundwaters have an unusual K-Fe-SO_4 composition because of the weathering of the altered mineralized rocks in the area. Seasonal variability was noted only in the shallowest groundwaters. All of the groundwaters appear to be of meteoric origin as indicated by tritium and stable isotope measurements. Shallow groundwaters are less than 40 years old, but deeper waters may be a mixture of younger and older fluids producing an apparent age of 40-60 years.

Ochiai, Y., M. Yamakawa, S. Takeda and F. Harashima. 1988. Natural analogue study on Tono Uranium Deposit in Japan. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting.* Snowbird, Utah: CEC:126-139.

The Tono uranium mine is the largest uranium reserve in Japan. Uranium is concentrated in paleochannels in a Tertiary sediment package composed of arkosic sandstone, tuffaceous sandstone, carbonaceous mudstone, and conglomerate. The deposit is less than 150 m deep. The uranium is characteristically associated with zeolites, clay minerals, and organic material. Only seldom are primary uranium minerals such as coffinite and uraninite observed. A 1 cubic meter block of ore from the Tono mine was subdivided into 64 blocks 25 cm on a side and the mineralogy, chemistry and isotopic compositions of the blocks determined to study the distribution and migration of uranium and related elements. It was found that equilibrium among 238U, 234U, and 230Th had been maintained and that 226Ra had been leached. The local groundwater is a stagnant, bicarbonate water.

Papike, J. J., J. C. Laul and P. Nabelek. 1982. Contact metamorphism between quartz monzonite and limestone/argillite: a natural analog study for radionuclide migration. *Geological Society of America Abstracts with Programs* 14:583.

The authors have studied elemental migration at the boundary of a quartz monzonite intrusion and the intruded argillites and limestones. Maximum temperatures are estimated to have been about 575-600°C and pressures to have been about 2 kb. Certain unspecified elements were found to migrate tens of meters in the argillites. They found that in general, domains of equilibrium were small and that the argillites tended to be more open to fluid flow that did the limestones.

Papp, T. 1987. The role of natural analogues in safety assessment and acceptability. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium.* Brussels: CEC.

Papp suggests that the protection principles designed into a repository be based on processes which can be evaluated in natural settings. He emphasizes the importance of natural analogs in increasing public confidence in any repository. He recognizes that formal, traditional validation of some processes will not be easy therefore scientific judgement and peer review will be important.

Papp, T. 1988. Natural analogues in SKB safety assessments. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting.* Snowbird, Utah: CEC:162-170.

The author describes the Swedish HLW program. The role of natural analogs in the program is briefly covered. A means of expressing "validity" and the level of validity required are considered very briefly. No conclusions or suggestions are offered.

Patyn, J., P. Del Marmol and M. Monsecour. 1987. Environmental tracers for validating predictive models. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium.* Brussels: CEC:444-448.

Patyn et al. are studying the Boom clay formation as a potential host for HLW. They have compared 14C measurements of groundwater aquifers above and below the clay horizon with data from hydrologic studies and attempted to reconcile them. Their success is variable. They are also using major and trace element compositions of the waters above and below the clay to describe the flow system. Their data do not lend themselves to simple interpretations.

Penrose, W. R., W. L. Polzer, E. H. Essington, D. M. Nelson and K. A. Orlandini. 1990. Mobility of plutonium and americium through a shallow aquifer in a semiarid region. *Environmental Science and Technology* 24:228-234.

Liquid wastes containing americium and plutonium are released in a canyon at LANL where they make their way into a shallow aquifer. Both elements are detectable in monitoring wells as far as 3390 m down gradient. Over that distance, plutonium concentrations decreased exponentially whereas americium concentrations varied, but did not increase or decrease systematically. Colloids between 25 and 450 nm appear to have been important to transport. About half of the americium appears to exist in a non-colloidal, stable anionic complex of less than 2 nm diameter. Other workers (Nyhan et al., 1985) have shown that plutonium and americium move further through the local volcanic tuff than through soils or sediments, but never more than a few meters. The authors have conducted isotope exchange experiments which indicate that the plutonium bound to the colloidal materials is not exchangeable.

Petit, J. 1990. Reasoning by analogy (rational foundation of natural analogue studies). *Applied Geochemistry* , in press.

Natural analogues are the only way to get at processes operating over geologic time. They provide the only means of testing model of such long term processes for pertinence (if not actual validation of the models). There is no consensus as yet with regard to the usefulness of natural analog studies. However, scientists use analogy everyday in classifying natural objects into groups. Items within a group are assumed to have more in common with each other than with items not in that group, regardless of the obvious differences among the items within the group. Many people have objected to the scientific use of analogs based on their generally qualitative character. Because of the difficulty of deciphering an often imperfect historical record, analog studies are often limited to qualitative descriptions, however, in some instances quantitative data have been obtained. Predicting the future based on the past is an uncertain business (witness the prediction of earthquakes and etc.). It is not the case that quantitative data are somehow of more inherent value than qualitative data. In fact, the choices made in setting up a mathematical model generally are made on the basis on qualitative information and it is only after those choices are made that quantitative data are introduced in the mechanical calculations. Therefore, the qualitative basis for the construction of the models is actually more important than the quantitative data input later.

Petit, J.-C. 1990. Design and performance assessment of radioactive waste forms: what can we learn from natural analogues? *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print.* Brussels: Commission of the European Communities: n° EUR 13014 EN.

Petit discusses the use of a number of analog materials with regard to designing waste forms: glasses, spent fuel, ceramics, cements, bitumens, resins, and metallic container materials. The review of natural and waste form glasses is extensive whereas the other parts are relatively limited in scope. Petit points out that the roles of natural analogs include: development of conceptual models, acquisition of data and definition of initial and boundary conditions, and validation of models. Petit considers "validation" to be the process whereby the results of short-term, small-scale laboratory experiments, and the long-term predictions of models based on the laboratory experiments, are compared to observations of natural systems which have operated for long periods at large scales. This process of testing by comparison is "validation." Such a process results in "reasonable confidence" in a predictive model.

Petit, J.-C. 1990. Migration of radionuclides in the geosphere: what can we learn from natural analogues? *Radiochimica Acta* in press.

Petit includes a long introduction in which he makes a philosophical case for the use of natural analogs. Natural analogs are the only way to identify very slow mechanisms and are the only way to assess the "pertinence" of models (even if true validation is beyond them). Natural analogs are important to safety assessment and to building confidence in models. It is often implied that qualitative data are somehow inferior to quantitative data; Petit disagrees. "Quantitative data for a given process ... can only be injected into the model subsequently to the decision that such a process ... must be taken into account, and at a particular place in the modelling scheme." Models are necessarily developed through a process of iterative interaction with natural analogs and lab and field experiments.

Petit, J. C. 1988. Analogue studies at the French Atomic Energy Commission during the period 1986-1988. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting*. Snowbird, Utah: CEC:75-87.

Petit discusses the French CEA natural analog research programs which include materials studies and geochemical systems research. Some of the programs of interest concern alteration of natural glasses (and laboratory dissolution experiments), smectite - illite transformations in geothermal systems, hydrothermal alteration of granites (elemental remobilization), radionuclide dispersion in clays, in situ injections of actinide analogs, and laboratory sorption experiments. One archeological analog program concerns gallo-roman cements. Very little detail of procedures or results is provided.

Petruso, K. M. 1978. Lead weights from Akrotiri: preliminary observations. *Thera and the Aegean World*. C. Doumas, ed. London: Thera and the Aegean World, Inc.: 547-553.

The balance weights at Akrotiri constitute one of the largest groups of prehistoric weights from the Aegean. Fifty seven lead disks have been found, along with a few stone weights (3). Petruso reports that lead objects "oxidize readily on contact with humic acids in the soil." A crust is formed by the oxidation with the result that the weight is then heavier than it was originally.

Phillips, F. M., S. N. Davis and P. Kubik. 1990. A proposal to use chlorine-36 for monitoring the movement of radionuclides from nuclear explosions. *Ground Water Monitoring Review* Summer 1990:106-121.

The authors suggest that 36Cl would make a better radionuclide tracer than 3H, 39Ar, or 129I because its mobility is "equal to or greater than water," it has a relatively long half-life (301,000 years), collection and storage of samples is easy, at common temperatures it is not subject to vapor transport, the natural background is low, and it does not form insoluble precipitates. A demonstration study is described at the Gnome Site (40 km southeast of Carlsbad, NM) where 36Cl was released to the atmosphere, along with other radionuclides.

Pichler, H. and W. Friedrich. 1976. Radiocarbon dates of Santorini volcanics. *Nature* 262:373-374.

The top layer (Bo) of the Santorini volcanics which buried the late-Minoan settlements is comprised of air fall pumice, ashes, and pyroclastic flows. The Upper Pumice Series was deposited on a soil horizon which contains wood from Minoan houses dated at 3,370 ± 100 yr

b.p. by C^{14}. The Upper Pumice Series contains horizons rich in plant fossils. The genera represented in these horizons are still present in the region indicating that the climate at the time of the eruptions was the same as the present.

Pichler, H. and W. L. Friedrich. 1980. Mechanism of the Minoan eruption of Santorini. *Thera and the Aegean World.* C. Doumas, ed. London: Thera and the Aegean World, Inc.:15-30.

At least 15,000 years of volcanic quiescence preceded the Minoan eruption. The Minoan volcanic sequence is called the Upper Pumice Series (Bo). The first phase (which probably lasted only a few hours) was air-fall pumice, 0.5 - 5 m thick on Santorini. Phase two was a base surge, phreatomagmatic eruption (which probably lasted a few days to a few weeks) depositing 0.5 - 7 meters of low temperature tuff on Santorini. The third phase consisted of at least five big ash flow eruptions, containing 25 to 30% fragmented older volcanic rocks, leaving deposits up to 40 m thick. The upper portions of the third phase were subsequently eroded, reworked and transported by "eruptive and post-eruptive rains."

Pichler, H. and S. Kussmaul. 1980. Comments of the geological map of the Santorini Islands. *Thera and the Aegean World.* C. Doumas, ed. London: Thera and the Aegean World, Inc.:413-427.

This paper provides a detailed chronology of the volcanic development of Santorini; various volcanic centers are described individually. A description of the basement rocks is given. The authors include maps of the evolution of the islands and stratigraphic sections for a number of localities on the islands.

Pichler, H. and W. Schiering. 1977. The Thera eruption and Late Minoan-IB destructions on Crete. *Nature* 267:819-822.

It appears to be unanimously agreed that the Upper Pumice Series (which covers the destroyed settlements on Santorini) was deposited in a single episode. Pichler and Schiering believe that there was no connection between the decline of Minoan civilization and the Thera volcanic eruption.

Pirc, S. and A. W. Rose. 1980. Uranium anomalies in paleo-aquifers near sandstone-type uranium deposits in the Devonian Catskill Formation of Pennsylvania. *Developments in Economic Geology - Geochemical Exploration 1980.* New York: Elsevier: 219-231.

The authors have located uranium anomalies in a paleoaquifer which suggests that the local groundwater added uranium to the aquifer rather than leaching it from the aquifer as is more commonly thought. This phenomenon has also been reported from sites in Wyoming where the anomalies may extend some miles up gradient from the uranium deposit. The authors suggest that such enrichment may occur in all roll front type uranium deposits. They note that although the high clay, mica, and iron oxide contents of the Catskill sandstones make them particularly good uranium sinks, the sands of the Morrison Formation are much purer and yet are uranium enriched.

Raloff, J. 1990. The Colloid Threat. *Science News* March 17:169-170.

W.R. Penrose and others from Argonne National Laboratory studied the migration of plutonium and americium in a shallow aquifer underlying Los Alamos National Laboratory. LANL had been

dumping waste water in Mortandad Canyon since 1963; their calculations anticipated radionuclide transport of only a few meters before soil retention. Penrose found migration over some 2 miles from the dump site. Mobility is ascribed to colloid formation (particles from a nanometer to a micron in size). Colloids responsible for americium mobility were found to be "much smaller" than those transporting plutonium a finding which corresponds to the apparent greater mobility of americium; americium levels were constant at various distances from the source whereas plutonium levels dropped off by a factor of one thousand with distance.

Rasmussen, J. D., C. G. Cunningham, T. A. Steven, R. O. Rye and S. B. Romberger. 1985. Origin of hydrothermal uranium vein deposits in the Marysvale volcanic field, Utah. *Uranium Deposits in Volcanic Rocks*. Austria: International Atomic Energy Agency, proceedings of a technical committee meeting, El Paso, TX April 1984. IAEA-TC-490: 317.

Exposure of the hydrothermal uranium veins at Marysvale occurs over a vertical range of about 300 m. The veins cut a 19 Ma rhyolite ash flow tuff. The mineralizing fluids are believed to have had low pH and fO2 and to have had temperatures of about 200°C. Precipitation of the uranium minerals occurred in response to increased pH after reaction with wall rocks. At the deepest levels exposed, alteration of the wall rocks was to kaolinite and sericite, with deposition of uraninite, coffinite, jordisite, fluorite, molybdenite, quartz and pyrite. Higher in the system the fluids were increasingly oxidized (wall rocks altered to hematite with deposition of "sooty" uraninite and umohoite).

Read, D. and P. J. Hooker. 1988. The speciation of uranium and thorium at the Broubster natural analogue site, Caithness, Scotland. *Scientific Basis for Nuclear Waste Management XII - Materials Research Society Symposium Proceedings*. Pittsburgh: Materials Research Society: 763-770.

The authors have studied uranium, thorium and REE transport using a combination of field studies and analyses, experiments, and mathematical modelling. At Broubster, the above elements leach out of a hydrocarbon-containing calcareous sediment, move downslope and are fixed in a peat bog about 100 m away. Uranium is oxidized and transported in "true solution" as carbonate and/or phosphate species. The mechanism of uranium fixation in the peat is not known but appears to have nothing to do with reduction or solubility constraints. Thorium is carried as a colloidal oxyhydroxide phase and may be lost from solution by co-precipitation on finely divided ferric flocs. Thorium fixation may also be partly a physical process as the colloids are trapped in the pores of the peat.

Read, D. and P. Hooker. 1990. Using hydrogeochemical data from natural environments to improve models of radionuclide speciation in groundwaters. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print*. B. Come and N. A. Chapman, eds. Brussels: Commission of the European Communities: n° EUR 13014 EN.

This paper describes investigations at four locations which exhibit different forms of uranium transport and fixation. Oxidation of U(IV) to U(VI) is the basis for mobilization at all four sites. At Broubster, U is fixed by organics; at South Terras U is fixed by iron oxyhydroxides, at Alligator Rivers U is precipitated as secondary uranyl phosphates and silicates, and at Pocos de Caldas redox precipitation plays a "significant" role. The authors maintain that analogs are useful because they are the only means of "observing the net effect of geochemical processes acting over timescales appropriate to a safety assessment."

Roberts, P. D., T. K. Ball, P. J. Hooker and A. E. Milodowski. 1988. A uranium geochemical study at the natural analogue site of Needle's Eye, S.W. Scotland. *Scientific Basis for Nuclear Waste Management XII - Materials Research Society Symposium Proceedings.* Pittsburgh: Materials Research Society: 933-940.

At Needle's Eye, Scotland, uranium is leached from pitchblende veins, transported and then trapped in estuarine silts. Transport is by drainage from a nearby cliff and by artesian flow. Uranium is transported readily whereas thorium and its daughters are relatively immobile and are retained in resistate detrital grains. Uranium fixation is controlled by humic substances in the upper silt layers and by sorption onto iron and manganese oxyhydroxides deeper in the silts. Prior to fixation, uranium is thought to be transported as "carbonato" complexes.

Roper, M. W. and A. B. Wallace. 1981. Geology of the Aurora Uranium Prospect, Malheur County, Oregon. *Uranium in Volcanic and Volcaniclastic Rocks- AAPG Studies in Geology No. 13.* El Paso, TX: American Association of Petroleum Geologists: 81-88.

The Aurora prospect is part of the McDermitt caldera complex on the Oregon-Nevada border. At Aurora, uranium mineralization is hosted by intermediate lavas. Uranium minerals include uraninite and coffinite which were emplaced by hydrothermal processes within a steeply dipping fracture system. There has been some weathering of the deposit which has redistributed uranium along the more porous lava horizons. The deposit was discovered in 1977 and contains some 17 million tons of U_3O_8 at an average grade of 0.05 wt% U_3O_8.

Rose, W. I., Jr. and T. J. Bornhorst. 1981. Uranium and thorium in selected Quaternary volcanic rocks of Guatemala and Sumatra: evidence for uranium redistribution. *Uranium in Volcanic and Volcaniclastic Rocks- AAPG Studies in Geology No. 13.* El Paso, TX: American Association of Petroleum Geologists: 13-21.

Studies of Quaternary volcanic rocks show significant U loss from low-U phases. The authors suggest that this loss may be due to defect siting of U in minerals that exclude U from normal lattice sites. In any event, this loss represents only a small loss of U from the whole rock. All samples showed some evidence of significant U and possibly Th mobility despite their young ages. By way of comparison, Zielinski et al. (1980) found very little U loss from extensively zeolitized 8 my old tuff from Utah (there was some redistribution).

Ross, C. A. M., C. Degueldre, M. Ivanovich and G. Longworth. 1987. Colloid benchmark exercise: an interlaboratory study of sampling and characterization techniques for natural colloids in oxic groundwater. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium.* Brussels: CEC.

Ross et al. collected samples of groundwater from a fractured Permo-Triassic sandstone in Britain and extracted the natural colloids from them by 2 different methods (pulsed cross-flow ultrafiltration and tangential diafiltration). Both methods were found to be effective and to produce no artifacts. Additionally, duplicate samples were taken, stored for 2 months and then run through the same 2 separation procedures; the results of these stored samples were not reported.

Ruskeeniemi, T., H. Niini, B. Sodernolm and M. Versterinen. 1989. The Palmottu U-Th deposit in SW Finland as a natural analogue to the behaviour of spent nuclear fuel in bedrock: a preliminary report. *Water-Rock Interaction.* Rotterdam: Balkema: 601-604.

At Palmottu, SW Finland, a Precambrian granitic pegmatite contains an average of 0.1%U. The redistribution of U has been studied petrographically and in the context of groundwater variations. Uranium occurs mainly as uraninite; the uraninite grains are extensively corroded with a distribution apparently independent of the present groundwater conditions. Shallow groundwaters are Ca-Na-HCO3 whereas deeper waters are Na-Cl-SO4-HCO3 fluids. The waters also change from oxidizing to reducing with depth and the pH increases with depth. At the bottom of the sample hole, the U concentration of the waters decreases whereas the U concentrations of the particulate fraction increases.

Saager, R., K. Thiel, G. J. Hennig and U. Bangert. 1980. Uranium redistribution in weathered conglomerates of the early PreCambrian Pongola Supergroup, South Africa - inferences from a study by alpha spectrometry and fission track micromapping. *Developments in Economic Geology - Geochemical Exploration 1980.* New York: Elsevier: 233-249.

Uranium fission track analyses and isotopic analyses on samples from three sites in South Africa were done to establish uranium mobility in the weathering environment. At one site there was no evidence of uranium mobility within the last 1 million years; at one site there had been recent leaching of uranium; and at the other site there had been an accumulation of uranium recently. Uranium was concentrated in the samples with iron and titanium hydroxides; concentrations with the titanium hydroxides were about an order of magnitude greater than those with the iron (an observation which supports Langmuir, 1978, who reported that titanium hydroxides are more efficient accumulators of uranium than iron).

Sargent, F. P. 1985. What can the earth scientists provide? B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, First Meeting.* Brussels: CEC:105-111.

This paper is largely a description of the Canadian Underground Research Laboratory and various tests which have been performed as the facility has been constructed. Particular mention is made of the differences between the predicted hydrologic response of the site and the observed flows. The models appear to have overestimated the inflow rates by a factor of about three.

Sargent, F. P. 1990. Natural analogues and performance assessment of the geological disposal of nuclear waste: a review. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print.* Brussels: Commission of the European Communities: n° EUR 13014 EN.

Sargent reviews the use of natural analogs in support of performance assessment of geologic HLW disposal. He notes that most natural analog applications have related to near field assessment rather than far field. He discusses the idea of "negative analogs" (for example the formation of ore deposits which emphasizes the mobility of the ore elements rather than their immobility). He calls for greater use of negative analogs.

Schorscher, H. D. and M. E. Shea. 1990. The regional geology, mineralogy and geochemistry of the Poços de Caldas alkaline caldera complex, Minas Gerais, Brazil. *Fourth Natural*

Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print. Brussels: Commission of the European Communities: n° EUR 13014 EN.

The Poços de Caldas caldera is the largest alkaline complex in South America (about 33 km average diameter). Early volcanism was followed by caldera subsidence and nepheline syenite intrusions along ring dikes. At Morro do Ferro a carbonatite intrusion resulted in the formation of stockwork magnetite veins. Local magmatic brecciation occurred in association with intense hydrothermal potassium- and sulfur-rich alteration. These processes caused the formation of a Th-REE concentration at Morro do Ferro and a U-Zr-REE deposit at Osamu Utsumi. Late stage events included intrusion of lamprophyre dikes followed by strong weathering which has developed redox fronts of enriched uranium mineralization. The mineralizing events ended about 76 Ma ago (Ar/Ar date on an unmineralized lamprophyre dike).

Sekine, K., T. Murakami, N. Yanase, T. Ohnuki, H. Isobe and A. Kasai. 1988. Migration behaviour of uranium and thorium series nuclides: relevant to alteration. Australian Nuclear Science and Technology Organisation. ANSTO Alligator Rivers Analogue Project - Progress Report, May 1988 - August 1988 :157-186.

Investigations necessary to understand the migration behavior of transuranic elements relevant to alteration include: paragenetic sequence, adsorption and desorption characteristics, geochemical modelling. Toward that end this work is underway: alteration mechanisms of chlorite, U adsorption/desorption onto chlorite and other clays, and modelling of uranium and thorium migration. The quartz-chlorite schist host rocks have been weathered to a depth of about 20 m. The authors infer that the migration modes for uranium series nuclides vary with depth, probably due to different mineral components. The mobility of the nuclides is in the order $^{238}U > ^{234}U > ^{230}Th$ in the Koongarra deposit.

Seward, D., G. A. Wagner and H. Pichler. 1980. Fission track ages of Santorini volcanics (Greece). *Thera and the Aegean World.* C. Doumas, ed. London: Thera and the Aegean World, Inc.:101-108.

The oldest subaerial volcanic activity on Santorini has been dated by fission track techniques at about 1 Ma. This activity deposited white vitric ash and pumice lapilli on the "strongly decomposed and reworked surface" of underlying phylitic rock (L. Tertiary). Fission track dating of obsidian of the Lower Pumice Series indicates an age of approximately 100,000 years, which is consistent with stratigraphic relations and 14C dating of overlying paleosols.

Shade, J. W. 1981. Comparison of glass and ceramic leaching behaviour by natural analogs. *Nuclear and Chemical Waste Management* 2:219-228.

Shade has characterized dissolution and leaching mechanisms in glass and crystalline nepheline and albite after laboratory leaching and etching. He reports a significant difference in the leaching mechanisms between the glassy and crystalline materials. Acid attack on crystalline surfaces is selective and tends to attack high energy sites whereas a "gel layer" which inhibits diffusion is the controlling mechanism for glass leaching. No such layer forms on crystalline materials except possibly through secondary precipitates.

Shea, M. 1985. Performance assessment input: Marysvale natural analog study. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, First Meeting*. Brussels: CEC:160-163.

The Marysvale natural analog study is funded by the DOE through their Office of Crystalline Repository Development (OCRD). The site is an inactive hydrothermal uranium/molybdenum vein ore deposit hosted by granitic rocks. They consider that this fossil hydrothermal system is a good analog to a HLW repository at some time after the cannisters have been breached and interactions between groundwater, rock, and the waste have occurred (initially at elevated temperatures). Some of the goals of the study are to determine: the spatial extent of the hydrothermal system; the nature of the hydrothermal fluid; the thermal gradient around the ore body; the duration of the mineralization; the suite of nuclides present in the ore; the extent of the nuclide migration from the veins into the country rock; the effects of hydrothermal alteration of the retentiveness of the minerals for uranium (and other elements); the effects of hydrothermal alteration on permeability and rock strength; the role of fractures and microcracks in nuclide transport; any perturbations to the system since the initial emplacement of the ore.

Shea, M. 1988. Marysvale fracture controlled mass transport study. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting*. Snowbird, Utah: CEC:11-25.

This paper reports the intermediate results of an ongoing investigation intended to evaluate the mass transport of nuclides or their proxies (Co, Ni, Se, Sr, Zr, Nb, Cs, Ba, Nd, Sm, Eu, Th, U) in a hydrothermal system in fractured igneous rock (plutonic and volcanic). Shea includes a summary description of the Marysvale system but focuses on detailed petrography, mineralogy and mineral chemistries. Shea emphasizes the importance of fault-controlled fluid flow and has selected his samples to follow that up. Most of the present work is descriptive.

Shea, M. E. 1990. Isotopic geochemical characterization of selected nepheline syenites and phonolites from the Poços de Caldas alkaline complex, Minas Gerais, Brazil. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print*. Brussels: Commission of the European Communities: n° EUR 13014 EN.

Isotopic studies were undertaken on a breccia pipe at Osamu Utsumi and on regional rocks. The regional rocks show ∂D and $\partial^{18}O$ evidence of meteoric alteration. Rb-Sr whole rock data for regional rocks did not result in an isochron nor did Sm-Nd data for the regional rocks. A mineral separate yielded a Rb-Sr age of about 78 Ma. Within the breccia, a nepheline syenite xenolith returned a whole rock age of 76 Ma which is interpreted as the age of the hydrothermal event due to the strong alteration of the sample. This data corresponds well to the age of a lamprophyre dike at 76 Ma.

Sidle, W. C., D. Sayala and T. Steinborn. 1985. Natural analogues in evaporites for the interpretation of mineralogic and geochemical variations in a nuclear waste repository system. *EOS, Transactions, American Geophysical Union* 66:1153.

The authors have studied contact metamorphism resulting from intrusion of mafic dikes into salt formations. They found aureoles ranging from <1 m to 7 m as a result of intrusions with temperatures of 600-800°C. Phase changes in the salt mainly were the recrystallization of halite and the incongruent melting of polyhalite and sylvite. No changes in Y, REE, Th or U

concentrations were observed around the intrusives. The authors conclude that there would be little disturbance to a salt host from the lower temperatures expected from HLW containers.

Sigurdsson, H., S. Carey, W. Cornell and T. Pescatore. 1985. The Eruption of Vesuvius in A.D. 79. *National Geographic Research* 1:332-387.

This article includes a detailed account of the progress of the eruption based on the eyewitness description of Pliny the Younger. Studies of the eruption began with Dolomieu in the 18th century. The rocks under which Herculaneum is buried are dominantly basic, silica - undersaturated, potassic tephrites, phonolites and leucites (aside: very different from Yucca Mountain). At Herculaneum, surge layers are associated with pyroclastic flows forming thick, partly indurated, poorly sorted tephra. The authors describe the sequence and aerial distribution of these layers and the apparent effects on property and people at the time of deposition.

Skytte-Jensen, B. 1985. Geochemical model needs. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, First Meeting*. Brussels: CEC:43-54.

The author points out that the one-dimensional migration equation needs no additional validation inasmuch as hundreds of chromatographic separations are made each day proving the equation. However, the care required to construct columns which produce the elution curves predicted by theory is some measure of what discrepancies will arise in applying those theories to the real world. In addition to the obvious problems of channeling, diffusion into deep pores, and variable particle size, there are the additional uncertainties of slow adsorption kinetics and saturation effects. The author lists the following as the main difficulties in predicting migration phenomena: insufficient knowledge of dispersion processes; insufficient knowledge of the effects of organics on migration; lack of adequate thermodynamic data for some species; poor characterization of mixed hydroxy-complexes; insufficient knowledge of which factors control adsorption processes.

Slater, E. A. 1980. Late Bronze Age Aegean metallurgy in the light of the Thera analyses. *Thera and the Aegean World.* C. Doumas, ed. London: Thera and the Aegean World, Inc.: 197-215.

14 neutron activation analyses of corroded bronze artifacts from Santorini show that they are generally 30 to 80% copper and that most were deliberate tin bronzes. No lead or nickel data are given. All of the artifacts showed at least some corrosion. The artifacts analyzed were: a tripod, a pin, a hook, a bronze sheet, and a bronze plate.

Smellie, J. 1985. Proposed programme of investigation at Pocos de Caldas, Minas Gerais, Brazil. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, First Meeting*. Brussels: CEC:171-174.

The Pocos de Caldas region is generally anomalous with respect to uranium, thorium, and REE's which may be considered chemical analogs to neptunium, plutonium, and americium/curium respectively. There are two sites of interest near the town of Pocos de Caldas: Morro do Ferro and the Osamu Utsumi Mine (within about 5 km of each other). The research plan calls for studying radionuclide behavior in contrasting redox environments, the importance of colloids on thorium transport, and element redistribution by hydrothermal activity.

Smellie, J. 1988. Pocos de Caldas, Minas Gerais, Brazil: a natural analogue study. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting*. Snowbird, Utah: CEC:57-73.

Smellie summarizes the status of investigations at Pocos de Caldas which began in 1986 and are scheduled to end in 1989. This paper includes descriptions of work at both the Osamu Utsumi Mine and at Morro do Ferro. The geology and U and Th distributions at Osamu Utsumi are described as well as high temperature studies, hydrogeology, groundwater chemistry, colloid studies, and microbiology studies. Work summarized at Morro do Ferro includes geology, natural decay series and LREE analyses, hydrogeology, groundwater chemistry, colloid studies, and microbiology studies. Several sections and figures are provided.

Smellie, J., N. Chapman, I. McKinley, E. Penna Franca and M. Shea. 1988. Testing safety assessment models using natural analogues in high natural series groundwaters. The second year of the Pocos de Caldas project. *Scientific Basis for Nuclear Waste Management XII - Materials Research Society Symposium Proceedings*. Pittsburgh: Materials Research Society: 863-870.

This project is a joint venture of Brazil, Sweden, Switzerland, UK, and the USA. The work takes place at two sites within the Pocos de Caldas caldera (a Cretaceous alkaline volcanic complex in Minas Gerais): the Osamu Utsumi open pit uranium mine and the Morro do Ferro thorium and REE prospect. This project is designed around four main objectives: testing chemical thermodynamic models, and studying redox front processes, colloids in groundwater, and near-field hydrothermal processes. Early results suggest that the mathematical models may have a difficult time explaining field observations; this trouble may be a function of the models used, inadequate data, or the unusual nature of these groundwaters.

Smellie, J. A. T. 1988. Some Swedish natural analogue studies: a review. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting*. Snowbird, Utah: CEC:96-103.

The author lists and summarizes several analog studies in Sweden. All of the analogs concentrate on low temperature (<80°C) studies. (1) A uraninite stability study looked at natural uraninites from depths of 50 - 130 m in crystalline rocks. Most of the samples are in radioactive disequilibrium, however, the reducing environment has preserved the uraninite such that it has remained "texturally stable" during its 1750 Ma existence. (2) A matrix diffusion study investigated fracture zones in differing hydrogeological environments intersected by drill core. They found that, in general, water-rock interaction has produced radioactive disequilibrium resulting from uranium migration on a time scale of 1 Ma; Th was immobile under the same conditions. A limit of 3 cm was suggested for the migration of radionuclides from fracture fluids into the saturated rock over the available time span. (3) A deeply penetrating fracture zone located in a groundwater recharge region was intersected by drill holes at several depths in an attempt to examine the changes in alteration mineralogy and chemistry as conditions changed from oxidizing to reducing with depth. At this time only samples from 50 m depth have been studied; these samples indicate significant oxidation is limited to 2-3 cm adjacent to the fracture/water interface. It is proving difficult to distinguish between hydrothermal alteration and low temperature weathering. (4) A bronze cannon partially submerged in the Baltic Sea and embedded in sand and clay since 1676 has been studied as an analog to copper cannister stability. Maximum corrosion related to a pitting factor of 5 is estimated to be <10 mm in 100,000 years. (5) Several long-term studies of clay alteration have been undertaken as analogs to bentonite barrier stability with the conclusion that at temperatures <100°C, most of the smectite in the clay should remain "chemically intact" for more than 1 Ma.

Smellie, J. A. T., A. B. MacKenzie and R. D. Scott. 1985. An analogue validation study of natural radionuclide migration in crystalline rocks using uranium-series disequilibrium studies. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analog Working Group, First Meeting*. Brussels: CEC.

Smellie et al. have studied the concentrations and isotopic ratios of U-series elements in sections of drill core from 3 locations. Distributions and ratios indicate rock-water induced disequilibria in 2 of the 3 samples. U appears to have migrated from the rock some 40 cm (or more) on a time scale of about 1 my while Th remained relatively immobile. A limit of 3 cm is suggested for radionuclides moving from fracture fluids into the rock.

Smellie, J. A. T., L. B. Magno Jr., N. A. Chapman, I. G. McKinley and E. P. Franca. 1987. The Pocos de Caldas project feasibility study: 1986-7. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogues in Radioactive Waste Disposal - A Symposium*. Brussels: CEC.

Smellie et al. describe the results of preliminary work at the Osamu Utsumi U mine and at Morro do Ferro. General descriptions are given of core sampling and logging and groundwater sampling procedures. Emphasis is placed on the importance of microbes with regard to U mobilization. There is only a limited discussion of results. Largely, they found the sites to be much more complicated than anticipated.

Smith, M. R., J. C. Laul and V. G. Johnson. 1987. Natural radionuclides in Hanford ground waters. *Scientific Basis for Nuclear Waste Management XI - Materials Research Society Symposium Proceedings*. Pittsburgh: Materials Research Society: 249-257.

Uranium, thorium, and radium concentrations in groundwaters at Hanford are very low with respect to radon concentrations which suggests that they are being sorbed and/or precipitated from solution, probably related to reduction with depth; concentrations of uranium are much higher in surface waters. Barium contents correlate very well with radium even though the concentrations of the two elements differ by some six orders of magnitude. Therefore, the authors suggest that barium may be a good elemental analog for radium.

Snelling, A. A. and B. L. Dickson. 1988. A study of the weathering history at Koongarra. Australian Nuclear Science and Technology Organisation. ANSTO Alligator Rivers Analogue Project - Progress Report, May 1988 - August 1988 : 13-20.

This paper attempts to resolve the question of what initiated the weathering of the ore deposit at Koongarra about 1-3 Ma ago. The authors hypothesize a "rapid scarp retreat and erosion of the schist" down to the top of the ore horizon followed by a stable situation since that event. They are pursuing the question through a literature search but have found no information about such a rapid erosion event in that time period. The paper summarizes the information on weathering in the area gathered to date from the literature.

Stege, B., N. E. Pingitore, P. C. Goodell and D. V. LeMone. 1981. Limestone bedrock as a barrier to uranium migration, Sierra Pena Blanca, Chihuahua, Mexico. *Uranium in Volcanic and Volcaniclastic Rocks- AAPG Studies in Geology No. 13*. El Paso, TX: American Association of Petroleum Geologists: 265-274.

The limestone bedrock at Pena Blanca is comprised of a bottom unit of "foraminiferal lime mudstone", followed upward by alternating layers of argillaceous limestone and calcareous shale. Fossils indicate an age of Albian to Cenomanian (mid-Cretaceous). No data are presented to support the authors' opinion that these limestone rocks are "impermeable" other than the presence of abundant mud in the sequence. Nevertheless they summarize: "These units formed a hydrologic barrier that prevented downward or lateral migration of uranium-bearing solutions."

Steven, T. A., C. G. Cunningham and M. N. Machette. 1981. Integrated uranium systems in the Marysvale Volcanic Field, West-Central Utah. *Uranium in Volcanic and Volcaniclastic Rocks- AAPG Studies in Geology No. 13*. El Paso, TX: American Association of Petroleum Geologists: 111-122.

At Marysvale, U occurs in a variety of geologic settings including: porphyry deposits, hydrothermal veins, dispersed hydrothermal deposits, roll-front and sedimentary trap deposits. So far the only production has been from hydrothermal veins. Portions of the Joe Lott Tuff Member in the southern part of the Big John caldera at Marysvale have been converted to clinoptilolite and have lost about half of their original U content (about 12 ppm). There is little known about the changing drainage patterns at Marysvale for the past 20 my or about the remobilization of U by surface waters. In the Mineral Mountain area there are springs with anomalously high radioactivity (Miller et al., 1979).

Stuckless, J. S. 1986. Applications of U-Th-Pb isotope systematics to the problems of radioactive waste disposal. *Chemical Geology* 55:215-225.

Stuckless has studied the concentrations of U, Th, and Pb and the isotopic compositions of Pb in several granitic plutons. He finds that open system behavior is common in the surface and near-surface environment, and that elemental mobility is possible down to several hundred meters depth. By using these techniques, one may determine whether or not a pluton has remained closed or has been isotopically undisturbed (i.e. isolated from circulating fluids and therefore the biosphere) for the last several hundred million years.

Sunder, S., P. Taylor and J. J. Cramer. 1987. XPS and XRD studies of uranium rich minerals from Cigar Lake, Saskatchewan. *Scientific Basis for Nuclear Waste Management XI - Materials Research Society Symposium Proceedings*. Pittsburgh: Materials Research Society: 465-472.

Primary mineralization at Cigar Lake has been dated at 1300 million years. Both uraninite and coffinite were identified by XRD; some of the samples contained organic carbon, probably in natural hydrocarbons. The uranium concentrations in groundwater are similar to those expected for uraninite equilibrium; measured values are $10^{-7.5}$ to 10^{-9} mol/dm^{-3}. The oxidation state of the uranium is equal to, or lower than, that of U_3O_7. The authors suggest that various redox couples are responsible for maintaining solution Eh and that the system is not significantly affected by radiolysis; Eh is estimated at about -0.2 to +0.2 volts. Radiogenic lead appears to have been leached from the samples whereas uranium appears to have been stable.

Sverjensky, D. A. 1988. Geochemical modelling of the Koongarra uranium deposit. Australian Nuclear Science and Technology Organisation. ANSTO Alligator Rivers Analogue Project - Progress Report, May 1988 - August 1988 : 21-64.

Sverjensky notes that the "complex" geologic history of the Koongarra deposit complicates the resolution of the present day processes. He has used measured water compositions, temperatures, pressures, oxidation states, and pH values to calculate the speciation and saturation states of the groundwaters, using EQ3NR. He reports that the redox state of the groundwaters are "poorly constrained" at present; that the Fe and Al in the analyses may be particulate rather than dissolved; that U is complexed by HPO4 or CO3 depending on the concentrations of those agents and the pH; and that waters from the weathered zone are undersaturated with respect to chlorite, illite, carbonate minerals, uraninite, uranophane, saleeite, torbernite, and carnotite, suggesting that the present fluids may actually be dissolving and dispersing the U of the deposit.

Tammemagi, H. Y., B. Haverslew and N. C. Sturchio. 1986. Investigations of the Empire Creek Stock, Montana, as an analogue to a nuclear waste repository. *Chemical Geology* 55:375-385.

This paper is a case history of a low temperature geothermal system. The system was unusual in that it had no surface manifestation such as hot springs. Maximum T was 95°C. Descriptions of the geology, petrography, permeability, and alteration of the site are given. They are attempting U disequilibrium studies in order to provide age limits on the present phase of hydrothermal activity.

Thompson, J. L. 1984. Laboratory and field studies related to the radionuclide migration project. Los Alamos National Laboratory. LA-10372-PR.

This paper is a report of activity in the Radionuclide Migration Project for FY84. The project was begun in 1973 "to determine the potential for movement, both on and off the NTS, of radioactivity from underground nuclear explosions." Work is reported for the Cambric Site (one of the largest studies of radionuclide migration in the world), the Cheshire Site, and the Nash Site. At Cambric, tritium, krypton, and iodine have continued to be monitored; so far "no radioactive cations have appeared" in the test well water. At Cheshire, lithium, tritium, and other elements have been measured; tritium appears somewhat lower than expected. At Nash (where the detonation occurred in alluvium above the water table) water samples have been restricted to fluids from the carbonate aquifer beneath the alluvium, to test the migration of radionuclides from the unsaturated zone into the saturated zone. However, it is not clear whether the nuclides measured in the waters originated in the explosion cavity or whether they represent "material driven by the explosion into fractures in the carbonate rocks."

Tsolis-Katagas, P. and C. Katagas. 1989. Zeolites in pre-caldera pyroclastic rocks of the Santorini volcano, Aegaen Sea, Greece. *Clays and Clay Minerals* 37:497-510.

This information is based on "about 60" samples from pyroclastic rocks immediately west of the Akrotiri area. The vitric portions of the silicic tuff near Akrotiri has been altered to a mixture of K and K-Ca rich clinoptilolite, opal-CT, and clays. There is no obvious vertical or lateral pattern to the mineral distributions. The authors attribute the random variations to differences in heat flow, ionic activity in interstitial waters, and permeability. The authors cite Nicholls (1971) who reports that the "Akrotiri volcanics" consist mainly of domes and flows of "basalts and andesites". These volcanics overlie Upper Triassic "marbles" which have been thrust over metapelites and metapsammites (Papastamatiou, 1958). Kavourides et al. (1982, unpublished data) report that the island is geothermally active with a geothermal gradient of about 15.7°C/100 m at Thermia (3.5 km NE of Akrotiri). At Thermia and Vlychadha (3.5 km SE of Akrotiri) there are thermal springs (T up to 52°C). In the Akrotiri area, the geothermal gradient in somewhat less, about 4.7°C/100 m (Kavourides et al. 1982, unpublished data). Zeolites volumes varied from trace amounts to about

60% of the rock. The alteration of the original dacites to the zeolite rich rocks was accompanied by an increase in H2O and MgO and a decrease in SiO2, Na2O, K2O, Al2O3, and CaO. In addition to clinoptilolite, some mordenite occurs, but no analcime was found. The composition of Akrotiri well water is reported and is described as similar to oil field waters (i.e. a sodium chloride brine).

Ulmer, G. C., G. H. Kacandes and D. E. Grandstaff. 1986. Icelandic geothermal fields as an analog for nuclear waste disposal in basalt. *Advances in Ceramics* 20:755-764.

The authors have conducted a series of experiments reacting Columbia River basalt with synthetic groundwater in autoclaves and have compared the results with parallel experiments using Icelandic basalt and with data from Icelandic geothermal fields to establish the ability of short term experiments to approach long term results. The rock compositions, temperatures, hydrologic residence times, glass compositions, and groundwater compositions of the Hanford site and the Icelandic geothermal fields are comparable. Experimental results for cation/proton ratios, neutral species concentrations, redox, and alteration phases are similar, indicating that short term experiments do approach long term conditions, however, there are differences (e.g. CO_2) which may reflect additions from volcanic gasses in the geothermal fields not present at Hanford.

Valkiainen, M. 1988. Finnish natural analogue research. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting*. Snowbird, Utah: CEC:110-118.

Some Finnish natural analog programs are described by the author. At Palmottu (a small uranium deposit consisting of uraninite in microcline granite dykes) hole have been drilled and the groundwaters sampled and analyzed. Downhole, the waters go from oxidizing to reducing and the pH increases. U concentration in the water is higher in the oxidizing upper waters whereas U concentration in the rock is highest in the bottom of the hole. About one third of the U in the deep water was bound to a particulate (>0.45 μm) fraction whereas only about 3% of the U from the middle part of the hole was bound to particulates. A corrosion study of copper coins from the Russian warship St. Nikolai (which sank in 1790) is planned. Some of the coins are badly corroded and others are not, presumably due to differences in local chemistry.

Van Luik, A. E. 1985. The use of natural analogs in the process of building confidence in performance assessment models. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analog Working Group, First Meeting*. Brussels: CEC.

Van Luik summarizes remarks made during a discussion of modeller's needs during Session I of the first meeting of the CEC's NAWG. They concluded that natural analog studies are fraught with uncertainties, but they will be useful if the analog work results in a "credible description" of a well-defined process and if it provides quantitative information that can be used to validate models.

Vilks, P., J. J. Cramer, T. A. Shewchuk and J. P. A. Larocque. 1988. Colloid and particulate matter studies in the Cigar Lake natural analog program. *Radiochimica Acta* 44-45:305-310.

AECL (Atomic Energy of Canada Ltd) has carried out a series of natural analogue studies to evaluate geologic HLW repositories. Among these are studies at Cigar Lake, Saskatchewan. Uranium ore at Cigar Lake occurs as an E-W trending lens 2 km long and 25 - 100 m wide at a depth of 400 m. There has been no disturbance by mining or weathering. The ore (uraninite) is up to 65% and is surrounded by a clay-rich zone. This study set out to assess the concentration, size

distribution, stability, and composition of natural colloidal material (<500 nm) in groundwater near the deposit. Concentrations ranged from 0.6 - 261 mg/l; most particles were in the 5000 - 10000 nm range, with a peak in colloid size between 50 and 100 nm; particles consisted of clays (mostly illite), Fe-Si precipitates, organics, rock particles, and drilling impurities. Both concentration and composition appear to have been determined by local alteration mineralogy and Fe oxidation. The authors found no evidence for U migration away from the deposit since the last hydrothermal event.

Vovk, I. F. 1988. The IAEA report of the role of natural analogues in performance assessment. B. Come and N. Chapman, eds. *Commission of the European Communities Natural Analogue Working Group, Third Meeting*. Snowbird, Utah: CEC:140-144.

This article summarizes the IAEA report on the role of natural analogs. Natural analogs are defined as "occurrences of materials whether man-made or natural, conditions and processes which are envisioned from an analogic viewpoint, justified by their similarity or their identity with occurrences known or predicted in some parts " of a waste disposal system. The conclusions of the report are included verbatim. Some of the conclusions follow. Natural analogs can help demonstrate the robustness of a performance assessment by showing that no important processes have been omitted. Natural analogs may be the only way to validate complex models of coupled processes. So far it has proved difficult to extract quantitative information from natural analog studies, however, they may prove important to providing limits and bounds to calculations of system performance. Natural analogs may also be of special importance in gaining public acceptance for waste disposal proposals.

Waber, N. 1990. Mineralogy, petrology and geochemistry of the Poços de Caldas analogue study sites, Minas Gerais, Brazil. II Morro do Ferro. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print.* Brussels: Commission of the European Communities: n° EUR 13014 EN.

Morro do Ferro is located near the center of the Poços de Caldas caldera complex and is the highest point in the caldera, evidence of its relative resistance to erosion. This Th-REE deposit was formed by supergene processes which developed elongated argillic lenses of ore which run down the hill slope. Major ore minerals include: bastnaesite, monazite, cheralite, goyazite, thorianite and thorite. This mineralization and the associated alteration suggests that a carbonatite intrusion was the source of the ore minerals. Within the orebody, Ce, U and Th tend to occur together, whereas La is associated with Nd and Y.

Waber, N., H. D. Schorscher, A. B. MacKenzie and T. Peters. 1990. Mineralogy, petrology and geochemistry of the Poços de Caldas analogue study sites, Minas Gerais, Brazil. I Osamu Utsumi uranium mine. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print.* Brussels: Commission of the European Communities: n° EUR 13014 EN.

The Osamu Utsumi uranium mine is an open pit of some 800 m diameter. Subvolcanic porphyritic phonolites are the main rock type and have been intruded by later nepheline syenites. These rocks were subjected to hydrothermal alteration which altered magmatic alkali feldspars to intermediate microcline and replace nepheline by mixtures of kaolinite and illite/sericite. Early hydrothermal alteration probably occurred at temperatures well below 200°C since kaolinite was stable. During the later potassic alteration, fluid inclusions recorded temperatures of 210-260°C. Maximum temperatures occurred at the end of the potassic stage and were probably in the range of 260 to

360°C as indicated by fluid inclusions and illite crystallinity data. Sulfur isotopic studies suggest that the hydrothermal fluids had a magmatic source.

Waite, T. D. 1988. Radionuclide sorption processes in the weathered zone: modelling and incorporation in the transport equation. Australian Nuclear Science and Technology Organisation. ANSTO Alligator Rivers Analogue Project - Progress Report, May 1988 - August 1988 :187-193.

Waite notes the previous reliance on Kd's and proposes an approach aimed at developing "surface coordination" or "site binding" models instead. The sorption research plan will include both batch and column investigations on both unconsolidated material from the weathered zone and on consolidated material; the problems associated with particle size reduction of the consolidated materials are discussed.

Walker, G. W. 1985. Geology of the Lakeview uranium area, Lake County, Oregon. *Uranium Deposits in Volcanic Rocks*. Austria: International Atomic Energy Agency, proceedings of a technical committee meeting, El Paso, TX April 1984. IAEA-TC-490: 412-447.

Near-surface, paleohydrothermal systems related to intrusion of rhyolite created argillic zones which are overlain by silicic caprocks and which are enriched in U, As, Mo, Hg, and Sb (at the White King and Lucky Lass deposits). Late Eocene basalt flows are overlain by a sequence of ash flow tuffs and interbedded tuffs, all of which is capped by Late Miocene basalt flows (7-8 m.y.). U mineralization is associated with altered rhyolite and altered tuffs and tuffaceous sediments.

Ward, D. B., D. G. Brookins, M. D. Siegel and S. J. Lambert. 1990. Natural analog studies for partial validation of conceptual models of radionuclide retardation. *Scientific Basis for Nuclear Waste Management XIV*. Boston: Materials Research Society Symposium Proceedings Series Vol. 212:472.

The authors are looking at U and trace metal distributions in groundwaters and fracture-filling clays to determine the extent of clay/solute interaction. They consider this interaction to be analogous to sorption of waste ions onto clays in an aquifer. They estimate U solid/liquid distribution ratios at 80 to 800 ml/g. Comparison of these measurement to actinide behavior requires quantification of the inert and exchangeable components of the U content of the clays which they are pursuing with selective extraction techniques and mineralogical studies.

Warren, P. 1984. Absolute dating of the Bronze Age eruption of Thera (Santorini). *Nature* 308:492-493.

Warren discusses dating of the Santorini eruption provided by frost damage in the bristlecone pine tree-ring sequence from Campito Mountain, eastern California (1628-1626 BC) and a date based on a peak of acidity in the Camp Century ice core from northwest Greenland (1390 ± 50 BC).

Watkins, N. D., R. S. J. Sparks, H. Sigurdsson, T. C. Huang, A. Federman, S. Carey and D. Ninkovich. 1978. Volume and extent of the Minoan tephra from Santorini volcano: new evidence from deep-sea cores. *Nature* 271:122-126.

The Santorini eruption (about 1500 BC) was one of the largest known explosive eruptions in post-glacial time; a caldera with an area of some 83 km^2 and a depth of 600 - 800 m was formed. Three phases have been identified in the eruption: 1) coarse tephra fall; 2) fine grained tephra fall deposits and base surge horizons overlain by mud flows; 3) non-welded ignimbrite flows, intraformational flood deposits and very fine grained co-ignimbrite tephra fall deposits. Assuming an average thickness of 15 m over 200 km^2, the volume of tephra on Santorini is estimated to be 3 km^3.

West, J. M., I. G. McKinley and A. Vialta. 1988. The influence of microbial activity on the movement of uranium at Osamu Utsumi mine, Pocos de Caldas, Brazil. *Scientific Basis for Nuclear Waste Management XII - Materials Research Society Symposium Proceedings.* Pittsburgh: Materials Research Society: 771-777.

Osamu Utsumi is a roll front uranium deposit. This study investigates the movement of natural radionuclides across redox fronts at Osamu Utsumi as an analogue to such migration across radiolytic redox fronts in a HLW repository. The authors estimate that the nutrients available from the rock and groundwater would support about 0.1 g/m^3 of biomass. The rate of movement of the redox front depends on the rate of supply of oxidants; this study indicates that microbes are present and are currently enhancing the supply of oxidants and hence the rate of advance of the front. These inferences are compatible with the observations that the redox front is moving faster than would be expected on the basis of simple dissolved oxygen concentration. The authors note, however, that at Cigar Lake, Canada, high concentrations of uranium remain immobile despite the presence of extensive microbial activity.

West, J. M., A. Vialta and I. G. McKinley. 1990. Microbiological analysis at the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print.* Brussels: Commission of the European Communities: n° EUR 13014 EN.

The authors have attempted to characterize the microbial populations and their influence on geochemical processes. Both rock cores and groundwaters were sampled for microbes; microbes were found in all samples with no depth correspondence. The authors estimate an annual production of about 0.01-0.1 g of dry biomass per square meter of redox front. They suggest that the local sulfur geochemistry may be mainly microbially catalysed and that such processes could be responsible for the formation of pitchblende concretions and the presence of secondary pyrite.

Wilde, A. R., T. P. Mernagh, M. S. Bloom and C. F. Hoffman. 1989. Fluid inclusion evidence on the origin of some Australian unconformity-related uranium deposits. *Economic Geology* 84:1627-1642.

Fluid inclusions from Koongarra, Nabarlek, and Jabiluka were examined using a variety of standard techniques. The data indicate that ore deposition occurred at 200-300° C at a depth of about 2 km. The mineralizing fluids were calcium and chloride rich and sulfur poor. Some post-ore inclusions contain methane and other hydrocarbons which may have provided reductants responsible for ore deposition. It is also possible that ore deposition occurred as a result of the interaction of an oxidized ore-bearing solution with graphite in the lower Proterozoic host rocks.

Winograd, I. J. 1986. Archaeology and public perception of a trans-scientific problem: disposal of toxic wastes in the unsaturated zone. U.S. Geological Survey. Open-file Report 86-136.

Winograd points out that archaeologic evidence can be particularly meaningful to the "public and courts who ... are reluctant to rely exclusively on computer-generated" models. He also notes that the archaeologic record also suggests that the likelihood of human intrusion into a repository is relatively great. Some problems with archaeologic analogs are noted: 1) determination of paleoclimate is difficult 2) it is hard to find good hydrogeologic matches for a repository 3) archaeologic artifacts were never subjected to a heat pulse. Many examples of artifacts which have been preserved in unsaturated environments are given. Most of these examples are caves and burial sites.

Wollenberg, H. A. and S. Flexser. 1986. Contact zones and hydrothermal systems as analogues to repository conditions. *Chemical Geology* 55:345-359.

Investigations of igneous contact zones which have been studied with regard to elemental migrations include: a Tertiary stock into Precambrian gneiss, a stock into ashflow tuff, a rhyodacite dike into Columbia River basalt, a kimberlite dike into salt. In general there has been little migration of radioelements from the more radioactive intrusives into the less radioactive country rocks. The lack of mobility is attributed by the authors to the location of the radioelements in resistant accessory minerals (zircon, sphene, monazite, allanite). They suggest that artificial versions of these accessory minerals would make effective waste forms. Active hydrothermal systems are suggested as good analogs to the convective flow which might be established around a HLW package during the period of high heat generation; the temperatures are comparable, and the lifetimes are similar. They suggest studying the distributions of radioelements with respect to the hydrology, water chemistry, and alteration mineralogy. One example of such a study is given (Newberry, Oregon). Researchers used whole rock g - spectrometric analyses to determine the distributions of U, Th and K in core. They found a general decrease in U and Th with depth that was independent of the degree of hydrothermal alteration, suggesting the presence of more oxidizing conditions at depth.

Yanase, N. 1988. Distribution of uranium and actinium series radionuclides in rocks and groundwater. Australian Nuclear Science and Technology Organisation. ANSTO Alligator Rivers Analogue Project - Progress Report, May 1988 - August 1988 : 123-146.

Rocks and groundwaters from Koongarra were studied by alpha and gamma spectrometry to measure the concentrations of uranium and actinium series radionuclides. The results generally supported the findings of earlier workers, but apparently there were some detection problems with the equipment. Yanase concludes that more sampling, additional work and better equipment are needed.

Yusa, Y., G. Kamei and T. Arai. 1990. Natural analogue studies on engineered barrier materials - recent activities at PNC Tokai, Japan. *Fourth Natural Analogue Working Group Meeting, Pitlochry, Scotland, 18-22 June 1990, Final Meeting Report Pre-Print.* B. Come and N. A. Chapman, eds. Brussels: Commission of the European Communities: n° EUR 13014 EN.

The Japanese natural analog program has three components: 1) study of alteration phenomena, 2) examination of environmental conditions, 3) performance of supporting experiments. They have investigated weathering of basaltic glass (280-2800 years old, alteration products and rates determined), corrosion of iron in soil(gas/water pipes in soil for 20-110 years), alteration of smectites after contact metamorphism (bentonite intruded by rhyolite), and alteration of cement (tunnel, river, and seawall concretes).

Ziegler, V. and J. Dardel. 1984. Uranium deposits in Europe. *Uranium Geochemistry, Mineralogy, Geology, Exploration and Resources*. England: The Institution of Mining and Metallurgy: 140-161.

This paper summarizes the geology of uranium deposits in Europe. Deposits are grouped according to their general tectonic setting and their characteristic host rock. The authors include an outline of the geologic structure of Europe. Deposits related to Tertiary volcanics are briefly described in the Macedonia area (Zletovska Reka in southeast Yugoslavia). Uranium mineralization is at least partially hosted by tuffs and ignimbrites and was emplaced by fault-controlled hydrothermal activity associated with intense alteration. These deposits are relatively low grade ("a few hundred ppm") and small ("several hundred tons of uranium").

Zielinski, R. A. 1981. Experimental leaching of volcanic glass: Implications for evaluation of glassy volcanic rocks as sources of uranium. *Uranium in Volcanic and Volcaniclastic Rocks-AAPG Studies in Geology No. 13*. El Paso, TX: American Association of Petroleum Geologists: 1-11.

Zielinski has studied the rate of uranium removal from volcanic glass by alkaline, oxygenated fluids. Uranium is removed as glass is dissolved; in all experiments, the removal rates of uranium and silicon were approximately equal. Temperature is the most important variable controlling removal rate. Less important are surface area (grain size), pH, glass composition, and the concentration of dissolved carbonate. In a low temperature, weathering environment, the most important factors are effective surface area (i.e. fine grained sediments are favored over massive, glassy units), the corrosiveness of the solutions towards glass, and fluid flow which allows frequent exchange of interstitial solutions.