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THE ROLE OF NATURAL ANALOGS IN GEOLOGIC DISPOSAL OF HIGH-LEVEL NUCLEAR WASTE

Prepared for

Nuclear Regulatory Commission
Contract NRC-02-88-005

Prepared by

Center for Nuclear Waste Regulatory Analyses
San Antonio, Texas

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Foreword to the Proceedings of the WORKSHOP ON THE ROLE OF NATURAL ANALOGS IN GEOLOGIC DISPOSAL OF HIGH-LEVEL NUCLEAR WASTE

1

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A Workshop on the Role of Natural Analogs in Geologic Disposal of High-Level Nuclear Waste (HLW) was held in San Antonio, Texas, on July 22–25, 1991. It was sponsored by the U.S. Nuclear Regulatory Commission (NRC) and the Center for Nuclear Waste Regulatory Analyses (CNWRA). Invitations to the workshop were extended to a large number of individuals with a variety of technical and professional interests related to geologic disposal of nuclear waste and natural analog studies. Participation by over 50 scientists and engineers included staff members of the NRC and CNWRA and representatives from the U.S. Department of Energy (DOE); the U.S. National Laboratories; the U.S. Geological Survey; several universities and private organizations; the Nuclear Waste Technical Review Board; the Advisory Committee on Nuclear Waste, Clark County, Nevada; and other organizations. Contributors to the workshop are identified in the summaries of the working groups proceedings (Chapters 14 to 17). The objective of the workshop was to examine the role of natural analog studies in performance assessment, site characterization, and prioritization of research related to geologic disposal of HLW.

Expert opinions were informally solicited from members of the nuclear waste management community and from individuals outside this field. Several presentations focused on natural analog studies mounted specifically in support of geologic disposal of nuclear waste. In addition, contributions were provided by scientists and engineers from other fields who routinely construct conceptual and computational models for the evolution of geologic systems and who have experience in model validation using data from natural systems. A theme of the meeting was the generality of reasoning by analogy in earth science applications.

In an opening session, presentations focused on relations between natural analogs and nuclear waste management and applications of reasoning by analogy in a variety of scientific and engineering endeavors. Subsequently, separate working groups addressed the use of natural analogs in four technical areas of nuclear waste management: waste package and waste form; near-field processes and environment; far-field processes and environment; and volcanism and tectonics. Working groups were instructed to define specific technical issues to which natural analog studies can contribute, to evaluate the status of studies on these issues, and to identify areas of additional fruitful research. Conclusions reached by the separate working groups were reviewed in a closing plenary session.

These proceedings comprise manuscripts written by plenary session speakers, additional papers contributed by workshop participants, and summaries of results from each working group. Five articles (Chapters 2 through 6) address the relation of natural analog studies to the regulation, performance assessment, and licensing of a geologic repository for HLW. A series of papers then focuses on applications of reasoning by analogy in other earth science applications, including the effects of earthquakes on engineered structures (Chapter 7) and exploration for ore deposits and petroleum (Chapters 8 and 9). In addition, an oral presentation at the workshop addressed natural analogs studies in the prediction of future volcanic activity and volcanic risk assessment. In Chapter 10, an overview is provided of a recently completed, internationally coordinated natural analog study at Poços de Caldas, Brazil. Papers are also presented on problems and applications of natural analog studies in each of the four technical areas addressed by the working groups (except volcanism/tectonics) (Chapters 11 through 13). Finally, the proceedings and conclusions of the working groups are summarized in Chapters 14 through 17.

Diverse subjects and points of view were encouraged and freely aired at the workshop. Both the utility and limitations of natural analog studies were stressed. Debate developed on many topics from the specifics of the thermodynamic properties of minerals to the generality of the range of systems for which natural analog studies are appropriate. All workshop participants were invited to provide written contributions to these proceedings, and divergent views are respectfully represented here. After review and revision, all submitted manuscripts have been included. Although many insights were gained and problems were clarified at the workshop, the role of natural analogs for geologic disposal of HLW continues to be an issue of debate and definition.

The organizers and editors desire that the workshop activities and these proceedings contribute to a greater definition of the utility of natural analog studies in site characterization and performance assessment for geologic disposal of HLW. The editors express their sincere appreciation for the insightful contributions made by workshop participants and the serious and time-consuming efforts of speakers, authors, working group coordinators, reviewers of manuscripts, and editorial assistants.

The chapters of this document represent contributions of the individual authors or workshop participants. They do not necessarily reflect the views or regulatory positions of the NRC, the DOE, or other organizations with which the authors are affiliated.

THE ROLE OF NATURAL ANALOGS IN THE REPOSITORY LICENSING PROCESS 2

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2.1 BACKGROUND

The concept of a permanent geologic repository for high-level nuclear waste (HLW) is implicitly based on analogy to natural systems that have been stable for millions or billions of years. The time of radioactive and chemical toxicity of HLW exceeds the duration of human civilization, and it is impossible to demonstrate the accuracy of predictions of the behavior of engineered or social systems over such long periods. In contrast, demonstrably stable geologic environments can provide the required isolation. Only geologic (or archaeologic) systems offer the opportunity for direct study of chemical isolation and transport phenomena over the time scale appropriate to nuclear waste isolation. Large time and space scales are prevalent themes in earth sciences, and reasoning by analogy can aid the scientific evaluation of geologic phenomena. For example, the history of the early Earth, for which no accessible record exists, has been largely deduced through investigations of meteorites and the moon. Key uses of natural analog studies are the identification and evaluation of large space- and time-scale processes and mechanisms and testing of qualitative and quantitative models of system behavior, for example, repository performance.

2.2 REGULATORY BASIS

U.S. Environmental Protection Agency (EPA) regulations stipulate that compliance with HLW cumulative release requirements for a period of 10,000 years is to be demonstrated by performance assessments (40 CFR 191.13) (EPA, 1985). Performance assessment analyses are to identify all significant processes and events and to examine their effects on the performance of the disposal system [40 CFR 191.12(q)] (EPA, 1985). EPA and U.S. Nuclear Regulatory Commission (NRC) rules acknowledge that absolute confirmation of repository performance is impossible and that a finding of reasonable assurance of environmental protection and public safety is the realistic requirement. NRC rules recognize that evaluation of waste isolation and identification of all significant processes and events on the EPA-mandated time scale are feasible only with supporting studies of analogous systems, and they specify that predictive analyses and models given in the license applicant's safety analysis report shall be supported by appropriate use of field tests, *in situ* tests, and natural analog studies [10 CFR 60.21(c)(1)(ii)(F)] (NRC, 1983a). The demonstration of compliance with objectives and criteria for repository performance over long times in the future imposed by 10 CFR Part 60 is stipulated to involve the use of predictive models that are supported by such measures as natural analog studies (10 CFR 60.101) (NRC, 1983a). The NRC staff has elaborated that methods such as natural analog studies will give confidence in the validity of models (response to comment No. 130 in NUREG-0804) (NRC, 1983b). These explicit references in NRC documents to natural analog studies and to studies of separate but representative geologic areas constitute the formal regulatory basis for the NRC program on natural analogs.

2.3 PROGRAMMATIC NEED

Although the logical basis and regulatory requirements for studies of natural analogs to support the licensing process are well established, practical applications of natural analogs to licensing of specific geologic repository systems have not been well developed. Essential questions remain unanswered. To what extent can data from analogous systems be extrapolated to assess processes, events, and occurrences at a particular repository site? In practice, how can reasonable assurance that performance objectives and technical criteria are satisfied be derived from natural analog studies? To what degree can performance assessment models be validated using data from natural analogs? Conduct of natural analog research and analysis is required to address questions such as these.

2.4 ROLE IN THE REPOSITORY LICENSING PROCESS

The explicit role of natural analogs in the licensing process is to support site characterization and predictive modeling of repository performance. This support will come in three forms as described in the following sections.

2.4.1 Identification of Processes and Events

The geologic tenant of uniformitarianism, commonly paraphrased as "the present is the key to the past," implies a regularity of natural processes governing the evolution of the Earth over time. The principle can be extended to indicate that the past is the key to the future. Observations and interpretations associated with repository site characterization will identify many important aspects of the geology (hydrology, geochemistry, etc.) that could affect waste isolation in the future. However, other significant phenomena are not expected to be manifested in the ambient site, including chemical and hydrologic processes and events associated with the introduction of foreign materials and with radiation and thermal effects. Studies of analogous systems will identify processes and events likely to influence the evolution of the perturbed geologic system, and they will enable evaluation of the importance of these phenomena. For example, rocks altered by natural hydrothermal solutions are likely to record changes analogous to those that will occur in the hydrothermal zone associated with the repository near field. The behaviors of uranium (and other) natural mineral deposits and of volcanic glasses in environments analogous to the repository site demonstrate processes and events that will affect nuclear waste forms over long periods of time. The performance of certain container materials can also be evaluated by analysis of analogs such as native copper deposits or archaeological metallic artifacts. Occurrences of natural resources in analogous geologic sites will assist evaluation of their likelihood at the repository site. Furthermore, natural analog studies can provide evidence for potential effects in scenarios for future disruptive events, such as seismicity and volcanism. Identification through analog studies of important interactions among processes in the complex engineering and geological environment of a HLW repository will permit their consideration in safety analyses. Conversely, identification of processes and events that would have insignificant effects can help justify their omission from predictive models. The development of relatively complete and realistic conceptual models and scenarios for performance assessments will require data from analog systems.

2.4.2 Calibration of Models

Performance assessment models used to support a finding of reasonable assurance of repository safety will depend in part on theoretical and empirical relations and parameters. Studies of systems analogous to the repository system, in conjunction with laboratory and field tests, will provide sources of empirical relations and parameters. For example, concentrations and variations of solutes, colloids, and microbes in natural groundwaters will help bound their likely concentrations in the repository environment. Inverse modeling of natural hydrologic systems can provide hydrologic parameters pertinent to large-scale, heterogeneous systems. Iterative modeling of systems that can be directly observed with progressive model refinement is a routine method of calibration. Errors and omissions in model parameters and relations can be identified in this process. Natural analogs will be the objects of exercises to calibrate models used in performance assessment to augment parametric values and empirical relations derived from laboratory studies of limited space and time scales.

2.4.3 Validation of Models

Strict validation of predictive models for repository performance is impossible because of the large time and space scales and the geologic and engineering complexity of the repository system. Nevertheless, for models to support a finding of reasonable assurance of repository safety, a judgment must be made of their accuracy and applicability to the system of interest. Both qualities can be evaluated, at least in part, using the degree of correspondence between model results and observable features of natural analog systems. Correct predictions of the characteristics of analog systems not involved in the calibration of the models will help to demonstrate model accuracy over the range of characteristics. Correct model predictions of processes in an analog system that are representative of specific repository processes will show applicability of the model to the repository system. Aspects of validation derived from analogs may be largely qualitative, because the representation of the repository system provided by analogs is approximate and because some quantitative features of natural systems are difficult to obtain (e.g., initial conditions). Nevertheless, evaluations of natural analogs will provide information on the completeness of performance assessment models, that is, the extent to which the models account for all important processes and events and their coupled effects. Furthermore, performance assessments will generate predictions of probabilistic distributions of consequences, and studies of the properties of a number of analogous systems will assist in validation of the predicted distributions.

2.5 CONCLUSIONS

In the United States, the licensing of a HLW repository will require reasonable assurance that the public radiological health and safety will be protected through compliance with regulatory objectives for repository performance. Reasonable assurance in the behavior of a unique and complex engineering and geologic system operating over a space scale of many cubic kilometers and a time scale of 10,000 years or longer is likely to be provided only through converging lines of evidence from a variety of investigations. Studies of analogous natural systems can support these investigations. Stable natural systems, analogous to hypothetical repository systems, provide the conceptual basis for permanent geologic disposal. Natural analogs offer field evidence for processes and events that could affect repository performance over large time and space scales. The usefulness of natural analog systems in calibration and validation of models required for predicting repository performance is an issue of active research. In combination with site investigations, laboratory studies, and scientific and engineering analyses, studies of natural analogs are expected to contribute to the reasonable assurance necessary for repository licensing.

2.6 REFERENCES

EPA (1985) Environmental Radiation Protection Standards for the Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Wastes: Final Rules. Title 40 Part 191. Code of Federal Regulations. Washington, D.C.

NRC (1983a) Disposal of High-Level Nuclear Wastes in Geologic Repositories. Title 10 Part 60. Code of Federal Regulations. Washington, D.C.

NRC (1983b) Staff Analysis of Public Comments on Proposed Rule 10 CFR Part 60, "Disposal of High-Level Radioactive Wastes in Geologic Repositories." NUREG-0804, Nuclear Regulatory Commission, Washington, D.C.

U.S. NUCLEAR REGULATORY COMMISSION NATURAL ANALOGUE RESEARCH PROGRAM

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3.1 INTRODUCTION

The following words can be extracted from 10 CFR 60.101(a)(2):

> Proof ... is not to be had in the ordinary sense of the word.

To those involved in the safe disposal of nuclear waste, these words have a special meaning. The regulatory periods, be they 300, 1,000, 10,000 or 1,000,000 years, place a burden of proof with regard to regulatory requirements which cannot be satisfied in ordinary engineering terms or even by heroic laboratory or real-time field investigations. Beyond this acknowledgement of the difficulty and unique nature of the demonstration that must be made, the scope and complexity of the problem have led many technical experts in this field to observe, correctly, that an overall performance assessment model can never be fully validated. The study of natural analogues to processes that may affect repository performance has been advanced as a way to approach this problem.

The performance assessment problem facing the waste disposal community is one that requires credible conceptual models of processes and events and a quantitative basis for exercising those models to describe the performance of real disposal systems over the period of interest. The U.S. Nuclear Regulatory Commission (NRC) has stated an approach in its regulations that includes natural analogue studies among "such measures" supporting predictive models [10 CFR 60.101(a)(2)]. Adherence to criteria advanced by the Commission of the European Communities Natural Analogue Working Group (NAWG) to judge the potential value of a proposed analogue study allows investigators to focus more clearly on ultimate objectives in the context of performance assessment by drawing specific attention to separability of effects, a clear statement of the analogous systems or processes being studied, independent means to establish basic parameters, well-defined boundaries and boundary conditions, and the ability to describe the temporal history quantitatively and with acceptable accuracy (Chapman et al., 1984).

3.2 REGULATORY CONTEXT

The primary responsibility of providing data for support of the license application rests with the U.S. Department of Energy (DOE). However, for the NRC to have an independent basis to evaluate the DOE work, the NRC will selectively investigate analogue work to support its evaluations. The NRC Office of Research is attempting to develop a systematic approach to natural analogue research that will represent a balanced approach to providing "Reasonable Assurance" (consistent with NRC regulations and as opposed to "proof" or "validation") that analyses are reasonable approximations to reality and that performance objectives will be achieved. Parallel to the efforts on natural analogues has been a broader effort to define an overall high-level waste (HLW) research program plan. The plan is structured around the regulatory performance objectives of Part 60 and is directly keyed to the most recent officially announced DOE schedule.

Figure 3-1 shows the regulatory structure as it is used to provide the format for the Research Program Plan. Conceptually, this simple approach organizes regulatory concerns into the engineered system,

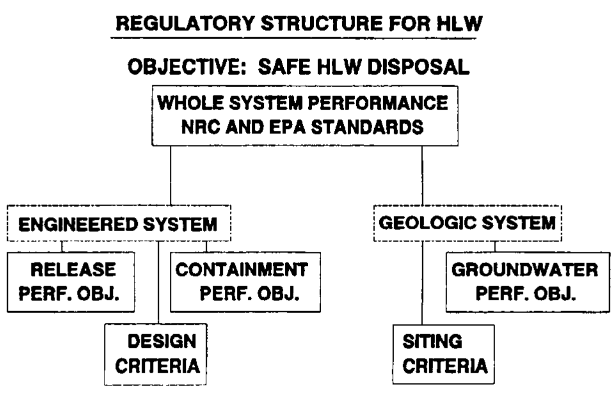

Figure 3-1. Organizational structure of high-level waste research program plan as it relates to regulatory requirements

within which the bulk of mechanical and thermal perturbation will occur, and the geologic system, within which the fundamental geologic processes will be largely undisturbed. The interface between these two areas is the "near field" where coupled thermal-chemical-hydrologic processes may significantly affect groundwater flow and contaminant transport and thus perturb the boundary conditions for the far-field transport evaluation. While the thermal perturbation may be fairly localized, its influence could extend a significant distance beyond the near field and be displayed in such processes as mineral dissolution and/or precipitation, moisture redistribution, and gas flow. Waste package/waste form and near-field processes loosely fall within the engineered system of Figure 3-1 and provide the source term for the far-field calculations. Far-field processes and volcanic/tectonic events fall under the geologic system and provide the final link to the overall performance assessment and consideration of disruptive scenarios.

Figure 3-2 displays the hierarchy of goals and objectives that must be satisfied through the regulatory framework, technical evaluations, and development of independent capability to assess DOE claims of facility performance. The goal of the NRC HLW research is to reduce uncertainty so that responsible regulatory decisions can be made in the HLW licensing program for the protection of public health and safety. The regulations and standards of the NRC and the U.S. Environmental Protection Agency (EPA) provide the framework for this evaluation, but they contain imprecisely defined terms, such as "substantially complete containment" and the "disturbed zone," which create uncertainty in their implementation.

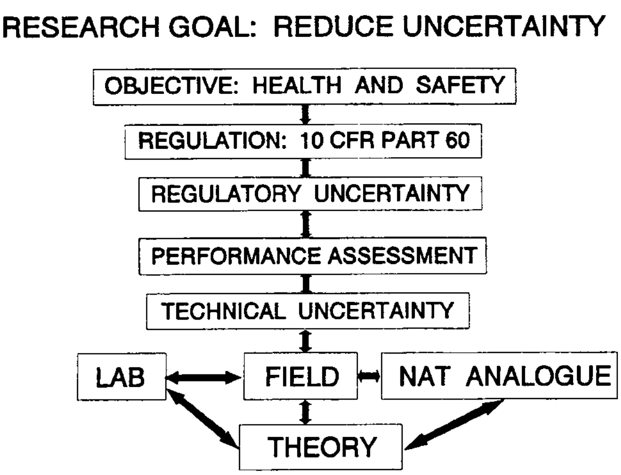

Figure 3-2. Hierarchy of goals and objectives requiring supporting data and analyses

Performance assessment is the process of systematic, quantitative evaluation of compliance with the standards established by the EPA and the NRC for both overall and subsystem performance. This evaluation is built on complex conceptual and computational models of the engineered and geologic systems and thus carries the technical uncertainties inherent in the evaluation of any complex engineered or natural system. Processes that are not well understood can generate large uncertainties when they perturb a system that may otherwise be well understood. The entire evaluatory framework is built on a combination of (i) scientific theories describing the systems, (ii) laboratory experiments testing processes amenable to small-scale and short-time-frame studies, (iii) field experiment and testing programs designed to provide both large-scale and real-time confirmation of laboratory tests, and (iv) the longer time frames attainable through the study of analogous natural systems. Technical uncertainty and the propagation of error through complex evaluations must be estimated and constantly reassessed to further focus efforts to provide credible analyses.

3.3 CONDITIONS AND PROCESSES CONSTRAINING SELECTION OF NATURAL ANALOGUES

Extensive progress in natural analogue research has been achieved over the last 10 years by such countries as the United Kingdom, Sweden, Switzerland, Canada, Japan, and the United States. Several large international projects have been sponsored by the Nuclear Energy Agency (NEA) and the Commission of European Communities (CEC), such as the Poços de Caldas Project, Cigar Lake Analogue Project, the Alligator Rivers Analogue Project to name a few. The completion of these projects and others provides extensive literature on subjects of common interest to the various international waste disposal programs, such as corrosion of waste packages, radionuclide mobility and retention, importance of colloids and redox fronts in radionuclide mobility, etc.

Unique aspects of the United States repository program drive the approach to the use of natural analogues. The United States repository will potentially contain younger fuel and a higher thermal loading than repository designs other countries are considering. This design will lead to higher temperatures in the host rock and, perhaps, significant alteration due to boiling of pore water in the unsaturated zone. The thermal regime for the repository host rock is graphically depicted in Figure 3-3, which is an approximation of the time-temperature curve anticipated for the United States repository (Pruess et al., 1990a and b). The distances shown are from the centerline of an individual waste container. Internationally, there is little interest in systems over 100 °C, because disposal sites and wastes will be managed to maintain temperatures below this figure. The current United States repository designs result in much higher temperatures over the first 1,000 years. In addition, the unsaturated, oxidizing environment at Yucca Mountain poses two other conditions unique to the United States program that are considered in the selection of appropriate analogue studies.

APPLICABILITY OF CATEGORIES OF ANALOGUES VERSUS TIME-TEMPERATURE OF REPOSITORY

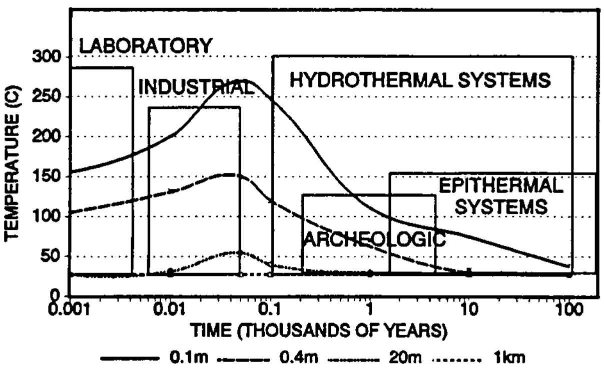

Figure 3-3. Application of analogue studies to provide understanding for time-temperature ranges for United States repository

Superimposed on the temperature profiles of Figure 3-3 are the sources of information that can be used to enhance our understanding of system performance for various parts of the time-temperature history expected for the United States repository. Laboratory and real-time field experiments yield information that extends, at most, to several years. With proper design and long-term funding, this period might be extended to tens of years. Modern industrial experience with high-technology alloys or other engineered materials and state-of-the-art underground excavation and construction techniques may span a period of 30–50 years. Archaeological analogues may span 100–5,000 years, but, except for some artifacts that may have been subjected to brief heating from a volcanic eruption, largely only relate to low-temperature conditions. Natural systems that may provide information over time periods from 100 to 1,000,000 years include hydrothermal systems (which can also represent the thermal effects) and epithermal systems (which are applicable to the lower-temperature, near-surface region).

In order to reduce concerns over uncertainties in extrapolation of laboratory data over large temporal and spatial scales, several different natural systems could be analyzed, which would bound the critical regions of regulatory or scientific uncertainty. Most natural systems leave a footprint in time, providing information regarding the final state of the system. It is often difficult to determine all the processes leading to the final observed state. Processes that are transient in nature cannot be examined at one particular site. In order to understand processes and synergistic conditions leading to the final state of a natural system, a well-planned matrix of studies could be developed to explore different aspects of the problem. If one axis represents potential variations in one parameter while another is held constant, a set of analogues might provide points on the isopleth where *in situ* values of the constant parameter are the same and the other takes on values unique to the system under study. Another example might be to test variations with scale by looking at the same processes in similar systems but over larger distances. A matrix of studies over a range of temperature, distance, and time would help to reduce uncertainty and bound parametric values of concern in both the robust performance assessment models, and, more specifically, in the more complex subsystem conceptual and numerical models.

3.4 INITIATIVES BY NRC

The structure of the NRC Natural Analogue Research Plan has evolved, in part, from consideration of the time-temperature curves. First, as noted above, the unique time-temperature aspects of the United States program lead to consideration of higher temperature regimes than other programs. Second, disruptive scenarios take on a greater importance because of tectonic and volcanic activity in the vicinity of the Yucca Mountain repository site. Other concerns of radionuclide mobility over long times and the performance of engineered containment systems are common to most disposal programs, and, hence, the NRC will make use of information from other programs as appropriate.

The high-temperature curve (Figure 3-4) is typical of the immediate vicinity of the waste canisters. Superimposed are idealized representations of the range of temperature versus time conditions of analogues currently in the NRC program designed to address the uncertainties of near-field processes. Projects at the Valles Caldera and Peña Blanca, Mexico, should provide information regarding the thermal stability of the host rock and the transport characteristics of the medium over a range of temperature and water saturation. The Akrotiri site on the isle of Santorini, Greece, may provide information on the corrosion and near-field transport of metallic artifacts. The Akrotiri site provides a well-constrained time of burial (3,600 years ago), well-defined exposure temperatures, and a chemical environment similar to Yucca Mountain. Most difficult to determine at the site will be the hydrogeologic conditions to which the artifacts were exposed.

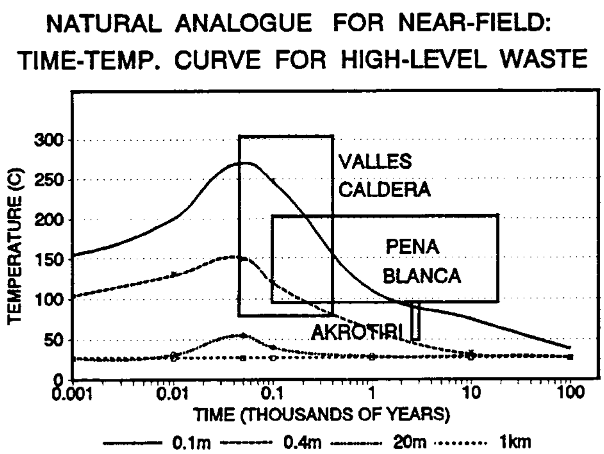

Figure 3-4. Applicability of near-field analogues to time-temperature curves for United States repository

The response of the host rock to a thermal pulse from one volcanic flow overlaying a second was the subject of studies at the Valles Caldera (see Figure 3-4). This project was specifically aimed at alteration observed near the contact between the two formations, and results have been reported concerning the differential migration of halogens away from the contact via vapor phase transport. The site was selected for study because many of the initial and bounding conditions are well constrained. The dates of the events are well established. The thermal history of the event has been reconstructed from direct physical evidence and knowledge of similar flows. The system has planar geometry and is well bounded. The tuff host rock is similar in chemical composition to the Yucca Mountain tuffs. The goal of the study was narrowly defined. While not as comprehensive nor as glamorous as the larger ore body studies, the results may be just as significant as any individual piece of those larger programs.

Conditions and processes affecting the stability of the waste form and source term will also be slightly different at the Yucca Mountain site than at other proposed disposal sites. Therefore, an attempt is being made to investigate the role of the unsaturated zone and elevated temperatures on waste package materials and waste form. Figure 3-5 identifies the natural analogue projects that are currently under consideration by the NRC.

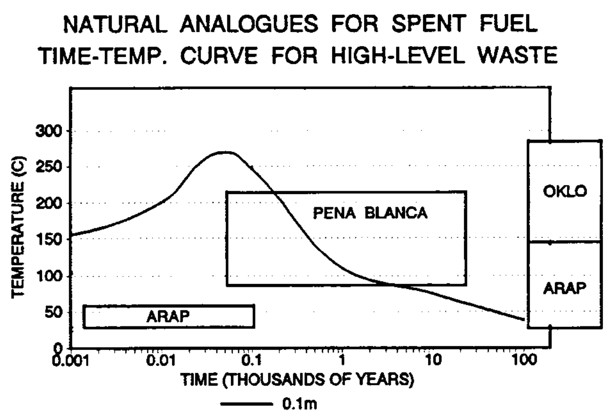

Figure 3-5. Spent fuel analogues versus peak repository temperature

The project at Nopal I, a tuff-hosted uranium ore body located in the Sierra Peña Blanca, Chihuahua, Mexico, is focused on source term degradation and transport processes. The alteration of uraninite under unsaturated oxidizing conditions is one aspect of the study. Transport processes of uranium in the unsaturated zone, and low-temperature alteration of a tuffaceous host rock are also being considered at this site as a natural analogue to processes expected to occur in the proposed United States repository. A preliminary investigation of the site has been completed, and a program of field investigations relevant to source term and contaminant transport is progressing (Murphy et al., 1990).

NRC work on the Oklo reactors [in cooperation with the Commissariat à l'Energie Atomique (CEA) investigations] is focused on source term (uraninite alteration) and characterization of the organic phases involved with radionuclide retention in and around the Oklo reactors. The much more extensive CEA and CEC investigations are concerned with the stability of uraninite and the mobility of fission products in and around the reactors. The NRC also hopes to benefit from investigations by the CEA/CEC that will provide data on the effect of igneous intrusions in the vicinity of a natural reactor zone.

The International Alligator Rivers Analogue Project is an international cooperative study of a uranium ore body that has been under intense investigation for the last 5 years, a program supported by organizations in the United States, Australia, the United Kingdom, Sweden, and Japan. The objectives of this project are to contribute to the development of realistic models for radionuclide migration within the geosphere, develop methods of validation of models using laboratory and field measurements, and encourage interaction between modelers and experimentalists in achieving objectives. This is being accomplished through six subprojects: (i) modeling of radionuclide migration (including the study of primary and secondary uranium ore dispersions in the matrix and soils determining the nature of radionuclide transport through the rock matrix and fractures), (ii) hydrogeology of the Koongarra uranium deposit, (iii) investigation of U/Th series disequilibria, (iv) the role of groundwater and colloids in radionuclide transport, (v) the study of naturally occurring fission products, and (vi) transuranic nuclide studies (Duerden, 1990).

Figure 3-6 shows another way to categorize information that may be obtained from the various natural analogue projects currently under investigation by the NRC. This diagram indicates processes affecting waste form stability, waste package, source term degradation, host rock stability, and transport of radionuclides under the two extreme hydrologic conditions. Natural analogue studies will also address the nature of fluid flow in an unsaturated fractured rock and transport under similar conditions. The Peña Blanca and Akrotiri sites will both address these issues.

CURRENT NRC NATURAL ANALOGUE STUDIES

HYDROLOGIC CONDITIONS	WASTE FORM SOURCE TERM	WASTE PACKAGE	HOST ROCK STABILITY	TRANSPORT
SATURATED	ARAP PENA BLANCA OKLO		PENA BLANCA	ARAP
UNSATURATED	PENA BLANCA ARAP	AKROTIRI	VALLES CALDERA PENA BLANCA	VALLES CALDERA ARAP PENA BLANCA AKROTIRI

ELEVATED TEMPERATURES, TIME > 100 YEARS

Figure 3-6. Breakdown of NRC analogue studies with respect to hydrologic conditions

3.5 THE ROLE OF ANALOGUES IN THE LICENSING PROCESS

The broad interpretation utilized in the NRC program for natural analogue studies is used as the framework for Figure 3-7: elevated temperatures and/or results pertinent to evaluations over times greater than 100 years. The emphasis on higher-temperature processes and the inclusion of disruptive scenarios constitute the expanded view taken by the NRC program.

The intransigence of the model validation problem has brought us to the point of no return. Neither real-time laboratory or field studies nor natural analogues can truly "validate" a performance assessment model. However, "validation" in its purest sense is not what we are after. "Reasonable assurance" is the term of choice, and the path to it is a reasoned and systematic approach building ***credibility and confidence*** into the use of models to simulate waste disposal system performance. Natural analogues can provide an important service in this role.

Scenario development is one of the ways in which natural analogues can contribute to disposal facility assessment. Not only disruptive scenarios, but expected normal and off normal scenarios, such as abnormal rainfall or cycles of climatic change, can be studied in analogous systems. When scenarios are advanced for review, it would be appropriate to ask if there are natural systems available for study in which the same phenomena have been observed and from which information might be extracted to quantify expectations of frequency and magnitude for these phenomena.

Sensitivity studies and coupled processes comprise additional areas where analogue studies can be very productive. In instances where coupled processes are involved, this may be particularly important, because the ability to vary parameters when studying the evolution of a natural system only exists through finding another system in which that parameter or series of parameters is different. Several analogues can thus begin to provide the same perspective as a

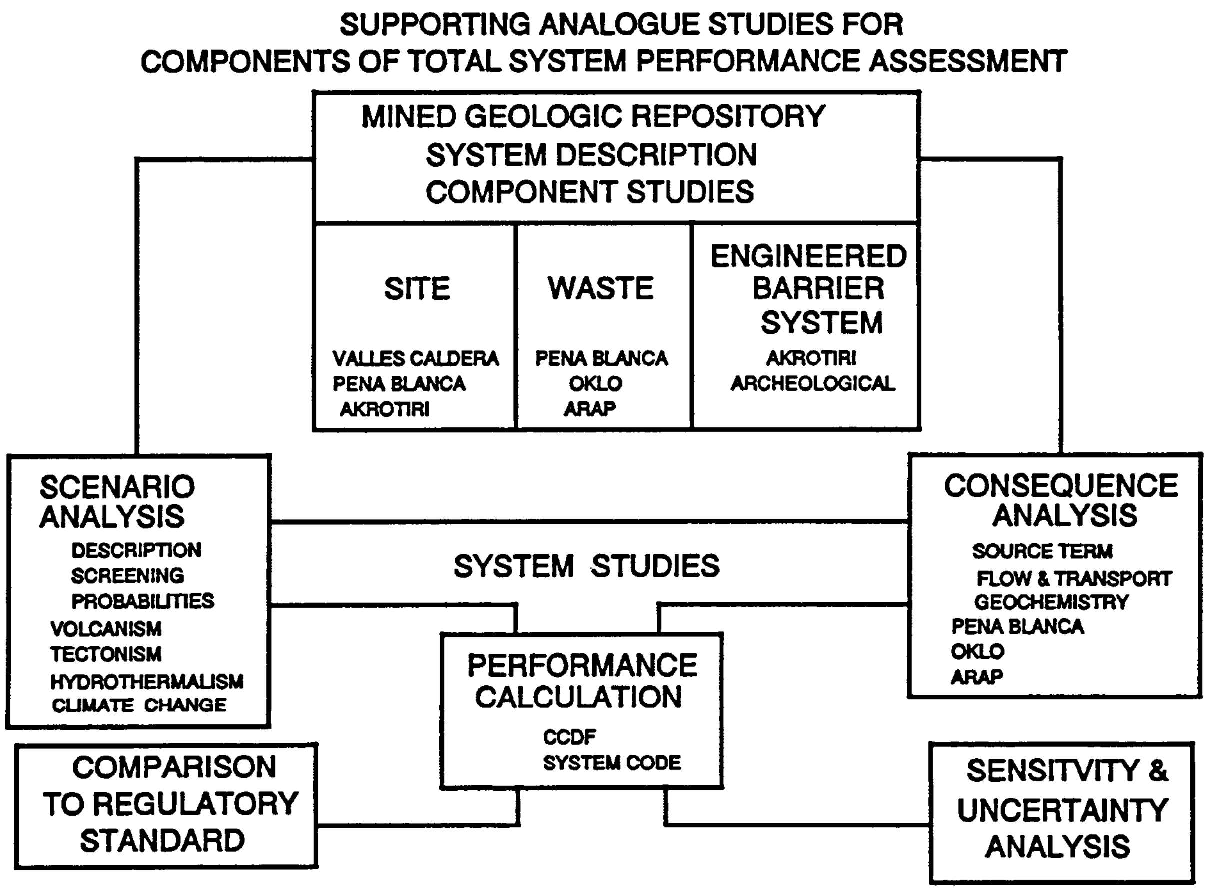

Figure 3-7. Conceptual flow diagram of performance assessment showing possible contributions from natural analogue studies

laboratory experiment in which critical parameters can be held constant or varied. In this example, selected comparison to laboratory experiments can be an informative complement to the natural analogue investigations.

Model development is also amenable to input from natural analogue studies. By testing both conceptual and computational models against descriptions of processes from natural analogues, weaknesses may be revealed that could be addressed by additional theoretical or laboratory work and augmentation of both models. This iterative process is now explicitly included in the formal process since it is now referred to as Iterative Performance Assessment. In the final analysis the most significant result of an analogue study will be to tell us under what circumstances models do not work or are not applicable. This, then, stimulates the next phase of model development and a more credible product for use in the review process.

Database validation is perhaps the most direct application of analogues. Comprehensive databases developed in laboratories can be spot-checked against field measurements under similar conditions. The same is true of extended databases developed by theoretical extrapolation of laboratory data.

A final area for consideration of natural analogue data is in site characterization. Insights gained from attempting to both study and model natural analogues yield important information about the type of data needed to support credible simulations of repository processes. The value of such information cannot be overstated. The analogy is in the ability to test the methods of data collection, treatment of samples, and effects of destructive and invasive techniques weighed against nondestructive and noninvasive methods. The analogue results provide insights for a more deliberate and, in the long run, more effective program of site characterization.

3.6 CONCLUSIONS

The NRC is the government agency responsible for licensing the HLW repository. Not only must the performance assessment models be tested, but the NRC must ensure that plausible scenarios of performance are considered, both favorable and unfavorable. The primary responsibility of providing supporting data for support of the license application rests with the DOE. However, for the NRC to have an independent basis to evaluate the DOE work, the NRC will selectively investigate analogue work to support our evaluations. To this end, natural analogue studies may play a key role in providing the necessary confidence in support of the DOE license application by (i) providing data to test the ability of models to address potential future states of the disposal system and (ii) providing insight through development of conceptual models for designing site characterization and data collection programs. Figure 3-7 presents a conceptual flow diagram for an iterative performance assessment. Indicated on this figure are the present and planned components of the NRC Natural Analogue Research Plan. It is a small start, as it must be consistent with NRC resources in this area, but it is systematic and focused to provide information in critical areas related to the nature of the problem.

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NATURAL ANALOG STUDIES: LICENSING PERSPECTIVE 4

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4.1 INTRODUCTION AND PURPOSE

This report is intended to describe the licensing perspective of the term, "natural analog studies," as used in 10 CFR Part 60 (the Rule), including a clarification of the range of topics to which these studies can apply. Evidence suggesting a misunderstanding of this term comes from a discussion on its definition at the U.S. Nuclear Regulatory Commission (NRC)-Center for Nuclear Waste Regulatory Analyses (CNWRA) Workshop on the Role of Natural Analogs in Geologic Disposal of High-Level Nuclear Waste, July 22–25, 1991. That discussion concerned the range of topics to which natural analog studies should apply. Since the workshop, an additional paper and report has come out recommending the range of topics appropriately covered by natural analog studies. Chapman (1992) states "a natural analog is an environment that has been perturbed in some way by materials or processes analogous to those in or around a repository, and resulting from its presence." Furthermore, he states, "the majority of analog studies concern geochemical processes." These ideas are reflected also in a report written by a panel of scientists [Natural Analogue Review Group (NARG)] selected "to provide guidance and recommendations to the U.S. Department of Energy's (DOE) Office of Civilian Radioactive Waste Management for the implementation of natural analog studies in the site characterization program" (letter from C.P. Gertz to T.H. Isaacs, 6/1/92). The report states that, "natural analog studies should be process-oriented and should basically address the issues resulting from the perturbation of a natural system (the geologic site) by the introduction of a technological system (the repository)." Furthermore, the report goes on to say that, "all investigations normally part of site characterization, even when considering comparisons with similar remote sites, such as (paleo)hydrology, etc., should not be considered as natural analog studies." The range of issues suggested in the NARG report to which natural analogs can apply is more restrictive than required by 10 CFR Part 60.

4.2 ANALYSIS

The term "natural analog studies" is used twice in 10 CFR Part 60. The first occurrence of the term is in the section describing License Applications, §60.21 Content of application, specifically in §60.21(c)(1)(ii)(F). The second occurrence is in Subpart E—Technical Criteria §60.101 Purpose and nature of findings. The text of 10 CFR Part 60 using the term "natural analog studies" is provided in the Appendix.

In Paragraph (F) of §60.21(c)(1)(ii), "natural analog studies" is one of the methods from an appropriate combination of methods that can be used to support analyses and models "to predict future conditions and changes in the geologic setting." The geologic setting is defined in the Rule as "the geologic, hydrologic, and geochemical systems of the region in which a geologic repository operations area is or may be located." The "changes in geologic setting" would necessarily result from various processes acting in and on the systems. The systems are, thus, composed of both conditions and processes, and the analyses and models are meant to support prediction of the future states of the systems. In turn, it is interpreted that these analyses and models will be part of the "explanation of measures used to support the assessments required in paragraphs (A) through (D)."

Paragraph (A) requires "an analysis of the geology, geophysics, hydrogeology, geochemistry, climatology, and meteorology of the site." This analysis involves determining both conditions and processes present at the site and, thus, can be considered site characterization. Site characterization is defined in the Rule as "the program of exploration and research, both in the laboratory and in the field, undertaken to establish the geologic conditions and the ranges of those parameters of a particular site relevant to the procedures under this part... ."

Paragraph (B) refers to "Analyses to determine the degree to which each of the favorable and potentially adverse conditions, if present, has been characterized. . . ." Favorable and potentially adverse conditions are described in §60.122 Siting Criteria, where some of the analyses involving favorable and potentially adverse conditions can be considered site characterization work [e.g., §60.122(b) and (c)] and some can be considered performance assessment [e.g., §60.122(a)].

A distinction can be made between site characterization and performance assessment. Whereas site characterization involves collecting, describing, and analyzing processes and conditions of the site, performance assessment specifically evaluates the site relative to the performance objectives described in the Rule. The information from site characterization thus feeds into performance assessment.

Paragraph (C) requires an "evaluation of the performance of the proposed geologic repository... ." Paragraph (D) refers to "The effectiveness of engineered and natural barriers... ." Both of these paragraphs refer to performance assessment.

The use of the term "appropriate combination of such methods" in paragraph (F) provides for flexibility in the choice of the methods used to support the analyses and models predicting future conditions and changes in the geologic setting. As a result, there is not a one-to-one correlation between the methods listed in the Rule "such as field tests, *in situ* tests, laboratory tests which are representative of field conditions, monitoring data, and natural analog studies" and the required analyses of paragraphs (A) through (D). However, the use of the term "conditions...in the geologic setting" in paragraph (F) could include conditions such as those listed as favorable and potentially adverse conditions in the Siting Criteria. Thus, an "appropriate combination of such methods" is to support site characterization work. The use of the term "changes in geologic setting" could refer either to changes caused by the repository, which would necessarily involve performance assessment, or to changes that occur naturally over the period of regulatory concern, which would involve site characterization. Consequently, §60.21 requires that an "appropriate combination of such methods" be used to support site characterization work and performance assessment. However, the Rule does not describe what constitutes an appropriate combination of methods to support the analyses.

The Staff Analysis of Public Comments on Proposed Rule 10 CFR Part 60 "Disposal of High-Level Radioactive Wastes in Geologic Repositories" (NRC, 1983) states that the "support for the models from an appropriate combination of methods concerns not only the reliability of the codes themselves, but also the representativeness of the models with respect to the physical conditions of the site." Thus, by referring to conditions, the paragraph is addressing aspects of site characterization.

Since the Rule does not explicitly restrict the application of natural analog studies to any one of the specified analyses in Paragraphs (A) through (D), it is prudent to assume that these studies could be applied to all of them. Consequently, a broad definition of the term "natural analog studies" would be appropriate.

The second occurrence of the term "natural analog studies" is in §60.101, where it states that natural analog studies are used to support predictive models to demonstrate compliance with objectives and criteria. The term "objectives and criteria" in the same sentence that contains "natural analog studies" can refer to either the phrases "performance objectives and site and design criteria" or "objectives and criteria for repository performance" in preceding sentences of §60.101. Thus, natural analog studies are, at least, to be used to support performance assessment and possibly to support analyses to demonstrate compliance with site criteria.

Finally, both occurrences of the term "natural analog studies" in the Rule relate it to describing the future, for example, "models that will be used to predict future conditions" in §60.21 and "predictive models" in §60.101. All information in a license application, whether representing conditions and processes from the past or the present, will be used to predict conditions and processes in the future that describe the ability of the site to isolate radioactive waste. Otherwise, the information would be unnecessary.

4.3 DISCUSSION

In the past the term "natural analog" has often been considered synonymous with a site with similar geochemistry. This is apparent in the DOE Site Characterization Plan (1988), where the term is found only in the chapter on geochemistry. There, the examples of natural analogs provided are warm and hot springs and uranium and thorium ore deposits. "The study of warm and hot springs in tuffaceous rocks provides information about several important aspects of a repository environment in tuffaceous rock including (1) the effect of the thermal pulse on the chemistry of groundwater; (2) the effect of heated groundwater on the host rock including dissolution and precipitation reactions; (3) the transport of certain elements (e.g., strontium, cesium, uranium, thorium, etc.) found in radioactive waste in a hydrothermal environment; and (4) hydrothermal fluid flow in fractured tuff" (DOE, 1988). "Uranium and thorium ore deposits are a source of data on the following: (1) the long-term stability of radioactive solids; (2) the long-term release of radionuclides from these solids; (3) the transport of radionuclides under various pH, Eh, temperature, and pressure conditions, ground-water and host rock compositions, and hydrologic regimes; and (4) the long-term effects of radiolysis" (DOE, 1988).

These examples of natural analogs are consistent with those recommended in the NARG report. However, they do not represent the full range of issues to which natural analog studies can apply as indicated by the Rule.

Consistent with 10 CFR Part 60, a natural analog can be defined as a condition, process, or event, or a combination of these, that is similar to the same in another environment and/or another time. The use of the term "natural analog" in 10 CFR Part 60 can be taken to mean that the other environment is the planned site of a high-level nuclear waste (HLW) repository, including the regions around this repository site that may affect its performance or may have had an effect on its current or past characteristics. Likewise, the other time is either the future when predicting the performance of the repository or site characteristics or the past or present when describing the site characteristics.

The term "condition" in the definition is meant to be very nonspecific. It can refer to a physical condition, like temperature or pressure, or a chemical condition, like a phase assemblage or composition, or a structural, temporal, or spatial condition, or conditions not yet considered or known. The term "process and event" likewise is meant to encompass a wide range of possibilities. For example, it could include dissolution, precipitation, erosion, groundwater flow, diffusion, faulting, volcanism, flocculation, or respiration.

The scope of natural analog studies is not specified by the Rule. Thus, it is conceivable that these studies could range from full-blown international efforts at one extreme to simple literature searches at the other. Given the broad definition of natural analogs, numerous examples of the use of natural analog studies exist in the DOE Site Characterization Plan. These range from development of the appropriate use of potassium-argon methods of age determination of volcanic rocks to the methods of measuring stream flow in an arid environment. In fact, prior to the collection of site-specific data, much of the information from natural examples used to develop the Site Characterization Plan can be considered to have been derived from natural analog studies.

As another example of the use of natural analog studies, if the elicitation of expert judgment is used to provide information in the license application, natural analog studies can support this information. The elicitation of expert judgment is considered to be a formal process where, when site-specific data are lacking, experts are called upon to provide their best estimates of the value of certain parameters at the site (Bonano et al., 1990). However, it is questionable if there is such a thing as an expert when there are no data. What, then, makes a person an expert? The answer must be an expert is one who has collected, studied, and analyzed data from analogous environments, under analogous conditions, and/or on analogous processes and events. This information, if from nature, comes from natural analog studies. It is expected that in the license application, in support of the expert judgment, information from natural analog studies would be provided.

A good example of the use of natural analogs to help describe a site condition is the characterization efforts of the calcite and opaline silica vein deposits. Vaniman et al. (1988) conducted a preliminary comparison of mineral deposits in faults near Yucca Mountain, Nevada, with possible analogs including hydrothermal, warm-spring, cold-spring, playa, and soil deposits. Since then, investigators from the U.S. Geological Survey (USGS) and Los Alamos National Laboratory (LANL) have continued the analog work as part of the study plan for Characterization of Yucca Mountain Quaternary Regional Hydrology. The presence of these deposits could indicate saturated conditions in the past as caused by an elevated water table or near-surface pedogenic conditions. The determination of the origin and age of these deposits could provide information suggesting the likelihood of hydrologic conditions of the site in the future.

To provide further support to the notion that natural analog studies address site characterization activities, one need only consider the work done on the Alligator Rivers Analog Project (ARAP).

The project has been active for several years and has involved numerous scientists from five countries. The final report of ARAP consists of 17 volumes describing the various studies of the Koongarra ore body in northern Australia. The bulk of the material describes the analog, its site characteristics. On the other hand, only two pages are devoted to calculating the quantity of uranium that has left the system since the deposit was formed. This is performance assessment information. Another example of the use of natural analogs is applied to determining the probabilities of volcanism at the Yucca Mountain site. Here basaltic volcanic fields that are most analogous to the Crater Flat volcanic field will be studied to determine their evolutionary cycles. This information will then be used to estimate probabilities of magmatic disruption of the repository.

The draft Regulatory Guide DG-3003 (NRC, 1990), Format and Content Guide for the License Application for the High-Level Waste Repository, can be used as an indication of the range of topics to which natural analog studies may be applied. In that document, the term "natural analog studies" is used numerous times in supporting predictive models applied to topics as diverse as geology, hydrology, geochemistry, climatology and meteorology, shafts and ramps, underground facility, and waste form and packages.

Studies of natural analogs require that two systems/sites have to be adequately characterized to show analogous behavior or conditions. Consequently, the initial identification and selection of natural analogs is often rudimentary. For example, uranium ore deposits have been assumed to mimic repository chemistry; the unsaturated zone intruded by magma has been assumed to mimic the heated hydrologic system of a HLW repository in the unsaturated zone; redox fronts mimic corrosion product—radionuclide interactions. In order to find out how good the analogs are, one must carry out a characterization program comparable to that of the site. Only as the characterization progresses can the selection of analogs become more refined and specific.

Furthermore, many of the techniques and models used to characterize a HLW repository are state-of-the-art. For example, prior to selection of Yucca Mountain as a possible site for a HLW repository, there had been little interest in understanding the flow of water in unsaturated fractured rock. Most hydrologists had been trained and focused their energies on systems where the presence of water was important, such as the saturated zone and soils. Now hydrologists are rushing to characterize a system where the absence of water is important. This is an area of active research, so techniques and models used to describe this system have yet to be applied to many analogous systems. Consequently, literature surveys of analogs of flow in unsaturated rock along with analogs of other aspects of a HLW repository would tend to be spotty or incomplete.

4.4 CONCLUSIONS

The Rule requires that an "appropriate combination of methods," one of which is natural analog studies, be used to support predictive models of performance assessment and site characterization activities. These studies supply information concerning conditions, processes, and events, both anticipated and unanticipated, at the site. Finally, it should be recognized that "natural analog studies" can be applied to aspects of the repository site characterization and performance assessment that are not necessarily geochemical in nature.

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4.6 APPENDIX: SECTIONS OF 10 CFR PART 60 REFERRING TO NATURAL ANALOG STUDIES

In §60.21(a) Content of Application, the Rule states that "An application shall consist of general information and a Safety Analysis Report."

Further, the Rule describes the information contained in a Safety Analysis Report in §60.21(c) where it states, "The Safety Analysis Report shall include: (1) A description and assessment of the site at which the proposed geologic repository operations area is to be located with appropriate attention to those features of the site that might affect geologic repository operations area design and performance." §60.21(c)(1)(ii) states that "the assessment shall contain:

(A) An analysis of the geology, geophysics, hydrogeology, geochemistry, climatology, and meteorology of the site,

(B) Analyses to determine the degree to which each of the favorable and potentially adverse conditions, if present, has been characterized, and the extent to which it contributes to or detracts from isolation. For the purpose of determining the presence of the potentially adverse conditions, investigations shall extend from the surface to a depth sufficient to determine critical pathways for radionuclide migration from the underground facility to the accessible environment. Potentially adverse conditions shall be investigated outside of the controlled area if they affect isolation within the controlled area.

(C) An evaluation of the performance of the proposed geologic repository for the period after permanent closure, assuming anticipated processes and events, giving the rates and quantities of releases of radionuclides to the accessible environment as a function of time; and a similar evaluation which assumes the occurrence of unanticipated processes and events.

(D) The effectiveness of engineered and natural barriers, including barriers that may not be themselves a part of the geologic repository operations area, against the release of radioactive material to the environment. The analysis shall also include a comparative evaluation of alternatives to the major design features that are important to waste isolation, with particular attention to the alternatives that would provide longer radionuclide containment and isolation.

(E) An analysis of the performance of the major design structures, systems, and components, both surface and subsurface, to identify those that are important to safety. For the purposes of this analysis, it shall be assumed that operations at the geologic repository operations area will be carried out at the maximum capacity and rate of radioactive waste stated in the application.

(F) An explanation of measures used to support the models used to perform the assessments required in paragraphs (A) through (D). Analyses and models that will be used to predictfuture conditions and changes in the geologic setting shall be supported by using an appropriate combination of such methods as field tests, in situ tests, laboratory tests which are representative of field conditions, monitoring data, and natural analog studies."

In Subpart E—Technical Criteria, §60.101, Purpose and Nature of Findings, requires "... a finding that the issuance of a license will not constitute an unreasonable risk to the health and safety of the public. The purpose of this subpart is to set out performance objectives and site and design criteria which, if satisfied, will support such a finding of no unreasonable risk."

Finally, §60.101(a)(2) reads, "While these performance objectives and criteria are generally stated in unqualified terms, it is not expected that complete assurance that they will be met can be presented. A reasonable assurance, on the basis of the record before the Commission, that the objectives and criteria will be met is the general standard that is required. For §60.112, and other portions of this subpart that impose objectives and criteria for repository performance over long times into the future, there will inevitably be greater uncertainties. Proof of the future performance of engineered barrier systems and the geologic setting 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, making allowance for the time period, hazards, and uncertainties involved, that the outcome will be in conformance with those objectives and criteria. Demonstration of compliance with such objectives and criteria will involve the use of data from accelerated tests and predictive models that are supported by such measures as field and laboratory tests, monitoring data and natural analog studies."

ROLE OF NATURAL ANALOGS IN PERFORMANCE ASSESSMENT OF NUCLEAR WASTE REPOSITORIES

5

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5.1 ABSTRACT

Mathematical models of the flow of water and transport of radionuclides in porous media will be used to assess the ability of deep geologic repositories to safely contain nuclear waste. These models must, in some sense, be validated to ensure that they adequately describe the physical processes occurring within the repository and its geologic setting. Inasmuch as the spatial and temporal scales over which these models must be applied in performance assessment are very large, validation of these models against laboratory and small-scale field experiments may be considered inadequate. Natural analogs may provide validation data that are representative of physico-chemical processes that occur over spatial and temporal scales as large or larger than those relevant to repository design. The authors discuss the manner in which natural analog data may be used to increase confidence in performance assessment models and conclude that, while these data may be suitable for testing the basic laws governing flow and transport, there is insufficient control of boundary and initial conditions and forcing functions to permit quantitative validation of complex, spatially distributed flow and transport models. The authors also express their opinion that, for collecting adequate data from natural analogs, resources will have to be devoted to them that are much larger than are devoted to them at present.

5.2 INTRODUCTION

The unusually large spatial and temporal scales associated with high-level nuclear waste (HLW) geologic repositories present a major challenge to radiologic safety assessment. While the basic scientific laws applicable to geologic waste disposal are the same as for other engineering projects, there are two main features that reduce the level of confidence with which the future performance of the repositories can be determined. First, uncertainties in site and design data tend to grow larger with increasing spatial and temporal scales. Second, the conditions under which the repository is expected to perform long into the future are hard to define and are, to some extent, speculative in nature. The first uncertainty results primarily form the fact that, with the current technology requiring drilling or excavation, it is difficult to fully characterize a heterogeneous site without seriously impacting its waste isolation capability. The second factor arises from the difficulty of predicting natural events and processes far into the future, a task that becomes more daunting when the effects of human actions must be considered.

Assuming that natural analogs are selected based on desirable attributes, which include spatial and temporal scales similar to those of repositories [see Pearcy and Murphy (1991) for further discussion of this aspect], they present unique opportunities for studying phenomena important to repository performance at those scales. A sampling of literature on natural analogs [e.g., see Commission of European Communities report EUR 13014 EN (Alexander and McKinley, 1991), and the literature reviews by Pearcy and Murphy (1991)] suggests that study of natural analogs may be used to:

(i) identify processes that operate at large scales;
(ii) determine how processes are coupled so that conceptual models can be developed;
(iii) estimate rates at which various processes operate so that appropriate constitutive equations can be formulated;
(iv) validate performance assessment models; and
(v) obtain qualitative corroboration of repository safety.

In some of the natural analogs literature, the terms validation and verification are applied interchangeably to models. For this paper, a model is defined as an abstract concept representing the complex physio-chemical processes—the abstraction being specific for the purpose for which the model will be used. In practice, the concept will be described by an algorithm, for example, complemented through computer code or software. These computer codes are verified to assure that the implementation of the underlying model is correct. However, the model itself is validated to assure that the conceptual abstraction of the processes is acceptable. Validation of performance assessment models with data from natural analogs is the most often cited reason for undertaking analog studies. It is this aspect of natural analog studies that will be examined in this paper.

5.3 BRIEF OVERVIEW OF PERFORMANCE ASSESSMENT

We shall restrict the definition of performance assessment for the purpose of this paper to quantitative estimates of measures of future repository performance. The performance measures is usually defined in regulations that vary from country to country. Annual risk is probably the most common measure of performance, human dose is another. In the United States, there are quantitative performance measures for both the total system and the subsystems. This is shown in the bottom line of the chart in Figure 5-1, where five regulatory requirements applicable to HLW repositories are identified. The three left-hand boxes identify the generally applicable environmental standards promulgated by the U.S. Environmental Protection Agency (EPA) (EPA, 1985). The EPA standards apply to the entire repository system. In contrast, the remaining two boxes identify the rules developed by the U.S. Nuclear Regulatory Commission (NRC) (NRC, 1983), and these apply to particular subsystem (e.g., Groundwater Travel Time for the Site subsystem and the Package Life and the Release Rate Rules for the Engineered Barriers subsystem). It may be noted that the EPA standard will eventually be integrated into the NRC rule for the purpose of its implementation.

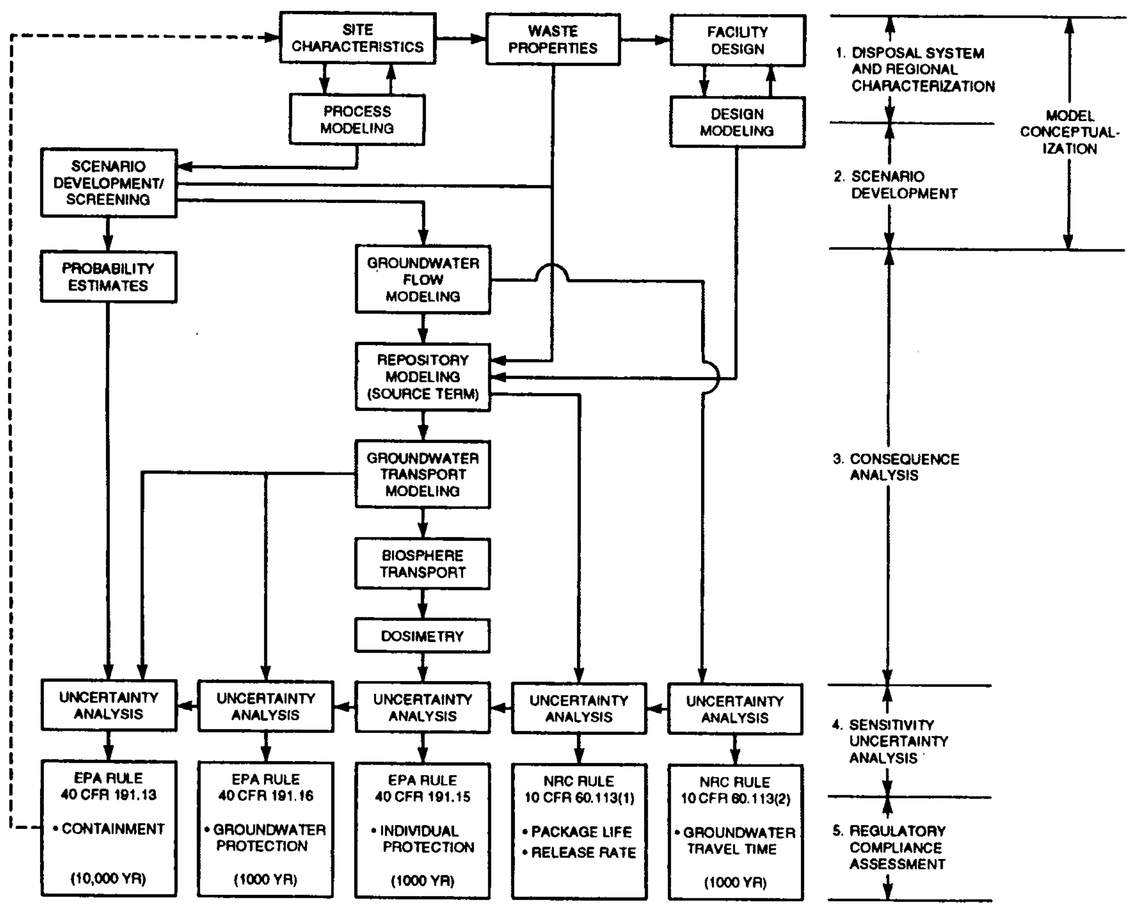

Figure 5-1. Performance requirements and steps for analysis

Figure 5-1 also summarizes various analyses that are thought to be required for assessing performance using the current methodology. It may be seen from Figure 5-1 that assessing performance requires modeling of geologic, hydrologic, geochemical, thermal, and mechanical processes. It is known that these processes are coupled in a complex way, although, with the current state-of-the-art, all of the couplings cannot be fully described. The representation of these couplings in the performance assessment models is commonly simplified to accomplish the calculations. One of the difficult strategic decisions in performance assessment is to balance the complexity of models against available data on site and engineered barriers. It is very tempting for the modeler to use an overly complex model even if data to support such a model do not exist. It is equally tempting for the data collector to over-sample one facet of the site or to emphasize one aspect of the design and neglect others. Some basic considerations in selecting models for performance assessment and their implementation as computer codes are:

(i) Mechanistic (in contrast to empirical) representation of processes is preferable. Mechanistic representation requires explicit use of the basic principles of conservation of mass, momentum, and energy at an appropriate scale. Constitutive laws and state equations used in the formulation of mechanistic models are normally derived from observations.

(ii) Models whose complexity is compatible with the complexity of site and design data are preferable.

(iii) Flexible implementations (e.g., numerical solutions) are preferable. Flexibility is essential to analyze system behavior under the widely varying conditions that may occur in the future.

(iv) Fast and efficient implementation is preferred so that sensitivity and uncertainty analyses can be performed.

Another strategic decision to be made in performance assessment modeling is whether to model "realistically" or "conservatively." Only a degree of realism or conservatism is implied here, since these terms cannot be defined in an absolute sense. Inclusion of greater detail regarding space-time dependence of processes leads to a higher degree of realism in the conceptual model. A higher degree of realism is preferable from a scientific viewpoint, while a pragmatic view may tolerate a higher degree of conservatism. In any case, knowledge of the "degree of conservatism" may be important for regulatory decision making. This is certainly the case in the United States, where the regulations acknowledge that strict mathematical proof of the future performance of the repository is impossible and, hence, require "reasonable assurance" or "reasonable expectation" in meeting the desired safety goals. Currently, it is common to conduct both detailed realistic simulations for certain individual processes or a critical part of a system and simplified conservative simulations for the total system.

We assume that the conceptual abstractions constituting a model will eventually be translated into mathematical models. Generally accepted mathematical forms suitable for simulating physical systems are parametric in nature. The uncertainties in these model parameters, and also in the form of relationships representing constitutive and state equations, can collectively be called "technical uncertainties." Usually, these technical uncertainties are required to be explicitly represented in performance assessment models. For example, the risk measure of performance incorporates in it not only the consequence, but also the probability of the causative event. The United States HLW regulations (EPA, 1985) incorporate probabilities explicitly; that is, they specify not only a level of performance, but also the probability level at which it must be met. This dictates that the performance assessment models be probabilistic in nature.

The fact that performance assessment models can vary in their degree of realism (or conservatism) and can be either deterministic or probabilistic can have a large impact on how model validation is to be defined and demonstrated.

5.4 BRIEF OVERVIEW OF MODEL VALIDATION

The concept of validation is generally defined from the view of realistic, deterministic models. In this context, model validation requires corroboration that, under site specific conditions, the abstracted model represents "reality" and, therefore, the model estimates of the (unverifiable) future state of the system are acceptable. Since the system states can be observed only in the present, there are no experimental means to determine its future states. Therefore, no means to compare model predictions to actual system states are available.

Therefore, for practical purposes, model validation is sought by comparing model results to experiments conducted by design (laboratory or field experiments) or by nature (natural analogs in the case of the HLW repositories). Natural analogs are systems whose behavior, at least in certain well-defined aspects, is analogous to the system under investigation. In addition, the analogous system has evolved so that many of its states have been observed. If a model can be validated against the analog, then this model may be assumed to apply to the system of interest.

We note that, based on Popper's (1959) philosophy, the very idea that a theoretical model can be validated by any one experiment on any spatial or temporal scale has been criticized on logical grounds. In the Popperian view, experiments may only refute (rather than validate) models. Thus, simply because model and experimental results compare does not constitute a proof of model validity. Only when no experiment can be found to refute a model may it be declared validated. Therefore, model validation is impossible in the strict sense. These and other considerations of model validation are discussed by Ababou et al. (1992) where it is accepted that a model cannot be absolutely validated, and the concept of "degree of validation" is introduced for practical applications. Admittedly, this concept is subjective in nature, but it may be of value in the regulatory environment.

The degree of validation of a model can be estimated by assigning weights that depend upon both the scope of the experiment and the goodness-of-fit between model and observed data. These weights are accumulated over the suite of experiments for which validation is attempted. With regard to the scope of an experiment, the validation weight assigned to the experiment is proportional to the broadness of the range of test conditions. In general, the broader the test conditions, the better test of the applicability of the model it is. Thus, a field-scale experiment with many scales of heterogeneity and varying boundary conditions will have a higher validation weight than an experiment on a small homogeneous sample. Again, a subjective judgment will have to be made regarding the weight assigned to a validation experiment based on its scope. In the regulatory arena, it may be possible to specify through agreement of involved parties a consistent set of rules which, when followed, will provide a meaningful estimate of the degree of validation. Although it is easier to define the goodness-of-fit weight in a quantitative manner, this measure is still dependent upon the objective for which the model is to be used. For example, if early arrival of low concentrations of contaminants is not of concern, it may not be necessary that the model accurately predict the entire shape of a contaminant plume; it may be sufficient that the model estimates the migration of the plume centroid and increase in local plume spread in a reasonable manner. Other such measures are discussed in the paper by Ababou et al. (1992).

5.5 MODEL VALIDATION WITH NATURAL ANALOGS

While most laboratory and field experiments have the advantage of human control, their spatial and temporal scales are usually much smaller than those of interest for the design of the actual repository. Even carefully designed field-scale experiments may still lack control at the boundaries or fail to measure important state variables with sufficient spatial and temporal resolution. An example of insufficient spatial resolution of field measurement locations is shown in Figure 5-2. It depicts contoured bromide concentrations from a model simulation overlain by dots which represent the actual solute sampling locations for a controlled test at the partially saturated Las Cruces Trench site (Wierenga et al., 1989). It is readily apparent that even though the measurement points are closely spaced, the computed plume shape is such that it is difficult to draw a conclusive inference regarding the match between the model results and observations. Different conceptual models have been developed in which the complexity of both the initial saturations and the spatial structure of the soil-hydraulic properties are varied. In support of the concept that the model must not, in some sense, incorporate more detail than is capable of being resolved in the actual experiment, the simple models produced simulated bromide plumes whose first and second moments most closely matched those observed (Sagar and Wittmeyer, 1991).

The Las Cruces Trench experiment is specifically designed for validating flow and transport models in unsaturated, unconsolidated soils similar to conditions expected at low-level waste sites. The spatial domain of the experiment is about $15 \times 15 \times 6$ m, and

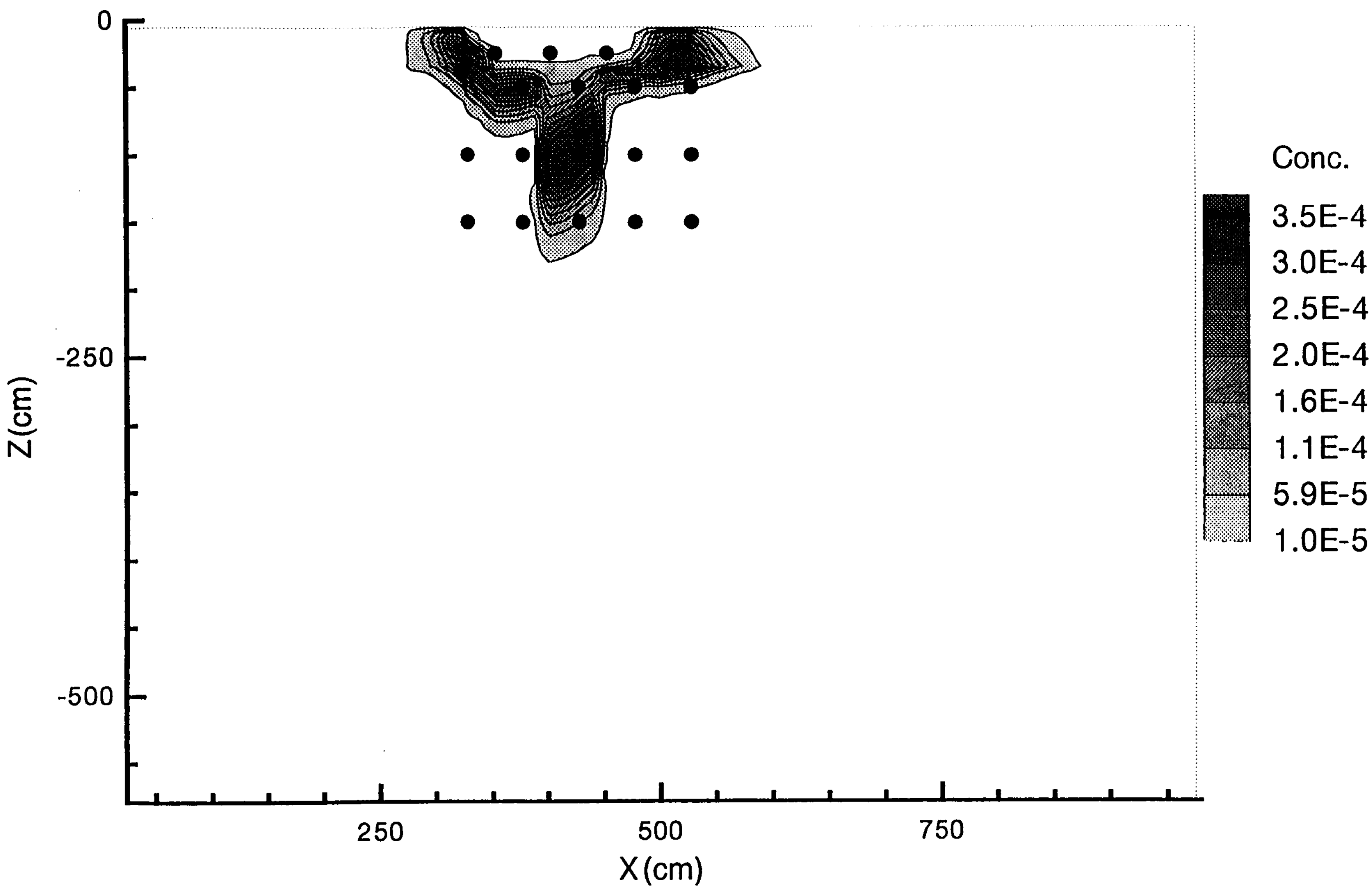

Figure 5-2. Simulation of Las Cruces Trench Validation Experiment. Note the difficulty of measuring the contaminant plume even when samples are located in a systematic manner.

the infiltration and redistribution of water and solute is monitored over approximately 400 days. While there is considerable heterogeneity in soil properties, there are no fractures or fracture-like features that would generally be expected in a repository located in consolidated materials. While consistent rules for assigning 'validation weights' have not been formulated yet, it is worthwhile to consider the Las Cruces Trench experiment as an example of how such rules may be formulated. The space scale of the experiment is two orders of magnitude larger than a laboratory core, and it is about two orders of magnitude smaller than that of a low-level waste (LLW) repository. The time scale of the experiment is about three orders of magnitude smaller than that of the LLW repository. Significant natural heterogeneities similar to those in the LLW repository are present in the experiment. There is considerable confidence in the data because of the level of control over the experimental conditions. A weighting scale can be assigned to all these factors for arriving at a composite validation weight for the experiment. Alternatively, rather than formulate explicit rules, an expert panel may be asked to consider all of these factors and assign such a weight. Note that the validation weight for the same experiment would be less for the case of models that are to be applied to the HLW repositories because of the absence of features (e.g., fractures) that may dominate the flow and transport in hard rock. Note also that the degree of validation of a particular model will be determined by combining the validation weight of the data set (or experiment) and the degree to which the model results (e.g., concentrations, centroid of the plume, etc.) compare with that of the experiment.

All natural analogs are only approximately analogous to the real system, if for no other reason than that the future evolution of the real system is not known and, therefore, it cannot be said that it will be similar to the analog. However, considering that subjectivity is inherent in determining the degree of validity, even approximate analogs can be of great utility when the degree of approximation is accounted for in the validation weight. Natural analogs may be assigned higher validation weights because these have space-time scales similar in magnitude to the actual system. But this has to be compensated by the fact that natural analogs suffer from the lack of experimental controls. The initial conditions from which a given analog has evolved are never known and may at best be arrived at through the use of other models. Consider the evolution of the Oklo ore body (Cowen, 1976), an important natural analog to spent fuel, since it contains transuranic activation products, and fission products. The Oklo ore body functioned as a natural reactor some 2 billion years ago with intermittent operation in different zones (see Figure 5-3). Significant site characterization (not too dissimilar from what will be needed for an actual site) would be required to estimate the present state of the system. The present system state, though imperfectly known, is but one point on the evolutionary curve. What went on in the more than 2 billion years of its evolutionary history (e.g., geologic changes, climatic variations, and geochemical and transport processes) can only be roughly estimated. As is true of most inverse problems, tracing the evolution backward in time is fraught with difficulties, such as nonuniqueness and mathematical instability. Particular care must be used with natural analogs so that one does not end up simply comparing results of one model (that used to generate the evolutionary history) with those of another (that is being used for performance assessment). Therefore, despite the fact that the

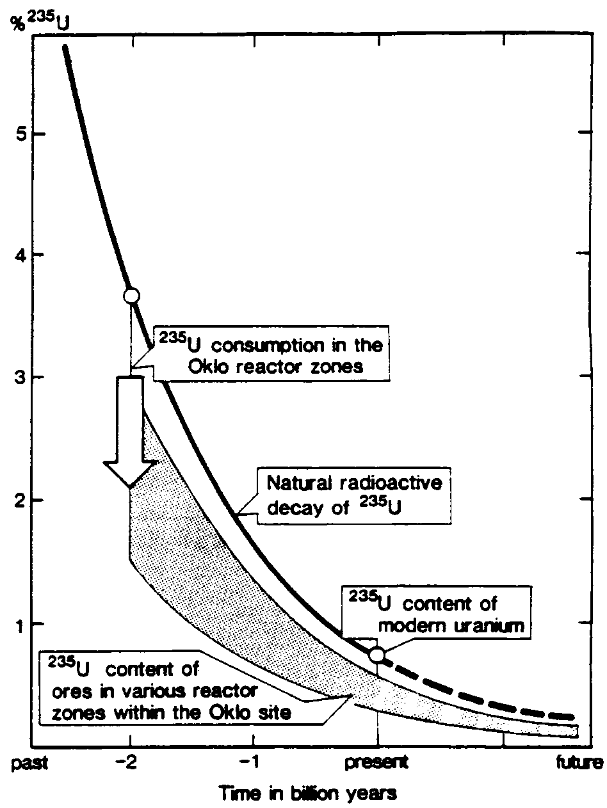

Figure 5-3. Evolution of the ore body at the Oklo (natural analog) site (McKinley, 1989)

space-time scales of analogs are comparable to those of the repository system, lack of knowledge of initial and boundary conditions will cause the validation weight assigned to natural analogs to be low. For quantitative model validation, it would be useful to adequately characterize the analog at this time and then monitor it (and also its boundary conditions) into the future for, say, many tens (if not hundreds) of years. Such data, if attainable, would have much higher validation weight for HLW repositories.

Even in the absence of the data suggested above, qualitative conclusions of great relevance can be drawn, for example, if Oklo has maintained its integrity (i.e., the radionuclides have migrated only so far) for over 2 billion years, then a HLW repository in a similar environment might be expected to be safe for a few million years. However, as indicated by Chapman and Miller (1993), caution should be exerted in drawing such general conclusions. In support, they cite the following excerpt from nuclear industry literature, "The Oklo reactors ran gently at the kilowatt-power level for millions of years. They never blew up. The radiation and waste from them did not deter surrounding life forms. Over immense timescales, the waste has barely moved away from the reactor site. As a result, scientists today are confident that waste in man-made stores and repositories is likely to move even less... ." It may be noted that an opposite argument can be made. The lack of abundance of similar natural reactors can be interpreted to mean that such a system is, in general, unstable. Of course, the scarcity of such systems may be merely a reflection of the lack of investigations and not of its inherent instability. In addition to qualitative understanding, important quantitative insights regarding elemental speciation and processes governing migration have been gained from the investigation of the Oklo analog site.

In the view of the authors, natural analog studies can be effectively used to ascertain, in a broad sense, the applicability of basic laws describing flow and reactive transport processes to greater spatial and temporal scales. In addition, as indicated by Pearcy and Murphy (1991), natural analogs may be useful in conveying to the public a sense of the long-term stability possible in a geologic environment.

Similar problems also arise in natural analog studies related to engineered barriers. Based on discovery of archeological artifacts, for example, the corrosion rate of iron and copper has been estimated to be 0.1 mm/yr (Johnson and Francis, 1980). It is generally accepted that the age dating of the artifacts is probably correct, but that it is impossible to define the environmental conditions under which degradation occurred. It is also argued that some metal artifacts may have corroded at a much higher rate and disappeared, thus biasing this estimate. McKinley (1989) argues in the safety assessment of the Swiss program that, based on observations from natural analogs, an assumption of corrosion rate of 0.1 mm/yr with a pitting factor of 3 is conservative. Such use of analog data to estimate the degree of conservatism is worthwhile, but it does not provide support to model validation.

From the limited literature study performed by these authors, it is apparent that qualitative arguments like that of McKinley (1989) are characteristic of natural analog studies more than quantitative model validation. Even such conclusions as those of Mckinley are limited to the near-field processes. For example, these are related to the leach rates and radionuclide solubilities. We have not come across many conclusions regarding far-field processes of even the qualitative kind.

Because of the relatively large cost of in-depth investigations of natural analogs, some of the these studies in the past have focused on narrow issues related, for example, to geochemistry. Alexander and McKinley (1991) and McCombie (1991) recommend that natural analog studies not remain focused on narrow issues but adopt a broader prospective. In the context of model validation, we believe that data from natural analog studies will have only low to moderate validation weight. Hence, it may, in fact, be more productive to plan analog studies to address well-developed but narrow specific issues. For example, inferences regarding average rates of various physical processes under conditions of natural analogs may provide useful bounds for assessing performance of HLW repositories under similar conditions. Such bounds are only marginally useful for model validation, but may be invaluable for providing qualitative assurances regarding the effectiveness of the repository system.

5.6 SUMMARY AND CONCLUSIONS

We are somewhat pessimistic regarding the use of natural analog data for the specific purpose of model validation. The primary reasons for this pessimism are:

(i) lack of experimental control of the natural analog;
(ii) unknown initial conditions from which the analog evolved;
(iii) need of relatively large resources to adequately characterize even the present state of the analog.

While useful qualitative results can be obtained by studying the natural analogs at the current level, it is doubtful that these would generate data that would have high validation weight in quantitative model validation.

We also believe that natural analogs alone, even if more resources are committed to their study, will not provide the preponderance of evidence that will be required for validating performance assessment models. Such evidence can be accumulated only by conducting a variety of tests under a variety of conditions. However, if a natural analog site can be examined in detail and monitored for the long term (at least tens of years), then it would be possible to construct an experiment with high validation weight.

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LONG-TERM PREDICTIONS USING NATURAL ANALOGUES

6

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6.1 ABSTRACT

One of the unique and scientifically most challenging aspects of nuclear waste isolation is the extrapolation of short-term laboratory data (hours to years) to the long time periods (10^3–10^5 years) required by regulatory agencies for performance assessment. The direct validation of these extrapolations is not possible, but methods must be developed to demonstrate compliance with government regulations and to satisfy the lay public that there is a demonstrable and reasonable basis for accepting the long-term extrapolations.

Natural systems (e.g., "natural analogues") provide perhaps the only means of partial "validation," as well as data that may be used directly in the models that are used in the extrapolation. Natural systems provide data on very large spatial (nm to km) and temporal (10^3–10^8 years) scales and in highly complex terranes in which unknown synergisms may affect radionuclide migration. This paper reviews the application (and most importantly, the *limitations*) of data from natural analogue systems to the "validation" of performance assessments.

6.2 INTRODUCTION

As societies move forward in their efforts to design, build, and finally, license and operate a nuclear waste repository, three phrases—"performance assessment," "validation" and "natural analogues"—become part of the common language and concern. Because the construction (no matter how difficult) of a repository is not a demonstration that it works, we rely on performance assessment to bound or limit the extrapolated long-term behavior of the repository. The performance assessment must represent a rather elaborate model of extrapolated behavior. There can be considerable uncertainty in such a model. Typical questions concerning the sources of error or uncertainties include:

(i) Are the physical and chemical processes modeled correctly (e.g., the corrosion mechanism of the waste form or sorption mechanisms during transport through an aquifer)?
(ii) Are the fundamental physical and chemical parameters accurately known and appropriate to the conditions in the repository (e.g., actinide solubilities in a concentrated brine)?
(iii) Are the scenarios that are selected to describe the possible release of radionuclides plausible or likely (e.g., human intrusion)?

At this time, one of the most detailed and elaborate efforts at performance assessment is the work at Sandia National Laboratories on the performance assessment of the Waste Isolation Pilot Plant in New Mexico (Hunter 1989; Bertram-Howery and Hunter, 1989; Bertram-Howery and Swift, 1989). A general description of the approach to performance assessment is given by Campbell and Cranwell (1988). Despite the mathematical sophistication of the approach used in a performance assessment, uncertainties can be large in the predicted performance, and the entire methodology must be "confirmed." At the simplest level, confirmation consists of three activities:

(i) Measurements according to accepted procedures of physical and chemical properties (e.g., actinide solubilities). This is quality assurance.
(ii) Verification of codes by comparing results to the results of other codes designed for the same purpose and by using generally consistent sets of data.
(iii) Finally, validation is obtained through additional laboratory or even field-scale tests (Geldhart et al., 1988; Kelmers et al., 1987). These tests are usually designed to test a proposed mechanism for radionuclide release, but the spatial and temporal scales of such experiments are extremely limited. Thus, this is a type of limited hypothesis testing. The length of time and the expense of such tests limit their number. Larger spatial and temporal scales may be tested against the

historic or geologic record. For groundwater models this is often referred to as calibration.

These processes are perhaps best illustrated by experience with groundwater models. The reader is referred to the work of Konikow and Bredehoeft (1992) which discusses these specific limitations. The levels of confirmation—acquisition of basic physical and chemical data, code verification, field-scale validation, and historic calibration—are all important, as well as difficult and time-consuming, but these efforts remain trivial in comparison to the higher level of confirmation that asks the fundamental question of whether the predicted or bounded performance will encompass the actual performance.

It is to this question that studies of natural systems, usually referred to as natural analogues, enter into consideration [Eisenberg, 1986; Kovach and McCartin, 1988; Birchard and Alexander, 1983; Petit, in press (a); Petit, in press (b)]. Natural analogue studies examine system behavior on the correct spatial and temporal scales, but there are many limitations (Ewing and Jercinovic, 1987), and there has been only a limited effort to explicitly use natural analogue studies in a performance assessment. In fact, there appears to be considerable confusion concerning just exactly how this might be done, particularly when data from natural systems are combined with the probabilistic analyses which are a common part of a performance assessment (Chapman and Côme, 1989). The public and licensing requirements for validation of performance assessment and the increased complexities with resulting delays in these efforts have lead finally to a certain note of despair (Krauskopf, 1990) and an effort to revise the expectations of the public and the regulatory agencies (National Research Council, 1990). There are special difficulties in describing the risks that have small probabilities in a long-term risk context (Svenson and Karlsson, 1989); here again, natural systems are used to communicate ideas to the public.

In all of these discussions, natural systems or natural analogues remain a "bullet on each viewgraph" which purports to describe the "validation" process. In this paper, I want to explore how natural systems might actually be used in the performance assessment process. I will consider the use and limitations of natural analogues, particularly limitations that are inherent to the processes of scientific proof and analogy.

6.3 SCIENTIFIC "PROOF" AND ANALOGY

The phrase "natural analogue" conveys the sense that in natural systems (usually of great age), there are situations or materials that are analogous to the conditions or materials of interest in a waste repository. It is important to define what is meant by such an analogy, as it leads immediately to the idea that there can be a "proof by analogy." In the broadest sense, an analogy refers to a similarity between things otherwise unlike, that is, a partial resemblance. In logic, analogy is an inference that certain resemblances imply a probable further similarity. Since the time of Aristotle, logicians have argued over whether the use of analogy is simply another form of induction or whether it represents a distinct class of arguments, and, if so, how the validity of an argument by analogy can be demonstrated (Aristotle, 1966; Niiniluoto, 1980). The most useful discussion is still to be found in John Stuart Mill's *A System of Logic* (Mill, 1874) in which he argues that the distinction between analogy and induction is an artificial one, that, in practice, both rest on the collection and correlation of observations. The two approaches, however, differ importantly in one's ability to demonstrate their validity. Induction is based on a scientific understanding of the causality between events or phenomena, while analogy, in the absence of proof, temporarily accepts a probable hypothesis. This is a common and legitimate approach in the physical sciences where conclusions based on an analogy are used until a negative instance has disproved the hypothesis. In the physical sciences, it is often easy to identify the variables that are important in the causal relationships of a particular phenomenon, and this lends strength to the analogy. The validity of the inferred relationship rests on the pertinence of the variables selected to describe the phenomenon. Mill's own words best make the point: "Since the value of an analogical argument ... depends on the extent of ascertained resemblance, compared first with the amount of ascertained difference and next with the extent of the unexplored region of unascertained properties, it follows that where the resemblance is very great, the ascertained difference very small and our knowledge of the subject-matter tolerably extensive, the argument from analogy may approach in strength very near to a valid induction... . It is hardly necessary to add that ... no competent inquirer into nature will rest satisfied with it when a complete induction is attainable, but will consider the analogy as a mere guidepost, pointing out the direction in which more rigorous investigations should be prosecuted."

The question of the pertinence of the selected variables used in an analogy is one of establishing cause-and-effect relationships. Bertrand Russell (1983) refers to this as a "fruitful analogy." "One of the most important and difficult things about the inductive method is the discovery of fruitful analogies, and the connected problem of the analysis of a complex phenomenon into elements that can be studied separately. The fruitful analogy is one that discloses a similarity in causation, and the investigator has to begin by guessing at the cause."

Russell (1983) goes on to point out that, "we cannot so easily, if at all, reach a numerical estimate of the probability of inductions." Unfortunately, this is inherent to the process of a probabilistic performance assessment, which requires this "numerical estimate." We are trapped between our inability to assign probabilities, and yet, "ultimately, we must reach a point where we use experience of what is known as a basis for inferring what is unknown, and this sort of inference is only valid if induction is valid." (Russell, 1983). As far as this author is aware, there is no rigorous proof available that demonstrates that induction is valid.

This view of "analogy" immediately limits what one may expect from this approach. Proof or "validation" of a hypothesis [e.g., the long-term durability of a borosilicate nuclear waste glass (Ewing and Jercinovic, 1987; Jercinovic and Ewing, 1988)] can only be approached (never arrived at), and then only to the extent that details of one system correlate to the details of another system (e.g., the correspondence between corrosion of basaltic glass at a mid-ocean ridge and the corrosion of a borosilicate glass in a bedded-salt repository). The selection of the pertinent variables that are used to describe the phenomenon (e.g., in the case of glass corrosion, these may include temperature, pH, surface area to solution volume ratio, flow rate) have a direct bearing on the validity of the conclusions. Finally, a probabilistic assessment of projected or predicted behavior may not be possible.

We should also note the historic role of analogy in developing an understanding of geologic processes over the expanse of geologic time. Charles Lyell, the founder of modern geologic methodologies, was firmly rooted in an actualistic philosophy that assumed the constancy of physical laws, "Their immutably constancy alone can enable us to reason from analogy, by the strict rules of induction, respecting the events of former ages, or, by a comparison of the state of things at two distinct geological epochs, to arrive at the knowledge of general principles in the economy of our terrestrial system" (Lyell, 1830). In nuclear waste disposal, we reason from our own geologic epoch to the next. Thus, analogy is (and must be) a powerful logical and pedagogical tool. But what are the special limitations of analogy when applied to a predicted behavior?

6.4 LIMITATIONS IN HISTORICAL SCIENCE APPLIED TO PERFORMANCE ASSESSMENT

Ewing and Jercinovic (1987) have discussed the nature and special "limitations" of proof in historical sciences. Geo-scale predictions over long periods of time (e.g., behavior of nuclear waste forms in nuclear waste repositories) have the same limitations as post-dictive confirmation of geologic hypotheses, only the direction of the time scale has been changed (the future instead of the past).

The scale in time and space of natural systems does not allow one to carry every hypothesis into the laboratory. The test of a geologic hypothesis rests on its compatibility with selected observations (often prejudiced by the hypothesis in hand) and extracted from a geologic record that is woefully incomplete. Geologists have wrestled with these limitations, always trying to put some distance between the false impression of others that their efforts are "merely descriptive," and they rather have strived to practice their craft with the same rigor as other physical scientists. Scientists in the nuclear waste community are confronted with the same difficulties when they try to use natural systems to predict long-term behavior. Each geologic system seems disturbingly unique in its occurrence, with a wide range of variables (e.g., solution composition, age, flow rate), many poorly defined or unknown. The importance of these variables to the phenomena being described may change over the course of time, and, most importantly, with such wide variations and uncertainties between supposedly similar occurrences, there seems to be little hope of arriving at useful generalizations.

The distinguished paleontologist, G.G. Simpson paid particular attention to this situation in an essay, "Historical Science," in which he outlines both the methodologies and limitations that are inherent in historical sciences (Simpson, 1963). Simpson defined historical science as the "determination of configurational sequences, their explanation, and the testing of such sequences and explanations." By "configuration," Simpson means to describe all aspects of the system as it changed through time during the past. For a geologist, this is a common process of writing a geologic history. The development of a geologic history proceeds by the typical accumulation of facts or observations welded together by normal inductive and deductive processes. The unusual aspect of the process is the "testing" of the hypothesis. There is no experiment that can be done that will repeat the activity on a part of the Earth's surface over long periods of time. The test can only be a comparison of deduced results of the hypothesis against the actual rock record.

As an example, if one proposes meteorite impact as the cause of late Cretaceous extinctions, where are the high pressure phases that would have formed during such an event? The correlation of late Cretaceous extinctions with an iridium anomaly, high-pressure silica polymorphs, and the graphitized carbon in thin layers of shale at the Cretaceous-Tertiary boundary is a convincing form of proof (Alvarez, 1987) that may still be contested by others (Archibald, 1982). In the parlance of Simpson, this is the process of "postdiction" (as compared with prediction) in which there is a correlation of the past and present. If the geologic record were complete, the process of hypothesis testing by postdiction would be tedious, but always rewarding. That is, we would always arrive at an answer that could be used. The fact that the geologic record is notoriously incomplete (Kerr, 1991), however, makes the process not only tedious, but often unrewarding. The absence of shock features at the Cretaceous-Tertiary boundary would not demonstrate that the extinctions were not caused by meteorite impact, but could simply be the result of a scanty geologic record. The rock record seldom provides a complete record of catastrophic events (Kerr, 1991), as they occur on such a short time scale. These are limitations unique to the limitations of the geologic record, but what are the additional limitations of our predictive efforts embodied in performance assessments of the long-term behavior of nuclear waste repositories?

The first, and obvious, limitation is that there is no rock record for future events. So, even though we can use postdiction to confirm that certain processes and mechanisms operate on the scale of earth systems, we cannot project their configurations into a future succession of "configurations" or scenarios. We can confirm large-scale, long-time mechanisms, but we can never be sure that these are the currently operative mechanisms. We can also, with certain limitations, use the rock record to establish probabilities for events in the natural system, but these estimates will remain largely subjective. This is why the development of release scenarios is so important and, at the same time, so difficult. We gain "hints" from past behavior, but finally only experience and expert judgment determine the probabilities and risk; hence, the importance that we ascribe to each scenario.

At this stage, it is important to distinguish between a scenario and an hypothesized future behavior. A hypothesis has the property that it can be disproved [in contrast, a hypothesis cannot be proved (Popper, 1961)], either by predictions and experiments or postdictions and careful observations. There is no part of a performance assessment that can be "proved." There is no experiment or observation that can validate the predicted performance of a nuclear waste repository. A scenario is instead a proposed performance, and the best that can be done with a scenario is that a probability of occurrence (perhaps based on the geologic record) be assigned and an evaluation made of the consequence. This is an important point, as scientists are trained to disprove hypotheses by looking for exceptions. As the exceptions mount in number, the theory or paradigm is disproved (Kuhn, 1970). One must realize that results of a natural analogue study may not be consistent with a performance assessment, but performance assessments (by definition) cannot be disproved.

Natural analogue studies can never be used to prove or disprove a proposed performance. Statements such as, "Natural glasses have existed for millions of years" or "Natural glasses are easily altered" do not speak for or against the long-term stability of nuclear waste glasses. The two statements only indicate a lack of correspondence between the historical configurations that characterized the corrosion environments of the glasses.

6.5 SUMMARY OF LIMITATIONS

This discussion has tried to emphasize some of the conceptual and philosophical issues that complicate the use of natural analogues. I end by classifying these limitations into two types: (i) the limitations of models and (ii) the limitations of "confirmation" or "validation."

Significant errors in performance assessment models may occur due to

- the selection of the wrong deterministic model
- an incorrect analytical solutions for the model
- an incomplete description of the system modeled
- the presence of nonlinear systems.

The last item on this list has not been discussed in this paper; but one should simply note that nonperiodic, irregular behavior may occur, and probably does occur, in nonlinear systems. The short-term temporal evolution of such systems can be accurately predicted, but the long-term behavior is highly unpredictable, and deviations may evolve rapidly with time.

The limitations of "confirmation" or "validation" include

- A performance assessment hypothesis, by definition, cannot be tested.
- A hypothesis can only be invalidated, not proven to be true. This is particularly true of argument by analogy or induction.

6.6 CONCLUSIONS

I should end by saying that this list of limitations does not mean that one should not move forward. The problem exists. Nuclear wastes must be permanently isolated from the accessible environment. However, one cannot use elaborate mathematical approaches, such as applied in performance assessments, as a way of verifying a predicted behavior. Nor should one expect the public to accept such a demonstration as final or convincing proof. Performance assessment is simply an organized and sophisticated way of thinking about the elements of the problem. Natural systems (the phrase "natural analogue" is probably not necessary) provide vital data [Jercinovic and Ewing, 1988; Finch and Ewing 1989 (a), (b) in press, for examples), as well as providing the "guideposts" of Mill for understanding complex systems over long periods of time. There is no method by which a long-term prediction can be validated.

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ANALOG EARTHQUAKES 7

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7.1 ABSTRACT

Analogs are used to understand complex or poorly understood phenomena for which little data may be available at the actual repository site. Earthquakes are complex phenomena, and they can have a large number of effects on the natural system, as well as on engineered structures. Instrumental data close to the source of large earthquakes are rarely obtained. The rare events for which measurements are available may be used, with modifications, as analogs for potential large earthquakes at sites where no earthquake data are available. In the following, several examples of nuclear reactor and liquified natural gas facility siting are discussed. A potential use of analog earthquakes is proposed for a high-level nuclear waste (HLW) repository.

7.2 THE CONCEPT

The use of analogs is the first stage of a better understanding of complex phenomena. Analogs are used to predict future happenings when too little is known about the phenomena being predicted or when theories are not completely accepted. Analogs may be used to add credibility to a theoretically derived prediction. A characteristic of an analog is the lack of a mathematically described statistical variability. It is usually unknown whether an analog represents the mean of a variable of interest or a rare extreme. Often there is only one analog to an anticipated event or condition, and it is not likely to be a perfect match.

Among dictionary definitions, an analog is something that is similar to something else. Definition of the word "analogy" yields further insight, for example, if something is similar to something else in some respect, it is likely to be similar in others. That the words "identical," "all" or "in every respect" did not appear in any definition encountered, is notable. An analog may be a model as inferred by the definition of "model" in Bates and Jackson (1980): "A working hypothesis or precise simulation, by means of description, statistical data, or analogy, of a phenomena or process that cannot be observed directly or that is difficult to observe directly."

Geological phenomena are generally observable only at the surface of the earth or in a one-dimensional bore through the earth's surface to a limited depth. However, a more complete understanding of a particular geologic feature may be obtained in regions of great topographic relief or in regions where geologic features have been turned on their side, and erosion has produced a natural cross section. Limited exposures of a geologic feature, that is similar to a feature of one of these relatively rare natural cross sections, may be used to infer that which cannot be seen. On-going depositional processes produce features reminiscent of those seen in sedimentary rocks. Therefore, by analogy, these processes are presumed to have occurred in the past. Alteration products of active hydrothermal regions, likewise, by analogy, are used to infer the cause of alteration products in geology elsewhere.

That earthquakes are observed to accompany fault movements implies that fault offsets observed elsewhere were also likely to have been accompanied by earthquakes. Instrumental recordings of earthquakes accompanying certain types of faulting at specific distances, by analogy, are attributed to earthquakes that have a similar origin but for which no instrumental recordings are available.

Much of the subject of geology has its origins in analogs that were often referenced, although not necessarily with the word "analog," by early writers, such as Hutton (1795). In a sense, all of geology is based upon analogs.

A past recorded earthquake whose characteristics or effects are sufficiently similar to those expected at a new facility site may be used to predict design loads or the consequences of potential structural degradation. Ideally, a strong motion record to be used as an analog should have been recorded from an earthquake having similar characteristics as that expected at the new site, for example:

- nature of the fault and the dynamics of its movement
- distance from fault to facility
- nature of the tectonic stress field and stress drop during an earthquake
- fault orientation to the facility and stress field, (Rogers et al., 1977; Boatwright and Boore, 1982)
- earthquake magnitude
- path geology
- depth of earthquake focus and depth of facility
- fault parameters, for example, length, width, and offset
- location, number, and size of asperities or barriers

Usually, not all variables will be identical or available. Consequently, modifications based on other incompletely analogous earthquakes will be required.

Predictions of earthquake ground motion are based on:

- direct analogs
- interpolation or extrapolation from near or partial analogs
- formulae or computer codes that reproduced ground motion of analogous or nearly-analogous earthquakes.

7.3 SOME EXAMPLES

Example 1: The Diablo Canyon Nuclear Power Plant.

In the initial license application, a magnitude 6.75 aftershock was proposed at a 6–12-mile depth, caused by a magnitude 8+ main shock on the San Andreas fault about 40 miles distant. The assignment was made largely on the supposition of an unknown but possible fault at depth. Also, a magnitude 7.25 on the Naciemento fault, about 20 miles distant was proposed. This earthquake was a scaled-up analog to the magnitude 6.3 Long Beach (1933) earthquake. Modified Mercalli Intensities of damage were documented for the 1933 earthquake. An equivalence between Modified Mercalli Intensities and peak ground acceleration compiled from many earthquakes provided a design basis.

Later, an offshore fault, the Hosgri fault, was determined to be of licensing significance. A magnitude 7.3 offshore earthquake in 1927 had caused rock slides, sand boils, water spurts, a tsunami of 6 feet and some fallen chimneys in the vicinity of Lompoc, California (Coffman and von Hake, 1973). The U.S. Geological Survey (USGS) and the U.S. Nuclear Regulatory Commission (NRC) concluded that there was sufficient uncertainty in the published location of this earthquake 60 km offshore that it was possible that this earthquake might have occurred on the Hosgri fault.

The Lompoc earthquake, therefore, became an analog for a 7.5-magnitude earthquake located offshore, 5 miles from the plant. There were no strong motion records for the Lompoc earthquake or from any other earthquake of this magnitude at this distance. Considerable effort was expended in extrapolating the effects of other earthquakes to this magnitude and distance. Dr. Robert Page of the USGS applied prior research on the number of cycles of strong motion at various levels for the Alaskan pipeline to this site. Dr. Nathan Newmark, consultant to the NRC, interpreted Dr. Page's information in terms of design criteria. Again, the analog earthquake was based on a past earthquake on what might have been a similar fault. The analogy was imperfect, however, because all desired data concerning the analog were not available. Consequently, extrapolations from the data of other imperfectly analogous earthquakes were employed to complete the necessary design criteria.

Continued research on this project has resulted in additional proposals, including earthquake source computer modeling to obtain or confirm adequacy of design criteria.

Example 2: NRC Task Action Plan A46 regarding the seismic qualification of nuclear power plant components for old plants.

The requirement for seismic qualification of some components was imposed after construction of the plants. These components had been used in conventional fossil fuel power plants throughout the world. Studies by the Brookhaven, Lawrence Livermore, and Sandia National Laboratories, Southwest Research Institute (SwRI), EQE Inc., and others documented that many of these plants had been subjected to earthquake shaking and that the components had not failed (Yanev, 1984; Smith and Dong, 1983; Chang, 1987; and Kana et al., 1983). The magnitudes and distances of the earthquakes to the plants and some records were available. These earthquakes became analogs for seismic shaking table input and, in turn, verified that the test shaking levels were analogous to real earthquake ground motion.

This example differs from the previous one and suggests a somewhat different use of analogs. It is to directly support the performance of structural or mechanical elements by using analog exposures to vibratory ground motion without the use of an intermediate approximate relationship or model.

This type of procedure eliminates the necessity of constructing approximate models of earthquake shaking, for example, peak acceleration as a function of distance and magnitude and appropriate spectral envelopes for test shaking or accepting a white-noise spectral shape for such test shaking. The method depends upon many analogs. Therefore, a statistical distribution of parameters may be possible, which might add credibility to the result. A possible negative aspect is that the details of the analogs may not be well investigated and compared to the site or sites in question. The question of whether foundation types, fault types, stress drops, etc. are similar to the site in question may not be possible to answer or may be largely ignored.

Example 3: The planned Grassy Point, British Columbia, liquified natural gas compression and storage facilities, and seaport.

This planned facility was located 90 km east of the offshore Queen Charlotte fault. The Queen Charlotte fault is a strike slip fault that is analogous to the San Andreas fault in California. Both faults have experienced magnitude (M_S) 8+ earthquakes. There were no strong motion records from magnitude 8+ earthquakes. The location of the facility and the Queen Charlotte fault are in sparsely populated areas. Consequently, reliable Modified Mercalli Intensities of damage also were not available. The San Andreas M_S = 8+ earthquakes, however, had well-documented damage intensities at distances of 90 km from the fault. Further, there was a strong motion record closer than 90 km to a M_S = 7.7 earthquake on the White Wolf fault near Bakersfield, California. An examination of seismic source theory indicated that, for frequencies of vibration that could affect the facility, the vibrations of a magnitude 7.7 earthquake would be similar in amplitude to those of magnitude 8+. Therefore, the M_S = 7.7 Kern County (also known as the Arvin Tehachapi) earthquake of 1952 could be used as an analog to predict ground motion at the Grassy Point facility. The shaking recorded for the Kern County earthquake was scaled down to represent the greater distance. With modification, the Kern County earthquake strong motion record became an analog for a larger more distant earthquake on the Queen Charlotte fault. This value was checked against a correlation with acceleration for Modified Mercalli Intensities observed for the M_S = 8+ earthquakes on the San Andreas fault in California (1872 and 1906) (Coffman and von Hake, 1973) and also against Canadian building code requirements. The analogs and the code requirements were in reasonable agreement (Hofmann et al., 1982).

Example 4: The Gros Cacauna liquified natural gas receiving terminal in eastern Canada (Fenco Consultants Ltd., 1982).

The site was located in an area of past seismic activity where magnitudes had reached 7 or slightly higher. These earthquakes became analogs for an earthquake near the site. However, no strong motion records were available from these M_S = 7 earthquakes. Consequently, the record from the Kern County 1952 M_S = 7.7 (Coffman and von Hake, 1973) earthquake was slightly adjusted for distance and magnitude and used as design criteria for the facility.

7.4 LESSONS LEARNED

At times, only the occurrence of an analog earthquake is known and no strong motion records may be available. The analogy is between the geologic conditions, for example, fault rupture length, and the magnitude of the earthquake. Under these circumstances, a record is interpolated or extrapolated from other imperfectly analogous earthquakes, or a record is derived from formulae or computer codes that were derived from the study of many earthquakes. It can be concluded that analogs of various types, some of them imperfect, are useful.

7.5 ANALOG EARTHQUAKES FOR A HIGH-LEVEL NUCLEAR WASTE REPOSITORY

A number of variables affect earthquake shaking at a site. They are in the source, path, site, and instrumentation categories. Source variables include those in Section 7.2 of this paper. Some of these variables also influence the displacement of faults possibly hidden at depth, that is inferred from the occurrence of an earthquake.

Path variables include:

- source to facility distance
- path geology
- characterization of sedimentary wedges and their effect on surface waves (Herrmann, 1978)

Site and instrument variables include:

- depth of facility and depth of the strong motion instrument
- facility and instrument sites—foundation geology and geomechanics
- frequency response of the strong motion seismograph

Knowledge of all of these variables is not usually available or possible to obtain for either an anticipated earthquake near a site or for potential analog earthquakes to be used to predict effects at the site. Many of these variables are discussed by Hofmann (1991). This lack of knowledge may be translated into an expected variability in the effects at a site. Often there is insufficient information to determine the mathematical nature of this potential variability. It can be a limitation to the application of analogs if several of them are not available.

The qualities of an analog earthquake to be applied to any facility design should fulfill the following criteria.

- The analog should have occurred in an environment such that the effects to be predicted at the repository could have been observed.
- The analog earthquake should have occurred in a tectonic and geologic environment much like that of the repository.
- If the analog includes a strong motion seismic record, it should have been recorded at a depth and in material that are similar to that of the repository.

Vibratory ground motion effects that may be of concern to a deep repository are:

- Shaking of canisters in their boreholes causing stress cracks and accelerated corrosion
- Spalling of tunnel walls, thereby enlarging the zone of higher permeability around tunnels and providing added avenues for groundwater or gaseous migration
- Shaking (or fault movement) may cause stress changes which squeeze groundwater from rock pores to higher elevations (Wood et al., 1985) that are closer to or encompass formerly dry repository shafts, thereby providing faster radionuclide pathways to the biosphere.

Fault movement, which usually, but not always, causes earthquake shaking, may produce undesirable effects at a deep repository such as:

- Faults may move, increasing gouge thickness and decreasing permeability, thereby diverting groundwater from an aquifer to higher elevations and reducing the distance of radionuclide pathways to the biosphere.
- Faults or fault intersections may open, creating permeable pathways along which groundwater or gases may migrate to the biosphere.
- Faults may intersect a waste package, thereby damaging this engineered barrier, causing leaks, which, in turn, reduce the time of radionuclide migration out of the repository. Such faults may also provide a low permeability pathway directly from the waste to the surface or to moving groundwater that may carry radionuclides to the surface.

Finding analogs for all these effects is not likely. For those that can be found, very site-specific characteristics may be needed to reduce uncertainties. Modification of analog observations may be necessary to better reproduce the desired conditions at the site. Modifications for ground motion may be accomplished by determining the desired maximum magnitude for the site and the potential source distance from the site. Ground motion amplitudes may then be adjusted using standard curves. Compensation for records of the analog being at the surface and the repository being at depth may be developed by computer modeling or by determining ground motion amplitude ratios from seismic recordings on the surface and at depth in mines. This would be another analog. Groundwater movement from strain changes might be determined from scaling of near-analog effects to the earthquake magnitude and groundwater table at the site. An alternative is finite-element strain groundwater flow modeling.

7.6 POSSIBLE EXAMPLE ANALOG EARTHQUAKES FOR YUCCA MOUNTAIN

The likelihood of strong shaking at or near Yucca Mountain, Nevada, has been estimated, for example, by Sommerville et al. (1987) and Rogers et al. (1977). Additional work performed may use other boundary conditions. Rogers et al. (1977) limit their hazard estimates to magnitude 7 or lower earthquakes. Sommerville et al. (1987) assigned maximum magnitude potentials to a number of faults in or near the Yucca Mountain site. The maximum magnitudes were about 7.4. Higher magnitudes on longer but more distant faults were also considered in their hazard estimations. The estimates in Table 3 of Sommerville et al.

(1987) correlate $M_S = 7.4$ with fault lengths of about 53–57 km in this region. The nearest fault of that length, in their study, was the Rock Valley fault, 20 km or more from the site. The largest fault closer to the site was the Paintbrush Canyon with a presumed maximum magnitude of 7 based on length and maximum Quaternary paleo-offsets. Further field work may better define fault length and offset and probable future slip in the current stress situation. These efforts may change the maximum magnitude for particular faults. As field work at Yucca Mountain progresses, other faults may be found to be near 57 km long.

Observations of the effects of the potential example analogs below may be adjusted if the desired magnitudes for faults at Yucca Mountain differ. These are possible examples of analog earthquakes for effects that may be possible at Yucca Mountain.

- 1983 Borah Peak, Idaho, $M_S = 7.3$
  - Occurred in an extensional environment on the border of the Basin and Range Province
  - Dip slip faulting
  - Occurred in carbonate rocks
  - Groundwater effects observed
  - Shallow groundwater table must be modified for the Yucca Mountain site.
- 1980 Vieste, Italy, $M = 6.5$
  - Occurred in an extensional environment
  - Dip slip faulting
  - Occurred in a tuff sequence
  - Groundwater effects observed
  - Shallow groundwater table must be modified for the Yucca Mountain site.

Near-field ground motion records were not available for the 1983 Borah Peak earthquake. Rovelli et al. (1988) summarize scaled accelerations for earthquakes from extensional areas in Italy. They do not verify theoretical results with an analog earthquake, suggesting that no suitable strong motion records are available. Another analog may be required for ground motion effects.

7.7 CONCLUSIONS

Although the entire complexity of an earthquake is seldom available from analog earthquakes, they remain good examples of natural analogs and their limitations. Analogs are a first step in a better understanding of complex natural processes. Partial analogs are useful, but modifications may be necessary to apply analogs in some, perhaps many, circumstances. Analogs do not usually include knowledge of potential variations in observations caused by the statistical or chaotic nature of the processes involved, or from overlooked, unknown, or ignored variables.

Analog earthquakes need not be perfect to be useful. Perfect analogs are seldom found. The depth where strong motion information is desired may differ from the depth of a strong motion seismograph that has recorded an earthquake of the proper magnitude and distance. The media within or upon which information is desired may be different from that on which a strong motion seismograph is located. The type of fault movement causing the earthquake may differ from that expected at the site of interest. A large number of differences degrades the utility of an analog, but one or a few differences may be accommodated.

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APPLICATION OF NATURAL ANALOG STUDIES TO EXPLORATION FOR ORE DEPOSITS

8

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8.1 ABSTRACT

Natural analogs are viewed as similarities in nature and are routinely utilized by exploration geologists in their search for economic mineral deposits. Ore deposit modeling is undertaken by geologists to direct their exploration activities toward favorable geologic environments and, therefore, successful programs. Two types of modeling are presented: (i) empirical model development based on the study of known ore deposit characteristics, and (ii) concept model development based on theoretical considerations and field observations that suggest a new deposit type, not known to exist in nature, may exist and justifies an exploration program.

Key elements that are important in empirical model development are described, and examples of successful application of these natural analogs to exploration are presented. A classic example of successful concept model development, the discovery of the McLaughlin gold mine in California, is presented.

The utilization of natural analogs is an important facet of mineral exploration. Natural analogs guide explorationists in their search for new discoveries, increase the probability of success, and may decrease overall exploration expenditure.

8.2 INTRODUCTION

Natural analog studies are used by exploration geologists in their search for economic mineral deposits. Geologists commonly refer to their exploration approach as ore deposit modeling or model development, and every economic geologist has a model in mind during his search, whether he knows it or not, based on studies and observations of known ore deposits.

E.C. Pearcy and W.M. Murphy (1991) recently defined natural analogs as "occurrences of materials or processes in nature that may be viewed as comparable to some aspect of a system of interest." Another way of defining natural analogs is that they are similarities in nature. Pearcy and Murphy's definition can be applied to ore deposit exploration by replacing "occurrences of materials" with "known ore deposit," "processes" with "known ore-forming processes, both chemical and mechanical," and "comparable to some aspect of a system of interest" with "the type of deposit the geologist is searching for and hoping to discover." A key statement in the definition is "comparable to some aspect of a system of interest." Since ore deposits are unique features in nature, they are never exactly the same. There are, however, enough similarities to justify developing a model to aid in the search for new discoveries.

8.3 MODELING

The first step in ore deposit modeling is the selection of the desired commodity to discover. The same commodity may occur in economic quantities in diverse geological environments, necessitating the study and construction of various model types. Two types of modeling can be undertaken.

Empirical Model Development—This approach involves the study of existing ore deposits, constructing a three-dimensional (3D) model of various characteristics, and applying this knowledge to the exploration for a similar deposit.

Concept Model Development—This approach is based on theoretical considerations and field observations. Concept development involves development of a new concept or deposit type not known to exist in nature, but thought to be possible.

8.3.1 Empirical Model Development

Key elements that are important and studies for empirical model development are as follows:

Age—The Proterozoic age hosts the majority of World Class deposits around the world. Figure 8-1 demonstrates the importance of the Proterozoic age rocks as the host for major deposits.

Host Rock—Certain host rocks are known to contain specific commodities. An example is that rare earth elements are hosted by carbonatites.

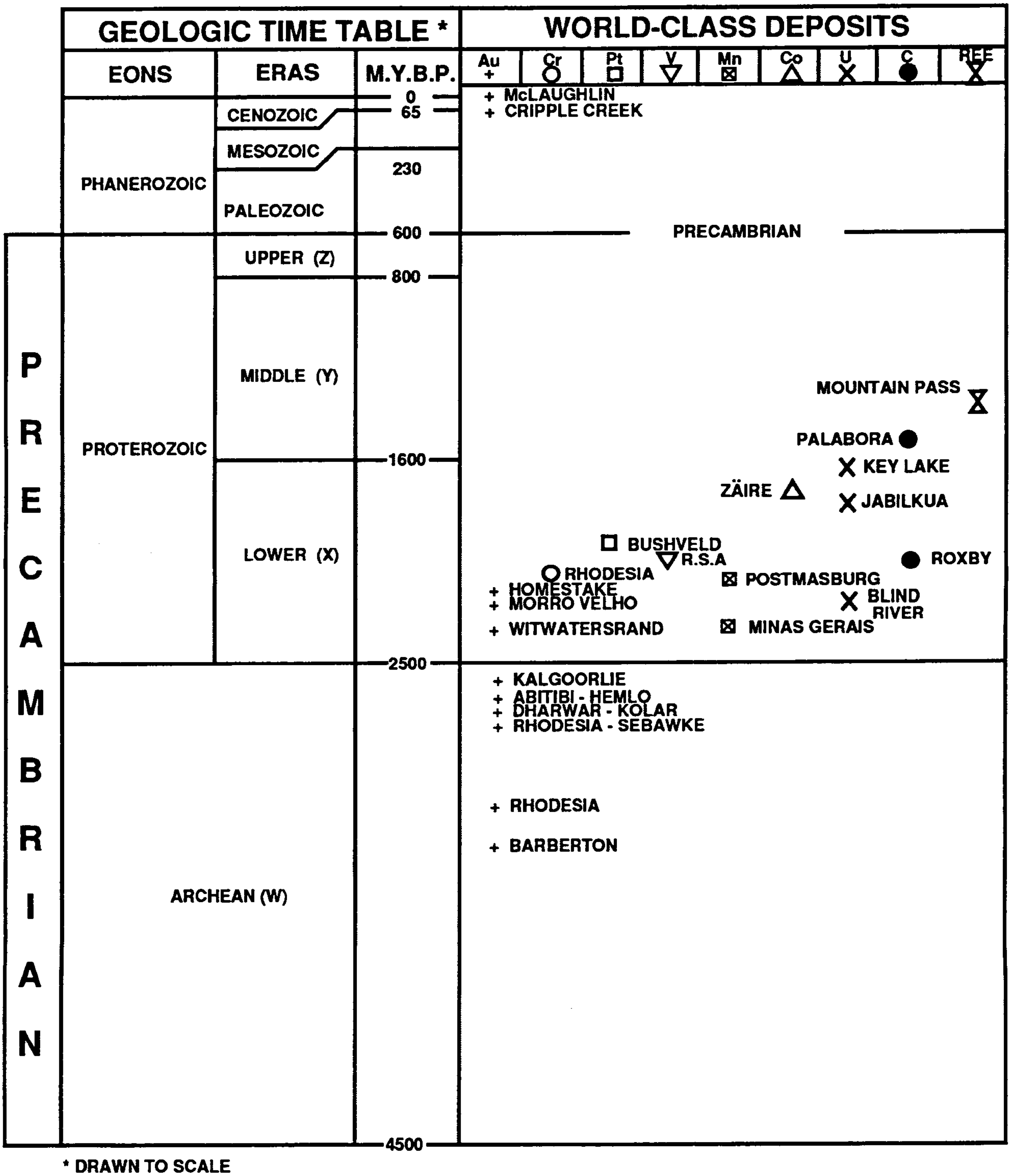

Figure 8-1. Geologic age of world class ore deposits

Structure—Major ore deposits are commonly located in or associated with rift zones.

Geologic Setting—Depending on the selected commodity of interest, a geologist may concentrate exploration in a closed basin environment versus a cratonic environment.

Alteration Patterns—Concentric alteration halos are particularly useful in porphyry copper exploration.

Geochemical Signature—Antimony, arsenic, and thallium display characteristic geochemical anomalies in gold deposit environments.

Sulfide Distribution—Pyritic halos occur above and laterally to copper deposits and contain increasing amounts of copper bearing sulfides as the central portion of the deposit is approached.

Mineral Association—Barite commonly occurs as a cap above stratiform lead-zinc-silver deposits, and cinnabar (mercury) is a significant pathfinder mineral in gold exploration.

Geophysical Characteristics—The geophysical characteristics associated with a deposit vary depending on host rock, alteration, and mineralization. A magnetite deposit generates a magnetic high in contrast to a magnetic low over an altered porphyry copper deposit.

Proper development of these characteristics and construction of a 3D model gives the exploration geologist a blueprint of a type of deposit and enables him to intelligently explore for and evaluate similar deposits with a minimum of time and expenditure.

8.4 EXAMPLES OF SUCCESSFUL APPLICATION OF EMPIRICAL MODEL DEVELOPMENT TO EXPLORATION

Probably the best documented successful application of natural analogs to mineral exploration is the discovery of the Kalamazoo segment of the San Manuel porphyry copper deposit. The porphyry copper boom of the 1960s prompted detailed studies of the known deposits by mining companies and individuals. Foremost in model development was David Lowell, consultant, who applied alteration zoning patterns and sulfide distribution to determine that a portion of the known San Manuel deposit was downfaulted along the San Manuel fault (Lowell, 1968). Deep exploration drilling discovered the Kalamazoo deposit at a depth of approximately 3,000 feet. This is a classic example of applying model development or natural analogs to exploration that led to discovery of a major copper resource. Based on comparison of observed alteration patterns to those relations at other deposits, geologists can determine if a prospect is located high in the system or deep in the mineralized system (Lowell and Guilbert, 1970).

A second successful application of empirical model development to porphyry copper exploration is the discovery of the world class Escondida orebody in Chile. David Lowell was also involved in this discovery and applied his knowledge of alteration patterns, sulfide distribution, and leached capping studies to explore this major system. The mine is currently operated by BHP-UTAH Minerals.

Numerous other examples of empirical model development are present in the literature, but their discussion is beyond the scope of this paper. The point to be made is that empirical model development, or application of natural analogs, is an important facet in exploration for mineral deposits and has been routinely applied with success.

8.5 CONCEPT DEVELOPMENT

As discussed above, concept development is the development of a model based on theoretical considerations and careful field observations to search for a deposit type not known to exist in nature, but thought to be a possibility. The development of the mercury-hot springs-gold model that led to the discovery of the McLaughlin gold deposit in northern California in 1978 is a classic example of successful application of concept development. The following is a brief description of the steps that led to the discovery of this significant gold deposit utilizing concept development (Gustafson, 1991).

In the mid-70s, Homestake Mining Company was actively exploring for gold deposits, mainly in the western United States, that could be mined by surface methods. Homestake geologists were encouraged by management to generate new ideas, concepts, and ore deposit models to use in their search for ore deposits. The exploration program included examination of old precious metal districts to determine their potential for open pitable ore left behind by previous miners, and the writer was involved in these examinations.

The fact that gold occurs in geothermal-hot spring environments is well documented in the literature. The Broadlands Geothermal Field in New Zealand and Steamboat Springs in Nevada are examples of occurrences where gold is reported in limited quantities and is actually precipitating from geothermal waters today. Physical and chemical conditions in hot spring systems are right for the formation of gold deposits, but these deposits were largely ignored by explorationists, because economic concentrations were not known to exist in presently active systems. Studies had previously been conducted by Homestake to determine the validity of a hot springs-gold model, but they revealed discouraging configurations. Geothermal systems do provide two important elements needed to form ore deposits: (i) a plumbing system, and (ii) hydrothermal solutions. Therefore, the hot springs-gold model was intriguing at this point from a theoretical standpoint, but, prior to the McLaughlin gold discovery, was only a concept.

The basic field observations made by the writer during the examination of numerous precious metal districts advanced a working hot springs-gold model supported by physical and chemical considerations. The occurrence of occasional active or fossil hot spring deposits, in the form of predominately siliceous sinter deposits, plus mercury mineralization in the form of cinnabar, was observed in close association with several known precious metal districts. Mercury had been used as a geochemical pathfinder for years by explorationists in their search for gold deposits, but geologists did not consider mercury mines as a potential location to look for gold deposits. Other common mineral associations recognized in known gold camps are sulphur and antimony mineralization.

These observations were instrumental in the development of the mercury-hot springs-gold concept, and they triggered the thought process of relating actual field observations to theoretical considerations. Since hot spring deposits and mercury mineralization occur near existing gold mines, why not consider searching for gold deposits near hot springs and mercury mines? Metal zoning in mineral deposits is a well-documented feature. It was envisioned at this point that low-temperature minerals, such as mercury, would form high in the hydrothermal system, and, if gold were present in the hydrothermal fluids, it should precipitate at a higher temperature and, therefore, lower elevation, below the mercury mineralization. Examples of gold districts examined that contain hot spring deposits and mercury mineralization in association with gold mineralization are (i) Bodie, California, (ii) Borealis, Nevada, and (iii) Goldfields, Nevada.

As part of Homestake's exploration activities in the mid-70s, a review of the numerous prospect examination reports in Homestake's exploration files was undertaken to determine if any prospects examined by Homestake over the past 75+ years justified re-examination. This activity is not a pre-requisite for concept development, but in this case, has important implications to the McLaughlin discovery. A review of these files in mid-1977 identified one area, first examined by Homestake geologists in 1926, as significant, justifying a follow-up examination. This project area, Cherry Hill, near Wilbur Springs, Colusa County, California, was described by Homestake geologists as containing hot spring deposits, mercury mineralization, and gold mineralization. Both mercury and gold had been mined from this area on a limited scale in the late 1800s and early 1900s.

Field examination of the Cherry Hill area confirmed the previous observations. The area contains active hot springs, hot spring sinter deposits, and widespread mercury and gold mineralization in altered Jurassic Knoxville sediments.

This property examination produced the necessary working model for the mercury-hot springs-gold concept and confirmed the earlier theoretical considerations and field observations. Additionally, it provided an area containing ore grade gold value in association with mercury and hot spring deposits. The hypothetical concept now became a working model. The Cherry Hill occurrence also directed Homestake's attention to the mercury districts of the California Coast Ranges, which were not known for gold production and, therefore, were long ignored by precious metal explorationists.

The Cherry Hill target was drill tested and a small, currently uneconomic, open pitable inventory delineated. The Cherry Hill project served an important role in Homestake's successful gold exploration program that followed by providing an area to study and refine the genetic target model.

8.6 MERCURY-HOT SPRINGS-GOLD EXPLORATION MODEL

A mercury-hot springs-gold exploration model was developed and presented to Homestake management by the writer at the Fall, 1977 budget meeting. The model, as presented, is shown in Figure 8-2. It consists of a geothermal system, structurally controlled, containing hot spring sinter deposits with cinnabar (mercury) mineralization at the surface, with anomalous to significant gold value changing downward to significant to economic gold value within a permeable host rock. Arsenic and antimony values were envisioned as additional significant geochemical indicators of potential gold mineralization at depth. The presence of a permeable host rock is important to provide dissemination of gold minerali-

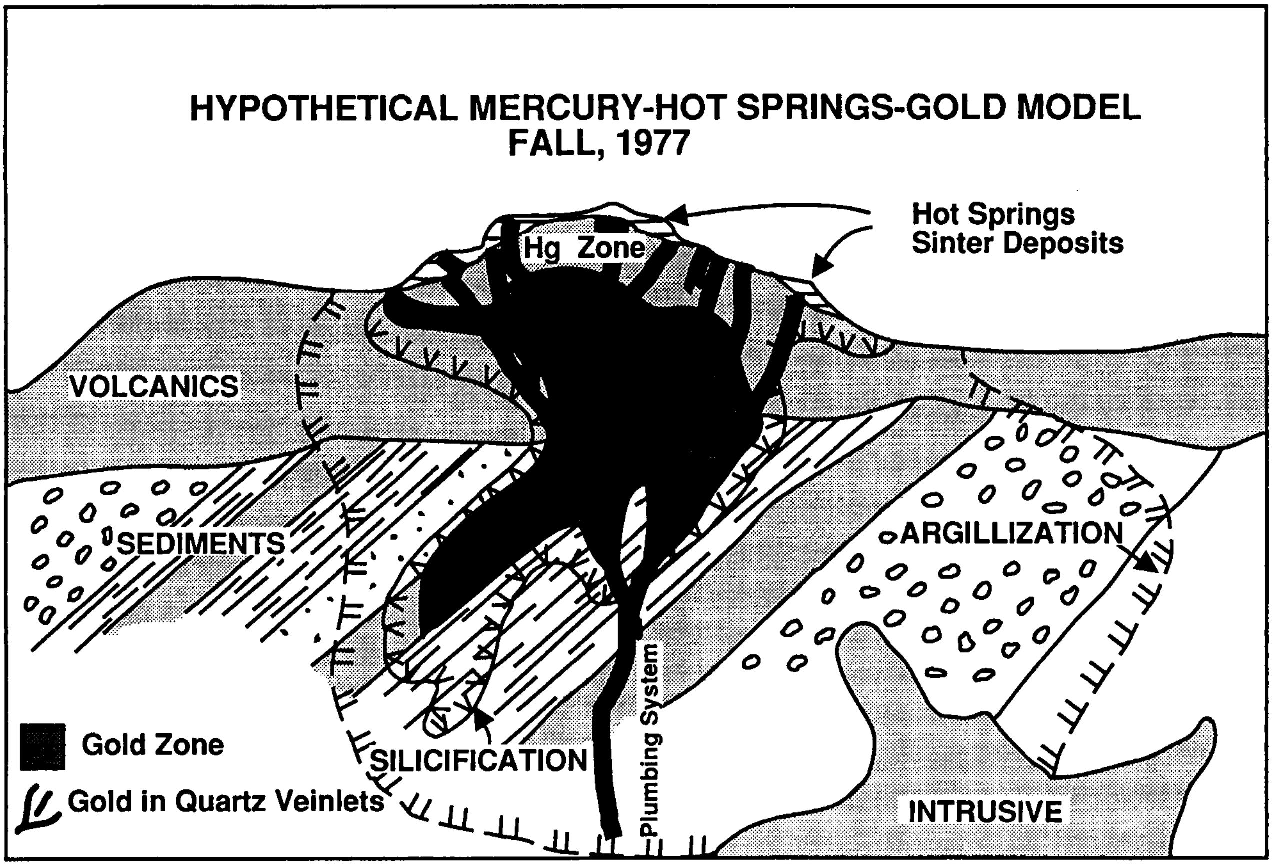

Figure 8-2. Hypothetical mercury-hot springs-gold model developed utilizing theoretical and field observations

zation over a large area that could be mined by surface methods rather than confining mineralization within a vein system that would dictate an underground mining situation.

With the working exploration model developed, and Cherry Hill presented as an example, a reconnaissance budget was requested to pursue the concept. Homestake management viewed the concept and reconnaissance program with enthusiasm and provided sufficient funds to conduct a reconnaissance program.

8.7 MERCURY-HOT SPRINGS-GOLD RECONNAISSANCE PROGRAM

The first question to answer was where to apply the concept to achieve success and accomplish Homestake's corporate goal of discovering a plus 1,000,000-ounce gold deposit. On a global sale, the Pacific Rim, with its active geothermal areas and metal provinces zoned around the Pacific, was considered potential prospecting territory, but it was decided to concentrate the initial reconnaissance program in the Coast Ranges of California near the working model, the Cherry Hill projects. The program was eventually expanded to include the western United States.

The program initially involved an extensive literature review of all published mercury-hot spring occurrences. Due to the location of Cherry Hill, the Clear Lake area received top priority, and reconnaissance began in this area. Eighty-eight mercury-hot spring areas were selected for examination in the field and prioritized from the literature search.

An initial examination, consisting of mapping and sampling, was performed in each area to determine geological characteristics and geochemical signature, particularly the presence or absence of gold values. The examination approach was to sample as deeply as possible in the mineralized system as topography would allow, that is, in drainages cutting the system, since gold was envisioned to be deposited at a lower elevation, in the higher temperature environments. Number ten on the list to examine was the Manhattan mercury mine near the intersection of Napa, Yolo,

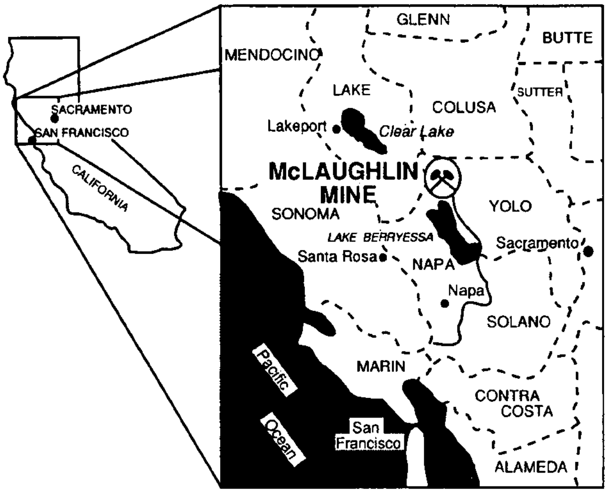

Figure 8-3. Map showing location of the McLaughlin Gold Mine, Napa and Yolo Counties, California

and Lake Counties, California. Figure 8-3 shows the location of the Manhattan mine, which was later changed to the McLaughlin mine in honor of Homestake's past chairman, Dr. Donald McLaughlin. The McLaughlin Gold Mine is located 13 airline miles south of the Cherry Hill area.

8.8 MANHATTAN MINE INITIAL EXAMINATION

The Manhattan mercury mine was examined on February 16 and 17, 1978. The extensive alteration and quartz veining observed on the surface were impressive and sampling of outcrops proved the presence of gold values. Initially 32 samples were taken and assayed for gold, with a high value of 0.34 oz Au/ton. Examination of this prospect and the assay results proved the concept, and a project was born. Optimism was high that the Manhattan area had potential to become Homestake's first open pit gold mine.

8.9 FOLLOW-UP ACTIVITIES AND OPERATION

The area was drill tested and an ore reserve of 20,000,000 tons @ 0.16 oz Au/ton calculated after the completion of 409 drill holes and underground testing. The project was turned over to operations in June 1982, and the first bar of gold was poured in March 1985. This classic epithermal mercury-hot springs-gold deposit is owned and operated by Homestake Mining Company and by March 1990, had produced 1,000,000 oz of gold. Current production is approximately 250,000 oz of gold per annum.

The exploration that produced this discovery is an excellent example of concept development and how natural analogs can be applied to mineral exploration.

8.10 DISCUSSION

This paper demonstrates the importance of natural analogs in mineral exploration and the approach exploration geologists use to discover new mineral resources. Application of modeling or natural analogs does have significance in the Yucca Mountain site characterization in that, once the Yucca Mountain site is fully described, the geological characteristics of known mineral deposit models can be applied to determine if any potential models fit the geological environment. If a reasonable model is suggested, knowledge of modeling can assist in the evaluation of potential mineral resources.

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NATURAL ANALOGS IN THE PETROLEUM INDUSTRY 9

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9.1 INTRODUCTION

The use of natural analogs in petroleum exploration predates the industry itself. The earliest oil fields were discovered by people who had only a rudimentary (at best) knowledge of geology, and they worked solely by analogy, generally looking for surface expressions of oil, such as seeps and tar pits. When the anticlinal theory (Figure 9-1) of gas and oil accumulation became popular, more geologists were employed in the search for hydrocarbons, and surface mapping of anticlines became a standard tool in the explorationist's toolkit. The advent of seismic techniques, in a way, simply extended this strategy by allowing geologists to "see" deeper into the subsurface. To a large extent, that is still current practice—one still looks for anticlines with closed contours as potential targets.

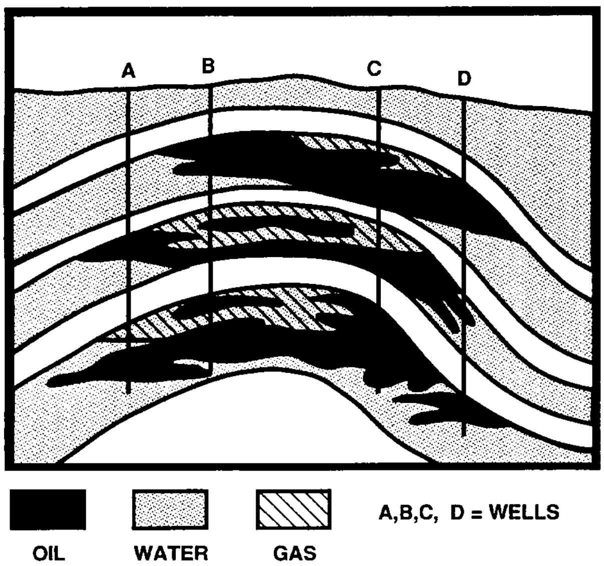

Figure 9-1. Anticlinal model for gas and oil accumulation showing irregular distribution of gas, oil, and water in an asymmetric anticline. This was one of the first natural analogs used by the petroleum industry and still dominates exploration strategies in some companies (Stewart, 1951).

Numerous generic models for gas and oil accumulations were amassed by the 1940s, which could be termed "natural analogs." These were catalogued and taught to succeeding generations of petroleum geologists. This period was perhaps the apex of the use of natural analogs for exploration, which are well exemplified by the diagrams reproduced in Figure 9-2. Perhaps not coincidentally, this period also coincided with the discovery of most of the world's major oil fields and virtually all of the world's major petroleum provinces.

From 1950 onward, as hydrocarbons became increasingly difficult to find, exploration strategies relied less and less on natural analogs and more and more on increasingly sophisticated technology, principally seismic technology, but also on such tools as remote sensing, as that science developed in the late 1970s. Today, the principal tools are computer models that "integrate" as much of the available data as possible and display it in ways that would be difficult if not impossible without computers. The principal objective is to "reduce risk," and any technique that accomplishes that goal is a candidate for inclusion in an integrated model.

To some extent, the transition to computer models reflects the increased capabilities of computers, particularly individual workstations, but it also reflects the significantly increased difficulty of finding gas and oil. Older, once reliable techniques, based primarily on mapping subsurface geology have largely failed the industry in the 1980s, and the increased emphasis on computerized models is an attempt to develop new strategies. However, overlying all of this is the increasingly evident fact that most of the accessible hydrocarbons have been discovered and much of that has been produced. Hydrocarbon exploration in the lower 48 states clearly peaked about 1984-85 and is now in a state of decline. Thus, the petroleum industry may serve as an analog itself in the development and utilization of technologies that include natural analogs. In particular it may serve as a guide to the

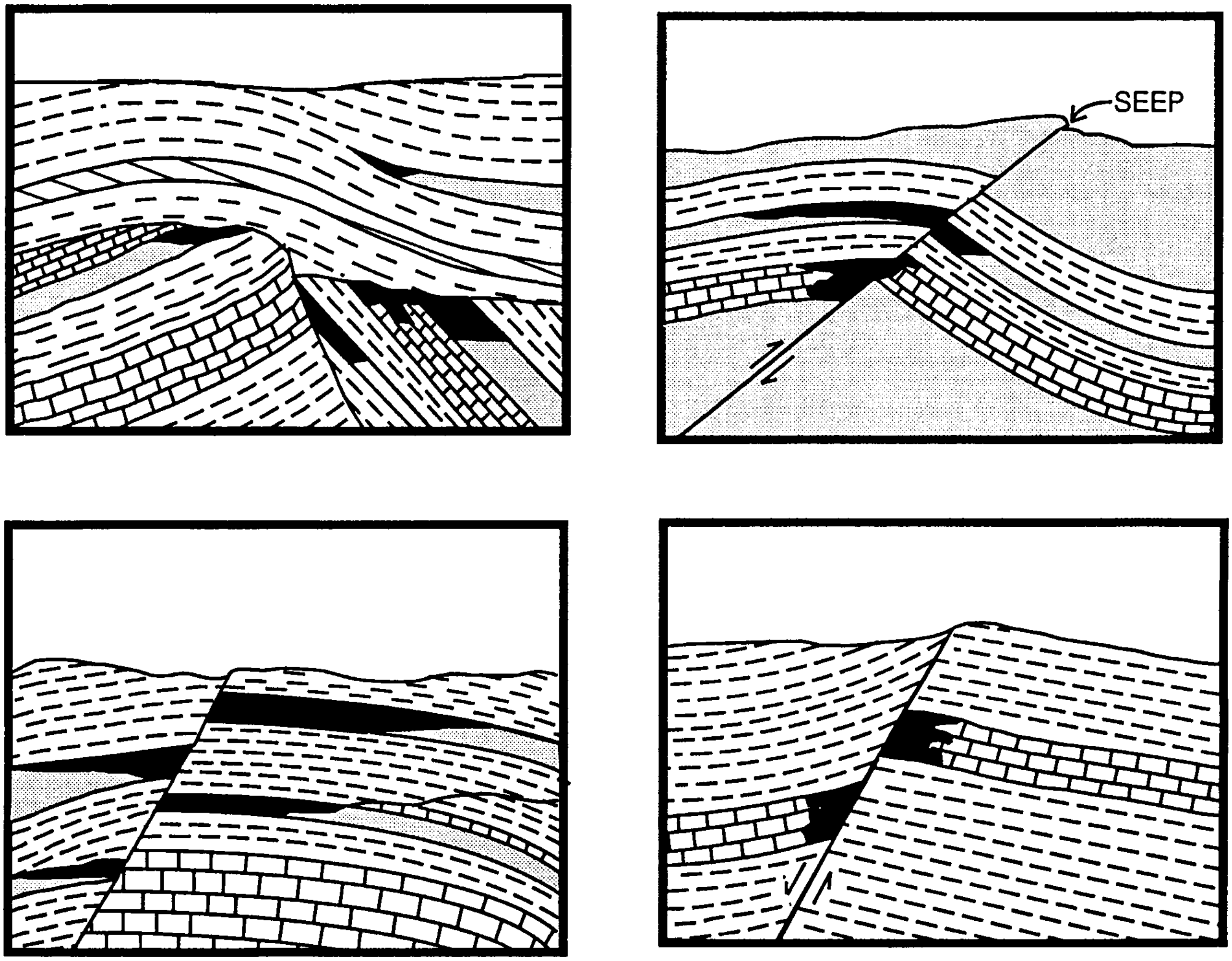

Figure 9-2. A series of natural analogs showing hydrocarbon trapping in faulted strata with erosional uncomformities (Stewart, 1951)

"life cycle" of natural analogs in a particular application.

Natural analogs played a large role in the early stages of the petroleum industry, but they came to be supplanted in the later, mature stages by technology. Specifically, the anticlinal model was joined by stratigraphic traps, fault traps, diagenetic traps, and hydrodynamic traps as natural analogs, but industry emphasis shifted toward developing better seismic technology beginning in the 1970s.

The natural analogs were not abandoned by any means; they were by this time a part of the background that every petroleum geologist was assumed to have coming out of school. But by themselves, the analogs no longer provided the competitive advantage that large companies required to survive. However, the latest trend in industry research could be described as quantifying the older natural analog models and combining them with "hard data" from seismic surveys and well logs. The recent industry emphasis on basin modeling is a good example of that trend.

The present era, which is a time of "old age" in the petroleum industry, is one in which attention is being directed toward integrated computer models that attempt to combine theory with hard data in an effort to simulate the evolution of a sedimentary basin on a large scale. These models are, for the most part, just in their infancy, although the mass-transfer models are an exception. However, only time will tell if this will be a successful approach; success for the industry being defined as reducing exploration risk.

As an example of the evolution from the use of natural analogs to models, we can consider two cases—the so-called Allan fault-plane maps and attempts to predict porosity "in advance of the drill."

The Allan fault-plane map can be regarded as a bridge between a true geologic analog and a purely theoretical model. Above all, the Allan fault-plane map does reduce exploration risk, and, mainly for that reason, it is widely used in the industry. At the other end of the spectrum, efforts to predict porosity in advance of the drill failed to reduce risk and were abandoned by the industry. It is instructive to examine both of these cases, one a success and the other a failure, as example of the transition from natural analogs to computer models.

9.2 THE ALLAN FAULT-PLANE MAP

The Allan fault-plane model has been discussed in detail (Allan, 1989). This model essentially relates faults to fluid migration and hydrocarbon entrapment. The basic assumption is that a fault is neither a seal nor a conduit and thus, that the effect of faulting on migration and entrapment is a function of the properties of the rocks that are brought into contact by faulting and on the geometry of the fault blocks.

As a simple example, consider a faulted anticline in which the strata on one side of the fault move down relative to the other. Further assume that the strata consist of interlayered sands and shales. The technique requires mapping the trace of the sands onto the fault plane for both the upthrown and downthrown blocks (Figure 9-3). This is the fault-plane map. From it, geologists can deduce the likelihood that hydrocarbons migrated from source beds to traps by crossing the fault where two permeable sands were juxtaposed. They can be done where hydrocarbons may be trapped by juxtaposition of shales opposite sands. Allan (1989) discusses several examples of the effects of varying sand/shale thicknesses on migration and trapping. That paper should be consulted for more detail on the method.

What is important here is the fact that a natural analog, the anticline, has been used in conjunction with another natural analog, the fault-plane, to infer a process, the migration of hydrocarbons. It is no longer sufficient to know that a faulted anticline exists; it is also necessary to access the probability that at least one of the sands is filled with hydrocarbons. The fault plane map provides a simple solution to that problem, and, for that reason, it has found wide application in the petroleum industry as a technique that reduces exploration risk.

It is interesting to note that the paper outlining the fault-plane technique appeared in 1989 and was first presented outside of Shell Oil in 1980. However, work had begun on the model in 1967, and one can infer that Shell Oil used the technique for a number of years before word leaked out to the rest of the industry. This is an aspect of industry research that sets it apart from either academic or government research in that results are not communicated in a timely fashion and cannot be used by others to build upon. Generally, one finds many wheels being rediscovered and results not published until either the competition clearly has acquired the expertise or it is no longer of any proprietary advantage. In addition, the fact that all research is driven by economic objectives seriously limits the directions researchers can pursue.

FAULT PLANE PROJECTION

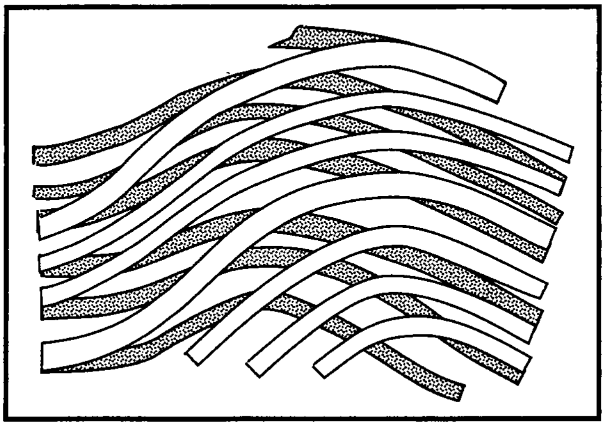

Figure 9-3. Example of Allan fault-plane for a faulted anticline illustrating structural and stratigraphic geometry. Downthrown block is in front of upthrown block; permeable beds are indicated by blocked ends, impermeable beds by open spaces. In this example, each permeable bed is in contact with another permeable bed at its highest point. As a result, hydrocarbons migrate vertically by passing from bed to bed across the fault (Allan, 1989).

9.3 POROSITY PREDICTION

Another example along these lines is the industry attempt in the late 1970s to predict porosity. Porosity is obviously an important reservoir parameter, and knowing beforehand if a target has adequate porosity would provide a significant advantage. Industry interest in secondary porosity was initially triggered by petrographic observations that showed most sandstones were subjected to dissolution processes that could only have occurred at depth. This dissolution led to large increases in porosity on a hand specimen scale, and it was thought that, if the processes occurred on a reservoir scale, then targets at depths once thought to contain only completely cemented rocks might in fact have adequate porosity.

Most oil companies adopted an aggressive research policy directed toward quantifying and predicting porosity trends with depth. At the time these studies were being initiated (~1978), diagenetic studies were a low priority in most oil companies. From 1978 to about 1984, diagenetic studies were in vogue, and geochemists and sedimentary petrographers were in high demand. However, around 1984, it became evident that the problem of porosity prediction would not have a quick solution, and attention began to wane.

There were several reasons for this. One was the fact that cementation and lithification processes were not well understood in terms of either the geologic settings or the basic physics and chemistry. Data showing the variation in porosity with depth began to show that the porosity variation at any one depth greatly exceeded the variation with total depth (Figure 9-4). Thus depth (e.g., overburden load) alone would not adequately account for porosity loss. The second reason for waning interest was that other techniques, such as basin history diagrams and thermal maturation models, were beginning to have some impact. Resources and attention shifted from porosity prediction to maturation prediction, and the problem of porosity, cementation, and lithification were largely relegated to the academic community, a situation that persists to the present.

The ultimate reason for the loss of interest was that 5 years of intense efforts did not produce a model that explorationists could use to "reduce risk." The 5-year moratorium appears to be a pretty general rule in the petroleum industry. Projects that do not produce useful results in that length of time are abandoned, or, if they have certain scientific merit, they are handed over to the academic community for further development. The current research effort in basin compartments, for example, stems almost entirely from that circumstance.

However, several things can be learned from this experience. One is that an adequate theory is necessary in order to develop a useful tool. In the case of the fault-plane maps, both anticlines and faults were well understood, and, in addition, the model itself was fairly simple. In contrast, rock alteration is much more complex; key questions remain to be answered, and critical experiments remain to be performed. In addition, the problem of model verification emerged as a central issue. It was not difficult to model porosity changes at depth, but proving the validity of any particular model has, so far, proved to be impossible.

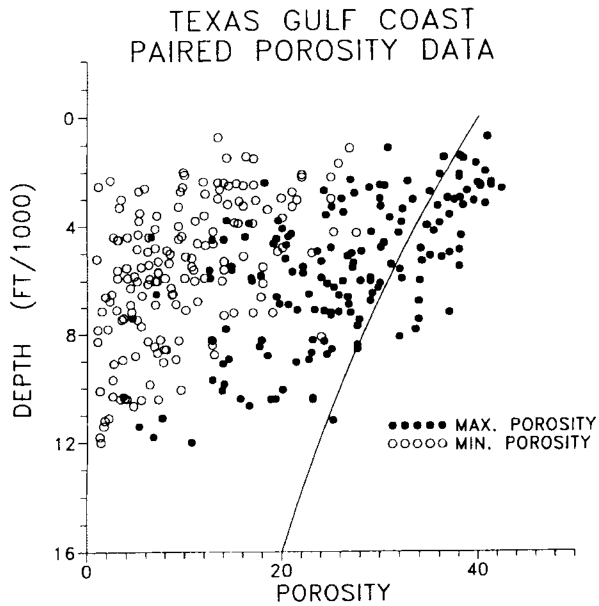

Figure 9-4. Porosity versus depth for a series of wells in the Texas Gulf Coast. Open circles indicate maximum porosity over a cored interval; open circles indicate minimum porosity. Length of the average cored intervals is 18–20 feet. Thus, there are wide swings in porosity over a short distance as well as a general trend toward lower porosity with depth.

Thus, the ability to move from natural analogs to theoretical models in an applied setting has proven enormously difficult in practice. The fault-plane model, which could be easily verified and understood, is an example of a successful transition in the petroleum industry. In contrast, the porosity prediction problem cannot even be stated in a simple, concise fashion that would be agreeable to most geologists. The bottom line is that moving from natural analogs to theoretical models has proven more difficult and treacherous than previously imagined. In addition, it appears that, where such transfer has been successful, the natural analogs were already in place and served to both guide and verify the model. In a practical or applications-oriented environment, model verification has to have a high priority; perhaps not to the point that models are not developed just because no one can yet think of a way to verify them, but verification needs to be considered at the time of initial model development.

9.4 BASIN MODELS

Currently, a significant fraction of the research effort in the petroleum industry is directed toward basin modeling in one form or another. The ultimate aim is to produce a computer code that will simulate the features in the evolution of a sedimentary basin necessary to access the hydrocarbon potential. Many codes, some produced in academia, have the ability to model certain aspects, but none are comprehensive and none operate in three dimensions (3D). Development of true 3D basin history codes is a high priority.

Conventional single-well burial history models take ages (time) and depth to formation tops from wells or measured sections and reconstruct a burial history by plotting time of deposition against rock thickness (Figure 9-5). The only significant complication is to account for sediment compaction during burial, but nearly all available models now do this. Once a burial history diagram is generated, the thermal history is reconstructed using vitrinite reflectance or fission track data (Naeser et al., 1990). Assuming conductive heat flow, the burial history diagram can be contoured for temperature (Figure 9-5).

These diagrams can be adapted to a variety of uses. For example, the application of burial history diagrams to diagenesis lies in being able to relate the cementation to a specific time and depth. Several ways have been proposed, but one method is to use O isotopes to estimate cementation temperatures, and then, use the known thermal history to locate the cementation event in time-depth space (Wood and Boles, 1991). The technique is relatively simple; once the temperature of cementation is established (via O isotopes) and the burial history diagram is contoured for temperature, then, knowing the present sample depth, one simply backtracks along the burial trajectory of the sample until it intersects the appropriate isotherm. For example, assume that a sample is taken exactly at the boundary between the Stevens sand and the Reef Ridge/McLure (Figure 9-6) and that the isotopic temperature is 80 °C. Then, the time and depth of crystallization occurred at the point on the diagram where the top of the Stevens intersects the 80 °C isotherm.

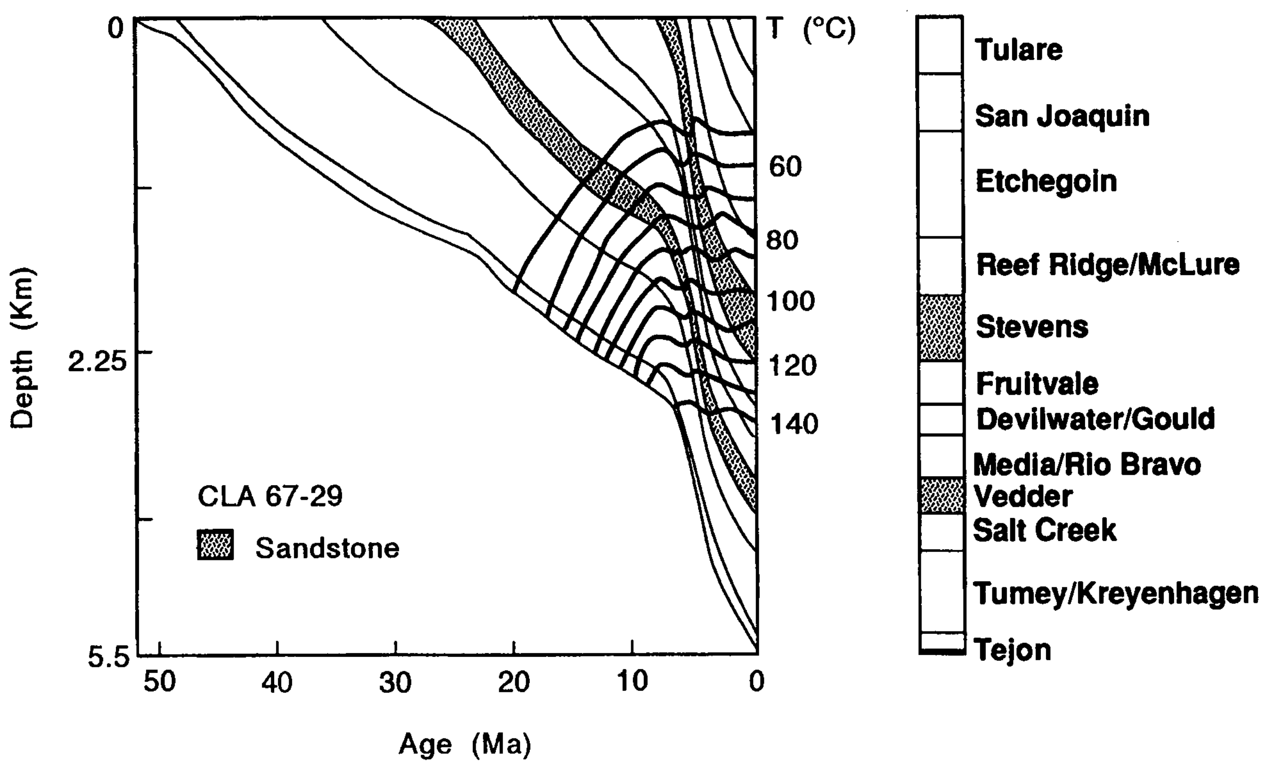

Figure 9-5. Typical geohistory plot for a well in the southern San Joaquin Valley of California. Plot has been contoured for isotherms and corrected for compaction (Wood and Boles, 1991).

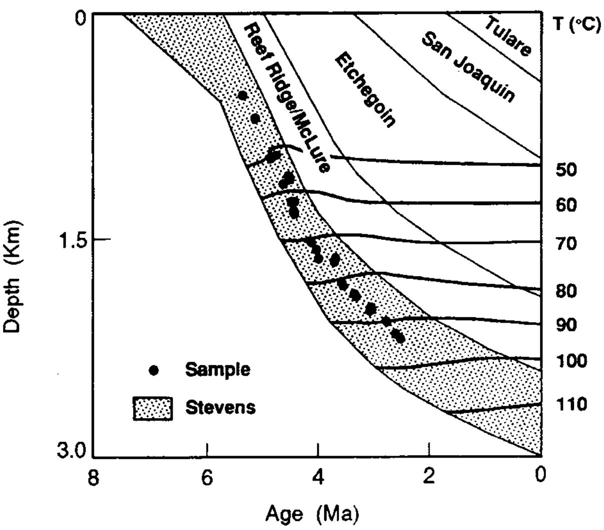

Figure 9-6. Geohistory plot for reservoir interval of Stevens sand at N. Coles Levee. Upper boundary corresponds to the approximate top of Stevens sandstone. Data points are calculated depths and times of crystallization for carbonate cements.

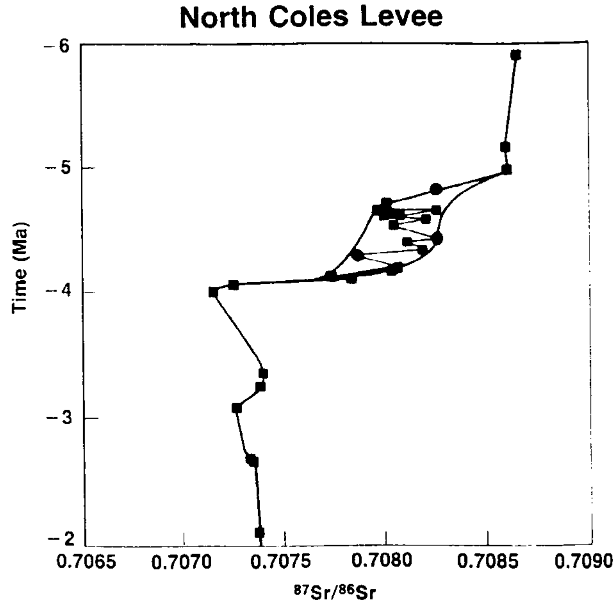

Figure 9-7. Plot of $^{87}Sr/^{86}Sr$ versus computed time of crystallization for strontium data from N. Coles Levee. Heavy curves outline envelope of values. Light lines connect samples in order of crystallization (Wood and Boles, 1991).

An additional application derives from the fact that it is then possible to construct time-series plots for any parameter that can also be measured in the same sample; for example, the C and Sr isotopes in the calcite cements. Time spectra (e.g., plots of $^{87}Sr/^{86}Sr$ against time) are shown for the North Coles Levee (NCL) strontium isotope data in Figure 9-7. Both the embedding of the samples in the burial history diagram (Figure 9-6) and the time spectra are techniques that provide a quantitative link between sample measurements and basin models.

9.4.1 The Martin Model

Burial history models that include inorganic diagenesis are relatively new tools for analysis of mineral paragenesis, and only a few papers have appeared on the subject (Woronick and Land, 1985; Burley et al., 1989; Wood and Boles, 1991). However in 1969, J. Martin at the Chevron Oil Field Research Company outlined an algorithm that computed pore fluid pressure as a function of burial history (Figure 9-8). Martin's intention was to model "abnormally high fluid pressures" in sedimentary basins, but in the course of looking at that problem he also essentially solved the problem of computing basin history well before the technique became popular outside the industry. Unfortunately, nothing was published externally, only an internal company memorandum was written. As a result, when the basin history codes were eventually written, the development team started from scratch and did not include the calculation of formation pressures. The new programs were, thus, more limited than the earlier program and consumed approximately 4 man-years of effort, much of which may have been unnecessary.

This brief sketch of the history of an industry research project highlights a recurring problem in industry research; the failure to keep new generations of researchers in touch with previous results. Corporate memory has proven to be remarkably short, perhaps only 10–15 years on average. It is considerably shorter in areas where all the investigators have retired or left the company.

The governing equations for Martin's model of a compacting basin may be written:

$$q - \varphi S = K/\mu \, (-\partial P/\partial z + \rho_w)$$
(Darcy's Law)

$$-\partial q/\partial z = \partial \varphi/\partial t$$
(Fluid continuity)

$$-\partial[S(1 - \varphi)]/\partial z = -\partial(1 - \varphi)/\partial t$$
(Solid continuity)

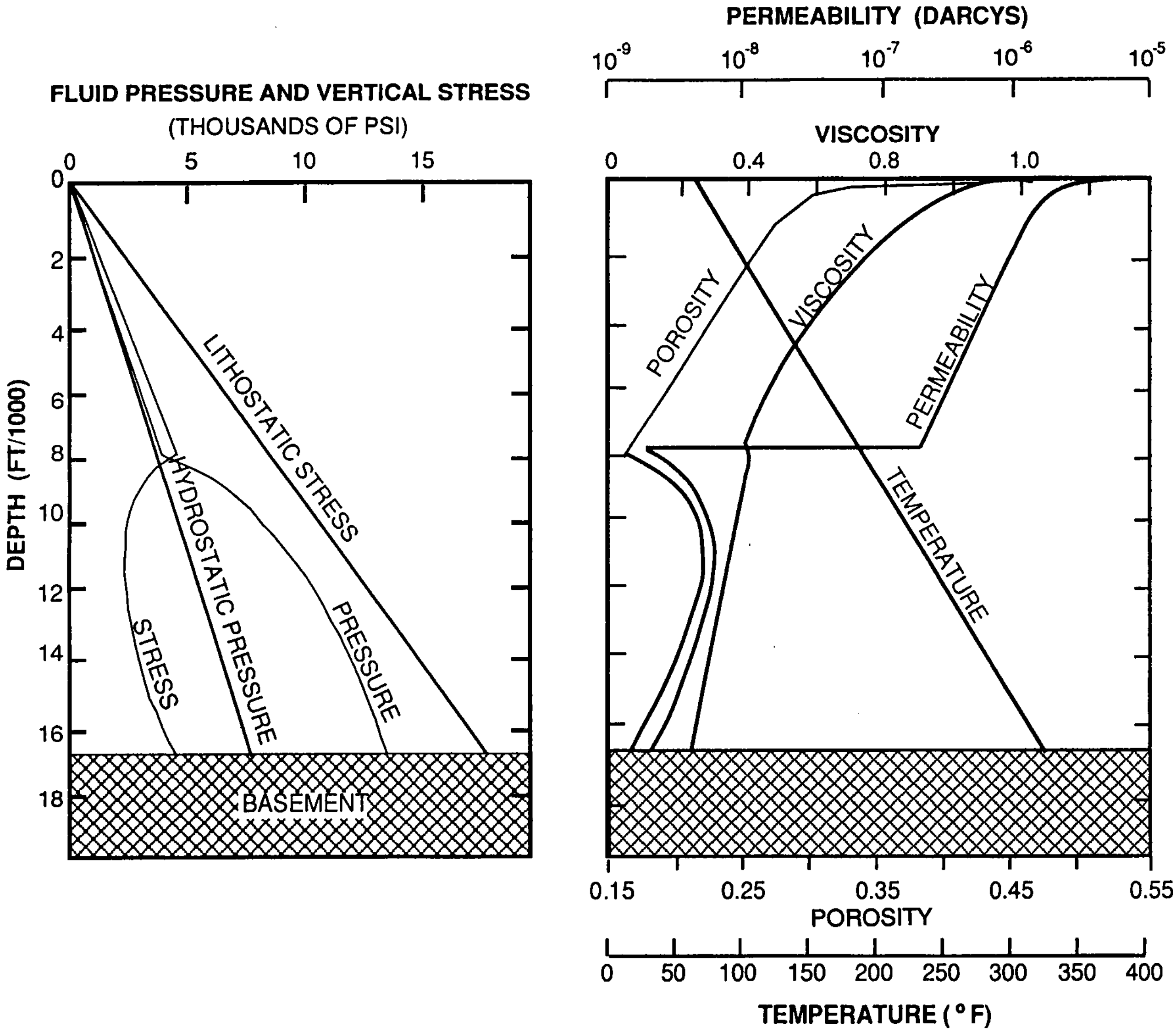

Figure 9-8. Variations in fluid pressure, rock stress, porosity, viscosity, and permeability calculated using Martin equations discussed in text. Results in figure are for after 40 My of constant sedimentation at a rate of 500 feet/My. The abrupt change in permeability corresponds to a change in deposition from a clay to silt.

$$\sigma = \sigma_s + P$$

(Effective stress)

$$\sigma = \int^{h} [(1-\varphi)\,\rho_r + \varphi\rho_w]\,dz$$

$$Q = -\lambda_z \nabla T$$

(Fourier's Law)

where:

ϕ = porosity
P = fluid pressure
K = permeability
q = fluid flow rate
S = velocity of solid matrix
t = time
z = vertical distance from top of basement
μ = fluid viscosity
ρ_r = density of solids
ρ_w = fluid density
σ = total vertical stress
σ_s = stress on solid matrix
Q = heat flow
λ_z = thermal conductivity
T = temperature

These equations represent six unknowns (q, S, T, P, σ, and σ_s). The porosity is assumed to be a known function of σ_s, while the fluid viscosity is a known function of temperature, T, and pressure P. The variation in permeability with depth, z, depends on the amount of compaction and the initial permeabilities in the sediments when they are deposited. Thus variations in K and z are calculated with the solution.

The boundary conditions require that q=0 at z=0 so that:

$$\partial P/\partial z = -\rho_w \quad \text{at } z = 0$$
$$\partial \sigma_s/\partial z = -(1-\varphi)(\rho_r - \rho_w) \quad \text{at } z = 0$$

At the surface,

$$\sigma_s = P = 0 \quad \text{for } z = h$$

where h is the total thickness of sediment, and the rate of deposition, d(t), at z = h is also a boundary condition. These equations constitute a moving boundary-value problem that has to be solved numerically. However, the solutions provide the dependence of the fluid pressure, porosity, permeability, and lithostatic stress, as well as the variation in rock thickness as a function of time (Figure 9-8).

Efforts are now under way at several institutions (Cornell, Michigan Technological University) to write a burial history code based on these equations, which should result in an improvement in the current practice, as well as an expansion of the capabilities of basin history models to handle situations involving geopressured rocks. In general, this study should provide a better understanding of the chemical and physical processes that give rise to fluid movements and rock alteration in basins. The timing and duration of cementation events in clastic rocks is of particular interest. If a case can be made that fluids move episodically through complex flow networks of porous sands connected by faults, then it would be worthwhile to try to establish a link between rock cementation and seismic activity in basins.

A logical follow-up to the Martin burial history model would be to develop a mass-transfer code similar to EQ3/6 or CHILLER that would model the geochemical and isotopic evolution of the cements and vein fill. However this step is beyond current capabilities and would require either massive rewriting of current mass-transfer codes or starting from scratch and writing a code specifically designed for diagenetic analysis. Some preliminary work is in progress on writing a new mass-transfer code based on the Simplex algorithm that will deal specifically with diagenesis and will include time-temperature dependence.

9.5 SEISMIC PUMPING AND FAULT VALVES

The seismic pumping model introduced by Sibson et al. (1975) attributed the movement of pore fluid in rocks to the dilation/collapse cycle associated with large-magnitude earthquakes. This is, in turn, a variation on the inclusion/collapse theory of deep earthquakes proposed by Brady (1975). This model (Figure 9-9) assumed that, prior to an earthquake, a volume of rock around the focus dilates in response to tectonic stresses by the opening of extension cracks and fractures. The development of this fracture porosity decreases the fluid pressure in the dilatant zone and induces a slow inward migration of pore fluid from the surrounding rock. When stress is released following an earthquake, the cracks in the dilatant zone close and expel the fluid rapidly upwards. The expelled fluids will follow a path of least flow resistance, which will generally be the more permeable

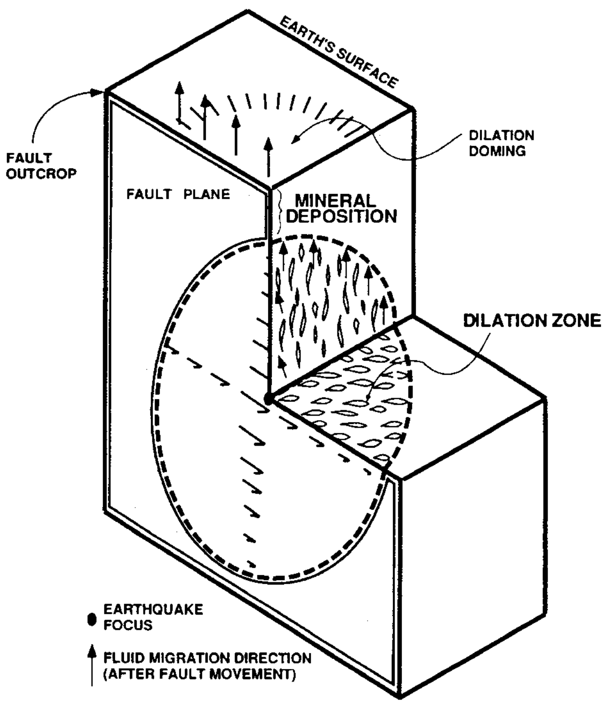

Figure 9-9. Initial model for seismic pumping based on concept of rock dilation in vicinity of a fault. This model assumed that pore fluid entering the dilatant zone is rapidly expelled following stress release after a seismic event

horizons encountered. At depth, the flow will likely follow faults, but, at shallow depths, high-permeability zones in sands and silts will offer alternative routes.

Sibson (1981) subsequently introduced the fault valve model as an alternative to the seismic pumping model. The basic tenet of this model is that overpressure seals in basins are episodically punctured by earthquakes, and fluid migration occurs until either hydrostatic conditions are reached or until the fault "self seals" by precipitating cements (Figure 9-10). This version of the seismic pumping model has obvious affinities through the overpressure connection to more conventional basin models.

Both of these models provide for a cyclic pumping of pore fluid, which could provide explanations for both the fluid driving force and the episodic nature of the fluid movement. They also provide a mechanism for mineral precipitation/dissolution in that the fluid pumping moves large volumes of fluid (e.g., 10^{10} liters of fluid per seismic event) rapidly from one pressure-temperature environment to another. Sibson et al. (1975) calculate that a fault with a displacement of 1 km could produce 10^3–10^8 fluid pulses. Sibson (1981) discussed direct evidence (e.g., elevated groundwater flow, vein fill, etc.) that channel flow of pore fluid accompanies shallow faulting.

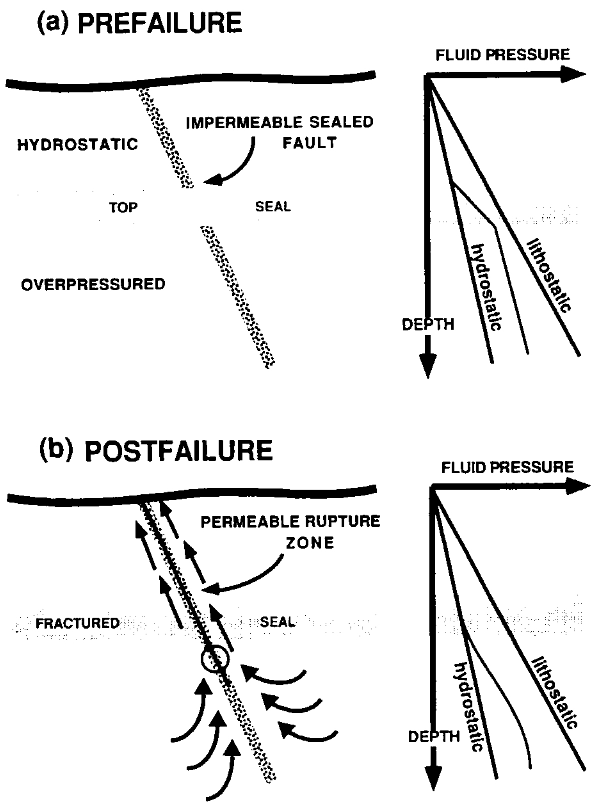

Figure 9-10. Fault-valve model which replaces seismic pumping model. In this model, the fluid movement following a seismic event is due to the puncturing of the overpressure seal by the fault (Sibson, 1981).

9.6 BASIN COMPARTMENTS

Another model closely related to the fault valve model that has been proposed recently is the basin compartment model. The essence of this model (Figure 9-11) is that basins are broken up into compartments or "bottles" separated laterally by faults and vertically by cement seals (Bradley, 1975; Powley, 1990; Hunt, 1990). The model is based primarily on measurements of fluid pressures in wells that suggest there are abrupt changes or discontinuities in fluid pressure laterally across faults and vertically across (top) cement seals (Figure 9-12).

The vertical seals are postulated to be zones in which large volumes of cements have been precipitated. It has been suggested that the vertical seals are carbonate cements that tend to occur in the vicinity of the 100 °C isotherm and that the cements migrate upwards as the basin subsides such that the cements remain more or less fixed on the 100 °C isotherm (Hunt, 1990). Whether this is exactly true or not, there does seem to be at least some evidence that certain diagenetic reactions, such as albitization and illitization, also occur near this temperature (Boles, 1979, 1984; Land and Milliken, 1981; Lundegard et al., 1984; Morad et al., 1990) and may be related to the formation of top seals.

There is clearly a connection between the fault valve model and the basin compartment idea. At-

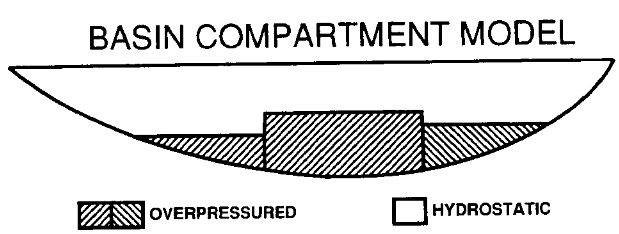

Figure 9-11. Model for basin compartments in which normally pressured rocks overlie several compartments by supernormally pressured rocks which are separated laterally by faults and vertically by shale or cement seals (Prowley, 1990)

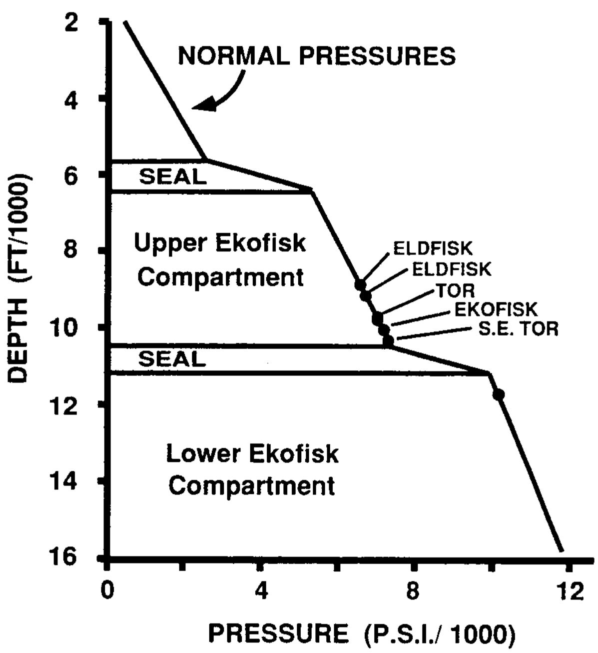

Figure 9-12. Model for pressure compartment at Ekofisk field in the Cental Graben of the North Sea. Note the paucity of data points the interpretation is based upon (Powley, 1990).

tempts are under way to link these two models into a more comprehensive basin model, an effort that illustrates the current trend toward building large basin models. The interdisciplinary nature of this type of research is also evident and partially explains the trend toward research teams composed of experts in allied fields, as well as the tendency toward including more personnel outside a company.

9.7 MASS TRANSFER AND DIAGENESIS

Finally, one of the last major areas to be incorporated into basin models is geochemical mass transfer. Although a number of codes currently exist in this area, EQ3/6 and CHILLER, for example, to date none have been combined with basin history models or with basin compartment models. This is almost certainly a shortcoming that will be addressed in the future, since the ability to predict diagenetic changes in rocks is still an industry priority.

Currently, one of the principal problems in diagenesis lies in understanding rock cementation (as distinguished from rock lithification), which requires consideration of: (i) the sources of the cementing materials, (ii) the transport of the cements, and (iii) the deposition (precipitation) of the cements. This problem has bearing on porosity evolution, reservoir quality, and hydrocarbon migration, as well as an understanding of one of the most basic geologic processes.

Recent thinking about processes occurring in sedimentary basins has led to models that propose long distance (>1 km) transport of fluids and cements. Models based on seismic pumping (Sibson et al., 1975), fault valving (Sibson, 1981) and basin compartments (Powley, 1990; Hunt, 1990) are good examples. However, with the exception of the work by Boles and Ramseyer (1987), hard evidence supporting or refuting such ideas is generally lacking.

A previous study of carbonate-cemented sand zones at NCL led to the conclusion that cements in some of the zones were precipitated episodically and could be related to seismic activity (Boles, 1987; Boles and Ramseyer, 1987; Schultz et al., 1989; Wood and Boles, 1991). In addition to the recent work at NCL, the regional study by Surdam et al. (1988), which modeled the geologic history of the southern San Joaquin Basin, and the work by Cathles and Smith (1983) on episodic ore deposition are relevant to this study. Boles (1991) discussed some petrographic observations that suggested hydrocarbons were involved in the dissolution of plagioclase at NCL. These observations would be consistent with earlier suggestions by Surdam et al. (1984) and Surdam and Crossey (1985) that organic acids leached from hydrocarbons are instrumental in feldspar diagenesis.

9.8 SUMMARY

The petroleum industry has used natural analogs practically from its inception at the turn of the century. Early analogs were simply basic geologic structures, which, although new at the time, were easily verified and put to practical use. From about 1900 to after World War II, these types of natural analogs were expanded and refined. However the rise of seismic techniques in the 1940s and 1950s began the shift in emphasis from purely natural analogs to geologic interpretation based on seismic data. In the late 1960s, computer modeling began to add a new dimension to the industry research efforts, and, by 1980, basin modeling had taken hold.

In its simplest form, basin modeling was the integration of natural analogs with models from other disciplines. Adding hydrocarbon maturation calculations to basin history models is typical of the direction. Today, the greatest research emphasis is on more comprehensive basin models, with the ultimate aim to be able to model the evolution of a sedimentary basin from the initial deposition of sediment to the present state. Progress has been made in this direction, but generally in isolated areas, and the effort is really in its infancy at the present time.

One major stumbling block has been in the area of model verification. It is obviously impossible to simulate basin development in the laboratory, and, thus, answers to key questions, such as, "What is the dominant mode of fluid flow in the subsurface?" remain unanswered. The issue of verification revolves around two points: (i) how should "ground truth" data be incorporated into theoretical models? and (ii), what degree of verification is necessary? Complete verification is out of the question for a comprehensive basin model, so the problem of just what data need to be acquired and how they should be integrated into the models is rapidly becoming the question of the day.

In addition, the move from purely natural analogs to more theoretical models represented by computer codes has presented a new set of problems for research managers in the petroleum industry and has required a change in research procedures. Coupled with the shrinkage of research budgets, program managers have begun to rethink the way in-house research is conducted. For most companies, including many of the larger ones, it is no longer possible to pursue all areas of potential interest in-house. Currently, the concept of "leveraged" research has arisen, the idea being that joint projects with universities will stretch research dollars and allow some projects to remain alive that would have otherwise been tabled. At the present time, perhaps as much as 70–80 percent of the basic research is being conducted as joint projects, particularly the basin modeling efforts, since this is an area of considerable academic interest anyway.

In general, the petroleum industry found that outside research programs were most beneficial when (i) they provided access to new technologies, and (ii) kept long-term research efforts alive that would have otherwise been abandoned. The main difficulties were in finding competent personnel who were not already working for a competitor and working on a time cycle centered around student thesis projects.

Future trends in long-term research in the petroleum industry will probably see even more emphasis on joint projects with universities and outside consultants and will focus on development of coupled models for basin processes. Key questions will involve model verification and moving new technology more rapidly and efficiently to practical application.

Finally, there is already a noticeable shift from exploration models to work on reservoir management and enhanced recovery techniques. This area offers considerable opportunity to combine natural analogs with quantitative models, since the "easy" oil has already been recovered and new techniques will require a better understanding of the natural environment and the effects of recovery on the rock matrix.

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THE POÇOS DE CALDAS INTERNATIONAL PROJECT: AN EXAMPLE OF A LARGE-SCALE RADWASTE ISOLATION NATURAL ANALOGUE STUDY

10

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10.1 INTRODUCTION

The proper isolation of radioactive waste is one of today's most pressing environmental issues. Research is being carried out by many countries around the world in order to answer critical and perplexing questions regarding the safe disposal of radioactive waste. Natural analogue studies are an increasingly important facet of this international research effort (Chapman et al., 1984; Chapman and McKinley, 1990).

The Poços de Caldas International Natural Analogue Project was designed to study radwaste-related processes occurring in the natural environment, and the study area contains many features analogous to those anticipated to impact the isolation of radioactive waste. The project was a multidisciplinary study, covering such diverse disciplines as geology, geochemistry, hydrology, geomorphology, and microbiology, as well as related modeling.

The Poços de Caldas Project represents a major effort of the international technical and scientific community towards addressing one of modern civilization's most critical environmental issues—radioactive waste isolation.

10.2 PREVIOUS STUDIES AT POÇOS DE CALDES

The Poços de Caldas area has been the subject of other long-term studies. In particular, these have focused on the Morro do Ferro Th/REE ore deposit. In 1977, an international conference on areas of high natural radioactivity was held in Poços de Caldas (Cullen and Penna Franca, 1977). Studies have also been conducted regarding the biological uptake of U, Th, and their daughter products (Eisenbud et al., 1984; Campos et al., 1986).

The geology and geochemistry of the Poços de Caldas area has also been previously studied. Examples of these earlier studies include those of Ellert et al. (1959), Amaral et al. (1967), Bushee (1971), and Ulbrich (1984). The regional geology, geochemistry, and hydrology are discussed in more detail by Holmes et al. (1991), Schorscher and Shea (1991), and Shea (1991).

10.3 CURRENT STUDIES

10.3.1 Project History

The Poços de Caldas Project was conducted for 3-1/2 years from June 1986 until December 1989, under the joint sponsorship of SKB (Sweden), NAGRA (Switzerland), the Department of Environment (United Kingdom), and the Department of Energy (United States), with considerable support from a number of organizations in Brazil, most notably Nuclebras (now Uranio do Brasil). A first-year feasibility study (Smellie et al., 1987) was followed by 2-1/2 years of data collection and interpretation. The U.S. Department of Energy (DOE) was involved in the technical and programmatic planning of the project from its inception, with members on both the Steering and Technical Committees, as well as in active research. The Commission of European Communities hosted the final symposium of the Poços de Caldas Project at Pitlochry, Scotland, in June 1990.

The project generated a series of technical reports, which are published in 15 volumes and a collection of scientific papers that will appear in a Special issue of the *Journal of Exploration Geochemistry*. These papers will be beneficial to the scientific members of the international radioactive waste community, as well as administrators and government officials responsible for the management of research projects, and they will serve as an important guidepost for other current and future studies. They will also be of interest to earth and environmental scientists for their technical and scientific information. Finally, applied modelers and mathematicians will find these papers to be a valuable example of a complete and interactive modeling exercise.

10.3.2 Study Sites

The study area, in the province of Minas Gerais, Brazil, is located within an 80-million-year-old alkalic volcanic/plutonic complex comprising a 35-km diameter subsidence caldera. A naturally high radioactivity is associated with the local volcanic rocks (mainly phonolites and nepheline syenites), geothermal springs, and uranium deposits. It contains two sites of particular interest, the Osamu Utsumi uranium mine and the Morro do Ferro thorium/rare-earth ore body. The first site is notable for the prominent redox fronts contained in the rock, while the Morro do Ferro is recognized as one of the most naturally radioactive locations on the surface of the Earth. The geology and mineralogy of these sites are discussed in more detail by Waber et al. (1991) and Waber (1991).

10.3.3 Principal Objectives

The project had four principal objectives that were used to focus the research of the project (Smellie et al., 1989), such that it remained as pragmatically oriented as possible towards the overall goal of studying processes as they related to radioactive waste isolation issues. Those objectives were: (i) assist in verification/calibration of hydrochemical models, codes, and databases used to evaluate rock/water interactions and the solubilities and speciations of elements; (ii) determine interactions of natural groundwater, colloids, radionuclides, and mineral surfaces with respect to radionuclide transport processes and colloid stability; (iii) produce a model of geochemical transport across redox fronts, with special attention to redox-sensitive natural series radionuclides; and (iv) model migration of REE/U-Th series radionuclides during hydrothermal activity similar to that anticipated in the near field.

10.4 OBSERVATIONS AND IMPLICATIONS

Many of the results of the project have a direct application, or at least an implication, towards performance assessment. Some of the natural processes and interactions observed at Poços de Caldas need to be incorporated into performance assessment models, particularly in terms of sorption, solubility/speciation, code/database comparison, colloid transport, microbial transport, redox transport, and hydrothermal transport. These observed processes/interactions include amorphous to crystalline phase transitions, microbiological chemical reactions, flow channeling, matrix diffusion, and redox retardation. These processes and interactions will be discussed further below.

The reader should note that this summary paper is highly-distilled and "punchy," in the spirit of the presentation at the San Antonio workshop, with an absence of pedagogical approach or discussion section. Therefore, I strongly encourage the reader to read the more thorough and explanatory Summary Chapter of the Poços de Caldas Report Series (Chapman et al., 1991), as well as any specifically referenced reports.

10.4.1 Sorption

Amorphous phases at Poços de Caldas were observed to reduce trace element mobility. As they age and crystallize, they may either release sorbed species into the groundwater or incorporate some given species from the groundwater into their crystalline structure (Nordstrom et al., 1991). Therefore, performance assessment models may need to account for the precipitation of an amorphous phase evolving to a crystalline phase, rather than only sorption onto crystalline phases. Some trace element fixation processes appear to be irreversible (MacKenzie et al., 1991). Thus, the reversible sorption mechanism models currently used in performance assessment codes do not appear to be appropriate. These performance assessment models tend to be too conservative and, in turn, overly pessimistic, which may have negative cost/benefit and siting criteria impacts.

10.4.2 Solubility and Speciation

The results of trace element solubility and speciation modeling for Poços de Caldas groundwaters were generously conservative, but several errors were noted in the thermodynamic databases that were used (Bruno et al., 1991). In particular, it was noted that a number of key observed mineral phases were missing in the databases. Therefore, it is important to ensure that the thermodynamic databases used in performance assessment include the appropriate minerals that control solubility and speciation for any given test case.

10.4.3 Colloid Transport

Evidence from the Morro do Ferro study site showed that groundwater particulates were not mobile and may actually have aided trace element retardation through an element fixation/particle filtration mechanism (Miekeley et al., 1991a; Miekeley et al., 1991b). These results suggest that there may not be a "colloid problem," but where they are broadly applicable to other geologic environments is not clear and needs further study.

10.4.4 Geomicrobiology

Microbially mediated chemical reactions at Poços de Caldas appear to be very significant, even in deep groundwaters (West et al., 1991). Therefore, if specific microbial reactions and their related enhanced kinetics are not accounted for in geochemical models, performance assessment results will not necessarily be conservative.

10.4.5 Redox Transport

Modeling of the redox fronts at Poços de Caldas (Cross et al., 1991) included simple mass-balance scoping calculations, chemical equilibrium modeling, kinetic chemical modeling, and modeling of specific features of the redox fronts, such as microbiological processes (West et al., 1991), natural-series radionuclide profiles (MacKenzie et al., 1991), and trace element redistribution (MacKenzie et al., 1991).

The simple mass-balance calculations explain the formation of redox fronts in very general terms, but greatly simplify the processes known to be occurring at such fronts. Coupled transport/chemistry models provide a better simulation of some aspects of the fronts, but they are really interpretive models without any convincing predictive abilities. In particular, they poorly simulate trace element chemistry in either solution or solid phases.

The process-specific modeling sheds some light on the inaccuracies of the chemical modeling. Microbial catalysis appears to be very significant in redox systems, particularly affecting the chemistry of sulfur. Natural-series measurements clearly show that redox fronts move very slowly. Further, trace element distributions reveal that the Poços de Caldas redox fronts appear to retard a wide spectrum of trace elements, even many nonredox sensitive elements, probably due to elemental sorption/fixation or solid solution in precipitating amorphous FeO(OH).

The above results support the far-field conceptual model of advective flow of oxidants along major fracture zones coupled with slow, diffusive solute exchange with the surrounding rock. The observed redox "retardation" adds a possible element of conservatism to transport models involving redox discontinuities.

10.4.6 Hydrothermal Transport

Cathles and Shea (1991) applied physical and chemical codes to model both the natural, intrusive-driven hydrothermal system at the Osamu Utsumi uranium mine, as well as a case in which hydrothermal processes were driven by a hypothetical underground repository. The hypothetical repository was modeled to be similar to a possible United States high-level nuclear waste (HLW) design, and placed within the Osamu Utsumi uranium mine host rock. The hydrothermal circulation system around the hypothetical repository proved remarkably similar to that observed at the mine. However, the calculated alteration around the repository was only 0.1 percent relative to the natural system. The relatively high temperatures operative in the natural system at Poços de Caldas, and as modeled for the hypothetical repository, are only probable for some United States HLW scenarios and possibly also for the French HLW repository concept.

10.5 LESSONS LEARNED

In a more general sense, there were many important lessons learned in the Poços de Caldas Project. Those outlined below are discussed in more detail by Chapman et al. (1991).

- Heterogeneities in the physical and chemical properties of the rocks and waters occur at all scales and are not always possible to characterize adequately.
- Robust models were required to interpret the sparse and heterogeneous data, and a similar approach will likely be needed to characterize a repository site.
- Although there has been mobilization and enrichment of uranium and other radionuclides, large-scaled rapid transport of radionuclides has not occurred at Poços de Caldas.
- The project has shown that data collection cannot be rushed, no matter how many resources are available at the outset.
- It is particularly important that hydrochemical speciation data be collected *in situ*.
- Any study site will be more complex, ill-defined, and perturbed than expected.

- It is not always possible to constrain a process adequately in order to study and interpret it.
- Fundamental refinements to hydrochemical trace element models are theoretically transferable and will be usable at any study site, if applicable.
- Analogue studies provide invaluable experience for conducting performance assessments.
- Modelers and investigators must coordinate data requirement at the outset.
- Some data needs may be impractical or impossible to fulfill.

10.6 SUMMARY

Data collected at Poços de Caldas were successfully used to verify/calibrate (first steps toward validation?) numerical models and to confirm or correct laboratory measurement. In particular, corrections were made to thermodynamic values as used in geochemical codes. Also, investigators identified materials and processes that had not previously been identified as related to radionuclide migration and needed to be incorporated into performance assessment models. The most specific example is the discovery of key mineral phases, observed to be present in the field, that were not included in current thermodynamic databases.

10.7 ACKNOWLEDGMENTS

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NATURAL ANALOGUE STUDIES AS SUPPLEMENTS TO BIOMINERALIZATION RESEARCH

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11.1 ABSTRACT

Chemical reactions can alter the chemistry and crystal structure of solid objects over archeological or geological times, while preserving external physical shapes. The reactions resulting in these structures offer natural analogues to laboratory experiments in biomineralization and to biologically influenced alteration of nuclear waste packages, and thus, they offer the only available way of validating models that purport to predict waste package behavior over archaeological or geological times.

Potential uses of such analogues in the construction and validation of hypothetical mechanisms of microbiological corrosion and biomineralization are reviewed. Evidence from such analogues suggests that biofilms can control materials alteration in ways usually overlooked. The newly hypothesized mechanisms involve control by biofilms of the cation flow near the solid surface and offer plausible mechanisms for the formation of mixed-cation minerals under conditions that would lead to dealloying in abiotic experiments; they also can account for the formation of unusual minerals [such as posnjakite, $Cu_4SO_4(OH)_6.H_2O$] and mineral morphologies unusual in corrosion [malachite, $Cu_2CO_3(OH)_2$, rarely forms botryoidally under corrosion conditions and its occasional presence on archaeological objects that appear to have undergone microbiological corrosion may be related to biofilm phenomena].

11.2 INTRODUCTION

The purpose of this paper is to show how studies of alteration products, particularly pseudomorphs and of corroded artifacts, can provide data that form a useful supplement to laboratory research data on biomineralization processes, and to laboratory research on microbiological corrosion of materials of importance to high-level nuclear waste (HLW) packages.

Before any data or arguments are presented, it will be useful to define the limits of the subject matter of this paper, and the sense in which certain words will be used. Biomineralization describes biological reactions leading to the creation of inorganic products, which need not be natural minerals, either by precipitation or by chemical replacement of other materials. Biocorrosion will refer to biomineralization reactions in which a solid metallic phase is oxidized. This paper will consider the study of mineral alteration products, generally pseudomorphs, or corroded artifacts, with the intention of developing an understanding of the reactions that led to their formation. These reactions will be regarded as natural analogues to the reactions that are expected to take place during degradation of a waste package. The intent of research in this field is to use these natural analogues to validate models for waste package degradation and codes based on these models.

A pseudomorph is defined mineralogically as a specimen that has been reacted so that the internal structure is altered, but the external form is preserved. For the study of natural analogues, it is useful to broaden the definition somewhat. In this paper a pseudomorph will describe an object (natural or an artifact) whose external shape has been preserved, but whose internal crystal structure or composition (usually both) has been changed. An example is a crystal of cuprite, cubic Cu_2O, that has altered to monoclinic malachite, $Cu_2CO_3(OH)_2$, while retaining its gross cubic shape. The term alteration will be used for all chemical reactions involving a change in the composition of an object, part of an object, or its dissolution. Corrosion will be used for alteration reactions involving oxidation of a metal species originally in a solid phase.

There are three commonly accepted classes of biomineralization and one subclass for which a new term is introduced. Microbiologically intermediated reactions are inorganic extracellular reactions caused by microbiologically influenced changes in the bulk electrolyte chemistry. Microbiologically induced reactions are those in which the reactions are extracellular and inorganic in nature but are controlled by the local biofilm chemistry. Microbiologically controlled reactions are intracellular reactions in which the composition, crystal structure, or form of the crystals, is controlled by the cell. An example would be the production of hexagonal prismatic crystals of greigite, Fe_3S_4 (conjecturally pseudomorphic after troilite, FeS) in magnetotactic bacteria; this terminology is adapted from Lowenstam (1989). A subclass of induced reactions that is not usually considered separately includes extracellular reactions in which the microorganisms act to control the morphology of the alteration products without affecting the composition or crystal structure. Outside the study of natural analogues this type of reaction is of little importance, but its appearance in archaeological applications appears to justify a separate designation, and it will be termed microbiologically structured or shaped alteration, though, under some circumstances, the mineral can be described as a pseudomorph of the microorganism (Watterson, 1991). The reason why a mineral specimen pseudomorphic after another mineral is of such importance is that the specimen itself displays the nature of both the reactant and of the product. For example, a specimen of malachite may have formed by corrosion of copper or by alteration of some other copper mineral. If the specimen has the form of a bowl, the starting material was almost certainly a copper alloy (though in a completely mineralized specimen it would be difficult to determine the original composition), but if the specimen is a crystalline mass with no pseudomorphic characteristics, determining the reaction path might be a matter of guesswork. Even if it were known that the original material were a sulfide, the identity of the sulfide might be in doubt, and the reaction path might have been any of several.

Microbiologically influenced corrosion (MIC) covers corrosion reactions that involve any of these types of biomineralization. In this paper, discussion of microbiologically intermediated corrosion will be limited; microbiologically intermediated corrosion is a very common phenomenon (for example, virtually all sulfiding corrosion outside chemical plants is intermediated, and much carbonate corrosion as well), and generally of only peripheral interest to bioprecipitation research. Microbiologically controlled reactions will not be treated extensively, because the detailed research required to discriminate them from induced reactions has not been performed, except perhaps, in the case of magnetotactic bacteria.

11.3 ALTERATION PRODUCTS AND PSEUDOMORPHS

Minerals may undergo reactions (biologically influenced or not) with their environment that result in changes in chemical composition, generally accompanied by changes in crystal structure. A crystal that has been subjected to this process without change in its gross shape is termed a pseudomorph. In a situation where one is dealing with metals, this definition needs to be broadened to include crystalline aggregates, since metal single crystals are laboratory curiosities. Pseudomorphs have long been treated as geological curiosities, and some of the most comprehensive work was done on them in the last century (Blum, 1843-1873). When one is attempting to extract information from a natural analogue, presumably to validate some model of a mineralization process, pseudomorphs are particularly useful, because the identity of the original mineral is generally known and because there is a lack of gross physical shape change. The same points are valid for altered archeological objects.

To extract information on corrosion processes from a pseudomorph or a corroded artifact, one must first observe the nature and morphology of the corrosion/alteration product, and then combine this with reasonable estimates of the local water chemistry over the period during which the reactions were taking place, and of the relevant thermodynamic (and sometimes kinetic) data. One considers various plausible alteration mechanisms and excludes those which, given known thermodynamic and kinetic data, could not have produced the observed structure.

Sometimes one observes phenomena, such as Liesegang patterns (Scott, 1985), alternating patterns of different minerals which provide periodically layered structure for the corrosion products. Such observations need to be interpreted in terms of models testable under laboratory conditions and offer interesting prospects for research.

11.4 MICROBIOLOGICALLY INFLUENCED PRECIPITATION OF MINERALS

Information on biomineralization reactions can be extracted from alteration products by comparing the structure and composition of the products to various conjectured reactions. If pseudomorphs of one mineral after another exist, or other altered structures make clear the identities of the reactant and product, one looks for a (biological or nonbiological) path for the reaction.

The absence of pseudomorphs of one mineral after another means nothing; the reaction may be a common one but may not occur pseudomorphically. The argument that a reaction transforming one mineral into another cannot be effectuated microbiologically can be made from the absence of the second mineral as an alteration product (pseudomorphic or otherwise) of the first, but this line of reasoning must be applied with great care to minerals that are found in only a few places. For example, it is unknown for reevesite [$Ni_6Fe_2(OH)_{16}CO_3.4H_2O$] to form as an alteration product of josephinite (FeNi) in nature, but it is possible to alter josephinite under a biofilm in such a way as to produce reevesite; it just happens that conditions at the one place in the world where there is still significant uncollected josephinite are not right for such alteration.

Isotope geochemistry may be useful in the study of biomineral pseudomorphs. It is known that the action of sulfate reducing bacteria (SRB) is isotopically preferential as far as sulfur is concerned, and it might be possible to discriminate sulfiding by an infinite, well-mixed sulfide reservoir (a situation which might be typical of intermediated reaction) and sulfiding by a limited sulfide population in a biofilm, with a long renewal time (which would be more typical of microbiologically induced corrosion), if there were some way of estimating the isotopic ratio in the bulk reservoir.

11.5 ARTIFACTS

Artifacts have been extensively studied from the corrosion standpoint. One reason is that archaeologists and museum curators need to understand corrosion reactions so as to ensure that these reactions do not accelerate once a specimen has been excavated, and to determine to what extent the consequences of past corrosion reactions can be reversed. There also may be interest in whether a particular mineral formed as part of a corrosion or alteration process, or whether it was deliberately applied (for example, as a pigment) or was formed as part of the artifact's manufacture.

The identity and structure of corrosion products on artifacts has been the subject of extensive literature, abstracted in Arts and Archeology Technical Abstracts. Gettens (1963) and Brown et al. (1977) prepared extensive reviews; a much more detailed bibliography on copper alloys, citing references as far back as Pliny, is contained in Sharkey and Lewin (1971). McNeil and Little (1990, 1991a, 1991b) contain some more recent citations.

11.6 MICROBIOLOGICAL CORROSION OF ARTIFACTS

The most important class of bacteria for artifact mineralization is SRB (Baas-Becking and Moore, 1961; Hamilton, 1985). SRB-induced biomineralization can affect any metal whose thermochemistry is such that the sulfides are reasonably stable with regard to the oxides, even iridium. The resistant metals appear to be gold, titanium (Little 1991), and zirconium, metals whose sulfides are stable in the presence of water only under extraordinary conditions. Aluminum, chromium, and magnesium sulfides are more stable, but reactions between ions of these metals and hydroxyl ions or dissolved oxygen are so favorable energetically that sulfiding corrosion in the biosphere seems relatively unlikely.

Surfaces of minerals and artifacts in the biosphere are colonized by bacteria, which produce biofilms. Microorganisms in the biofilm are capable of maintaining an environment radically different from the bulk in terms of Eh, pH, and concentrations of various species (Walch, 1989; Newman et al., 1991); in consequence, it is possible to form beneath the biofilm various compounds that are not stable in the bulk environment. An example of such biofilm-dominated mineralization is the conversion of metal to a sulfide mineral by the action of biofilms containing both SRB and oxygen-consuming bacteria (Pope, 1986). Since the biofilms are nonuniform, it is possible for the local environment to vary chemically on a submillimeter scale. This can produce complex mineralogical assemblages on a fine scale (Gouda et al., 1993).

Sulfide biomineralization is probably the most comprehensively studied subset of biomineralization, the one where there has been some study of microbiologically controlled mineralization. SRB have been observed to produce sulfide mineralization of Cu, Fe, Ni, Cd, Ag, Pb, and Ir (Baas-Becking and Moore, 1961). In some cases they can produce a sulfide of one metal on a substrate of another, or even on a silicate (Duncan and Ganiaris, 1987).

In the sulfide-rich reducing environment at the solid surface, minerals are formed that, while they persist for long periods at standard temperature and pressure (STP, 273 K, 1 atm.) because of slow kinetics, they are not stable in the bulk environment for thermodynamic reasons. The formation of such compounds, including covellite (CuS) and chalcocite (Cu_2S) on copper and mackinawite (FeS_{1-x}) and greigite (Fe_3S_4) on iron by SRB-containing consortia is well documented (Baas-Becking and Moore, 1961; McNeil and Little, 1990) and can, to a degree, be understood in terms of stability diagrams (Garrels and Christ, 1965). However, simple application of stability diagrams prepared for pure metals to alloys or to pure metals in groundwaters of complex ionic chemistry can lead to misleading predictions because of metastability or because of stabilization of phases by impurities. Eight different copper sulfides have been observed in SRB-induced corrosion of Cu-Ni alloys (McNeil et al., 1991); and five iron sulfides are characteristic of MIC (McNeil and Little, 1990).

11.7 MICROBIOLOGICAL CORROSION OF IRON

The SRB-influenced sulfidation of iron displays all three of the recognized types of biomineralization, and it was the first process in which microbiological corrosion was correctly identified (Gaines, 1910) and for which a mechanism was proposed (van Wolzogen Kuhr, 1934).

Iron and carbon steel are subject to SRB-intermediated reactions during use in connection with sour gas and related waters. There is also ample evidence of microbiologically induced corrosion under biofilms (Baas-Becking and Moore, 1961; Hamilton, 1985; McNeil and Little, 1990). Iron also displays the most studied case of a microbiologically controlled reaction, the simultaneous formation of pyrite and greigite in anaerobic magnetotactic bacteria (Bazylinski et al., 1990).

Consider the biomineralization of an iron surface under a biofilm containing SRB and an oxygen consumer. The original, uncolonized iron surface is generally coated with a very thin layer of dense magnetite, overlaid by more porous outer layers of magnetite and/or hematite, depending upon surface treatment. Fe^{++} must be solubilized, perhaps with the assistance of local acidification due to occluded cells; then the reactions:

$$Fe^{++} + HS^- \Leftrightarrow FeSH^+$$

$$2\,FeSH^+ \Leftrightarrow Fe_2S_2 + 2H^+$$

(very rapid)

$$Fe_2S_2 \Leftrightarrow \text{mackinawite}$$

appear to account for the formation of mackinawite, FeS_{1-x} (Goldhaber and Kaplan, 1975; Taylor, 1980). Berner (1970) showed that, when elemental sulfur is present, the mackinawite then alters to pyrite (FeS_2) without formation of any persistent intermediates in detectable amounts. However, alteration to pyrrhotite ($Fe_{1-x}S$) by way of greigite (Fe_3S_4) appears to be typical of microbiologically induced corrosion of iron (McNeil and Little, 1990), and this may be indicative that SRB, in the usual corrosion conditions, cannot produce significant elemental sulfur. The details of the reaction process and the role of smythite (Fe_9S_{11}), are not fully understood and appear to depend on the details of the suite of microorganisms in the biofilm (Bazylinski et al., 1993).

The apparent end product of such biomineralization can be any of several compounds. Thermodynamically, pyrite is the stable phase, and this is frequently observed in geological situations (Morse et al., 1987); pyrrhotite appears to be more common in engineering corrosion applications (McNeil and Little, 1990), though there are certainly cases when the sulfides oxidize to produce "green rust II," an oxidized sulfate mineral (Olowe et al., 1989).

11.8 MICROBIOLOGICAL CORROSION OF COPPER

The situation of SRB-induced mineralization of copper is even more confused. If one performs laboratory experiments on pure copper with SRB, the usual product is chalcocite (Cu_2S), though covellite (CuS), can be produced, and minor amounts of other minerals are sometimes observed. Corrosion in nature produces chalcocite as well as covellite (Baas-Becking and Moore, 1961; Gettens, 1963). If alloys are corroded, the situation is much more complex, and a number of other copper sulfide minerals are generated (McNeil et al., 1991).

A model for SRB-induced corrosion of copper and copper-nickel alloys that accounts for most of the observations is as follows. The copper surface, at the beginning of the reaction, is covered with Cu_2O. When the surface is colonized by a consortium of SRB and oxygen consuming bacteria, the cuprite is destabilized and solubilized in some way. This is in contrast to the nonbiological mineralization of copper artifacts by waters containing chloride, carbonate, or sulfate. In these cases, large amounts of cuprite are retained in the corrosion products, while in the case of SRB-induced corrosion, the cuprite is wholly consumed. The first sulfide corrosion product is chalcocite, Cu_2S, which precipitates on the surfaces of microbes and forms a very porous layer. If the groundwater contains significant iron, the precipitate may be chalcopyrite ($CuFeS_4$) instead.

In the case of pure copper, the first deposits of copper sulfide corrosion product are extremely porous and nonadherent. If the reaction is allowed to proceed for a few months, more and more chalcocite is formed. Only when the chalcocite/copper layer has receded some distance from the solid surface are compounds richer in sulfur formed in quantity. The final compound formed is generally blue-remaining covellite (CuS_{1+x}). Evidence from abiotic measurements (Woods et al., 1992) suggests that, so long as copper ions are available, all reduced sulfide is consumed as rapidly as it is produced, and alteration of chalcocite to more sulfide rich minerals can proceed only when there is no competing rapid sulfide consuming mechanism at the SRB surface.

The interaction of microbiological action with dealloying is significant. When an alloy corrodes in a natural environment, sometimes corrosion proceeds by the formation of a mixed cation mineral, for example:

$(Fe,Ni) \Leftrightarrow (Fe,Ni)_9S_8$	pentlandite
$(Fe,Ni) \Leftrightarrow Ni_6Fe_2CO_3(OH)_{16}.4H_2O$	reevesite
$(Cu,Zn) \Leftrightarrow (Cu,Zn)_2(OH)_2CO_3$	rosasite

On the other hand, the corrosion can proceed by dealloying. For example, in a Cu-Sn alloy, the Cu may dissolve and reprecipitate as a Cu mineral, or it may be transported away in solution (Geilmann, 1956; Robbiola and Fiaud, 1992), leaving an artifact with the approximate shape of the original bronze artifact but composed largely of tin or tin minerals. In different environments, Sn can dealloy from very similar alloys, leaving a copper mineral structure (Tylecote, 1979).

Dealloying is commonly observed and studied in laboratory environments, but the formation of mixed-cation minerals as corrosion products is generally observed only under natural conditions. This may be due to the biofilm acting to limit the escape of ions of the dealloying species, maintaining high local concentrations favorable to mixed-cation mineral precipitation. Biofilms may also be responsible for unusual physical forms observed in natural corrosion but not in laboratory experiments, such as botryoidal malachite [$Cu_2(OH)_2CO_3$]. Malachite, a familiar corrosion product on copper alloys, is common in geological setting in botryoidal form; that is, with a grape-bunch-like structure. This type of structure, common in geological situations, is scarce on archeological objects (Gettens, 1963; Zycherman, 1982) and is never seen in laboratory tests. Botryoidal rosasite [$(Cu,Zn)_2(OH)_2CO_3$] is also known in nature but it has never been formed in laboratory corrosion and appears to be unknown in archeological corrosion studies. This type of morphology may be due to control of mass transfer by biofilm effects.

11.9 CONCLUSIONS

Biomineralization reactions are important alteration mechanisms for a wide variety of solids. Believable projections of such reactions and estimations of rates over periods inaccessible to laboratory experimentation requires the construction and validation of models for very long-term corrosion behavior of waste packages. Validation of such models, and the codes based on them, is possible only through the study of the products of natural and archaeological corrosion and alteration and consideration of the reaction processes leading to these products as test cases for model validation.

11.10 ACKNOWLEDGEMENTS

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NATURAL GEOCHEMICAL ANALOGUES OF THE NEAR FIELD OF HIGH-LEVEL NUCLEAR WASTE REPOSITORIES

12

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12.1 ABSTRACT

United States practice has been to design high-level nuclear waste (HLW) geological repositories with waste densities sufficiently high that repository temperatures surrounding the waste will exceed 100 °C and could reach 250 °C. Basalt and devitrified vitroclastic tuff are among the host rocks considered for waste emplacement. Near-field repository thermal behavior and chemical alteration in such rocks is expected to be similar to that observed in many geothermal systems. Therefore, the predictive modeling required for performance assessment studies of the near field could be validated and calibrated using geothermal systems as natural analogues. Examples are given which demonstrate the need for refinement of the thermodynamic databases used in geochemical modeling of near-field natural analogues and the extent to which present models can predict conditions in geothermal fields.

12.2 INTRODUCTION

The disposal of HLW from commercial power reactors in subsurface geologic repositories is generally viewed as the most practical means of dealing with such material. The manner in which it is or will be emplaced underground varies from country to country. Among the variables are the type of waste, the duration of aging of the waste prior to emplacement, the packing density of the waste containers and the concentration of radioactive waste in the containers, the nature of the host rock, the use of engineered barriers, and whether or not the system will be saturated with water. All of these variables affect the maximum temperature excursion experienced in and around the repository after burial. Early practice in the United States was to design for maximum temperatures in water saturated host rock to range from about 160 °C in salt to 260 °C in basalt (Raines et al., 1981). These maxima would be attained close to the container-host rock interface and occur between 35 and 60 years after burial of the waste (Wang et al., 1979). The temperature of the waste would still be 50 to 100 °C above the ambient temperature in basalt, some 1,000 years after burial, and the region affected by elevated temperature would extend up to 500 m from the waste containers. The temperature in the presently proposed repository in the vadose zone at Yucca Mountain will not exceed 180 °C in the host rock adjacent to the waste some 15 years after closure (Tsang and Pruess, 1987; Tsang and Pruess, 1992). In other countries, for example, Switzerland and Japan, designs usually limit the maximum temperature to <100 °C to ensure minimal alteration of the bentonite clay barrier surrounding the waste containers.

Various arguments can be advanced for or against operating a waste repository so that temperatures significantly exceed 100 °C after closure. Advantages are that the repository is more compact and cheaper to build and that the thermal excursion of the repository host rocks will induce the formation of secondary minerals that act as radionuclide hosts in the event of container failure. On the other hand, fracturing and groundwater convection could be enhanced in water saturated systems, and physicochemical processes will occur that are more difficult to quantify.

Many questions arise regarding the consequences of near-field alteration when repository ambient temperatures significantly exceed 100 °C. How will the host rock alter and at what rate? How will alteration affect the permeability and porosity of the surrounding rock? Will radionuclides be retarded more effectively than they would in bentonite backfills below 100 °C? How will the groundwater composition be modified, and how will this affect the concentration of radionuclides in solution? What will be the effect of groundwaters interacting with the waste containers, and how will the oxidation state of the groundwater influence the secondary mineral composition? Hence, there are arguments for the more conservative philosophy of building a repository to operate at lower temperatures, where confidence in predicting the chemical behavior of backfill barriers and the surrounding host rock is enhanced by laboratory experiments and field observations at earth surface temperatures.

12.3 PERFORMANCE ASSESSMENT REQUIREMENTS

Performance assessment studies are conducted prior to construction of a repository in order to predict the fate of the radioactive waste, given all conceivable release scenarios. These studies involve the use of mathematical simulators whose purpose is to predict repository behavior for as long as the radioactive waste remains hazardous. Sometimes time periods of up to 100,000 years must be considered, although shorter durations are more common. In the United States, regulations require consideration of time periods of 50, 300, 1,000, and 10,000 years following waste emplacement. The first 50 years is the period of monitored retrievable storage required by U.S. Nuclear Regulatory Commission (NRC) regulations 10CFR, Part 60. The waste containers are also required under these regulations to retain their integrity for at least 300 years and up to 1,000 years after repository closure. The 10,000-year time period is the length of time that the radioactive waste must be isolated from the accessible environment as required by Environmental Protection Agency (EPA) regulations 40CFR, Part 191. Mathematical models should, therefore, be constructed to determine near-field system behavior and release scenarios in conformity with design criteria imposed by these regulations.

If radionuclides are released in a water saturated repository, they migrate through convective and advective groundwater transport and through diffusion. But they are also retarded by chemical interactions, such as adsorption, ion exchange or coprecipitation with the host rock. Simultaneously, the radionuclides decay to daughter products, some of which could also be hazardous. In the far field, where the host rocks are unaffected by thermal perturbations due to radioactive decay, radionuclide transport can be modeled assuming that the host rock matrix remains unaltered over the time interval during which the radionuclides remain hazardous. It may also be assumed that the system everywhere is locally at (metastable) equilibrium and that the temperature remains constant.

The implicit assumption that local (metastable) equilibrium is achieved in the far field automatically implies that the kinetics of chemical reactions are fast in relation to groundwater velocity, which commonly ranges from millimeters to meters per year. In consequence, laboratory experiments lasting, at most, a year can be conducted to measure far-field chemical reactions with a reasonable expectation that (metastable) equilibrium will be substantially achieved within the duration of the experiment. Modeling far-field phenomena is, therefore, concerned less with a comprehension of the chemical processes than with their quantification, and with other uncertainties, such as the physical heterogeneities of the rock and their effect on the hydrologic behavior of groundwater flow.

The near field, in contrast, is spatially constrained, and physical heterogeneities, while not necessarily quantifiable in every detail, will at least be observable during repository construction. The host rock matrix alters and, therefore, comprehension and quantification of radionuclide transport is much more difficult under such conditions, particularly if temperatures exceed 100 °C. Rock alteration takes place at elevated temperatures, and the system is not locally at equilibrium, because of the relatively slow reaction kinetics involved in mineral transformations and the nonisothermal nature of the near field, which varies both temporally and spatially.

The chemical processes in the near field are unlikely to achieve equilibrium in times sufficiently short to permit meaningful results to be obtained from laboratory or field experiments. Indeed, even if experiments were to be conducted for as long as 100 years, the duration would still be short compared to that needed to observe chemical phenomena of concern in the near field. For obvious reasons, it is impractical to consider such experiments as a basis for predicting repository behavior when decisions regarding the construction of a repository must be made in much less time. Therefore, some other means of acquiring the needed information must be found. The only practical approach is to observe natural analogues of the waste repository. Natural analogues must, therefore, play a vital role in elucidating near-field processes.

Models accounting for all relevant chemical and transport phenomena in the near field have not been developed. Even though partial models describing either the geochemistry, heat transfer, or hydrology are available, natural analogues are limited in their application until comprehensive simulators are developed. For performance assessments of the near field to be successful, both model development and natural analogue studies should be integrated in order to meet performance assessment needs.

12.4 STATUS OF GEOCHEMICAL MODELS

Complex systems comprising many chemical components and many phases at elevated temperatures require computational methods for their interpretation and quantification. Sophisticated geochemical models and suitable coding with supporting thermodynamic and kinetic data are needed to interpret natural analogue behavior for performance assessment. Relevant computer codes to solve geochemical models currently fall into four classifications: (i) calculation of phase equilibria, (ii) calculation of the distribution of species in the aqueous phase, (iii) reaction progress simulators, and (iv) reactive chemical transport simulators.

12.4.1 Calculation of Phase Equilibria

Codes to calculate phase equilibria, usually in the form of meshes of univariant curves in P-T space, are useful in defining the stability fields of secondary minerals in hydrothermal systems of the type likely to be encountered in the near field. Other features include the ability to plot phase diagrams as a function of P, T, and X, where X is some independently variable chemical component in the system. An example of such a code is GEO-CALC (Perkins et al., 1986; Berman et al., 1987; Brown et al., 1989). Another, SUPCRT92 (Johnson et al., 1992), permits calculations of the position of univariant curves in P-T space, as well as standard-state thermodynamic properties of phases as a function of pressure and temperature. Other computer codes of a similar type have been reported in the literature, for example, Powell and Holland (1988).

12.4.2 Distribution of Species

Many computer codes are available to perform the task of distributing species in solution using mass action and mass balance laws. Such codes are useful in interpreting groundwater analyses in relation to the thermodynamic parameters affecting their composition. Most codes in use in the United States employ the equilibrium constant approach as opposed to the mathematically equivalent free energy minimization approach to obtain a solution. An important feature of these codes is that they can also calculate whether the aqueous solution is saturated with respect to various minerals. Conversely, if a mineral assemblage is specified, the aqueous phase composition can be calculated. In rock dominated systems, such as the repository near-field environment, this capability is particularly useful, as it allows the calculation of the maximum possible concentration of radionuclides in the groundwater. Examples of such codes are EQ3 (Wolery, 1983, 1992), PHREEQE (Parkhurst et al., 1980), SOLMINEQ.88 (Kharaka et al., 1988), and SOLVEQ (Spycher and Reed, 1989). All permit calculation of solution equilibria at temperatures to 300 or 350 °C along with the water saturation surface. Other distribution of species codes are available that incorporate adsorption and ion exchange reactions, such as MINEQL (Westall et al., 1976; James and Parks, 1976), MINTEQ (Felmy et al., 1984; Krupka and Morrey, 1985), and ECHEM (Morrey, 1988). They might find limited application to near-field sorption phenomena, but are better equipped to deal with far-field chemical equilibria at 25 °C. In Russia, the Gibbs free energy minimization approach is preferred. Example codes include GIBBS (Shvarov, 1976; 1992) and SELECTOR++ (Karpov, 1981; Karpov et al., 1992). See also Mironenko et al. (1992).

12.4.3 Reaction Progress and Reaction Kinetics

Reaction progress codes simulate the evolution of a chemical system as a function of reaction progress, ξ, or as a function of time. The reaction progress variable is usually chosen instead of time, because so little is known regarding the rates of dissolution or precipitation of mineral phases. In using reaction progress codes, it is assumed that the reactants, such as the rock-forming minerals, dissolve according to a preset ratio, usually in proportion to their molar concentrations in the rock. Homogeneous equilibrium in the aqueous phase and reversible equilibrium with respect to product (i.e., secondary) minerals and the aqueous phase are assumed. With increasing knowledge regarding the dissolution kinetics of minerals, the reaction progress variable may be disregarded in favor of time as a variable. Indeed, this option has been included in one reaction progress code, EQ3/6, by Bourcier (1985). The principal reaction progress codes available at present are EQ6 (Wolery, 1984;

Wolery and Daveler, 1992), PHREEQE (Parkhurst et al., 1980), and CHILLER (Reed and Spycher, 1989).

12.4.4 Reactive Chemical Transport

Many reactive chemical transport codes are currently under development, and successful simulations reflecting various natural geochemical processes have been reported in the literature. Unfortunately, complex simulations reported so far are isothermal and have been conducted only at 25 °C. While satisfactory for far-field predictions, such modeling is of limited value for the near field. Non-isothermal simulations at elevated temperatures have been limited to relatively simple systems involving few chemical components, for example, CHMTRNS (Noorishad et al., 1987) and THCC (Carnahan, 1986). To properly model the near field, significant advances in the present capabilities of reactive transport simulators will be required.

12.5 GEOTHERMAL SYSTEMS AS NATURAL ANALOGUES OF THE NEAR FIELD

12.5.1 Selection of Natural Analogues of the Near Field

For natural analogues to be relevant and useful to performance assessment, several criteria should be met:

- Except for specialized partial validation needs, the analogue should be active, rather than extinct, that is, the chemical processes to be characterized should be going on at present.
- The temperature should be in the range between 25 and 300 °C.
- Water must be present, saturating or partially saturating the rock and be the primary agent involved in mass transport.
- The groundwater composition should be controlled by the host rock mineral assemblages.
- The chemical environment of the natural analogue should be similar to that of the repository, that is, the host rocks should be of a similar type and chemical composition.
- The natural analogue must be quantifiable in terms of the parameters used in the predictive models for performance assessment.
- The performance assessment simulators must incorporate thermodynamic and kinetic models that are relevant to both the repository and natural analogue environments.
- The natural analogue should be sufficiently well characterized to permit semi-quantitative, if not quantitative, estimates of chemical reaction rates.
- The magnitude of the natural analogue process and its lifetime should approximate that of a waste repository.
- Sufficient analogues should be available to permit multiple validations over a range of parameter values of significance to the repository near-field environment.

Finding a perfect analogue to a nuclear waste repository is probably impossible. Most will correlate with only some of the design criteria for the repository under consideration. For example, although the Oklo reactor in Gabon meets criteria for studying the fate of extinct radionuclides, the host rocks might differ from those of the planned repository. Because the Oklo reactor is extinct, it is not possible to examine the radionuclide transport mechanisms or the solubility of those radionuclides under natural conditions at elevated temperatures. In contrast, an active hydrothermal system could meet many of the criteria for host rock secondary alteration, but would not contain many relevant radioelements. Natural analogues of the near field, therefore, are never complete in every respect, and will necessarily provide only partial validation to predictive models. Examination of many natural analogues, however, should permit validation over a sufficiently broad range to give confidence in the predictive capabilities of the models.

Various rock types have been examined over the years as potential hosts for geologic repositories. They include granite (Canada, France, Sweden, Switzerland, United Kingdom, United States), clay (Belgium), basalt and vitroclastic tuff (United States), shale (Japan), and bedded salt (USA). Because of the interest shown by the United States Government in the burial of HLW in basalt and vitroclastic tuff, the use of natural analogues in such host rocks is emphasized in the remainder of this paper.

Basalts and tuffs are extrusive igneous rocks that are frequently associated with volcanically-driven hydrothermal systems. Active hydrothermal systems are of economic interest in many parts of the world as they can be exploited for geothermal energy. Such systems are often drilled to recover steam or heated water, and consequently, both their geology and geochemistry are sometimes characterized in considerable detail. These geothermal systems persist for hundreds and even thousands of years, because their heat source is usually an underlying magma body of substantial size. Heat transfer is accomplished through thermal conduction and convection of water in the rock fractures. Such mechanisms are also expected in HLW repositories, because heat transfer in geothermal systems is somewhat similar to the persistent heat production from decaying long-lived radionuclides. The temperature range of most geothermal systems also falls within the design range of planned waste repositories in the United States, although many geothermal systems are recorded with temperature maxima exceeding those contemplated in repositories. The composition of geothermal waters is also determined mainly by mineral alteration processes; that is, the system is "rock dominated" rather than "water dominated." Similar groundwater compositional control is expected in waste repositories. Although comparisons have not been made, the circulating volume of water in a convecting hydrothermal system is probably much larger in scale than that in a nuclear waste repository. Therefore, the closest analogues to a potential waste repository are probably not of commercial interest and have, therefore, not been examined closely. This divergence is one area that will require particular attention in modeling studies.

12.5.2 Alteration Mechanisms

Volcanic rocks often contain natural glass. The glass is unstable in geothermal systems and tends to decompose into suites of secondary minerals. Natural glasses decompose in a complex manner that is not fully understood. Observations reported in the published literature show that the alteration mechanisms are strongly influenced by compositional variations in the glass, which results in at least two distinct structural types (Apps, 1987). Rhyolitic glasses form an open "stuffed tridymite" type structure (Taylor and Brown, 1978) which can easily hydrate and exchange cations without destruction of the aluminosilicate framework. Such glasses sometimes remain in the vitreous state for tens of millions of years (Forsman, 1984). In contrast, glasses of basaltic composition do not appear to retain their vitreous aluminosilicate framework upon hydration, but decompose directly into a proto-smectite structure upon contact with liquid water, resulting in the formation of palagonite (Eggleton and Keller, 1982). Figures 12-1 and 12-2 taken from Apps (1987) illustrate schematically the sequence of steps believed to occur in rhyolitic and basaltic glasses. It should be noted in passing that the residual glasses in massive basaltic flows, such as are observed in Iceland or the Columbia River basin, can approach rhyolite in composition as a result of crystal differentiation.

Natural silicate glasses contain between 45 and 75 wt. percent SiO_2. If they were to dissolve and achieve equilibrium with the groundwater, they would supersaturate the solution with respect to both quartz and cristobalite. Figure 12-3, modified after Apps (1970), illustrates the solubility relationships between various silica polymorphs. If the glass were to consist only of silica, the mineral cristobalite would precipitate in preference to quartz because it is kinetically favored. It is generally true that the least stable mineral forms in preference to more stable phases when the solution is supersaturated with respect to all of them. Ostwald (1897), using thermodynamic arguments, reasoned that an unstable system would approach equilibrium through a sequence of progressively lower energy states. Although a more meaningful approach to explain the observed sequences, which are essentially kinetic in nature, would be through the application of classical nuclea-

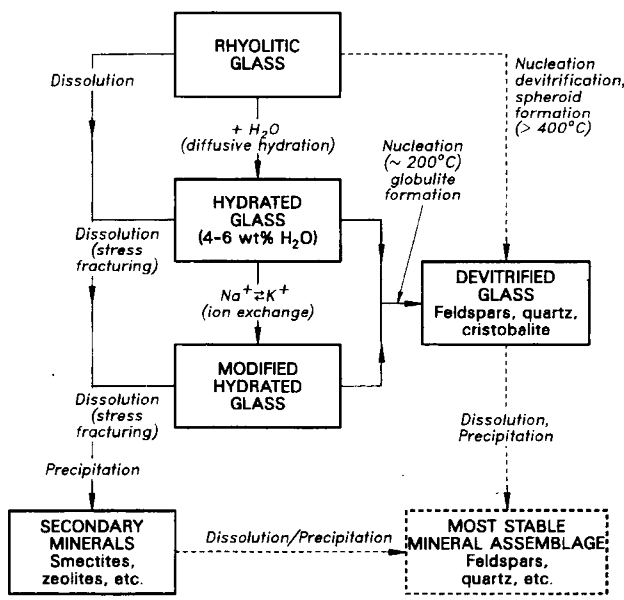

Figure 12-1. Schematic diagram to show the decomposition paths of rhyolitic glass when exposed to the aqueous phase

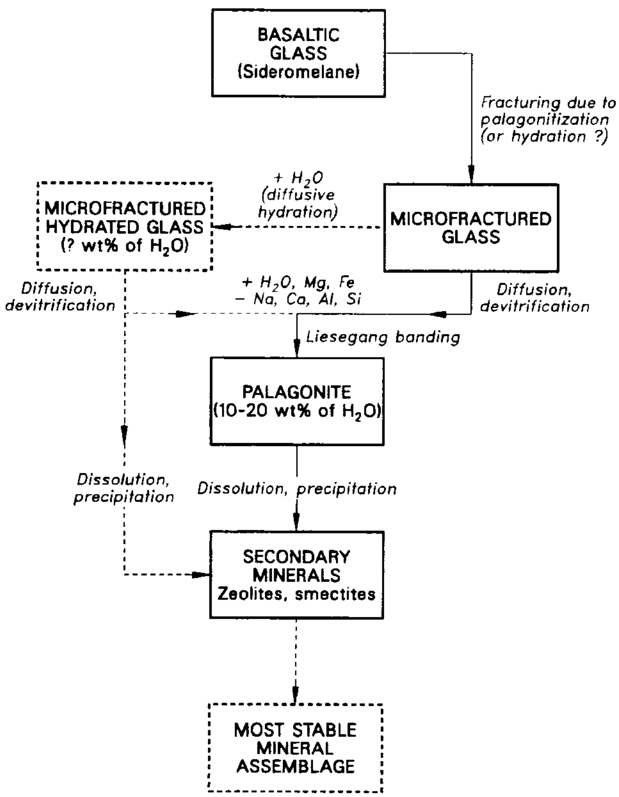

Figure 12-2. Schematic diagram to show the decomposition paths of basaltic glass when exposed to the aqueous phase

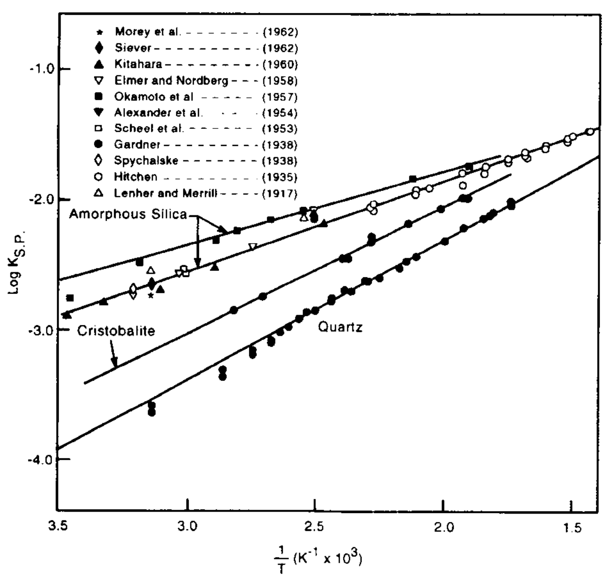

Figure 12-3. Solubility products of silica polymorphs as a function of temperature (Apps, 1970)

tion theory. No satisfactory explanation using the latter approach has been derived so far.

In hydrothermally altering vitric volcanic rocks, the so-called "Ostwald Rule of Stages" is amply demonstrated, a sequence of metastable phases forming that gradually decompose to more stable assemblages over time (Dibble and Tiller, 1981). With increasing temperatures in geothermal systems, the rates of dissolution and precipitation are enhanced, and, consequently, the glass and early formed least stable phases are rapidly destroyed, leaving more stable phase assemblages containing quartz. The secondary mineral assemblages observed in altering volcanics are, therefore, metastable assemblages that are not strictly in thermodynamic equilibrium, because they are slowly recrystallizing to progressively lower energy states represented by more stable mineral assemblages.

Dibble and Tiller (1981) have described the conceptual basis for such alteration as illustrated in Figure 12-4. Here, a more soluble phase, r, is dissolving. It releases its chemical components to the aqueous phase through a diffusion boundary of thickness, δ_{rs}. At some finite distance, x, from the reactant phase, a product phase, p, is precipitating. Phase, p, is also surrounded by a diffusion boundary, δ_{sp}. Transport between the diffusion boundaries shielding the reactant and product phases is accomplished in geothermal systems by aqueous diffusion and convective flow.

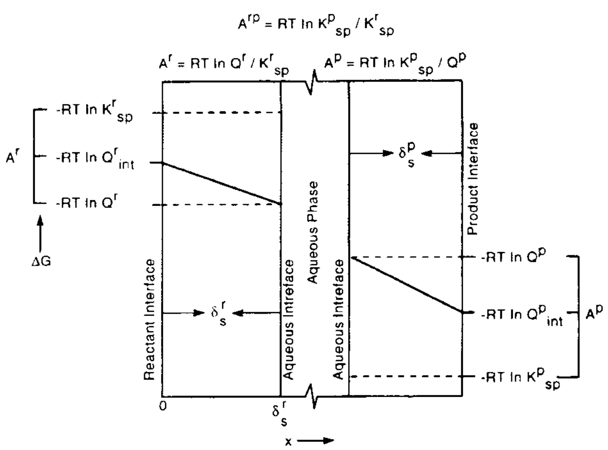

Figure 12-4. Schematic diagram to show thermodynamic and mass transfer considerations during irreversible dissolution and precipitation (Dibble and Tiller, 1981)

The affinity, A, of a chemical reaction is defined as

$$A = RT \ln K/Q$$

where Q is the ion activity product in the aqueous phase, which is negative for reactants and positive for products. Hence:

$$A^r = RT \ln Q^r/K^r_{sp}$$
$$A^p = RT \ln K^p_{sp}/Q^p$$
$$A^{rp} = Rt \ln K^p_{sp}/K^r_{sp}$$

Field evidence suggests that groundwaters in fractures and pores are relatively close to equilibrium with respect to secondary (metastable) minerals forming in a geothermal system, that is, A^p is small.

This conclusion can be inferred from the uniformity of groundwater compositions and mineral assemblages, as noted earlier, the commonly observed close approach to equilibrium with respect to quartz above 200 °C and the general level of crystal perfection in many zeolitic assemblages growing in host rock voids. Such perfection is unlikely at high degrees of supersaturation. As a first approximation, it may be assumed that groundwater in geothermal systems reflects a quasi-equilibrium state with respect to co-existing secondary mineral assemblages, provided that the sampling point is not in a region of rapid convection, or that the system has not been exploited extensively for geothermal energy. Because the accuracy of thermodynamic data of secondary minerals in geothermal systems is commonly less than that necessary to resolve A^p, the assumption that secondary minerals in geothermal systems are in equilibrium with the groundwater is a reasonable approximation at this time.

At relatively low temperatures, distinctive reaction rims penetrating vitric volcanic rock matrix blocks are sometimes observed, suggesting that the alteration rate of the rock matrix is the rate controlling step. But in most geothermal fields, the host rock is pervasively altered. Under these conditions, it is more likely that the secondary matrix minerals, rather than the residual glass, are the primary source of reactants in the aqueous phase. Because many of these minerals are fine-grained phyllosilicates, the excess surface free energy might provide the affinity, A^{rp}, for the crystallization of secondary minerals. Further study of the reaction affinities of altering rocks in geothermal systems is needed to resolve these issues

The isotopic dating of zeolitic assemblages and $\delta^{18}O$ and δD measurements in altering vitric volcanics could provide a wealth of information regarding the rates of crystal growth. Together with kinetic models of glass alteration and grain coarsening (Ostwald ripening), such information could allow scoping studies to be made of the actual rates of alteration in geothermal systems, and could predict near-field rock alteration in a repository.

In basalts, the mineral zonation observed as a function of temperature is very consistent, although minor variations can be attributed to compositional variations in the basalt (Walker, 1960 a,b), or if seawater rather than meteoric water is present. Figure 12-5 shows the approximate zonation associated with alteration in Icelandic basalts summarized from several investigations (Apps, 1983). Surprisingly, very similar zonations are observed, often with identical secondary mineral assemblages, although in different proportions, in volcanic rocks with compositions ranging through andesitic to dacitic, and even rhyolitic. Similar zonation is even observed in hydrothermal systems occupying sedimentary terrains, such as those at the Salton Sea, California, and Cerro Prieto, Baja, California.

The mineralogical uniformity suggests strongly that the composition of the groundwater coexisting with altering volcanic rock might also show a similar consistency. This indeed proves to be the case for basaltic terrains, as is illustrated in Figure 12-6. In this figure, the calculated log activity ratios of major chemical components are plotted as a function of temperature from data by Arnorsson et al. (1983) of waters taken from wells from several different geothermal fields in Iceland. The values were calculated using the EQ3 code (Wolery, 1983). The temperature-dependent trends of all illustrated component activity ratios are quite systematic, with a scatter of about ±1–1.5 log unit. Most of the scatter is probably due to errors in the estimated pH, (-log[H^+]), as other element activity ratios not incorporating [H^+] show smaller deviations, for example, log [Na^+]/[K^+], and log [SiO_2(aq)], illustrated in Figure 12-7. Groundwater compositions from other geothermal systems in rocks varying from basic to acidic also display similar temperature-dependent ion activity ratios. Consistent temperature-dependent trends in the fugacities of various gases from geothermal fields are also observed as illustrated by D'Amore and Gianelli (1984). Figure 12-8, adapted from their paper, shows a sympathetic variation in the calculated fugacity of oxygen and sulfur from several geothermal fields, these

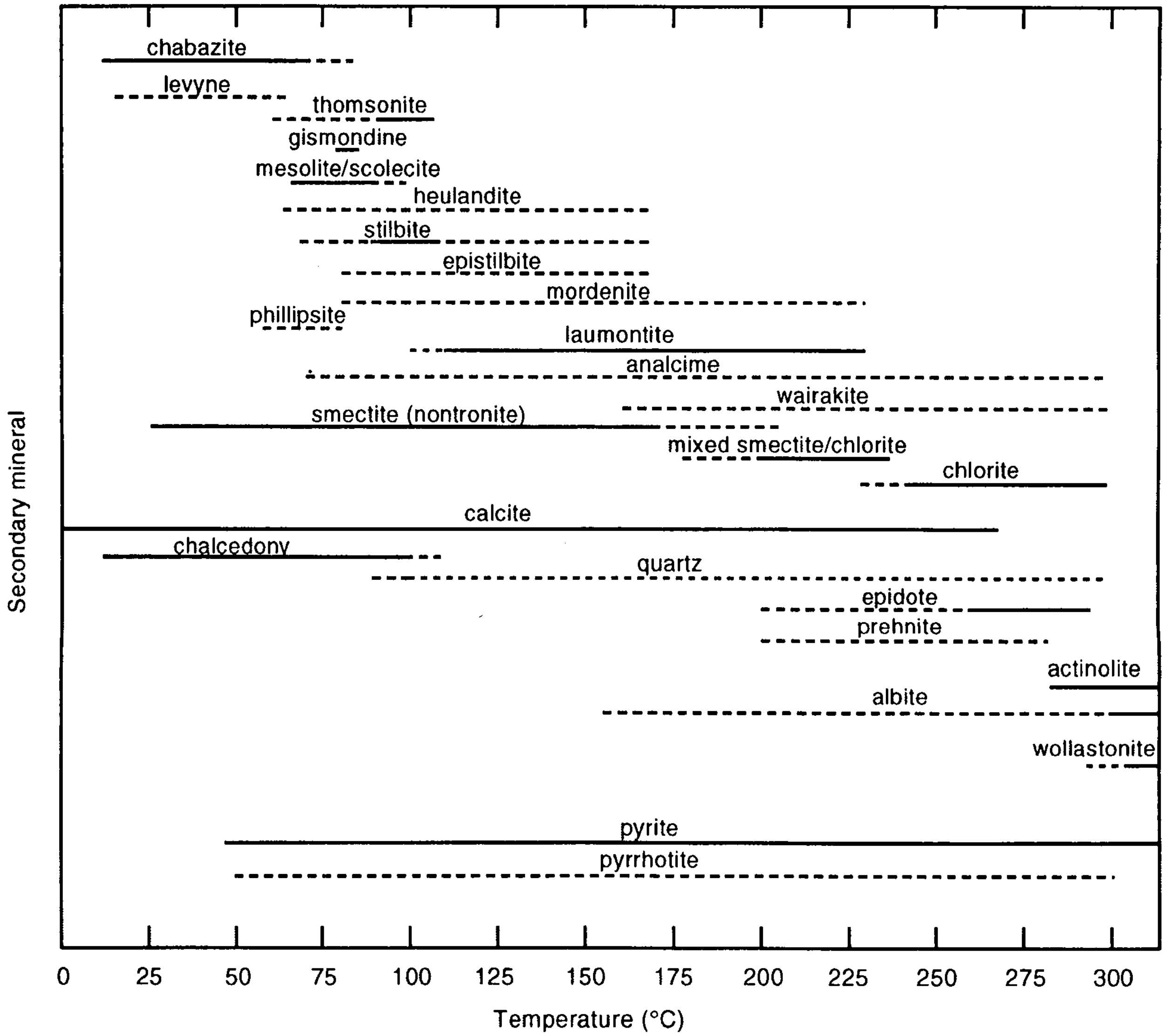

Figure 12-5. Observed stability ranges of secondary minerals in hydrothermally altered Icelandic basalts

fugacities being based on observed H_2, CH_4, CO_2, and H_2S concentrations in the steam phase from producing wells.

The remarkable correlations in secondary mineralogy and groundwater and vapor phase chemistry between geothermal fields strongly suggest that a geochemical model describing the hydrothermally altering volcanic rocks could not only be validated over a wide range of volcanic rock types and temperatures, but could also be used in predicting the thermodynamic behavior of rock alteration around HLW in similar host rocks.

12.5.3 Application of Geochemical Models

Geothermal systems can be used at several levels for the development of geochemical models of near-field behavior. They can be used:

- for the description of the mineralogy and distribution of secondary alteration at the observational level
- for the purpose of calibrating equilibrium rock-water models
- for the formulation and calibration of nonequilibrium kinetic models obeying the Ostwald Rule of Stages

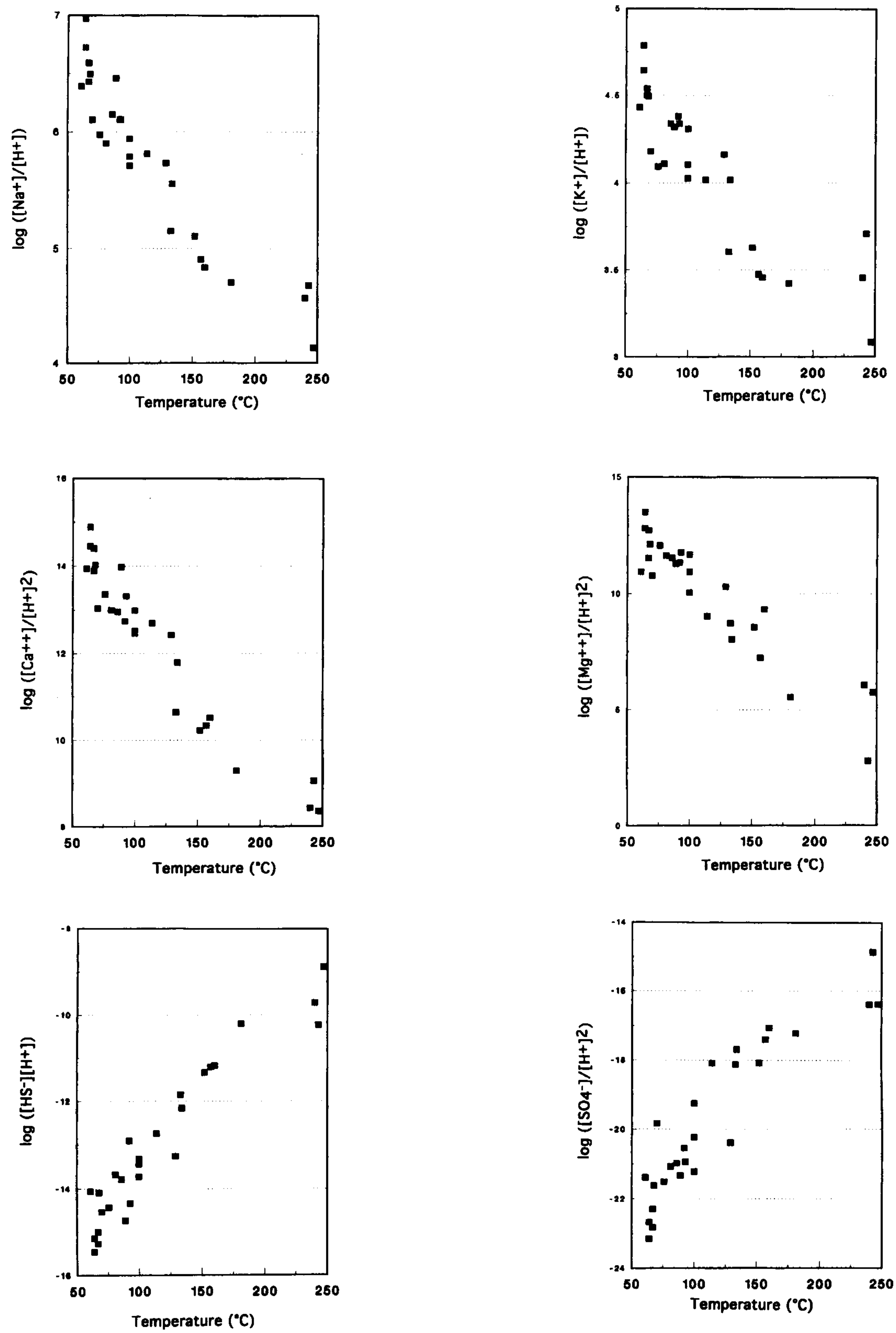

Figure 12-6. Activity ratios of major elements as a function of temperature in well water from Icelandic geothermal wells (calculated from chemical analyses cited in Arnorsson et al., 1983)

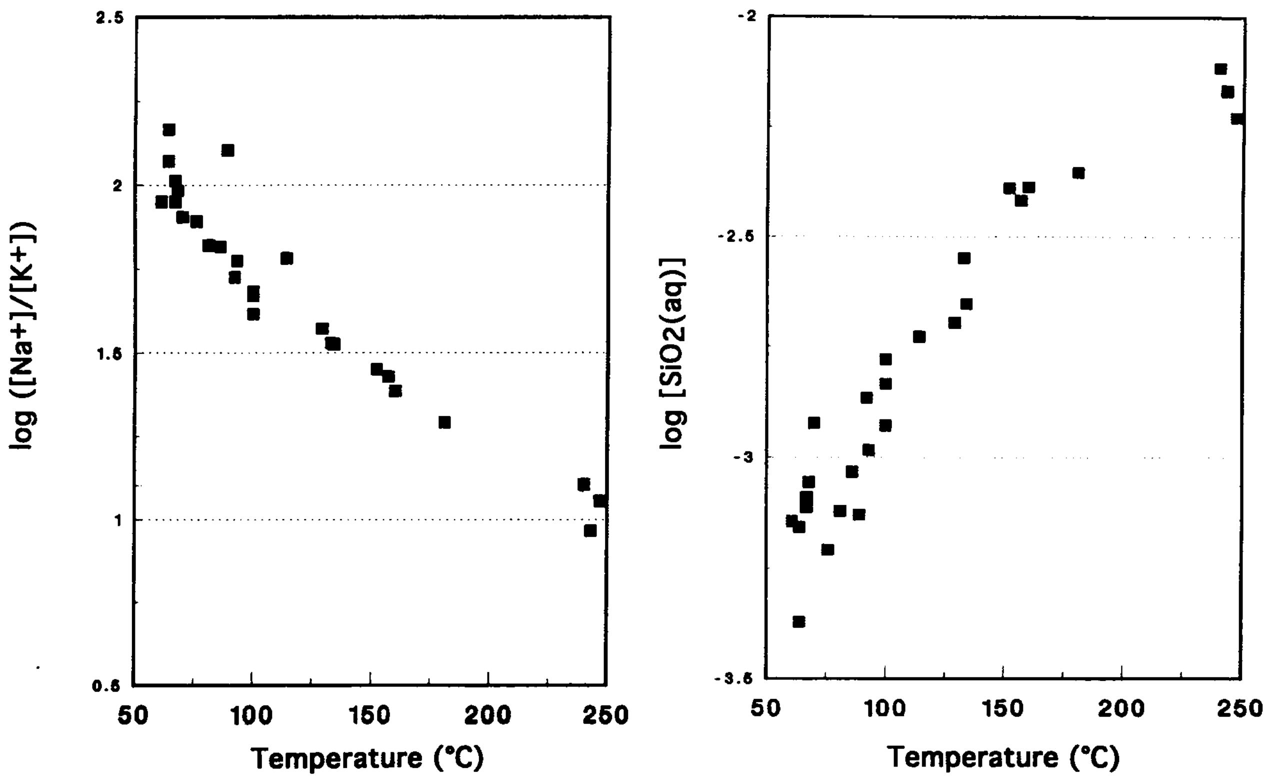

Figure 12-7. Activity ratio of $[Na^+]/[K^+]$ and saturation index of quartz as a function of temperature in well waters from Icelandic geothermal wells (calculated from chemical analyses cited in Arnorsson et al., 1983)

- for the repeated partial validation of reactive geochemical transport models simulating near-field behavior.

In order to make the modeling efforts tractable, the development work should be broken down into the steps enumerated above. In the following sections of this paper, the author discusses his experience in addressing the second level of modeling, that is, the procedures adopted in analyzing and interpreting samples of geothermal fluids taken from geothermal wells, as well as that of developing models of geothermal waters in equilibrium with secondary mineral assemblages.

The principal uncertainty with the application of such model development to a waste repository in volcanic rocks is the degree of alteration. The cumulative quantity of heat released by the waste is relatively small compared with geothermal fields having commercial potential. It would be desirable to study small geothermal fields with transient heat production, but, as noted earlier, such fields are of limited economic interest and are, therefore, unlikely to be studied in sufficient detail. Another problem concerns the behavior of the long-lived hazardous radionuclides in such an environment. These radionuclides include actinides, such as ^{241}Am, ^{237}Np, $^{238,239}Pu$, ^{233}U and fission products, such as ^{135}Cs, ^{59}Ni, ^{107}Sn, ^{129}I, ^{79}Se, ^{126}Ra, and ^{14}C. Very little of a quantitative nature can be derived from the geothermal analogues regarding the transport of the transuranic actinides, as their presence in nature, even under favorable conditions, is at vanishingly small concentrations. The chemical behavior of fission radionuclide elements can be investigated, however, even though the concentrations in natural systems might differ significantly from those in a repository. Of particular interest is variation of the concentration of the radioelement in solution as a function of temperature and its concentration in coexisting secondary minerals in a geothermal system. Such information, in conjunction with geochemical models, could be used to validate partially a geochemical transport model concerning those radioelements.

Information that is incidental to the mobilization of elements can also be derived by studying the loss of coherence between immobile and potentially mo-

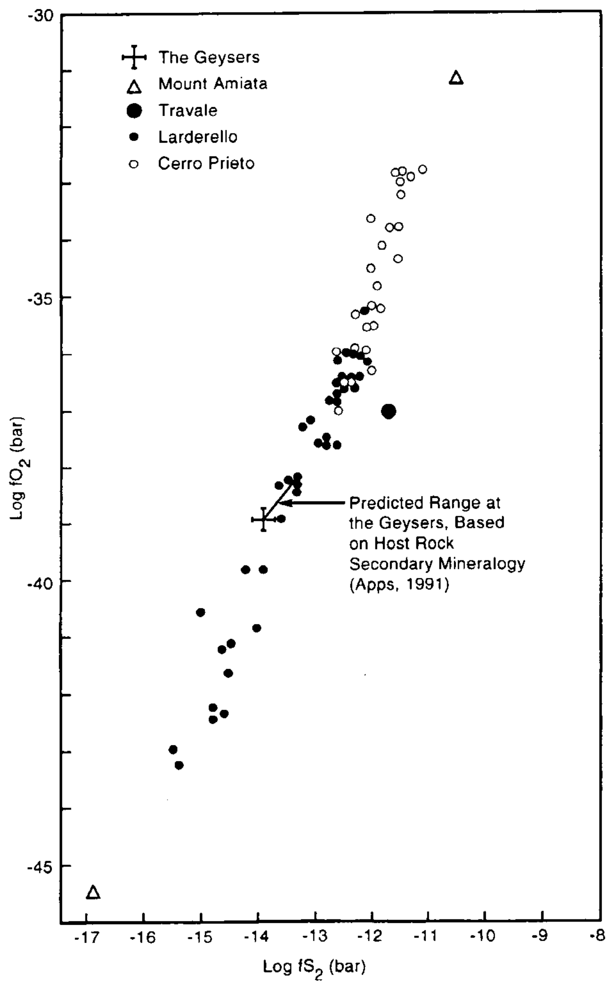

Figure 12-8. Variation in log fO2 versus fS2, calculated from volatile and noncondensible gas concentrations in stream from various geothermal fields (D'Amore and Gianelli, 1984)

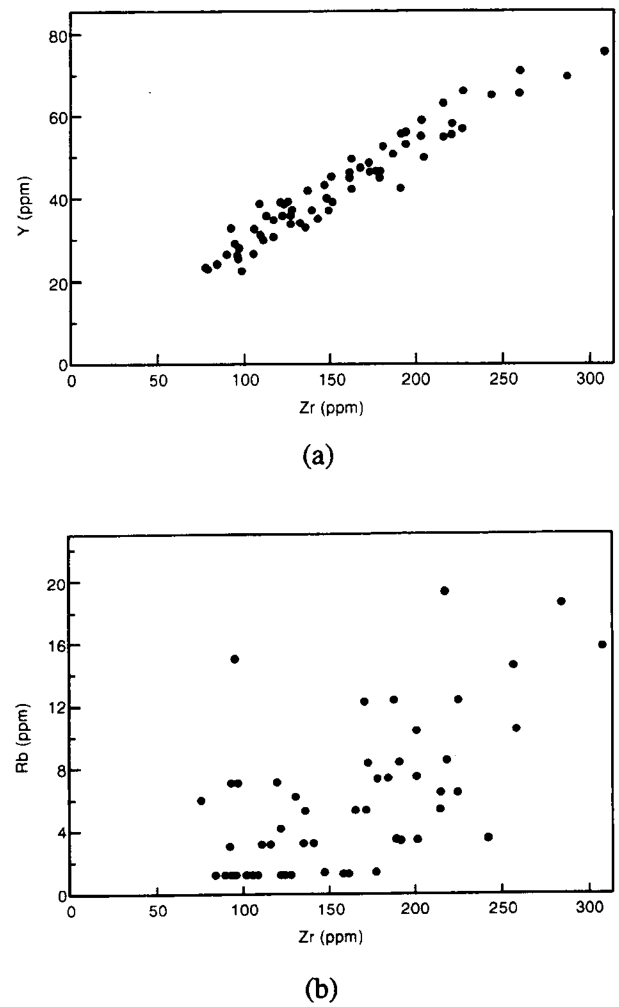

Figure 12-9. Dispersion of yttrium and rubidium in relation to zirconium in Icelandic basalts (Wood et al., 1976)

bile elements in volcanic rocks during hydrothermal alteration. This is illustrated in Figures 12-9a and b, from Wood et al. (1976), which show the relationship between yttrium and zirconium and rubidium and zirconium in altered Icelandic basalts. Zirconium is extremely insoluble in geothermal waters, and is, therefore, unlikely to be mobilized in a volcanic rock when altered. Yttrium, a trivalent rare earth element, is likewise unlikely to be mobilized and will remain in aluminosilicate structures. In contrast, rubidium, an alkali metal, is easily solubilized and dispersed during alteration. This is reflected in the substantial scatter in the correlation plot illustrated in Figure 12-9. Similar comparisons could be made of the dispersion of other radioelements versus zirconium.

12.6 VALIDATION OF AQUEOUS GEOCHEMICAL MODELS THROUGH WELL WATER ANALYSIS FROM ACTIVE GEOTHERMAL SYSTEMS

12.6.1 Background

Geochemical codes necessarily require extensive thermodynamic data, $\Delta H^{\circ}_{f,298}$, S°_{298}, C°_{p} (T) for example, and V° for minerals and the corresponding partial molal properties of aqueous species in order to calculate thermodynamic relations between minerals and the coexisting aqueous phase. Creation of databases of the needed scope for such modeling is costly in time and effort. Therefore, existing critically evaluated, internally consistent thermodynamic compilations, for example, those by Helgeson et al. (1978), Robie et al. (1979), Berman (1988), Holland and Powell (1990) for minerals, and those by Tanger and Helgeson (1988), Shock and Helgeson (1988) and Shock et al. (1989) for aqueous species are used, together with miscellaneous data of dubious heritage, to fill omissions in the primary sources. Most of the mineral thermodynamic data in the above cited references have been compiled from a systematic analysis of high-temperature, for example, 400 °C, phase equilibria to define univariant curves in P-T space, coupled with a smaller data set obtained from low- and high-temperature calorimetric studies. The resulting data are represented in the standard state at 298.15 K and 1 atm or 1 bar pressure, which necessitates significant extrapolations from the temperatures and pressures at which the phase equilibrium measurements were made. To be assured that such extrapolations are meaningful, accurate corrections for C_P^o and V^o must be made, and the participating phases must be adequately characterized, for example, order-disorder phenomena, the existence of displacive phase transitions, variations in chemical composition, crystallographic properties, crystallite size, evidence for metastable equilibrium or nonattainment of equilibrium, etc., in addition to such frequently observed details as the uncertainties in temperature and pressure. Unfortunately, many of these important factors were not reported in the earlier literature, from which most of the current thermodynamic data have been derived. The data are, therefore, of questionable accuracy for the evaluation of natural waters over the temperature range of 0–300 °C, the range of interest for performance assessment studies.

In contrast to the abundance of published phase equilibrium studies at elevated temperatures, studies reporting aqueous solubility measurements of minerals are sparse in the critical 0–300 °C range, and they are confined mainly to salts, such as carbonates, sulfates, and phosphates. With the exception of quartz and its polymorphs, few solubility studies are available for any aluminosilicates commonly found in geothermal systems. In principle, it should be possible to measure mineral equilibria in aqueous solutions quite precisely in the laboratory, as temperature and pressure can be closely controlled, and the chemical components in solution can normally be analyzed with an accuracy of less than ±5 wt. percent. Unfortunately, many experimental uncertainties make successful determinations a difficult proposition. Questions concerning the damage to the crystal structure during sample preparation, incongruent dissolution, metastability, nonattainment of reversible equilibrium, or the extreme duration of experiments required to demonstrate reversible equilibrium, the characterization of microscopic amounts of secondary product phases, problems in measuring pH, and difficulties associated with sample collection, preservation and analysis all degrade the accuracy of the resulting data. Problems of data reduction due to the presence of ill-defined complexation, uncertainties regarding the true pH, or correction for activity coefficients in strong mixed electrolytes also increase the difficulties of satisfactory interpretation of experimental results and render such investigations a challenge to the most dedicated investigator. Furthermore, the systematic study of mineral solubilities at elevated temperatures is expensive. Therefore, it is unlikely that resources will be available in the near future to conduct the experiments needed to validate the required thermodynamic databases. An interim solution to this dilemma is to use natural analogues as a means of validating and/or calibrating the thermodynamic database.

Calculations of mineral solubilities from chemical analyses of geothermal well waters would initially appear to be an even more daunting task than that of acquiring thermodynamic data by other means. Groundwaters might not be in equilibrium with coexisting minerals, mixing and convection or advection could be taking place, and the collection of samples could be difficult and involve contamination or the loss or gain of volatiles and gases. The cooling of the sample during and after collection might cause transient precipitation or adsorption of chemical components before chemical analysis. Yet there are also significant advantages. The well water has often been in contact with the host rock for hundreds or even thousands of years, allowing for closer approach to (metastable) thermodynamic equilibrium than is achievable in the laboratory. Groundwater samples can be collected in relatively large sample volumes, and their transit from the host rock environment to the surface is short, if collected from a producing well. As a consequence, groundwaters are often closer to equilibrium with respect to secondary minerals than is achievable in solubility studies in the laboratory, and, if the problems inherent in the collection and handling of natural samples can be overcome, groundwaters could prove to be better indicators of thermodynamic equilibrium than laboratory experiments.

Recognition that the groundwater can be close to equilibrium with respect to certain minerals is not new, (Garrels and Christ, 1965; Browne and Ellis, 1970; Arnorsson et al., 1983; Gunlaugsson and Arnorsson, 1982; Senderov, 1980; Aargaard and Helgeson, 1983), but studies that demonstrated this were generally conducted with objectives limited to illustration or the independent prediction of the thermodynamic properties of isolated minerals, rather than for the comprehensive validation of a complex geochemical model. An exception is the already cited work of Arnorsson et al. (1983), who not only developed their own thermodynamic database and model (Arnorsson et al., 1982), but also analyzed a large number of groundwaters from geothermal wells and hot springs.

In order to test the above approach, the author conducted such a study using information in the published literature. Chemical analyses of groundwaters covering a range of host rocks and temperatures were assembled. Wherever possible, mineralogical descriptions of the host rocks were also compiled. The quality of mineralogical information varied greatly. In several cases, mineralogical data were obtained from sources spatially separated from the formation from which the water sample was drawn, but where the temperature profile and rock type was similar. The thermodynamic database used for the study was compiled by Berman (1988), augmented with data from Helgeson et al. (1978) and the calculated thermodynamic data for clays from Wolery (1978), corrected using a more generally accepted Berman (1988) value of $\Delta H_{f,298}$ for corundum. Solubility products for all minerals were calculated using the thermodynamic data for aqueous species compiled by Tanger and Helgeson (1988), Shock and Helgeson (1988), and Shock et al. (1989) and incorporated in the 1987 version of SUPCRT, a revised version of which is now available (Johnson et al., 1992). Solubility product data at 0, 25, 60, 100, 150, 200, and 300 °C were formatted for entry into the database of a somewhat modified 1986 version of EQ3 (Wolery, 1983).

12.6.2 Evaluation of Chemical Analysis

The first step in evaluating the groundwater is to check the quality of the chemical analysis by performing an initial distribution of species at the temperature at which the pH was measured and checking for consistency between charge balance, pH, alkalinity, pCO_2, and the gross chemistry of the sample. If the conductivity of the sample had been measured, it should be compared with that calculated by the method of A.P.H.A. (1985). Sometimes it was found necessary to compare the chemical analysis with those obtained in neighboring wells to identify discrepancies in individual components. Where no obvious source of error could be identified, balancing on Cl^- was preferred to achieve electrical neutrality, as this component does not significantly affect the calculated ion activity products of minerals. These initial comparisons were usually successful in identifying gross errors and the chemical component(s) requiring adjustment to achieve electrical neutrality. With high-quality chemical analyses, only minor correction(s) to one or two species of a magnitude of less than 5 wt. percent, were required, which is well within the magnitude of uncertainties due to other causes. The *in situ* groundwater composition was then reconstituted at the measured down-hole temperature, adjustments being made for the loss of volatiles and gases and the amount of steam flashed from the sample, when such had occurred prior to sampling, electrical neutrality being maintained in all these corrections.

12.6.3 Comparison of Calculated Saturation Indices with Mineralogy

As an initial test of the model, derived analyses of producing wells for Icelandic basalts by Arnorsson et al. (1983) were evaluated. Calculated saturation indices of selected minerals as a function of temperature are illustrated in Figure 12-10. Although the scatter of the data in some cases was greater than desired, most mineral saturation indices fell within the range expected, or they revealed systematic deviations suggestive of errors estimated in the thermodynamic properties of either the minerals or the chemical potential of one or more of the aqueous components. Results were sufficiently encouraging to broaden the scope of the study to include analyses from deep-seated groundwaters and well waters on a worldwide basis. In the following paragraphs, some illustrations reflecting the thermodynamic validation possibilities are given with respect to such a global data set, and some unresolved issues are raised that require further study.

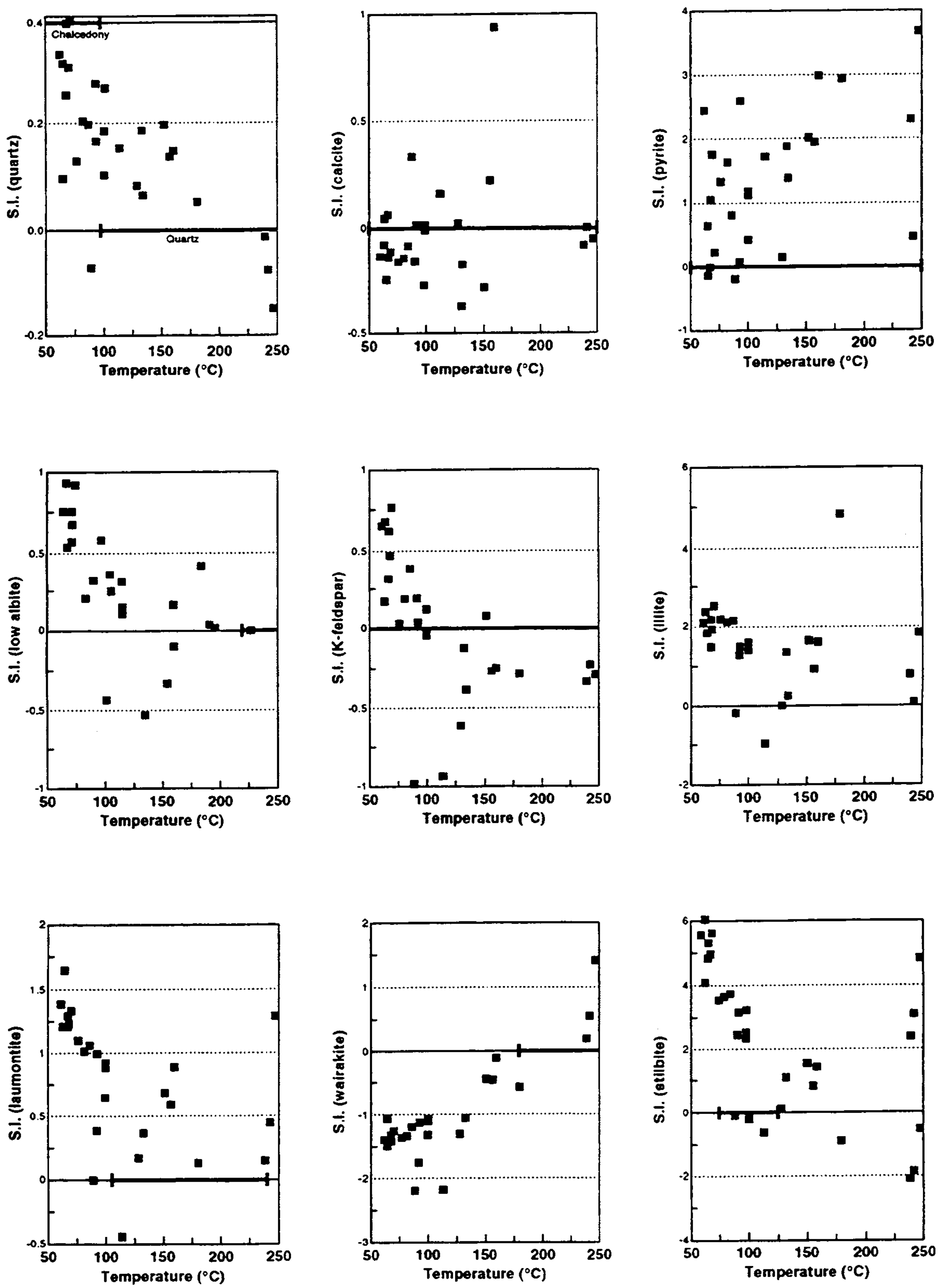

Figure 12-10. Saturation indices of quartz, calcite, pyrite, low albite, potash feldspar, illite, laumonite, wairakite, and stilbite as a function of temperature in Icelandic well waters. Horizontal bars represent temperature ranges of observed occurrences (chemical analyses cited in Arnorsson et al., 1983).

12.6.4 Refinement of the Gibbs Free Energy of Minerals from Field Data

12.6.4.1 Potash Feldspar and Low Albite

For many years, the element concentration ratio, Na/K, in the liquid aqueous phase has been used to estimate the source region temperature of hot springs and geothermal effluent. As a concentration ratio, it possesses the advantage that it is unaffected by transient boiling or condensation, and it is affected only slowly by conductive cooling. Fournier and Truesdell (1973) recommended its use only where source region temperatures are greater than 150 °C.

The thermochemical basis for the Na/K geothermometer is not well defined. Usually, discussion centers on the "exchange" reaction between plagioclase (low albite) and potash feldspar (adularia or microcline)

$$NaAlSi_3O_8 + K^+ = KAlSi_3O_8 + Na^+ \qquad (1)$$

where

$$\log K(T) = \frac{[Na^+]}{[K^+]} \qquad (2)$$

Past attempts to reconcile field observations with calculations using published thermodynamic properties of the participating species have not been particularly successful, greater faith being placed on the accuracy of thermodynamic data obtained from calorimetric studies and phase equilibrium than on groundwater analyses.

The coexistence of secondary low albite and potash feldspar in geothermal systems is frequently mentioned in the literature. Tomasson and Kristmannsdottir (1972), in discussing mineral alteration in the geothermal area of Reykjanes, Iceland, refer to the occasional presence of albitized plagioclase, as well as the sporadic occurrence of newly formed potash feldspar in all geothermal holes. Mehegan and Robinson (1982) and Viereck et al. (1982), in describing secondary hydrothermal alteration in the Reydarfjordur drill core from Eastern Iceland, mention that low albite and adularia coexist in most of the intersected volcaniclastic ricks, whereas authigenic albite replaces primary plagioclase crystals in some of the interdigitated basaltic flows. Browne and Ellis (1970) noted the presence of adularia and secondary albite in hydrothermally altered intermediate and acid lavas and volcaniclastic rocks intersected by boreholes in the Ohaki-Broadlands hydrothermal area in New Zealand. On the Kamchatka Peninsula, Naboko et al. (1965) refer to secondary adularia and albite in dichotic and andestic volcaniclastics of the Pauzhetka geothermal field, whereas Trukhin and Petrova (1974) describe alteration zones containing secondary albite and adularia in andesitic lavas and andesitic and dichotic tuffs of the Bolshe-Bann geothermal field.

In contrast, the coexistence of low albite with potash feldspar is never mentioned in mineralogical studies of cores penetrating sea floor basalts, where the temperature ranges from between ~4 and 70 °C. Frequent reference is made instead to the presence of potash feldspar, sometimes replacing plagioclase. Plagioclase in sea floor basalts is commonly replaced by secondary clays instead of low albite. Analcime is also observed as an authigenic phase, although it is rarely found in basalts saturated with meteoric waters at similar temperatures. As noted earlier, minor variations in mineral assemblages can be expected. Whether this particular deviation is due to the lower temperatures, the presence of seawater, or some other cause remains to be studied further.

Because of extensive mineralogical observations confirming the coexistence of secondary low albite and potash feldspar in geothermal fields and the consistency of groundwater compositions, it is reasonable to assume that the Na/K ratio in the aqueous phase reflects a near equilibrium state between these two minerals.

In Figure 12-11, the calculated values of log K(T) for Eq. (1), using $\Delta G^{\circ}_{f,298}$ for low albite and potash feldspar from Helgeson et al. (1978), Robie et al. (1979), Berman (1988), Holland and Powell (1990), and Kiseleva et al. (1990), are compared with the analytical determinations of the Na/K ratio in well waters from geothermal fields and deep water-saturated formations from around the world. Field temperatures were measured down hole or computed from well discharge data. The log K(T) values are calculated along the water saturation curve, employing the entropies of low albite and potash feldspar cited by Robie et al. (1979), accepted by all sources, and Maier-Kelley heat capacity functions, cited by Helgeson et al. (1978), for low albite and potash feldspar. The thermodynamic properties for the ionic species, Na^+ and K^+, are given by Shock and Helgeson (1988). The illustrated uncertainty is estimated from those given in the cited references.

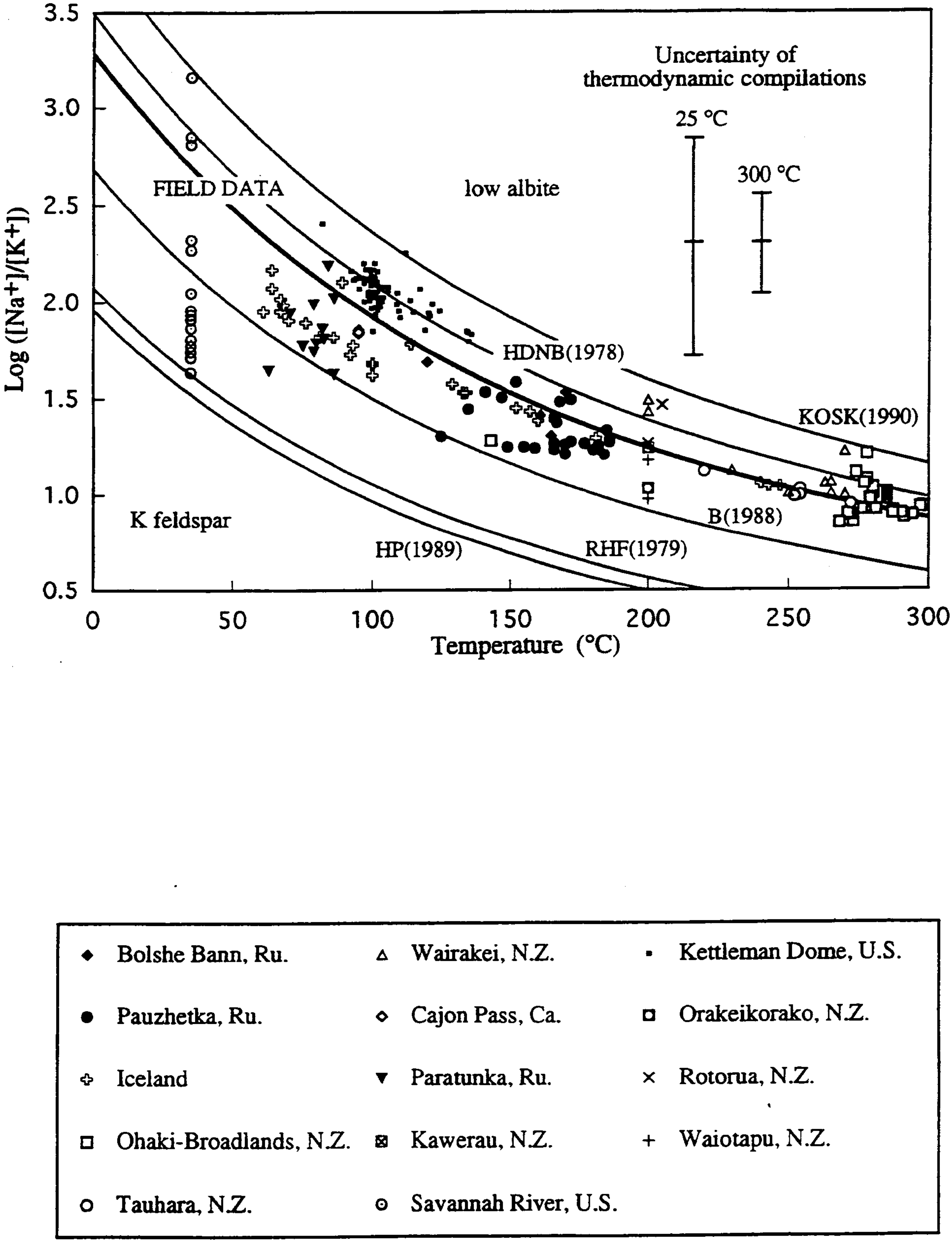

Figure 12-11. Log $[Na^+]/[K^+]$ calculated from compiled thermodynamic data as a function of temperature, compared with the corresponding ion activity products from geothermal well waters

The field data are generally consistent and can be fitted by a univariant curve, positioned as indicated on Figure 12-11 to within ±0.2 log(Na^+)/(K^+) or 1 kJ in ΔG_r° for reaction (1) at 25° and 2 kJ at 300 °C. This contrasts with an uncertainty of nearly 3.5 kJ for the log K(T) predicted from calorimetry of phase equilibrium measurements. The fitted curve closely follows the equation proposed by Fournier (1981) for the Na/K geothermometer and the data reported by Il'in et al. (1979) for the Pauzhetka geothermal field, but it does not fit the latter investigators' data from the lower temperature Paratunka field in the same region.

The chemical analyses of geothermal wells below 200 °C reported by Arnorsson et al. (1983) include aluminum concentration. The saturation indices of low albite and potash feldspar can, therefore, be computed for those well waters and their solubility products compared with those predicted from calorimetry and high-temperature phase equilibria. The results, illustrated in Figure 12-10, show the saturation indices referenced to the data by Berman (1988), who used the thermodynamic properties of low albite taken from Hemingway and Robie (1977). The saturation indices of both feldspars show trends towards supersaturation below 100 °C, which might be indicative of the sampled waters originating at temperatures higher than those measured. In spite of the scatter, the saturation indices suggest that $\Delta G_{f,298}^\circ$ of low albite is more nearly correct than that of potash feldspar in Berman's database.

A correction to $\Delta G_{f,298}^\circ$ for potash feldspar alone using the field correlation of Na/K yields a revised value, which is 6.3±3.7 $kJ.mol^{-1}$ more negative than that of Robie et al. (1978) or 3.2±3.7 $kJ.mol^{-1}$ more negative than that of Berman (1988), but it is 5.6±3.7 $kJ.mol^{-1}$ less negative than $\Delta H_{f,298}^\circ$ of microcline determined by Kiseleva et al. (1990).

12.6.5 Laumontite and Wairakite

The correlation of the Gibbs free energy of low albite and potash feldspar is but one of several exercises in the calibration of mineral thermodynamic properties using geothermal fluids and groundwaters. Other examples include the coexistence of laumontite or wairakite with low albite and potash feldspar, represented by the equilibrium reactions:

$$\underset{\text{laumontite}}{CaAl_2Si_4O_{12}.4H_2O} + \underset{\text{quartz}}{2SiO_2} + Na^+ + K^+ = \underset{\text{low albite}}{NaAlSi_3O_8} + \underset{\text{potash feldspar}}{KAlSi_3O_8} + Ca^{++} + 4H_2O \quad (3)$$

and

$$\underset{\text{wairakite}}{CaAl_2Si_4O_{12}.2H_2O} + \underset{\text{quartz}}{2SiO_2} + Na^+ + K^+ = \underset{\text{low albite}}{NaAlSi_3O_8} + \underset{\text{potash feldspar}}{KAlSi_3O_8} + Ca^{++} + 2H_2O \quad (4)$$

where

$$K = \frac{[Ca^{++}]}{[Na^+][K^+]} \quad (5)$$

An attempt at calibrating the Gibbs free energies of laumontite and wairakite using a similar scheme was first made by Senderov (1980). Figure 12-12 is a comparison between the logarithm of ion activity products calculated from analyses of geothermal waters and log K calculated from thermodynamic data of the participating minerals. The low albite and potash feldspar Gibbs free energies were like those described in the preceding section. Those of laumontite and wairakite were calculated from phase equilibrium and heat capacity measurements. There appears to be a discrepancy of approximately 0.7 in log K between predicted and field values. The causes of the discrepancy have yet to be identified, but may be due in part to attainment of equilibrium with respect to cristobalite below 150 °C. Line A–A' represents the position of the reaction:

$$\underset{\text{laumontite}}{CaAl_2Si_4O_{12}.4H_2O} + \underset{\alpha\text{-cristobalite}}{2SiO_2} + Na^+ + K^+ = \underset{\text{low albite}}{NaAlSi_3O_8} + \underset{\text{potash feldspar}}{KAlSi_3O_8} + Ca^{++} + 4H_2O \quad (6)$$

which gives better agreement with field data.

12.6.6 Other Minerals

A serious difficulty with such procedures is the frequent need to know the down-hole pH of the chemical analysis, as many reactions involve hydrolysis. Unfortunately, measurements of this parameter are normally made only after a sample has been retrieved and cooled to surface temperatures. The down-hole pH must then be calculated using known thermodynamic data for dissolved aqueous species at the surface and down-hole temperatures. As noted earlier, it appears that the calculated down-hole pH is a major source of inaccuracy in validation studies. The cause of the inaccuracy is not well understood, but it could be related to the fugitive behav-

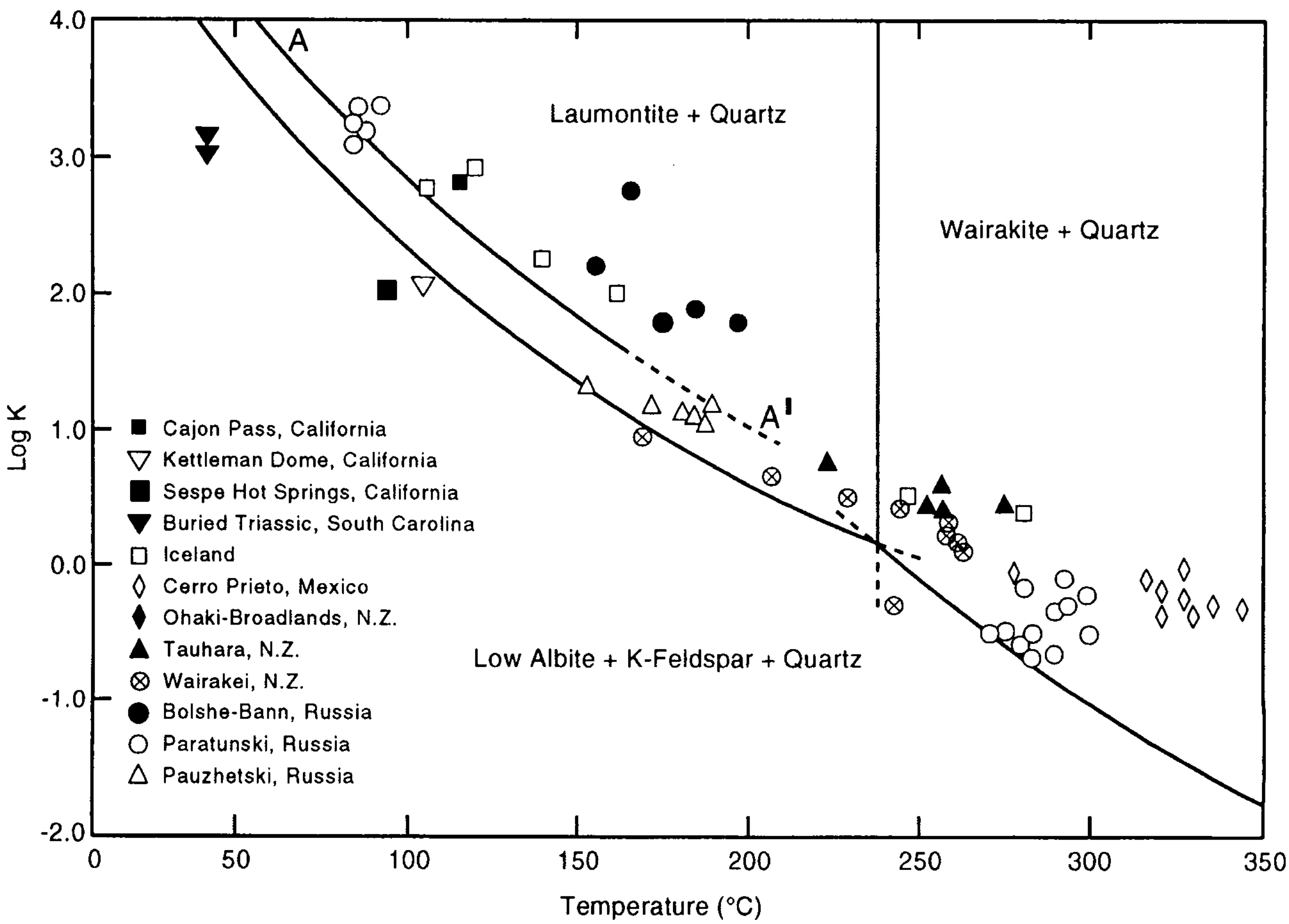

Figure 12-12. Log K = $[Na^+][K^+]/[Ca^{++}]$ calculated from compiled thermodynamic data as a function of temperature, compared with the corresponding ion activity products from geothermal well waters

ior of dissolved CO_2 during sample collection and analysis, thus:

$$HCO_3^- + H^+ = H_2O + CO_2 \quad (7)$$

Understanding the inter-relationship of pCO_2 with pH in brines of different salinities is an important step in reducing uncertainties associated with pH values in geothermal systems.

12.6.7 Pyrite

Calculations of the saturation index of pyrite from geothermal well waters in Iceland by Gunnlaugsson and Arnorsson (1982) and those reported in this paper in Figure 12-10, show that they are supersaturated with respect to pyrite by several log units over the range of temperatures where pyrite is observed. Such large discrepancies are quite unrealistic. Of the many potential sources of error, one often proposed is the contamination of the water sample by ferrous iron due to dissolution of the steel casing in the well. Another source of error might be the thermochemical properties of pyrite, although the uniformity of thermodynamic values in the literature would suggest otherwise. The thermodynamic properties of ferrous ion, Fe^{++} (Nordstrom, 1984; Vasil'ev et al., 1985) could also be a source of error. In predicting the groundwater composition from the secondary mineralogy of geothermal fields where pyrite is present, the author (Apps, 1991) found significant discrepancies in the predicted concentrations of Fe^{++} and SO_4^{--} when compared with measured values using the dissolution reaction:

$$FeS_2 + H_2O = 0.25H^+ + 0.25SO_4^{--} + Fe^{++} + 1.75HS^- \quad (8)$$

The cause of the discrepancy between predicted and observed pyrite solubility in geochemical systems requires urgent attention. It is hoped that natural analogues will help in tracing the source of the problem and aid in its resolution.

12.6.8 Comments on the Observed Scatter in Field Data

As is observed in Figure 12-6 and 12-7, the scatter in the trends of potentials of chemical components varies from ≈±0.2 for log $[Na^+]/[K^+]$ and log $[SiO_2(aq)]$ to ≈±1.5 for the logarithms of activity ratios incorporating $[H^+]$. In computing saturation indices, Figure 12-10, the scatter ranges from ±0.3 S.I. units for quartz and calcite in their presumed stability fields to about +3–0.5 S.I. units in the case of pyrite. It should be noted, however, that the magnitude of errors in S.I. is a function of the number of atoms in a mineral formula unit. Thus, for example, in comparing the S.I.s of quartz and albite, S.I.(albite) should be divided by three, because it contains three SiO_2 units in one formula unit, $NaAlSi_3O_8$.

The scatter can be attributed to any of several variables in what is sometimes a poorly constrained system. In the following discussion, the effect of several of these variables will be examined.

12.6.9 Sampling and Analysis

The principal problems are preservation of sample integrity and determination of down-hole or *in situ* formation water pH. Loss or gain of CO_2 or H_2S during sampling and subsequent handling can cause substantial shifts in sample pH, particularly if the TDS content of the water is low. Still more errors are introduced if the pH has been determined on corrupted samples. Errors of ±0.5 pH and even greater are not uncommon and would easily account for much of the scatter observed in the log activity ratio trends of Figure 12-6. Uncertainties in sample pH also arise when the pH of high ionic strength groundwaters are measured. Errors of as much as 0.5 pH units can arise due to liquid junction errors in the reference electrode when the pH meter is calibrated using standard buffer solutions.

Errors introduced through loss of NH_3 and H_2S could also contribute to the lack of precision in pH measurement and calculation of some mineral S.I.s, for example, pyrite. The author need not elaborate on the problems associated with sample collection from flashing geothermal wells. It suffices to note that calcium carbonate and silica precipitation will introduce significant errors unless corrected. The dissolution of steel casing and its impact on the saturation indices of pyrite and Fe(II)-bearing silicates has already been noted.

12.6.10 Disequilibrium Introduced by Groundwater Transport

Geochemical systems convect, causing local supersaturation and precipitation with respect to some minerals wherever groundwater from an elevated temperature source migrates into cooler regions of the geothermal system. The kinetics of precipitation under falling temperature gradients has not been modeled, except in a few cases (Verma and Pruess, 1988), but it is observable in several geothermal fields. At Wairakei, New Zealand, for example, wells adjacent to major fractures are supersaturated with respect to potash feldspar (Ellis and Wilson, 1960). In Icelandic wells, many groundwaters less than 150 °C are supersaturated with respect to quartz (see Figure 12-10). At 250 °C, substantial equilibration with respect to quartz can be achieved in a few days, but at 25 °C, equilibrium is achieved only after several thousand years (Rimstidt and Barnes, 1980). Therefore, convecting groundwaters, initially saturated with respect to quartz, can become supersaturated with respect to chalcedeny upon cooling. It should be noted, however, that supersaturation with respect to quartz in Icelandic groundwaters is also achievable through dissolution of natural glasses in hyaloclastites or basalt flows.

Thermodynamic analyses of hot spring data usually show significant variations in the predicted source region temperatures when using different geothermometers. Furthermore, calculated S.I.s of many minerals known or inferred to exist at depth indicate that the hot spring water is no longer in equilibrium with the source region. Evidence of chemical modification of the groundwater during transport and cooling is very evident. Each field occurrence must be examined carefully, and the extent of disequilibrium determined. Further investigations of these phenomena are needed, and caution must be exercised in assuming that local metastable thermodynamic equilibrium is generally valid.

12.6.11 Solid Solutions

Where minerals are pure or nearly pure substances (e.g., quartz, albite, pyrite, and anhydrite), the mineral activity product should be fixed at some finite value, and S.I. should be zero at any given temperature, provided that the mineral is present and at equilibrium with the coexisting groundwater. This assumption has been tested by the author and by others and appears to be generally valid for hydrothermal systems. Several classes of minerals are not pure substances, however, and vary in composition depending on the bulk chemistry of the host rock and the alteration kinetics of the primary minerals and glasses. Of greatest importance are the phyllosilicates and zeolites. Compositional variability in these classes of minerals can be described in terms of solid solutions of defined end members. In many cases, the solid solutions behave ideally, for example, the substitution of Fe^{++} for Mg^{++} in chlorite (Walshe, 1986). In others, such as the substitution of Fe^{+++} for $Fe^{++} + H^{+}$ in biotites, the solid solution is far from ideal (Beane, 1972). If the substitutions are minor, the solid solution can be approximated to the composition of the dominant member component, and the S.I. will deviate only incrementally from zero in making this approximation. The activity product of minor component end members, however, can be expected to vary substantially from one geothermal site to another. Unfortunately, the quality of thermodynamic data for phyllosilicates and zeolites is generally inadequate to correct for solid solution substitutions. Therefore a significant scatter in the activity products of solid solutions is to be expected when these minerals are approximated to their end member compositions.

Another feature of minerals displaying solid solution properties is that the composition can vary both with the state of alteration of the rock matrix and with temperature. As the rock alters, the composition of the geothermal fluid changes in response to changing chemical conditions. Succeeding layers of crystals aggregating on a fracture surface or vesicle wall will, therefore, reflect these changes. Only the composition of the mineral at the water interface could be in equilibrium at the time of sampling. Bulk chemical analyses of solid solutions are, therefore, not appropriate for equilibrium thermodynamic calculations in geochemical systems.

12.7 CLOSING COMMENTARY

Geothermal systems in volcanic rocks can serve as suitable analogues of near-field geothermal processes. They can be used to calibrate thermodynamic data, and their relatively uniform behavior permits the validation of groundwater compositions calculated from observed secondary mineral assemblages. Although further study is required to resolve a number of details, it appears likely that natural analogues provide a sound basis for predicting equilibrium between groundwater and secondary minerals. With the current state of knowledge, field data can be correlated with thermodynamic data, and the thermodynamic data for pure substances can be beneficially adjusted in certain circumstances to refine model predictions.

Predictions of groundwater chemistry on the basis of the observed secondary mineralogy in a geothermal system generally correlate well with the observed composition of the geothermal fluids, provided that the concentration of Cl^{-} is specified (Apps, 1991). Most aqueous species concentrations can be predicted to within a factor of five, and some to within 20 mol. percent. Exceptions are the Fe^{++} and SO_4^{--} as noted earlier.

Although the overall level of precision might be improved incrementally with the further refinement of thermodynamic data, present modeling and validation of geothermal systems as natural analogues are sufficient to make preliminary predictions of many radioelement source term concentrations, establish the corrosivity of the groundwater to various waste container materials, and initiate preliminary studies of chemical transport in the near-field environment.

The chief problem remaining is the observed scatter in activity ratios of ionic species and mineral saturation indices calculated from chemical analyses of groundwaters. The principal causes of this scatter should be identified, and if possible, accounted for in subsequent field sampling programs. Model refinement, including the recognition of solid solution models for clays and zeolites, would also be advantageous. Enhanced precision might also be achieved through the application of more sophisticated electrolyte models to describe the thermodynamic properties of groundwaters with ionic strengths exceeding 0.1.

The next step in using geothermal systems as analogues is in the development of kinetic models. This phase of the work will undoubtedly provide a serious challenge to the geochemist, but it is essential if evaluations of the rates of alteration in the near field of geologic repositories are to be predicted. The problem could be tackled in six steps.

(i) Measurement of glass devitrification kinetics in the laboratory by means of flow-through reactors at elevated temperature.

(ii) Measurement of crystal growth kinetics at elevated temperatures in the laboratory through small displacements from equilibrium of selected secondary minerals.

(iii) Development of crystal growth models of secondary minerals at low levels of supersaturation.

(iv) Integration of glass devitrification/dissolution kinetics and crystal growth in a model that includes diffusive and convective transport, as well as surface reactions of dissolution and precipitation. It is probable that surface reaction rates at the low levels of supersaturation observed in the field are fast in relation to diffusive and convective transport. Hence, the latter transport processes would control the rate.

(v) Inclusion of step (iv) into a reactive chemical transport model of a convecting geothermal reservoir.

(vi) Validation of the model in step (v) using well-characterized geothermal reservoirs.

The model developed in step (v) could be used to explore the rates of dispersion of soluble and insoluble elements as illustrated in Figure 12-9 in addition to more general validation studies of geothermal fields. Although the program suggested above is quite demanding, it is not unrealistic given the current state of the art in model development.

The final step in model development involves the incorporation of radioelement transport in the near field. Although some fission product radioelements might be correlated with field observations of the behavior of their nonradioactive counterparts, there will be no such opportunity to observe the behavior of actinides other than uranium and thorium. Reliance must instead be placed on laboratory experiments under simulated near-field conditions. This small step beyond the domain of natural analogues will, however, be buttressed by the confidence gained from model development and validation of the geochemical framework in which the radionuclides would migrate.

In conclusion, it can be confidently stated that natural analogues in the form of geothermal systems in volcanic rocks are not only desirable, but necessary for the development of performance assessment models of the near field of repositories in volcanic rocks, such as that planned at Yucca Mountain, Nevada. The preliminary results given in this paper suggest that such optimism is well founded. Nevertheless, the geochemist should not underestimate the challenges that lie ahead.

12.8 REFERENCES

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NATURAL ANALOGS FOR FAR-FIELD ENVIRONMENT/HYDROLOGY 13

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13.1 INTRODUCTION

The term, "natural analog," most frequently refers to a natural setting in which materials, conditions, and processes are considered to be similar to those that may occur within an engineered structure or system following the system's placement within the natural environment. For example, the geochemistry of a naturally occurring uranium ore body may provide insight into possible rates and mechanisms of radionuclide transport and retardation that could be expected to occur near a geologic repository for the disposal of high-level radioactive waste (HLW). The application of analog studies, however, need not be restricted to engineered systems; the concept of "natural analog" can be extended to include the study of natural systems that possess characteristics and features similar to those of a particular natural system of interest. As with engineered systems, natural-analog studies for application to natural systems tend primarily to be of heuristic value, allowing insight into poorly understood processes and conditions that may be occurring within the system of interest or that may be expected to occur within the system in response to possible future changes of external environmental conditions. In this context, analog studies are applied widely in the natural sciences as part of the long-standing method of scientific induction. Natural-analog studies also can provide quantitative data by which to test and validate the application of conceptual and numerical predictive models to a natural system of interest. Clearly, the value of natural-analog studies depends critically on the extent to which information and data are transferrable from the analog system to the system of interest.

The present discussion considers the applicability of natural-analog studies to characterize far-field conditions in the vicinity of geologic-repository systems for the disposal of HLW. The far field is that region within the geologic host medium that is sufficiently distant from the repository such that the immediate effects of repository construction and the heat generated by emplaced waste can be regarded to be negligibly small. Conditions in the far field, therefore, are determined by the natural state and evolution of the repository geosphere environment.

Because moving groundwater is considered to be the primary transport mechanism for radionuclide release to the accessible environment from geologic repository systems, characterization of the present state and expected evolution of the geohydrologic system is of major concern. Geohydrologic conditions in the far field will control the flux of groundwater reaching the repository environment (which, therefore, may be available to contact emplaced waste) as well as the flux of groundwater available for radionuclide transport between the repository and the accessible environment. Changes in far-field geohydrologic conditions during a mandated repository lifetime of 10,000 years or more are expected to occur principally in response to future climatic change. The potential geohydrologic consequences that could be caused by climatic change include possible increases in the flux of groundwater reaching the repository and shorter groundwater travel times from the repository to the accessible environment. The significance of climatic change for waste containment and isolation will depend on the response characteristics of the geohydrologic system and are likely to be of greatest potential importance for repositories located in unsaturated-zone environments. Unsaturated-zone sites are of major concern, because the United States repository program is presently evaluating the suitability of unsaturated tuff at Yucca Mountain, Nevada, as a host rock for the nation's first repository for commercially generated HLW. Consequently, discussion here will be directed principally at the application of natural-analog studies to characterize hydrologic far-field conditions for repositories sited within thick unsaturated-zone environments.

13.2 UNSATURATED ZONE FLOW AND TRANSPORT

The quantitative description of groundwater flow in geologic media requires the development of conceptual models for the flow processes and the translation of these models into an appropriate mathematical framework to permit calculation of flow rates and directions. The putative theory of groundwater flow in saturated media derives from a Darcian continuum model of flow. This model is based on Darcy's law, which states that the flux of groundwater at any location within the flow region is proportional to the gradient of the hydraulic head at that location. With specific regard to characterizing the moisture balance in soils, the Darcian continuum theory has been generalized and extended for application to characterizing the storage and movement of water in unsaturated media. The underlying conceptual model is based on the hypotheses (i) that the medium can be represented as a macroscopic continuum of interconnected pores and (ii) that capillary and adsorption forces under gravity control water storage and flow within the pores. Because the pores are occupied by both liquid-phase and gas-phase fluids, the resulting Darcian flow equation, unlike its saturated-zone counterpart, is highly mathematically nonlinear, which makes the definition and measurement of hydrologic properties difficult in unsaturated media and often poses problems for conceptual and numerical model validation in specific applications. An additional complication arises under transient flow conditions when the dynamics of the gas phase within the air-filled pores may influence liquid-phase conditions and flow.

Although the Darcian model for groundwater flow has been successfully applied to both field and laboratory studies in hydrophilic soils, the direct applicability of the model to unsaturated-zone environments in general has yet to be adequately demonstrated. Of particular concern for geologic repositories located in thick unsaturated zones is the characterization of moisture flow in variably saturated, spatially heterogeneous indurated rocks, such as occur at Yucca Mountain, Nevada. The major problems in extending the soils-based model concern scale and composition. Unsaturated zones in soils typically do not exceed a few meters in thickness, and soils generally are high-porosity (30–60 percent) media composed of unconsolidated materials. The unsaturated zone at the Yucca Mountain site, on the other hand, ranges from 500 to 750 m thick and consists of a layered sequence of unsaturated, variably fractured, welded and nonwelded tuffs of low matrix porosity (generally ranging from 10 to 30 percent). In spite of these differences, however, the present approach is based on the presumption that the Darcian soils-based model is appropriate to describe moisture storage and flow within the unsaturated rock matrix. In this context, thin unsaturated zones in soils constitute a fundamental analog for thick unsaturated zones in layered rock. Specific issues that remain unresolved include (i) the validity of the macroscopic continuum model for characterizing the possibly complexly interconnected pore space in unsaturated rock, (ii) proper accounting for the interaction and coupling of liquid-water flow in the rock matrix and that possibly occurring in open fractures, (iii) incorporating the effects of spatial heterogeneity that could lead to the occurrence of preferential flow pathways and localized regions of enhanced water saturation, and (iv) allowing explicitly for high-intensity transient events involving phenomena such as rapid two-phase flow and wetting-front instabilities. In order to resolve these issues, new theoretical and modeling approaches may be required, and natural systems displaying some or all of these features can be expected to provide analogs for developing and testing new and refined models.

In addition to the difficulties in characterizing the flow of groundwater in unsaturated geologic media, the generally accepted concepts of solute dissolution and transport as they apply to saturated conditions may not be straightforwardly applicable to unsaturated environments. For example, the continuum approach may not be appropriate in the presence of geologic heterogeneity that may occur over a range of scales and may lead to preferential flow and transport pathways. The general concepts of "retardation" and "dispersion" may take on new meanings in unsaturated-zone settings. Furthermore, the presence of air within unsaturated transport pathways will need to be taken into account not only as it affects the liquid-water flow field but also as a medium for potential gas-phase radionuclide transport and as a chemical reactant along the transport pathways.

13.3 COUPLED FLOW AND TRANSPORT PROCESSES

Under the most general set of circumstances in the far field, coupled processes involving simultaneous heat and moisture flow and solute transport in the presence of chemical reactions will need to be considered. Heat flow will occur in the far field in response to the natural geothermal gradient and may consist of both conductive and convective components. In nonisothermal unsaturated-zone environments, the moisture distribution generally will be determined both by liquid-phase flow and advective gas-phase water-vapor transport. Radionuclide dissolution and transport will depend principally on the magnitude and direction of liquid-water flux through the repository system; although gas-phase transport of some radionuclides, such as carbon-14, may occur within the air-filled pore space. The inclusion of coupled interactive processes introduces additional complexities, which, however, may be most severe in the near-field repository environment where the effects of heat generated by emplaced waste may lead to strong thermal gradients and elevated ambient temperatures. Although they may not be directly applicable to far-field unsaturated-zone environments, hydrocarbon and geothermal resource evaluation problems may provide insights and bounds on conditions in the repository far field. Petroleum engineering is concerned with the general problem of multi-phase fluid transport in diverse geologic media and settings. Geothermal-resource evaluation is concerned with multi-phase moisture storage and flow under strongly nonisothermal conditions. In addition to their possible heuristic value as analog systems, both of these fields have contributed significantly to the development of field and laboratory techniques and numerical-modeling methods that will be applicable to the problem of repository siting in unsaturated-zone environments.

The principal geochemical issue with respect to radioactive-waste isolation in geologic media concerns the potential for radionuclide retardation along the transport pathways. In the low-temperature, far-field environment, the identification and characterization of the relevant retardation processes is straightforward, at least in principle. The major source of uncertainty derives from the unknown consequences for radionuclide retardation of possible future changes in far-field environmental conditions that could lead, for example, to *in situ* mineral alteration or to the creation of new transport pathways. Because of the expected long residence time of groundwater in an unsaturated rock matrix, the kinetics of retardation processes will not need to be considered as long as unsaturated conditions are maintained in the far field. Consequently, as long as unsaturated conditions prevail in the far field and significant fast flow and transport pathways are absent, equilibrium chemistry under fixed or only slowly varying ambient conditions may suffice to characterize the dominant retardation processes.

13.4 CLIMATIC CHANGE

Because climate ultimately determines the amount of water available to infiltrate into the unsaturated zone, future climatic change may pose significant consequences for waste containment and isolation in repositories sited in thick unsaturated zones in arid regions, such as the southwestern United States. Of major concern is the possible occurrence of significantly wetter conditions of sufficiently long duration to increase groundwater flux in the unsaturated zone and, thereby, to increase the amount of water available to contact emplaced waste and to transport radionuclides in solution. In particular, depending on the specific geohydrologic setting, increased net infiltration could initiate water flow in fast pathways, such as fractures and faults, that could reduce appreciably the time required for water to reach the repository from land surface, as well as the groundwater travel time from the repository to the accessible environment.

In order to resolve the concerns posed by the possibility of future climatic change, information is needed regarding not only the likelihood for the occurrence of climatic change during the lifetime of the repository but also the expected effects on repository performance that could be induced by climatic change. Because moving groundwater is expected to be the primary mechanism for radionuclide release and transport, the effects of climatic change on waste containment and isolation will be mediated by the site geohydrologic system. In unsaturated-zone systems, climatic change will be translated into changes in the distributions of water content and groundwater flux within the system. The consequences of climatic change for waste containment and isolation will depend on the magnitude of change and the time required for the effects of change to propagate through the system. Consequently, in order to evaluate the effects of future climatic change on repository performance, site-specific models and data will be needed to enable quantitative prediction of the response of the geohydrologic system to specified changes in climatic conditions.

Because the factors controlling long-term climatic evolution remain incompletely understood and quantified, reliable prediction of future climatic change at either global or regional scales is not yet feasible. Consequently, based on the premise that the past is the key to the future, the evidence for past climatic conditions is taken to be at least indicative of possible future climatic variability and extremes. In this sense, past climate is regarded to be a natural analog for future climate. The expectation that past climate can serve as a guide to future climate is based, in part, on the evidence for cyclic climatic variability that is implied by presently available data. The data indicate, for example, that glacials and pluvials recur with periods of several thousands of years. Climate data for the past 30,000 years indicate that shorter-term climatic fluctuations of variable amplitude are superimposed on the long-term climatic cycles.

Although the evidence for past climatic change indicates that future climatic change occurring within the lifetime of a radioactive-waste repository is likely, the effects of climatic change on a geohydrologic system and, especially, the consequences for waste containment and isolation, cannot be evaluated directly. Consequently, both paleohydrologic studies and studies of geohydrologic systems in a variety of different climatic settings can be used to estimate the effects of future climatic change on a particular geohydrologic system. The correlation of past climatic change with the paleohydrologic record provides insight into the magnitude and timing of the effects produced by climatic change on geohydrology. The study of systems in different climatic conditions provides insight into the end states produced by a specific climatic setting. The combination of paleoclimatic and paleohydrologic studies together with the study of analog geohydrologic systems in a variety of present-day climatic environments can provide baseline data for qualitative, if not quantitative, extrapolation of geohydrologic-system response to possible future climatic change. The principal geohydrologic-system response to climatic change will include changes in the rainfall-runoff and groundwater recharge-discharge relations as well as possible change in water-table or potentiometric-surface altitudes. These geohydrologic-system variables and their response to climate change will depend complexly on both the geohydrologic setting and existing climatic conditions.

13.5 MODEL VALIDATION

Numerical models for natural or engineered systems are developed in order to quantitatively describe the state and predict the evolution of these systems in response to changing external conditions. Model validation consists of demonstrating that the numerical model and its underlying conceptual model provides an adequate and appropriate representation of the system. In general, models can be validated only for a particular system under a known set of conditions. Models to be implemented to predict changing far-field conditions near a radioactive-waste repository during a 10,000-year or longer repository lifetime, however, cannot be validated directly. Consequently, such models must be indirectly validated by demonstrating their ability to adequately represent a variety of similar, or analog, systems subject to differing sets of known external conditions. By proceeding in this manner, the limits of model applicability can be established and confidence developed that the model is appropriate for use within these limits. Therefore, natural-analog systems are expected to be of indispensable use as part of the overall model-validation process, especially for those models invoked to predict the long-term performance of a repository system and its environment.

WASTE FORMS, PACKAGES, AND SEALS WORKING GROUP SUMMARY

14

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14.1 GENERAL OBSERVATIONS

The group decided to limit the discussion to waste forms and waste packages. The scope of the discussions involved both natural and anthropogenic analogues. The majority of the group felt that research in the United States on natural and anthropogenic analogues has lacked stable funding, with a consequent destruction of institutional memory. The group felt that a stable, regularly assembled body of scientists, perhaps organized under the aegis of a national technical society, such as Materials Research Society (MRS), should exist in the future. As an initial task, the group recommended that a comprehensive literature survey of natural and anthropogenic systems/reactions relevant to alteration of waste glass and spent fuel, degradation mechanisms of container materials, and mechanisms of alterations of chemical battier backfill should be prepared. There was a consensus that issues in analogues should be considered in connection with model verification and performance assessment. In contrast, analogs cannot generally be regarded as simulations of waste package performance in a repository.

The engineered barrier system may be classified as shown in Figure 14-1. It is apparent from Figure 14-1 that the approach to analogues for addressing containment issues would be different from that for release rate. There seems to be a longer history of research into analogues of vitrified waste and spent fuel than metallic container materials. While some container materials, such as copper, lend themselves to the study of natural analogues, for materials, such as stainless steels, anthropogenic analogues of more recent origin (50–75 years old) should be considered.

14.2 USE OF ANALOGUES FOR WASTE FORMS

The issues discussed with respect to spent fuel analogues included:

- the need to develop a better understanding of the crystal chemistry, phase equilibria, and mineralogy of actinide oxide and silicate phases in order to project behavior of spent fuel in terms of changes in the alteration mechanisms over time.
- the need to understand the relationship between alteration reactions of natural uraninite and other minerals to those of spent fuels.
- the need to understand the effects of environmental factors on alteration mechanisms.

14.3 USE OF ANALOGUES FOR CONTAINER MATERIALS

Copper has been examined in the Swedish and the United States program using both archeological and natural analogues. Iron has been examined using anthropogenic analogues, such as Roman nails. Potential uses of analogues include:

- exercise models of corrosion product mineralogy and morphology, maximum corrosion depth (if possible), and existence of various corrosion mechanisms against observations on the analogue.
- examination of materials that can be plausibly argued to have existed in environments similar to the repository environments, but to have been wholly reacted.

While copper and iron may be natural choices for an analogue program because of their long history and, in the former case, because of its presence in certain geologic formations in the native state, more recent (30–100 years old) analogues of these and other alloys should not be ignored.

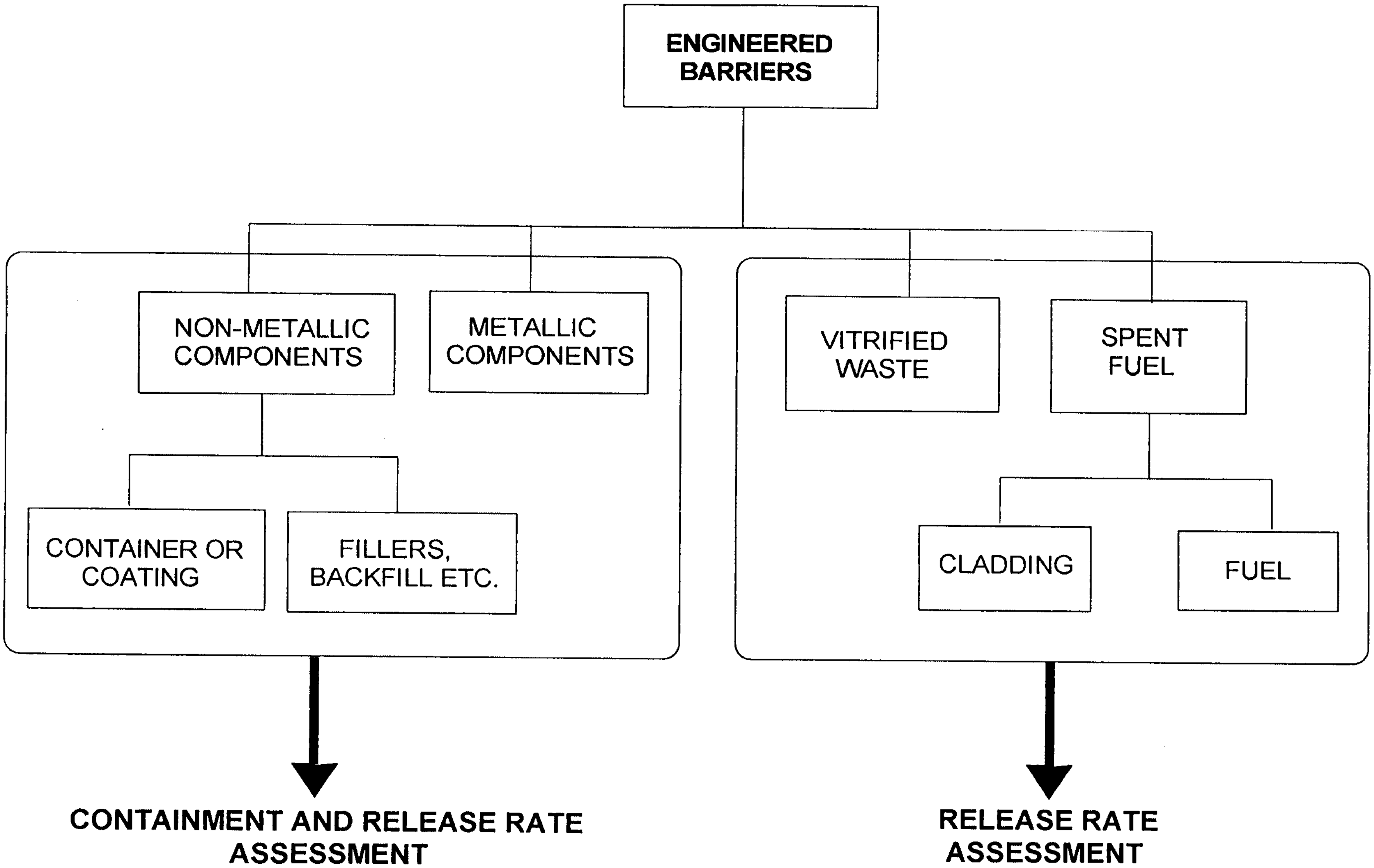

Figure 14-1. Classification of the engineered barrier systems

NEAR-FIELD ENVIRONMENT/PROCESSES WORKING GROUP SUMMARY

15

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15.1 GENERAL OBSERVATIONS

Several themes generally applicable to natural analog studies were developed in the course of working group discussions. A consensus prevailed that there exists a compelling philosophical rationale for natural analog studies in support of the geologic disposal of high-level nuclear waste (HLW) largely because the long time scale of concern exceeds direct laboratory or human experience. Phenomena relevant to long-term isolation of nuclear waste can be identified in natural systems. Analogous natural (and archeological) systems provide the only means to study some problems or issues that are truly inaccessible in laboratory studies. A broad view of natural analogs was advocated. Many subjects can be addressed in natural analog studies, and a variety of approaches may be appropriate. Literature reviews to discover reports of natural occurrences of predicted or speculated repository materials or processes can constitute a valuable analog study. Research can be conducted at scales that range from microscopic examinations of processes and properties of materials to multidisciplinary and integrated studies on a geologic scale. Much research in the geosciences employs reasoning by analogy. Recognition of this research and experience (e.g., methods and successes) can benefit applications of natural analog studies to nuclear waste issues.

A challenge for natural analog studies is integration with system modeling and performance assessment. Confidence in the safety of geologic systems for disposal of nuclear waste requires an identification and understanding of significant processes in the natural and engineered systems and the use of that knowledge to evaluate (i.e., model) repository performance. Two objectives of analog studies are to develop and test hypotheses and to attempt to validate both conceptual and numerical models. Research should be oriented to obtain results that can contribute to performance assessments. Relevant analog data may consist of identified processes or properties and their coupling, or they may provide bounds or examples for reasonable system behaviors. Results are likely to be both qualitative and quantitative. The results of analog studies should be transmitted to performance assessment modelers.

15.2 THE NEAR-FIELD ENVIRONMENT: ISSUES AND PROCESSES

The near-field environment is generally defined as the region significantly affected by thermal perturbations associated with the HLW and by construction and the introduction of exotic materials. Thermal effects on the geochemical, hydrological, and mechanical properties of repository components are issues to be addressed in natural analog studies relevant to the near field, with regard to an estimation and evaluation of the waste isolation characteristics of the system. The consequences of the introduction of exotic materials, for example, the effects of the geologic setting on the materials, and the effects of these materials on the geologic environment, are also near-field analog issues. Coupling of thermal, chemical, hydrological, and mechanical processes is an important characteristic of the near-field environment that may be addressed by study of analogous natural systems. Particularly in the near-field environment, the coupling of performance-related processes necessitates interdisciplinary studies.

Chemical reactions can be promoted by near-field temperature changes due either to changes in equilibrium conditions or increases in reaction rates. These reactions can affect solute concentrations (e.g., by dissolution or evaporation) and speciation, precipitation or dissolution of minerals, changes in mineral compositions or sorption properties, and the generation and composition of a gas phase (e.g., by volatilization or consumption of dissolved gases or H_2O). Geologic environments are typically metastable, and thermally activated reactions producing more stable phases can be anticipated in the near field. The normal metastability of natural systems over geologic time suggests that local chemical equilibrium would not be expected to be achieved during transient near-field thermal perturbations. Particularly significant near-field analog studies could be devoted to reaction rates at relevant elevated temperatures over periods that are long relative to laboratory accessible time scales, but nevertheless short relative to most geologic systems (e.g., tens to thousands of years).

The chemistry of radioelements can be affected by near-field phenomena. Solubilities of radioelement-containing solids, ion exchange equilibria and kinetics, coprecipitation relations, colloid generation, and other processes controlling radioelement concentrations are temperature dependent. In addition, the oxidation state of the system can influence radionuclide concentrations in solution. Variations in the redox conditions in the near field can be a consequence of reactions promoted by temperature variations, by introduced materials, or by the thermohydrological phenomena (i.e., coupled heat transfer and fluid flow).

Near-field thermal loading can cause thermal convection of gas and liquids. In unsaturated media with two fluid phases, the distribution of fluids can be strongly altered leading to phenomena such as a liquid saturation halo, capillary flow due to saturation gradients, or to thermal heat pipe effects (i.e., counter current flow of gas and liquid). In addition, osmotic flow can be induced in the near field by thermally driven changes in solution concentrations, for example by vaporization or water-rock reactions.

The near-field environment can provide an energy source for microbial activity either through radioactive decay or irreversible reactions of repository materials, for example, corrosion. Microbial activity can have important effects on such processes as corrosion, colloid formation, and complexation of aqueous species with organic ligands. Microbes can generate local chemical environments with ramifications for radionuclide isolation. In addition, biomass generation can affect hydrologic characteristics.

15.3 NEAR-FIELD ANALOGS

Having developed a sense of the near-field system and significant processes and issues, the group assembled a list of potential near-field analog systems. These systems were then divided in six general categories, with some subcategories, based on their natural (e.g., geologic) occurrences.

1. Hydrothermal systems
   - A. Fossil
   - B. Active
   - C. At elevated temperatures along the geothermal gradient at the repository site or in an analogous setting
2. Contact zones around dikes, sills, or plutons
3. The natural reactors at Oklo
4. Shallow earth systems under the influence of diurnal or seasonal temperature variations
5. Natural redox fronts, natural redox processes
6. Special mineral and material deposits
   - A. Ore deposits
   - B. Cement (e.g., portlandite) deposits
   - C. Meteor impact sites
   - D. Archaeological materials
7. Modern analogs:
   - A. Nuclear device test sites
   - B. *In situ* vitrification sites
   - C. Contamination, waste, and test sites associated with nuclear research and technology
   - D. Biological effects on metallic well casings
   - E. Mine leaching, mineral beneficiation sites
   - F. Modern materials behavior in geologic environments

A matrix was developed relating the issues and processes to the outline of potential natural analogs (Table 15-1). The relations in this matrix are not intended to be exhaustive or absolute.

15.4 FOCUS: HYDROTHERMAL SYSTEMS ANALOGS OF THE NEAR FIELD

The group chose to evaluate hydrothermal systems in greater detail as natural analogs of the near-field environment and processes. Many active and fossil hydrothermal systems have been studied in the context of geothermal energy resources and hydrothermal ore deposits. These systems generally record the effects of interactions of hot water with rock. What

Table 15-1. Matrix of nuclear waste repository near-field issues (Section 15.2 of text) and analog systems that may be used to address the issues (Section 15.3 of text). Numbers refer to elements of the outline of analogs given in Section 15.3 of the text.

Analogs	Hydrothermal Systems	Igneous Contacts	Natural Reactor	Shallow Systems	Redox Fronts	Mineral Deposits	Modern Analogs
Issues							
Thermal effects on chemistry	1A, 1B, 1C, 1D	2	3			6A, 6C	7B
Thermal effects on mechanics	1A, 1B, 1C, 1D	2	3			6A, 6C	7B
Thermal effects on hydrology	1A, 1B, 1C, 1D	2	3	4			7B
Thermal effects on gases	1A, 1B, 1C	2		4			
Redox relations	1A, 1B, 1D	2	3		5	6A, 6C, 6D	
Radionuclide chemistry			3		5	6A, 6C	7A, 7C
Microbial activity					5	6A	7D, 7E
Construction materials						6B, 6D	7F

are the general characteristics of hydrothermal systems, and how do these characteristics compare to the near field of a HLW repository? Hydrothermal systems can be characterized according to the duration of hydrothermal activity, the fluid flux, the chemistry of hydrothermal solutions, fluxes of chemical components through the altered rock, the heating rate and integrated heat load, and gas phase evolution and chemistry. These characteristics should be evaluated to establish the closeness of the analogy of particular hydrothermal systems to expected characteristics of particular repository near-field environments, and, hence, their relevance to evaluations of repository performance.

In general, the thermal loading and near-field temperature evolution can be closely estimated for various repository designs. Good analogies for the effects of heat and fluid-rock interactions at elevated temperatures in the near field can be provided by natural hydrothermal systems. However, many hydrothermal systems or aspects of these systems may have little apparent relevance to a particular repository system. A number of general characteristics of hydrothermal systems may differ significantly from repository near-field environments. In particular, heating in repository systems is of short duration relative to most natural hydrothermal systems. Also, total fluxes of water and chemical mass transfer are likely to be small in a repository relative to larger hydrothermal systems. Solutions with aggressive behavior, for example, acidic hydrothermal waters associated with magmatic activity, may not be representative of heated groundwater in a repository environment. Pervasive alteration in hydrothermal systems may leave a sparse record of many phenomena relevant to relatively short-term alteration of the repository near field.

The working group suggested that hydrothermal events of relatively short time and small space scales bear the greatest analogy to the repository near field. For example, distal sectors of active hydrothermal systems may be affected over relatively short time periods. In the outflow zones of active caldera hydrothermal systems, hydrothermal flow paths may have only recently transected country rock, and the solutions may be near-neutral to slightly alkaline waters of meteoric origin at 60° to 120 °C. Evidence for the effects of hydrothermal activity on spatial scales analogous to a repository may also be found near igneous dikes or at the margins of larger hydrothermal systems.

In the context of an unsaturated environment, thermohydrologic phenomena, such as a heat pipe, may be significant in the near field. It would be of interest to examine natural environments and, particularly, hydrothermal systems for the occurrence or evidence for natural heat pipes and their consequences. Evidence might be obtained regarding heat-pipe effects on redox phenomena, mineral precipitation, permeability changes, and heat-transfer mechanisms.

FAR-FIELD ENVIRONMENT WORKING GROUP SUMMARY 16

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16.1 GENERAL OBSERVATIONS

It was generally agreed among the participants in the Far-field Working Group that transferability of data will determine the usefulness of natural analog studies for development of a geologic high-level waste (HLW) repository. The extent to which data from any one geologic site may reasonably be transferred for use at any other geologic site is not adequately known. In practice, how does one use data derived from an analogous system to establish with reasonable assurance that performance objectives will be met in a repository system?

Selection criteria were recognized as the first and perhaps most important opportunity to improve the transferability of analog data to a repository system. Obviously, transferability is enhanced by having as close a match between the analog and the system of interest as possible. The criteria proposed by Chapman et al. (1984) emphasize the necessity of such a close comparison and were broadly affirmed. However, in addition to having as close a match as possible, it is important that the question to be addressed by a given analog be well defined. A narrowly defined question that is resolvable at an analog site may provide useful (i.e., transferable) data even from an analog site, which in other regards, differs substantially from the repository conditions. This line of reasoning is especially important for analog sites that provide a unique opportunity to test a contentious hypothesis (e.g., fission product geochemistry at Oklo).

In addition to considerations for data transferability, to be most useful within the context of the HLW program, selection criteria for an analog should consider a variety of practical aspects. Can the study be completed using currently available technology? Is the study likely to yield useful results in a timely manner? What is the potential for multiple benefits from the study?

Although this workshop was intended to cover the general applicability of analog research to the long-term geologic storage of HLW, much of the discussion focused on the proposed United States HLW repository at Yucca Mountain, Nevada. Consequently, many of the considerations raised here are site specific.

16.2 THE FAR-FIELD ENVIRONMENT

The working definition of "far field" was found to vary among the researchers present. No clear boundary between the "near field" and the "far field" exists. The "near field" is generally considered to be that volume surrounding the waste which will experience significant thermal effects. In practice, "far field" appears to encompass the volume beyond that range as well as overlapping substantially with what may be considered in other forums to be the "near field."

16.3 FAR-FIELD PHENOMENA

Many issues, processes, and events were identified as potentially significant for the far-field environment. Broadly, these can be considered to fall into two categories—hydrologic and geochemical. Of course, there is considerable overlap and feedback between processes occurring within these two general categories. Nevertheless, such a division provides a useful framework in which to consider relevant phenomena. This summary presents a subset of the identified hydrologic and geochemical phenomena considered by the working group to be of particular importance for the performance of a HLW repository.

16.3.1 Hydrologic Processes

16.3.1.1 Fracture Connectivity, Fracture Flow and Large-Scale Effective Hydraulic Properties

The Yucca Mountain site is underlain by fractured, welded tuffs. The degree to which the fracture systems are pneumatically and hydrologically connected has significance for gas-phase radionuclide transport and the possible presence and creation of fast liquid-phase flow pathways. Both the degree of fracture connectivity and the pneumatic and hydrologic significance of interbedded unfractured, non-welded tuffs is highly uncertain. On a large scale (space and time), an average moisture field, which is not necessarily conservative from a performance assessment point of view (for unsaturated sites and flow field at saturated sites) develops. In an unsaturated site, depending on the stratigraphy and location of fault zones, perched water tables may form.

Treatment of fracture paths is currently based on the hypothesis that fractures can be treated as continua of distinct properties. Mechanisms of fluid and contaminant interchange between fractures and matrix are not well understood. In modeling large-scale unsaturated flow through thick geological deposits, the fine-scale flow behavior that actually occurs cannot be simulated by deterministic techniques. This is because: (i) the entire heterogeneous media property field can not be practically sampled and tested, and (ii) even if one could completely define the media heterogeneities, the current generation of flow codes based on Richards' equation are limited by their computational efficiency in obtaining a solution for a deep water table problem (based on the fineness of the numerical grid required). In recent years, effective (average) properties which can be used for large-scale, heterogeneous systems have been developed. Unfortunately, little experimental work has been performed to assess the validity of these new effective property models, particularly at the flow rates/time scales relevant to the radioactive-waste disposal problem. Determination of appropriate effective flow properties will strongly affect prediction of flow rates and directions in the vadose zone.

An analog study may help in understanding this effective behavior if a method can be found to reconstruct the flow history of the analog system. Such an understanding may lead to basic hypotheses that are independent of the analog system and can be applied to other sites. The kind of investigations and the level of characterization that will lead to a reconstruction of the past effective flow behavior of a site remains problematic. Pneumatic testing at an analog site, for example, Apache Leap, Arizona, may provide insight to, and the properties of, fracture-system processes. It may be possible to assess effective flow properties by performing a detailed mapping of the subsurface distribution of several environmental tracers, both at the proposed repository site and at analog site(s). Careful definition and limitation of the questions to be addressed at any analog site are required; otherwise, characterization of the analog site may become as involved as that of the proposed repository site.

16.3.1.2 Net Infiltration

Net infiltration refers to the flux of water entering the unsaturated zone below the plant-root zone and is the primary source of water for downward gravity-driven percolation through the unsaturated zone.

Present-day rates of net infiltration at the Yucca Mountain site are considered to be small (<1 mm/yr averaged over the surface area of the site). Future rates of net infiltration in response to climatic change are highly uncertain at present. (Increased net infiltration rates could create fast-flow pathways that could transmit water rapidly to the repository horizon and subsequently to the water table.) Fast-flow pathways also could cause the creation of perched-water bodies in the unsaturated zone.

Future changes in net infiltration will depend on the effects of climatic change, specifically enhanced precipitation, on the unsaturated-zone geohydrologic system. Limits on future climatic change may be inferred from past paleoclimatic change (i.e., the past may be an analog for the future). The effect of climatic change on the geohydrologic system may be accessible to analog study at sites with similar geologic settings but which are located in wetter environments than the Yucca Mountain site (e.g., Apache Leap, Arizona, and Rainier Mesa, Nevada). Direct transferability would be problematic, but relationships and processes might be transferrable.

16.3.2 Far-Field Heating

What effects will the heating of the host rock by a repository (temperatures up to 100 °C are anticipated in the far field) have on the far-field mineralogy, rock properties (e.g., rock strength, porosity, permeability), water composition, and degree of saturation?

Because of the relatively low-temperature nature of this process, laboratory experimental data, hampered by metastability and kinetic problems, will probably be of limited use in understanding the effects. An appropriate natural analog may be ideal for determining some of the long-term effects although adequate definition of past conditions will be challenging.

Several technical issues are raised by the possibility of far-field heating including: (i) Will the present-day minerals be altered (this is a particularly important question for the unsaturated zone)? (ii) Will the rock be "plugged" by mineral precipitation? (iii) Will an unsaturated repository be dried, inducing a saturation halo? (iv) Will the water composition change sufficiently to affect the stable mineral assemblage?

As discussed previously, it is unlikely that laboratory studies can answer these issues. Analog investigations may be able to provide some answers, but success is uncertain. Possible analog sites include geothermal systems and the north end of Yucca Mountain itself. Additionally, steam flooding of oil fields such as the Kern River field could provide important information.

16.3.3 Geochemical Processes

16.3.3.1 Colloidal Transport of Radionuclides

At present, it is highly uncertain whether or not colloids will form and be transported through a Yucca Mountain repository flow system. Colloid transport could be a significant mechanism for the transport of elements such as Am, Pu, Cm, Th, etc. Colloid transport has been proposed as the transport mechanism for Am and Pu at several U.S. Department of Energy (DOE) sites. Colloid transport is addressable through analog research, and has been studied previously [e.g., Poços de Caldas, Brazil (Miekely et al., 1990), Alligator Rivers, Australia (Edghill, 1988)]. Meaningful measurements are difficult, and extrapolation of results to a repository system is uncertain.

16.3.3.2 Microbial Activity

Microorganisms may have a significant effect on radionuclide transport by either directly changing the oxidation state of a given radionuclide, or indirectly, by maintaining a steady-state system of mineral phases that sorb radionuclides. The importance of such processes is uncertain; present understanding is limited by assumptions concerning available nutrients, as well as amounts and identities of microorganisms.

It is very likely that microbes are present at most, if not all, natural analog sites. Appropriate analog sites should be able to be studied for the possible influence of any present microbes on other applicable studied processes at that site. For example, microbial activity plays a key role in the transport of uranium at the Poços de Caldas natural analog site. Both sulfur oxidizers and reducers are found to affect the oxidation of pyrite, producing intermediate sulfur species (polysulphide or colloidal sulfur), which, in turn, form secondary pyrite and sulfate and possibly the reductant needed to form the observed pitchblende nodules. This mechanism is supported by both sulfur isotope analysis of the secondary pyrite and the shape of the pitchblende nodules. Due to the lack of thermodynamic and kinetic data, this mechanism cannot as yet be analyzed quantitatively.

16.3.3.3 Speciation and Solubility Limits of Key Radionuclides

Speciation and solubility limits for key radionuclides are critical aspects for considering repository performance and remain poorly defined. Speciation and solubility limits will determine the forms and amounts of hazardous radionuclides available for transport out of a repository. The complexes formed by the radionuclides will vary in composition and stability according to local groundwater conditions. The secondary geochemistry of the waste form constituents (i.e., the minerals formed after corrosive oxidation and dissolution of the waste form and the compositions of the solutions in contact with those minerals) as they move into the far-field will control the concentrations of radionuclides in solutions that may move away from the repository area into the accessible environment. Table 16-1 provides an outline of present knowledge.

Potential analogs for these radionuclides include uranium ore deposits, global fallout from nuclear testing, radionuclide waste disposal sites, and underground nuclear test sites. Speciation and solubility of the species listed above (as for others) depends critically on the composition of the groundwaters in the analog environment. Extrapolation of speciation and solubility measurements made at an analog site to anticipated repository conditions requires judicious selection of analog systems and thoughtful applica-

Table 16-1. Speciation and solubility limits of key radionuclides: present knowledge

Species	Level of Uncertainty in Thermodynamic Databases and in Transport Models	Need to Reduce Uncertainty	Availability of Suitable Analog
U	Moderate	Low	High
Pu	High	Moderate	Moderate
Np	Low	Moderate	Low
Tc	Low	Low	High
I-129	Low	Low	Moderate

tion. Such considerations provide the bases for ranking the need for and likely usefulness of analog work on individual species.

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VOLCANISM/TECTONICS WORKING GROUP SUMMARY

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17.1 GENERAL OBSERVATIONS

The overall impetus for studying geologic analogs of Yucca Mountain is to improve definition and analyses of geologic hazards and to improve estimates of risk for repository design, performance assessment, site characterization, and review of a license application. In particular, analog studies should be directed toward: (i) reduction of key technical uncertainties (KTUs) related to site characterization; and (ii) refinement of constraints on initial and boundary conditions important for modeling and simulation of waste-isolation performance.

Analog regions should be treated as models, essentially as one geological system used to represent another. Analogs should be used to improve understanding of processes and conditions at Yucca Mountain (YM) that cannot be investigated directly by site characterization. Studies of analog sites are likely to suggest alternative methods and directions of site characterization by identifying important processes not directly observable at YM. Analogs provide important additional constraints on initial and boundary conditions of mathematical models and laboratory experiments. Investigations and analyses of analog regions are generally considered to be indispensable as field-scale experiments to explain and predict volcanic and tectonic processes and to assess related waste isolation hazards. This is of particular importance because time-space scales of geological processes are difficult to simulate under laboratory conditions.

In general, for crustal-scale (>10^2 kms^2) geologic processes, a natural analog is a selected part of the earth's crust that is similar to another part of particular interest. More specifically, natural analogs are viewed here as geographic regions or geologic settings that are substantially similar to YM in age and style of Neogene and Quaternary (15 Ma to present) tectonic deformation and volcanism. A less ambiguous, more descriptive general term for such regions is geologic analog. A more specific term may be appropriate for focused studies of certain processes, such as volcanic analog or structural analog.

Use of a properly chosen geologic analog may provide added information and additional insight into the critical dimensions of depth and time that are only indirectly available through investigations restricted to YM. That is, the subsurface at YM can only be studied indirectly. Borehole data (i.e., core samples and analyses, and geophysical logs), seismic surveys and geophysical potential field surveys at YM may not yield models of the deep subsurface that are complete enough for reliable hazard assessment. Development of conceptual tectonic models of YM and subsequent estimates of related natural hazards depend on interpretations of geologic structures that exist as deep as 10–20 kms below the surface at YM. Analog regions that have been uplifted and eroded offer a more direct view of deeper levels of geologic structures similar to those at YM.

Assessment of risk related to earthquakes, fault rupture, and volcanic eruption requires analyses of the time and space patterns of these processes. Time series and spatial distributions cannot be reliably determined from only a few events. Probabilistic methods especially are degraded by lack of critical data. Even a comprehensive site characterization program may not yield the necessary data; it simply may not be available at the site. Indeed, data required to formulate probability distribution functions for risk assessment models may only be available from a range of analog regions. In particular, studies of modern analogs are essential for characterization of transitory dynamic processes, such as earthquake and volcanic eruptions. For example, the probability of large earthquakes (>6.5) at YM cannot be determined from the modern seismicity record of faults at YM. There have been no large historical earthquakes at YM that directly correlate to faults with known surface traces. Thus, one interpretation is that YM may be essentially aseismic. A reasonable alternative interpretation is that the recurrence period of large earthquakes at YM may be longer than about 200 years, a real possibility in this area. A promising partial solution to this problem is to supplement the local seismic record at YM by examining the historic and paleoseismic record for similar structures elsewhere within the Basin and Range (BR) region. This approach essentially substitutes a wide spatial sampling (i.e., all of the BR region) for the short temporal record at a specific site (YM). Seismicity records from potential analog regions must be used carefully, however, because structural style influences seismicity. An important concern is, then, proper definition of criteria used to determine structural and volcanic similarity of potential geologic analogs of YM.

Similar problems exist in risk assessment related to disruption of a proposed repository due to potential future volcanic activity in the vicinity of YM. Data available at the site may not be sufficient to formulate reliable probability distributions of volcanic disruption. Adequate data on eruptive styles and recurrence periods of mafic vents similar to Lathrop Wells can be acquired by studying a suite of geologically analogous areas. Certainly, the potential physical, chemical, and hydrological effects of an eruption similar to Lathrop Wells can only be studied in regions where modern analogs of the Lathrop Wells cone exist.

Conditions which should be examined to properly compare, and to establish some measure of the similarity of a volcanic/tectonic analog include: (i) *in situ* stress state; (ii) age of deformation; (iii) structural style (type of deformation); (iv) age of volcanism; (v) eruptive style, composition, source depth, and ascent history (type of volcanism); (vi) finite strain state and strain rates, local and regional displacement fields, fault-slip histories; (vii) surface and subsurface hydrologic and hydrogeologic conditions; (viii) crustal stratigraphic sequence (rock types) and thickness, and associated physical (e.g., gravity, magnetic, and velocity structure) and; (ix) chemical properties [rare earth element (REE) and isotopic compositions] pertinent to volcanic/tectonic processes. Depending on the specific problem being addressed by the analog study, some of these conditions may be substantially more important than the others.

General recommendations are: (i) take as quantitative an approach as possible; (ii) structure investigations to answer specific questions; (iii) select analog areas carefully, based on definition of specific problems; (iv) use analogs to develop probability distributions for important parameters that are not measurable at YM; (v) thoroughly document how potential analogs are similar to and different from YM, and thoroughly consider how differences may bias results.

17.2 MAGMATIC/VOLCANIC PROCESSES

Studies of geologic analogs are important to obtain critical data and gain new insight into assessment of hazards related to volcanic processes and in assessment of repository risk. Hazard assessment consists of two basic parts: (i) identification of potential sources and (ii) estimation of probabilities of occurrence. Risk assessment combines hazard assessment with estimates of potential effects on a repository. Site characterization may be adequate to determine potential sources of eruption (e.g., existing vents and vent alignments, fault zones), but it is not sufficient to obtain data to reliably estimate probabilities of eruption (eruption recurrence, characteristic periodicities). There are simply too few eruptive episodes and too much uncertainty about age of eruption to clearly establish eruption recurrence periods at YM. Thus, adequate data on patterns of spatial distribution and timing of volcanic vents is only available by investigations conducted at a suite of analog sites.

Analyses of potential effects of an eruption on a repository (probability of disruption) should include observations and analyses of modern analogs. Studies of active vents and Holocene vent systems are likely to yield information that can be used to estimate direct and indirect dynamic effects of intrusion and eruption on repository systems. Because unsaturated conditions are an important part of the natural barrier system, studies of the physical and thermal effects of volcanic activity on local water table elevation and groundwater flow patterns may be particularly important at YM. Historical information on pre-eruption water table elevations may be available from areas of recent basaltic cone eruptions, such as Parícutin (Mexico).

Significant uncertainties remain in estimates of ultimate source depth, magma ascent rates and ascent pathways. Data on patterns and rates of magma ascent are critical to explain the occurrence and characteristics of eruptive systems, to predict eruptions, and to estimate probabilities of repository disruption. However, adequate data on these processes are not available from a single locale. Rather, multiple analog sites, that encompass a range of models, will be required.

Important questions and issues related to volcanism which require investigations at analog sites include:

- Estimates of subcrustal flux of material: (i) Can useful estimates be made of the volumes and rates of magma accumulation in the lower crust and upper mantle? (ii) Can the Quaternary eruption history of BR basaltic systems be related to magma flux?
- What is the flux of magma into the middle and upper crust? How effective are seismic tomographic and heat flow analyses for determining instantaneous flux?
- How complete are models of BR magmatism? How well do existing models represent coupled thermal, mechanical, and magmatic processes.
- Are models of basaltic dike intrusion and cone eruption at YM adequate for reliable estimates of volcanic hazard and consequence.
- What are potential effects of lithospheric conditions on magma transport and storage? For example, what are relationships of extant stress and strain states, and finite tectonic extension (strongly extended versus less extended regions), on evolution of small basaltic systems, as well as the large Neogene silicic caldera systems.
- Is magma stored in the crust? Does magma pool in a mid-crustal chamber, or is the source in the mantle, with no pooling? How are feeder dike systems for basaltic vents localized at upper mantle/lower crust depths (30–50 kms)? How are potential instabilities that localize magma ascent related to extensional strain? Can seismic tomography be used to detect magma chambers? How can seismic tomographic data be used to improve models of magma storage and ascent?

In general, does a lack of modern extrusive volcanism indicate a lack of subsurface magmatism? Does this hold for YM?

- How can the magnitude of potential magmatic and volcanic processes be determined?
- How will magma, magmatic fluids, and additional heat alter the near-field environment? How might these changes influence the chemical and physical stability of canister materials, waste materials, and the potential repository host rock (Paintbrush tuff)?

KTUs reflected in recent research at Lathrop Wells include: (i) ages of eruptions; (ii) style, duration, and cyclicity of eruption (e.g., mono- versus polygenetic); (iii) effects on groundwater flow and water table elevation, and influence of water table elevation on eruptive style; (iv) relationship to existing faults; (v) potential for coupling of intrusive/eruptive processes and fault slip; (vi) potential for earthquake-triggered eruptions. These issues need to be explicitly considered to properly formulate probabilistic estimates of future volcanic activity and repository disruption.

Phreatic eruptions are of particular importance because of potentially widespread effects on both near-field and far-field conditions. Interaction of preexisting or synchronous fractures or faults with ascending magma and groundwater may result in highly localized conduits for gas/fluid exchange and shallow convection. Physical barriers or fluid-flow pathways may be created by emplacement of dikes.

17.2.1 Potential Magmatic/Volcanic Analogs

Proposed criteria for selecting Quaternary basaltic volcanic analogs of YM/Crater Flat include: (i) evidence of hydrovolcanic processes; (ii) approximately Hawaiite composition—somewhat more differentiated; (iii) geochronologic analyses comparable to Lathrop Wells cone—sufficient isotopic and radiogenic dates should be available to establish the age of the analog; (iv) similar Neogene silicic eruptive history(?); and (v) similar Neogene and Quaternary deformation history.

Proposed magmatic/volcanic analogs include:

Lunar Crater-Reveille Range (LC-RR). The LC-RR volcanic field may be a good analog site for investigating the influence of faults on vent location and alignment. Caution should be exercised initially, however, until additional studies show how similar the Reveille Range bounding fault is to faults at YM.

Black Mountains (eastern Death Valley). The Black Mountains area may offer a view of both silicic and basaltic magmatic plumbing systems. The Black Mountains are a relatively intact block of the upper crust that has been rotated and uplifted by extensional faulting, and subsequently denuded by erosion. Important investigations that may be possible in the Black Mountains include studies of patterns and spatial distributions of magmatic dike systems and relationships of dikes to surface vents. These studies are important to constrain groundwater flow models used to assess the hydrologic effects of potential magmatic processes at YM. Studies of the Black Mountains may provide improved constraints on orientation, spatial extent, spacing, and the detailed patterns of dikes represented in groundwater flow simulations.

Cima; Coso. Studies of the Cima and Coso volcanic fields may provide additional information about the influence of faults on vent locations and alignments. Studies of the regional tectonic setting of these fields, in conjunction with recent space geodetic data, may also provide insight into relationships between finite strain and strain rate on localization of volcanism.

Erupting mafic cinder cones do not occur in the northern, primarily extensional BR region. Modern mafic volcanoes in North America are restricted primarily to the Pacific magmatic arc region of the southern BR. Thus, the modern analogs suggested here are within plate-tectonic domains of convergence and active subduction, rather than within the broad continental extensional environment of the BR province. Locally, however, extensional deformation may characterize areas of active cinder cone eruption. Proposed Holocene-modern basaltic eruptive analogs include:

Jorullo (Mexico), Parícutin (Mexico), Cerro Negro (Nicaragua). Investigations of these modern basaltic volcanoes are likely to improve existing concepts of eruptive style, and to provide important data on associated dynamic and hydrothermal processes. Because magmatic volatile content strongly influences the dynamics of volcanic eruptions, comparative analyses of volatile contents and eruptive styles at modern mafic vents may significantly improve conceptual models of potential eruptions at YM. Studies of the extent, intensity and longevity of diffuse degassing of magmatic volatiles and hydrothermal alteration of the surrounding rock will contribute substantially to development of performance assessment scenarios of volcanic disruption.

Heater tests conducted in G-tunnel, within the Nevada Test Site, may provide useful information on the far-field effects of magmatic heating of the Paintbrush Tuff. Additional analog sites will be considered, as needed, depending on emerging priorities in site characterization and performance assessment.

17.3 TECTONIC PROCESSES

Investigations of structural/tectonic analogs are important to predict and analyze a range of future potential deformation states at YM. Specifically, prediction of hazards at YM related to coupled earthquake and fault-rupture processes is likely to depend heavily on forward models of coseismic and aseismic slip. Constraints on fault geometry, incremental slip, and associated distributed deformation should be developed from both site characterization and studies of similar structures elsewhere in the BR region. For example, measurements of fault slip at YM suggest that the system is extended only about 10–60 percent. Studies of analog systems that are more strongly extended (e.g., >100 percent in the Bullfrog Hills area) may substantially improve predictions of potential future deformation due to fault slip. Indeed, it may be viable to use multiple analog sites as a forward modeling process to examine how deformation might progress from the current state at YM to a more extended condition. Analogs may also show how the fault system evolves. Current models include systems that evolve as active low-angle sliding surfaces, as well as systems that evolve by high-angle cross-cutting of pre-existing, uplifted, low-angle fault surfaces.

Important questions and issues related to tectonics and structural deformation which would benefit from investigations at analog sites include:

- Do detachment systems evolve as low-angle faults, or do they evolve into low-angle faults?
- What role do high-angle fault elements play in the overall kinematic evolution of detachment systems?
- What surface-geological criteria can be used to discriminate between high-angle (domino style) fault systems and detachment systems?
- How do high-angle dip slip, low-angle dip slip, and strike slip (transform) faults interact?

- What are the implications of fault geometry for earthquake seismic and fault rupture hazards?
- What is the neotectonic deformation style at YM? Has the structural style at YM changed significantly over the last 10 million years?
- How does tectonic extension influence the location and style of volcanism within the central BR region? Do eruptive volumes correlate to finite extensional strain or to strain rate?
- How are extant or incipient faults influenced by intrusion of magmatic dikes or by eruption of vent systems?

Answers to these questions, and data necessary to develop and adequately constrain prediction of future tectonic deformation at YM are not attainable solely by site characterization. Important data that is difficult to acquire at YM includes:

- direct determination of subsurface fault geometries
- direct determination of depths of potential detachment faults
- slip and paleoseismic histories of faults.

Investigations of analog regions is necessary to supplement data acquired by site characterization to estimate earthquake hazards and repository risk at YM. Data that must be acquired from regions of historic seismic activity and from fault systems with a discernable paleoseismic record, preferably both, include:

- rate and style of seismic strain release within the region that comprises the tectonic setting of YM
- vibratory ground motion (shaking)
- ground accelerations
- attenuation characteristics
- aftershock characteristics
- length-area-magnitude relationships
- segmentation
- associated groundwater effects.

An appropriate approach to identify analog fault systems includes use of existing studies, along with reconnaissance trenching and characterization studies to determine the paleoseismic record at potential analog sites. In concert with these fault studies, appropriate seismo-tectonic (i.e., earthquake) analogs may be further defined by examining existing focal mechanism solutions and selectively re-computing seismic source characteristics and focal mechanisms. Information on the dynamic response of underground systems at YM to future potential earthquake seismicity may be gained by reviewing studies of the effects of underground nuclear tests on tunnels at the Nevada Test Site. Such studies may be particularly appropriate to predict near-field effects, such as seismic slip on the Solitario Canyon fault or the Paintbrush-Stagecoach Road fault.

17.3.1 Potential Tectonic/Structural Analogs

In practice, candidate structural analogs of YM may be restricted to the BR region. Structures are well exposed in the mountain ranges, and alternative Neogene structural styles applicable to YM are widespread within the region. Also, analogs from within the BR region are more likely to have a similar overall Neogene and Quaternary geologic history, as well as comparable *in situ* stress and strain conditions. However, depending on acquisition of additional information about deep fault geometry at YM (i.e., from reflection seismic surveys), regions such as the East Africa/Red Sea Rift system, the North Sea/Viking Graben, or the Aegean may provide good faulting-process analogs.

The YM region is structurally complex, and no clear consensus has emerged on the detailed structural style. Generally, YM is considered to be part of an extensional system that includes both strike-slip and dip/oblique slip normal faults. Uncertainty exists in describing how these different faults interact to accommodate modern regional displacements and in determining the relative mix of potential seismic and aseismic slip. Debates about basic subsurface fault geometry (planar versus listric) and slip history are common. However, YM is mapped in considerably more detail than most areas that would qualify as analogs. Thus, the structure of YM is uncertain, and the structure of potential analog areas is likely to be even less certain. Consequently, the primary value of structural analogs is in the opportunity to study similar processes, rather than as "look-alike" models of YM.

Proposed criteria for selecting candidate tectonic/structural analogs of YM include: (i) late Neogene and Quaternary geologic history of tectonic extension and associated volcanism (generally satisfied by potential analogs within the BR region); (ii) evidence of association with regional detachment fault systems and related development of metamorphic core complexes; (iii) detachment system crosscut by high-angle normal faults (i.e., Bare Mountain); (iv) association with crustal-scale strike slip fault systems; (v) erosion to a deeper structural level than YM; and (vi) associated basaltic volcanism.

Proposed tectonic/structural analogs include:

Black Mountains (Death Valley area). The Black Mountains may be a reasonably useful general tectonic/volcanic analog for YM. Neogene volcanism within the Black Mountains may be similar to YM in that silicic ash flow and rhyolite lava sequences cap the stratigraphic section and occupy a structurally high position on the Black Mountains fault block. However, silicic eruption volumes may be significantly less than at YM. The Black Mountains are in a more strongly extended region than YM, and the fault block has been rotated above a regional detachment fault system. The block thus lies essentially on its side, exposing a cross section of the upper crust to a depth of about 6–8 km. Processes and features that may be studied include deep fault geometry, interaction of sequential generations of faults, and relationships of basaltic dike networks to the extensional fault system.

Bullfrog Hills. This area may be a good analog for a more strongly extended YM system. Neogene and Quaternary tectonic extension in the Bullfrog Hills regions is in excess of 100 percent. Detailed review of existing geologic maps and sections, supplemented with focused field studies, may provide useful examples of listric fault systems at various intermediate stages of extension. These may be useful as natural forward models of the YM system.

Dixie Valley, Cedar Mountain, Borah Peak. These areas may be appropriate to develop and constrain models of normal and normal-oblique mainshock sources and coupled models of coseismic fault slip and ground rupture. These regions are particularly useful for investigations of fault segmentation. Paleoseismic records (from trenching studies) may provide additional information on regional-spatial/temporal clustering and on local recurrence periods.