Department of Energy
Washington, DC 20585

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Repository Licensing & Quality Assurance
Project Directorate
Division of High-Level Waste Management
Office of Nuclear Material Safety
and Safeguards
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555

Dear Mr. Holonich:

Enclosed is the U.S. Department of Energy's (DOE) response to the State of Nevada's comments on DOE's use of the rock varnish dating technique.

If you have any questions, please contact Mr. Chris Einberg of my office at 202-586-8869.

Sincerely,

Linda J. Desell

for John P. Roberts
Acting Associate Director for
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Enclosure:
Ltr, Gertz to Loux, dtd 8/21/92

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RESPONSE TO STATE OF NEVADA COMMENTS ON ROCK VARNISH DATING METHOD

Reference: Ltr, Gertz to Loux, dtd 7/24/91

In the U.S. Department of Energy's (DOE) response to the State of Nevada's comments on Study Plan 8.3.1.8.5.1, "Characterization of Volcanic Features" (reference), we suggested that Study Plan 8.3.1.5.1.4, "Analysis of the Paleoenvironmental History of the Yucca Mountain Region," be consulted to attain further background on DOE's plans regarding the rock varnish (cation ratio) dating technique. In their comments on Study Plan 8.3.1.8.5.1, the state included an appendix with comments specifically on this technique. Because DOE does not know if the state intends to offer comments on Study Plan 8.3.1.5.1.4, and because a topical report on erosion is now being prepared, we wish to clear the administrative record regarding the state's comments on the rock varnish dating technique prior to completing the topical report. These comments were furnished to Los Alamos National Laboratory for an assessment of their impact on the planned program. Our responses tend to focus on generic application of this dating technique for site characterization rather than on its use for any specific study.

An enumeration of the state's comments is contained in Enclosure 1. DOE's responses to those comments relative to the utility and validity of the rock varnish dating technique are contained in Enclosure 2. The 16 comments on that subject have been consolidated into eight concerns to reduce the redundancy in the state's comments. The remaining 12 comments dealt with geochemical aspects bearing on formation of rock varnish, as a phenomenon, that are not directly relevant to the dating technique. These were Comments 5, 6, 7, 16, 20, 21, and 23-28.

6. Specific Comments on Appendix A-Rock-Varnish Dating

Cation-ratio dating using rock varnishes for the purpose of obtaining relative ages of geomorphic surfaces is a relatively exciting new field where techniques and methods are being developed which may prove to be valuable to interpretive research some time in the future. Because this dating approach is still in the developmental stage, controversy among researchers over techniques and methods is found throughout scientific literature. The Yucca Mountain site characterization program must provide analytical efforts that have reasonable confidence levels considerably above that which is currently available for rock varnish dating. It is questionable whether the general scientific community will accept the results of these proposed investigations given the current state of dating techniques and methodologies. Rock varnish appears to be a complex mixture of transition metal oxyhydroxides containing various organics (see Nagy, et. al., 1990, GSA Abstracts No. 09137) and detrital components. The genesis of the material is poorly understood; its behavior in the weathering environment is also poorly understood. To utilize this material and method to develop age data for studies deemed critical for the characterization of Yucca

Comment 1

ENCLOSURE 1

Mountain appears to be inappropriate because of the uncertainties inherent in the methods and therefore the results.

In a recent publication on rock varnish dating, D. H. Krinsley, R. I. Dorn, and S. W. Anderson (1990) briefly discussed nine general factors that may interfere with rock-varnish dating of geomorphic surfaces. This publication provides a more complete list of pertinent references than offered by Appendix A.

Rock varnish dating is an analytical method which to date has not been refined. In theory, K and Ca trapped in rock varnish should be leached at a constant rate through time. These cations (K and Ca) are then compared to Ti whose mobility should be insignificant. The cation ratio K + Ca/Ti provides therefore an estimated age of surface stability for geomorphic features and surfaces within a particular region. Figure A-1 (Appendix A, page 10) indicates gross regional ratios with age for particular regions. Regionality effects on varnish dating (cation depletion) are presumably a factor of local K and Ca sourcing and regional climatic influences on weathering reactions including local biotic transfer activity. Variations of weathering (leaching) reactions within subregional areas such as Forty Mile Wash, Yucca Mountain, Crater Flat have not been characterized. Changes in climate regime through time, potentially affecting leaching rates over time are not addressed. Curves are presumed to be linear. Section 2.3, Appendix A, pages 6 to 7, provide the rationale behind using rock varnish dating and the laboratory techniques that will be applied. In essence, chemical composition of the varnish will be determined by SEM-EDX. Harrington, et. al., 1989, have indicated their awareness that Ba and Ti peaks overlap with EDX. Thus, the method of analysis does not produce or does not always produce: (K + Ca)/Ti results, but rather produces or sometimes produces: K + Ca/Ti - Ba. The behavior of Ba in leaching systems should be similar to Ca, therefore, there is no surety as to what is being measured and how this affects the theory behind the method. This problem is not addressed in Appendix A. Krinsley, et. al., (page 103, 1990), suggest that WDX analyses are considerably better for deconvoluting Ti and Ba. Yet, there is no mention of utilizing WDX analyses in Appendix A. Electron Microprobe Analyses will apparently be used for mineral composition analyses but apparently not for cation ratio determinations discussed above (Appendix A, section 3.4.7, page 19).

Comment 1

The following are specific page-by-page comments. We are providing these comments only because of the level of emphasis placed on rock-varnish studies in the Study Plan.

Pages 2 to 3.

2

1. It is doubtful that the stated purpose will be met if rock-varnish studies are not augmented by additional dating techniques that are supported by sound theory and are reproducible by standard practices.

3

2. The results will have little utility for the Yucca Mountain site characterization process as the technology to utilize cation-ratio dating is at best a poorly understood relative dating method. This method is not regarded by the scientific community as an absolute dating technique.

Pages 4 to 8.

4

1. The rock varnish dating curve constructed for the Yucca Mountain area requires significantly more data points using standard and acceptable dating tools than has been offered. Sections 2.1 and 2.2 only mention 14-C data collection of the basal layers of rock varnish for volcanism studies. It must be shown that for 14-C dating, rock varnish is a reasonable material. Amino acid work by [illegible]gy, et. al., (1990) suggests that organics are quite mobile in rock varnish.

5

2. It is not clear why PIXE analyses are proposed in section 2.2 in light of the comments in section 2.3. The problem with Ba and Ti will still be significant.

6

3. XRD analyses of rock varnish minerals will probably only identify those of greater than 5% and will not assist in identifying glasses.

7

4. XRF analyses on SEM prepared samples should contain the substrate rock surface. It is unclear as to the purpose of this activity. XRF analyses will not affect elements lighter than 22. Choice of XRF standards for rock varnish may be difficult.

8

5. SEM analyses of rock-varnish by EDX will not resolve the Ti and Ba peak interference problems. WDX analyses should be used as an appropriate substitute.

9

6. It is difficult to see how rock varnish dating could be used in the Yucca Mountain site characterization process if the sampling activity to acquire rock varnish clasts is developmental. The high selectivity of samples appears to suggest that data may not be reproducible. As stated above, acceptance of the dating technique is questionable by the scientific community. Acceptance

...be necessary if the results are presented in licensing.

10

It is difficult to see how the rock-varnish dating curve could be established with adequate error bounds without the extensive use of other dating methods which are not discussed in section 2.

Pages 9 to 19.

11

1. "The processes of rock-varnish formation and accretion on rock surfaces are not yet clearly understood but likely involve both geochemical and biological agents." (page 9, section 3.1, paragraph 1). This statement is probably true. What is also true is cation-ratio dating of rock varnish is not yet clearly understood. On the basis of those statements, we do not understand why the method is being used to characterize a potential high-level nuclear waste repository.

12

2. Rock varnish dating curves are based upon K-Ar and U-trend dated deposits. No documented case has been made that the number of well dated K-Ar and U-trend deposits that have been used to obtain standard data for rock-varnish calibration is a statistically representative sample. For example, literature containing K-Ar dating of volcanic lava flows and ash in the Yucca Mountain region does not appear to provide an abundance of sound reproducible dates.

13

3. In section 3.3.2, there appears to be a strong sampling bias for varnish samples which could diminish the potential for reproducible results. It is unclear how such a sampling approach satisfies QA level 1 requirements. A more representative approach would be to collect all variations of varnish and report the range. The thickest, darkest, and most complete coatings are judgmental factors unless some measuring equipment is used in the field to measure thickness, color, and completeness.

14

4. During sample preparation, clasts are hand washed in deionized water to remove surficial detritus. Is there documentation that the deionized water wash process does not leach K and Ca? Is there a scientifically-accepted and QA approved procedure for washing varnish?

15

5. In section 3.3.6, the ratio of K + Ca/Ti is calculated for 6 overlapping sites and the lowest five are averaged for the sample. Why are the lowest five averaged? What ranges are found? The calculation of the cation-ratio appears to require statistical manipulation. The

approach suggests that any one analytical point does not provide useable cation-ratio data for that sample because there is a wide range of cation-ratios within any one sample. Therefore, if the range of cation-ratios were plotted, the result would not have dating utility. It is unclear why the Study Plan concludes that the average figures are potentially age related.

15 Additionally, in section 3.3.6, K - Ca/Ti is not necessarily what is being measured in the laboratory. A full discussion of the Ba problem is appropriate in this section and should be included.

In section 3.3.6, there appears to be a significant number of anomalies: statistical manipulation of data, and a lack of understanding of the actual geochemical, biogeochemical, and sedimentological processes which occur in rock-varnish. It is difficult to justify using this dating technique given those uncertainties.

6. Section 3.0 appears to emphasize the process of characterization of rock varnish (minus some critical laboratory procedures, and with the addition of several questionable procedures) rather than Yucca Mountain site characterization. There are other dating methods available based upon sound theory and scientific acceptance that have potentially more utility than what is attempted here.

16

Further questions and comments derived from the Appendix A review are as follows:

1. The field methods proposed for sample collection require specific judgement calls on the collection of desert varnished materials. What are the criteria which will be used to make the field judgement decisions? Without such criteria, the data collected may not be representative of the feature analyzed and the data will not be reproducible by independent analyses. Alternative field methods are available to collect representative samples.

17

2. The proposed laboratory methods for obtaining cation-ratios are technically inappropriate. Other methods are available that would supply more accurate data.

18

3. It must be demonstrated that regional dating curves apply for the full range of time to all of the site specific geomorphic regimes within the regional area. For example, why would washes such as Forty Mile Wash (and its terraces) have the same weathering cation behavior as rock outcrops on top of Yucca Mountain? An effective demonstration would utilize another dating tool. Further, geomorphic environments on a

19

local scale should vary their cation weathering profiles with time, especially if that time span is as great as suggested on page 15 (section 3.4.2 Sample collection, 6,000 to 700,000 years old). Theory of varnish genesis and behavior with respect to its chemical composition, digenesis, and organic behavior must be developed prior to use of varnish cation-dating for Yucca Mountain characterization.

20

4. The relationship between varnished pebbles and the geomorphic surface hosting the varnished material must be known for each type of landform investigated.

21

5. Some varnish surfaces appear to be unstable as they are themselves weathered. These would presumably yield ages which are erroneous.

22

6. All varnish layers are not of the same composition or structure. Therefore the chemical composition of various varnish varieties will vary. How does this affect dating?

23

7. Organic acids produced in the soil and within the varnish would affect varnish stability and chemical composition (especially mobilized cations). Organic composition would be affected by changes in climate and microtopography. Thus, cation leaching in varnishes may vary on the basis of time, locale, and presumably even within a single varnish sample.

24

9. Fractures (tensile displacement) within varnish are not homogeneous. These fractures can transport leaching liquids differentially. Cation compositions, therefore, could vary within a single sample. Cation stratigraphy from the surface of a varnish to its substrate probably show little if any pattern and therefore from a cation-ratio dating concept are not time stratigraphic.

25

10. Remobilization of transition-metals within varnish appears active along aqueous transportation paths. What is the fate of K, Ca, and Ba during remobilization digenesis?

26

11. How do varnish deformation structures affect the chemical composition of the rock/varnish interface?

27

12. To what extent does rock composition influence varnish chemistry?

28

13. What is the behavior of Ti relative to Al during chemical weathering in the desert environments? And how do these data support the cation-ratio used?

6

REFERENCES

Harrington, C.D., R. Raymond, Jr., D. J. Krier, and J. W. Whitney, 1989, "Barium Concentration in Rock Varnish: Implications for Calibrated Rock Varnish Dated Curves", Geological Society of America Abstracts with Programs, Vol. 21, p. A 343, No. 20471

Krinsley, D. H., R. I. Dorn, and S. W. Anderson, 1990, "Factors that Interfere with the Age Determination of Rock Varnish", Physical Geography, Vol. 11, No. 2, pp. 97-119.

Nagy, B., L. A. Nagy, M. J. Rigali, W. D. Jones, W. K. Bilodeau, D. H. Krinsley, K. H. Schram, and P. F. Baker, 1990, "Sedimentological Processes Affecting the Development of Rock Varnish", Geological Society of America Abstracts with Programs, No. 9137.

1. UNDERSTANDING OF THE PROCESS OF CATION DEPLETION IN ROCK VARNISH

The rock varnish (cation ratio) dating technique is one of a large number of calibrated dating techniques that can be used for dating Quaternary events, which include lichenometry, amino acid racemization, obsidian hydration, etc. This technique is especially appropriate for surface exposure dating of deposits made up of coarse clastic deposits, such as colluvial boulder deposits on hillslopes.

As a calibrated technique, it relies on comparison to deposits of known age to establish the calibration and does not necessitate a complete understanding of the calibrated process to utilize the dating technique. A complex process can be calibrated even if all of the relationships and processes contributing to the trend are not completely understood. Such calibrated techniques are commonly used in Quaternary studies; including soils dating techniques, such as the Harding Index and carbonate soils technique, and geomorphic dating techniques. Even cosmogenic dating necessitates utilizing a production rate for the cosmogenic isotope that must be calibrated to another dating technique.

Although more data points might reduce the curve uncertainty to a minor degree, the purpose for applying the technique and an investigator's judgement cannot be separated from the determination for what constitutes an "adequate" concentration of data points for a calibration curve.

2. ACCEPTANCE OF THE TECHNIQUE BY THE SCIENTIFIC COMMUNITY AND THE NATURE OF THE DEBATE IN THE LITERATURE ABOUT THE TECHNIQUE

Nothing has been published in the scientific literature that calls into question the trend of decreasing cation ratios with increasing varnish age. In contrast, a number of studies have been published that have noted such a trend does occur and can be calibrated. Among these is an article by Whitney and Harrington, (in press), to be published in the Geological Society of America Bulletin, that utilizes cation ratio dating to establish estimated ages of hillslope boulder deposits. The acceptance of this peer-reviewed article for publication indicates the acceptance of the cation ratio dating technique as employed in this type of study. Additionally, the contractor for the State of Nevada doing rock varnish dating of geomorphic surfaces, in a comment on an article by Bierman and Gillespie (1991), concludes by noting that "Five different laboratories around the world have all found a time dependent decrease in the varnish cation ratios with time. The method appears to work." Also, in reporting on work done by the State of Nevada in Crater Flat (Bell and others, 1991), it was noted that "Rock varnish dates verify the mapped allostratigraphic relations and provide minimum limiting ages for the geomorphic surfaces. Based on consistent cation leaching relations . . . calibrated cation ratio dates provide minimum age estimates."

Thus, both the work done by investigators on the Yucca Mountain Site Characterization Project, and work done by the State of Nevada, have demonstrated that rock varnish dating of deposits at Yucca Mountain provide reasonable age estimates of Quaternary events.

ENCLOSURE 2

3. ANALYTIC TECHNIQUES USED TO MEASURE CATION DEPLETION ARE NEITHER THE BEST NOR MOST APPROPRIATE TECHNIQUE TO USE

All of the cation ratios used in rock varnish studies have been calculated using the scanning electron microscope with an energy dispersive system (SEM-EDS). This technique has been described in detail in a number of publications, including Whitney and Harrington, (in press). Recently, Bierman and Gillespie (1991) examined the analysis of rock varnish with a variety of analytic techniques, including both the SEM-EDS and the PIXE-EDS at the University of California, Davis, which has been used for all analyses performed by State of Nevada contractors. Bierman and Gillespie (1991) concluded in their study "that PIXE-UCD could not accurately analyze standards of varnish-like composition." Additionally, they note that, "The chemical composition and cation ratios of synthetic rock-varnish standards determined by quantitative, standard based SEM-EDS agree with known compositions and are similar to those determined by most other methods." Bierman and Gillespie's study demonstrates that the SEM-EDS technique produces the same quality of analytical results as produced by microprobe analyses and possesses the distinct advantage of allowing larger areas of the rock varnish to be incorporated in each analysis than with a standard microprobe. This same study calls into question the quality of rock varnish analyses performed for State of Nevada studies by the PIXE-UCD.

4. COMMENT ON THE ACCURACY OF THE AGE ESTIMATES MADE USING ROCK VARNISH TECHNIQUE

Los Alamos has evaluated rock varnish age estimates within the geologic context and constraints of both the Espanola Basin in New Mexico and the Yucca Mountain area. In the Espanola Basin, age estimates derived from rock varnish dating have been compared to amino acid racemization ages for deposits underlying the rock varnish-covered surfaces and the rock varnish ages are found to be reasonable. Additionally, a rock varnish age of 550 ka was obtained for a surface overlying deposits containing the Lava Creek B tephra (620 ka), which also supports the geologic validity of the rock varnish age estimates.

In southern Nevada, similar geologic comparisons have found that varnish thickness is greatest on the deposits that yield the oldest age estimates. The thickest carbonate soil horizons are likewise noted in the deposits with the oldest estimated ages. Finally, rock varnish on a surface in Las Vegas Wash yields a 600 ka age and is underlain by deposits which contain the Lava Creek B tephra (620 ka) at a depth of two meters. Thus, the validity of this dating technique has been demonstrated within the geologic constraints of southern Nevada, outside the Yucca Mountain area. Nowhere have geologic constraints demonstrated that age estimates from this technique are in error.

5. USE OF OTHER DATING TECHNIQUES FOR QUATERNARY DATING

The rock varnish cation ratio dating technique is one of a large number of calibrated dating techniques that can be used for dating Quaternary deposits; others include soils dating, carbonate soils techniques, lichenometry, obsidian hydration dating, etc. The cation ratio dating technique is especially appropriate for surface exposure dating of deposits made up of coarse clastic deposits, such as colluvial boulder deposits on hillslopes. While other Quaternary dating techniques might be employed to date Quaternary surfaces, they, like rock varnish dating, are also in the developmental process. As such, they are likewise controversial.

6. PRECISION OF AGE ESTIMATES MADE USING ROCK VARNISH DATING

The precision delivered by a dating technique must be evaluated within the context of the geologic problems one seeks to solve. Los Alamos is not applying the rock varnish dating technique to solve geologic problems that require extremely precise age estimates, as would be needed to resolve age differences between events that had occurred within the Holocene. If ages within the the early and mid-Quaternary (200 ka to 1400 ka) are at issue, greater uncertainty can potentially be tolerated. For example, uncertainties of as much as 10% do not alter the erosion rates at Yucca Mountain calculated by investigators to any significant degree. Even if the age estimates were older by 25% than the true ages (making erosion rates too low by 25%), the average hillslope degradation would only increase from 0.1 mm/ka to 0.125 mm/ka, an insignificant amount within the 10,000-year period. Depending on the purpose for applying the technique, some uncertainties may not turn out to be sensitive to the results of the application.

7. INCLUSION OF BARIUM WITHIN ROCK VARNISH ANALYSES

The presence of barium in rock varnish was first discussed by Harrington in an abstract for the 1990 annual Geologic Society of America meeting, and was further detailed in Harrington and others (1989), and in Whitney and Harrington (in press). DOE contends that barium occurs in all rock varnish and in all rock varnish analyses. There is reason to suspect that it may in fact contribute to the decreasing cation ratio with increasing varnish age.

8. SAMPLING PROCESS FOR PERFORMING ROCK VARNISH STUDIES

The method of sampling rock varnish for cation ratio dating of geomorphic surfaces by Los Alamos/USGS investigators has been discussed in detail in Harrington and Whitney, 1987; Harrington and others, 1989; and Whitney and Harrington (in press). All criteria utilized to assure the collection of appropriate samples are addressed in these publications, as is the sampling rationale.

REFERENCES

Bierman, P.R. and A.R. Gillespie, 1991, Accuracy of Rock-Varnish Chemical Analyses: Implications for Cation-Ratio Dating: Geology, v. 19, p. 196-199.

Bell and others (1991), State of Nevada publication.

Harrington, C.D., 1987, Scanning Electorn Microscope Method for Rock-Varnish Dating: Geology, v. 15, p. 967-970.

Harrington, C.D., R. Raymond, D.J. Krier, and J.W. Whitney, 1989, Barium Concentration in Rock Varnish: Implications for Calibrated Rock Varnish Dating Curves: (abs) Geological Society of America Abstracts with Programs, v. 21, p. 6.

Whitney, J.W. and C.D. Harrington, in press, Relict Colluvial Boulder Deposits: Indicators of Climatic Change and Long Term Slope Stability in the Yucca Mountain Region, Southern Nevada: Geological Society of America Bulletin.

If you have any questions, contact Thomas W. Bjerstedt at (702) 794-7590.

J. Maxwell Blanchard
Carl P. Gertz
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Enclosures:
1. Enumerated Comments on Study Plan 8.3.1.8.5.1, Regarding Rock Varnish Dating Technique
2. Responses to Eight Concerns

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