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**TRACE ELEMENT AND REE COMPOSITION
OF FIVE SAMPLES OF THE YUCCA MOUNTAIN
CALCITE-SILICA DEPOSITS**

SPECIAL REPORT No. 8
CONTRACT No. 92/94.0004

RECEIVED
FEB 27 1993
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SPECIAL REPORT Submitted to the
Nuclear Waste Project Office
State of Nevada

July, 1993

Assembled by:

Don Livingston

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**Trace Element and REE Composition of Five Samples
of the Yucca Mountain Calcite-Silica Deposits**

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Dr. D. T. Vaniman

PART 1

Introduction

INTRODUCTION

The attached materials document the results of part of our recent effort of geochemical sampling and analysis at Yucca Mountain and nearby regions. Our efforts in regard to these analyses come as a result of our interest to obtain comprehensive analyses of rare earth elements (REE), lanthanum (La) through lutecium (Lu). We were pleased to learn that we also obtained several additional, non-REE analyses as well. Commercially available REE analyses have proved to be insufficiently sensitive for geochemical purposes. Upon recommendation of scientific colleagues we contacted Dr. Roman Schmitt at the Radiation Center at Oregon State University in Corvallis. Dr. Schmitt expressed considerable interest in our project and we sent five samples as a trial effort. The results are very encouraging. The purpose of compiling Dr. Schmitt's report and the other materials is to inform the sponsor of his independent observations of these results and other information that we have sent to him. To provide a more complete appreciation of the utility of REE analyses we have included a copy of Dave Vaniman's recent article in which he notes that REE analyses from Yucca Mountain indicate the occurrence of two distinctly different REE patterns as do several other chemical parameters of the calcite-silica deposits. Our four samples with high equivalent CaCO_3 were collected from sites we believe to be spring deposits. One sample, 24D, is from southern Crater Flat which is acknowledged by U.S.G.S. investigators to be a spring deposit. All four of these samples have REE patterns similar to those from the saturated zone reported by Vaniman.

PART 2

Correspondence with A. Johnson & Technical Report

April 16, 1993

Mr. Arthur Johnson
Director
Radiation Center
Oregon State University
Corvallis, OR 97331

Dear Mr. Johnson:

In accordance with the telephone conversation with Mr. Roman Schmidt of your staff, we are sending 5 samples of calcite for neutron activation analysis. We are interested in the REE abundances of these materials. This work is being performed on behalf of the State of Nevada, Nuclear Waste Projects Office. The samples were collected at and in the region around Yucca Mountain, Nevada. Those samples collected from Yucca Mountain have been checked for radiation and cleared by the radiation personnel at the NTS. The samples were collected from calcite silica veins and travertine of Quaternary age. These and other samples are being analyzed also for O^{18} , C^{13} , Strontium Isotope Ratios, and U-Series ages. These REE analyses have an important bearing on alternative possible genetic models being considered.

It is our understanding that a fee of \$80.00/sample is appropriate for these analyses. A check for \$400.00 is enclosed. If at all possible, we would appreciate having the results of these analyses by the end of June. If you have any questions regarding these samples, please contact me at home 1108 Rock Springs Dr., Las Vegas, NV 89128, (702) 363-6257.

Sincerely Yours,

Dr. Donald Livingston
Geochemical Director
TRAC

OREGON STATE UNIVERSITY
Radiation Center A100 Corvallis, Oregon 97331 · 5903
Telephone 503 · 737 · 2341 Fax 503 · 737 · 0480

June 21, 1993

Dr. Donald Livingston
1108 Rock Springs Dr.
Las Vegas, NV 89128

Reference: Radiation Center
Project No. 926

Dear Dr. Livingston:

We have completed the analyses associated with OSU Radiation Center Project No. 926, which consisted of your five calcitic samples. Accompanying this cover letter is a technical report containing a tabulation of the analytical results and other pertinent information.

To assist us with our reporting requirements, we would greatly appreciate being informed of any publications or oral presentations of data obtained with the help of the Radiation Center. Normally, we will contact you by letter in early May to request any information you may have regarding publication or other presentations of such data. It is very important to the continued success of our program at OSU that we receive feedback on the support we provide, and we will greatly appreciate whatever assistance you can give us.

Thank you for your cooperation and for allowing the Radiation Center to assist you with your research. I trust you will find our report to be complete and in line with your expectations.

Yours sincerely,

A. G. Johnson
Director

AGJ/dd

Enclosures

cc: S. C. Campbell
J. F. Higginbotham
R. A. Schmitt

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TECHNICAL REPORT

RADIATION CENTER PROJECT NO. 926

Dr. Donald Livingston
1108 Rock Springs Dr.
Las Vegas, NV 89128

OREGON STATE UNIVERSITY

Radiation Center A100 Corvallis, Oregon 97331-5903

Telephone 503-737-2341 Fax 503-737-0480

June 17, 1993

Dr. Donald Livingston
1108 Rock Springs Dr.
Las Vegas, NV 89128

Dear Don:

The Radiation Center has completed the INAA of five calcitic samples that you provided. The INAA was done by Dr. Y.-G. Liu, my postdoc, who has analyzed >300 worldwide marine carbonates of 0-550 Ma. He used the same INAA procedures as were used for the >300 carbonates. Standards were CRB (equivalent to BCR, Basalt Columbia River; CRB and BCR samples were taken from the same quarry), NBS 1633A, and JB-1 basalt.

The attached table lists the data with estimates of overall errors (± 1 s.d.). For ranges in uncertainty, the lower uncertainty value corresponds to the high abundance values. $Ce^A \equiv Ce$ anomaly calculated relative to N.A.S.C. (North American Shale Composite, Gromet et al. G.C.A. 48, 2469-2482, 1984). $(CaCO_3 \%) \equiv$ calcite, assuming all measured Ca is in calcite. $(La/Lu)_{NN}$ and $(Eu/Sm)_{NN}$ are ratios normalized to N.A.S.C. $(La/Lu)_{CN}$ and $(Eu/Sm)_{CN}$ are ratios normalized to C1 chondrites.

Two figures show the abundance ratios relative to N.A.S.C. and non-volatile C1 abundances. The Gd* points are not measured but interpolated between Sm and Tb.

Below are some comments and tentative interpretations.

Sample 38F: $\leq 9\%$ $CaCO_3$. The C1 normalized pattern is consistent with a granitic or rhyolitic pattern. Abundances of Na, Cr, Co, and Sb are also consistent with a granitic/rhyolitic rock. Also the normalized $(La/Lu)_{CN}$ and $(Eu/Sm)_{CN}$ are consistent with the high silica ($> 70\%$) granitic (or rhyolitic) ratios. Since $CaCO_3 \leq 9\%$, the chemical composition of the remaining $\geq 91\%$ of the sample is consistent with a granitic/rhyolitic-like composition.

Samples 24D, 36N, 4D, and 5C all exhibit roughly parallel patterns with C1 normalized (-)Eu anomalies. The estimated $CaCO_3$ contents range from 35 to 64%. In general these four patterns for the Rb, K, Th, REE (except Eu), Sc, Hf, and Ta parallel the 38F pattern. Of interest is the similar normalized Sr and Eu abundances in 38F, and the much higher normalized Sr abundances in 24D, 36N, 4D and 5C relative to the corresponding Eu in these samples. I will discuss its significance below. Also of some

interest are the rather similar U abundances in the four samples 36N, 38F, 4D and 5C. The enhanced mobility in hydrothermal solutions of UO_2^{2+} relative to Th^{4+} can account for some of this observation.

Some investigators assume Ti is immobile in rock-water interactions and use Ti for normalizations of the chemical compositions of residual weathered rocks. Because the K_{sp} s of $\text{Th}(\text{OH})_4 \sim 10^{-50}$, $\text{Hf}(\text{OH})_4 \sim 10^{-55}$ and $\text{Ti}(\text{OH})_4 \sim 10^{-58}$, one can assume that all three of these elements will be relatively immobile during cold-hot water interactive leachings. However, sufficiently acidic waters will enhance their leaching characteristics.

The lower ratios of La/Th and La/Hf in the four samples 24D, 36N, 4D and 5C relative to La/Th and La/Hf ratios in 38F are not consistent with hot water leaching of rhyolitic basement rocks like 38F to yield the REE, Hf, and Th abundances in the four samples.

Returning to the interesting Sr-Eu abundances, we observe higher Sr abundances in the four samples relative to 38F. Now in granites/rhyolites, both Sr and Eu probably reside mainly in the feldspars as $2+$. Hydrothermal leachings of feldspars should yield comparable losses of these divalent ions in the feldspars. After leachings, the Eu^{2+} is oxidized to Eu^{3+} in the hot/cold water, and subsequent precipitations will favor coprecipitation of SrCO_3 rather than $\text{Eu}_2(\text{CO}_3)_3$ with CaCO_3 crystallization. This could explain the disparity in the observed abundances of these two elements in the five samples.

I have also plotted the element abundances vs N.A.S.C. to search for possible relationships between pedogenic water leachings. It has been found by investigators that the relative REE pattern in river water is roughly parallel to the N.A.S.C. pattern. I am not aware of REE patterns in soil pore waters. Such patterns will vary from soil to soil because they will be complex functions of many parameters; viz. water pH, soil mineral compositions, anion concentrations in the water, temperature, etc.

The rather flat NASC-normalized REE patterns for 24D, 36N, 4D and 5C do suggest leachings of soils may have occurred with preferential leachings of Sr from feldspar minerals in the soils and subsequent precipitation with CaCO_3 . However, to account for the observed abundances for the rather similar La/Th and La/Hf ratios argues against a pedogenic mechanism involving leaching of soil minerals. Also the roughly similar NASC normalized Cs, Rb, Th, REE, Sc, and Hf abundances (all these elements exhibit different chemical properties) are not compatible with a pedogenic mechanism. Leachings of the alkalis, Cs and Rb, are very different from Hf and Th, as extreme examples. It seems that the NASC normalized trace element pattern in sample 36N suggests that most of the Cs, Rb, K, Th, REEs, Sc, and Hf did not result with coprecipitation with CaCO_3 , but that these trace elements were transported by water as tiny clay particulates and deposited during the precipitation of CaCO_3 .

Likewise for 24D, 4D and 5C, one can argue that the generally flat elemental patterns vs N.A.S.C. suggest water transport of clay particulates from the sources followed by their deposition with the precipitated CaCO_3 . The high Sr abundances suggest preferential dissolution and leaching of Sr from the sources (soils?) followed by coprecipitation of SrCO_3 with CaCO_3 . As discussed previously, the high U abundances reflect the high

solubility of UO_2^{2+} , complexing with CO_3^{2-} in the hydrothermal water, and followed by coprecipitation with CaCO_3 .

For some carbonates, 24D and 5C, the NASC normalized Ba is higher relative to the normalized REEs. This may reflect preferential leachings of Ba salts in the source minerals. Note that Ba ratios in 4D and 5C are normal relative to the REEs etc.

Slight (-)Eu anomalies in the NASC normalized plots are observed in 24D and 5C. These may be attributed to slight anomalies in the leached source minerals. Similar arguments may be advanced for the (-)Sc anomalies in 24D, 4D and 5C.

In conclusion, the INAA data, limited to five carbonate samples, indicate that hydrothermal transport of clay particulates seems to account best for the observed elemental abundances in samples 24D, 36N, 4D, and 5C. The sample 38F with $\leq 9\%$ CaCO_3 has a chemical composition similar to a granite/rhyolite composition.

Best Regards,

R. A. Schmitt

RAS/clp\don.liv

Sample: Wt. g	24D 1.1721	36N 0.8192	38F 0.9507	4D 0.9722	5C 1.2736	Uncertainty %
Fe %	0.25	0.13	0.85	0.61	0.32	3
Ca	25.5	21.9	3.7	14.0	18.4	5-10
Na	0.22	0.059	1.97	0.31	0.27	2
K %	0.32	0.075	3.57	0.70	0.40	5-10
Sc ppm	0.71	0.40	4.55	1.51	0.97	2
Cr	7.8	2.3	4.8	7.0	7.6	3-5
Co	1.00	0.78	0.73	6.39	3.59	2
As	4.2	4.6	6.7	10.6	8.3	5-10
Sb	0.24	0.49	0.29	0.77	0.47	5-10
Rb	13.4	5.9	98.8	22.7	16.8	5-10
Sr	392	567	306	1244	754	5-10
Cs	2.5	0.38	2.7	2.1	0.77	5-10
Ba	660	114	1924	209	139	5-10
La	7.3	1.36	87.1	11.5	12.1	2
Ce	13.7	4.0	163.1	22.3	19.1	5-10
Nd	5.2	1.6	55.1	9.6	10.7	5-10
Sm	0.88	0.36	6.97	1.64	2.11	2
Eu	0.133	0.049	1.94	0.26	0.26	3
Tb	0.098	0.041	0.58	0.157	0.27	5-15
Yb	0.34	-	1.64	0.62	0.94	5-15
Lu	0.055	0.017	0.31	0.072	0.13	5-15
Hf	0.76	0.22	7.8	1.56	1.22	3-5
Ta	0.19	0.084	0.82	0.26	0.22	3-5
Th	1.88	0.76	15.9	3.23	3.16	3-5
U ppm	1.3	2.5	3.4	2.6	3.7	5-15
Ce ^{A*}	0.98	1.34	1.01	0.98	0.78	
CaCO ₃ (%)	64	55	9	35	46	
(Eu/Sm) _{NN}	0.78	0.70	1.44	0.82	0.64	
(La/Yb) _{NN}	2.1	-	5.3	1.9	1.3	
(Eu/Sm) _{CN}	0.40	0.36	0.74	0.42	0.32	
(La/Yb) _{CN}	13.7	8.3	29.1	16.5	9.6	

Oregon State University Radiation Center
 #926/Donald Livingston
 Yucca Mountain

Oregon State University Radiation Center
 #926/Donold Livingston
 Yucca Mountain

PART 3

Letter to D. Livingston (June 21, 1993)

OREGON STATE UNIVERSITY

Radiation Center A100 Corvallis, Oregon 97331-5903

Telephone 503-737-2341 Fax 503 737-0480

June 21, 1993

Dr. Donald Livingston
1108 Rock Springs Dr.
Las Vegas, NV 89128

Dear Don:

This letter will summarize my telephonic discussion you on 6/21/93 about our INAA interpretations of the five calcitic samples 24D, 36N, 38F, 4D, and 5C. Also my letter of 6/17/93 to you consisted of a tentative interpretation of our INAA data before I received the Y.M. (Yucca Mountain) documents that you sent to me. After reading your Mar'93 TRAC report and abstracts and some USGS reports on Y.M. research, I will reinterpret our INAA data based on a better knowledge of the local geology.

Recall that we plotted our INAA-whole rock data vs C1 chondrites and N.A.S.C. (North America Shale Composite, which represents fairly well the average continental crust composition). For the carbonate samples 24D, 36N, 4D and 5C, the NASC-normalized compositions of the alkalis, Th, REE, Hf, and Ta are roughly flat and parallel. The different pattern for 38F reflects its predominant rhyolitic composition.

Sample 24D represents an uncontested spring deposit-brecciated carbonate (J.B. Paces et al, Rad. Waste Manag. 1573-1580, 1993). We note that the NASC normalized pattern for 24D is rather similar to the patterns in the other three samples, 36N, 4D and 5C. We also note that the C1-normalized REE patterns that we observed in the four samples 24D, 36N, 4D and 5C are also rather similar to those reported by D.T. Vaniman (Rad. Waste Manag., 1935-1939, 1993) for calcite minerals, separated from fracture-lined calcites below the present static water level in four drill cores at Y.M.

I note the generally enriched normalized abundances of U and Sr in 24D, 36N, 4D and 5C and the enriched Ba in 24D and 36N. I suggest that these data strongly support your hypogene hypothesis for the origin of these carbonate samples, namely that "veins and strataform calcite and silica deposits were formed from upwelling ground water driven intermittently by forces related to tectonic processes," and, "For the Yucca Mountain environment, however, the most reasonable cause would seem to be upwelling through , or from, subjacent Paleozoic and Precambrian limestones." These quotes are taken from your Mar '93 Report No.4, Contract No 92/94.0004.

During the past decade, my present postdoctoral student, Dr. Y.-G. Liu, and I have analyzed >300 worldwide marine 0 - 550 Ma carbonates. Many of these were deposited

in the central USA, Iowa, Illinois, and Ohio (see attached tables which we will publish in the very near future). During the Ordovician, Silurian, and Devonian Periods, most of the present USA was covered with shallow (<50m) seawater. (e.g. see A. M. Ziegler, et al. Paleobotany, Paleoecology, and Evolution, Vol.2, 231-266, 1981.) Therefore, the midwest carbonates deposited ~330-470 Ma ago that we have studied are expected to have rather similar chemical compositions to the lower Paleozoic carbonate formations near the Y.M.. We note that the detrital compositions in these midwest limestones and dolomites exhibit N.A.S.C.-like compositions and therefore represent fallout of aeolian transported detritus over the continental USA. Such detritus, ranging from 0.2-10% in the midwestern lower Paleozoic whole rock carbonates, was deposited with the biogenic carbonates. The above summary has an important bearing in the interpretation.

The INAA data are most compatible with the following scenario based on the hypogene hypothesis. Hydrothermal waters within limestones and dolomites below the Y.M. dissolve some of the carbonates thereby enriching the fluids in Ca and Sr and also in Ba. I note that Ba has low to intermediate values in the midwestern lower Paleozoic carbonates, e.g. <10-170 ppm Ba, and Sr ranges from 57-430 ppm. Reiterating, we expect some fluids will be Ba enriched and others, not.

I also note that the ranges of the alkalis, e.g. Rb, REE, Hf, and Ta in the four carbonate samples 24D, 36N, 4D and 5C are much greater than the Sr range in these samples, which is expected from a range of limestone-dolomite leachings, if the limestones/dolomites below or adjacent to the Y.M. are similar to the midwestern USA limestones/dolomites of comparable age.

How to explain the enriched normalized U in the four carbonates relative to the rather flat NASC-normalized alkali, Th, REE, Hf, and Ta pattern in 24D, 36N, 4D and 5C samples. We have observed in nearly all marine carbonates that were deposited in shallow <100m deep seas, e.g. over the midwestern USA, central Europe, Saudi Arabia, China that we have analyzed via INAA, that the U concentrations are generally >10X greater relative to U abundances in marine carbonates deposited in the deep oxic Pacific and Atlantic Oceans. Because the U/Th ratio is >30,000 in present seawater, organic debris present in shallow seas is able to reduce a small fraction of U^{6+} in the uranyl carbonate complexes to U^{4+} , resulting in precipitation of the very insoluble $U(OH)_4$ onto the sedimentary carbonate and detritus matter. The K_{sp} of $U(OH)_4$ is $\sim 10^{-56}$. The hypogenetic fluids flowing through the lower limestones/dolomites will dissolve some of the carbonates resulting in Sr and Ba enrichments and transport the exposed detritus (NASC-like particulates) that had been relatively enriched in U relative to N.A.S.C. matter.

For example, an excellent element indicator or proxy for NASC is Th. Because the concentration of Th is very low in seawater ($\sim 0.00003 \pm 0.00002 \mu\text{g/L}$; Huh et al, Geochim. Cosmochim. Acta **53** 1357-1366, 1989) and $Th(OH)_4$ exhibits such a low K_{sp} , $\sim 10^{-50}$, trivial Th is expected to precipitate out of seawater onto carbonate and detrital clay particulates. I note that the U/Th ratios in 23 midwestern Paleozoic carbonates (see attached tables) range from 0.3-11.8 with a median of 0.80 relative to the $U/Th = 0.22$ in NASC. For 24D, 36N, 4D, and 5C, the geometric mean (most probable value) of the NASC-normalized U/Th ratio values is ~ 6 (range of 3-15), which compares very well with the expected ratio of $0.80/0.22 \sim 4$, cited above.

Finally, the relatively flat and parallel NASC-normalized patterns for the alkalis, Th, REEs, and Hf and Ta are attributed, as mentioned above to hypogenetic water transport of the detritus in the carbonates exposed by the dissolution of calcitic or dolomitic carbonates.

As discussed in my previous letter, the observed NASC-normalized patterns for 24D, 36N, 4D and 5c are not compatible with a supergene mechanism. Clearly, leachings of rhyolitic rocks and derivative soils would have fractionated very greatly the alkalis, Cs, Rb, and K, relative to the very immobile elements Hf and Th. Yet, within the fluctuations of continental crustal values, as exemplified by average NASC, these elements exhibit roughly the same NASC-normalized ratios for a given carbonate. These observations are not compatible with a supergene hypothesis, but are with a hypogene mechanism involving hydrothermal reactions with deepseated limestone/ dolomite formations.

To reconcile the differences in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios observed in lower Nevada Paleozoic limestones/dolomites and in the carbonate veins, I suggest that the sedimentary limestones/dolomites were layered between metavolcanics, >500 Ma. In fact, the trends observed for $^{87}\text{Sr}/^{86}\text{Sr}$ in seawater during the Phanerozoic (J. Veizer, Ann. Rev. Earth Planet. Sci. 17, 141-167, 1989) are not at variance with extrapolations of the 87/86 line from a minimum of ~ 0.7078 at ~ 460 Ma to ~ 0.7091 at ~ 510 Ma; i.e. 87/86 ratios > 0.7091 would have been expected from dissolved carbonates that were older than ~ 510 Ma. Also, it is possible that the hypogenetic water originated from greater depths with higher Rb/Sr ratios and therefore with higher indigenous 87/86 ratios. Such fluids could have interacted with the lower Paleozoic carbonates to yield the observed 87/86 ratios of ~ 0.7125 (B.D. Marshall et al. Rad. Waste Manag. 1948-1952, 1993.)

A brief discussion of the slight negative Eu anomalies in samples 24D, 36N, and 5C is in order. Now the average Eu/Sm ratio is 0.25 ± 0.05 in 24 midwestern lower Paleozoic limestones/dolomites (see attached two tables) relative to a corresponding ratio of 0.19 in NASC. A ~ 0.02 s.d. is expected for the 0.19 value for a realistic uncertainty. This would yield a (+) Eu anomaly of $0.25/0.19 = 1.32$ if hypogenetic fluids leached and dissolved lower Paleozoic carbonates! However, the 0.25 ± 0.05 range indicates many lower Paleozoic formations exhibit Eu/Sm ratios of ≤ 0.20 , which overlaps the NASC ratio. Therefore, the very slight (-) Eu anomalies in three of the four samples could represent the Eu/Sm present in the lower Paleozoic of preCambrian limestones/dolomites, i.e. in the combined carbonate-detritus whole rocks that were leached by hypogenetic fluids without any significant Eu loss through the $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+} + \text{F}^- \rightarrow \text{EuF}_2$ (with CaF_2); i.e the D. T. Vaniman mechanism (Rad Waste Manag., 1935-1939, 1993).

For the carbonates studied by Vaniman, very severe (-) Ce anomalies were reported, some of which were even more severe than the (-) Ce anomaly observed in present Pacific seawater, e.g. 0.06 ± 0.01 relative to NASC. Some Vaniman calcites exhibited Ce anomalies of ~ 0.01 , in USW G-2, 476L. The mechanism proposed by Vaniman, namely oxidation of $\text{Ce}^{3+} \rightarrow \text{Ce}^{4+}$ followed by $\text{Ce}(\text{OH})_4$ formation or equivalent $\text{CeO}_2 \cdot x\text{H}_2\text{O}$ with coupled $\text{MnO}_2 \rightarrow \text{Mn}^{2+}$ reactions can account for the Ce depletions in the calcites.

(A few years ago, I was able to calculate that the upper limits of Ce at ~ 2000 ppm in deep ocean Mn modules were consistent with the redox reactions of $\text{Ce}^{3+} + 4\text{OH}^- \rightarrow \text{Ce}(\text{OH})_4 + \text{e}^-$ and $\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$.)

In all four whole rock samples, 24D, 36N, 4D and 5C, we did not observe significant Ce anomalies, i.e. in samples with CaCO_3 contents of 35-64%. Also the La contents ranged from 1.36-12.1 ppm. From Vaniman's chondritic patterns, I calculate that Vaniman obtained La contents ranging from 7-60 ppm in separated USW G-2 calcites. For USW G-4 calcites, he reported ~3-30 ppm La in calcites. In general, the REE content in the Vaniman calcites were higher than the four whole rock carbonate samples 24D, 36N, 4D, and 5C. Comparison of these data and the Ce anomalies data may indicate that the REEs in our four samples are not associated with the calcite phase, i.e. largely absent in the CaCO_3 contents of 35-64%, but present as accessory minerals in the whole rock, and that the REEs in our four calcitic carbonates were derived from deepseated hypogenetic fluids. The four samples 24D, 36N, 4D and 5C exhibit slight (+) and (-) Ce anomalies ranging from 0.78 - 1.34 relative to N.A.S.C.. The 24 midwestern lower Paleozoic carbonates also exhibit (+) and (-) Ce anomalies in the whole rocks ranging from ~0.4 - 1.1 (Please note that the Ce anomalies reported in the bottom rows of the two attached tables represent the Ce anomalies of the seawater parental to the biogenic carbonates and not the Ce anomalies in the whole rocks relative to N.A.S.C.). The Ce and Eu anomalies discussed above are compatible with the hypogene hypothesis and that no significant loss of Ce and Eu occurred from the ascending hypogenetic fluids.

(We calculated Hg INAA abundances in the five carbonate at: 24D, < 0.03 ppm; 36N, 0.21 ± 0.02 ppm; 38F, < 0.06 ppm; 4D, < 0.04 ppm; and 5C, < 0.03 ppm. < values indicate 99% reliability of value.)

If the hypogenetic fluids were parental to the four carbonate samples (24D, 36N, 4D and 5C of this study) that exhibited very slight and variable Ce and Eu anomalies and for the drill core separated calcites analyzed by D. T. Vaniman, that exhibited very large (-) Ce and (-) Eu anomalies, then it seems very evident that the parental fluids to our four carbonates were not equilibrated with the wallrocks while the D. T. Vaniman calcites were equilibrated with the wallrock. This deduction assumes the validity of the causal mechanisms, cited by Vaniman, for generation of the severe Ce and Eu anomalies.

Another crucial anomaly observed in the N.A.S.C.-normalized abundances is the (-) Sc anomaly relative to the heavy REE, e.g. Yb which is better determined than is Lu, and to Hf in the four carbonates 24D, 36N, 4D and 5C. The average Sc/Yb ratio is 2.2 ± 1.0 in the above four Y.M. carbonates and 1.8 ± 0.9 in 24 midwestern lower Paleozoic, Iowa, Illinois and Ohio limestones/dolomites. Clearly these overlap well within their $\pm$ s.d. uncertainties. Again this agreement is entirely consistent with the hypogene mechanism; i.e. hypogenetic fluids dissolving >500 Ma carbonates layered between metavolcanics will expose N.A.S.C.-like detrital clay particulates that are transported in the fluids to upper regions in the Y.M., followed by rapid crystallization of $\text{CaCO}_3(\text{SrCO}_3)$ and coprecipitation of the detritus.

I have referred to the assumption that limestones/dolomites (or their metamorphosed equivalents) are very likely layered between the metavolcanics below the lower Paleozoic limestone/dolomite basement at the Y.M. From biogeographic maps of continental regions during the Paleozoic (see A. M. Ziegler et al, 1981 reference cited previously) the oldest map for the middle late Cambrian (Franconian) shows the present USA under shallow seas and as part of the Laurentia assembly directly over the equator. Laurentia is also separated considerably from the main Gondwana continent. Extrapolation to 600 Ma suggests that

considerable biogenic activities could have generated thick layers of limestone. Furthermore, extrapolation of the J. Veizer (1989, cited previously) $^{87}\text{Sr}/^{86}\text{Sr}$ curve to ~ 600 Ma could result in 87/86 ratios of ~ 0.7100 or higher. The above comments are consistent with polygenetic fluids responsible for the observed $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

Future Researches

My postdoctoral student, Dr. Y.-G. Liu and I are sufficiently intrigued by this carbonate study that we wish to suggest a proposed 3-year draft plan for research, focussed on testing the supergene and hypogene mechanisms as causes of fluid transport into the Y.M. complex. Let me first state that I have been supported with continuous NASA funding for meteoritical, lunar, and geological research over the past years. Currently, my NASA grant is extended to Feb 1, 1994, and my proposal for extension is currently under review.

Also, as of Oct 1, 1993, I am retiring from my teaching duties at OSU, but I plan to continue research activities as Professor Emeritus with full use of the 1 MW TRIGA research reactor and laboratory facilities for INAA. Dr. Liu plans to continue as my postdoc. He has been over 20+ years doing both the INAA and R (radiochemical) NAA.

A. Very briefly, I proposed the following INAA studies of carbonates, opals, opaline crusts, brecciated carbonates, travertines collected by your TRAC group over the entire Y.M.C. (Yucca Mtn. complex). From the Geologic Map of Nevada, J.H. Stewart and J.E. Carlson (Nev Bureau of Mines and Geology, 1977) it is evident that the overall Y.M.C of ~ 50 km x ~ 50 km is riddled with numerous fractures. A large number, ~ 300 of the above identified samples should be collected over the entire complex, say ~ 100 over the Y.M.C. and ~ 100 near the proposed waste repository including samples from the holes already drilled into the Y.M.C.. Also, ~ 100 carbonate etc samples should be obtained vertically and across several veins in order to search for elemental fractionation patterns resulting from wall-rock interactions.

B. A large number of the samples, > 100 of interior unweathered lower Paleozoic limestones/dolomites from the carbonate and transitional assemblages exposed east and southeast of the Y.M.C. and also directly west of Crater Flat should be analyzed by INAA. The elemental patterns of these assemblages will be compared to those of the lower Paleozoic midwestern Illinois, Iowa, and Ohio limestones and dolomites. Also ~ 25 samples from the upper Paleozoic carbonates and siliceous-detrital rock immediately adjacent and east of the Y.M.C. should be analyzed. Samples, say ~ 50 , from outcrops of pre-Cambrian dolomites and limestones or their metamorphosed equivalent should be sampled and analyzed.

C. After the INAA of the above whole rock samples, mineral separates should be obtained for uniquely identified samples and the separates should be analyzed by INAA.

D. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios should be determined by the USGS team on aliquants of carbonates or other minerals, selected from chemically unique whole rocks that have been previously analyzed by INAA. In addition to 87/86 ratio measurements, U series disequilibrium, lead isotopic, and C isotopic studies by the USGS or other teams could be done on unique chemically identified samples.

E. Our INAA technique, which has been applied to > 1000 individual lunar samples by our group over the past 24 years, consists briefly of a ~6 hour activation in a thermal neutron flux of $\sim 3 \times 10^{12}$ n/cm²/sec in the OSU 1 MW TRIGA reactor, located in the Radiation Center Annex. (The OSU reactor "celebrated" its 25th birthday this year!) The 25 elements analyzed via INAA are Fe, Ca, Na, K, Sc, Cr, Co, As, Sb, Rb, Sr, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Th, and U. Activated samples are generally counted with ~15-25% relative efficient Ge detectors. For more accurate determinations of Ce anomalies, we also count 32.5 d ¹⁴¹Ce (145.4 keV γ) and 11.0 d ¹⁴⁷Nd (91.1 keV γ) with a thin LEPD Ge detector to obtain more accurate Ce and Nd abundances. For samples that have yielded unique normalized elemental patterns from the long activations, we also plan to activate representative aliquants for short times, say ~5-10 minutes, at lower thermal neutron fluxes of $\sim 3 \times 10^{11}$ n/cm²/sec in order to determine additional elements, viz. Ti, Al, Mg, Mn, V, Dy and other elements via measurements of short-lived radionuclides. For samples that contain very low U and Th abundances, say <0.1 ppm, we employ epithermal NAA for accurate determinations of U and Th. This technique would be restricted to unique samples.

F. The INAA data from this proposed study will be normalized to chondritic and N.A.S.C. abundances in order to search for geochemical clues which will permit us to ascertain reasonable conclusions for testing the supergene or hypogene hypotheses. Throughout this proposed study, we will keep in contact with other waste repository research groups through and with the TRAC personnel.

Accustomed to writing contractual reports, we intend to write quarterly reports, if required, and scientific papers for the High Level Radioactive Waste Management proceedings.

G. To accomplish the objectives of this draft plan, I suggest ~2 months per year of my efforts and ~10 months per year by my postdoctoral student. The approximate costs would be ~\$100 k/yr which would include salaries, overhead, indirect costs, supplies, reactor charges, travel and miscellaneous costs. If the outline draft plan seems appropriate for DOE or Nevada funding, I would plan to submit a proposal, formally endorsed by Oregon State University administrators.

I look forward to your comments. You have my permission to show this draft plan to DOE or Nevada officials for their perusal.

Best Regards,

Roman A. Schmitt
Professor of Chemistry, Geosciences, and
Oceanography

RAS/clp\don2.liv
Enclosures

Addendum to letter:

Comparisons of Cr, Fe, Co and Sb to Th (a N.A.S.C.-detrital proxy) in Y.M. samples 24D, 36N, 4D and 5C relative to the ratios in 23 midwestern (Iowa, Illinois, and Ohio) lower Paleozoic limestones and dolomites.

Y.M.	Cr/Th	Fe(%) /Th(ppm)	Co/Th	Sb/Th
24D, 36N, 4D, 5C	2.9 ± 0.9 (2.7)	0.15 ± 0.04 (0.15)	0.94 ± 0.27 (1.0)	0.29 ± 0.24 (0.19)
24 Midwestern lower Paleozoic limestones/ dolomites	8.4 ± 5.2 (6.5)	0.64 ± 0.42 (0.57)	2.4 ± 3.4 (1.4)	0.39 ± 0.51 (0.12)

() Values are median values.

Within the large uncertainties, the respective ratios agree generally within ± 1 s.d. and all within ± 2 s.d. These correlations support the hypogene mechanism as discussed in the letter.

Table 4. Element abundances in Illinois and Iowa limestone and dolomites from the Paleozoic Era*

Period Formation Age(Ma) Sample	Carboniferous				Silurian				Silurian		Ordovician		Ordovician		Uncertainty	
	Burlington-Keokuk		Mississippian	Racine				Kankakee		Fort Atkinson		Guttenberg				
	-330	-340		-420				430	-450	-470						
	D60 ^a	D58 ^b	MA-4 ^a	D56 ^c	D55 ^a	D68 ^e	D59 ^f	D63 ^g	D65 ^h	D62 ⁱ	D57 ^j	D64 ^k	D61 ^l	D66 ^m	D67 ⁿ	
Ti(%)	0.004	0.005	0.02	0.03	0.02	0.001	0.01	0.05	0.05	0.01	0.03	0.006	0.02	0.004	0.006	20-60
Al	0.012	0.065	0.29	0.65	0.48	0.048	0.058	0.91	0.91	0.17	0.37	0.13	0.08	0.24	0.38	2-30
Fe	0.089	0.059	0.62	0.22	0.18	0.11	0.091	0.37	0.49	0.26	0.43	0.25	0.50	0.26	0.28	2-3
Mg	0.16	0.35	0.38	11.5	10.0	12.2	12.8	10.5	10.5	11.7	11.7	11.1	11.3	0.65	0.61	2-20
Ca	41	39	33.6	20.5	17.4	21.1	22.7	18.8	19.1	20.7	21.5	20.7	20.7	39	36	5
Na	0.015	0.013	0.019	0.027	0.025	0.032	0.027	0.033	0.036	0.023	0.031	0.047	0.045	0.013	0.013	2-5
K(%)	-	-	0.15	0.36	0.29	-	-	0.61	0.57	0.15	0.24	-	-	0.28	0.38	5-10
Sc(ppm)	0.30	1.78	0.73	1.20	1.03	0.17	0.12	1.54	1.53	0.33	0.74	1.33	0.43	0.54	0.81	3
V	1	3	-	9	8	1	2	12	12	2	7	3	3	2	3	10-50
Cr	0.5	3.2	8.7	7.2	6.5	0.6	0.6	8.6	9.4	2.7	6.8	3.9	1.5	1.3	1.0	5-10
Mn	510	330	180	77	85	116	85	155	194	290	250	1120	800	330	330	2
Co	0.24	0.74	6.3	0.40	0.55	0.81	0.46	1.10	1.57	0.78	0.58	0.27	0.22	0.54	0.61	2-5
Rb	0.2	1.8	5.7	12	9.6	-	1.2	15	16	3.5	7.1	2.7	1.5	2.2	3.9	6-50
Sr	120	155	280	74	80	76	57	102	61	71	60	99	100	430	400	6
Sb	0.02	0.06	0.92	0.06	0.08	0.08	0.15	0.15	0.14	0.08	0.05	0.04	0.03	0.02	0.02	10-30
Cs	0.02	0.12	0.33	0.49	0.35	0.05	0.05	0.45	0.49	0.14	0.31	0.13	0.07	0.08	0.13	5-50
Ba	8	13	92	33	34	-	-	55	57	13	24	26	9	8	21	10-30
La	3.8	10.5	2.8	6.5	8.2	1.87	1.46	10.1	8.9	3.9	4.3	11.8	5.9	4.4	5.1	2
Ce	2.8	11.1	3.7	9.7	13.0	1.28	1.47	16.0	14.3	5.1	10.1	17.4	7.9	8.3	9.1	2
Nd	4.5	13.3	2.1	6.7	7.6	1.20	0.75	10.1	9.3	4.2	5.3	14.9	5.1	3.7	4.3	5-10
Sm	0.95	2.5	0.55	1.15	1.10	0.18	0.16	1.18	1.20	0.49	1.05	2.5	0.95	0.42	0.54	2
Eu	0.27	0.67	0.085	0.25	0.23	0.056	0.040	0.31	0.32	0.13	0.23	0.75	0.22	0.096	0.13	5
Tb	0.19	0.45	0.068	0.17	0.14	0.060	0.035	0.21	0.21	0.083	0.16	0.56	0.15	0.072	0.09	3-10
Yb	0.39	0.95	0.22	0.61	0.45	0.15	0.106	0.62	0.66	0.19	0.38	1.18	0.40	0.22	0.31	5-15
Lu	0.044	0.11	0.032	0.085	0.066	0.019	0.011	0.088	0.092	0.024	0.055	0.16	0.052	0.029	0.039	5-10
Hf	0.007	0.05	0.27	0.45	0.57	0.029	0.037	0.55	0.53	0.16	0.38	0.08	0.07	0.13	0.23	3-30
Ta	-	0.015	0.027	0.090	0.067	-	0.002	0.11	0.10	0.023	0.061	0.029	0.016	0.028	0.041	6-50
Th	-	0.47	0.52	1.13	1.09	0.06	0.10	1.33	1.45	0.42	1.11	1.69	0.41	0.31	0.63	5-10
U	0.10	0.13	0.93	0.56	0.61	0.05	0.05	0.75	0.76	0.18	0.53	1.48	0.49	0.12	0.20	10-30
CaCO ₃ (%) ^a	100	98	84	51	44	53	57	47	48	52	54	52	52	98	90	
MgCO ₃ (%) ^a	0.5	1	1.3	40	34	42	44	36	36	40	40	38	39	2	2	
Detritus(%) ^a	0.2	1.4	4.5	8	7	0.5	0.6	10	10	2.7	6	~2	1.2	2.3	3.8	
Ce ^{err}	0.32	0.44	0.29	0.51	0.69	0.30	0.49	0.64	0.62	0.50	1.08	0.63	0.64	0.94	0.86	

* 24 Illinois, Iowa, and Ohio carbonates (330-470 Ma) were analyzed. These were deposited in the shallow Panthalassa seas. * Along Hwy. 36-59, 12-13 mi NW of Pittsfield, Pike Co., IL (SW SE 29-4S-5W; Barry 7.5m Quad.). * Outcrop along Douglas Creek, Henderson Co., IL (SE SW-8N-5W; Lomax 7.5m Quad.). * McCook Quarry, Lyons, Cook Co., IL (Sec. 15-38N-12E; Berwyn 7.5m Quad), ~124 ft. above base of Racine. * Ditto, ~3 ft. above base of Racine. * Thornton Quarry, Thornton, Cook Co., IL (SW Sec. 28-36N-14E; Calumet City and Harvey 7.5m Quad), ~100 ft. below top of quarry and top of Racine Dolomite. * Ditto, ~250 ft. below top of quarry. * Ditto, south face, from interreef rock near top of quarry in SE Sec. 33-36N-14E, ~7 ft. * Ditto, ~21 ft. * Elmhurst Quarry, Elmhurst, Cook Co., IL (SW NW 2-39N-11E; Elmhurst 7.5m Quad), ~44 ft. above quarry floor-Blaines member of Kankakee. * Ditto, ~2 ft. above quarry floor, probably Elwood dolomite. * National Quarry, Joliet, Will Co., IL (ESE Sec. 21-35N-10E; Joliet and Elwood 7.5m Quads.) 6.5-12.5 ft. above base of Fort Atkinson. * Ditto, from basal 6.5 ft. of dolomite. * Roadcut on west side of Hwy. X-56 ascending hill, 3.2 km N of Guttenberg, Clayton Co., Iowa (SENNW sec. 32-93N-2W; Guttenberg 7.5m Quad.). * Estimated ranges are for samples with highest to lowest concentrations. * Observed Mg and Ca assumed to be MgCO₃ and CaCO₃. * Detrital component was calculated by assuming all Al, K, Cr, Rb, Cs, Hf, Ta, and Th abundances were present in N.A.S.C. (North American Shale Composite) -like matter. * Ce anomalies were calculated relative to N.A.S.C. after subtraction of La, Ce, and Nd in N.A.S.C.-like detrital matter. * West central Iowa, Eilscheid Well; analyzed by C. Koeberl and J.B. Hartung, *Proc. Lunar & Planetary Science* 22, 111-126 (1992).

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Table 5. Element abundances in Ohio limestones from the Paleozoic Era

Period Formation Location Age (Ma) Sample	Devonian					Silurian		Ordovician		Uncertainty ^j (%)
	Columbus		Eiferian			Alexandrian		Champlainian		
	385		385			430		470		
	a	b	c	d	e	h	i	f	g	
Ti(%)	0.012	0.016	0.012	-	-	0.016	0.019	-	-	20-30
Al	0.151	0.118	0.019	0.039	0.051	0.170	0.246	0.050	0.093	2-15
Fe	0.189	0.154	0.035	0.029	0.046	0.31	0.56	0.038	0.095	1-3
Mg	1.6	4.1	0.38	0.13	1.4	2.9	0.33	0.59	0.84	3-15
Ca	35.6	32.7	38.9	39.3	36.1	34.2	37.0	36.3	38.1	3
Na	0.0147	0.0197	0.0184	0.0081	0.0190	0.0146	0.152	0.0085	0.164	2-9
K	0.092	0.070	-	0.023	0.040	0.10	0.14	0.044	0.095	15-30
Sc(ppm)	0.39	0.37	0.059	0.109	0.185	0.49	1.34	0.095	0.151	2
V	6.0	7.0	2.4	2.9	3.9	4.1	11.6	1.0	1.8	7-30
Cr	3.4	4.5	0.87	0.68	1.2	2.2	6.2	0.59	0.92	1-6
Mn	204	117	171	152	211	249	400	21	32	2
Co	0.33	0.20	0.096	0.092	0.37	0.49	1.85	0.092	0.17	1-6
Rb	2.9	2.4	0.34	1.1	1.3	4.1	5.7	1.5	2.6	5-12
Sr	110	130	110	140	130	80	150	140	340	5
Sb	0.086	0.106	0.028	0.047	0.062	0.046	0.107	-	0.014	7-14
Cs	0.143	0.117	0.026	0.040	0.030	0.135	0.22	0.038	0.071	6-20
Ba	42	25	11	12	15	9	170	42	9	3-15
La	4.5	4.6	1.89	1.55	2.59	2.28	5.8	0.57	0.68	1-2
Ce	3.7	4.8	2.47	2.10	3.15	3.7	10.5	0.95	1.14	2-4
Nd	3.0	3.0	1.82	1.17	2.24	1.9	5.2	0.44	0.53	2-7
Sm	0.75	0.83	0.38	0.198	0.61	0.400	1.65	0.104	0.118	1-2
Eu	0.149	0.160	0.113	0.071	0.145	0.107	0.41	0.022	0.021	2-5
Tb	0.122	0.117	0.049	0.049	0.100	0.083	0.32	0.008	0.010	4-30
Dy	0.89	0.66	0.51	0.27	0.44	0.51	1.86	0.061	0.11	5-30
Yb	0.37	0.37	0.151	0.085	0.190	0.32	0.91	0.036	0.035	2-10
Lu	0.053	0.057	0.024	0.010	0.030	0.037	0.106	0.0052	0.0064	2-20
Hf	0.13	0.36	0.015	0.021	0.24	0.17	0.14	0.022	0.044	2-20
Ta	0.005	0.020	-	0.011	0.015	0.019	0.034	-	0.011	10-30
Th	0.26	0.35	0.034	0.047	0.13	0.32	0.98	0.082	0.12	2-10
U	1.9	3.2	1.13	1.44	1.54	0.15	1.06	0.14	0.34	1-8
CaCO ₃ (%) ^k	89	82	97	98	90	86	93	91	95	3
MgCO ₃ (%) ^k	6	14	1	0.4	5	10	1	2	3	3-15
Detritus(%) ^l	2.2	2.1	0.3	0.5	1.0	2.4	4.5	0.7	1.0	-25
CeA ^m	0.32	0.47	0.61	0.66	0.55	0.72	0.86	0.75	0.71	

a #25-2055A. b #21-2092. c #20-2083E. d #192A. e #189G f #13-2080-14. g #09-2082-b. h #55-2075. i 14-2045B. j Estimated uncertainty ranges correspond to highest to lowest abundance ranges for a given element. k All Ca and Mg abundances are assumed to be equivalent to CaCO₃ and MgCO₃, respectively. l Detrital component was calculated by assuming all Al, K, Cr, Rb, Cs, Hf, Ta, and Th abundances were present in N.A.S.C. (North American Shale Composite)-like matter. m Ce anomalies relative to N.A.S.C. were calculated after subtraction of La, Ce, and Nd abundances in N.A.S.C.-like detritus.

(INAA data by Drs. Y.-G. Liu and R.A. Schmitt, 1991)

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PART 4

Letter to D. Livingston (July 6, 1993)

OREGON STATE UNIVERSITY

Radiation Center A100 Corvallis, Oregon 97331-5903

Telephone 503-737-2341 Fax 503 737-0480

July 6, 1993

Dr. Donald Livingston
1108 Rock Spring Dr.
Las Vegas, NV 89128

Dear Don:

Below is a list of fission track experts who used our 1 MW TRIGA reactor thermal column for activations of their samples in 1992 and 1993.

H. Wollenberg and S. Flexser, L.B.L. (CA)
J. Steidtmann, P. Groll, and G. LeFebre, Dept. of Geol., University of Wyoming
D. Miller, M. Roden, and R. Donelick, Dept. of Geol. Rensselaer Polytechnic Institute
B. Kowallis, Dept. of Geol., Brigham Young Univ.
J. Vance, Dept. of Geol. Sci., Univ. of Washington, Seattle (zircons)
B. Patrick, Dept. of Geosciences, New Mexico Tech. (zircons and apatites)
T. Dumitru, Dept. of Geology, Stanford U.

R.E. Zartman and L.M. Kwak (H.L.W.M., 1953, 1993) contend that their observed Pb isotopic data are compatible with the supergene mechanism, including Trench 14 shallow vein system, if the eolian particulates from the surrounding lower Paleozoic marine carbonates are abraded to smaller and smaller sizes and eventually are totally dissolved during periods of rainfall and surface water accumulation. They further indicate that cycles of wet and dry weather rework the resulting secondary carbonates so eventually the Pb isotopic signatures are preserved in calcretes and veins.

I claim that these deductions are not consistent with the chemistry of meteoric and ground waters. First, I note the M.R. Smith (1991) report ("Natural Radionuclide Element Hydrochemistry, Characterization of the Yucca Mountain Saturated (well waters) and Unsaturated (pore waters) Zone Ground Water") (Monty Smith was one of my latest Ph.D. students before he returned to the P.N.L.) analyzed samples listed below. I have normalized selected alkalis (Rb and Cs) and the very insoluble Hf and Th and also La as a representative REE to N.A.S.C. abundances.

Element	J12 well water pH = 7.3	J13 well water	UZ#4 pore waters	
			6110926 pH = 6.5	6110923 pH = 6.5
Rb	0.074	0.052	0.18	0.096
Cs	0.11	0.18	0.096	0.085
La	0.000013	0.000009	<0.003	0.00023
Hf	0.00016	<0.0003	0.0016	0.048
Th	0.000008	0.00003	0.00020	<0.00081
U	0.045	0.033	0.17	0.05

A few observations are summarized below.

1. The normalized abundances of Rb, Cs, and U are rather similar in both Y.M. well water and UZ (Unsaturated Zone) pore water.
2. Very low abundances of La, Hf, and Th were found in well waters and UZ waters; e.g., Th/Rb $\sim 1.1 \times 10^{-4}$ in J12 and $\sim 1.1 \times 10^{-3}$ in UZ 6110926 pore waters, and La/Rb $\sim 1.8 \times 10^{-4}$ in well waters and $\sim 2 \times 10^{-3}$ in UZ pore water.
3. The pHs of these waters range from 6.5 - 7.3.

Clearly, the data above indicate that the contributions from contrasting trace elements (e.g., the very soluble alkalis and very insoluble elements like La, Hf, and Th) to the calcite/opal samples like Trench #14, 36N are very different. Also, their observed abundances reflect their respective solubility products, which controls the fractions leached from soil, rocks, carbonates and minerals therein.

We will approach the Zartman-Kwak scenario from expected solubilities. Suppose 1g N.A.S.C.-like very fine grained particulates and $\sim 15\text{g CaCO}_3 + \text{SiO}_2$ (roughly equivalent to 36N composition) are placed in a 1L flask and various pH waters are added. We will neglect CaCO_3 dissolution which will only raise the pH. Now the average pH of Nevada rain is expected to be ~ 5.5 in the absence of anthropogenic activities (John Hart, O.S.U. priv. com., 1993). He also indicated that soil pH=5 and below are apparently reached only in high mountain meadows which traps runoff. If such low pH=5 waters react with soil carbonates as envisioned by Zartman and Kwak, the pH will increase.

We will first assume that the $\text{pH} \leq 6.5$ soil waters dissolve all the alkalis in the very fine grained N.A.S.C.-like particulates. How much Th is dissolved?

Below I have calculated the expected [Th], i.e., activity of Th, and (Th), i.e., concentration of Th. Assume $\gamma(4+ \text{ ion}) \sim 0.005$.

Expected Th in Solutions

pH	[Th]	(Th)
6.5	$\sim 2 \times 10^{-12} \mu\text{g/L}$	$\sim 5 \times 10^{-10} \mu\text{g/L}$
6.0	$\sim 2 \times 10^{-10}$	$\sim 5 \times 10^{-8}$
5.5	$\sim 2 \times 10^{-8}$	$\sim 5 \times 10^{-6}$
5.0	$\sim 2 \times 10^{-6}$	$\sim 5 \times 10^{-4}$
4.5	$\sim 2 \times 10^{-4}$	$\sim 5 \times 10^{-2}$
4.0	$\sim 2 \times 10^{-2}$	~ 5

The above rather simple calculations based on the K_{sp} of $\text{Th}(\text{OH})_4 \sim 10^{-50}$ indicate that the pHs of Y.M. rainfall and surface waters must have been ≤ 4.0 in order to satisfy the Zartman-Kwak scenario. In view of the high pHs of Y.M. well waters of ~ 7.3 , Y.M. UZ pore waters ~ 6.5 , average rainfall of ~ 5.5 , the expected eolian mix of ~ 15 fine grained lower Paleozoic calcitic/1 fine grained N.A.S.C.-like detritus in them yielding a pH > 5.5 in the Zartman-Kwak solubilization solutions that were hypothesized as possible parental to Y.M. veins like Trench #14, we assert that the extremely low quantities of dissolved Hf and Th relative to the high quantities of dissolved Rb and Cs rule out the Zartman-Kwak hypothesis for a supergene genesis of the Trench #14 carbonates.

Such low calculated N.A.S.C. normalized ratios of dissolved alkalis and Hf, Th, e.g., from a very fine grained 1g N.A.S.C. Rb/Th $\sim 125/5 \times 10^{-6} \sim 2.5 \times 10^7$, relative to N.A.S.C. normalized ratios of Rb/Th ~ 0.8 in Trench #14, 36N, rule out the Zartman-Kwak scenario and strongly support the hypogene hypothesis that hydrothermal fluids, within the tectonic rearrangements regime, flow through Paleozoic and Cambrian carbonates below and subjacent to Y.M. and dissolve some of the Ca, Mg carbonates and mix in the exposed fine grained N.A.S.C.-like particulates scattered throughout these Paleozoic and Cambrian carbonates. Such fluids migrate to higher stratigraphic regions along fractures and crystallize very rapidly, yielding the observed microcrystalline CaCO_3 minerals, e.g., at Trench #14.

In conclusion, the very important Pb isotopic constraints reported by Zartman and Kwak (1993) are satisfied by their scenario of total dissolution of Paleozoic eolian particulates only if the pHs of rain and surface waters are ≥ 1 , i.e., low enough to dissolve not only the eolian detritus grains but also the predominant eolian carbonate grains and other carbonate minerals in the soils yielding a final pH ≤ 4.0 . Invoking such a low pH is entirely unreasonable and untenable.

Best regards,

R.A. Schmitt

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P.S. Please send me a copy of Jerry Szymanki's 1989 unpublished DOE report that other Y.M. workers cite. Also, send me a copy of the E.M. Taylor and H.E. Huckins (1986) paper.

PART 5

Calcite Deposits in Fractures at Yucca Mountain, Nevada

CALCITE DEPOSITS IN FRACTURES AT YUCCA MOUNTAIN, NEVADA

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ABSTRACT

Calcite is one of the latest-formed minerals within fractures at Yucca Mountain. Petrographic and chemical studies of these calcites have the potential, in conjunction with fluid-inclusion and isotopic studies, of determining the locations of transmissive regions in unsaturated tuffs. Preliminary chemical data for fracture calcites from Yucca Mountain indicate a common composition for most unsaturated-zone calcites (low abundances of transition elements; chondrite-normalized lanthanide-element patterns with prominent negative Ce and Eu anomalies) that is distinct from most calcites in the saturated zone. Exceptions to this general characterization occur in drill core USW G-4; the reasons for these deviations are as yet unknown, but the rich variety of calcite compositions suggests that much information is to be gained from further studies.

INTRODUCTION

Yucca Mountain, in southern Nevada (Figure 1), is being studied as a potential site for deep geologic disposal of high-level radioactive waste. Should a repository be developed at Yucca Mountain, the preferred location is within the upper unsaturated tuffaceous volcanic rocks. In this location, one factor of concern is the amount and rate of aqueous transport through the unsaturated rocks toward the underlying saturated intervals. Calcite, one of the most recently-formed minerals at Yucca Mountain, is of minor abundance in the unsaturated rocks but is widely distributed. Studies of calcite ages, isotopic systematics, chemistry and petrography could lead to a better understanding of transport processes at Yucca

Mountain. Specifically, the study of past calcite precipitation can provide several types of information about the Yucca Mountain site:

- (1) Calcite deposits are markers of where water has been in the unsaturated rocks; preferred pathways may be marked by calcite deposits.
- (2) Dated calcite deposits indicate when water was there.
- (3) In some cases, models of carbonate transport and precipitation may allow estimation of minimum quantities of flow.
- (4) Reconstructions of the aqueous chemical environments of most recent calcite deposition may help to evaluate the potential future coprecipitation of waste with carbonate or other fracture minerals at Yucca Mountain.

Preliminary data on the ages of fracture- and cavity-filling calcites at Yucca Mountain have been obtained by uranium-series dating.¹ These dates indicate episodic deposition of most unsaturated-zone calcite during meteoric recharge episodes occurring within the past 400 Ka. The uranium-series dates further suggest that distinct calcite precipitation episodes may have been concentrated at 28, 170, and 280 Ka.

The $\delta^{13}\text{C}$ compositions of calcites differ markedly above and below the static water level (SWL), with lighter carbon ($\delta^{13}\text{C}$ of -9.5 to -4‰ vs. PDB) in the unsaturated zone and heavier carbon ($\delta^{13}\text{C}$ of -2 to 3‰) in the saturated zone.² The carbon isotope data suggest that most calcites above the SWL precipitated from waters that had reacted with the overlying soils and their plants, whereas the calcites beneath the SWL precipitated from

waters of the deeper Paleozoic aquifer, although there is considerable overlap of the two $\delta^{13}\text{C}$ groups in a zone from 300 m below to 500 m above the present SWL.

Strontium isotope data on the calcites reinforce the fundamental distinctions between calcites above and below the SWL.³ Calcites of the unsaturated zone within 400 m of the surface have more radiogenic Sr ($^{87}\text{Sr}/^{86}\text{Sr}$ av. 0.71215) than those below the SWL ($^{87}\text{Sr}/^{86}\text{Sr}$ av. 0.70909). Intermediate $^{87}\text{Sr}/^{86}\text{Sr}$ values occur in the unsaturated zone within 100 m of the SWL, perhaps related to past rise in the water table.

DESCRIPTION OF RESEARCH

For this research the chemistry and petrography of 19 calcites from fractures both above and below the present static water level (SWL) are described. Mineral separates of calcite were hand-picked from fractures in Yucca Mountain drill cores USW G-1, USW G-2, USW GU-3/G-3, and USW G-4 (Figure 1). Calcite samples were obtained from fractures above and below the SWL in each drill core (depths to the SWL are 572 m in USW G-1, 525 m in USW G-2, 750 m in USW G-3, and 540 m in USW G-4). The hand-picked separates were used for instrumental neutron activation analysis (INAA). Thin sections and sample chips were examined by optical methods and by backscattered-electron, secondary-electron, and energy-dispersive X-ray methods in a scanning electron microscope (SEM). Mg and Mn compositions, not determined by INAA, were measured by electron microprobe. Abundances of minor mineral contaminants (quartz or mordenite) in some calcites from below the SWL were determined by X-ray diffraction. Abundance of opal contamination in one calcite from above the SWL was estimated by SEM image analysis and by comparing the INAA-determined Ca composition to the Ca content of ideal calcite. In the text and figures that follow, calcite samples are identified by their drill core of origin and depth in meters (e.g., USW G-4, 107).

RESULTS

Petrographic studies reveal a variety of bladed rhombohedral and rarer pyramidal-scalenohedral calcite forms above the SWL. Deeper calcites generally fill fractures and are

Figure 1 - Drill cores USW G-1, USW G-2, USW GU-3/G-3, and USW G-4 located relative to the outline of the potential repository at Yucca Mountain.

typically anhedral. Calcites in fractures above the SWL in USW G-2 are commonly intergrown with small amounts (<1%) of Ca-rich zeolites (e.g., USW G-2, 477). Calcites above the SWL in other drill holes may be intergrown with variable amounts of opal and/or sepiolite (USW GU-3, 295 and USW G-4, 107). Calcites below the SWL may be intergrown with dolomite (USW G-2, 1640: <1% dolomite), quartz (USW G-2, 1756: 5% quartz), mordenite (USW G-1, 1179: 5% mordenite), or analcime.

A. Drill Cores USW G-1, USW G-2, and USW GU-3/G-3

In drill cores USW G-1, USW G-2, and USW GU-3/G-3 the fracture calcites of the unsaturated zone are chemically distinct from those of the saturated zone. In particular, some transition metals are much higher in the deeper calcites (e.g., Sc of 0.5-6 $\mu\text{g/g}$ in the saturated-zone calcites vs. <0.02 $\mu\text{g/g}$ in the

Figure 2 - Chondrite-normalized lanthanide-element patterns for fracture-lining calcites above and below the present static water level (SWL) in four drill cores at Yucca Mountain. Sample numbers indicate depth in meters. Circles or polygonal symbols are used for calcites from above the SWL; crosses (+, x) are used for calcites from below the SWL. The percentages of intergrown mineral contaminants are indicated where calcite separates of >99% purity could not be obtained. Arrows drawn for some Ce points indicate that only a maximum Ce content could be determined and the Ce anomaly is actually deeper than shown. Error bars (one standard deviation) are smaller than the symbols used except for Nd and for exceptionally low Ce values, where standard deviations are ~4x the symbol size.

unsaturated zone). The enrichment in transition metals is most notable in MnO, which is measurable by electron microprobe at 0.25 to >2% in the deeper calcites but is <0.05% in the shallower calcites.

In addition to these differences in element abundances, the chondrite-normalized REE patterns are markedly different in calcites above and below the SWL. The development of

strong negative Eu and Ce anomalies in calcites above the SWL distinguishes them from calcites below the SWL. Figure 2 illustrates these differences.

B. Drill Core USW G-4

The calcite chemical analyses available from USW G-4 contrast with those from the other drill cores. Calcites in USW G-4 appear to

have low concentrations of transition elements at all depths (e.g., Sc of 0.006 $\mu\text{g/g}$ in calcite below the SWL), although only one sample from below the SWL has yet been analyzed (USW G-4, 810). Not only does this one calcite sample from 270 meters beneath the SWL have an REE pattern similar to that of unsaturated-zone calcites, but one of the unsaturated-zone calcites (USW G-4, 107) has a smaller Ce anomaly and lacks the Eu anomaly seen in all other unsaturated-zone calcites (Figure 2). The close intergrowth of this particular calcite sample with small ($\sim 40 \mu\text{m}$) spheres of opal makes it the least pure sample of calcite analyzed; however, the 10% opal contamination can not account for the reduction in heavy REE (Tb, Yb, Lu) by factors >10 in this fracture calcite (Figure 2).

DISCUSSION

The prominent negative Ce and Eu anomalies in most calcites above the SWL suggest that these calcites are, as a group, distinct from calcites below the SWL. Most lanthanide elements are trivalent; however, Ce may be depleted by precipitation as Ce^{IV} (CeO_2) from waters that are oxidizing or of high pH. The well-studied coprecipitation of Ce^{IV} with Mn^{IV} in oceanic manganese nodules⁴ may be relevant to the formation of unsaturated-zone calcites in fractures at Yucca Mountain, where manganese minerals in which Mn^{IV} predominates (lithiophorite or rancieite) are common in unsaturated-zone fractures. Rancieite in fractures at Yucca Mountain may contain as much as 8% CeO_2 by weight.⁵ If the fluids from which these shallow calcites have formed were modified by manganese-mineral precipitation and if many of these calcites are as young as the data suggest,¹ then the formation of Mn-oxides as well as calcite may be an ongoing process at Yucca Mountain. Alternatively, Ce^{IV} may be actively scavenged from calcite-forming waters by Mn-oxides that have already formed.

In contrast to the negative Ce anomalies attributed to Ce oxidation, negative Eu anomalies are typically attributed to Eu reduction, from Eu^{III} to Eu^{II} . In divalent form, Eu readily substitutes for Ca in many common minerals. If incorporated into precipitating minerals under the appropriate reducing conditions, Eu is depleted from the remaining solution.

It is possible that the exceptionally low Eu contents of some shallow calcites may be caused by scavenging of Eu by another Ca-rich mineral. Ca-zeolites (probably heulandite or stellarite) are intergrown with some shallow calcites in USW G-2. However, in other drill cores fluorite (CaF_2) rather than Ca-zeolite is commonly associated with the calcites above the SWL. Early precipitation of fluorite could deplete Eu from waters that later precipitated calcite. If fluorite is an important factor in generating the exceptionally deep negative Eu anomalies in calcites of USW GU-3, then either (1) fluorite formation is a thing of the past, and very deep Eu anomalies are not forming in the younger calcites, or (2) fluorite formation is an ongoing process. The latter option is unlikely, because all fluorite occurrences yet observed in association with shallow calcites indicate that the fluorite is overlaid by later-formed calcite. Furthermore, fluorite is likely to be an earlier, higher-temperature phase formed from F-rich fluids generated by F loss from glassy tuffs during devitrification.

The possible involvement of Mn-oxides, fluorite, and perhaps other minerals in the formation of Ce and Eu anomalies is not the only potential explanation for these features. These anomalies need not have formed solely as calcite (and/or other minerals) precipitated from the source waters. Experimental studies suggest little fractionation of REE during calcite precipitation from dilute solutions.⁶ However, it is uncertain whether the source waters would develop the same REE patterns as the tuffs, soils, or other solids that provide lanthanide species to solution. The behavior of lanthanides during weathering is a poorly understood process.⁴ This uncertainty in source-water chemistry is particularly relevant if most of the calcites above the SWL were deposited by downward-flowing water.

The chain-structure clay sepiolite is an important associate of the calcite and opal that form in calcrete at the surface of Yucca Mountain.⁷ It is noteworthy that some fracture calcites above the SWL also contain sepiolite and opal, resulting in mineral assemblages that are similar to the calcretes at the surface of Yucca Mountain. The occurrence of sepiolite and opal in shallow fracture calcites is a further indication of linkage between soil mineralogy and the minerals precipitating along fracture surfaces above the SWL at Yucca Mountain.

The anomalous calcite compositions in USW G-4 appear to violate the otherwise general character of high Sc and Mn abundance for calcites below the SWL and large negative Ce and Eu anomalies above the SWL. Sample USW G-4, 810 carries the chemical signature of a shallow calcite even though it is 270 m below the SWL. This sample might be explained as calcite that formed in the unsaturated Bullfrog Member of the Crater Flat Tuff prior to deeper burial and water-table rise, but there is as yet no independent evidence to support this hypothesis. More perplexing is sample USW G-4, 107 that is 433 m above the SWL with the expected low Sc content and negative Ce anomaly, yet having a heavy carbon isotopic composition ($\delta^{13}\text{C}$ of 0.6 to 4.9‰; sample G-4 108 of ref. 2) and normal Eu pattern similar to calcites from below the SWL. This "hybrid" calcite, which is closely intergrown with opal, indicates that a single simple model of calcite formation is unlikely to explain all of the calcite precipitation mechanisms at Yucca Mountain.

CONCLUSIONS

There is an apparent set of chemical distinctions that separates most calcites at Yucca Mountain that formed in the unsaturated zone from those that formed in the deeper, saturated rocks. Negative Ce and Eu anomalies are common in calcites above the SWL yet not below; high contents of Sc and Mn are common in calcites below the SWL but not above. The violation of this simple distinction in some calcites from one drill core (USW G-4) indicates that a single model of calcite precipitation is probably inadequate for explaining the origins of all Yucca Mountain fracture calcites. However, the rich variety of calcite chemical compositions and mineral associations, coupled with isotopic and fluid-inclusion data, may provide a broad enough data base to unravel the various regimes of calcite precipitation that have occurred - and perhaps are still occurring - at Yucca Mountain.

ACKNOWLEDGEMENTS

This work was supported by the Yucca Mountain Site Characterization Project as part of the Civilian Radioactive Waste Management Program. This Project is managed by the U. S. Department of Energy, Yucca Mountain Site Characterization Project. INAA data were

obtained at the trace-element geochemistry laboratory of Washington University, St. Louis, Missouri. Review comments by D. Broxton and A. Simmons are greatly appreciated. The Yucca Mountain Project Technical Data Catalog Data Tracking Number for this paper is LA000000000025.001.

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