

CONF- 860858--3

RECEIVED BY OST: MAY 12 1986

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7408-ENG-36.

TITLE: OCCURRENCE OF FRACTURE-LINING MANGANESE MINERALS IN SILICIC TUFFS,
YUCCA MOUNTAIN, NEVADA, USA

LA-UR--86-1412

AUTHOR(S): Barbara Arney Carlos

DE86 010199

SUBMITTED TO: Fifth International Symposium on Water-Rock Interaction
Reykjavik, Iceland
August 7-12, 1986

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

new

OCCURRENCE OF FRACTURE-LINING MANGANESE MINERALS IN SILICIC TUFFS, YUCCA MOUNTAIN, NEVADA, USA

Barbara Arney Carlos
Los Alamos National Laboratory, Los Alamos, NM 87545, USA

INTRODUCTION

Yucca Mountain, in southern Nevada (Fig 1), is being studied by the Nevada Nuclear Waste Storage Investigations (NNWSI) Project as a potential site for an underground high-level nuclear waste repository. The site is within Miocene volcanic rocks that are 1.5 to 4 km thick and range in age from 12.5 to 14 MY (Marvin et al., 1970; Carr et al., 1984). Several holes have been drilled in Yucca Mountain for geologic and hydrologic studies. Drill hole USW G-4 (G4 on Fig. 1), the most recently cored hole within the potential repository block, was chosen for detailed study of fracture-filling minerals because it is closest to the planned NNWSI exploratory shaft. Drill hole USW G-4 was drilled to 914.7 m (3001 ft) and continuously cored from 6.7 m (22 ft) to total depth (TD). The drilling history, lithology of the core, and geophysical logs of the well are given in Spengler and Chornack (1984). Manganese minerals are mentioned briefly, but not identified, by Carlos (1985). Manganese fracture coatings in a few samples from drill holes UE-25b#1H, USW G-3 (G3 on Fig. 1), and USW G-4 are described and discussed briefly in Caporuscio and Vaniman (1985). Because manganese oxides in fractures may act as a natural barrier to radionuclide migration (Means et al., 1978; Zielinski, 1983), it is important to determine exactly which manganese minerals are present, in what intervals they occur, and how extensive these fracture coatings are.

METHODS

The manganese oxides coating fractures in drill hole USW G-4 were examined using a binocular microscope (50x magnification). Samples of open fractures were examined using an ISI scanning electron microscope (SEM) up to 3000x magnification, and qualitative energy dispersive (EDS) analyses were obtained. Closed fractures were thin sectioned, and coatings were chemically analyzed on a Cameca electron microprobe. Microprobe analyses of manganese dendrites on nearly planar open fractures were also attempted as there was no way to thin section across these samples. The results are probably less quantitative than the results for thin sections but are more reliable than the EDS analyses obtained on the SEM. Whenever open fractures contained enough coating material, these were scraped and hand picked under 25x magnification for x-ray powder diffraction (XRD) using a Siemens D-500 diffractometer. Because of the small amounts of material available, samples were all run as water smears on a glass plate, usually for at least 15 minutes per degree 2θ . The results are only qualitative due to orientation

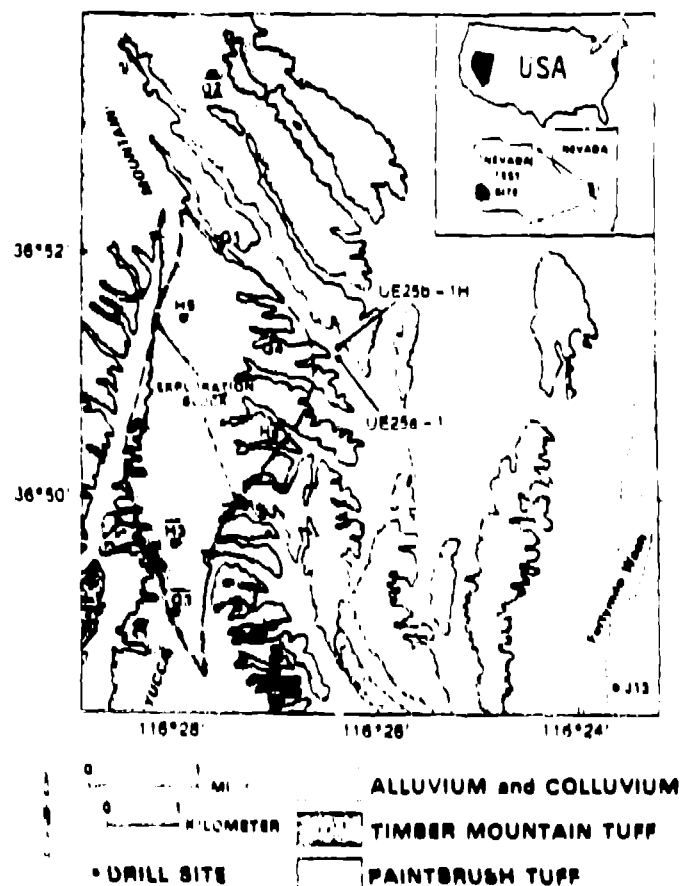


Fig. 1. Location of Drill Holes at Yucca Mountain, Nevada.

effects and small sample size, but the constituent minerals were identified from the XRD patterns.

RESULTS

Fracture coatings from the complete length of core from drill hole USW G-4 were examined. Manganese oxide coatings occur in discrete intervals (Fig 2): from 12 to 40 m (40 to 131 ft) depth, from 207 to 400 m (680 to 1312 ft), minor amounts from 500 to 509 m (1640 to 1670 ft), along faults and shear fractures from 585 to 607 m (1920 to 1991 ft), from 638 to 640 m (2093 to 2100 ft), from 783 to 818 m (2570 to 2684 ft), and from 863 m to 915 m (2830 to 3000 ft)(TD). The static water level is at approximately 540 m (1770 ft) (Robison, USGS, personal communication, 1984).

The manganese oxides in the upper interval occur as well-formed dendrites, 1-10 mm in diameter, on fractures in densely-welded tuff. They occur over cristobalite, mordenite, and smectite or illite fracture coatings and on bare rock. X-ray diffraction indicates they are romanechite. Microprobe analyses show that the dendrites from 21.3 m (70 ft) (Table I) do not contain Ba; Ca and possibly Mg apparently take its place in the romanechite structure. Although the analyses were performed on dendrites, the silica content shows that the Mn oxide is intergrown with other minerals. The XRD pattern shows that in this sample romanechite occurs with cristobalite, quartz, feldspar, mordenite and a small amount of clay (illite?).

Many fractures between 207 and 400 m (680 and 1312 ft) depth contain manganese dendrites or crusts, but they are usually small (1-2 mm) and cover less than 1% of the total fracture surface. Manganese oxides increase in abundance with depth in this interval, and two samples, at 306 and 383.4 m (1201 and 1258 ft) contained

enough manganese oxide (~4% coverage of the fracture surface) to appear in the XRD pattern. The manganese oxide crusts in these intervals are either todorokite or lithiophorite. Manganese oxides occur over quartz, feldspar, cristobalite, tridymite, under mordenite, and, below 379.5 m (1245 ft), under heulandite. SEM and microprobe analyses of manganese patches on open fractures indicate Al and possibly traces of Zn in the manganese minerals; Al suggests lithiophorite, but the analyses are not quantitative enough to provide positive identification.

From 500 to 509 m (1640 to 1670 ft) manganese oxide occurs in the zeolitized rock matrix more than in fractures. The manganese oxide in fractures does not form distinct patches but rather gives a grey tint to the fine-grained coatings on the fractures. The sample at 500.7 m (1643 ft) is one of the darkest of these and consists of tiny (<5 micron) specks embedded in a mordenite mat. The amount of manganese mineral is insufficient for XRD analysis. SEM analyses of several of these specks show minor amounts of Ni. The large Ca and small K peaks may reflect the composition of the manganese mineral or may actually reflect the mordenite composition.

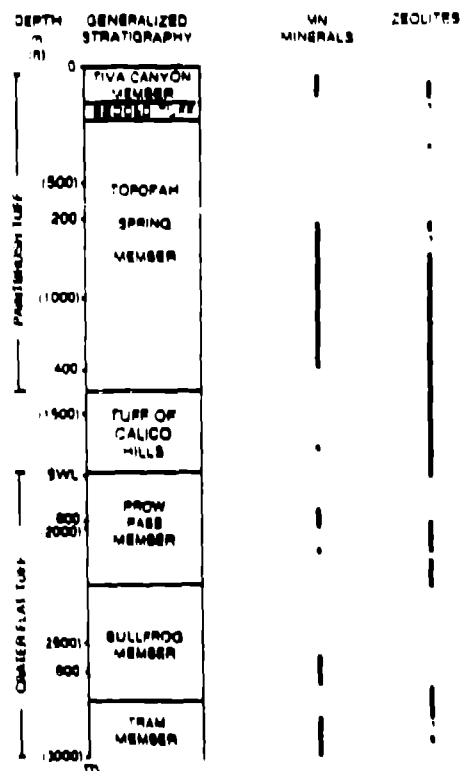


Fig. 2. Manganese and Zeolites in Fractures, USW G-4.

TABLE I. MICROPROBE ANALYSES OF MANGANESE MINERALS IN FRACTURES, USW G-4

Sample Depth (ft)	70* av of 4	1258* av of 3	1990A 1 pt	1990B av of 2	2099 shard av of 4	2099 vein 1 pt	2615 av of 3	2620 av of 3	2656 av of 5	2947 av of 3
SiO ₂	22.53	2.90	21.74	31.35	0.23	5.68	0.46	0.96	1.23	0.90
TiO ₂	0.17	0.17	0.23	0.18	N/D	N/D	0.29	1.41	1.06	0.59
MnO ₂	53.47	51.34	51.95	41.98	85.40	81.26	73.74	74.87	75.47	74.04
Al ₂ O ₃	4.27	23.54	7.92	10.71	0.79	2.19	0.16	0.61	0.33	0.82
Fe ₂ O ₃	5.82	0.87	3.92	2.38	0.16	0.27	2.28	7.52	4.44	3.57
MgO	2.62	0.55	N/A	N/A	N/A	N/A	0.22	N/D	2.77	N/A
CaO	6.01	0.53	0.46	0.39	0.13	0.38	2.13	0.29	1.19	0.63
BaO	N/D	N/D	5.70	3.26	11.49	9.80	3.39	8.02	2.21	6.29
SrO	N/D	N/D	N/A	N/A	N/D	N/D	2.12	3.25	0.52	N/A
ZnO**	0.56	1.04	N/A	N/A	N/A	N/A	N/D	0.53	N/D	N/A
NiO**	N/A	N/D	N/A	N/A	N/A	N/A	N/D	0.32	N/D	N/A
K ₂ O	0.91	0.25	3.52	6.26	2.24	2.03	0.88	1.43	0.17	3.20
Cl	0.16	N/D	N/A	N/A	N/A	N/A	N/D	N/D	N/D	N/A
Total	96.52	81.19	95.44	96.51	100.44	101.61	85.67	99.21	89.39	90.04

* Surface of open fracture

** av detected for pure Mn standard : Zn 0.40, Ni 0.15

N/A not analyzed

N/D none detected (amount \leq backgrounds).

Manganese oxides are not common fracture-coating minerals between 585 and 607 m (1920 and 1990 ft). They occur primarily along fault planes and shear fractures where they either surround or replace pulverized zeolitic rock matrix. In the sample from 607 m depth the manganese oxide cryptomelane fills in between shards. Microprobe analyses of manganese oxides in this sample revealed much Si (and probably K) from the rock matrix but also show a variation in Ba content from one area to another on the sample.

The manganese oxides from 638 to 640 m (2093 to 2100 ft) closely resemble those in the lowest intervals but are separated from that series of Mn-filled fractures by 143 m (470 ft). These fracture fillings are thick sooty black. The sample from 640 m depth has tufts of acicular crystals which are visible at 50x magnification. SEM images show that they either precede mordenite or were co-deposited, as hollandite needles appear to penetrate through clouds of mordenite and some have short fibers that are probably mordenite growing on them. Manganese oxide lines the fractures and fills in shards lined with clinoptilolite. Microprobe analyses indicate high Ba contents, both for vein and shard-filling material. XRD analysis indicates the manganese mineral is hollandite.

The manganese minerals hollandite or cryptomelane form continuous black coatings on the surface of fractures from 783 to 818 m (2570 to 2684 ft) depth, usually over quartz and under calcite. They have similar acicular or stubby filiform morphology as seen in the SEM, but they have very different minor element chemistry as determined by microprobe (Table I). From 863 to 915 m (2830 to 3000 ft) manganese coatings are less continuous and often occur with red-brown hematite staining. In other fractures the manganese minerals occur with quartz. In this interval, as in the one above, the manganese minerals are hollandite or cryptomelane and the minor element chemistry is variable even within a single sample.

DISCUSSION AND SPECULATION

Based on mineralogy, chemistry, morphology, and separation of manganese-bearing intervals by barren intervals, it is concluded that the manganese minerals were deposited by at least 4 separate and isolated solutions. The upper interval of large and well-formed romanechite dendrites is interpreted to be derived from waters percolating down from the surface, one of the possibilities mentioned by Caporuscio and Vaniman (1985). The Ca and Mg contents of these dendrites support this interpretation. The small dendrites and scales of todorokite and/or lithiophorite in the densely-welded rock from 207 to 400 m (680 to 1312 ft) may well have formed from Mn dissolved from the host rock as was suggested by Caporuscio and Vaniman (1985). The manganese deposits from 500 to 509 m (1640 to 1670 ft) are unique in the core from this drill hole in morphology and chemistry and may be related to the manganese in the host rock in that interval. Additional XRD and microprobe work are being done on this interval. The remaining manganese minerals, below 585 m (1920 ft), are all hollandite and cryptomelane and may have precipitated from an upwelling fluid with differences in chemistry caused by temperature gradient and rock matrix variations. Alternatively there may have been a sequence of fluids over a period of time, or separate fluids in the apparently separated intervals of manganese deposition, but all are interpreted as being early, hydrothermal-type deposits. Information from additional holes may help constrain these interpretations.

REFERENCES

- Caporuscio, F.A. and Vaniman, D.T. (1985) Iron and manganese in oxide minerals and in glasses: preliminary consideration of Eh buffering potential at Yucca Mountain, Nevada, Los Alamos National Laboratory report LA-10369-MS.
- Carlos, B.A. (1985) Minerals in fractures of the unsaturated zone from drill core USW G-4, Yucca Mountain, Nye County, Nevada, Los Alamos National Laboratory report LA-10415-MS.
- Carr, W.J., Byers, F.M., Jr. and Orkild, P.P. (1984) Stratigraphic and volcano-tectonic relations of Crater Flat Tuff and some older volcanic units, Nye County, Nevada, US Geol. Surv. Open-file report 84-114.
- Marvin, R.F., Byers, F.M., Jr., Mehnert, H.H., Orkild, P.P. and Stern, T.W. (1970) Radiometric ages and stratigraphic sequence of volcanic and plutonic rocks, southern Nye and western Lincoln Counties, Nevada, Geol. Soc. Am. Bull. 81, 2657-2676.
- Means, J.L., Crerar, D.A. and Borcsik, M.P. (1978) Adsorption of Co and selected actinides by Mn and Fe oxides in soils and sediments, Geochim. Cosmochim. Acta 42, 1763-1773.
- Spengler, R.W. and Chornack, M.P. (1984) Stratigraphic and structural characteristics of volcanic rocks in core hole USW G-4, Yucca Mountain, Nye County, Nevada, section on geophysical logs by D.C. Muller and J.E. Kibler, US Geol. Surv. Open-file report 84-789.
- Zielinski, R.A. (1983) Evaluation of ash-flow tuffs as hosts for radioactive waste: criteria based on selective leaching of manganese oxides, US Geol. Surv. Open-file report 83-480.