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# CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES

## TRIP REPORT

**SUBJECT:** 8th European Commission Natural Analogue Working Group (NAWG) Workshop
20-1402-561/20-1402-871

**DATE/PLACE:** March 23–25, 1999
Strasbourg, France

**AUTHOR:** William M. Murphy and David A. Pickett

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**BACKGROUND AND PURPOSE OF TRIP:**

The NAWG brings together experts on natural analogues to nuclear waste disposal to discuss results, applications, and future directions of natural analogue studies. The workshop consisted of three days of oral and poster presentations, supplemented by open discussion sessions. CNWRA staff attended in order to make presentations in a session on Peña Blanca and to promote possible international cooperative studies at Peña Blanca. Abstracts and a list of attendees are available from the authors.

**SUMMARY OF PERTINENT POINTS:**

**Session 1: Natural Analogue Overview**

Overview presentations were given by J. Cramer (Craton Corp., Norway), B. Côme (ANTEA, France), and H. von Maravic (EC, Belgium). Cramer summarized the role of the NAWG in promoting use of analogues in support of geologic disposal of nuclear waste, emphasizing the large projects that have been promoted by NAWG and the emphasis participants have placed on making contributions to performance assessments (PA). Côme summarized a French initiative to expand analogue studies to consideration of the stability of binders (stabilizers) for toxic wastes such as asphalt and glass. Objectives of the study were emphasized rather than results. von Maravic expressed an optimistic view of the benefits of EC sponsorship of the MIRAGE project and the NAWG. He noted an evolution in analogue studies from large scale projects to small scale single process studies.

**Session 2: Natural Analogue Projects 1**

Discussions of specific natural analogue sites opened with a presentation by J. Smellie (CONTERRA, Sweden) on the Maqarin cementitious materials analogue in Jordan. At this site, bituminous coals spontaneously combusted due to sudden exposure to oxygen, producing natural cement. Studies are geochemical in nature, focused on hyperalkaline groundwaters resulting from interaction with the cements and interaction of the waters with host sedimentary rocks (e.g., alteration and porosity reduction). V. Havlova

(Nuclear Research Institute, Czech Republic) then described pilot studies at the Ruprechtov site in the Czech Republic, where argillaceous sediments are being studied as analogues to bentonite/clay repository materials. Work so far has focused on water chemistry and uranium-series data. Moderate U accumulations in this reducing system are observed associated chiefly with organic matter and amorphous Fe minerals.

**Session 3: Natural Analogue Projects 2**

Two presentations on thermal effects on clay deposits were followed by a summary of studies sponsored by the Spanish ENRESA. R. Pellegrini (U. Rome) described mechanical effects at three sites where igneous intrusions occur in clay formations: Isle of Skye (UK), Col du Perthus (France), and Orciatico (Italy). Clay formations become harder and more compact and develop fractures due to heating and subsequent cooling. A. Bouchet (ERM, France) presented mineralogical analyses from the same sites. Generally, a swelling smectite phase is generated in the short duration heating events. Quartz and carbonates are depleted from the zones closest to the heat source. Where temperatures did not exceed 100 °C, no major mineralogical changes were observed.

The Spanish program is focused on three projects, as described by P. Hernan (ENRESA, Spain). The objective of the BARRA project is to examine effects on clay barriers. Thermal effects are being examined at Cabo de Gata where an igneous dome intruded bentonites. Loading of bentonites by overlying strata is being examined as an analogue of stresses induced by a waste container. The MATRIX project involves investigations of uranium transport in fractures around a uranium deposit in metamorphic rocks. In the ARCHEO project an effort is being made to investigate corrosion of ancient metals in natural environments. Few results of these projects were presented as they all appear to be in initial stages of investigation.

**Session 4: Natural Analogue Projects 3**

P. Airey (ANSTO, Australia) provided a summary of the completed ASARR project (Analogue Studies in the Alligator Rivers Region). Included was a classification system for analogue studies that places them in the context of repository relevance. Notable ASARR results were discussed at site scale (e.g., U mass balance calculations), sample scale (e.g., surface complexation modeling and *in situ* $K_d$), and micro scale (e.g., mineral chemistry). Of possible relevance to Peña Blanca studies were successful ion probe U-Pb and U isotope analyses of fine-grained uraninite. The role of a fault in radionuclide migration was the theme of presentation by H. Yoshida (JNC, Japan) on the Tono uranium deposit, Japan. Preliminary results suggest that fault gouge tends to retard migration, meaning that the fault does not serve as a conduit for transport to greater distances.

**Session 5: Poster Session**

A. Simmons (LBNL) presented a poster on the DOE analogue program for YM. The emphasis was on future work. A variety of studies were highlighted including hydrothermalism at Taupo, New Zealand, but an emphasis was on Peña Blanca. (see discussion of Peña Blanca session below.)

P. Ildefonse (Université Paris) gave a poster on Nopal, mainly covering elemental and stable isotope data. Oxygen isotope ratios suggest temperatures of 50–75 °C for kaolinite (presumably coeval with uraninite), 20–45 °C for smectites and opal, and around 10 °C for caliche. These calculations involve assumptions about water isotope ratios, and the temperatures are not well constrained. Rock and mineral chemical data were interpreted in terms of mobility during U mineral genesis. For example, there is some evidence for rare earth

element mobilization within the ore body, analogous to the observed U depletion in the center of the ore body. These data may be useful in the CNWRA's studies at Nopal.

**Sessions 6 and 7: Palmottu 1 and 2**

Seven talks in two sessions covered results from a major program at the Palmottu analogue, Finland, the final report for which is soon to be submitted. At the site, U and Th are hosted in hydrothermal veins cutting fractured crystalline bedrock in a water-saturated, reducing environment. R Blomqvist (Geological Survey of Finland) opened the sessions with an overview emphasizing groundwater flow and geochemical models. A notable surprise was a deep, slightly oxidizing flow system apparently originating in 10,000 yr-old glacial melt waters. T. Ruskeeniemi (Geological Survey of Finland) then spoke on uranium mineralogy at the site. Major U phases are uraninite and an amorphous silicate resembling coffinite, both dominated by the reduced U(IV) state; U concentrations of up to thousands of ppm are noted in calcite and other fracture-filling phases. The only occurrence of uranyl minerals is uranophane found at shallow depths where waters are more oxidizing. Ruskeeniemi reported discordance and open-system effects on U-Pb and U-series geochronological systematics in the U minerals.

P. Pitkänen (VTT, Finland) and M. Gimeno (CIEMAT, Spain) presented results on modeling of the hydrogeochemical evolution of Palmottu to provide a basis for understanding element transport. This work, benefitting from extensive well-drilling at the site and incorporating mineralogical data, involved statistical analyses to delineate four groundwater types and geochemical modeling that included both mixing and reaction path computations (using PHREEQC). Key processes include (i) weathering of the crystalline host rocks to produce young, more shallow bicarbonate waters and (ii) mixing between these young waters and deep, glacially-derived saline waters. J. Bruno (QuantiSci, Spain) finished the session with a discussion of the consistency between water redox conditions (Eh-pH) and host rock mineralogy at Palmottu. For example, in the mineralized zone, redox is consistent with control by the $UO_2$-$U_3O_7$ pair. This result suggests the potential importance of spent fuel control of redox after package failure. More generally, the results lend confidence to modelers' ability to predict water chemistry based on site data.

The first talk in the second Palmottu session, by D. Arcos (QuantiSci, Spain), concerned attempts to model kinetically and thermodynamically the aqueous behavior of trace elements at analogue sites (the discussion included U in Oklo waters). The investigators developed co-dissolution/co-precipitation models that fit the data better than pure phase equilibria. Included was modeling of the frequently noted (including at Nopal) association of U with Fe oxyhydroxides. D. Read (ENTERPRIS, UK) and K. Rasilainen (VTT, Finland) then discussed detailed modeling of U migration using data—including U series results—along a groundwater flow path in the upper oxidizing zone from six wells. A major conclusion of the study is that, even in the oxidizing zone, U is not dispersed on a large scale; it is, rather, "reconcentrated." To wrap up the Palmottu sessions, B. Grundfelt (KEMAKTA Konsult, Sweden) summarized implications of the program for PA. He concluded that Palmottu had proven most useful in identifying processes (such as water-rock interaction effects on water chemistry) and scenarios (such as deep infiltration of glacial water), and in lending credibility to the notion of geological disposal of nuclear waste. Model validation—an oft-stated natural analogue goal—was less than satisfying due to uncertainties in initial and boundary conditions in the natural system.

**Sessions 8 and 9: Oklo 1 and 2**

F. Gauthier-Lafaye (CNRS, France) summarized the geologic and exploration history of the natural fission reactor deposits at Oklo, recounting the conventional interpretation of association of the uniquely rich deposit with oxygenation of the atmosphere. The Oklo deposit is now closed, samples have been archived in Franc and present studies focus on the nearby Okelobondo natural reactor deposit. J. Bruno (QuantiSci, Spain) described petrographic and dissolution studies of Oklo uraninite as an analogue of spent fuel. Observations included the effects of bicarbonate and dissolution rates of trace elements. M. Del Nero (CNRS, France) presented data on the distribution of uranium and rare earth elements (REEs) in materials surrounding the reactor zone uraninite deposits at Bangombe, which is near Oklo. The strongest affinity was with iron oxyhydroxides and phosphates associated with iron oxyhydroxides. Sorption on clay minerals is also important and is reasonably modeled using a surface complexation approach. E. Ledoux (Ecole des Mines, Paris) presented local equilibrium reaction path calculations of the evolution of water and mineral chemistry for the present deposits around Oklo. A primary constraint was water chemistry analyses from boreholes. A variety of redox buffers was investigated with the conclusion that reactions among iron minerals (e.g., siderite and ferrihydrite) reasonably account for the redox potential of the waters. Redox buffering by graphite, representing organic material, can lead to stabilization of observed sulfide minerals (e.g., galena and pyrite), but the corresponding redox potentials are inconsistent with values measured for the waters. M. Cuney (CREGU, France) described petrographic studies identifying multiple stages of deformation and mineralogical alteration throughout the history of the Okelobondo reactor zone. Basin-scale transport of light REEs and uranium by phosphate rich and saline solutions circulating in fractures is indicated. Relevance to nuclear waste disposal was not addressed explicitly. A hydrological and geochemical study of the Okelobondo uranium deposits was presented by C. Ayora (CSIC, Spain). The deposit is presently located in the mixing zone of a relatively reducing solution resulting from reaction of meteoric water with iron silicates and more abundant solutions buffered at a higher oxidation potential by reactions with manganese phases. In a summary talk, V.M. Oversby (VMO, Sweden) described efforts to integrate field and lab studies associated with the Oklo project with performance assessments. A series of meetings was held to coordinate between the groups, with some exchange of information and understanding, but generally Oklo data have not been adopted in PA to date. Oversby criticized analogue studies in general as failing to represent repository systems and failing to provide well constrained hydrologic data, and advocated studies of processes. J. Cramer objected, noting that the Cigar Lake analogue system was well characterized and representative.

**Sessions 10 and 11: Peña Blanca 1 and 2**

W. Murphy (CNWRA) presented a brief introduction describing the relations between YM and Peña Blanca, emphasizing similarities in geology, hydrology, climate, and uranium mineralization as an analogue of spent fuel. He also noted differences including the engineered barrier system at YM and acid sulfate alteration at Peña Blanca. I. Reyes (U. Chihuahua, Mexico) continued the introduction with an overview of the carbonate and volcanic stratigraphy of the Peña Blanca district including age dates, the general structural features of the area, the lithology of the volcanic units, and the character of uranium mineralization. Detailed mapping of the Nopal I deposit as the primary analogue site was described.

P. Ildefonse (Université Paris) discussed the use of radiation-induced defects in kaolinite for interpreting U migration at Nopal. (This study has been published in *Applied Geochemistry*.) The principle behind the method is that a specific, measurable crystalline defect in kaolinite can act as a radiation dosimeter, indicative of adjacent radionuclide-rich materials. At Nopal, the method suggests long-term U concentrations in rocks

outside the ore deposit that are much greater than the measured concentrations. This interpretation is consistent with CNWRA models of late-stage remobilization of U out of these rocks.

A summary of CNWRA work concerned with uranium evolution at Nopal was presented by D. Pickett. The talk was posed as a history of uranium behavior, supported by mineralogic, chemical, and isotopic data. Implications for YM repository performance were highlighted. This talk was followed by a presentation by M. Murrell (LANL) on U-series data on three Nopal samples provided by the CNWRA. As has been presented previously, the LANL data are consistent with closed-system evolution of fracture U for over 400,000 yrs, in contrast with CNWRA interpretations. This conclusion is regarded as favorable with regard to radionuclide retention in the YM environment. (Murrell does, however, conclude that radium has been recently mobile.) Murrell is likely to request more samples from CNWRA in order to resolve these conflicting interpretations. With regard to other DOE natural analogue efforts, Murrell has indicated that field work at Nopal is planned for June; it is not yet clear what specific investigations will be undertaken.

W. Murphy (CNWRA) described the focus of analogue studies at Nopal I to be on source term and transport issues relevant to the proposed YM repository. Citations to Peña Blanca data in recent NRC, DOE, and EPRI PAs were noted. In general the alteration of uraninite at Peña Blanca was recognized in all three PAs as an analogous system. In the NRC PA, a module was developed to permit analogue data to be used as an alternate source term constraint. In the DOE TSPA-VA, Peña Blanca data are cited repeatedly as qualitative support for spent fuel alteration models. In the EPRI PA, uraninite alteration at Peña Blanca is cited as support for a questionable notion of metastability of $UO_2$. The alternate source term sensitivity study conducted for the NRC PA was described in some detail. It is based on the maximum average oxidation rate of uraninite at Nopal I derived from mass and age constraints and limiting estimates of water flux and uranium removal from the system.

**Session 12: General Discussion**

The session organizer A. Simmons (LBNL) posed the following questions to the panel members (R. Blomqvist-Palmottu, F. Gauthier-Lafaye-Oklo and W. Murphy-Peña Blanca): (i) what are the primary contributions of specific analogue studies; (ii) what are primary contributions to national programs; (iii) what issues are still to be addressed; (iv) what guidance can be provided to new analogue programs; and (v) what is the future of analogue work and NAWG? Murphy mentioned site specificity, source term and transport issues addressed by the Peña Blanca analogue, noted recognition in national programs of PAs for YM, cited ongoing work on episodicity of release and mobilization processes at the analogue site, suggested that new analogue programs use caution not to oversell the potential use of analogue data, and promoted an international program of studies under the EC at Peña Blanca. Gauthier-Lafaye emphasized process studies at Oklo and its unique character as a natural reactor providing information on radiolysis effects and the fate of fission products. Blomqvist emphasized the controls on oxidation potential in groundwaters in cratonic environments subject to glacial cycles. He emphasized the importance and time requirements for thorough site characterization for successful natural analogue studies. Guidance for site selection and scenario development for PA were also noted as key objectives of new analogue studies. The following group discussion tended to focus on the value of process oriented studies, and mechanistic understanding of processes as a goal of analogue studies in contrast to global system studies such as those that have been conducted (for example, at Pocos de Caldas and Alligator Rivers).

B. Miller (QuantiSci, UK) discussed ways to use natural analogues to help promote geologic disposal of nuclear waste, including such tools as web sites, field trips, and educational materials. This approach to the

waste issue seemed out of place in the workshop, in that most attendees were rather more interested in better *understanding* disposal. The talk seemed particularly inappropriate to those of us working on the regulatory side of the issue.

**NAWG members meeting**

About 20 national representatives met to discuss the organization and future of the NAWG. A NAWG web site is under construction and feedback was requested. The role of the NAWG in public relations was discussed, and the natural analogue video produced by NAGRA was noted for its good intentions and limited exposure. The structure of the next meeting, which is intended for spring 2001, will be workshop oriented rather than exposition oriented. Volunteers are requested to host this meeting. The advantages of having an associated field trip to an analogue site were generally endorsed. Some informal discussions were held subsequently with I. Reyes regarding the possibility of hosting the meeting in Chihuahua with a field trip to Peña Blanca.

**Observations**

Advances by the NAWG appear rather modest considering the large number of participants in the workshop. A concern expressed repeatedly was that most analogue studies have so far failed to prove applicable to PA. The need for process studies was another recurring theme. Despite the DOE presence at the workshop, DOE natural analogue work in relation to YM is limited in scope. Peña Blanca analogue work is receiving increasing attention and recognition, partly due to PA applications and partly due to its potential for process studies. This was the first NAWG workshop to offer more than a general description of work at Peña Blanca and/or a contributed poster. Few new initiatives were identified in the workshop or members meeting, although the role of analogues in public relations and the web site were discussed at some length.

**Pending Actions**

Papers will be prepared for publication in the proceedings on subjects covered in CNWRA contributions to the Peña Blanca sessions. Discussions will continue on the possibility and desirability of hosting the 2001 NAWG workshop. A summary of the workshop will be distributed by email to individuals in the US with an interest in analogue studies.

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