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Fluid inclusion studies of samples from the Exploratory Study Facility, Yucca Mountain, Nevada

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Foreword

Arjun Makhijani

In July 1998 IEER commissioned Dr. Yuri Dublyansky of the Siberian Branch of the Russian Academy of Sciences to prepare and study mineral samples that he collected in the previous month from the Yucca Mountain tunnel in Nevada. This five-mile tunnel has been drilled to study the suitability of the site for disposal of spent fuel from US nuclear power plants and highly radioactive waste from military plutonium production. Dr. Dublyansky is a geologist who specializes in fluid inclusions in minerals.

Fluid inclusions are small amounts of liquid and/or gas trapped in tiny cavities in mineral deposits. Study of these inclusions can yield information about whether an underground area had been dry or saturated in the past. When analyzed using isotopic dating techniques, such inclusions can also be used to estimate the date(s) in the past when water may have entered a particular area. It should also be possible to distinguish whether the water entered into the repository zone as a result of percolation from above or an upwelling from below. Finally, estimates can also be made of the temperature of the water.

Water is expected to be the main pathway by which the radioactive materials in spent nuclear fuel and other highly radioactive waste would reach the human environment. Water is also a principal means by which the containment of the wastes may become compromised. Hence, the question of whether a repository location has been dry or saturated in the past is an important one. This is especially the case when metal canisters are to be used in an oxidizing environment, as the Department of Energy is proposing to do at Yucca Mountain.

IEER's purpose in commissioning this report was to enable an independent assessment of these crucial questions. This study will help concerned policy-makers and the public to examine independently collected evidence important in evaluating the official study of the Yucca Mountain site, known as the Viability Assessment, which is to be issued in December 1998.

There has long been a controversy as to the presence of groundwater at some time in the past in the region of the proposed repository. This controversy has not yet been resolved. It is of the utmost importance to resolve it, since the presence of warm or hot water in the repository would change considerably the assessment of its suitability. For instance, technical details of the Viability Assessment revealed so far show that the DOE will be relying heavily on the integrity of the canisters containing the wastes over tens of thousands of years to keep long-lived radioactive materials out of the groundwater. But under saturated, warm conditions these canisters could deteriorate very rapidly. Dr. Dublyansky's study does not resolve all the questions and should be regarded as preliminary. But its findings are very disturbing and call for careful and intensive further work, especially as regards the age of the formation of the minerals in which the fluid inclusions have been found.

The subject matter is as complex as it is important. Questions relating to the management of long-lived radioactive wastes are among the most difficult that we face. The science is difficult enough. If it is confounded with opportunistic politics, as it has been throughout the DOE repository program, it will be impossible to make the sound technical judgments that are necessary to protect future generations. IEER's previous work has discussed many reasons that DOE's repository program should be terminated, not least because of the severe institutional problems in its management. Further, the radiation doses estimated for Yucca Mountain, should the groundwater become contaminated, have been far higher than for other sites that have been studied. The fact that historical claims of Native Americans to the land are not an important part of the official evaluation of the site or of the broader debate about it continues to be very troubling. But we have not before this time issued a special report dedicated to the specific issue of the geologic suitability of the Yucca Mountain site.

We have had Dr. Dublyansky's report extensively reviewed by independent scientists unaffiliated with the Yucca Mountain program as well as by scientists who are one way or another involved in evaluating that effort. We sent a draft copy of Dr. Dublyansky's report to Dr. Lake Barrett, Acting Director of the Office of Civilian Radioactive Waste Management (OCRWM), so that scientists of his choosing could review it. Generally, the reviews found Dr. Dublyansky's work to be of exemplary quality. The one exception was the review arranged by the DOE and compiled by Joe Whelan.[1]

I have worked closely with Dr. Dublyansky to ensure that all comments, including those made by DOE-selected reviewers, have been carefully addressed on their merits. When warranted, Dr. Dublyansky has made changes to his draft report. In other cases he has provided clarifications and additional explanations. Of course, since he is the author of the study, he has had the normal prerogative of making the judgment of how each review comment should be addressed.

One of the most interesting things about the DOE-arranged review compiled by Joe Whelan is its misrepresentation of some of the reviewers own data regarding certain mineral deposits at Yucca Mountain. As one who has had occasion to review many studies, I also found the *ad hominem* tone of some of the remarks highly inappropriate. This was not a final report we sent for review. It was a draft, sent out for review in the full expectation and commitment that we would take reviewers comments seriously. The *ad hominem* comments were therefore completely uncalled for and are not in keeping with normal scientific discourse. Despite the personal innuendoes, gross misreading of evidence clearly presented in the report, and misrepresentation by the reviewers of their own data, IEER has worked to treat their comments fairly. To enable the public to see all the evidence, IEER is going to the extraordinary length of publishing some of the reviews, including the DOE-arranged review compiled by Joe Whelan. A reply by Dr. Dublyansky on a point-by-point basis to the DOE-arranged review is also published in an appendix to this report.

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[1] Joe Whelan, James Paces, Brian Marshall, Zell Peterman, John Stuckless, Leonid Neymark (all of the US Geological Survey) and Edwin Roedder (Harvard University), "Review of 'Fluid Inclusion Studies of Samples from the Exploratory Studies Facility, Yucca Mountain, Nevada,'" forwarded to IEER with a cover memo by Joe Whelan to Dennis Williams, dated November 9, 1998 and a cover letter from J. Russell Dyer to Dr. Arjun Makhijani, dated November 13, 1998. Review "compiled by" Joe Whelan.

The DOE has an unfortunate history of rushing into large projects with huge budgets and jumping to conclusions about them before the scientific work is complete.[2] This Yucca Mountain project is no exception. The Department claims that it has completed work on assessing the viability of Yucca Mountain as a repository site. Yet, at the same time, it is preparing to conduct joint sampling and study of the critical issue of fluid inclusions (the subject of this report) with Dr. Dublyansky. The DOE-appointed reviewers of this report, while highly critical in their detailed remarks, agree that further work is warranted:

> *"Although we question Dublyansky's science and biases, we cannot reject his fluid inclusion data out of hand. Despite the fact that calcite is a notoriously difficult mineral for fluid inclusion studies, those difficulties are surmountable with care, and Dublyansky claims to have taken all reasonable precautions in conducting his studies. The fluid inclusion data should therefore be verified…and the timing of their formation should be constrained by isotopic dating of the host minerals."*[3]

Dr. Dublyansky's recommendations are very similar. He does not claim to know the date of the mineral deposits that have the fluid inclusions studied in this report. That remains to be established. Other crucial facts, such as the presence of high molecular weight hydrocarbons in a few samples, provide further indicative, though not definitive, evidence of water ingress into the Yucca Mountain repository location. Further work is also needed in this respect.

Dr. Dublyansky's work has impressed the independent reviewers immensely. These reviewers, who have never before done any work with IEER, concurred in their evaluation of the high quality of the report and the research on which it is based. One of them, Professor Larryn W. Diamond, of the Department of Mineralogy and Petrology, Institute of Earth Sciences in the University of Leoben in Austria, conducted an independent evaluation of some of the mineral samples. It is also noteworthy that the principal expert on fluid inclusions of the Congressionally-mandated Nuclear Waste Technical Review Broad, Dr. Robert Bodnar, reassessed some of his previous opinions of the subject after he worked with Dr. Dublyansky in June 1998 and had a chance to study some of the samples Dr. Dublyansky had taken in 1995. In a letter to the NWTRB, dated July 8, 1998, Dr. Bodnar agreed that elevated-temperature fluid inclusions were present in the samples and that they were not artifacts of the preparation of the samples. Further, he found evidence, though not conclusive, of the presence of aromatic hydrocarbons. Finally, he also recommended further sampling and study.[4]

When Dr. Dublyansky visited Nevada earlier this year, he discussed the subject of a joint sampling program with DOE and the US Geological Survey. There was interest on the part of some scientists but the USGS refused to go ahead with it.

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[2] IEER analyzed this tendency in DOE's Environmental Management program in a report by Marc Fioravanti and Arjun Makhijani, entitled *Containing the Cold War Mess*, published in October 1997.

[3] Joe Whelan to Dennis Williams, memorandum regarding review of Yuri Dublyansky's report, November 9, 1998.

[4] Robert Bodnar to Leon Reiter (Nuclear Waste Technical Review Board), letter dated July 8, 1998.

Dr. Dublyansky collected his own samples from the Yucca Mountain tunnel in June 1998. The locations have been marked and bar-coded by the Yucca Mountain Characterization Project. The present study is based on data derived from that sampling.

The DOE will be making a grave technical mistake if it declared Yucca Mountain to be a viable site, as it seems set to do later in December 1998, before this crucial issue is resolved. Such a finding, issued in the face of considerable agreement about the need for further examination of fluid inclusions would be at variance with sound scientific practice.

IEER believes that it is crucial that a joint sampling program be established, that careful joint studies be done, and that they be subjected to truly independent review. Draft findings should be presented to the public with the underlying data so that the broadest possible scrutiny is possible. This will likely take two years or more. The issuance of the Viability Assessment should be put off until that time.

Given the many problems with Yucca Mountain, and the possibility that these joint studies will yield further negative findings for the suitability of Yucca Mountain as a repository, it would be prudent for the DOE to begin making back-up plans for long-term management of spent fuel and military high-level waste. The DOE has typically failed to provide any insurance for many of its key programs, resulting in higher expenditures, greater delays, and larger environmental risks. IEER has put forward such a plan, but the DOE has ignored it.[5] We believe that it is high time for the DOE to address our specific recommendations.

Financial support for IEER's work on nuclear waste (including DOE's Yucca Mountain program) and other environmental and security issues related to nuclear weapons and nuclear power is provided by support from individual donors and the Beldon II Fund, the C.S. Fund, the DJB Foundation, the HKH Foundation, the John D. and Catherine T. MacArthur Foundation, the John Merck Fund, the New Land Foundation, the Ploughshares Fund, the Public Welfare Foundation, the Town Creek Foundation, the Turner Foundation, the Unitarian Universalist Veatch Program at Shelter Rock, and the W. Alton Jones Foundation. Their generous support makes our independent work and outreach possible. We hope and expect that Dr. Dublyansky's report will initiate a new and more scientifically thorough phase of work on one of the most vital environmental issues that we all face.

Arjun Makhijani, Ph.D.
President, IEER
Takoma Park
November 25, 1998

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[5] See *Science for Democratic Action*, vol. 6, no. 1, May 1997.

Main Findings and Recommendations

This report analyzes mineral samples of calcite collected from Yucca Mountain in June 1998 by the author. Calcite (calcium carbonate) is a mineral that often forms veins and incrustations in rock fractures. It is practically always formed by precipitation from water. Calcite can be formed in geologic media by percolation of water from the surface or by upwelling of water from below.

Examination of calcite samples from the Yucca Mountain subsurface discussed in this report leads to two principal conclusions:

- the studied calcite was formed by upwelling of water and not from percolation of surface water; and
- the water that entered the Yucca Mountain repository area in the past from below was at elevated temperatures.

The main evidence for these findings is as follows:

1. Water was found trapped in tiny cavities in the calcite samples. These trapped water bodies are called fluid inclusions. Many fluid inclusions had vapor bubbles formed in them, indicating that the water had shrunk after it became trapped. The shrinkage of water evidences that the water has cooled from its original temperature. This is evidence of the presence of water at elevated temperature in the repository zone in the geologic past that could not have come from surface sources.
2. A few samples showed the presence of hydrocarbons. These are all-gas inclusions in calcite, in which traces of aromatic hydrocarbons were found. Aromatic hydrocarbons are heavy molecules that could not have originated in surface sources. There is evidence of hydrocarbons in the geologic media beneath Yucca Mountain area. Hence, the trapped hydrocarbons provide supplementary, though at present, fragmentary additional evidence of upwelling of water into the repository horizon.
3. Veins and crusts at Yucca Mountain besides calcites contain other minerals such as opal, quartz, and minor fluorite. These minerals are typically precipitate from warm or hot water. In particular, it is extremely rare for quartz and fluorite to be formed from surface water percolation. Hence, the presence of these minerals is strong evidence of past presence of upwelling warm water in the Yucca Mountain area.
4. Minerals formed in unsaturated zone, that is, above the water table, are typically deposited in laminated formations consisting of millions of tiny crystals. For example, stalactites in caves are created in this way. By contrast, large individual perfectly shaped crystals require a saturated environment to form. The calcite at Yucca Mountain often forms perfectly shaped individual crystals, clearly indicating that the area was, at some time in the past, saturated.

The study also addresses the question of the age of the calcites. This is because the only way to estimate the future performance of any site as a geologic repository is to study its past. The timing of the formation of the calcites is important because it provides evidence of when the area was saturated and hence of the probability of its becoming saturated in the future during the period relevant to repository performance.

Peak radiation doses from Yucca Mountain are expected to occur in the period between 100,000 years and one million years from now. Saturation in the recent geologic past would have serous negative repercussions for the suitability of Yucca Mountain as a repository. This is because saturation of the Yucca Mountain repository after burial of highly radioactive waste may cause the waste canisters to corrode far more rapidly than if the area remained dry. On the other hand, if water entered Yucca Mountain many millions of years ago, and not since then, this specific issue would be of far less consequence.

The findings of the research for the timing of past repository saturation are only tentative and indicative. There are indications that the calcite may have been formed in the recent geologic past (less than one million years). This is a very complex and difficult area of work and considerable further research is needed to clarify this crucial question.

Recommendations

Much more data need to be acquired and analyzed in order to assess the implications of the new findings on the repository suitability. Specifically, three questions need to be addressed:

1. What is the age and what was the recurrence period of water upwelling?
2. What was the volume of fluids involved at different stages of this activity?
3. What was the spatial structure of ancient hydrothermal system?

This may be accomplished through concerted effort of researchers, involving:

a. Detailed fluid inclusion studies in calcite and other minerals from Yucca Mountain. Such study may provide important information on the spatial structure of the ancient hydrothermal system;

b. Careful dating of calcite samples hosting fluid inclusions indicating elevated entrapment temperatures. Such study would constrain timing of ancient hydrothermal system; and

c. Detailed isotopic study of mineral phases may provide important information on the origin of fluids and pattern of fluid migration.

Fluid inclusion studies of samples from the Exploratory Study Facility, Yucca Mountain, Nevada

1. Introduction

This report summarizes results of research on fluid inclusions from the calcite samples gathered in the Exploratory Study Facility (ESF), Yucca Mountain, Nevada in June, 1998.

The purpose of this research was to get insight into the paleo hydrology of Yucca Mountain and specifically address one important question: was the currently unsaturated zone[1] of the mountain unsaturated during the formation of these calcites, or did the deposition occur in a saturated environment?

According to the presently accepted concept by the Yucca Mountain Project, the unsaturated zone at Yucca Mountain was formed 9-10 million years ago and since that time the water table has never risen more than 85-100 m above its present level (e.g., Marshall et al., 1993), which is 300 m below the repository horizon. This would mean that the water table never reached zone where the high-level nuclear waste repository is planned to be constructed. The concept of the Yucca Mountain repository relies on the unsaturated environment as a major barrier that will prevent migration of radionuclides from repository into the accessible environment.

According to current regulations, performance of the repository must be ensured for at least 10,000 years in the future (10CFR60). Moreover, peak doses are expected to occur after 100,000 years or more. Therefore, the viability of the site critically depends on whether or not the hypothesis on the long-term stability of the unsaturated zone is correct.

Calcite-opal veinlets found in drill cores from unsaturated zone on the early stages of Yucca Mountain characterization indicated that water with chemistry “alien” to silicate bedrock tuff moved through the mountain in geological past. In 1995-1997, when a 7.8 km long tunnel (Exploratory Study Facility or ESF) was excavated into Yucca Mountain, many more occurrences of secondary minerals become available for study.

The origin of these secondary minerals, or, strictly speaking, the origin of the waters that deposited them, is of great importance, because it may provide information regarding the long-term stability of the unsaturated zone.

From the onset of the studies on Yucca Mountain calcite and opal, they were presumed to be formed in unsaturated zone from gravitation-driven water films that percolated down along open interconnected fractures (Szabo and Kyser, 1985; 1990; Whelan and Stuckless, 1992; Vaniman and Whelan, 1994, etc.). Calcite and opal were extensively studied in terms of their stable (carbon, oxygen) and radiogenic (strontium, uranium, thorium, lead) isotope compositions, and isotopic ages (U-series disequilibrium, ^{14}C, and U/Pb methods).

The fluid inclusion method, probably the only method capable of unequivocal determination of mineral origin, has never been adequately applied in these studies. To date, the U.S. DOE has published only 7 temperatures measured by the fluid inclusion method (DOE, 1993). The DOE has published no data since the ESF was actually constructed.

These (elevated) temperatures were either attributed to calcite of old, 8-10 million years age, or simply dismissed (Roedder et al., 1994). Recent work by the DOE contractors on calcite samples removed from ESF have failed to discover fluid inclusions suitable for determination of paleo temperatures. The research concluded that calcite in the ESF was formed from low-temperature waters in un-

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[1] Unsaturated, or vadose, zone extends from water table upwards to land surface, as opposed to saturated, or phreatic, zone extending from water table downwards.

saturated environment (Roedder and Whelan, 1998).

In 1995 I had an opportunity to collect and study samples from the first 200 m of the ESF tunnel excavated by that time[2]. I was able to make 82 measurements of paleo temperatures from 6 samples. Obtained temperatures along with auxiliary data on calcite textures clearly indicated that calcite in question was formed in saturated environment from aqueous fluids with slightly elevated temperatures (Dublyansky and Reutsky, 1995; Dublyansky et al., 1996a,b; Dublyansky, 1998a).

My fluid inclusion data have been evaluated by the U.S. Nuclear Waste Technical Review Board (NWTRB). In the course of this evaluation, I spent one week at Virginia Technical Institute and State University, carrying out a verification study with the Board's consultant, Dr. Robert Bodnar.[3] I its follow-up letter to the Board, Dr. Bodnar wrote:

> *"The most important result of the work conducted in the Fluid Research Laboratory during the week of June 15-19, 1998, is that the high temperatures reported earlier by Dublyansky were confirmed to be real and not an artifact of sample preparation or data collection. There is little doubt that the calcite in sample SS#85-86 either formed at or was later exposed to aqueous fluids with temperatures of at least 72 °C. The important question, then, that must be answered is "What is the age of the calcite being studied?"*[4]

In June 1998 I collected more samples from the entire extent of the 8.7 km-long ESF tunnel, and in October 1998 I performed a study of the fluid inclusions in them. This report discusses the results of my study.

Altogether I obtained about 300 measurements of fluid inclusion temperatures. Along with other features of the studied samples, they represent compelling evidence indicating that during the deposition of calcite, a saturated environment existed within Yucca Mountain at the level of planned repository.

This issue has direct and significant bearing on the suitability of the site as a potential host for the high-level nuclear waste repository. The critical questions remaining to be resolved are:

- When did it happen?
- Did it happen as one-stage process, or water was upwelling and receding intermittently?
- If the upwelling occurred in pulses, what was the recurrence period of these pulses and what was the duration of each pulse?
- How much water was involved?
- What was the spatial distribution of this upwelling?
- What was the cause of the upwelling?

Only when all these questions have been satisfactorily answered can we address the ultimate question:

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[2] The study of the 12 samples collected in 1995 was carried out in the Institute of Mineralogy and Petrography in Novosibirsk, Russia. The results are briefly summarized in this report.

[3] Report on this study is attached as Appendix 1.

[4] Letter of July 8, 1998 from Robert J. Bodnar to Dr. Leon Reiter of the Nuclear Waste Technical Review Board. Available at the official NWTRB web site at http://www.nwtrb.gov.

- Could it happen in the future, on time scales comparable to those during which radiation doses could be significant?

Without theses answers, any assessment of the site viability or suitability will necessarily be incomplete.

2. Fluid inclusions and the information that may be obtained from them

Fluid inclusion method is an established research tool extensively used by economic and petroleum geologists for prospecting and exploration of ore deposits and oil fields. Principles of the method are described in the pioneering treatise by Edwin Roedder (1984). This book is an encyclopedia of fluid inclusion information from different geological settings – from magmatic and high-grade metamorphic to hydrothermal and sedimentary.

Sedimentary systems encompassing relatively low-temperature and low-pressure geological environments have become a subject of vigorous study in early 1980s, which was driven, at least in part, by urgent needs of oil companies exploring sedimentary terrains. An excellent book, summarizing methodologies and possible pitfalls of fluid inclusion studies in this area of relatively low-temperature inclusions was published by Goldstein and Reinolds (1994).

A short explanation of the basics of the fluid inclusion method is provided below.

Fluid inclusions are fluid-filled vacuoles sealed within minerals. When a crystal precipitates from a fluid (e.g., water) the surface of the crystal is never perfect. Such imperfections on the crystal surface become engulfed by the crystal as it grows. This process creates tiny, commonly tens of microns in size, vacuoles containing the fluid present at the moment of sealing. Such inclusions are called *primary* fluid inclusions.

After mineral precipitation is complete, the crystals may be deformed and micron-wide cracks may develop. These micro-cracks may be filled with fluid present during or after the deformation. Concurrent re-crystallization leads to so-called “healing” of fractures, during which process the liquid-filled fracture transforms into a group of fluid inclusions aligned along the fracture surface. Since these inclusions contain fluids present after mineral growth, they are called *secondary* inclusions.

A similar mechanism may be responsible for entrapment of inclusions before crystal growth is complete; they are termed *pseudo-secondary*.

Groups of secondary inclusions cut across growth zones of a crystal and terminate at the crystal surface; groups of pseudo-secondary inclusions terminate up against a growth zone boundary inside the crystal. Natural crystals may contain primary, pseudo-secondary and secondary inclusions.

If a vacuole has trapped a portion of an aqueous solution and was sealed at some elevated temperature it will experience significant change upon cooling to room temperature. Both the solid crystal containing the vacuole and liquid inside it will shrink upon cooling. The thermal expansion of liquids (e.g., water) is significantly larger than that of solids (e.g., calcite). Therefore, as crystals cool from the temperature of formation to ambient temperature, the pressure in the sealed inclusion decreases. At a certain point homogeneous one-phase inclusion splits onto two phases: a low-density vapor bubble appears in the liquid filling the vacuole – a process called *heterogenization*. (An inclusion trapped at the temperature close to ambient will not heterogenize. The inclusion must be sealed at temperatures of at least 35-40 ^{o}C to nucleate a bubble upon cooling.)

As long as the vacuole remains sealed (i.e., its volume does not change), this process may be reversed. Upon heating, the liquid in such two-phase inclusion will expand and the vapor bubble will disappear at a temperature which called *homogenization temperature* (T_h). This temperature provides the estimate of the entrapment (sealing) temperature for given inclusion.

The interpretation of the homogenization temperature depends on the type of inclusion for which it was measured. T_h's obtained for primary and pseudo-secondary inclusions reflect temperatures of fluids from which the crystal was precipitated. In case of secondary inclusions, information may be obtained on the temperatures of fluids present after the crystal growth ceased.

Important information which might be derived from fluid inclusions is the *salinity of ancient waters*. Pure water freezes and melts precisely at 0 ^{o}C; the addition of salts is known to depress the freezing temperature. Therefore, by cooling inclusions to low temperatures and then measuring the temperature of the disappearance of ice upon thawing (called *final melting temperature*, T_{fm}), it is possible to estimate the concentration of dissolved salts. This parameter is conventionally expressed in weight percent of sodium chloride (wt % NaCl) equivalent. NaCl is the most common salt found in fluid inclusions.

In some instances, the aqueous liquids from which a crystal grows may be not homogeneous, but contain separate gaseous phases, immiscible with the liquid. For example, boiling or effervescent fluids are examples of such heterogeneous mixtures that may be present during the time of entrapment.

Inclusions may trap such gases and form all-gas or gas-rich inclusions. Such inclusions may also provide quite valuable information. By crushing them and releasing gas into a non-reactive liquid (e.g., glycerol) it is possible to estimate the *pressure during the inclusion entrapment*. Gas bubbles may expand, maintain the same size, or contract upon crushing. This will indicate pressure higher than, equal to, and lower than ambient atmospheric pressure, respectively.

The composition of gases trapped in inclusions may be studied by means of Raman spectrometry. An inclusion is irradiated with a laser beam whose energy changes in response to its interaction with the polyatomic molecules of the fluids inside inclusion – an effect called Raman scattering. This method allows the identification of some components of fluid inclusions (CO_2, CH_4, N_2, NH_3, CO, H_2S, C_2H_6, etc.). These are called Raman-active components. Details on the Raman microspectrometry may be found in the paper by Burke (1994).

Summary. Fluid inclusions may provide information on: (a) the temperature of fluids during and after the crystallization of minerals; (b) the chemistry of fluids; and (c) the pressure of fluids from which minerals grow. This information is necessary to determine the origin of minerals and the environment in which they were formed.

3. Technical details on sampling, sample preparation, equipment and techniques used

3.1. Sampling

Samples for this study were collected on June 8 and 9, 1998 from the Experimental Study Facility (ESF), which is a horseshoe-shaped 7.8 km-long tunnel excavated in the tuffs (Fig. 1). In compliance with the Integrated Sampling program adopted by the Yucca Mountain Characterization Project, the locations of each sample were marked on the tunnel walls by plastic plates, and each sample was assigned an individual number and bar code. Besides the 1995 sample set, I will also discuss the data from our first set of samples (set-1995) that was collected in March 1995 when only the first 200 m of the tunnel had been excavated. This first set of samples was collected from stratigraphically higher welded tuff Tiva Canyon, located above the design repository level and separated from the potential repository horizon – welded tuff Topopah Spring – by a layer of a highly-porous non-welded bedded unit (see Appendix 2). One sample from the 1998 set (number 2206) is also from Tiva Canyon tuff. The remainder of the 1998 set was gathered from the Topopah Spring tuff at the potential repository level.

3.2. Sample preparation

Fluid inclusions are typically quite small (tens of microns), therefore all studies and observations need to be done under the microscope. In order to study fluid inclusions, the doubly polished wafers 0.2-0.4 mm thick need to be prepared from a mineral.

Calcite is soft and cleavable mineral (which means its crystals tend to break along some directions much easier than along others). This property of calcite creates a potential hazard of stretching or damaging inclusions due to stress or vibration (e.g., when cutting sample on a diamond saw) or heating (e.g., during polishing or mounting the sample with some epoxies). Stretched or leaked inclusions yield homogenization temperatures which do not reflect natural processes and are therefore meaningless.

In preparing samples from Yucca Mountain, all possible precautions have been taken to avoid any mechanical or thermal damage to the inclusions during sample preparation. Working with the first set of samples we used cleavage chips instead of polished plates. The samples from the second set have been cut using a low-speed *Buehler Isomet* saw set at ~120 rpm with cold water as a coolant. The freshly cut surfaces were manually ground and polished using grinding powder (600 grit and 5 micron) and *Buehler Metadi* water-based diamond fluid (1 micron). The polished surfaces were mounted on glass slides using cyanoacrylic glue. The operations were repeated to produce doubly polished sections.

The procedures adopted ensured that during sample preparation the samples were never heated to a temperature in excess of 35 ^{o}C. This may be shown through the following observation. Relatively low-temperature inclusions (T_h of 35 to ~50 ^{o}C) being homogenized and then cooled back to room temperature virtually never heterogenize again – i.e., they do not re-nucleate the bubble after the cooling. Instead, they remain as a one-phase liquid. The reason for this behavior will be discussed later (Section 6.6). The fact that in my studies I observed two-phase inclusions with homogenization temperatures as low as 35 ^{o}C indicates that the samples were not heated above this temperature during preparation.

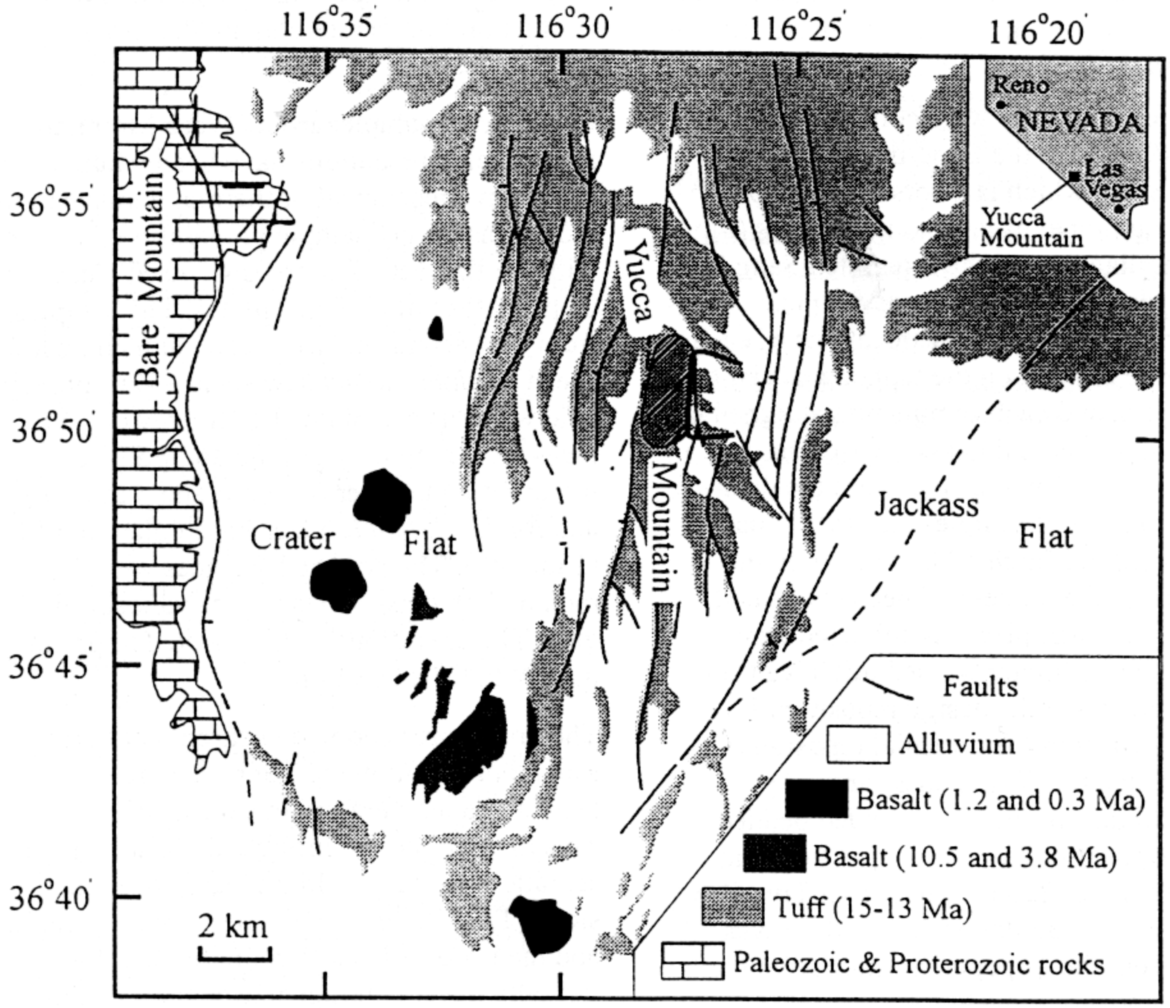


Fig. 1. Schematic geologic map of Yucca Mountain area. Patterned ellipsoid shows the exploratory block. Bold C-shaped line represents projection of the Experimental Study Facility tunnel

3.3. Analytical procedures and equipment used

The prepared doubly polished sections were examined under an *Olympus BX-60* microscope at different magnifications. The inclusions were documented with a *Polaroid* digital camera; sometimes, a *Sony* video printer was used for the purpose of rapid mapping.

After preliminary observations, sections were taken off glass slides (the cyanoacrylic glue having been dissolved in acetone). Typically, after the ungluing, the doubly polished sections broke onto numerous fragments, each 1 to 10 square mm in size. These fragments were examined under the microscope one by one to find groups of inclusions. Generally, I examined 20-50 such fragments from each sample. Typically only two to five fragments among these were found to contain two-phase inclusions which are needed for carrying out thermometric study.

Thermometric studies were conducted on a *Linkam THMSG* stage. Part of the homogenization temperature measurements on the 1995 sample set was made on a stage manufactured at the Institute of Mineralogy and Petrography in Novosibirsk, Russia.

Homogenization. As discussed above, researchers working with soft cleavable minerals should always keep in mind the possibility that inclusions may have been stretched by some natural process or during sample preparation. Such “disturbed” inclusions may produce temperatures which are meaningless in terms of genetic interpretations. Problems associated with sample preparation can be minimized by careful sample handling; the possibility of inclusion stretching by some natural process (e.g., mechanical stress, or thermal impact) needs to be evaluated. The safest way to avoid this problem is to measure homogenization temperatures not on single inclusions, but on *fluid inclusion assemblages* (FIA’s) – finely discriminated and pertographically associated groups of inclusions (Goldstein and Reinolds, 1994). Variability of data within an FIA will alert the researcher of the possible stretching, re-equilibration, necking or immiscibility – factors which make the interpretation of measured temperatures much more complicated and sometimes problematic. By contrast, consistency of data obtained from many inclusions in an FIA will indicate that the measured temperatures reflect the true temperatures during inclusion entrapment.

The question: What is a “consistent” result? has no straightforward answer. Goldstein and Reinolds (1994) recommend that FIAs with 90 % of inclusions homogenizing within a 10-15 ^{o}C interval should be considered as showing a consistent result (p. 151).

Taking into account this guideline, I measured homogenization temperatures on petrographically defined groups of fluid inclusions, FIAs. Some of my samples contained groups of the vapor-liquid inclusions with similar vapor-to-liquid ratios. In association with a few such groups I observed inclusions with elevated contents of gas in them. This may reflect hetrogeneous entrapment and/or necking-down. Since measurements on such inclusions may yield erroneous temperature estimates, such groups were not used for thermometric studies.

A cycling technique was applied to measure homogenization temperatures. Temperature in the stage was increased in increments of 1 ^{o}C. The sample was held at each temperature for 1 or 2 minutes for thermal equilibration. Each inclusion in the analyzed group was examined for the presence of a bubble, after which the next heating step was performed. If the presence or absence of a bubble in an inclusion at a certain temperature was not apparent (typically, for small inclusions less than 5 micron in size) the sample was cooled down to 20 ^{o}C (homogenized inclusions would not heterogenize after such cooling). This procedure made it possible to obtain measurements on assemblages of up to 20-25 inclusions, with an accuracy of 1 °C.

Freezing. The inclusions in Yucca Mountain calcites have proved to be difficult subjects for freezing studies due to their small sizes and the low salinity of entrapped fluids. The results of freezing experiments can only be interpreted if all three phases, solid, liquid and vapor, are present in an inclusion during the final melting. In comparatively low-temperature minerals such as the Yucca Mountain calcite, inclusions that are homogenized by heating virtually never heterogenize upon cooling to room temperature. Therefore, to carry out freezing experiments I had to artificially stretch the inclusions. This was done by heating them to 250 °C (the pressure in an inclusion increases very rapidly with increasing temperature) and/or cooling to the temperature of liquid nitrogen (inclusion may be stretched by expanding ice when water freezes).

An interesting outcome of the “overheating” experiments was the finding that most of inclusions did not stretch upon heating to 200-250 °C, i.e., they did not nucleate bubbles. Rather, they remained as one-phase liquids. (I held some of my samples for 10-25 minutes at these temperatures.) This applied equally to inclusions that initially were two-phase (T_h=35-70 °C) and those that originally were all-liquid. This result seems to be in conflict with the H_2O phase diagram, which indicates that the pressure in such inclusions should increase very rapidly and be very high (~4.5 kbars) at 250 °C. It is also in conflict with common perception of the fluid inclusions in calcite as being susceptible to stretching upon slightest overheating.

A possible explanation of this behavior is that calcite may accommodate very high internal pressures in inclusions through elastic deformations. Therefore, the time of overheating may be more important than the temperature. At the present stage, this effect cannot be quantified.

Many inclusions that I studied revealed the final melting temperatures of >0 °C which indicates possible metastable behavior in the system (pure water ice should melt at 0 °C and ice of saline water melts at <0 °C). To ensure that this was not related to a too-fast heating, I routinely held such inclusions at 0 (+0.1/-0.1) °C for 5-10 min., which typically did not led to melting.

Other methods. Gas chromatographic analyses (discussed in Appendix 1) were carried out at the Institute of Mineralogy and Petrography, Russian Academy of Sciences, Novosibirsk, Russia on the chromatograph *LHM-8* with two different types of gas detectors (flame-ionisation detector and catharometer). Gas was extracted from samples by heating them to 250-500 °C. Raman spectrometric analyses were performed at Virginia Tech, Blacksburg, VA using a *Dilor XY* Raman microprobe with *Princeton Instruments* CCD detector and *Lexial* Argon ion 5 watt laser. Analyses of carbon and oxygen isotopes in calcite were carried out at McMaster University, Hamilton, Ontario, Canada, using a *VG SIRA* mass spectrometer with an *Autocarb* analyser and U-series disequilibrium analyses were performed using VG354 mass spectrometer.

4. Occurrences of calcite in the ESF

Calcite in the ESF occurs as various epigenetic formations. In places it forms “common” veinlets (i.e., veinlets in which the opening of a fissure is entirely filled with calcite). An example of such veinlet is given in Fig. 2.

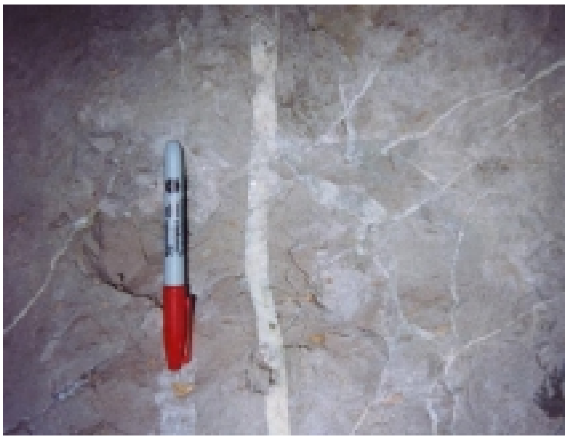


Fig. 2. Station 67+81.0. Dune Wash fault zone. Sample 2210. Calcite veinlets in Topopah Spring welded tuff.

Such veinlets, however, are rare.

Another rare, but fascinating occurrence is calcite coating floors of small tectonic cavities, like one shown in Fig. 3. Thin and apparently stress-related fissures propagate in various directions from such cavities; some of such fissures are filled with milky-white calcite.

Fig. 3. Station 28+27, Alcove 5. Tectonic cavity in Topopah Spring tuff with crystalline calcite deposited on its floor.

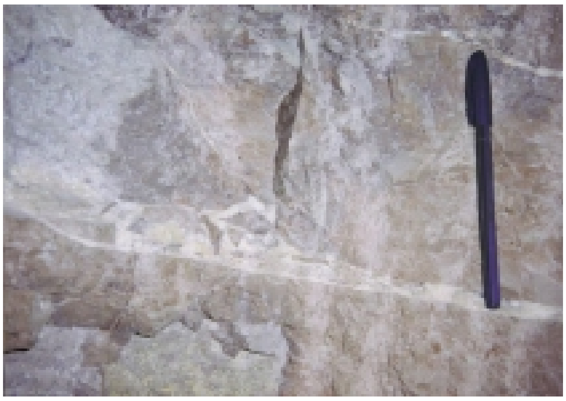


Fig. 4. Station 37+37.0. Alcove 6, station 0+55.1. Northern Ghost Dance Fault zone. Sample 2222. Low-angle veinlet and micro-breccia.

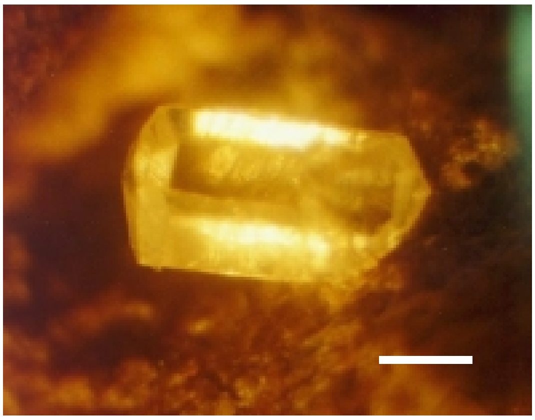
Calcite also occurs along low- to steep-angle fractures forming complex bodies, which consist of “common” veinlets build up of massive milky-white calcite, calcite-cemented breccias, and crusts featuring free-growth crystals in fissure’s opening. The shape of such bodies is often irregular, as it is shown in Fig. 4.

Calcite forms crusts, 1 to 3 cm thick on the floors of lithophisal cavities (Fig. 5). I did not observe calcite in thin fractures, intersecting these cavities.

Fig. 5. Station 38.37. Sample 2220. Lithophisa in Topopah Spring tuff featuring calcite lining on the floor.

Calcite also coats fracture walls or, in fractured zones, surfaces of broken fragments of bedrock tuffs (Fig. 6-A). On some occasions, it forms small individual euhedral crystals (Fig. 6-B).

A.



B.

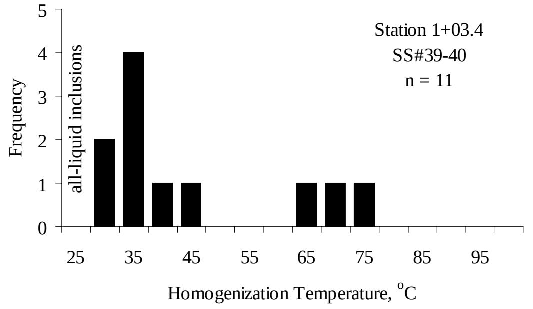
Fig. 6. Station 52.13. Sample 2215. A – Translucent blocky calcite, coating broken fragments of tuff (scale bar is 2 cm); B – Close up: individual euhedral calcite crystal crystallized on tuff surface (arrow on A; scale bar is 5 mm).

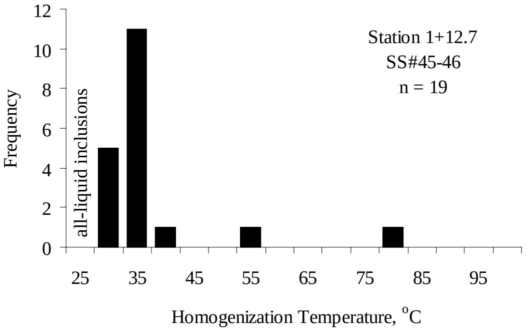
5. Fluid inclusion results

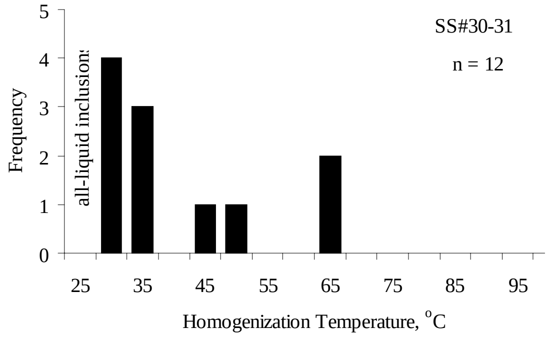
5.1. Samples from the first 200 m of the ESF (set-1995, results of previous studies)

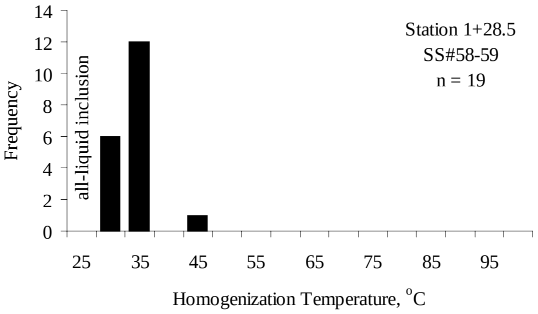
The samples, collected on March 1, 1995 and studied in Novosibirsk in 1995 and partly in Blacksburg, VA in June 1998 (see Appendix 1) are labeled according to the numbers of the steel sets between which they were taken. All samples are from Tiva Canyon tuff (Tpc unit).

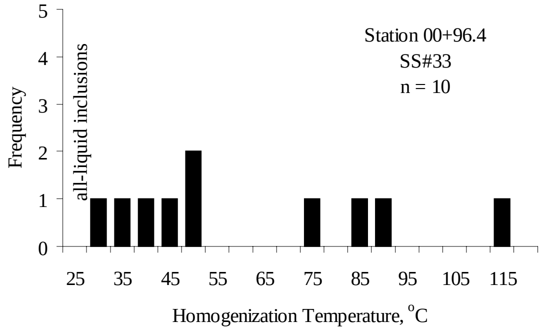
Thermometric data are given below:

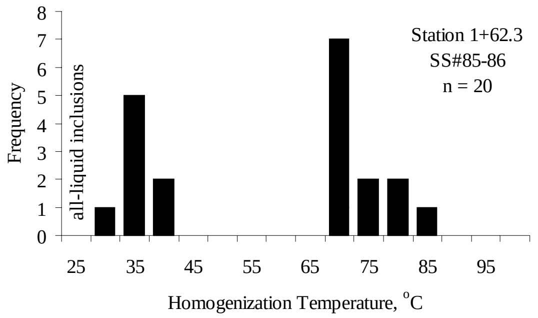












5.2. Samples from the ESF (set-1998)

Samples collected in the ESF in 1998 were assigned numbers from SPC00532201 through SPC00532232. Below we use the last four digits to identify the samples. The numbers of the stations reflect their distance from the north portal in meters, except for the alcoves, where the distance is indicated from the main tunnel.

Quantitative fluid inclusion results were obtained on seven samples. In three more samples, two-phase gas-liquid inclusions suitable for thermometry have not been found.

A brief summary on the fluid inclusion distribution in studied samples is given in table below. The table also indicates the presence or absence of fluorite in the samples.

Sample		***Inclusions***		***Fluorite***
	All-gas	*Gas-liquid(*)*	All-liquid	
2206	+	+	+	+
2215	-	-	+	+
2217	+	+	+	-
2218	+	-	+	-
2220	+	+	+	-
2221	-	+	+	-
2222	+	+	+	-
2224	+	+	+	+
2225	-	-	+	-
2226	+	+	+	-

* Only gas-liquid inclusions suitable for thermometry are indicated

Detailed results obtained on individual samples are given below.

Sample 2206

Station: 76+00.6

Field description. Calcite crust on the foot wall of the opening, up to 2 cm thick. Bedrock tuff appears to be altered (calcitized). In one location, the crust has pink color (possible presence of disseminated fluorite).

Bedrock: Tiva Canyon Tuff (Tpc unit).

Depth from land surface: ~70 m.

Minerals and textures. On a visual basis, there occur at least two generations of *calcite*. (1) ~1 mm-thick layer of slightly brownish calcite on the contact with the bedrock tuff. White empty globules 0.1-0.2 mm in size (opal?) often occur on its surface. (2) ~1 cm-thick layer of translucent large-crystalline calcite with free-growth crystals at its top. Under the microscope, up to four generations of calcite, separated by hiatuses (caused by dissolution) or layers of opal can be distinguished. The outer layer contains crystals of free growth with well-developed pinacoidal face and intergrowth.

Colorless and violet globules of *fluorite* are associated with the latest stages of calcite growth. They are often overgrown by calcite and make the latter look violet. Part of the globular aggregates reside on the calcite surface. Sometimes fluorite forms individual crystals on the calcite surface up to ~0.2 mm in size. Crystals are irregularly colored from light- to dark-violet. Crystals are isometric (simple forms100, 111, 110) but often distorted.

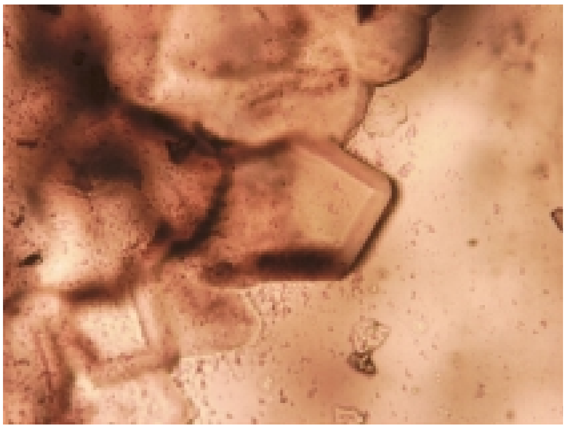


Fig. 7. Sample 2206. Quartz and calcite. Scale bar is 1 mm.

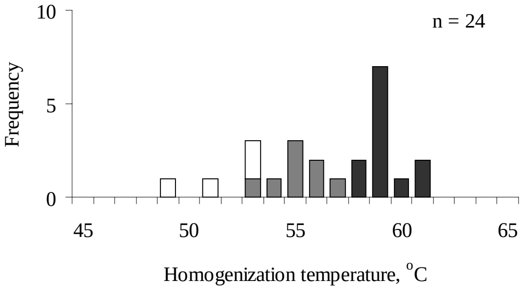


Fig. 8. Sample. 2206. Black – group of inclusions along growth zone; gray – inclusions along low-angle plane; white – inclusions forming a 3-D group.

Opal has a botrioidal appearance. *Quartz* occurs as globules 1-2 mm in diameter, composed of radially aligned micro crystals. The tips of crystals in globules are <0.1 mm in size. Some individual quartz crystals have size of up to 2 mm (Fig. 7). They have a perfect shape and a diamond luster; they are translucent. Some of them are overgrown by a thin layer of opal. Crystals of fluorite were also observed on the surface of quartz.

Fragments of tuff 2 to 15 mm in size occur in the middle of the crust. They are cemented by opal and calcite. Translucent euhedral crystals (*zeolite*?) occur on the surface of these fragments.

Fluid inclusions. Calcite contain numerous all-gas inclusions. All-liquid aqueous inclusions are abundant. Two-phase gas-liquid inclusions are rare. They occur as 3-D groups, groups along low-angle planes and along growth zones.

The results of thermometric studies are shown in Fig. 8. Homogenization temperatures for each group of inclusions cluster within narrow, 4-5 °C interval. The result, therefore is quite consistent and measured temperatures may be considered true temperatures of paleo fluids.

Sample 2215

Station: 52+13

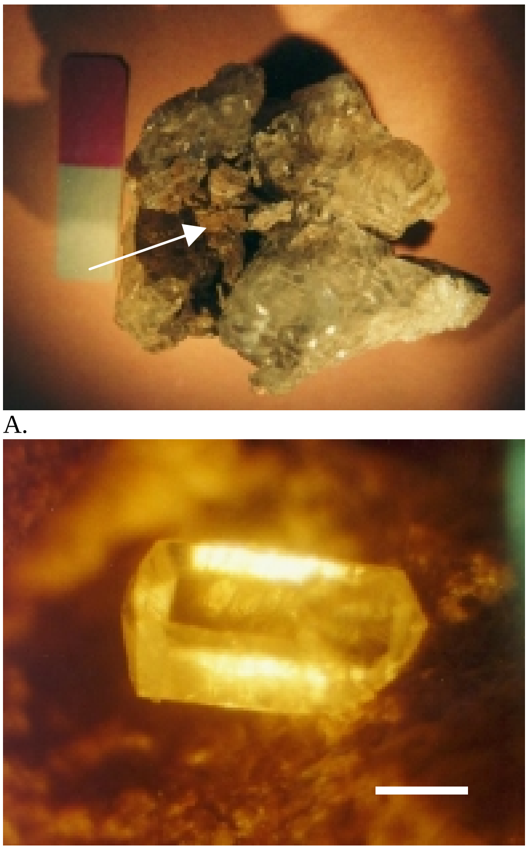
Bedrock: Middle Nonlythophisal crystal poor Topopah Spring Tuff (Tptpmn unit)

Depth from land surface: ~ 260 m.

Field description. Steep-angle fracture lined with thin, ~0.5 mm, crust of dark powdery to violet micro crystalline fluorite (subsample 2215A). In places this layer of fluorite is covered by a crust of translucent blocky calcite crystals (subsample 2215B).

Minerals and textures, subsample 2215B. *Calcite* is water-clear, blocky. It forms 0.5 to 3 mm thick crust on the fracture wall, as well as coats broken fragments of tuffs (Fig. 9-A). Sometimes it forms individual crystals (Fig. 8-B). Tuff on the contact with calcite and fluorite appears to be unaltered. Calcite contains globules of slightly brownish *fluorite* up to 1 mm in diameter, as well as numerous angular solid inclusions (they have not been identified).

Fluid inclusions. Calcite contains all-liquid inclusions. Two-phase gas-liquid inclusions suitable for thermometry have not been found.



A.

B.

Fig. 9. A - calcite coating fragments of tuff (scale bar is 2 cm); B – close up: individual calcite crystal on the surface of tuff fragment (arrow in A). Scale bar is 0.5 mm.

Sample 2217

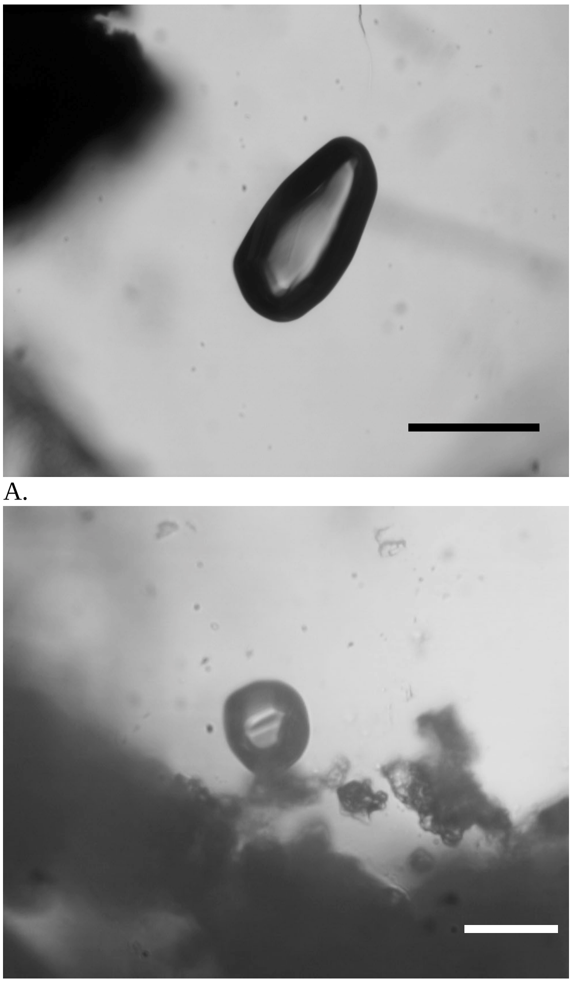
Station: 38+64.0

Bedrock: Middle Nonlithophysal crystal-poor Topopah Spring Tuff (Tptpmn unit).

Depth from land surface: ~260 m.

Field description. Local opening in a vertical fracture (otherwise closed) 5-10 cm wide. Calcite encrusts one wall of the opening but does not occur in the fracture.

Textures. Water-clear calcite forms crystals 1-4 mm in size. The shape of crystals is distorted: their dimensions perpendicular to the bedrock are significantly smaller than in other directions. Calcite is crystallized on the agglomerations of the sand-sized particles and entrap these agglomerations. Outer layers of calcite are typically translucent, and this mustard-colored material is readily visible through them. In some instances, sandy material forms elongated layers 0.1-0.3 mm thick. Calcite sometimes grows on both sides of these layers.


A.

B.

Fig. 10. All-gas inclusions. A – scale bar 100 μ; B – scale bar 25 μ.

Fluid inclusions. Calcite contains all-gas (Fig. 10), all-liquid, and gas-liquid inclusions.

All-gas inclusions occur randomly and typically are restricted to the portions of calcite closest to the substratum. On one occasion, however, I observed gas inclusions clearly restricted to calcite growth zones (Fig. 11). This indicates the primary character of these inclusions.

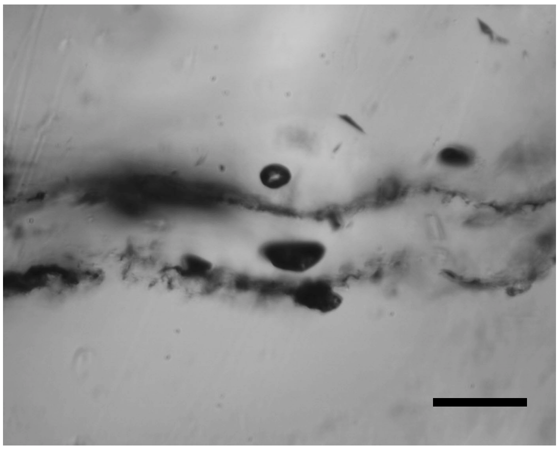


Fig. 11. All-gas inclusions aligned along the growth zones (two of them are not in focus). Such alignment indicate the primary character of inclusions. Scale bar is 100 μ.

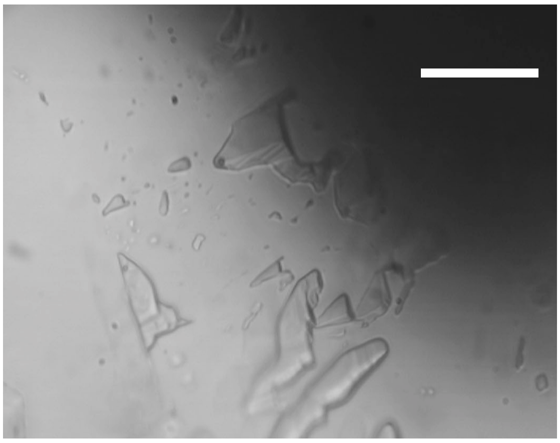


Fig. 12. Group of vapor-liquid inclusions. Scale bar is 20 µ.

The two-phase gas-liquid inclusions are rare. They are restricted to zones of calcite closest to the tuffaceous substratum. Blocky sparry calcite of outer parts of the crust is devoid of the two-phase inclusions and contains only all-liquid inclusions. Two-phase inclusions form groups along the low-angle planes (Fig. 12) or along steep-angle curvilinear surfaces (probably, healed fractures). The results of thermometric studies are given in Fig. 13. As is apparent from the figure, homogenization temperatures exhibit significant scatter, which indicates possible “disturbed” character of inclusions in this sample (stretching or leakage). The highest temperatures (>50 °C) should probably be disregarded.

Freezing experiments.

Freezing experiments were carried out on four inclusions from two groups. Two inclusions from the group shown in Fig. 12 yielded final melting temperature, T_{fm}’s of –0.9 and –0.95 °C, which correspond to the salinity of 1.57 and 1.65 wt. %, NaCl-equiv. Two inclusions from another group yielded T_{fm} of –0.3 and –0.4 °C (0.53 and 0.71 wt. %, NaCl-equiv.).

I attempted to perform a freezing experiment on one all-gas inclusion (shown in Fig. 14). Some tiny light-colored phases appeared upon rapid cooling to a temperature of ~-100 °C. On heating, these phases re-grouped to form one rounded phase. The phase disappeared in this inclusion at temperatures from –30 to –10 °C. The behavior of this phase did not show any dependence on the temperature regime: in a number of experiments it disappeared when the temperature in the stage was increasing and when it was decreasing.

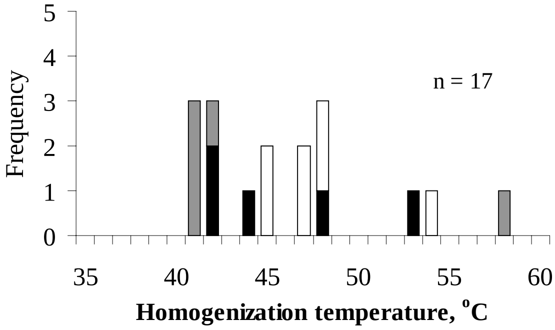


Fig. 13. Sample 2217. Black and gray – inclusions along low-angle plane (see Fig. 12); white – inclusions along steep-angle bent zone (healed fracture). Measurements show significant scatter, indicating possible “disturbed” character of fluid inclusions in this sample. The highest temperatures (>50 °C) should probably be neglected.

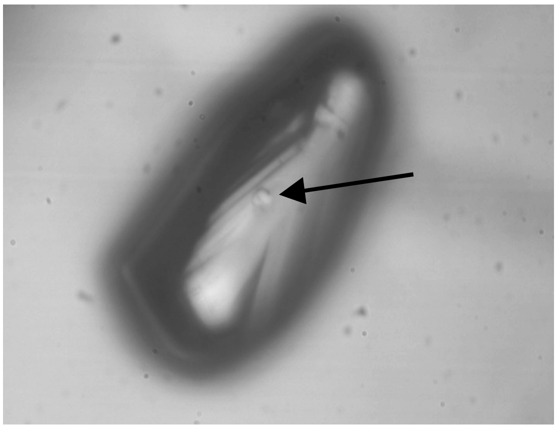


Fig. 14. Sample 2217. All-gas inclusion (see Fig. 10-A) containing unidentified phase (arrow) at –35 °C.

Sample 2218

Station: 45+26

Bedrock: Middle Nonlythophisal crystal poor Topopah Spring Tuff (Tptpmn unit)

Depth from land surface: ~ 230 m.

Field description. Lithophisa ~60 cm wide and 40 cm high. No other cavities around. The bottom of the cavity is lined with calcite. The walls of the cavity are covered by a ~1 mm thick layer of white α-quartz and tridimite crystals (identified by XRD).

Minerals and textures. Tuff on the contact appears to be altered to a depth of 3-8 mm. Two individual crystals of ***garnet*** (~3 mm in size; identified by XRD) were found in this altered zone and one in calcite. Calcite often appears to be crystallized as porous mass, composed of isometric crystals ~ 1mm in size. In other places calcite is massive. Fragments of tuff (3 to 10 mm in size) incorporated in the calcite look altered, almost decomposed.

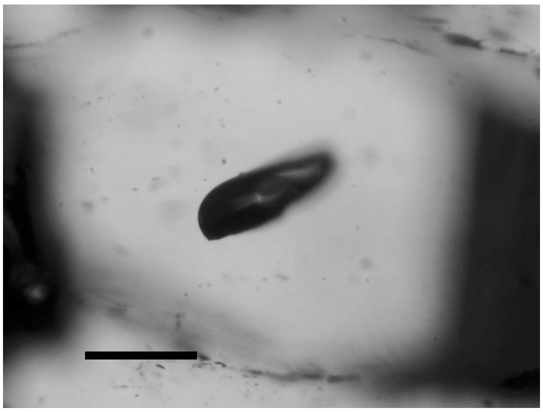


Fig. 15. All-gas inclusion in the middle of an individual grain of calcite. Scale bar is 50 µ.

Fluid inclusions. Calcite contains all-liquid inclusions, as well as all-gas inclusions (Fig. 15). Two-phase gas liquid inclusions suitable for thermometric studies were not found.

Sample 2220

Station: 38+37.0

Bedrock: Middle Nonlithophysal crystal-poor Topopah Spring Tuff (Tptpmn unit).

Depth from land surface: ~260 m.

Field description. Cavity in the bedrock tuff, 60 cm wide and 35 cm high. Thick, up to 2 cm crust of calcite coats cavity floor, as well as the lower part of hanging walls. There are individual euhedral crystals of calcite up to 1.0-1.5 cm large. No apparent feeder-fissure.

Minerals and textures. A 1 mm-thick layer of white *quartz* (alteration?) occurs on the contact with the bedrock tuff. After that a 1.5 cm layer of milky-white *calcite* is deposited. It reveals traces of competitive growth, induction surfaces. In places, this zone is strongly corroded; a new-formed water-clear and well shaped crystals of calcite < 1mm in size are present in the corrosion cavities. This calcite also occurs as thin, ~1 mm, veinlets in bedrock tuff. The described "Calcite-1" is cut by nearly horizontal and rough surface of dissolution, on which "Calcite-2" is deposited. It is also milky-white, but somewhat more translucent. Both calcites form flattened crystals of free growth; crystals of the "Calcite-1" are "blade-shaped", whereas crystals of the "Calcite-2" are blocky. The orientation of crystals is also different.

Opal is often present as primary solid inclusions, which have a half-spherical shape with the flat side aligned along the growth zones. Such inclusions often occur at the latest stages of calcite growth, close to the surface of blocky sparry crystals (Fig. 16).

Fluid inclusions. *All-gas inclusions* are abundant in this sample. In contrast to most other samples studied from the ESF, where all-gas inclusions are mostly restricted to the earliest generations of calcite, in this sample such inclusions occur throughout the calcite crust.

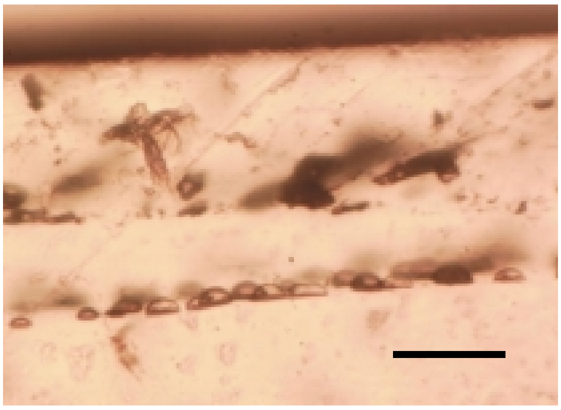
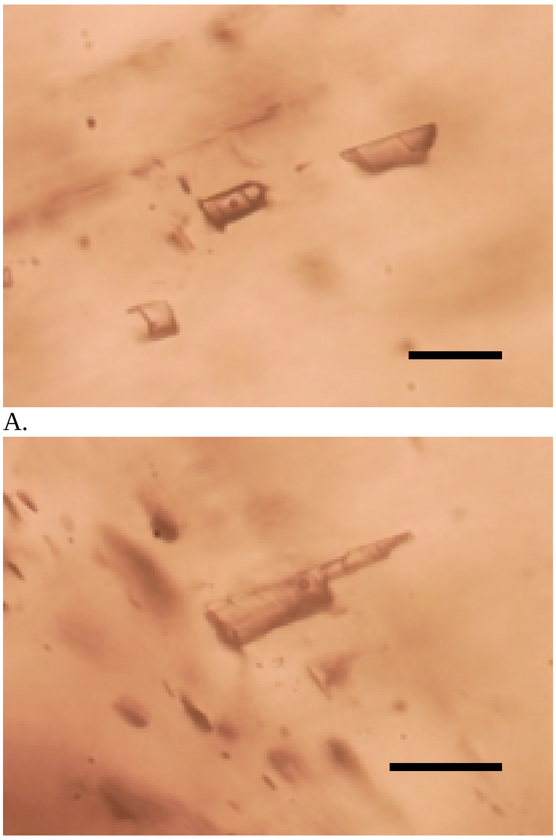


Fig. 16. Primary inclusions of opal in calcite near the crystal surface (top of the picture). Scale bar is 100 μ.



A.

B.

Fig. 17. Two-phase inclusions from a group along growth zone. Homogenization temperatures are 37 (A) and 38 °C (B). Scale bars correspond to 10 μ in both images.

All-liquid inclusions are also abundant. Gas-liquid inclusions suitable for thermometry are rare. They occur along growth zones (Fig. 17), low-angle planes and form 3-D groups.

The results of thermometric studies are shown in Fig. 18. Inclusions in individual groups homogenize within narrow temperature intervals (3 to 8 °C). This indicates that obtained temperatures reflect true temperatures of paleo fluids.

Freezing experiments performed on several inclusions with T_h = 36-40 °C yielded no numeric results. Two inclusions from a growth zone showed T_{fm} = +0.3 and +0.4 °C. Ice in two inclusions from another group melted at exactly 0 °C (ice crystals grew and diminished very fast as the temperature in the stage oscillated between –0.1 to +0.1 °C). The data suggest that aqueous fluid in inclusions is very diluted (essentially, it is fresh water).

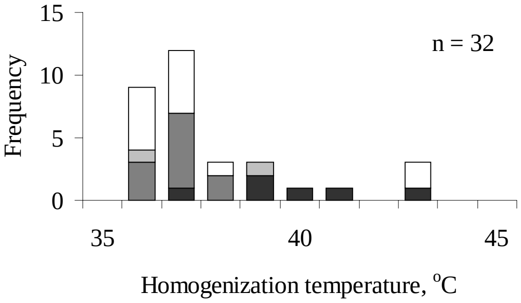


Fig. 18. Sample 2220. Black – group of inclusions along growth zone; dark gray – inclusions along low-angle plane; light-gray – inclusions forming a 3-D group; white – individual inclusions.

Sample 2221

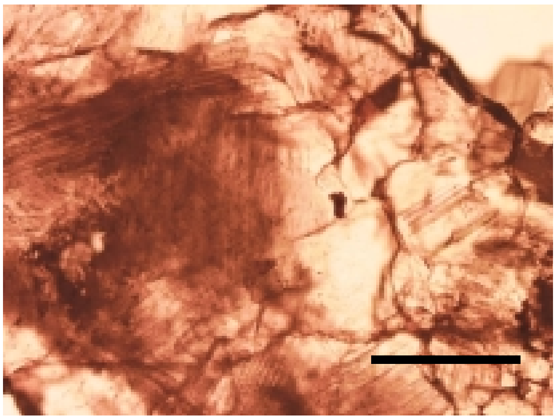
Station: 37+37.0 Alcove 6 - Northern Ghost Dance Fault Alcove, S.D.4

Station within alcove: 0+12.6

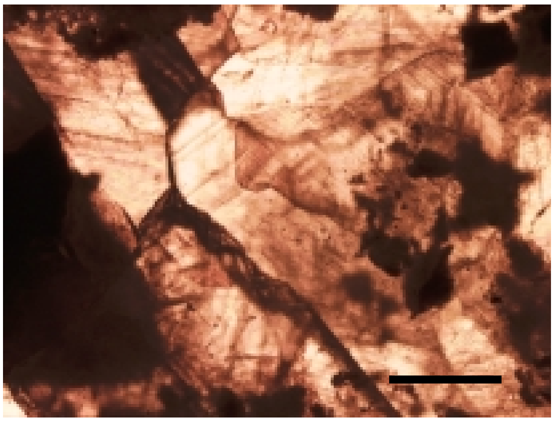
Bedrock: Middle Nonlithophysal crystal-poor Topopah Spring Tuff (Tptpmn unit).

Depth from land surface: ~230 m.

Field description. Vertical opening associated with calcite-cemented breccia-vein. Calcite encrusts both walls of the opening. Sometimes it forms near horizontal plates with crystals on both sides. These may be fragments of wall linings fallen on the cavity floor and overgrown by later-stage calcite.



A.



B.

Fig. 19. “Stressed” calcite in the basement of a crust. Outer parts of the sample are not damaged. Scale bars correspond to 5 mm in both images.

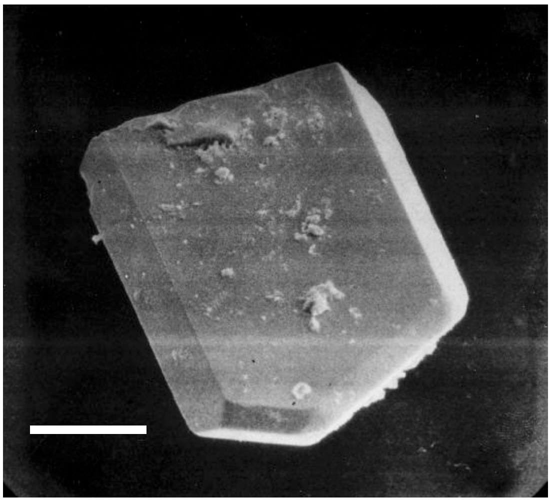


Fig. 20. Scanning Electron Microscope (SEM) microphotograph of a mineral (hematite?) from tuff alteration zone, overgrown by calcite. Scale bar is 50 µ.

Textures. *Calcite* occurring as breccia cement is milky-white semi-translucent. It cements small angular fragments of the tuff. The latter appears to be altered. Calcite in crusts is water-clear translucent. It forms nearly isometric blocky crystals growing on tuff or clay substratum.

A white powdery layer occurs on the contact between one crust and the bedrock tuff. This layer consists of *tridimite* (supposedly, early vapor-phase alteration of tuff). The layer also contain tabular crystals with metallic luster (*hematite*?) (Fig. 20). Similar crystals analyzed from another sample (2226) appeared to be a mixture of oxides of Fe, Mn and Ti.

Calcite in the basement of the crust often appears to be mechanically stressed and exhibits twinning (Fig. 19). The latest euhedral crystals do not bear indications of mechanical damage.

Calcite contains solid inclusions of an unidentified translucent cubic mineral (possibly *fluorite*).

Fluid inclusions. All-gas inclusions have not been found in this sample. All-liquid inclusions are abundant. Gas-liquid inclusions are rare. They occur as groups along healed fractures. Inclusions in such groups are typically small (1-5 μ in size).

Results of thermometric studies are shown in Fig. 21. The scatter in the data is significant. It should be noted, that inclusions associated with healed fractures yield larger scatter (up to 13 °C within a group), than isometric, possibly primary inclusions forming a 3 D group (8 °C). At this stage, the high-temperature part of the data (>40 °C) should probably be disregarded.

Freezing experiments were carried out on several large inclusions, bubbles in which were generated by stretching. They yielded T_{fm} of +0.2 to +0.3 °C. This indicates metastable ice melting and low-salinity fluids.

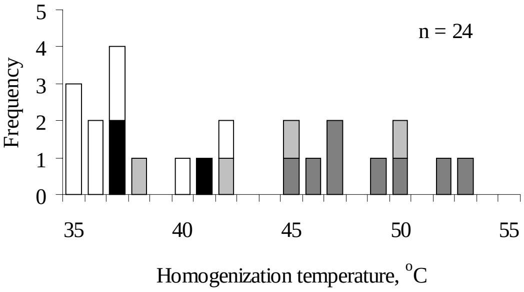


Fig. 21. Sample 2221. Black and gray – inclusions along healed fractures; white – inclusions in 3-D group (possibly primary).

Sample 2222

Station: 37+37.0 Alcove 6 - Northern Ghost Dance Fault Alcove.

Station within alcove: 0+55.1

Bedrock: Middle Nonlithophysal crystal-poor Topopah Spring Tuff (Tptpmn unit).

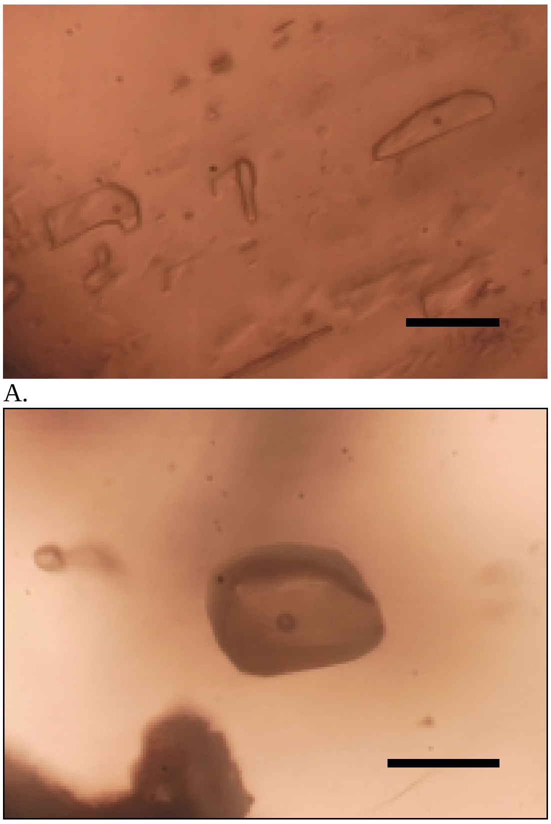
Depth from land surface: ~ 230 m.

Field description. Low-angle veinlet partly made up of crystalline calcite, partly cementing breccia fragments of tuff (Fig. 22). At both ends, when it enters shattered tuffs, veinlet splits into several discontinuous fragments.

Fig. 22. Low-angle veinlet and breccia (sample 2222)

Textures. Calcite is milky-white, massive. It completely fills the fracture opening. In places this massive calcite contains cavities (dissolution?) with their inner surfaces composed of the euhedral heads of tabular calcite crystals. Near the contact (2-4 mm), calcite is small-crystalline, granular.

Fluid inclusions. In the vicinity of the tuff fragments, calcite contains numerous and large (visible under binocular microscope) all-gas inclusions. All-liquid inclusions are also abundant.



A.

B.

Fig. 23. Gas-liquid inclusions: A - group of fluid inclusions along a low-angle plane (T_h = 36-37 ^oC); B – individual inclusion (T_h = 35 ^oC). Scale bars correspond to 10 μ in both images.

Gas-liquid inclusions are rare. They occur in groups (also containing all-liquid inclusions; Fig. 23) aligned along low- to steep-angle planes.

Thermometic study. The results of thermometric study are shown in Fig. 24. All studied inclusions (35) homogenized within a very narrow interval of 5 ^oC. The results are quite consistent. The measured temperatures may be considered true temperatures of ancient fluids.

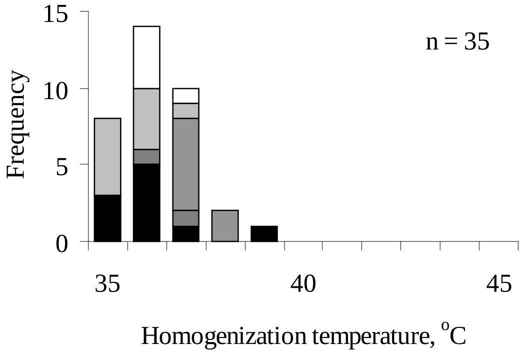


Fig. 24. Sample 2222. Five groups of inclusions (2 to 10 inclusions each).

Freezing experiments. One large artificially stretched inclusion was subjected to freezing (Fig. 25). The ice in inclusion melted at +0.35 °C suggesting low salinity of trapped fluids.

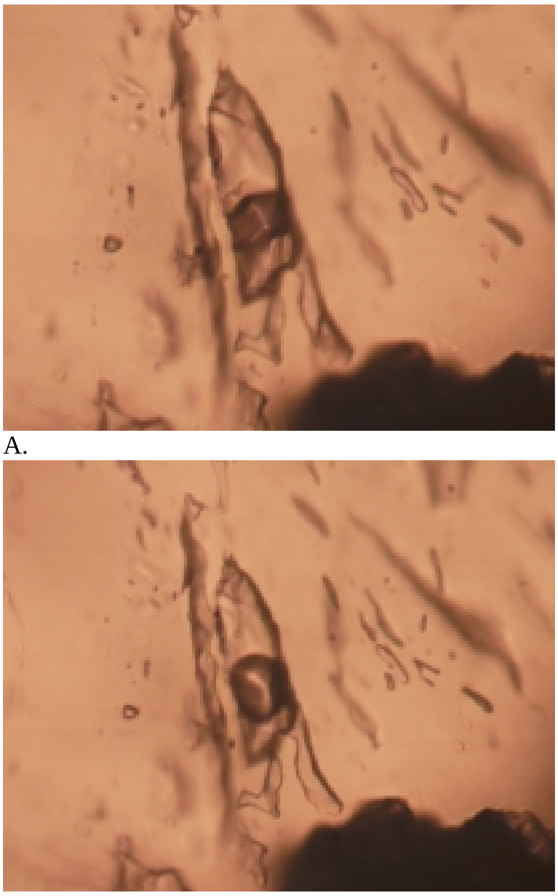


Fig. 25. Freezing experiment on artificially stretched inclusion. A – T = -20 °C, inclusion is frozen; B – T>+0.35 °C.

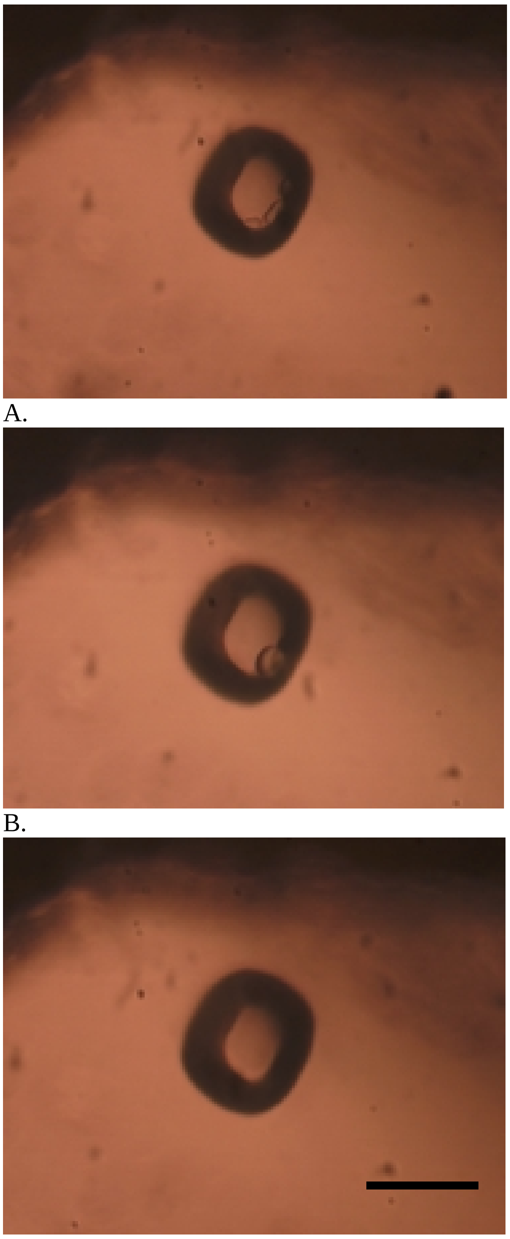


Fig. 26. Freezing experiment on the all-gas inclusion: A – three phases at T < -30 to -50 °C; B – one condensed phase; C – homogeneous inclusion (at T >-30 to -5 °C). Scale bar is 20 µ

In one all-gas inclusion, several segregations of a condensed phase appeared upon fast (50

^{o}C/min) cooling at T <~60 ^{o}C (Fig. 26-A). They re-grouped in one location to form one light-colored condensed phase with rounded shape (Fig. 26-B). The shape of this phase did not change on cooling or heating. Upon heating, the phase disappeared at random temperatures varying from –30 to –5 ^{o}C. The phase does not luminesce under UV excitation (vide-band UV-filter, 330-385 nm). The behavior is similar to one observed in the sample 2217.

Sample 2224

Station: 37+37.0 Alcove 6 - Northern Ghost Dance Fault Alcove

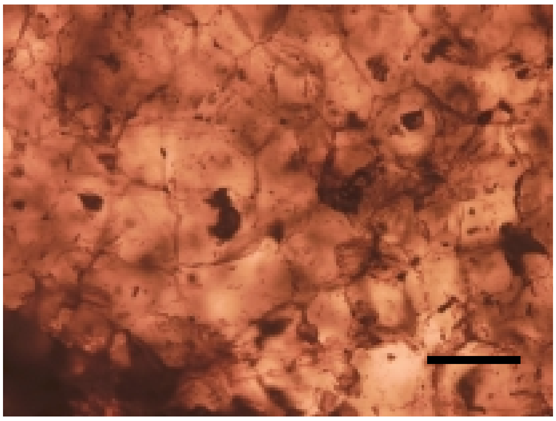
Station within alcove: 0+40.5

Bedrock: Middle Nonlithophisal crystal-poor Topopah Spring Tuff (Tptpmn unit).

Depth from land surface: ~220 m.

Field description. Calcite crust lining the wall of a steep-angle open fracture.

Minerals and textures. *Calcite* forms crystals on both sides of the crust. From one side, closest to the tuff contact, crystals have an appearance of a confined growth: their shape is distorted. Textural relationships reveal presence of the two generations of calcite, which grew in opposite directions from central "seam".


A.

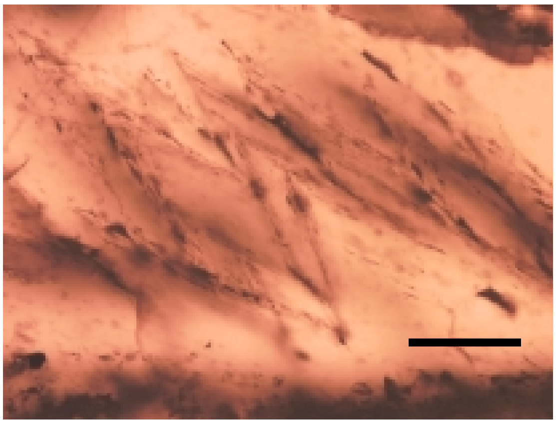

B.

Fig. 27. Granular character of Calcite-1 (A) and sharp "phantom" crystals in Calcite-2 (B). Scale bars correspond to 0.5 mm in both images.

Calcite-1 probably grew within some porous medium. Crystals are <1 mm in size, semi-translucent. Calcite-1 often has a granular appearance (Fig. 27-A) and associates with delicate "nets" composed of filamentous silica, as well as with micro druses of *quartz* and micro inclusions of *fluorite*. Calcite-2 does not contain silicate phases, but traps abundant all-gas inclusions. Its translucent crystals, 2-5 mm in size, are equant, blocky. They often exhibit zoning that reveals shape of crystals during the formation of the crust (Fig. 27-B).

Quartz forms micro-druses composed of perfectly shaped water-clear crystals up to 2 mm in size.

Fluorite occurs as cubic violet micro crystals (0.1-0.2 mm in size), aggregates of several crystals (Fig. 28), as well as slightly brownish spherules inside calcite and quartz. The relationships with host minerals indicate its syngenetic character.

Fluid inclusions. Calcite-2 contain abundant all-gas inclusions (Fig.29). All-liquid inclusions are present in both generations of calcite. Two-phase gas-liquid inclusions occur along curvilinear low-angle planes (healed

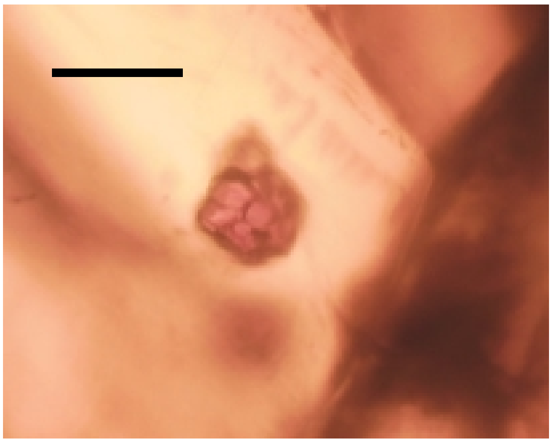


Fig. 28. Fluorite near the surface of the calcite crystal. Scale bar is 30 µ

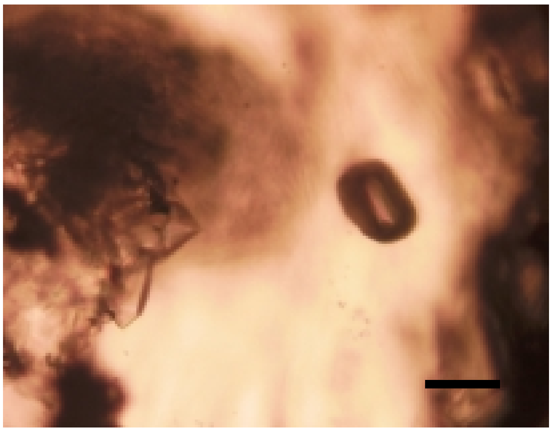


Fig. 29. All-gas inclusion in calcite and quartz crystals. Scale bar is 20 μ

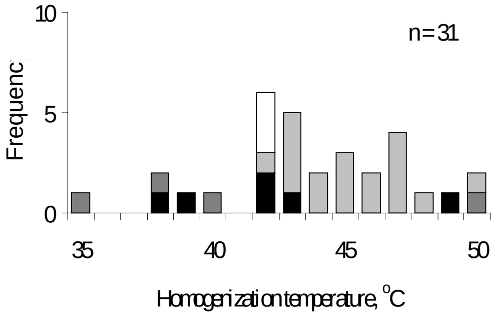


Fig. 30. Sample 2224. Black and dark-gray – groups of inclusions along healed fractures; light-gray and white – groups of large inclusions along low-angle planes (growth zones?)

fractures; inclusions are small, 4-10 μ); large inclusions with slightly flattened shape were found in low-angle planes.

Thermometric study. The results of the thermometric study are shown in Fig. 30. The data display substantial scatter. Larger scatter is characteristic for inclusions associated with healed fractures. Thermometric data on large inclusions associated with low-angle planes (possible growth zones) are somewhat more consistent.

Sample 2225

Station: 29+76

Bedrock: Middle Nonlythophisal crystal poor Topopah Spring Tuff (Tptpmn unit)

Depth from land surface: ~ 290 m.

Field description. Lithophisa 60 cm wide and 30 cm high. Calcite coats the floor of the cavity forming crust up to 1.5 cm thick. Bedrock of the inner surface of the lithophisa is covered by a ~1 mm thick layer of quartz crystals (vapor-phase alteration?).

Minerals and textures. *Calcite* is milky-white, semi-translucent. Tabular crystals are present, which in places are cut by corrosion and covered by layers of opal. This sequence again is cut by corrosion, after which another “portion” of calcite and opal was deposited.

Opal also occurs as primary inclusions, group of which follow the growth zones. The surface of calcite crystals is often covered by small, several micron in size “droplets” of ideally translucent opal.

Fluid inclusions. Calcite contain abundant all-liquid inclusions. Two-phase gas-liquid inclusions suitable for thermometry have not been found.

Sample 2226

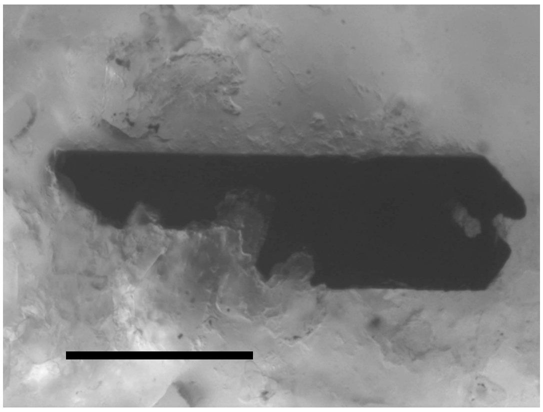
Station: 0+28.5 - Alcove 5.

Field description. Low-angle veinlet. There is a gradual transition from a hair-wide fissure with alteration zone of ~ 1 cm on both sides (bleached tuff), to calcite-cemented micro breccia (cement is not abundant), to large calcite crystals on the floor of the fissure's widening, to massive crystalline calcite filling (partly or entirely) a 1.0-1.5 mm wide fissure.

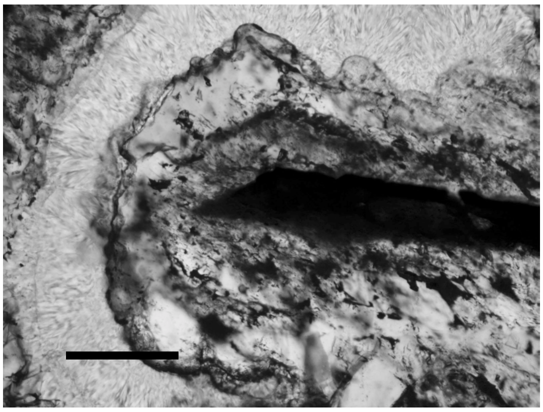
Minerals and textures. There is a ~1 mm-thick layer of α-*quartz* (identified by XRD) on the contact between tuff and calcite. Similar rims are typical of samples from lithophisae, where they are often composed of *tridimite*. Also, stringers and tabular crystals of a mineral containing Fe, Mn, and Ti (*hematite*?)[*]. It occurs in altered tuff, as well as in calcite-opal crust where it sometimes serve as a "seed" for crystallization of opal and calcite (Fig. 31).

Thin, ~0.5 mm fractures in tuff are often filled with *calcite*.

Botrioidal *opal* forms a layer within calcite crust. It also occurs as water-clear blobs and thin films on the surface and at the tips of calcite crystals. Besides, opal is present as solid inclusions in calcite (Fig. 31). The shape

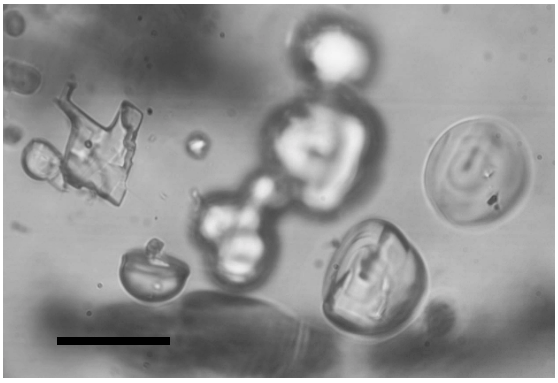


A.

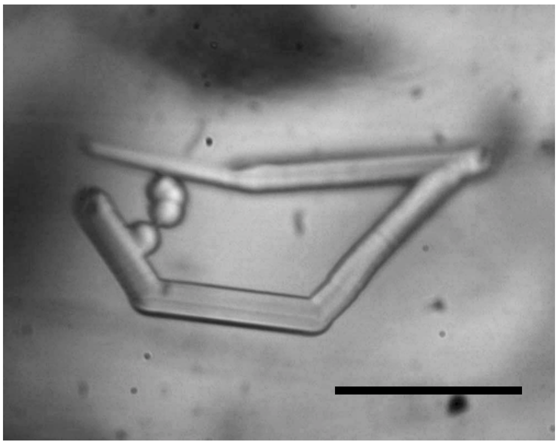


B.

Fig. 31. Hematite (?). A – embedded in calcite; B – overgrown by layers of opal and calcite. Scale bars correspond to 1 mm in both images



A.



B.

Fig. 32. Solid inclusions of opal in calcite + one two-phase aqueous inclusion (T_h = 37 °C). Scale bar corresponds to 25μ in both images.

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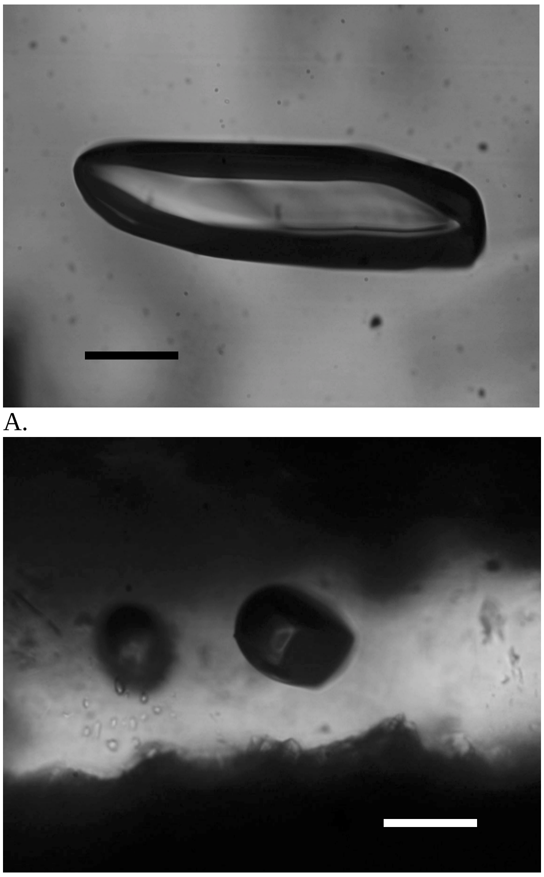
[*] Analysis on microprobe Cameca yielded concentrations: TiO_2 (2.16), MgO (0.38), MnO (6.22), FeO (81.12)



A.

B.

Fig. 33. All-gas inclusion in calcite crust (A, scale bar is 25 μ) and in calcite veinlet in tuff (B, scale bar is 100 μ).

of these inclusions and their association with growth zones indicate that deposition of these two minerals occurred simultaneously.

Fluid inclusions. All-gas inclusions often occur near the contact between calcite and tuff, calcite and opal, as well as in thin, ~0.5 mm wide, veinlets penetrating the bedrock tuff (Fig. 33).

Gas-liquid inclusions are rare. They occur as groups along growth zones (Fig. 34) and low-angle planes.

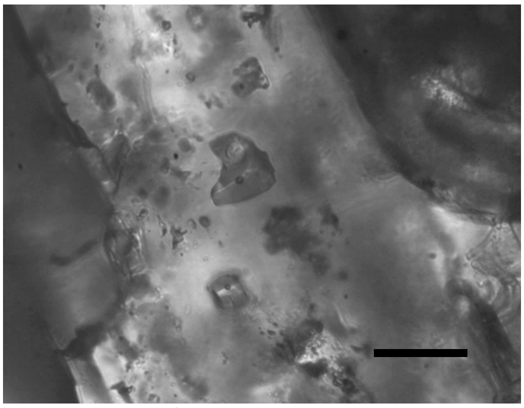


Fig.34. Group of gas-liquid inclusions in calcite near the contact with opal (upper right corner). T_h = 39-40 °C. Scale bar is 20 μ

Thermometric study. The results of the thermometric study are given in Fig. 35. All inclusions (42 from 3 groups) homogenized within a narrow interval of 7 °C.

The results are quite consistent; the measured temperatures may be considered true temperatures of paleo fluids.

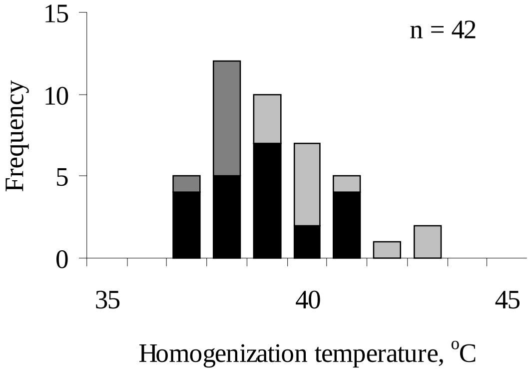


Fig. 35. Sample 2226. Black – inclusions along growth zone; Gray – inclusions in low-angle zones.

5.3. U-series dating

The age of the hydrothermal activity at Yucca Mountain is of critical importance from the standpoint of the suitability of the site as a potential host of a high-level nuclear waste disposal facility. With this in mind we made an attempt to measure absolute ages of calcites, for which hydrothermal origin was proven through fluid inclusion studies.

Four samples from the first sample set-1995 were subjected to TIMS U-series dating at McMaster University, Hamilton, Ontario, Canada (laboratory of Prof. D.Ford).

Three analyses (SS#30-31, SS#39-40, and SS#58-59) failed. One sample, SS#45-46, yielded the following results:

- Sample weight = 4.5945 gm;
- Spike = 0.484 gm;
- Concentration of U = 0.1396 ppm;
- Activity ratio $^{234}U/^{238}U = 1.4734 \pm 0.44$ (2σ);
- Calculated initial value $^{234}U/^{238}U = 1.7648 \pm 0.008$ (2σ);
- $^{230}Th/^{234}U = 0.8416 \pm 3.37$ (2σ);
- $^{230}Th/^{232}Th = 14 \pm 3.41$ (2σ);
- Age (in thousands of years, uncorrected for detrital thorium) = 169 (+13/-12) years; and
- Age (in thousands of years, corrected for detrital thorium) = 160 (+13/-12) years (two standard deviation errors).

The data above were treated by program for data reduction (Code and Algorithm by S.E.Lauritzen and J.Lundberg, 1997, Dept. of Geology, University of Bergen, Norway).

The sample that was dated was relatively large in size. Calcite crust ~10 mm thick was build up of two layers of slightly different color. Opal was not identified in the calcite. A layer of drusy quartz occurred at the bottom of sample.

The concentration of uranium in the sample is approximately equal to the average value of the samples from ESF analyzed by the USGS researchers (average U concentration from 20 samples is 0.139 ppm; Paces et al., 1996)

The analysis is internally consistent. The age, 160,000 years, reflects an average age of the crust; ages of inner layers may be older and outer layer – younger than this age. It is unlikely, however, that the ages of the early parts of the crusts are older than 1 million years. If it were so, the average measured age would have been much older than 160,000 years.

Although the average includes deposits over a significant time span, it represents the first direct datum on a sample with a known saturated-zone origin. Since it appears to be in conflict with findings of the DOE researchers on the old ages of early calcites at Yucca Mountain, the analysis needs to be reproduced and verified in the course of the subsequent studies.

6. Discussion

6.1. The issue: Saturated vs. Unsaturated paleo hydrology at Yucca Mountain

The origin of the epigenetic calcite and associated minerals (opal, quartz, zeolites, fluorite) found at Yucca Mountain is a subject of ongoing debate. The concept presently accepted by the U.S. Department of Energy and endorsed by a 1992 National Research Council report is that they were formed from rain waters percolating along interconnected fractures in the unsaturated (vadose) zone and carrying dissolved carbonate from overlying soils (NAS/NRC, 1992; Roedder et al., 1994; Stuckless et al., 1998; and many others).

A competing hypothesis envisages deposition of these minerals from deep-seated, elevated-temperature waters that welled up through the mountain and discharged on the surface (Szymanki, 1989; Hill et al., 1995; Dublyansky at al., 1998).

The issue is of great importance from the standpoint of the suitability of the Yucca Mountain site to host the high-level nuclear waste repository. Recent works by the U.S. Geological Survey group have demonstrated that calcite and opal at Yucca Mountain were deposited over an extensive period of time from 7-9 million years ago to as recently as ~20,000 years ago (Whelan and Moscati, 1998; Paces et al., 1998; Neymark at al., 1998). These age data are being used to estimate the percolation flux through the Yucca Mountain unsaturated zone. This concept is used as the basis for the Total System Performance Assessment by the U.S. DOE (see, e.g., the U.S. Nuclear Waste Technical Review Board's Report to the U.S. Congress and the U.S. Secretary of Energy; NWTRB, 1998).

The plausibility of this approach is critically dependent on the interpretation of the origin of secondary minerals at Yucca Mountain as being formed by rainwater in the unsaturated zone. However, if this interpretation is proven to be in error, the whole concept of the performance of the Yucca Mountain repository will need to be re-evaluated.

6.2. A few words on the terminology

There is some ambiguity in applying the term "hydrothermal" to fluids with temperatures of 35-75 ^{o}C, like those from which calcite at Yucca Mountain was deposited. The term has been used by researcher in the past including the present author. The terms "hydrothermal" fluid or "thermal" water do not have strict definitions, and the perception of these terms strongly depends on the specific field of expertise of a geologist who uses it. For instance, an ore geologist would not consider fluids with the temperature of less than 50-100 ^{o}C as hydrothermal. There is also perception, that "true" hydrothermal fluids should reveal some links with the source of heat, like cooling magmatic bodies, etc.

In hydrology, however the threshold for thermal water is much lower. For instance, a definition accepted by most European hydrologists calls the water thermal if its temperature *at the orifice* is 4-6 ^{o}C higher than the mean annual temperature of the area. (Schoeller, 1962). In this context the temperatures in subsurface environments above those to be expected from normal thermal gradients are also considered hydrothermal (Dublyansky, 1997).

In order to remove any ambiguity regarding the use of terms I am specifying that the terms thermal and hydrothermal are used in this study to refer to waters if they reveal temperatures higher than may be expected at a given depth within the unsaturated zone.

6.3. Methodology: the study of epigenetic calcite for paleo hydrologic reconstruction

Long-term stability of the regional hydrogeologic system is of significant concern for all sites intended for geological isolation of nuclear or other hazardous wastes. Fracture-filling calcites in crystalline and other rocks represent “footprints” of paleo hydrologic systems. Integrated studies of stable and radiogenic isotopes and fluid inclusions in calcite veinlets, accompanied by U-series and/or U/Pb dating are used in a number of national programs to constrain the past thermal and fluid history of the prospective waste disposal sites. Pertinent examples are: Chalk River Site in Canada (Bukata et al., 1998), Olkiluoto Site in Finland (Blith et al., 1998), and Äspö Hard Rock Laboratory in Sweden (Wallin and Peterman, 1995).

At Yucca Mountain, the “descending meteoric water” interpretation was based on extensive isotopic studies; one crucial method, fluid inclusion studies, was either not applied, or its results were inadequate (Dublyansky, 1994).

6.4. Discussion: Why isotopic methods are not sufficient for paleo hydrologic reconstructions?

Paleo-hydrologic reconstructions based solely on isotopic methods contain an inherent uncertainty. The isotopic composition of calcite ($\delta^{18}O$ and $\delta^{13}C$) deposited from an aqueous fluid depends on the two parameters: initial composition of these isotopes in the mineral-forming fluid, and the fractionation coefficients, governing partitioning of isotopes between the fluid and the depositing calcite. The fractionation coefficients are temperature-dependent. Therefore, we have two equations with three unknowns (the isotopic composition of carbon, that of oxygen in mineral-forming fluid, and the temperature). Evidently, such a system of equations can only be solved by assigning one of the unknowns with some arbitrary value (that was done, for example, by Szabo and Kyser (1990) who managed to “prove” the rainwater origin for the Yucca Mountain calcite this way).

Fluid inclusion studies provide independent information on the temperature of calcite deposition. This eliminates one of the unknowns and makes it possible to calculate initial values of the mineral-forming fluids.

My opinion is that the absence of adequate fluid inclusion research is one of the major and most regrettable deficiencies in the Yucca Mountain characterization activities.

6.5. Origin of secondary minerals in the ESF

The results of my studies show that hydrothermal origin for 13 calcite samples removed from the ESF is fairly certain. Below, I summarize results that imply deposition of these calcite in the saturated environment.

Mineralogy

The presence of crystalline quartz and fluorite within calcite crusts is not compatible with the postulated by the DOE rain water origin of the mineral-forming fluids. Quartz and fluorite were reported by the USGS researchers (Paces et al., 1996):

> *“Nearly all low-temperature secondary mineral occurrences consist of calcite and various silica phases including quartz, chalcedony and opal.” (p. 8)*

and

> *“Other phases are present (fluorite, clay minerals, zeolites, Mn-oxides, organic phases) but are volumetrically inconsequential.” (p. 9)*

No explanation have been offered for their presence, although the fluorite and quartz are typical minerals of the low-temperature hydrothermal assemblages:

> *"Fluorite occurs as a typical hydrothermal vein mineral with quartz, barite, calcite, sphalerite, and galena" (McGraw-Hill…, 1988, p. 195).*

Coarse crystals

The coarse-crystalline character of the calcite, predominance of euhedral sparry crystals in the Yucca Mountain crusts are not compatible with the meteoric water-film model of deposition. The "per-descensum" (meteoric) concept essentially ascribes the calcites at Yucca Mountain to a speleothemic, or flowstone, origin. Flowstones (i.e., layered formations deposited from gravitational water films), are well studied in natural caves (e.g., Hill and Forti, 1997).

Although the chemistry of the bedrock in carbonate caves and at Yucca Mountain is quite different, the analogy with speleothems is, in my opinion, justifiable. Caves represent not only the closest, but probably the only known natural analog for the postulated "descending film water" origin of the Yucca Mountain calcites. Such peculiar depositional setting imposes constraints on the textures of depositing minerals. These constraints have to do with physics, rather than with geology. In other words, if postulated "descending film water" origin of calcite at Yucca Mountain is correct, this calcite should not necessarily "*mimic*" speleothems, but it should comply with the physical laws (gravitation, surface tension, etc.) governing speleothemic growth. In this context, parameters such as rates of deposition, chemistry of host rocks, liquid and gas flux rates play a secondary role.

Due to their deposition from thin films of water, flowstones are always built up of tiny palisade calcite crystals and do not form large euhedral crystals:

> *"… distinctive fabrics of palisade calcite are formed because precipitation usually occurs from thin water films that flow over the growing speleothem surfaces. Large crystal terminations do not form on the speleothem surface because they form projections that disturb the water flow away from the projections which, as a consequence, are gradually eliminated." (Kendall and Broughton, 1978, p. 519)*

The size of the free-growth crystals forming on the outside layer of flowstone is controlled by the thickness of the water film from which the flowstone grows (typically, < 1 mm). By contrast, at Yucca Mountain calcite often forms well shaped free-growth crystals up to 1.5 cm in size. Such textures are not compatible with the postulated film-water origin for the Yucca calcite crusts; instead, they clearly indicate a phreatic (saturated) environment during their formation. To my knowledge, nowhere in the world (except for the publications of the USGS scientists on Yucca Mountain) large free-growth calcite crystals were reported to form from film waters.

Growth layers

Another generic feature of the flowstones is fine rhythmic lamination. This lamination appears due to the fact that the waters depositing calcite seep through from the soil. Biological activity of the latter varies with the seasons of the year, as well as in concert with the longer-period climatic changes. Percolating soil waters carry varying amounts of humic substances (humic and fulvic acids) and layers of calcite deposited from these waters acquire different coloration as a consequence. Even in apparently colorless specimens typical of speleothems from cold climatic settings this banding is readily revealed through luminescence under the UV or other excitation. This feature makes flowstone an excellent source of information on past environments (Shopov, 1997).

In contrast, the calcites from the ESF do not reveal rhythmic lamination, either on a visual basis or under UV luminescence. I examined all my samples under microscope using a wide-band UV filter (330-385 nm). None of samples revealed growth banding or luminescence. I also used more energetic impulse UV excitation, provided by powerful photographic flash to study 12 samples from the 1995 set. After such excitation, the Yucca Mountain samples typically yielded 1-8 s-long bluish-white luminescence (Dublyansky and Reutsky, 1995) that is characteristic of the low-temperature hydrothermal calcite from elsewhere (Dublyansky, 1997).

One calcite sample studied by means of Raman spectrometry did not show luminescence under Ar-laser excitation (see Appendix 1, Fig. 5).

Character of fluid inclusions

The issue, critical from the standpoint of the suitability of Yucca Mountain as a potential high-level nuclear waste site is whether the calcite found in its interior was deposited in saturated (phreatic) or in unsaturated (vadose) zone. Fluid inclusions trapped in calcite which was deposited in the unsaturated, vadose zone should reflect this setting. The vadose zone is (by definition) located above the water table and contains both water and air at atmospheric pressure. Goldstein and Reinolds (1994) note that

> *"Cementation and crack healing may trap fluid inclusions representing the vadose zone's fluid heterogeneity. Fluid inclusions from the vadose zone are characterized by all-liquid fluid inclusions … and two-phase (liquid + vapor) fluid inclusions characterized by highly variable L:V ratios. … Two-phase inclusions result from heterogeneous entrapment of the two fluid phases in the vadose zone. … Inclusions in which the bubble dominates the cavity volume are to be expected. Bubbles in two-phase inclusions are at about one-atmosphere internal pressure. … There should be no confusion between an FIA from the vadose zone and those from other environments." (p. 81).*

By contrast, most of inclusions in the Yucca Mountain calcites are all-liquid. Two-phase gas-vapor inclusions are rare and typically occur as groups with consistent liquid-to-vapor ratios. Such inclusions strongly suggest entrapment from homogeneous liquid.

All-gas fluid inclusions and, in some samples, all-gas + gas-rich inclusions reflect, most probably, heterogeneous entrapment (i.e., system where gas bubble existed as a separate phase in liquid during entrapment. Two observations, however, made such inclusions non-attributable to vadose zone setting: (1) less-than-atmospheric internal pressures; and (b) presence of aromatic hydrocarbons in some of them.

In many instances, all-gas inclusions were found to occur as individual inclusions, with no apparent relation to aqueous inclusions.

In summary, the types of inclusions found in calcite samples from ESF are not characteristic of the vadose zone setting. Instead, they reflect saturated, phreatic environment during the formation of the minerals.

Elevated formation temperatures

The geological history of Yucca Mountain precludes any thermal event such as burial or intrusions of magmatic bodies that could have led to thermal re-equilibration of the inclusions studied in the calcites. Therefore, the measured temperatures, 35-75 ^{o}C, may be considered to reflect the formation temperatures for these calcite samples. Such elevated temperatures are not compatible with the postulated vadose zone setting.

According to normal practice of the fluid inclusion studies, inclusions, for which primary, pseudo secondary of secondary origin cannot be determined with certainty, are treated as secondary. Some of our inclusions fall in this category. In the case of Yucca Mountain, however, secondary inclusions are of no lesser (and, perhaps, of even greater) importance than primary ones. Trapped at elevated temperatures, they indicate saturated environments within Yucca Mountain after the crystal growth ceased. Therefore, secondary inclusions characterize fluids younger than secondary minerals.

Presence of gases at less-than-atmospheric pressure

Several crushing experiments were performed on the all-gas inclusions (see Appendix 1). In all experiments the matching fluid entered the inclusion vacuole upon rupture, and the bubble shrank. To eliminate the possibility that bubbles contracted due to the absorption of a gas in the matching fluid, two different types of the latter were used. One was standard immersion oil (A) the second was glycerol which is known to be non-reactive with regard to most gas chemistries encountered in fluid inclusions. The degree of bubble contraction remained the same in both fluids.

A pair of equations may be written:

$$P_{NOW}V = nRT_{NOW},$$

$$P_{ENT}V = nRT_{ENT},$$

where P is the pressure, V is the volume of an inclusion (or a bubble), n is the number of moles of a gas in the inclusion, R is the gas constant, and indices *NOW* and *ENT* denote parameters in the unbroken inclusion now, at room pressure and temperature, and parameters during the inclusion entrapment. Since we are discussing unbroken inclusions, the volume V should be held constant. Assigning $nR/V = a =$ cons., equations may be re-written as:

$$P_{NOW} = aT_{NOW},$$

$$P_{ENT} = aT_{ENT}.$$

The temperature at the moment of entrapment may be determined as:

$$T_{ENT} = (P_{ENT}T_{NOW})/P_{NOW}.$$

The pressure of entrapment, P_{ENT}, of less than 1 bar is highly unlikely. It should be approximately equal to 1 bar in vadose setting and be >1 bar in saturated, phreatic, setting. On another hand, from crushing experiments we know that $P_{NOW} < 1$ bar. Therefore:

$$P_{ENT}/P_{NOW} > 1, \text{ and } T_{ENT} > T_{NOW}.$$

In other words, the entrapment temperature for all-gas inclusions should have been higher than the present-day ambient temperature.

Presence of inclusions filled with gases with pressures less than 1 atmosphere argues against the vadose zone setting. If these inclusions were trapped "*air-water wapor-*CO_2" phase, representative of the unsaturated zone atmosphere, as was suggested earlier (Roedder et al., 1994), these gases in inclusions should have retained pressures of about 1 atmosphere. This criterion is successfully used to tell apart the vadose unsaturated and phreatic saturated environment (Goldstein and Reinolds, 1994).

Roedder et al. (1994) suggested that less-than-atmospheric pressures revealed by crushing may be explained by condensation of water vapor in a trapped air bubble. This mechanism, although physically plausible, needs to be supported by numerical calculations. How much water needs to be condensed to decrease the pressure in inclusion to the extent that it will contract upon crushing (volumetric change of ~20 %)? How much water may be condensed in the inclusion from water vapor due to cooling from, 40 to 25 ^{o}C? Also important is that this hypothetical mechanism requires temperatures of entrapment higher than ambient (condensation of water vapor requires decrease of the temperature). Finally, this model does not account for the presence of hydrocarbons in inclusions.

Another question which was raised during the review of this report was: How can inclusions with internal pressure <1 atmosphere be formed in the saturated zone, where the pressure changes with depth according to the hydrostatic law (which is, approximately 1 atmosphere per 10 m depth)?

A possible explanation is that the gas bubbles were trapped at shallow depth, close to contemporaneous water table. The saturated zone extends from the water table downward. Therefore, hydrostatic pressure in this zone is ~ 1 atmosphere near the water table and increases with depth. The actual pressure in the entrapment zone will depend on the depth from water table.

Presence of gaseous aromatic hydrocarbons in all-gas inclusions

Aromatic hydrocarbons cannot be attributed to soil- and other unsaturated-zone environment. The presence of aromatic and probably other hydrocarbons suggests the relation of studied calcite with the presence of natural gas potential of the Paleozoic sedimentary rocks underlying Yucca Mountain. Existence of such potential was suggested by Mattson et al. (1992) on the basis of the Conodont color alteration index (CAI) analysis[5]. This matter will be discussed in more detail in Section 6.7.

Stable isotopic properties of calcite

Stable isotopic studies of speleothems represent an established method of paleo climatic reconstruction. Changes in delta ^{18}O values from one growth layer to another provide a proxy of the paleo temperature record, whereas the changes of the delta ^{13}C may be used to constrain the evolution of vegetation on the land surface (Ford, 1997). Stable isotopic data provide another insight into the origin of the Yucca Mountain calcites.

Typically, vadose-zone speleothems formed from water films (e.g., stalactites) display stronger response to the climate change as compared to phreatic, subaqueous speleothems. Variations of delta ^{18}O are greater in a meteoric water flowstone (e.g., 8 ‰ for Jewel Cave, South Dakota) and smaller in a subaqueous speleothem (2.5 ‰ for Devil's Hole, Nevada; Ford, 1997). At Yucca Mountain, calcites display variations of delta ^{18}O much smaller than would be expected for vadose speleothems deposited over long time intervals during the late Tertiary and Quaternary. In some samples they are less than 0.5 ‰ (Fig. 36). Such "dead-flat" behavior of oxygen is not compatible with the vadose-zone speleothemic (or film water) origin. At the same time, such behavior is quite typical of the low-temperature hydrothermal calcite from elsewhere (Dublyansky and Ford, 1997).

Isotopic parameters of parent fluids

Calcite studied from the ESF has isotopic values: δ^{18}O from -10.6 to -12.14 and δ^{13}C from -2.6 to -6.0 ‰ PDB. According to the fluid inclusion results, it was deposited from waters with the temperature of up to 50 ^{o}C. By applying well-established temperature-dependent fractionation coefficients (Friedman and O'Neil, 1997; Faure, 1986) it may be calculated that the parent waters that deposited calcite crusts had δ^{18}O of -4.6 to -6.2 ‰ SMOW

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[5] Conodonts are microfossils that occur in marine rocks of Late Cambrian to Triassic age. Conodonts change color in response to heating due to carbonization of organic matter sealed in them. Color of conodonts indicates the highest temperature reached by rocks containing them. This method is used to assess thermal history and evaluate the degree of thermal maturation of rocks with respect to oil and gas generation.

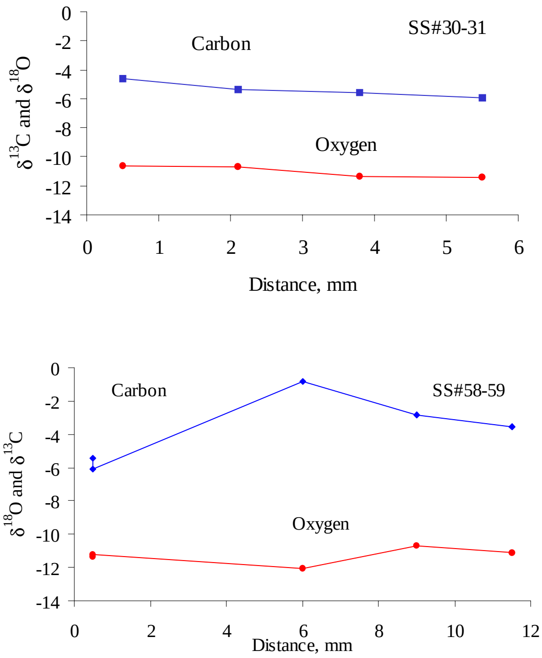

Fig. 36. Stable isotopic properties of hydrothermal calcite from the ESF across crusts.

and δ^{13}C varying from +0.2 to -3.2 ‰ PDB (calculated for 50 °C)[6]. These values deviate significantly from the modern values of waters in the Yucca Mountain Tertiary aquifer (δ^{18}O -14.0 to -12.8 ‰ SMOW and δ^{13}C -12.7 to -4.9 ‰ PDB; NAS/NRC, 1992, p. 157).

Salinity of fluids

Most of fluid inclusions studied so far did not yield numeric results regarding the salinity of trapped waters. This indicates low concentrations, probably close to fresh waters.

Some inclusions, however, yielded apparent concentrations of dissolved salts (expressed in conventional NaCl-equivalent) as high as 0.7 to 1.7 wt %. As in the case of fluid inclusion temperatures (see Section 6.2), these concentrations will be considered as "very diluted" or "fresh" waters by geologists, dealing with ore deposits. A hydrologist, however, would call such waters "brackish" or even "saline". Such salt concentrations are not expected for meteoric waters in volcanic rocks. They are compatible, however, with the salinity of the semi-confined Paleozoic carbonate aquifer (1.5 wt % of NaCl; Peterman et al., 1994).

6.6. Origin and significance of all-liquid inclusions

All studied samples from ESF contained, besides rare two-phase vapor-liquid and monophase all-gas inclusions, abundant all-liquid inclusions.

The appearance of a shrinkage bubble in an inclusion strongly depends on the two parameters: (a) difference between the temperature of entrapment and ambient temperature, and (b) size of inclusion. In order to appear, a bubble must cross a "thermodynamic threshold": some excess of energy needs to be spent on the creation of its surface. The surface tension relates to the curvature of the surface (i.e., to the size of a bubble) as $1/r^3$, where r is radius of the bubble. In other words, the lower the entrapment temperature (and, respectively the difference $T_{entrapment}$-$T_{ambient}$) and the smaller the size of the inclusions – the lower are chances that a bubble will appear in inclusion upon its cooling from $T_{entrapment}$ to $T_{ambient}$. Relatively small inclusions (ca. 10-20 micron) trapped at relatively low temperatures (ca. 30-70 °C) have small chances to heterogenize (which is, nucleate a shrinkage bubble) upon cooling to room temperature. Fluid in such inclusions may exist in "stretched" state for millions of years. Roedder (1984) noted that

> *"…inclusions as large as 20 µm in some minerals formed at 100 °C seldom show bubbles. Aqueous inclusions formed 70 °C may be as large*

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[6] $\delta^{18}O_{caclite}$ -$\delta^{18}O_{water}$ = 2.78(10^6T^{-2})–2.89 (where T is absolute temperature) and

$\delta^{13}C_{water} \cong \delta^{13}C_{calcite}$ +2.8 (at 50 °C)

> *as 100 μm and still not nucleate vapor bubble…" (p. 292).*

The appearance of bubbles in such inclusions is a stochastic process, so it is expected that populations trapped at low temperatures will typically be represented by mostly all-liquid inclusions and only small proportion of the two-phase vapor-liquid inclusions.

6.7. Relation of epigenetic minerals to the hydrocarbons in the Paleozoic rocks

A gas inclusion composition with aromatic hydrocarbons (see Appendix 1) is not compatible with the aerated vadose, unsaturated setting. Perhaps the only reasonable source of such hydrocarbons is organic matter in the Paleozoic carbonates, which underlay the Tertiary volcanic rocks of Yucca Mountain. These Paleozoic carbonates are known to have limited natural gas potential (Mattson et al., 1992; Grow et al., 1994; Fig. 37). Grow with co-authors (1994) pointed out that:

> *"While much of the Cambrian through Triassic rocks have thermal potential for gas, extensive Late Tertiary faulting at Yucca Mountain suggest that seals might be inadequate for retaining gas." (p. 1298).*

In the context of this study, however, we are interested not in *economic* hydrocarbon potential, but in possible explanations for the appearance of hydrocarbons in calcite.

Restricted data available to-date indicate that thermal history of Paleozoic carbonaceous rocks under Yucca Mountain was such as to allow organic matter trapped in these sedimentary rocks to be transformed into oil and gas. The only drill hole which penetrated Silurian dolomite under Yucca Mountain (UE25p#1) produced Conodonts having color alteration index, CAI, of 3 (Grow et al., 1994). Such a value is typical of rocks that have reached temperatures of ~180 ^{o}C and is in the range where:

> *"… oil is no longer generated, but in the range where gas is generated and previously generated oil is being converted to gas" (Grow et al., 1994. p. 1301).*

Although the amount of these hydrocarbons in Paleozoic rocks may presently be quite small, they represent a plausible source of tiny amounts of gases trapped in fluid inclusions. Moreover, it should be noted that the fluid inclusions were formed in the geologic past, so that the oil-to-gas ratio yielded by current exploration would not necessarily be relevant to the time of calcite formation.

6.8. A hint on the spatial structure of the system

In terms of the spatial distribution of measured homogenization temperatures, the following observation may be important. Two samples that yielded temperatures higher than other samples (SS#85-86 and 2206) are both from Tiva Canyon tuff. Also, both these samples are from the eastern part of the exploratory block (see Appendix 2), closest to the Paintbrush (~2 km to the east of the repository block). Fault zone which might have served as major avenue for upwelling fluids.

The reason for this suggestion is that there is a present-day thermal anomaly associated with this fault (locally elevated groundwater temperatures as indicated by borehole temperature measurements, reported by Sass et al., 1987). This anomaly may represent an "echo" of ancient activity (Fig. 38).

Although it is premature to make strong conclusions on the basis of only two samples, this hypothesis needs to be addressed in the future, when the spatial structure of the ancient upwelling system is studied.

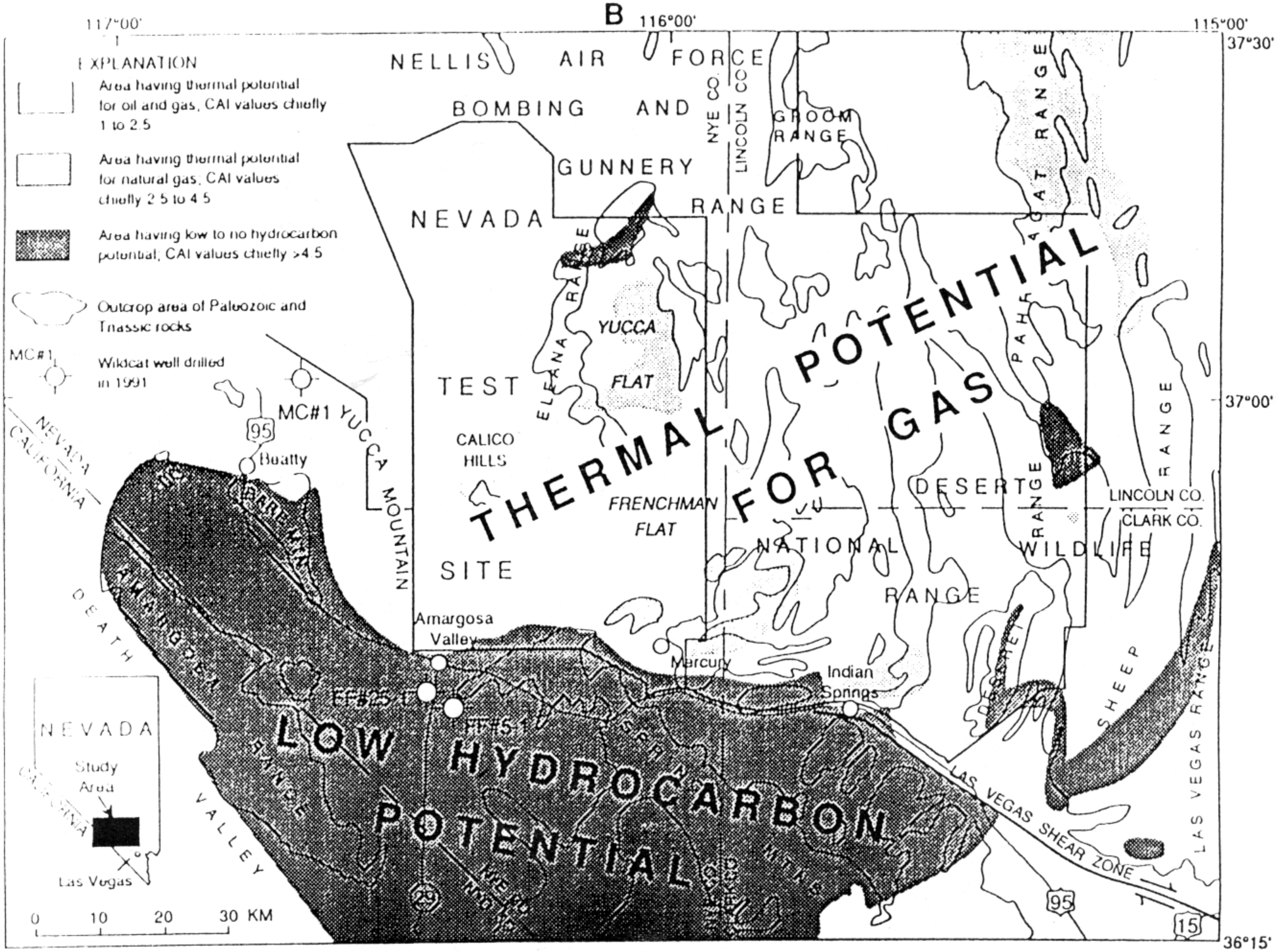

Fig. 38. Thermal potential for gas in Southern Nevada based on Conodont color alteration indexes (CAI). From Grow et al., 1994.

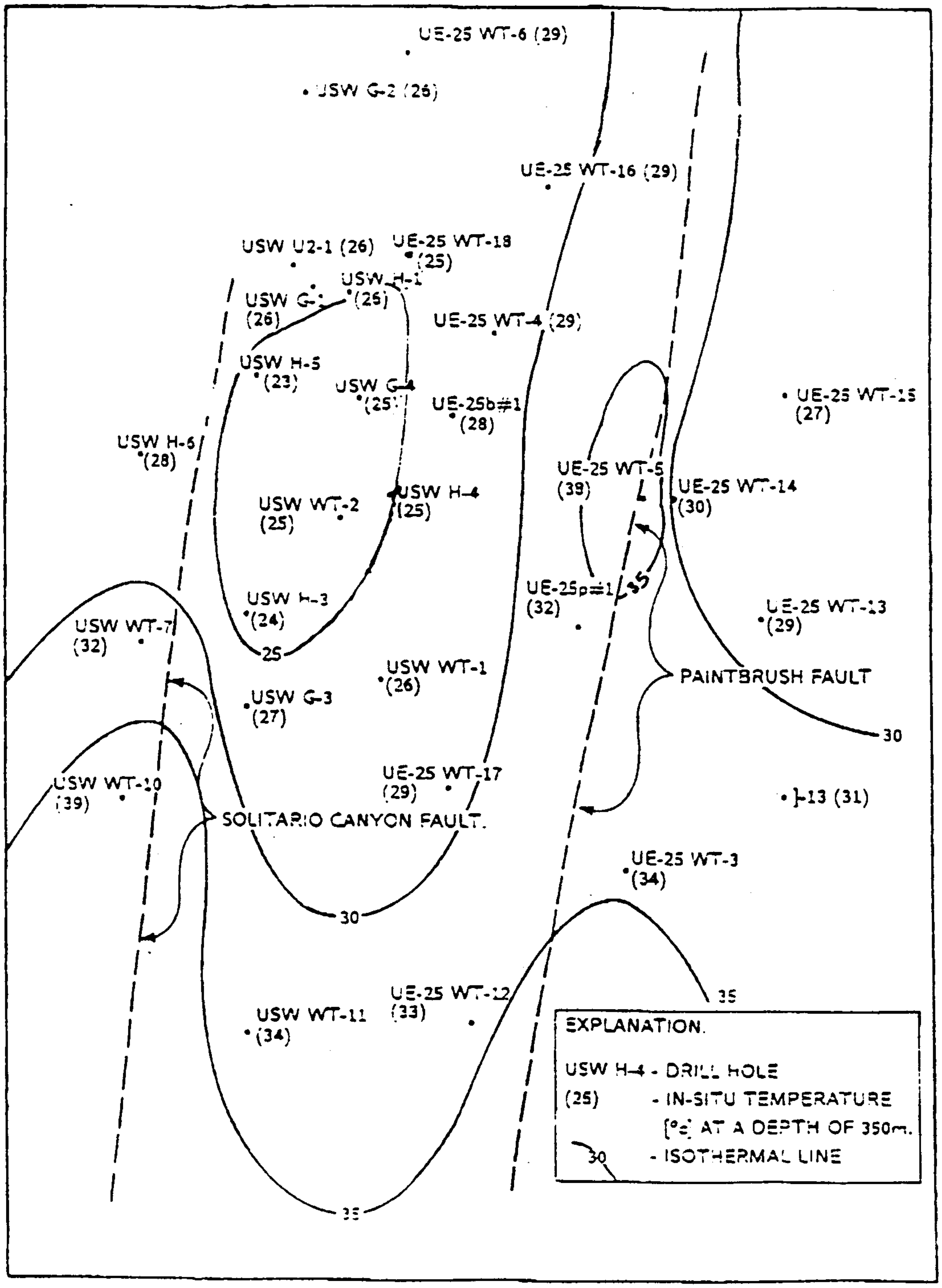

Fig. 38. Borehole temperatures at depth 350 m and isothermal lines suggested by them. Data from Sass et al., 1987; modified from Szymanski, 1987.

6.9. Discussion: Use of the Yucca Mountain calcites for paleo climatic reconstructions

It has been suggested (Whelan et al., 1994) that the stable isotopic record of calcites from Yucca Mountain may be used as a paleoclimatic proxy. They wrote:

> *"Fluids infiltrating into the UZ* [unsaturated zone] *should contain dissolved carbonate species derived from interactions within the thin soils atop Yucca Mountain, with* $\delta^{13}C$ *largely controlled by the plant assemblage … and* $\delta^{18}O$ *reflecting that of meteoric waters." (p. 2741).*

They also suggested that:

> *"Past climate changes in southern Nevada, such as during the most recent glacial stage, were accompanied by profound changes in mean annual air temperature and regional air mass circulation patterns – and, presumably, significant changes in the* $\delta^{18}O$ *of precipitation at Yucca Mountain." (p. 2743).*

In the most recent work, Paces et al. (1998) and Marshall et al. (1998) develop this approach further, claiming that:

(a) opal-calcite coatings were formed over a time period ranging from 7-9 Ma to as little as 16 Ka BP with the "remarkably constant" growth rate of between 1 and 5 mm per million years (Neymark et al., 1998);

(b) this time span included major, but gradual shift in climate from one favoring grasses in the Miocene to one favoring abundant shrubs and trees in the Quaternary; and

(c) the depositional environment involved water moving down through connected fractures as sheets or films.

However, as is apparent from the data discussed above, a significant part of calcite crusts studied by me from the ESF was formed from ascending heated aqueous fluids. Therefore, their stable isotopic properties may have little to do with past climates. Also, no isotopic changes, which could represent a "response" of calcite to climatic change have been detected in my samples (see Fig. 36).

Theoretically, it is possible that the calcite at Yucca Mountain is composed of the two types: older hydrothermal and younger, formed by rain waters. This would mean, however, that methods applied by the DOE and USGS researches studying this calcite are not capable of distinguishing between these two origins. None of the most detailed studies published by them indicates an option for this calcite of being polygenetic. I view the possibility of such interpretation of being correct as remote.

6.10. Evaluation of the "slow continuous deposition" model

Models of "continuous" mode of deposition and the "remarkably constant" 1 to 5 mm per million years deposition rates postulated by the USGS researchers for the Yucca Mountain calcite (Neymark et al., 1998; Paces et al., 1998, etc.) raise serious questions.

It appears that physical plausibility of this model has never been seriously analyzed and the model as a whole was not developed beyond a vague concept. Here is the best descriptions of the suggested mechanism of mineral deposition I have found so far:

> *"To explain bladed calcite textures and the presence of opal at crystal tips, solutions must transport ions to crystal extremities, where solutions reach oversaturation in mineral constituents. A depositional environment consistent with observed textures involves water moving down connected fractures as sheets*

> *or films where it can enter intersected rock cavities. Interaction between the liquid and an independently migrating gas phase at these sites result in CO_2 evasion or evaporation, oversaturation of mineral components in solution, and precipitation of slow-growing secondary minerals." (Paces, et al., 1998, p. 38).*

Firstly, I have observed under the microscope up to four distinct depositional episodes in some of my samples. These episodes are separated by hiatuses (dissolution, deposition of impurities, deposition of opal or quartz). Examples are shown in Figs. 11 and 27-B.

My observations are consistent with early, as well as recently published observations of the USGS scientists:

> *"The cathodoluminescence studies have revealed at least 4 major stages of calcite deposition in some samples, commonly separated by dissolution unconformities." (Whelan et al., 1994, p. 2741)*

or

> *"Secondary mineralization sequences in the UZ may be sorted into early, middle, and late stages … A sparsely distributed early stage consists of silica phases … locally associated with sparry, but often corroded, calcite. Main stage mineralization contains blocky to thick-bladed calcite +/-opal, frequently with dusty growth zones marked by abundant semi-opaque inclusions. Late stage calcite, again locally with opal, occurs as euhedral, clear, thin-bladed, spade- or fan-shaped crystals and as overgrowth on older calcite." (Whelan and Moscati, 1998).*

Therefore, petrographic features clearly indicate that: (a) there have been several stages of calcite deposition at Yucca Mountain, and (b) that depositional environment changed with time (at times, the fluids even become corrosive and dissolved calcite). This is inconsistent with the theory of "continuous deposition of calcite at a remarkably constant rate through the last 7-9 million years".

Now, let us make a simple calculation. Many of my samples contain large, 20 to 100 microns, all-gas inclusions (see Figs. 10, 11, 14, 15, 26, 29, and 33). They were trapped as gases immiscible with aqueous fluid. If the rate of calcite precipitation was 1 mm per million years, as suggested by the USGS researchers, it would take some 20,000 to 100,000 years to create a 20 to 100 micron-thick layer of calcite (such as shown in Fig. 11) in which inclusion is trapped. It is inconceivable that a gas bubble would remain in the same position for 100,000 years "waiting" until it becomes overgrown by calcite. Even if one invents some mechanism to "glue" the bubble to the growing surface, during such an extended period of time it would be destroyed by diffusion.

The problematic "continuous" concept becomes even more problematic when we apply it to the unsaturated environment (as the USGS researchers do). In the unsaturated zone aqueous fluids are supposed to move down as thin sheets along the surfaces of the interconnected air-filled fractures. The air is not stagnant in these fractures; it moves in response to changes of barometric pressure (for Yucca Mountain it is shown by recent studies in the tunnel). Accordingly, the CO_2 degassing or intake occurs in water films. Since the deposition of calcite is mostly controlled by the regime of CO_2, the rate of deposition would be expected to vary drastically in such a system. The amount of percolating water would be correspondingly variable. (The time of calcite formation spans several major climatic changes; therefore significant changes in the rate of atmospheric precipitation are expected.) Finally, an “unsaturated” setting cannot explain the newly obtained fluid inclusion data presented in this report.

My conclusion is that the hypothesis of “continuous deposition of calcite at a very constant and low rate” is in contradiction with empirical data (textures, petrographic observations, fluid inclusions) and does not comply with basic physical laws.

6.11. Ages of secondary minerals at Yucca Mountain

One sample analyzed by fluid inclusion method yielded the average age of about 160,000 years (see Section 5.3). This date should be considered as an estimate. A large sample, weighing ~4.5 gm, was analyzed.

Publications of the USGS scientists indicate that calcite and particularly opal at Yucca Mountain were formed over extended period of time of about 7-9 million years (Paces et al., 1998; Neymark et al,. 1998). The latest parts of calcite crusts, however, were found to be deposited quite recently (in terms of geological time). Paces et al. (1998) determined ages as young as 20,000-28,000 of years and older for calcite samples removed from the ESF.

Whelan and Stuckless (1992) and Whelan et al. (1994) reported U-series ages of 310, 280, 227, 190, 185, 170, 142, 30, and 26 and ^{14}C ages of 45, 44, 43, 42, 40, 39, and 21 (in thousands of years) for calcite samples recovered from drill cores from the upper 400 m of the Yucca Mountain vadose zone. Scarce fluid inclusion measurements reported for calcite from these boreholes (7 temperatures measured by Edwin Roedder; DOE, 1993) range from 57 to 114 ^{o}C (sample depth from 178 to 347 m). The outer layers in two samples were dated at ~21,000 and 45,000 years (radiocarbon dating).

Unfortunately, the fluid inclusion method was not used in characterization activities at Yucca Mountain to the extent it should have been used. As a result, the DOE currently possesses extensive database of ages measured on secondary minerals, the origin of which is not constrained by fluid inclusion studies. The absence of adequate fluid inclusion information limits usefulness of this database.

In the absence of the data on samples containing fluid inclusions, no strong conclusion can be drawn regarding the age of hydrothermal activity at Yucca Mountain. However in general, mineral-forming process for calcite and opal from ESF is reasonably well-constrained by the DOE dating (i.e., from ~7-9 million years to ~20,000 years).

In process of the reviewing of this report, an argument was made that calcite with elevated temperatures may be related to old, several million years old, parts of calcite. Because of this old age, the thermal-water origin of this calcite does not imply any potential threat to the suitability of the site.

This suggestion is in agreement with petrographic observations in a sense that the elevated-temperature inclusions are typically found closer to the contact with tuff (i.e., in older parts of calcite). The argument, however, is flawed. Hydrothermal origin of calcite is important mostly because it indicates saturated environment of formation. Outer parts of crystals in the Yucca Mountain calcite, do not typically contain two-phase inclusions; however, they do not contain inclusions typical of vadose zone, either. On top of that, they have a number of other features (see section 6.5) giving a compelling evidence of the saturated environment of formation.

On the basis of the available data, formation of calcite-opal-quartz-fluorite mineralization at Yucca Mountain can be envisaged as deposition in saturated zone from waters with elevated temperature. The temperature decreased at the latest stages of mineral formation; saturated environment of the deposition, however, persisted.

More data need to be obtained in order to constrain the timing of this fossil hydrothermal (lukewarm) activity. The relatively youthful age of the later stages of this activity, however, is fairly certain.

6.12. Implications of the data obtained from fluid inclusions on the Yucca Mountain Total System Performance Assessment

The possibility that saturated thermal environment may occur at certain stage of the planed repository life needs to be fully appreciated. This should lead to a re-consideration of many key-elements of the Total System Performance Assessment for the Planed Yucca Mountain repository. As far as I am concerned, the scenario of repository flooding by thermal waters is not considered in any of the recent versions of the TSPA.

One example emphasizing the importance of such re-assessment is the issue of the waste package degradation. It was explicitly stated in the Third Interim Report of the Peer Review Panel on the TSPA[7] that:

> *"No rational materials selection can be made without knowledge of the characteristics of the waters in contact with the waste packages. These characteristics include: temperature, pH, Eh and ionic concentrations (Cl, SO_4, NO_3, CO_3, Fe^{+++}, Ca, etc.)."*

Clearly, decisions based on the typical meteoric water compositions found in the Yucca Mountain subsurface will be inadequate in case of the intrusion of the deep-seated thermal fluids into the repository zone.

Also emphasized in the Report is the fact that the most corrosion-resistant and recently chosen as a base-case option, alloy C-22

> *"…is susceptible to localized corrosion only when wet in a critical temperature range. If C-22 remains passive in this range, its anticipated life, prior to penetration, is thousands of years. If it is not passive, then its life, prior to penetration, is as little as a few tens of years."*

Therefore:

> *"There is a need to determine the critical temperature range, and the times in this range when different scenarios can occur."*

Such vital determination cannot be made without scientifically sound and sufficiently detailed understanding of the hydrological history of Yucca Mountain.

Fluid inclusion studies may provide necessary information with regard to the expected compositions and temperatures of waters in contact with the waste packages. Coupled fluid inclusion, isotopic and absolute-age studies are required for determining the pattern and timing of the past excursions of thermal waters into the repository zone.

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[7] Available from the web page of the Yucca Mountain Site Characterization Project at http://www.ymp.gov/nonjava/index.htm

7. Conclusions and recommendations

Although the presence of fluids with elevated temperatures (ca. 35-75 ^{o}C) within the modern unsaturated zone at Yucca Mountain in the geological past is reasonably certain, this conclusion only indicates the possibility of the hazard for the potential high-level nuclear waste site. Much more data need to be acquired and analyzed in order to assess the degree of this hazard. Specifically, three questions need to be addressed:

1. What is the age and what was the recurrence period (if any) of the hydrothermal activity?

2. What was the volume of fluids involved at different stages of this activity? and

3. What was the spatial structure of ancient hydrothermal system?

This may be accomplished through concerted effort of researchers, involving:

a). Detailed fluid inclusion studies in calcite and other mineral phases from the ESF as well as from drill cores. Such study may provide important information on the spatial structure of the ancient hydrothremal system;

b). Careful dating of calcite samples hosting fluid inclusions with elevated homogenization temperatures. Such study would constrain the temporal structure of ancient hydrothermal system; and

c). Detailed isotopic study of mineral phases (C, O, Sr, He) may provide important information on the pattern of fluid migration, origin of fluids, etc.

Acknowledgments

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Of course, as the author of the report I am solely responsible for its contents and conclusions, any omissions and any errors that may remain.

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Appendix 1

Fluid Inclusions in Calcite Samples from the ESF, Nevada Test Site, Nevada

Study performed by Yuri Dublyansky

on June 15-19, 1998 at Virginia Tech, Blacksburg, Virginia

Report assembled by Yuri Dublyansky
for the Office of the Attorney General of the State of Nevada

July 1998
Washington, DC

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Introduction

This study was performed on June 15-19, 1998, in the Fluid Research Laboratory at Virginia Tech, Blacksburg, Virginia.

The purpose of the study was to check the validity of the fluid inclusion results obtained during my studies at the Institute of Mineralogy and Petrography, Russian Academy of Sciences in Novosibirsk in 1995-1998. These results were published (Dublyansky & Reutsky, 1995; Dublyansky at al., 1996-a, -b, 1998) and presented at the 7th PACROFI Meeting on June 2, 1998, in Las Vegas.

Four samples collected by me in 1995 in the first, approximately 300 m long section of the ESF (North portal) have become the subject of this study. Samples represent calcite and opal-quartz-calcite incrustations on the fracture walls or on the gravel-sized fragments found in local fractured zones of the welded tuff Tiva Canyon.

Sample preparation

All possible precautions have been taken to avoid any mechanical or thermal damage to the inclusions, as well as contamination of the samples.

The samples have been cut using low-speed *Buehler Isomet*® saw set at ~120 rpm with cold water as a coolant. Freshly cut surfaces have been manually ground and polished using grinding powder (600 grit and 5 micron) and *Buehler Metadi*® water-based diamond fluid (1 micron). Polished surfaces have been mounted on glass slides using polyacrylic “Crazy Glue” and the operations were repeated to produce doubly polished sections.

I have prepared sections from three samples; in one more sample calcite appeared to be too fractured, and the section was not prepared.

Optical observations

I examined prepared doubly polished sections under the microscope *Olympus BX-60* at different magnifications (objectives 10x, 40x, and 80x). Inclusions were photographed with *Polaroid Digital Camera*. Sometimes, for the purpose of the fast mapping of inclusion locations, I used *Sony* video printer.

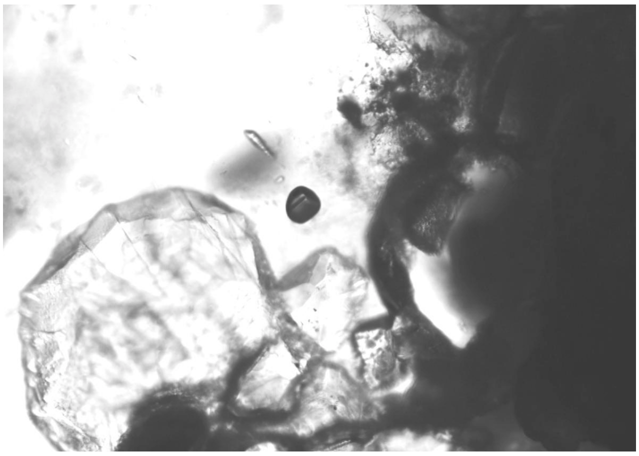


Fig. 1. All-gas inclusion in calcite near the contact with tuff (dark) and some unidentified epigenetic euhedral minerals. Size of the inclusion is ~ 40 μ. Sample SS#85-86.

All-gas inclusions

All-gas inclusions have been observed in one sample, SS#85-86. Inclusions occur in the apparently oldest parts of the calcite crust, more or less close to the contact with the bedrock tuff (Fig. 1). Inclusions are dark (Fig. 2) and often have equilibrated shape (Fig. 1, 3, and 4).

UV-luminescence

All three calcite samples prepared in Blacksburg, as well as sections of the SS#85-86 sample brought by me from Novosibirsk were studied for the UV-luminescence. The purpose of this was to check possible presence of the liquid hydrocarbon (oil) inclusions. One such inclusion has been found by me in the course of crushing tests in Novosibirsk and reported in my talk at the 7th PACROFI Meeting. None of the samples revealed luminescence.

Conclusion. Negative result of the UV-luminescence test indicates that studied inclusions apparently do not contain liquid hydrocarbons.

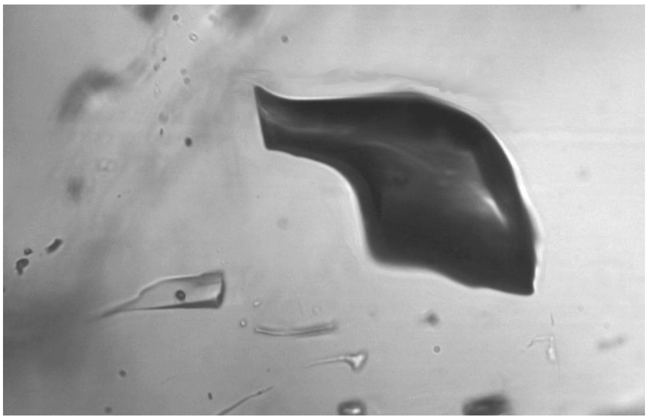


Fig. 2. All-gas and gas-liquid inclusions. Size of the all-gas inclusion is ~ 60 μ. Sample SS#85-86.

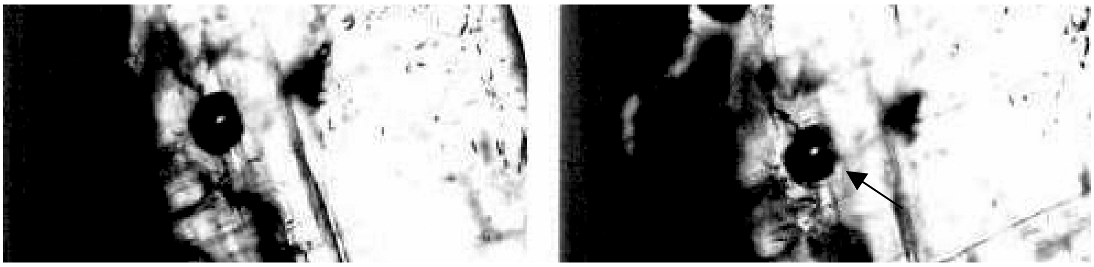


Fig. 3. Inclusion before (left) and after the rupture (right). Note the appearance of meniscus (arrow) in the inclusion on the right picture (oil entered the inclusion). Size of the inclusion is ~25 µ. Sample SS#85-86.

Crushing

I performed several crushing experiments on all-gas inclusions. In four experiments I was able to observe the moment of the rupture when the crack intersected the inclusion. None of the bubbles in inclusions increased in size. In all four cases oil entered the inclusion vacuole and the bubble shrank. Typical example is shown in Fig. 3. Out of the four successful experiments, in the three I used standard immersion oil (A); in one experiment I used glycerol. For these two fluids, I was unable to detect any difference in the degree of bubble contraction.

I have made an estimation whether the observed volumetric changes can be explained by difference in barometric pressure between Yucca Mountain and Blacksburg, located at different altitudes:

$$P_B V_B = nRT_B,$$

$$P_Y V_Y = nRT_Y,$$

where P is the pressure, V is the bubble volume, n is the number of moles of a gas in bubble, R is the gas constant, T is the temperature, and indices B and Y stand for Blacksburg and Yucca Mountain, respectively. Holding the term nRT as a constant, obtain:

$$P_B V_B = P_Y V_Y \quad \text{or} \quad P_B / P_Y = V_Y / V_B$$

Substitution of actual mean barometric pressures at Blacksburg and Yucca Mountain (ESF) yields:

$$0.957/0.913 = V_Y / V_B \quad \text{(pressure in bars).}$$

This means that the difference in altitude between the two sites can contribute no more than 5% of volumetric change. For example, for a 25 µ bubble, this would translate in the change of bubble diameter of about 0.5 µ; by far less than I have observed in crushing experiments.

I have established, therefore, that the pressure in non-broken inclusion at room temperature is less than 1 at. or 1 bar. Again, a pair of equations may be written:

$$P_{NOW} V = nRT_{NOW},$$

$$P_{ENT} V = nRT_{ENT},$$

where indices *NOW* and *ENT* denote parameters in the unbroken inclusion now, at room pressure and temperature, and parameters during the inclusion entrapment. Since we discuss unbroken inclusions, the volume *V* should be held constant. Assigning $nR/V = a$ = cons., equations may be re-written as:

$$P_{NOW} = aT_{NOW},$$

$$P_{ENT} = aT_{ENT}.$$

The temperature in the moment of entrapment may be determined as:

$$T_{ENT} = (P_{ENT}T_{NOW})/P_{NOW}.$$

It is highly unlikely that the pressure of entrapment was $P_{ENT} < 1$ at. (it should be approximately equal to 1 at. in unsaturated, or vadose, setting and higher than 1 at. in saturated, or phreatic, setting). On another hand, from crushing experiments we know that $P_{NOW} < 1$ at. Therefore:

$$P_{ENT}/P_{NOW} > 1 \quad \Rightarrow \quad T_{ENT} > T_{NOW}.$$

In other words, the entrapment temperature should have been higher than the present-day ambient temperature.

Conclusion. Crushing data indicate internal pressures in the SS#85-86 all-gas inclusions of less than 1 at. Similarity in the bubble behavior upon crushing in two different fluids (one of which, glycerol, is known to be non-reactive with regard to the most gas chemistries encountered in fluid inclusions), as well as very fast, almost immediate, contraction of bubbles, both argue against the possibility that the bubble contraction might be related to the dissolution of the gas in the fluid in which the crushing is performed. Inclusions in their pristine state, therefore, contain gas with low density. To allow the less-than-atmospheric pressures in unbroken inclusions, elevated entrapment temperatures are required.

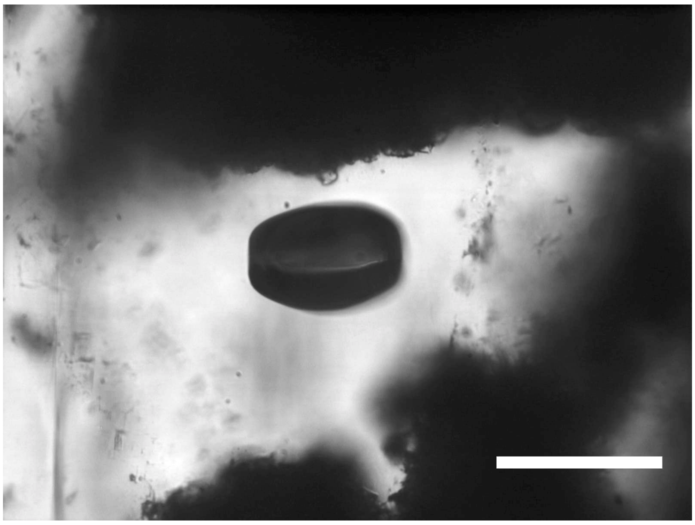


Fig. 4. Inclusion 2 studied by Raman spectrometry. Bar scale is 50 μ

Raman spectrometry

I analyzed two all-gas inclusions from the sample SS#85-86 (Fig. 4) on the Raman spectrometer (analyst Frank Harrison). The results are shown in Fig. 5.

Inclusion 1. First short, 1 and 2 min., analyses did not reveal any discernible signals on the Raman spectra. Longer, 20 min., run yielded broad hump of the Raman spectrum, characteristic of the fluorescence. Repeat 20 min. long run on the same inclusion yielded similar broad hump, with overall intensity decreased by ~20%. Analysis of the matrix calcite near the inclusion did not show any fluorescence.

Inclusion 2. This inclusion (Fig. 4) was analyzed by me in Novosibirsk (exposure to laser excitation 60 min. has led to overall decrease of fluorescence by an order of magnitude, from 360.000 to 36.000 counts per second). Being subjected to the two consecutive 20-min. analyses, inclusion have shoved the pattern, identical to the one observed for the Inclusion 1, except the intensity of fluorescence was significantly lower (see Fig. 5).

Interpretation. Fluorescence of fluid inclusions is typically caused by the presence of cyclic and aromatic hydrocarbons possessing benzene rings (which is, C_6 and higher). It might be concluded, therefore, that the gas in studied inclusions contains a certain amount of such aromatic hydrocarbons. Because the density of the gas is low in these inclusions (as it is apparent from crushing experiments), the amount of molecules in the analyzed volume is also very small, which makes it impossible to see peaks of individual gases on the Raman spectra. Prolonged exposure to the laser beam causes decomposition of organic compounds, which is expressed in the decrease of the fluorescence intensity. Direct correlation between the exposure time and the intensity of fluorescence can be observed in Fig. 5.

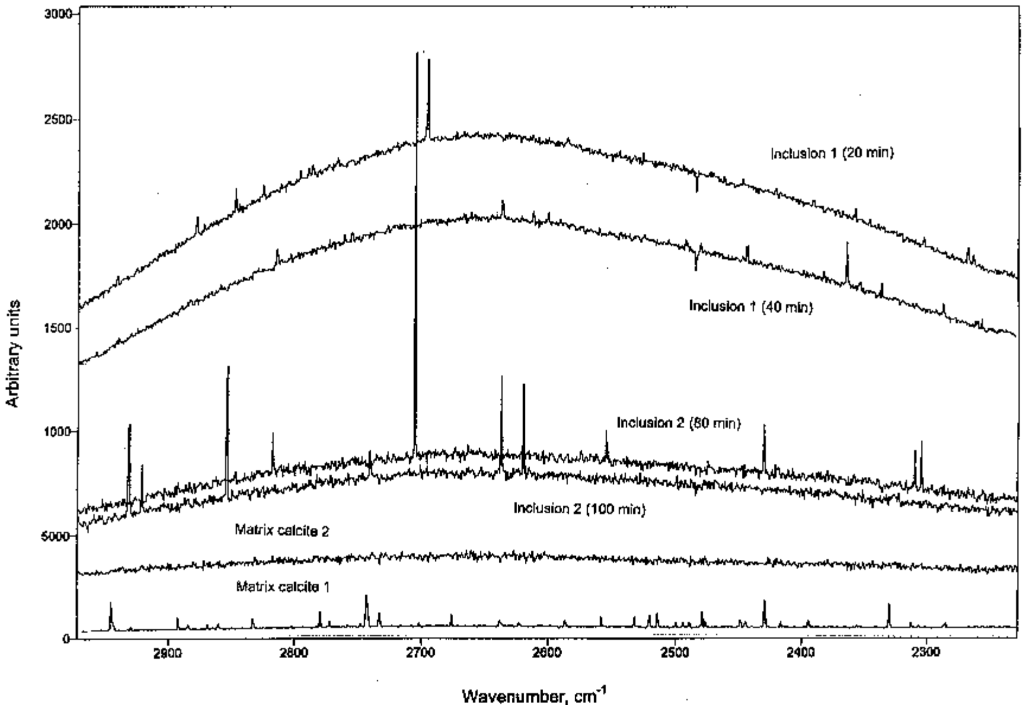


Fig. 5. Raman spectra obtained from two inclusions and matrix calcite. Sample SS#85-86. Analyst F.Harrison. Inclusion 2 was exposed to laser beam for 60 min in Novosibirsk and then twice for 20 min. in Blacksburg. Sharp peaks on the spectra are noise.

Two separate lines of evidence reinforce this interpretation.

1. Selective absorption analyses of individual bubbles released from the all-gas inclusions by crushing have been performed in Novosibirsk (sample SS#85-86; analyst Nina Shugurova). Bromine water, used in the analysis, removes cyclic and straight- and branched-chain alkanes:

$$C_nH_{2n} + Br_2 = C_nH_{2n}Br_2$$

$$C_nH_{2n-2} + Br_2 = C_nH_{2n-2}Br_4$$

Six bubbles analyzed by this technique revealed significant, ~80%, decrease in volume when submerged in the bromine water. By contrast, neither the gas bubbles from the “vapor phase” quartz (collected at Yucca Mountain), nor bubbles of the ambient air analyzed by the same method and with the same reagents, have shown any decrease in the bromine water. The selective absorption results, therefore, suggest the presence of the unsaturated hydrocarbons in the all-gas inclusions of the SS#85-86 calcite.

2. Bulk gas chromatographic analyses of calcite (as well as quartz, opal, and welded tuff samples) from the ESF have been performed in Novosibirsk (analyst Liubov Egorova). All samples, including SS#85-86, have shown presence of methane, acetylene, as well as heavier hydrocarbons C_3 to C_6 (Fig. 6). Several more peaks have been recorded on the chromatographic spectra. Apparently, they represent hydrocarbons heavier than C_6. These gases have not been identified so far, pending calibration of the equipment.

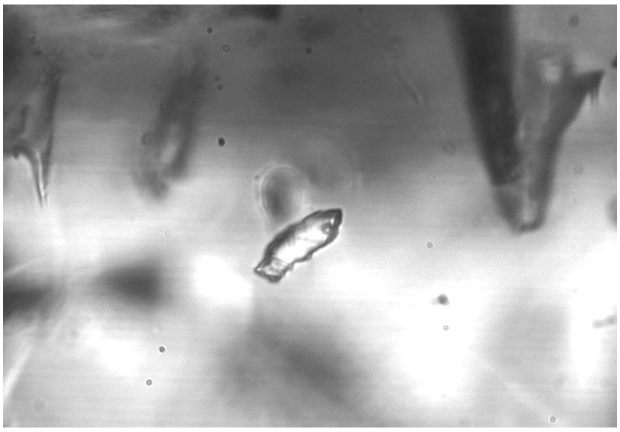
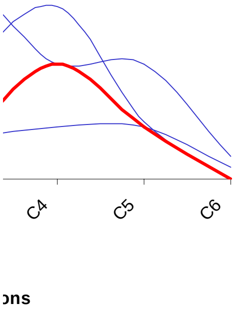


Fig. 8. Gas-liquid inclusion. Size is ~ 25 µ. Sample SS#45-46.



calcite samples from ESF. Sample SS#85-86 analyst L.Egorova.

Conclusion. On the basis of the data available, the conclusions regarding the presence of heavy (aromatic) hydrocarbons in the all-gas inclusions of the SS#85-86 sample seems to be warranted.

Gas-liquid inclusions

All three studied samples contain all-liquid inclusions, sometimes bearing indications of their primary origin (e.g., alignment along growth layers in sample SS#45-46). Besides, in all three samples I observed gas-liquid inclusions with apparently consistent and generally low vapor-to-liquid ratios. In two samples (SS#39-40 and SS#45-46) such inclusions are very rare. One of such groups is shown in Fig. 7; individual inclusion with characteristic vapor-to-liquid ratio is shown in Fig. 8.

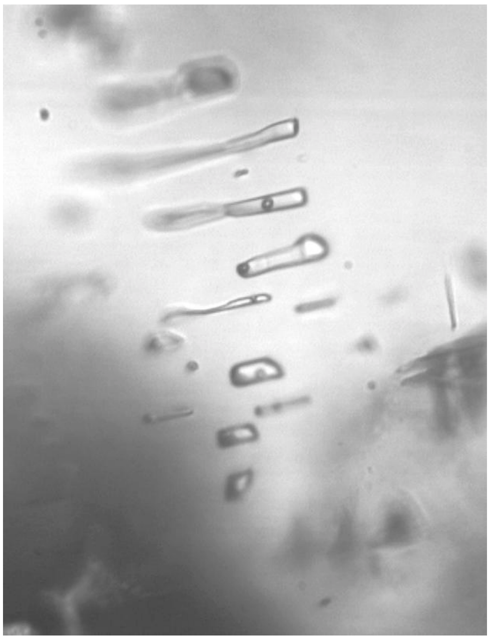


Fig. 7. Group of inclusions with apparently consistent vapor-to-liquid ratio. Size of the inclusion in the center (bubble in left corner) is about 25 µ. Sample SS#45-46.

In sample SS#85-86 gas-liquid inclusions were found to occur along growth zones of the calcite crystals. In several cases I was able to observe more than ten inclusions apparently belonging to the same growth zone within the same view field. Photo mosaic displaying the characteristic shapes and distribution of such inclusions is given in Fig. 9.

Thermometry

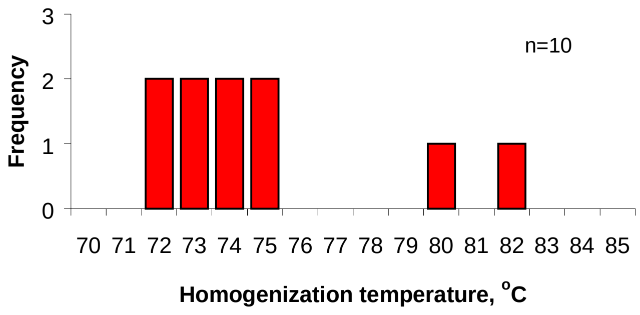
Thermometric study has been performed on the *Linkam THMSG 600* stage. I selected a group of inclusions, apparently representing the one growth zone and having (on the visual basis) similar vapor-to-liquid ratios. The data obtained by such fluid inclusion associations, FIAs, are considered the most reliable information in fluid inclusion thermometry. I located and mapped 10 inclusions within the same field of view. To be able to observe homogenization temperatures of all inclusions, I performed heating in cycles. The sample was heated to 30 ^{o}C and hold for 1-2 min. for thermal equilibration. Each inclusion was checked for the presence of a bubble. The temperature was increased at an increment of 1 ^{o}C. After every heating step I checked each inclusion. When I was unable to identify the presence of a bubble (this began to happen at temperatures in excess of 68 ^{o}C), I lowered the temperature by 10-20 ^{o}C, which typically was enough to see the bubble. The detailed chart of the experiment is given in the Appendix.

As it is seen from Fig. 10, the studied FIA yielded quite consistent homogenization temperatures. Eight out of ten inclusions homogenized within the 4^{o}-interval from 72 to 75 ^{o}C.

Conclusion. Homogenization temperatures indicate that studied calcite was formed from hot water with the minimum temperature of 75 ^{o}C.

In this experiment I obtained the data for the stratigraphically early part of the SS#85-86 calcite that was not available for the analysis in my early studies in Novosibirsk due to the fact that I had to work with cleavage chips, rather than with cut and polished sections. Results from the report Dublyansky & Reutsky (1995) characterize the outer parts of the calcite crusts. Respectively, lower temperatures have been obtained from these parts of the calcite

Fig. 9. Ten inclusions with apparently uniform vapor-to-liquid ratio in the same growth zone (FIA). Size of the largest inclusion is ~150 µ. Sample SS#85-86. Mosaic.



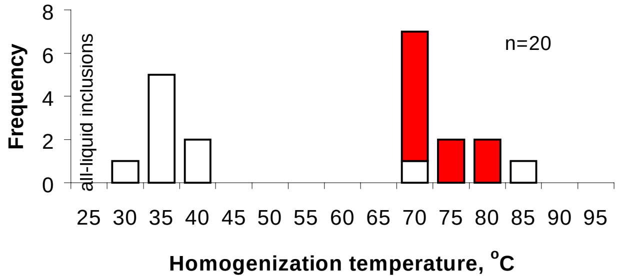


Fig. 10. Frequency histograms for the SS#85-86 sample. Upper histogram - this study; lower histogram - results by Dublyansky & Reutsky (1995) and this study (dark)

(Fig. 10).

Discussion

Thermometric data – are they reliable?

All necessary precautions have been taken to assure the absence of any heating, stretching, or other damage to the inclusions during sample preparation and thermometric studies. Besides, I am not aware of any "technical" process that could have led to the appearance of fluid inclusion groups yielding so consistent homogenization temperatures, as I have measured.

Geological history of Yucca Mountain precludes any thermal event (like burial or intrusion of magmatic bodies) that could have led to thermal re-equilibration of inclusions in studied calcite.

Therefore, the result may be considered as quite consistent, and the obtained homogenization temperatures, 72-75 ^{o}C, as reflecting the minimum possible formation temperature for the studied part of the calcite sample.

What is the age of the studied calcite?

To assess possible bearing of our results on the suitability of the Yucca Mountain site, we need to know the age of the studied calcite.

The authors of one of the latest papers dealing with the Yucca Mountain mineralization (Stuckless et al., 1998) state:

> *"… many calcite occurrences are related to a hydrothermal event (probably the synvolcanic Timber Mountain even, 9-11 ma). To our knowledge, all of these occurrences have been found only at great depth … but other hydrothermal minerals formed during this event are found closer to the modern surface…" (p. 73)*

Calcite that I studied was collected from depth of ~50-70 m below the topographic surface. If the observation above is correct, this calcite should be young, "post-Timber Mountain" one.

In the absence of the absolute age dating, discrimination between old (c.10-11 Ma) "Timber Mountain" hydrothermal calcite and younger "post-Timber Mountain" calcite at Yucca Mountain is possible on the basis of its isotopic properties. "Old" calcite invariably displays characteristic enrichment in ^{13}C (δ^{13}C –2 to +5 ‰ PDB) and depletion in radiogenic Sr (^{87}Sr/^{86}Sr from 0.7085 to 0.7100), whereas "young" calcite is depleted in ^{13}C (-3 to -10 ‰ PDB), and enriched in ^{87}Sr (0.7110 to 0.7130). Pertinent discussion can be found in papers by Vaniman & Whelan (1994), Whelan & Stuckless (1991) and elsewhere.

The problem of the age, therefore, may be dealt with in two steps: (1) determination of ^{87}Sr/^{86}Sr and δ^{13}C values; and (2) for calcites with "light" carbon and "heavy" strontium compositions – absolute dating by means of U-series, U/Pb or ESR methods.

Aromatic hydrocarbons in all-gas inclusions

The presence of aromatic hydrocarbons in all-gas inclusions, along with alkanes (as indicated by significant, up to 80%, decrease of the bubble volume in bromine water) and, probably, other hydrocarbons (methane, acetylene, C_3 to C_6; gas chromatographic analysis) may be indicative of the possible connection of the studied calcite with the petroleum (essentially, gas) potential of the Paleozoic sedimentary rocks underlying Yucca Mountain.

Conclusions and recommendations

Conclusions

1. All-gas inclusions from the studied sample SS#85-86 contain, at room temperature, a gas or mixture of gases with the pressure less than 1 at. This suggests entrapment of gas from heterogeneous fluid at elevated temperature;
2. All-gas inclusions from the sample SS#85-86 apparently contain aromatic hydrocarbons;
3. Gas-liquid inclusions from the sample SS#85-86 indicate the temperature of calcite formation in excess of 75 ^{o}C; and
4. The presence of groups of gas-liquid inclusions with apparently uniform vapor-to-liquid ratios in two more samples (SS#39-40 and SS#45-46) suggests formation of calcite in these samples at temperatures, exceeding ambient ones. This conclusion should be checked out by further thermometric studies.

Recommendations

The following set of research activities may be suggested for the purpose of the evaluation of the timing and extent of the migration of water with elevated temperatures within the presently unsaturated zone of Yucca Mountain in the past:

1. Extensive and comprehensive study of fluid inclusions in calcite, quartz, and fluorite from the entire extent of the ESF, as well as from existing boreholes in order to determine:

    a. abundance of minerals formed by warm/hot (>35 ^{o}C) fluids;

    b. spatial distribution of such minerals;

2. Isotopic analyses of calcite samples that yield elevated homogenization temperatures (^{13}C, ^{18}O, and ^{87}Sr) in order to attribute them to “old” Timber Mountain or “young” post-Timber Mountain lithofacies; and

3. Absolute dating of the identified “young” carbonates (U-series, U/Pb, ESR) in order to assess the timing of the calcite-forming processes.

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Appendix

Chart of the thermometric experiment

(√ - bubble present; 0 – inclusion homogenized)

T, °C	**Inclusion #**										**Cool to, °C**
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	
34	√	√	√	√	√	√	√	√	√	√	-
35	√	√	√	√	√	√	√	√	√	√	-
36	√	√	√	√	√	√	√	√	√	√	-
37	√	√	√	√	√	√	√	√	√	√	-
38	√	√	√	√	√	√	√	√	√	√	-
39	√	√	√	√	√	√	√	√	√	√	-
40	√	√	√	√	√	√	√	√	√	√	-
41	√	√	√	√	√	√	√	√	√	√	-
42	√	√	√	√	√	√	√	√	√	√	-
43	√	√	√	√	√	√	√	√	√	√	-
44	√	√	√	√	√	√	√	√	√	√	-
45	√	√	√	√	√	√	√	√	√	√	-
46	√	√	√	√	√	√	√	√	√	√	-
47	√	√	√	√	√	√	√	√	√	√	-
48	√	√	√	√	√	√	√	√	√	√	-
49	√	√	√	√	√	√	√	√	√	√	-
50	√	√	√	√	√	√	√	√	√	√	-
51	√	√	√	√	√	√	√	√	√	√	-
52	√	√	√	√	√	√	√	√	√	√	-
53	√	√	√	√	√	√	√	√	√	√	-
54	√	√	√	√	√	√	√	√	√	√	-
55	√	√	√	√	√	√	√	√	√	√	-
56	√	√	√	√	√	√	√	√	√	√	-
57	√	√	√	√	√	√	√	√	√	√	-
58	√	√	√	√	√	√	√	√	√	√	-
59	√	√	√	√	√	√	√	√	√	√	-
60	√	√	√	√	√	√	√	√	√	√	-
61	√	√	√	√	√	√	√	√	√	√	-
62	√	√	√	√	√	√	√	√	√	√	-
63	√	√	√	√	√	√	√	√	√	√	-
64	√	√	√	√	√	√	√	√	√	√	-
65	√	√	√	√	√	√	√	√	√	√	-
66	√	√	√	√	√	√	√	√	√	√	-
67	√	√	√	√	√	√	√	√	√	√	-
68	√	√	√	√	√	√	√	√	√	√	-

Chart of the thermometric experiment (continued)

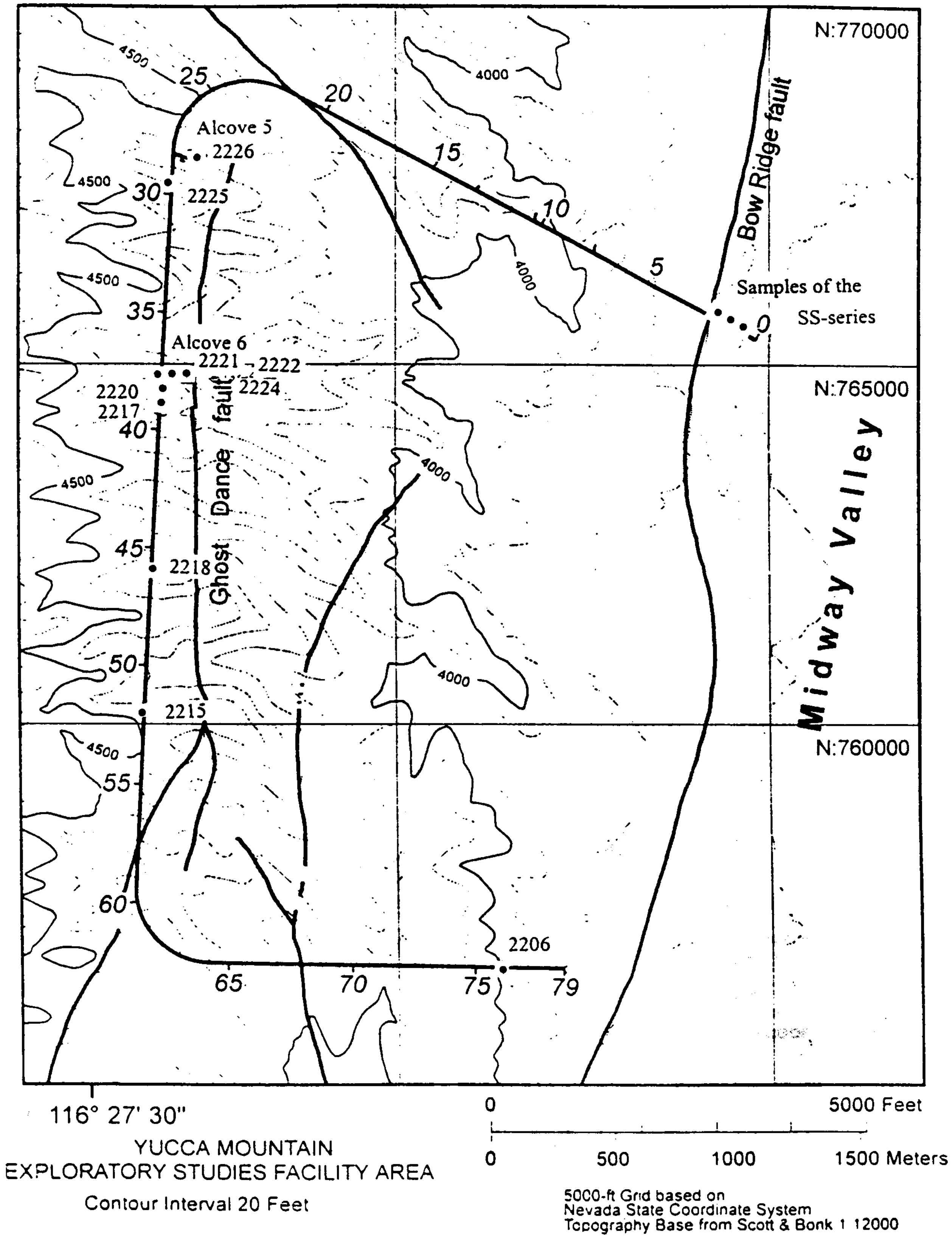
(√ - bubble present; 0 - inclusion homogenized)

T, ^{o}C	Inclusion #										Cool to, ^{o}C
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	
69	√	√	√	√	√	√	√	√	√	√	60
70	√	√	√	√	√	√	√	√	√	√	60
71	√	√	√	√	√	√	√	√	√	√	60
72	√	√	√	0	√	√	√	0	√	√	30
73	√	0	√	0	√	√	√	0	0	√	60
74	√	0	√	0	√	0	√	0	0	0	60
75	0	0	0	0	√	0	√	0	0	0	55
76	0	0	0	0	√	0	√	0	0	0	65
77	0	0	0	0	√	0	√	0	0	0	65
78	0	0	0	0	√	0	√	0	0	0	60
79	0	0	0	0	√	0	0	0	0	0	60
80	0	0	0	0	√	0	0	0	0	0	50
81	0	0	0	0	√	0	0	0	0	0	50
82	0	0	0	0	0	0	0	0	0	0	

Note. Studied sample was mounted on a piece of cover glass, which means it wasn't in direct contact with the silver block (heater). Possible shift in homogenization temperature should be checked. Since I allowed time (ca. 1 min) for thermal equilibration, this effect should not be significant.

Appendix 2: Schematic plan and geological cross-section of the ESF

(courtesy U.S. DOE Nevada Yucca Mountain Operation Office)



Plan view of the Exploratory Study Facility (adopted from Paces et al., 1996). Numbered ticks represent station numbers given at 500 m intervals. Locations of several major faults are shown schematically with bold lines. Locations of studied samples are shown as dots.

SYMBOLS

GROUP	FORMATION		INFORMAL UNITS	THERMO-MECHANICAL UNITS
		▧	Qac: Alluvium	UO
TIMBER MOUNTAIN TUFF	*RAINIER MESA*	▩	Tmr: Rainier Mesa Tuff Tmbt1: pre-Rainier Mesa Tuff bedded tuff	
PAINTBRUSH TUFF	?	░	Tpki: tuff unit "X" Tpbt5: pre-tuff unit "X" bedded tuff	
	TIVA CANYON	▨	Tpc: Tiva Canyon Tuff	TCw
		□	Tpbt4: pre-Tiva Canyon Tuff bedded tuff	PTn
	YUCCA MTN.	▩	Tpy: Yucca Mountain Tuff	
		▩	Tpbt3: pre-Yucca Mountain Tuff bedded tuff	
	PAH CANYON	▧	Tpp: Pah Canyon Tuff	
		■	Tpbt2: pre-Pah Canyon Tuff bedded tuff	
	TOPOPAH SPRING	░	Tptrn: Crystal-rich nonlithophysal crystal-rich vitric zone	TSw1
		▨	Tptpul: Upper Lithophysal crystal-rich and crystal-poor parts	
		░	Tptpmn: Middle Nonlithophysal crystal-poor	TSw2
		▨	Tptpll: Lower Lithophysal crystal-poor	
		░	Tptpln: Lower Nonlithophysal crystal-poor	
		▣	Tptpv: Vitric vitrophyre and non welded subzones	TSw3
		□	Tpbt1: pre-Topopah Spring Tuff bedded tuff	
CALICO HILLS		░	Tacf: Calico Hills lava flow	
		▩	Tacb: Calico Hills bedded tuff	

Appendix 3. Reviews and Evaluations

Reviews by

- Dr. Larryn W. Diamond, University of Leoben, Austria (also includes discussion with Yuri Dublyansky)
- Dr. Bruce Yardley, University of Leeds, UK
- Dr. Jean Dubessy, CNRS, France
- Dr. Jean S. Cline, University of Nevada, Las Vegas
- Dr. Joe Whelan, Dr. James Paces, Dr. Brian Marshall, Dr. Zell Peterman, Dr. John Stuckless, Dr. Leonid Neymark (all USGS) and Dr. Edwin Roedder (Harvard University)

Evaluation of the review by Whelan et al. by

- Yuri Dublyansky

UNIVERSITY OF LEOBEN
INSTITUTE OF GEOLOGICAL SCIENCES
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22 November 1998

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Evaluation of unpublished draft report by Dublyansky:

"Fluid inclusion studies of samples from the Exploratory Study Facility, Yucca Mountain, Nevada"
by Dr. Yuri Dublyansky, October 1998, Blacksburg, VA - Washington, D.C.

The major question addressed by this report is whether the fluid inclusions sampled from the ESF at Yucca Mountain represent meteoric waters trapped on descent, or warm deep waters trapped upon ascent. With this question in mind I have spent approximately seven hours carefully reading Dublyansky's report and using a high-powered optical microscope to examine the samples he provided me (thick-sections numbered 2206 and 2226, presumably corresponding to samples SPC00532206 and SPC00532226). My comments (see following numbered points) deal with the fluid inclusion, mineralogic, and stable isotope evidence adduced in favour of the report's conclusions. I am not sufficiently expert in radiometric dating to evaluate the results of uranium-series dating of calcite.

I find the report prepared by Dr Dublyansky to be of very high quality. It contains a large amount of meticulously collected data of relevance to the question of interest. The results are clearly presented and observations are adequately distinguished from interpretations.

The evidence in favour of warm, ascending water is summarized in section 6.2 of the report. I entirely agree with the compelling nature of most of the evidence adduced, including that listed under the headings: "Mineralogy and textures", "Presence of gases at less-than-atmospheric pressure", "Presence of gaseous aromatic hydrocarbons", and "Isotopic parameters of parent fluids". I find the evidence of "Stable isotope properties" consistent with the warm ascending water hypothesis, but not compelling, in that a cold-water meteoric environment could be envisaged in which the observed patterns could be generated. I have doubts about the remaining point, "Elevated formation temperatures", for the following reasons:

1) According to the report, both primary all-gas inclusions and primary liquid-vapour inclusions are present in the calcites, but no information is given with regard to the relative timing of the two types. In my examination of the samples I confirmed, to my satisfaction, that there are indeed primary inclusions of both types, but in addition I found evidence that the two inclusion types are, at least in part, contemporaneous. In particular, I found what appear to be mixed inclusions, containing large vapour bubbles (> 50 vol%) but also water. If this interpretation of contemporaneity is correct, then it would imply that the all-gas inclusions and the primary liquid-vapour inclusions are mutually saturated with respect to hydrocarbons and water (i.e. heterogeneous entrapment). Incidentally, since the all-gas inclusions probably contain some water, the enigmatic solid observed in a few all-gas inclusions could well be ice or a gas-hydrate clathrate that sublimes upon warming.

2) The report recommends that homogenization temperatures above a certain value should be ignored, but I find this procedure arbitrary. For example, if values above 50°C are to be ignored because of the danger of stretching, then how do we know that the values around 30°C are also not elevated due to stretching? To be convinced that the reported homogenisation temperatures are significant, I would like to see data on the reproducibility of the homogenisation temperatures (I could not find any such data in the report) – irreproducible values would indicate that the inclusions had stretched during heating on the microthermometric stage. I would also like to see, from overheating measurements, exactly at which temperature the inclusions in calcite do begin to stretch. Also, no explicit mention is made in the report of necking-down as a possible explanation for the spread in temperatures, yet I saw in the samples many possible candidates for necking-down, which could conceivably yield unrealistically high temperatures.

3) I cannot reconstruct from the histograms of homogenisation temperatures, whether the spread in values corresponds to inclusions in the same assemblage (FIA, e.g. primary growth zone or healed fracture), or whether the data derive from inclusions in different assemblages. The

distinction is important, because if the all-gas and liquid-vapour inclusions formed by heterogeneous entrapment, as I suggest above, it would mean that only the lowest of the homogenisation temperatures from each assemblage would be significant, and these lowest values would represent the exact temperatures of entrapment, not minimum temperatures (the internal pressure of the hydrocarbon inclusions should be equal to the internal pressure of the liquid-vapour inclusions at the homogenisation temperature of the latter, presumably only slightly in excess of 1 bar). From what I can judge, this way of treating the data could result in interpreted formation temperatures which are actually quite low (e.g. ~35 °C?), and hence the evidence for an origin as warm, hydrothermal fluid would not be compelling.

From the information in the report I cannot tell if the strontium-isotope evidence for upwelling is compelling or not. The report points out that the $^{87}Sr/^{86}Sr$ ratios of the studied calcite are consistent with the ratios of the semi-confined Paleozoic carbonate aquifer that underlies the modern aquifer beneath Yucca Mountain. However, what are the $^{87}Sr/^{86}Sr$ ratios of reactive minerals in the tuffs that host the calcite vein deposits. Are they also compatible with the calcite values?

Having pointed out these ambiguities in the microthermometric data, I am still of the opinion that, viewed collectively, the remaining "compelling" evidence is good support of the report's conclusion, that the calcite + opal + fluorite fracture coatings precipitated from warm, upwelling fluids, and not from descending meteoric water.

Finally, I have a comment regarding the danger of future upwellings. It is very important that further research be directed at understanding why the fluid ascended into the tuffs. If the ascent was driven by topographic flow through the deep carbonate semi-confined aquifer, then perhaps erosion in the region of Yucca Mountain has already removed the topographic highs, such that no future flow is possible.

Larryn W. Diamond

Dr Larryn W. Diamond
Professor of Mineralogy and Petrology

Note: "Chart of thermometric experiment" on page 15 of Appendix 1 seems to be incomplete (no zeroes indicating homogenisation).

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Re:	Comments	CC:	

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● Comments:

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Dear Dr. Diamond:

Thank you very much for evaluating my report and examining two of my samples. I greatly appreciate your time and the thoroughness of your review.

I would like to discuss some of your comments and provide clarification on the questions you raised.

Comment 1.
a. Contemporaneous liquid-vapor and all-liquid inclusions. I agree with your observation that there are apparently contemporaneous inclusions of both types; on several occasions I saw the same relationships. I should have and I will incorporate this observation in the report. (Most unfortunately, I have had only 3 weeks to do the original work at Bob Bodnar's lab and then only 4 days to compile the report; some of the deficiencies of the latter stem from this tight schedule).

I need to point out (here, as well as in the report) that I never carried out thermometric studies on liquid-vapor inclusions associated with gas-rich or all-gas inclusions. All my numeric data are from groups with regular liquid-to-vapor ratio (determined on visual basis). Therefore, I do not think that I should worry about the possible influence of the heterogeneous entrapment on my numeric data.

b. Phase which appears in all-gas inclusion upon freezing. You know, it seems unlikely to me that it was water, because it always had a rounded shape – whether I cooled or heated it. Quite possibly it was clathrate, as you suggested. I did not want to engage in much discussion on this matter before I have more data. We discussed with Bob Bodnar the possibility of analysis of this phase on Raman microprobe using cooling stage, and I plan to attempt this analysis as soon as I can (most unfortunately, during my 3-week stay in Blacksburg in October, Bob's Raman was out of order).

Comment 2.
a. Arbitrary elimination of temperatures. You are right, this is more or less arbitrary approach. However, when we speak of "tight clustering" of the temperatures measured from FIAs, or of "consistent results", don't you think that our judgements are equally arbitrary? Should we consider a 5 ^{o}C-interval of T_h's obtained from an individual FIA sufficiently "narrow"? Or 8 ^{o}C? Or 10 ^{o}C? For instance, Goldstein and Reinolds (1994) suggest: "For diagenetic applications, the class interval for T_h's should usually be 5 ^{o}C" (p. 123). For some of my samples (e.g., Fig. 23), data measured on as much as 5 FIAs fell ENTIRELY within one class interval!

Therefore, my approach to “disturbed” inclusion assemblages was like follows: to treat them not as “consistent”, but as “moderately consistent” (terms of Goldstein and Reinolds, 1994).

Since I did not observe indications of “creation” of the two-phase inclusions with visually similar liquid-to-vapor ratios from all-liquid inclusions by heating (see below my comment on inclusion overheating), I assumed that the same should apply to mechanical stress. In this case, I think, it is even more unlikely to “stretch” all inclusions in a group of all-liquid inclusions to produce two-phase inclusions showing similar liquid-to-vapor ratio. However, minor mechanical stress may slightly change the volume of already-two-phase inclusions; this change, not recognizable visually, will lead to the scatter of the measured T_h’s towards the higher temperatures. It is probably safe to consider the temperatures of 35-40 ^oC as not-altered, because they are so low that simply could not be lower. Again, I want to emphasize here (as I will do in the final report) that the data obtained on “disturbed” samples are considered as “suggestive” rather than “definite”.

I thank you for bringing up this point, because I now realize that I have to explain the rationale of my approach in the report.

b. Reproducibility of the homogenization temperatures. Most unfortunately, it is impossible to reproduce homogenization temperatures of my inclusions. It is inherent and unavoidable problem when working with so low-temperature material. Inclusions which homogenize at 35-50 ^oC virtually never heterogenize upon cooling, even when you cool them to <0 ^oC and hold them at these temperatures for weeks (back in Siberia, I try to do that once a while just putting my samples outdoor in winter). From 100 inclusions with T_h of 50-70 ^oC, only one or two would, probably, heterogenize.

This holds true not only for the Yucca Mountain samples but for all samples of the low-temperature hydrothermal calcites I worked with during the last 18 years (e.g., samples from Hungary, Algeria, Italy, Central Asia, USA, etc.). Physical explanation for such behavior is: since the difference between T_h and $T_{ambient}$ is small, the pressure drop upon cooling is not sufficient to overcome the thermodynamic barrier and create the bubble. This problem becomes even more significant if the size of inclusion and, respectively of a bubble which may appear in it, is small (the energy depends on the bubble size as $1/r^3$). Therefore, the criteria of reproducibility cannot be applied in my case. Instead, I used the criteria of “tight clustering” for homogenization temperatures measured on groups of inclusions associated with petrographically defined zones (FIAs).

c. Stretching of inclusions upon heating. Your comment on the temperatures of inclusions stretching upon overheating is quite important, and I definitely need to include the discussion of this matter in my report. As a matter of fact, I plan to perform an experiment, trying to “create” two-phase liquid-vapor inclusions from all-liquid ones. Presently I have observations on the behavior of inclusions which I heated trying to stretch them and generate bubbles to enable freezing experiments. Most of inclusions did not stretch upon heating to 200-250 ^oC, i.e., they did not nucleate bubbles and remained one-phase liquid (I hold some of my samples for 10-25 minutes at these temperatures). This applies equally to inclusions that initially were two-phase (T_h=35-70 ^oC) and those that originally were all-liquid.

This result seems to be in conflict with the H_2O phase diagram, which indicates that the pressure in such inclusions should increase very rapidly and be very high at 250 ^oC. It is also in conflict with common perception of the fluid inclusions in calcite as being susceptible to stretching upon slightest overheating. I suspect that calcite may accommodate very high internal pressures in inclusions through elastic deformations. Therefore, I feel that the time of overheating may be as important, or even more important than the temperature.

Inclusions that nucleated bubbles upon heating or freezing had quite irregular and typically high liquid-to-vapor ratios (see, e.g., Fig. 24 in my report).

c. No mention of necking-down. You are right, I did not mention that in my report. The reason is that I tried to avoid groups of inclusions which, on the visual basis, may have experienced necking-down or heterogeneous entrapment. Typically, results obtained by individual FIAs clustered within a 5-6 ^oC interval, therefore I did not feel it necessary to invoke necking to explain this (quite insignificant) spread. In three samples which yielded large scatter of the measured T_h's, I also measured inclusions which did not show indications of necking on the visual basis. And in one of these samples (see Fig. 18 in my report) I observed clear indications of mechanical twinning, which may account for the "disturbance" of inclusions.

Comment 3.
a. Spread of temperature. I am afraid that you were sent a xero-copy of my report, rather than original printout. Sorry, I could not control it, for during that time I was in Canada and then in Nevada. As I figured out, the different shades of gray which I used to represent each FIA on the histograms are not always recognizable on the xero-copy. I apologize for this. For four samples which do not show substantial scatter these data are:

Sample 2206 (Fig. 7):
FIA 1 – 49(1), 51(1), 53(2) – 3D group (white)
FIA 2 – 53(1), 54(1), 55(3), 54(2), 53(1) – low-angle plane (gray)
FIA 3 – 58(2), 59(7), 60(1), 62(2) – growth zone (black)

Sample 2220 (Fig. 17)
FIA 1 – 37(1), 39(2), 40(1), 41(1), 43(1) – growth zone (black)
FIA 2 – 36(3), 37(6), 38 (2) – low angle plane (dark gray)
FIA 3 – 36(1), 39(1) – 3D group (light gray)
Individual inclusions – 36(5), 37(4), 38(1), 43(2)

Sample 2222 (Fig. 23)
FIA 1 – 35(3), 36(5), 37(1)
FIA 2 – 36(1), 37(1)
FIA 3 – 37(6), 38(2)
FIA 4 – 35(5), 36(4), 37(1)
FIA 5 – 36(4), 37(1)

Sample 2226 (Fig. 34)

FIA 1 – 37(4), 38(5), 39(7), 40(2), 41(4) – growth zone (black)
FIA 2 – 37(1), 38(6) - low angle zone (gray)
FIA 3 – 39(3), 40(5), 41(1), 42(1), 43(2) - low angle zone (gray)

As you can see, some of my FIAs homogenized within 2 ^{o}C interval (e.g., sample 2222, FIA 3).

b. Possible influence of heterogeneous entrapment on data interpretation. As I indicated above, I did not use for thermometric studies groups of inclusions for which heterogeneous entrapment might have been suspected (see Comment 1-a in this letter). The higher-temperature samples, like 2206 and SS#85-86, yielded temperatures of 58-61 and 72-75 ^{o}C from FIAs of 8-12 individual inclusions. Taking into account these two facts, I believe I have reason to consider these "elevated" temperatures to be real (meaningful).

Strontium-isotope evidence. You are quite right, Sr data are not compelling. My purpose was simply to show that they are not in conflict with the upwelling model. I realize, however, that they may be interpreted (and, as a matter of fact, are interpreted by the U.S. Department of Energy researchers) differently. Generally, Sr in the bedrock tuffs is much less radiogenic than that in epigenetic calcites.

Note: Incomplete chart from page 15 of Appendix 1. Sorry about that. Copy is attached.

I hope I addressed most of your questions. Since your opinion on the non-compelling character of the fluid inclusion results seem to have been influenced by some technical failures from our part (poor quality of the copy sent to you, which made it impossible to see scatter for individual FIAs on histograms; may failure to mention the fact that I did not analyze groups showing potential of heterogeneous entrapment, etc.), I would like to ask you: does you opinion remains the same after you examined information provided in this letter? If I succeeded in clarification of the questions and problems you have had with my data, I would greatly appreciate if you could update you review. And of course, if you do not agree or not satisfied with my comments – please feel free to leave you review unchanged, or make more comments. The release of my report is scheduled for December 1st, so I still have some time to address them.

As a final remark, I would like to say that it was great pleasure to work with your review, which emphasized many points that either were inadequately addressed in my draft report, or that might have raised questions of a reader. I greatly appreciate your help!

Sincerely yours,

Yuri Dublyansky

Date: Thu, 26 Nov 1998 22:24:58 +0100
To: "Yuri Dublyansky" <kyoto_yuri@hotmail.com>
From: diamond@unileoben.ac.at (Larryn Diamond)
Subject: Re: Yucca Mtn Report

Dear Dr Dublyansky,

Thank you for the e-mail and FAX replies to my evaluation of your report. I find your points very interesting and mostly they answer the questions I raised in my evaluation. I have made some brief comments to your points, inserted into your text below (numbered 1,2,3...).

Dear Dr. Diamond:

Thank you very much for evaluating my report and examining two of my samples. I greatly appreciate your time and the thoroughness of your review. I would like to discuss some of your comments and provide clarification on the questions you raised.
Comment 1.
a. Contemporaneous liquid-vapor and all-liquid inclusions. I agree with your observation that there are apparently contemporaneous inclusions of both types; on several occasions I saw the same relationships. I should have and I will incorporate this observation in the report. (Most unfortunately, I have had only 3 weeks to do the original work at Bob Bodnar's lab and then only 4 days to compile the report; some of the deficiencies of the latter stem from this tight schedule). I need to point out (here, as well as in the report) that I never carried out thermometric studies on liquid-vapor inclusions associated with gas-rich or all-gas inclusions. All my numeric data are from groups with regular liquid-to-vapor ratio (determined on visual basis). Therefore, I do not think that I should worry about the possible influence of the heterogeneous entrapment on my numeric data.

(1) This answer does not really address the problem to which I was referring. See my point 9 below.

b. Phase which appears in all-gas inclusion upon freezing. You know, it seems unlikely to me that it was water, because it always had a rounded shape - whether I cooled or heated it. Quite possibly it was clathrate, as you suggested. I did not want to engage in much discussion on this matter before I have more data. We discussed with Bob Bodnar the possibility of analysis of this phase on Raman microprobe using cooling stage, and I plan to attempt this analysis as soon as I can (most unfortunately, during my 3-week stay in Blacksburg in October, Bob's Raman was out of order).

(2) I forgot to mention in my review that the reason that the solid comes and goes at different temperatures may be due to sublimation and Ostwald ripening of larger crystals. This is just a suggestion, but for example, each time you freeze the inclusion you may nucleate a different number of crystals at different locations in the inclusion. Then as you heat, the larger of these crystals should grow (by precipitation from the vapour) at the expense of the smaller crystals. Sometimes the larger crystals (the survivors) may be visible, and sometimes they may be hidden in the dark rims of the inclusions.

Comment 2.
a. Arbitrary elimination of temperatures. You are right, this is more or less arbitrary approach. However, when we speak of "tight clustering" of the temperatures measured from FIAs, or of "consistent results", don't you think that our judgements are equally arbitrary? Should we consider a 5 ^{o}C-interval of T_h's obtained from an individual FIA sufficiently "narrow"? Or 8 ^{o}C? Or 10 ^{o}C? For instance, Goldstein and Reinolds (1994) suggest: "For diagenetic applications, the class interval for Th's should usually be 5 ^{o}C" (p. 123). For some of my samples (e.g., Fig. 23), data measured on as much as 5 FIAs fell ENTIRELY within one class interval! Therefore, my approach to "disturbed" inclusion assemblages was like follows: to treat them not as "consistent", but as "moderately consistent" (terms of Goldstein and Reinolds, 1994). Since I did not observe indications of "creation" of the two-phase inclusions with visually similar liquid-to-vapor ratios from all-liquid inclusions by heating (see below my comment on inclusion overheating), I assumed that the same should apply to mechanical stress. In this case, I think, it is even more unlikely to "stretch" all inclusions in a group of all-liquid inclusions to produce two-phase inclusions showing similar liquid-to-vapor ratio. However, minor mechanical stress may slightly change the volume of already-two-phase inclusions;

this change, not recognizable visually, will lead to the scatter of the measured T_h's towards the higher temperatures. It is probably safe to consider the temperatures of 35-40 ^oC as not-altered, because they are so low that simply could not be lower. Again, I want to emphasize here (as I will do in the final report) that the data obtained on "disturbed" samples are considered as "suggestive" rather than "definite". I thank you for bringing up this point, because I now realize that I have to explain the rationale of my approach in the report.
b. Reproducibility of the homogenization temperatures. Most unfortunately, it is impossible to reproduce homogenization temperatures of my inclusions. It is inherent and unavoidable problem when working with so low-temperature material. Inclusions which homogenize at 35-50 ^oC virtually never heterogenize upon cooling, even when you cool them to <0 ^oC and hold them at these temperatures for weeks (back in Siberia, I try to do that once a while just putting my samples outdoor in winter). From 100 inclusions with Th of 50-70 ^oC, only one or two would, probably, heterogenize.

(3) This is clear to me now. I accept your explanation.

This holds true not only for the Yucca Mountain samples but for all samples of the low-temperature hydrothermal calcites I worked with during the last 18 years (e.g., samples from Hungary, Algeria, Italy, Central Asia, USA, etc.). Physical explanation for such behavior is: since the difference between T_h and $T_{ambien}t$ is small, the pressure drop upon cooling is not sufficient to overcome the thermodynamic barrier and create the bubble. This problem becomes even more significant if the size of inclusion and, respectively of a bubble which may appear in it, is small (the energy depends on the bubble size as $1/r^3$).

(4) I am familiar with this phenomenon. Initially I was not sure if it applied to your inclusions, hence the comments in my review.

Therefore, the criteria of reproducibility cannot be applied in my case. Instead, I used the criteria of "tight clustering" for homogenization temperatures measured on groups of inclusions associated with petrographically defined zones (FIAs).

(5) See my point 8 below.

c. Stretching of inclusions upon heating. Your comment on the temperatures of inclusions stretching upon overheating is quite important, and I definitely need to include the discussion of this matter in my report. As a matter of fact, I plan to perform an experiment, trying to "create" two-phase liquid-vapor inclusions from all-liquid ones. Presently I have observations on the behavior of inclusions which I heated trying to stretch them and generate bubbles to enable freezing experiments. Most of inclusions did not stretch upon heating to 200-250 ^oC, i.e., they did not nucleate bubbles and remained one-phase liquid (I hold some of my samples for 10-25 minutes at these temperatures). This applies equally to inclusions that initially were two-phase (Th=35-70 ^oC) and those that originally were all-liquid. This result seems to be in conflict with the H_2O phase diagram, which indicates that the pressure in such inclusions should increase very rapidly and be very high at 250 ^oC. It is also in conflict with common perception of the fluid inclusions in calcite as being susceptible to stretching upon slightest overheating. I suspect that calcite may accommodate very high internal pressures in inclusions through elastic deformations. Therefore, I feel that the time of overheating may be as important, or even more important than the temperature. Inclusions that nucleated bubbles upon heating or freezing had quite irregular and typically high liquid-to-vapor ratios (see, e.g., Fig. 24 in my report).

(6) These are all very revealing observations, and they would calm a lot of doubts (including my own) if you include them in your report.

c. No mention of necking-down. You are right, I did not mention that in my report. The reason is that I tried to avoid groups of inclusions which, on the visual basis, may have experienced necking-down or heterogeneous entrapment. Typically, results obtained by individual FIAs clustered within a 5-6 ^oC interval, therefore I did not feel it necessary to invoke necking to explain this (quite insignificant) spread. In three samples which yielded large scatter of the measured T_h's, I also measured inclusions which did not show indications of necking on the visual basis. And in one of these samples (see Fig. 18 in my report) I observed clear indications of mechanical twinning, which may account for the "disturbance" of inclusions.

(7) Good. I think it is important to mention in the report that you explicitly searched for evidence of necking-down and avoided inclusions which were suspect.

Comment 3.
a. Spread of temperature. I am afraid that you were sent a xero-copy of my report, rather than original printout. Sorry, I could not control it, for during that time I was in Canada and then in Nevada. As I figured out, the different shades of gray which I used to represent each FIA on the histograms are not always recognizable on the xero-copy. I apologize for this. For four samples which do not show substantial scatter these data are:
Sample 2206 (Fig. 7): FIA 1 - 49(1), 51(1), 53(2) - 3D group (white) FIA 2 - 53(1), 54(1), 55(3), 54(2), 53(1) - low-angle plane (gray) FIA 3 - 58(2), 59(7), 60(1), 62(2) - growth zone (black)
Sample 2220 (Fig. 17) FIA 1 - 37(1), 39(2), 40(1), 41(1), 43(1) - growth zone (black) FIA 2 - 36(3), 37(6), 38 (2) - low angle plane (dark gray) FIA 3 - 36(1), 39(1) - 3D group (light gray) Individual inclusions - 36(5), 37(4), 38(1), 43(2)
Sample 2222 (Fig. 23) FIA 1 - 35(3), 36(5), 37(1) FIA 2 - 36(1), 37(1) FIA 3 - 37(6), 38(2) FIA 4 - 35(5), 36(4), 37(1) FIA 5 - 36(4), 37(1)
Sample 2226 (Fig. 34) FIA 1 - 37(4), 38(5), 39(7), 40(2), 41(4) - growth zone (black) FIA 2 - 37(1), 38(6) - low angle zone (gray) FIA 3 - 39(3), 40(5), 41(1), 42(1), 43(2) - low angle zone (gray)
***** Attached is an Excel file which contains original data *****
As you can see, some of my FIAs homogenized within 2 ^{o}C interval (e.g., sample 2222, FIA 3).

(8) The data are much more understandable to me now. I agree that the individual fluid inclusion assemblages have very narrow T_h ranges, and this explains the spreads I assumed to be present in the poorly copied diagrams of your report.

b. Possible influence of heterogeneous entrapment on data interpretation. As I indicated above, I did not use for thermometric studies groups of inclusions for which heterogeneous entrapment might have been suspected (see Comment 1-a in this letter). The higher-temperature samples, like 2206 and SS#85-86, yielded temperatures of 58-61 and 72-75 ^{o}C from FIAs of 8-12 individual inclusions. Taking into account these two facts, I believe I have reason to consider these "elevated" temperatures to be real (meaningful).

(9) I am now convinced that the T_h values you report are meaningful. In particular, the range of 72-75 ^{o}C is very relevant to the Yucca Mountain repository issues. However, we may still disagree on what the "meaning" actually is. I do not view these homogenisation temperatures as representing "minimum entrapment temperatures". Rather, I think they represent the "exact" entrapment temperatures. The reason is that the calcite samples I looked at show evidence for a heterogeneous phase state during calcite growth. There are many fluid inclusion assemblages that show variable phase volume proportions, and these are spatially (and temporally in the growth sequence) close to fluid inclusion assemblages with constant phase volume proportions, be they all-gas or liquid-vapour. In my experience it is common to find all three types of assemblages when two phases coexisted in a vein environment. We can imagine that in two-phase system, pure end-member "liquid" may be trapped in some areas, pure end-member "gas" may be trapped in others, and mechanical mixtures of the two phases may also be trapped nearby.

Now if the two-phase state was prevalent during the period of calcite growth that contains the inclusions you measured, we must assume that the homogenisation temperatures of the liquid-vapour inclusions (representing the pure end-member liquid phase in the veins) is equal to the entrapment temperature, i.e. the isochores of the inclusions above T_h are meaningless. This deduction follows from the phase relations of immiscible fluids. The fact that you measured inclusions in assemblages with constant phase volume proportions does not change this interpretation. I therefore think you should state in your report that the T_h values as high as 72-75 ^{o}C represent the exact fluid temperatures during calcite precipitation. This does not greatly change the significance of your results for Yucca Mountain.

If you wanted to insist that the homogenisation temperatures are "minimum" entrapment temperatures, then I would suggest that you must prove that the liquid-vapour inclusions you measured are NOT saturated with respect to the hydrocarbons in the all-gas inclusions.

You may be already familiar with these arguments regarding heterogeneous entrapment, but if not, you may be interested to see the discussions in the following papers:

Diamond L. W. (1990) Fluid inclusion evidence for P-V-T-X evolution of hydrothermal solutions in Late-Alpine gold-quartz veins at Brusson, Val d'Ayas, NW Italian Alps. American Journal Science 290, 912-958.

Diamond L. W. (1994) Introduction to phase relations of CO_2-H_2O fluid inclusions. In Fluid Inclusions in Minerals: Methods and Applications (ed. B. De Vivo and M. L. Frezzotti), pp. 131-158. Virginia Tech.

Strontium-isotope evidence. You are quite right, Sr data are not compelling. My purpose was simply to show that they are not in conflict with the upwelling model. I realize, however, that they may be interpreted (and, as a matter of fact, are interpreted by the U.S. Department of Energy researchers) differently. Generally, Sr in the bedrock tuffs is much less radiogenic than that in epigenetic calcites.

Note: Incomplete chart from page 15 of Appendix 1. Sorry about that. Copy is sent by fax.

I hope I addressed most of your questions. Since your opinion on the non-compelling character of the fluid inclusion results seem to have been influenced by some technical failures from our part (poor quality of the copy sent to you, which made it impossible to see scatter for individual FIAs on histograms; may failure to mention the fact that I did not analyze groups showing potential of heterogeneous entrapment, etc.), I would like to ask you: does you opinion remains the same after you examined information provided in this letter? If I succeeded in clarification of the questions and problems you have had with my data, I would greatly appreciate if you could update you review. And of course, if you do not agree or not satisfied with my comments - please feel free to leave you review unchanged, or make more comments. The release of my report is scheduled for December 1st, so I still have some time to address them.

(10) I think it is clear from my comments in this message where I agree or do not agree with your explanations. If you find it necessary for me to update my review, I would have to read the new version of your report first. I do not know if there is time for that, in view of your December 1st deadline. Perhaps you can discuss the question with Dr. Arjun Makhijani, since he is paying me for my time.

As a final remark, I would like to say that it was great pleasure to work with your review, which emphasized many points that either were inadequately addressed in my draft report, or that might have raised questions of a reader. I greatly appreciate your help!

Sincerely yours,
Yuri Dublyansky

(11) One last point: could you please confirm that the samples you sent me have not been heated already during microthermometry. I just want to be sure.

Please write back to me if the comments I have made here are not clear to you.

Good luck with the revisions. By the way, you will receive essentially the same comments from me in my review of your manuscript submitted to Chemical Geology.

Best regards,
Larryn Diamond

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Review of: Y. V. Dublyansky, "Fluid inclusion studies of samples from the exploratory study facility, Yucca Mountain, Nevada" - draft version.

This report is primarily concerned with the results of a fluid inclusion study of vein and cavity-lining calcite from the ESF.

Calcite is a less robust host for fluid inclusions than some other minerals, but considerable care has been taken during sample preparation to avoid possible leakage. I consider that the procedures followed accord with best practice, and the results are quite distinct from those that would result if damage had occurred during preparation.

The procedures followed for data acquisition accord with best practice and the data presentation and interpretation are clear and consistent. The distribution of homogenisation temperatures obtained for individual samples and for the suite as a whole are consistent with the interpretation presented, and in particular the well clustered homogenisation temperatures of L-V inclusions are typical of warm water trapped originally as a single phase, rather than accidentally trapped mixtures of liquid and air liquid-only inclusions are typical of low salinity fluid trapped at sufficiently low temperatures that a vapour bubble fails to nucleate on cooling down to the freezing point. There is no simple rule for estimating the maximum of trapping from which this metastable behaviour may result, but small inclusions trapped at temperatures as high as 80°C may nevertheless display this behaviour.

The report marshals a number of other arguments in support of a hydrothermal, rather than pedogenic, origin for the calcite: presence of fluorite and especially quartz, homogeneous stable isotope composition and presence of hydrocarbons. These interpretations are soundly based by comparison with results from geothermal systems in my opinion.

Bruce Yardley
12th November 1998

COMMENTS ON THE REPORT
"FLUID INCLUSION STUDIES OF SAMPLES FROM THE EXPLORATORYSTUDY FACILITY, YUCCA MOUNTAIN, NEVADA"
from Dr. Yuri V. Dublyansky

This report contains two parts, one corresponding to results obtained before june 1998 and additional results obtained in june 1998.

This report demonstrates clearly a very careful and high quality work on natural samples which are not easy to study.

The second point concern the detailed description of the samples at all the scales: bedrock, field scale, mineralogical and textural descriptions, and finally the petrography of the fluid inclusions. Most of descriptions are supported by photographs.

The microthermometric study is also very carefully conducted in such a manner it can never overestimate the homogenization temperatures, which are the critical parameters for the estimation of the minimum temperature of fluid trapping or fluid palaeo-circulation. Consequently, values obtained by this microthermometric study can be trusted and stronlgy favour the interpretation of circulation of ascending "hot" waters in the past.

More generally, it is worth noting that descriptions are strictly disconnected from the interpretation, which allows the reader to make his own interpretation and to compare it with the interpretation of the author. The reviewer appreciated also the citations from previous works which favoured the vadose hypothesis.

U and Th isotopic dating of calcite gives an age consistent with previous dating carried out with the same method by other authors. These data are preliminary and much more data, coupled with microthermometric studies and detailed calcite geochemistry, are required for identifying the different fluid pulses.

Stable isotope data demonstrate the absence of variations typical of climate changes.

About the use of the UV luminescence (under which wavelength ?) for the identification of hydrocarbons, I have a minor disagreement with the author. The absence of fluorescence does not mean necessarily the absence of hydrocarbons because alkanes do not exhibit fluorescence under excitation with radiations around 300 nm. However, I admit that strictly alkane oil is scarce because oil contains usually fluorescent species (aromatic, etc...), even at low concentrations.

The dicussion is well conducted and compares the data with the vadose hypothesis. However, it is clear that the data given in this report validate the hypothesis of ascending <<hot>> fluids. It is worth noting that more recent observations, including crush experiments, support the previous interpretation and gives more constraints on fluid temperature circulation up to 75 ˚C.

I fully agree with the recommendation of the autor for further studies in order to establish the timing and extent of fluid migration within the presently unsaturated zone of Yucca mountain. However, the main question of interest for waste disposal repository, which arises from this careful study but which could not be solved at this stage, is the following: could these circulations of fluids, probably originating from underlying Paleozoic sedimentary rocks, percolate again through Yucca mountain ? This addresses also the question of the estimation of potential fluid reservoir in these Paleozoic sedimentary rocks.

In conclusion, the report of Dr. Yuri Dublyansky contains high quality data, their interpretation is reasonable and indicates the additional ways of research for a better characterization of these <<hot>> paleo-fluid circulations.

Vandœuvre, 4 th of november, 1998

Jean Dubessy
Director of Research at CNRS

Comments on
"Fluid Inclusion Studies of Samples from the Exploratory Study Facility, Yucca Mountain, Nevada"

by Yuri V. Dublyansky

October, 1998

Prepared at the Request of the Department of Energy

Jean S. Cline
Associate Professor
University of Nevada, Las Vegas

November 5, 1998

Introduction

These comments address three microthermometric studies conducted by Yuri Dublyansky and described in a report on samples from the Exploratory Study Facility at Yucca Mountain, Nevada. The first study was conducted on samples collected at Yucca Mountain in 1995; these samples were evaluated at the Institute of Mineralogy and Petrography in Novosibirsk, Russia. The second study was conducted on the same sample suite, but at Virginia Polytechnic Institute (VPI) in Blacksburg, Virginia, in the Fluids Laboratory of Robert Bodnar, in June, 1998. The third study was conducted at VPI in October, 1998, and evaluated samples collected at Yucca Mountain in June 1998.

Summary of Data

Section 2 of the report describes the methodology employed during the third study conducted at VPI in October, 1998. The homogenization and freezing techniques described are appropriate for these samples and should preclude or minimize stretching of inclusions during collection of microthermometric data. These methods include heating each chip and monitoring all inclusions during a single heating run to obtain homogenization temperatures. Heating experiments were conducted prior to freezing experiments so that inclusions were not stretched prior to heating by fluid freezing. In addition, prior to freezing experiments, inclusions were artificially stretched so that vapor was present during ice melting and correct ice melting temperatures could be determined. The methodology used in the Novosibirsk study is not described.

The first two pages of section 4, which summarizes fluid inclusion results, presents microthermometric data collected in both Russia and at VPI on six samples collected in 1995. No descriptions of samples or inclusions are provided. The data generally show two ranges of homogenization temperatures. All six samples contained inclusions which homogenized between 25° and as high as 55°C (modes generally at 30° to 35°C). Five of the six samples have inclusions that homogenized between 60° and 90°C, plus one additional data point occurs at 110° to 115°C. The lower temperature data show fair to good consistency for the six samples; the high temperature data are consistent in a 20-point data set in sample SS#85-86, but are less consistent and there are fewer data points (1 to 4) for remaining samples.

The next 17 pages of the report provide data on the third fluid inclusion study of ten samples collected in June, 1998. Each sample is described, as are identified minerals. Fluid inclusion discussions list the various inclusion populations present, and describe inclusions as occurring along growth zones, along planes, or in three dimensional arrays. Homogenization temperatures for each inclusion group are provided in histograms, and successful and unsuccessful attempts at determining a small number of ice melting temperatures are described.

In summary, these ten samples were collected from a variety of physical locations including: high angle and vertical fractures, lithophysal cavities, calcite cemented breccias, and low angle veinlets. All samples contain principally calcite; many samples contain opal, dispersed within or forming layers in the calcite. Some samples contain rare to trace fluorite and quartz. Additional minerals identified, generally in association with basal tuff or in calcite adjacent to the tuff, include alpha quartz, tridymite, and hematite(?).

All samples, except possibly 2226, contain liquid-only inclusions. In sample 2217, liquid inclusions are described as occurring in outer, blocky calcite. No further descriptions are provided for liquid inclusions. Seven of the ten samples are described as containing abundant vapor inclusions. In sample descriptions for which the locations of vapor inclusions are noted (2217, 2222, 2226), they are described as occurring in calcite near the calcite-tuff contact. The single exception is sample 2220, in which vapor inclusions occur throughout the calcite. This sample is described as being unique in this respect.

Seven of the ten samples have inclusions containing liquid plus vapor which are suitable for microthermometry. It is unclear whether or not the remaining three samples do not contain liquid plus vapor inclusions, or whether liquid plus vapor inclusions are present, but not suitable for microthermometry. These inclusions are described as occuring along growth zones, along planes (sometimes further described as secondary inclusions in fractures), and distributed in three dimensions in the calcite. Homogenization temperatures range from 29° to 61°C and most inclusions homogenize at lower temperatures. Many, but not all, samples have restricted ranges of data; this is especially true for some inclusions that lie within planes or growth zones. In samples 2220, 2222, and 2226, inclusions exhibit tight ranges of homogenization temperatures, all of which are below 50°C. Sample 2224 contains inclusions, all of which homogenize at temperatures less than 50°C, but these temperatures show a 16° temperature range. Samples 2217 and 2221 exhibit some homogenization temperatures greater than 50°C, but Dublyansky recommends ignoring the higher temperatures owing to the large spread of a small number of data points. Sample 2206 contains homogenization temperatures which range from 47° to 61°C. Restricted temperatures were obtained for inclusion groups: inclusions in growth zone, 57° to 61°C; inclusions in a plane, 52° to 57°C; and inclusions in a three-dimensional array, 49° to 53°C. In sample 2217, liquid plus vapor inclusions are described as occurring in calcite near the tuff contact. Homogenization temperatures for these inclusions range from 41° to 58°C. No other inclusion locations within the samples are provided.

Ice melting temperatures were obtained for four inclusions in 2217. These temperatures, -0.3°, -0.4°, -0.9° and -0.95°C, indicate very low fluid salinities. Additional attempts at freezing studies were not successful, and temperatures in the positive range indicated the metastable presence of ice. Collectively, freezing studies suggest that fluids are nearly pure H2O.

In the summary discussion of the fluid inclusion data, Dyblyansky points out that the two samples that contained the highest temperature data, samples 2206 (just described) and SS#85-86 (from the first and second studies) were collected from Tiva Canyon tuff in the eastern part of the exploratory block, close to the Paintbrush Fault zone.

Section 5 describes an effort to date four calcite samples. Only one of these samples (SS#45-46) provided a date. There is no description of the material analyzed, or relationship of analyzed material to fluid inclusions.

In appendix 1, the second study, a reevaluation at VPI of samples collected in 1995, is summarized. Vapor inclusions in SS#85-86 were studied using UV-luminescence, crushing, and Raman spectrometry. These analyses were interpreted to indicate that inclusions do not contain liquid hydrocarbons, have internal pressures of < 1 atmosphere, and contain aromatic hydrocarbons. Microthermometric data were collected on liquid plus vapor inclusions in SS#85-86; homogenization temperatures range from 71° to 75°C for 8 inclusions, and 2 additional inclusions homogenized at 80° and 82°C. Dublyansky notes that these data were collected from stratigraphically early calcite (calcite near tuff), whereas, data collected in Novosibirsk during the first study, were collected from the outer part of the calcite. This study produced homogenization temperatures of 25° to 40°C for 8 inclusions, plus two inclusions that homogenized at 70° to 75° and 80° to 85°C.

Discussion of Data

The fluid inclusion data that are presented do not lend themselves to a simple interpretation. This is because of the presence of three inclusion populations. If only liquid and vapor inclusions were present, a logical interpretation would be that the inclusions trapped immiscible fluids. However, the presence of liquid plus vapor inclusions that exhibit consistent homogenization temperatures suggests that a homogeneous fluid with an elevated temperature was trapped by these inclusions. If this interpretation is correct, this suggests that the three inclusion populations were trapped at different times during the growth of the calcite crystals.

Descriptions of inclusion locations for four samples indicate that most vapor inclusions were trapped in the paragenetically older part of the calcite crystals (2217, 2222, 2226). A few of these inclusions are interpreted to be primary; the origin of most vapor inclusions is not given. These descriptions suggest, but do not prove, that the trapped vapor phase may have been present when the first parts of the crystals grew. During later crystal growth either this phase was not present or it was not trapped. The presence of vapor inclusions throughout the calcite in 2220 may reflect a greater volume of early calcite, or, trapping of spatially restricted vapor at a later time.

Liquid inclusions are abundant and, in sample 2217, were trapped in the outer blocky, sparry calcite. The locations of liquid inclusions in other samples, and the origin of liquid inclusions are not given. Thus, few constraints can be placed on the timing of trapping of these inclusions. The inclusions in outer calcite in 2217 must be relatively late, paragenetically.

Liquid plus vapor inclusions suitable for microthermometry are rare in all samples in which they are present. Their location is given only for samples 2217 and SS#85-86, in which they occur in paragenetically older calcite near the tuff. Inclusion occurrences within growth zones, along planes and in three dimensional arrays suggests that inclusions are both primary and secondary. More information on the location of these inclusions within the calcite crystals is necessary to place age constraints on the inclusions, however, there is at least a suggestion that some of these inclusions may have been trapped early.

In summary, these observations and data suggest, but do not conclude, that the vapor, and vapor plus liquid inclusions may have been trapped when the earlier parts of the calcite crystals were growing. Liquid inclusions may have been trapped during growth of the outer, younger parts of the crystals. A detailed paragenetic study which documents the locations and origins of all inclusions is necessary to understand the temporal relationships of these inclusion populations. A better understanding of the location and distribution of each inclusion population with respect to other populations is also needed. Without greater paragenetic control on the described inclusions, it is not possible to determine their timing or origin. A model which explains and describes the trapping of *all* inclusion populations is necessary for complete understanding of the physical and chemical conditions during the formation of these crystals.

Liquid plus vapor inclusions, in all samples in which they occur, indicate minimum elevated temperatures as high as approximately 40°C (a few samples indicate higher temperatures). These elevated, but still low homogenization temperatures may reflect temperatures of fluids which were greater than ambient temperatures when trapped, or they may indicate temperatures related to the geothermal gradient. A study should be conducted to determine overburden thicknesses, the possible depth to sample sites over the past 12 million years, and the geothermal gradient during that time, to learn if the geothermal gradient can explain these elevated temperatures. Two samples exhibit consistent homogenization temperatures that reach 61° and 75°C. The highest temperature inclusions (SS#85-86) are described as being located in the paragenetically older portion of the calcite. Dublyansky notes that both of these samples were collected from near the Paintbrush Fault. These data do suggest that fluids with elevated temperatures were present and were trapped by these inclusions. Additional work is needed to identify the timing of formation of these inclusions as well as their spatial distribution in each sample and the extent of these inclusions within the ESF, to determine the significance of these inclusions with respect to the siting of the repository.

Two additional minor comments follow.

1. There is no description of the sample that was dated and no relationship to fluid inclusions or homogenization temperatures is provided. Thus it is not possible to evaluate the results.
2. I am not familiar with the selective absorption analyses that were conducted in Russia and I question analyses that rely on a visual estimate of the shrinkage of the vapor bubble.

Comments from Prof. Derek C. Ford

McMaster University, Hamilton, Ontario, Canada

Dear Yuri,

I have been over the work with Nicki and here are my comments on the USGS remarks. I have sent you by FAX a copy of the print-out for that result and an outline of our standard operating procedure in the clean room.

Points are as follows:

1/ The USGS is correct to write that it is wrong to attribute the failure of analyses of 30-31, 39-40 and 58-59 to too high detrital thorium. My fault entirely - I was writing to you and to Andrea Borsato on a day when I was also completing moving house and I became confused. For Andrea I was dating speleothem calcites and calcite cements in Quaternary fanglomerates. The cements all failed because of very high 232Th contents; his speleothems were fine.

Your samples simply failed to run sufficiently strongly during the thorium measurement stage on our VG354 mass spec for a statistically sound calculation of their ages. One was close but the program rejected it. This happens quite often with low U speleothem calcite samples in our experience. We can say no more than that. It is very annoying because a great deal of work is wasted.

2/ The analysis was carried out by Mrs Nicki Robinson, who has worked as our U technician since 1981. She is very experienced in the extraction work but has only recently been running the mass spec. Previously she was in charge of all our alpha-counting U analysis. Spiking, digestion and chemistry procedures are noted in the Extraction flowsheet Faxed to you. We use a Class 100 clean room and all acids are double-distilled. We cannot report yet on the reagent blanks; they are programmed into a new program by Lauritzen and Lundberg (my former students) that was prepared and checked on the Finigan mass spec at Bergen. We can't unscramble it here. We have asked Joyce (Lundberg) for the details.

3/ The successful sample, 45-46, was in three layers totalling ~10 mm in thickness. You requested separate analyses of each layer if possible. This was not possible because the total amount of sample was small and we anticipated (from previous alpha analyses of Yucca Mtn calcite powders supplied to us by Carol Hill) that the U content would be low. Nicki found that the sample was "very crumbly" and so separation of the layers would not have been easy in any case. She dissolved the entire sample in 7.5M HNO3 and reported that there was no insoluble residue.

4/ The total weight of sample consumed was 4.5945 gm and 0.484 gm spike was added to the solution. I do not accept the USGS contention that most of the U in the solution must have come from any quartz dissolved because the U conc of pure calcite is 0.01 to 0.05 ppm - we are not dealing with pure calcites in most subaerial environments. Most speleothem calcites (with which I have vast experience now) score between 0.05 and 0.5 ppm U and are entirely devoid of quartz. Some have as much as 100 ppm U.

Sample 45-46 was ~10 mm thick, with an uneven 1-2 mm layer that you identified as quartz at the base. There was no sign of any weathering between the individual layers, implying a more or less continuous sequence of growth to me. The age obtained, 169+/-13 ka, thus applies to a point at 5 mm above the base in the mean. If corrections are made for the density of quartz and for higher U content in the quartz, the effect is to move the applicable point closer to the base, i.e. to make the whole sample a bit younger, perhaps. It is difficult to imagine the base of that sample being as old as 1 million years or thereabouts (ages described by USGS as characteristic) if the age we obtained is correct.

5. I am not qualified to comment upon initial 234U/238U ratios and their interpretation in this specific region. I have worked on thermal water and meteoric water phreatic calcites and on vadose meteoric water calcites, precipitated in caves all over the world. Most of the initial ratios I have encountered have been at or below 2. The 1.764 in SS 45-46 is not exceptional in global terms.

6. To write " ...the 160 ka date, meaningless as it is....." is a prejudiced statement. That age result is internally consistent. It would seem to me that the proper procedure is not to ridicule it but to revisit it; have the USGS lab analyse it and also some third party lab also.

Derek Ford

Department of Energy
Office of Civilian Radioactive Waste Management
Yucca Mountain Site Characterization Office
P.O. Box 30307
North Las Vegas, NV 89036-0307

NOV 13 1998

Dr. Arjun Makhijani
Institute for Energy and Environmental Research
6935 Laurel Avenue, Suite 204
Tacoma Park, MD 20912

Dear Dr. Makhijani:

Lake H. Barrett asked that I arrange for reviews of Yuri Dublyansky's draft on fluid inclusion sampling from Yucca Mountain and forward them to you.

The reviews were conducted by two groups:

1. Dr. Jean Cline of the University of Nevada, Las Vegas, is an acknowledged expert on the techniques and interpretation of fluid inclusion studies. Dr. Cline has had no previous involvement with the Yucca Moutain Site Characterization Project, but we are discussing the possibility of her heading up an independent study of these features and deposits.
2. The second set of reviews is from a team of U.S. Geological Survey geologists. Members of this team have been dealing with this issue for over a decade.

Enclosed is the set of reviews by the team of U.S. Geological Survey geologists. Dr. Cline will forward the results of her review directly to you in the near future.

I trust this information will satisfy your needs. Feel free to use or distribute this information as you wish. Please do not hesitate to call me at (702) 794-1300 if I can be of further assistance.

Sincerely,

for J. Russell Dyer
Project Manager

PM:JRD-0310

Enclosure:
As stated

cc w/encl:
J. S. Cline, UNLV, Las Vegas, NV
Zell Peterman, USGS, Denver, CO
L. H. Barrett, DOE/HQ (RW-1) FORS
Records Processing Center = "14"

MP-5

MEMORANDUM

November 9, 1998

To: Dennis Williams, Yucca Mountain Project, DOE

Through: Bob Craig, Chief, Yucca Mountain Project Branch, USGS

Through: Zell Peterman, Chief, Environmental Science Team, USGS

From: Joe Whelan, USGS

Subject: Review of Yuri Dublyansky's reports entitled "Fluid inclusion studies of samples from the Exploratory Studies Facility, Yucca Mountain, Nevada" and an attachment entitled "Fluid inclusions in calcite samples from the ESF, Nevada Test Site, Nevada

The attached is a compilation of review comments from James Paces, Brian Marshall, Zell Peterman, John Stuckless, Leonid Neymark and Joe Whelan of the USGS and Edwin Roedder of Harvard University. In the subject reports, Dr. Dublyansky claims that (1) the secondary mineral assemblages are not compatible with ambient formation temperatures; (2) fluid inclusion temperatures as high as 75°C and internal pressures of gas-rich inclusions support formation of calcite from upwelling, hydrothermal solutions (3) the ages of the calcite containing the fluid inclusions are young; (4) volatile organic compounds, suggestive of oil generation, are present in the inclusions; and, (5) the stable carbon and oxygen isotopic compositions of the host calcite are incompatible with unsaturated formation.

In reviewing this report, we were disturbed by Dr. Dublyansky's shrewd and nonscientific arguments that seem to be crafted for readers unfamiliar with the specific Yucca Mountain geologic relations or the intricacies of specific analytical techniques being discussed:

- Poorly substantiated conclusions are presented as established facts.
- Data used to support his contentions are carefully selected whereas conflicting or refuting data are ignored
- He postulates a false corollary to someone else's hypothesis, then demonstrating that the corollary is false, concludes that the hypothesis is incorrect.
- Important spatial or temporal relationships (which are critical in geologic investigations) are misrepresented or ignored to confuse those unfamiliar with the subject matter.

Our most serious objections to Dr. Dublyansky's arguments for periodic and relatively recent upwelling of "hydrothermal" fluids are summarized below:

- What is meant by "hydrothermal"? In typical usage, it is restricted to fluids with temperatures greater than 50°C; whereas here it seems to apply to minerals formed at temperatures as low as ~30°C, or any temperatures higher than present ambient values.
- If an ~75°C hydrothermal event took place, why is it recorded in only one occurrence out of the 24 samples that Dr. Dublyansky has examined? Such an event should have left its mark on many different occurrences and affected most of the calcite already present at that time.

ENCLOSURE

- A large data base of published and available ages for the timing and rates of formation of the secondary mineralization is ignored, even though the reports that contain these data are cited. This data set, as a whole, clearly shows that the bulk of calcite present, and probably that which hosts the supposed "hydrothermal" fluid inclusions, is so old that it is of no consequence to the future performance of the potential repository.

- Dublyanski asserts that flowstone formed in caves is a reasonable analog for Yucca Mountain secondary minerals. In spite of having read the USGS reports, he either chooses to ignore our interpretation or displays poor scholarship when he argues that perceived differences between cave mineralization and that in the Yucca Mountain unsaturated zone precludes formation of the unsaturated zone deposits from descending meteoric waters.

- Calculations of the $\delta^{13}C$ and $\delta^{18}O$ for calcite are based on questionable assumptions and assertions, and $^{87}Sr/^{86}Sr$ values of unsaturated zone calcite and regional ground water are grossly misused to argue that the calcite formed from upwelling water.

- Crushing experiments, which determine the internal pressure of fluid inclusions, are said to provide strong evidence for the hydrothermal hypothesis. However, when properly interpreted, they offer strong evidence that the calcite formed in an unsaturated zone, or vadose, setting.

Although we question Dublyansky's science and biases, we cannot reject his fluid inclusion data out of hand. Despite the fact that calcite is a notoriously difficult mineral for fluid inclusion studies, those difficulties are surmountable with care, and Dublyansky claims to have taken all reasonable precautions in conducting his studies. The fluid inclusion data should therefore, be verified; the paragenetic relations of any two-phase inclusions found should be described; and the timing of their formation should be constrained by isotopic dating of the host minerals.

Review of "Fluid inclusion studies of samples from the Exploratory Studies Facility, Yucca Mountain, Nevada"

by Yuri Dublyansky

Comments from Joe Whelan, James Paces, Brian Marshall, Zell Peterman, John Stuckless, Leonid Neymark (USGS) and Edwin Roedder (Harvard University)

Compiled by Joe Whelan

As with previous reports arguing for upwelling of heated groundwater into the unsaturated zone at Yucca Mountain, this is not a scholarly investigation. Strong but careless conclusions are drawn from offhand observations and possible interpretations of data are presented as established fact with no effort to objectively consider plausible alternatives.

The comments below focus on points or arguments that seem unclear, on interpretations that seem to be poorly rooted in reliable data or clearly ignore conflicting evidence. We have consciously tried to ignore errors that may have resulted from an unfamiliarity with English or which probably represent minor typographical or proofreading mistakes. Numbered comments below are keyed either to numbers in the margin of the included text or to section headings.

Section 2. Technical details on sampling...

1. Stretching of Inclusions - Here it is stated: "The fact that fluid inclusions with homogenization temperatures as low as 35°C were preserved in the prepared sections indicates that during the preparation, the samples cannot have been exposed to temperatures higher than 34°C". Although the concept is correct and significant, the statement is wrong. Fluid inclusions normally stretch only by heating above their temperature of homogenization (Th), not below. But on heating above Th, inclusions in calcite may stretch with as little as 10 degrees of overheating. This is because each degree over T_h increases the internal pressure in the inclusion by about 12 atmospheres, and about 100 atmospheres is generally sufficient to cause the host calcite to stretch or decrepitate. Dublyansky is obviously aware of this process, but nowhere does he address the major problem presented by his own homogenization data. We address it in more detail under Item #7.

2. "Disturbed" Inclusions - We are curious as to how the criteria for "disturbed" and undisturbed fluid inclusions are implemented. Several of the samples described fit the definition of significant scattering of T_h values, and the author suggests that in some instances T_h values from these samples that are above a minimum T_h (as low as >40°C) are suspect. If some inclusions in a sample are suspected of being disturbed due to stretching or leaking, why aren't all of the inclusions in that sample suspect? Especially when the same sample contains myriad all-liquid inclusions indicating low formation temperature.

Section 3. Occurrences of calcite in the ESF

3 "Tectonic Cavities" - By "tectonic cavities" we presume that the author means fracture cavities where intersecting fractures or dilation of individual fractures has produced open cavities in the tuff. In the photo (Fig.2), he notes that the calcite is coating the floor of the cavity. He makes the same observation for lithophysal cavities (Fig. 4) and further on (p. 8, sample 2206) he observes that his sample came from "...the footwall of the [fracture] opening...". Although Dublyansky apparently does not draw the same conclusion, we take this restriction of secondary minerals to the floors of cavities and the footwalls of fractures as conclusive evidence that the minerals formed in an unsaturated zone setting. This is in direct contradiction to his arguments that the fluid inclusions in these minerals require past upwelling of hydrothermal fluids and at least locally saturated rocks. Certainly such upwelling fluids would precipitate calcite and/or opal around the entire periphery of cavities and on both walls of fractures. This is an example of ignoring an obvious spatial relation.

4. Fracture Pathways - Dublyansky states that "... thin fractures, intersecting these [lithophysal] cavities, if present, do not contain calcite." This is contrary to our experience based on line surveys of ~2500 meters of secondary mineralization and collecting from nearly 300 secondary mineral occurrences. In general, we commonly observe mineralized fractures both above and below mineralized lithophysal cavities.

Section 4. Fluid inclusion results

5. Distribution of T_h - The homogenization temperatures reported by Dublyansky, especially from the 1995 data set, are apparently bimodal with modes near 35°C and 75°C. Are these two modes from different generations of calcite? Do they occur together? The lower temperature inclusions would have to be later because otherwise they would have been altered by the later event, but Dublyanski never comments on this problem. Here, and throughout the report, the reader is left to wonder what portion of the long depositional history of calcite formation was sampled; i.e., what part of the paragenetic sequence hosts the inclusions? What are the spatial and temporal relations? Without paragenetic description, it is impossible to either relate the data to the 9-m.y. history of unsaturated zone calcite deposition, or to assess its significance to site performance. For example, figure 7 plots three different fluid inclusion types but the reader is told nothing about their spatio-temporal relations to each other or to the sequence of mineral deposition at this sample site. This deficiency underscores the need to describe the fluid inclusion assemblages within a paragenetic context and to then place geochronological constraints on the fluid inclusion assemblages whenever possible.

6. Resetting of T_h? - Dublyansky's descriptions of the fluid inclusion assemblages present in his samples are consistent with our observations in this respect: he finds abundant all-liquid inclusions, common all-gas inclusions, and only rarely does he encounter 2-phase, liquid-plus-gas inclusions. This raises a number of questions that he ignores. First, he doesn't explain the numerous all-liquid inclusions coexisting with the rare 2-phase inclusions. Second, where he finds 2-phase inclusions that indicate "elevated" temperatures and which occur other than at the base of a mineralization sequence, why hasn't that thermal event affected the paragenetically older, all-liquid, inclusions present in the sample. He presents histograms showing the T_h of inclusions in 13 samples. In each of these samples, there is a range of values. The difference between the highest and lowest values for each given sample ranges from 4 to 85 degrees Celsius, and averages 28 degrees Celsius. Unless all inclusions were formed in the order of their T_h values, from hottest first to coldest last, the lower temperature inclusions should have "stretched".

Calcite-hosted all-liquid inclusions are extremely susceptible to "stretching", enlargement of the inclusion cavity, by increase of internal pressure during heating. This is why great care is taken to prevent thermal stressing during preparation of plates for study of calcite-hosted fluid inclusions. Dublyansky says that some higher temperature two-phase inclusions were found near the tuff, at the base of the calcite, but presents no paragenetic data for most of his samples. Yet Dublyansky also reports that single-phase, all-liquid inclusions are common in most of these samples, and Roedder and Whelan have reported that they can be found even near to the tuff substrate. Such all-liquid inclusions would be the first to stretch on even gentle warming. So the higher temperature data present a paradox. In this connection it is important to note that when ALL his T_h data are plotted, they show a relatively smooth, unimodal curve, with a very strong mode at about 35°C, a sharp drop to 1/10th the number of data by 50°C, and a long "tail" out to 130°C. Similar higher-temperature "tails" have been reported in many fluid inclusion studies, and are generally attributed to sample and/or laboratory irregularities, rather than to real temperature variations.

Taking the sample SS#85-86 as an example, if a hydrothermal environment existed which precipitated calcite at 75°C in the Tiva Canyon Tuff, this event should have reset the all-liquid inclusions present in the pre-75°C stage calcite of that sample. Indeed, such an event could realistically have reset all of the pre-existing, calcite-hosted, all-liquid inclusions present in the unsaturated zone at that time. Because this would be a powerful argument for the hydrothermal scenario, we presume that Dublyansky would have emphasized this relationship, were it present. Since he didn't, it seems likely that older all-liquid inclusions in this and other samples have not been reset and, therefore, it is unlikely that a hydrothermal event ever occurred.

Alternatively, there may be no all-liquid inclusions that pre-date the higher temperature inclusions. In this case, the 2-phase inclusions must be early in the paragenesis, probably at least 8 m.y. old, and of no consequence to the recent or future hydrologic regime of the potential repository. Again, we are left to ponder the possible spatio-temporal relations.

7. Paragenesis of Fluorite - Dublyansky's statement that "Colorless and violet globules of *fluorite* are associated with the latest stages of calcite growth." is misleading. We have seen occurrences of fluorite visible through calcite coatings but to argue that this is "late" calcite is not warranted; calcite deposition in the unsaturated zone is extremely slow, and the calcite coating the fluorite may also be millions of years old. Inasmuch as the author later goes on the claim that the fluorite is a hydrothermal phase, he is here trying to set the stage to argue for recent hydrothermal activity. This provides two assertions of facts that are incorrect: 1) fluorite is probably not late, and 2) fluorite does not require high temperature to form.

8. Sample 2217 - Here Dublyansky reports that "...two-phase gas-liquid inclusions are rare. They are restricted to zones of calcite closest to the tuffaceous substratum." This description provides the sort of paragenetic information largely lacking elsewhere in the report, as well as probably indicating that the homogenization temperatures, at least in this sample, are immaterial to recent unsaturated zone hydrology and, therefore, to performance assessment.

9. Freezing Metastability - In the discussions of freezing temperatures, the author states that freezing temperatures above 0°C are "from metastability" or "metastable ice melting". Based on his descriptions of the tested inclusions, this statement is wrong. Metastability commonly occurs during freezing temperature determinations, yielding temperatures above 0°C, but only when a vapor phase is not present. The nature of the inclusions run shows that vapor phase must have been present during the "metastable" tests. We suggest that the reports of temperatures over 0°C

could result from either calibration errors or instability (not metastability) from too-fast warm-up.)

10. Paintbrush Fault – The Paintbrush Fault is at least 2 km east of these samples. It seems unlikely that upwelling along this fault could explain higher elevation deposits to the west. Perhaps Dublyansky intended to invoke the Bow Ridge Fault, which is in closer proximity to the samples, even though underground exposures of the fault show no evidence of hydrothermal alteration. In either case, this provides an example of trying to misrepresent geologic information to those unfamiliar with the Yucca Mountain area.

Section 5. Age of calcite from the ESF

Paragraph 1: A "hydrothermal origin" has not been proven through the fluid inclusion studies described in this report. The evidence remains equivocal at best.

Paragraph 2: Our analytical experience with subsurface calcite and opal has shown that when the samples are carefully prepared prior to subsampling (removal of rock powder from the outer surfaces that has accumulated as a result of the mining procedures) there is usually no problem in obtaining elevated ^{230}Th/^{232}Th activity ratios (>20). Exceptions to this are when the total uranium is very low (less than several nanograms) or when samples are very young (less than ten to thirty thousand years in age). It is curious, then, that three of the four samples "failed because of high content of detrital thorium." This quotation is untrue; otherwise, it could not be stated. The analyses must have been successful in order to know that ^{232}Th contents were too large to calculate a meaningful ^{230}Th/U age. This is presumably not an analytical problem, but a sample deficiency. Therefore, the results from the three samples that yielded large ^{232}Th contents should be published along with the preferred sample results. This way, the reader can gain additional information about the natural system and the analytical methods as well as gaining proof that the authors are not being misleading by selecting only the results that support their preconceived ideas.

Results of SS#45-46: The methods and results are inadequately described. The reader should be told the methods of sampling, spiking, digestion, chemistry, measurement, and the methods of detrital thorium correction. Subsample size and the blank levels are also critical pieces of information. Uncertainties in the measured ratios should also be given.

With the information given, we calculated an age of 169.2 ± 11 ka (95% confidence level) using values of 2% for the errors on the isotopic measurements. The measured ^{232}Th/^{238}U is low (0.0886), so the corrected age of 160 ka is reasonable although without knowing what values were used to make the correction, I could not reproduce this number exactly. The number of significant digits appropriate for the stated errors should be reported ((i.e., 3 not 6; ages should be quoted as 169 +13/-12 ka, and 160 +13/-12 ka).

Our TIMS U-series dating has focused on small sample sizes (<5-10 mg for opal and <50-100 mg for calcite). In spite of these efforts, we have identified a striking negative relation between ages and initial ^{234}U/^{238}U ratios for these small samples. We chose not to interpret this trend as an indication that the ^{234}U/^{238}U composition of the solutions responsible for mineral deposits was changing with time. No substantial changes are seen in either saturated-zone waters, as demonstrated by Ludwig and others (1992) in their Devils Hole work, nor in the surface environment as demonstrated by our own work with calcrete in the region. Instead, we have interpreted this trend, along with other evidence, as an indication that growth in these materials is extremely slow, and that a sample of even small size will average older and younger materials and the result will be an intermediate age. If the youngest, outermost material is included in the sample, the resulting apparent age will be substantially younger than the true age of the material at the base of the sample. For example, if a 1-mm-thick calcite consisted of 0.5 mm of calcite with an age of 1 million years, and 0.5 mm of recently deposited calcite, and if the entire calcite were crushed and analyzed, a ^{14}C analysis would yield an apparent age of 50% modern carbon (i.e., about 5.8 thousand years) whereas the true average age for this calcite would be 500,000 years. Dublyanksy is aware of this work, as he quotes from several of our reports that describe these effects, yet he does not acknowledge this hypothesis and ignores its implication to the simple interpretation he promotes. This is a prime example of selective use of information.

Derek Ford who analyzed this sample spoke with Brian Marshall at the 1998 GSA meeting in Toronto and indicated that the dated sample weighed 6 grams. Such a large sample would be severely impacted by mechanical mixing of older and younger materials, and the resulting age would clearly be meaningless in terms of dating a specific layer containing two-phase fluid inclusions. The uranium concentration of 0.1396 ppm is 5 to 10 times larger than uranium concentrations for pure calcite (0.01 to 0.05 ppm). This indicates that opal was probably present in the sample. If the included opal came from near the outer surfaces of the coating, as is common for many crusts, the isotopic composition of the opal would strongly dominate the sample. This would strongly bias the sample to an even younger apparent age because the opal will have 3 to 5 orders of magnitude more U than the calcite.

An additional flaw in Dublyansky's evidence and theory is implicit in the stated initial $^{234}U/^{238}U$ ratio of 1.7648. If a saturated-zone, hydrothermal origin for this sample is correct, the calcite should have inherited an initial $^{234}U/^{238}U$ ratio identical to that of its source. Shallow, saturated-zone water beneath Yucca Mountain has anomalously large $^{234}U/^{238}U$ activity ratios (7 to 8). Nor is this value close to the ratio of 2.3 determined for the Paleozoic aquifer water as sampled from UE-25 p#1 at Yucca Mountain. On a regional basis, $^{234}U/^{238}U$ values in ground waters as small as 1.8 are rare, largely being restricted to high-elevation springs with very short flow paths. Instead, the sample has an initial ratio within the range of values observed for pedogenic calcite and opal (1.4 to 1.9). Although it is likely that this initial ratio represents an apparent rather than a true value based on the large sample size, Dublyansky must discuss these inconsistencies in order to make a credible attempt to support his hypothesis. These arguments about the genetic implications of initial uranium ratios are not new, but continue to be selectively ignored by Dublyansky.

Paragraph 3: The statement that "This age, 160 ka, represents the first direct datum on the age of hydrothermal activity at Yucca Mountain." is nonsense for at least three reasons. First, the presumption of "hydrothermal activity" is ill-defined and has by no means been convincingly demonstrated. Second, the large sample size does not provide a "direct datum on the age" of the six-gram sample for the reasons described in the last several paragraphs. Third, the statement ignores a large amount of geochronological data recently produced by the USGS indicating that only the outermost layers in any crust have ages less than 500,000 years, and that ages of interior portions of the mineral coatings yield ages between 1 and 8 Ma (Paces and others, 1996; Neymark and others, 1998; Paces and others, 1998). Dublyansky is aware of this work but apparently ignores it because our results do not support his hypothesis. This is another example of selective use of available data.

It is also interesting to note that the 160 ka date, meaningless as it is, that is used by Dublyansky to support "the age of hydrothermal activity at Yucca Mountain" is from a sample with 16 out of 19 homogenization temperatures between 25 and 35°C The two outliers above 45°C must be tossed out by Dublyansky's own criteria of clustering temperatures. Therefore, his stated geochronological evidence for hydrothermal activity is from a sample lacking convincing evidence of hydrothermal activity.

Paragraph 4: The youthfulness of calcite and opal with respect to the age of the host rocks is not in question, although it is unfair to compare data from pre-1995 studies with more recent ones due to extreme differences in the methods used. It should be noted that the post-1995, technically advanced, dating efforts have focused on the outermost surfaces of calcite and opal. Materials lower in the microstratigraphy of individual coatings have U-Pb ages greater than 1 Ma. Dublyansky cites our most recent reports, but completely ignores these data and the implications they have on his fluid inclusion studies.

Paragraph 5: Awkwardly written and seemingly at odds with the last sentence of paragraph 1 of this section.

Section 6 – Discussion

11. "Hydrothermal Fluids" - The statement that "The results of our studies show that hydrothermal origin of 13 calcite samples is beyond reasonable doubt." is a clear instance of stating a possible conclusion as fact.

    Furthermore, there is considerable ambiguity and inconsistency of usage for various terms for water temperature in this report. Thus, the fluids had "Elevated temperatures", were "Hot waters", or "Deep seated thermal fluids", and a "Hydrothermal origin is beyond reasonable doubt." In part of the report, these terms are used for fluids that show maximum T_h values as low as 45°C (1995 data set) and 39°C (1998 data set). Elsewhere, for example sample 2221, which has a range of T_h from 35 to 58°C, it is suggested that "the high-temperature part of the data (>40°C) should probably be disregarded." Yet other samples, having much higher T_h values, as high as 75°C, are considered evidence of hydrothermal fluids.

12. Origin of Quartz and Fluorite - Dublyansky's statement that "The presence of crystalline quartz and, particularly, fluorite within calcite crusts is not compatible with the postulated rain-water origin of these mineral-forming fluids." is wrong. Cave Minerals of the World (ed. by Hill and Forti and which contains a chapter authored by Dublyanksy) indicates that both of these minerals, although commonly a result of hydrothermal fluids, can and have formed at ambient temperatures in cave environments.

13. Trace Minerals - We are chided for offering no explanation for the presence of trace minerals present in the secondary occurrences, "Other phases are present (fluorite, clay minerals, zeolites, Mn-oxides, organic phases) but are volumetrically inconsequential." (p.9, Paces and others, 1996). Inasmuch as all of these phases occur only sporadically and are all amenable to low-temperatures of formation, no special explanation was then or is now called for.

14. Speleothem Comparisons - Here, Dublyansky contends that if the Yucca Mountain unsaturated zone secondary minerals formed from descending percolation of meteoric origin, that they should mimic speleothem deposits in caves, which are also formed from descending meteoric waters. Although both form from descending water in a vadose environment, and Yucca Mountain percolation may have hydrochemical similarities with cave water, caves are not a good analog for Yucca Mountain secondary mineralization largely because of the gross differences in calcite growth rates.

    Dublyansky advances the false hypothesis that all calcite derived by descending meteoric water must have fine-grained, mammillary forms that are common in speleothems found in limestone caves. Because subsurface calcite at Yucca Mountain commonly consists of large, free-growing crystals, it is dissimilar to speleothem deposits and must therefore not have the same meteoric origin. The comparison is and incorrect as the two environments have very different host rocks, liquid and gas flux rates, which, in turn, result in very different calcite growth rates. The slowest rates of speleothem formation discussed by Hill and Forti (1997) are on the order of 10 mm/ k.y., or 10,000 mm/m.y. Calcite in the unsaturated zone at Yucca Mountain formed at rates of 1-5 mm/m.y. (Paces and other 1996; Neymark and others, 1998; Paces and others, 1998), or as much as 4 orders of magnitude more slowly. We have argued that this slow growth rate accounts for the unique calcite forms found in Yucca Mountain (Paces and others, 1996). Furthermore, the coarse crystal forms of calcite found in the Yucca Mountain unsaturated zone do not occur along steep flowpaths that would be analogous to water films producing flowstones, but in subhorizontal settings where crystal growth is less dependent on flow patterns.

Speleothems display layering, or depositional laminations, that reflect cyclical changes in fluid flux and composition resulting from long- and short-term climate variability. Dublyansky states that the Yucca Mountain unsaturated zone calcite does not show such layering and, therefore, can't represent climate-driven percolation fluxes. Again he is wrong as both the calcite, which shows growth banding under cathodoluminescent illumination (Whelan and others, 1994), and the opal, which displays extremely clear laminated structure in the SEM and in thin section (Paces and others, 1996), are layered at the micron scale.

Here Dublyansky has postulated a spurious corollary to a proposed mode of origin (i.e., that the unsaturated zone mineralization should mimic speleothems), then, when the corollary fails to pass his tests, uses this failure to reject the proposed mode of origin.

15. Stable C and O Isotopes of Calcite - Figure 35 depicts the variability of calcite $\delta^{13}C$ and $\delta^{18}O$ values across two mineralization sequences from the North Ramp (i.e., the Tiva Canyon Tuff). Both sequences display near constant calcite $\delta^{18}O$ values, from which Dublyansky concludes that the calcite can not represent formation from percolating meteoric waters because the C and O isotopic compositions of such waters should display a wide range over time due to climate variability. We agree with his logic, but find his data puzzling. We have repeatedly published C and O isotopic data showing wide variations in these parameters within individual samples. For example, figures 4.5 a and b in Paces and others (1996) show ranges of $\delta^{13}C$ of −7.2 to 6.3‰ and −6.2 to 6.9‰, respectively; and ranges of $\delta^{18}O$ of 12.8 to 16.8‰ and 13.7 to 17.8‰, respectively. Such ranges are common and we take them, as Dublyansky would suggest, as evidence of meteoric-water percolation fluxes.

16. Isotopic Signature of Mineralizing Fluids – Dublyansky derives the $\delta^{18}O$ of fluids responsible for calcite deposition at 50°C from calcite-H_2O fractionation factors and his measured calcite $\delta^{18}O$ values. The water $\delta^{18}O$ values he calculates range from −4.9 to −5.7‰ (we performed the same calculation and got −3.5 to −5.1‰). He notes these $\delta^{18}O$ values are considerably larger than those of modern Tertiary-aquifer ground waters, which range from −14.0 to −12.8‰. He performs a similar calculation to estimate the $\delta^{13}C$ of the dissolved inorganic carbon (DIC) of the calcite-forming water and arrives at a water with a DIC $\delta^{13}C$ of +0.2 to −3.2‰. Again, we tried to duplicate his calculation, but with even more problematic results; we calculated waters with DIC $\delta^{13}C$ of −4.4 to −7.8‰. In either case, we assume that he wishes to imply that the difference between his calculated water and the modern ground water is significant - that it is meaningful. It does show that the waters required to form calcite at 50°C would be much different than today's Yucca Mountain groundwater. In fact, his argument demonstrates that such water is much different than regional ground waters during the past 500,000+ years (e.g., Winograd and others, 1992) although we suspect that that was not his intent.

17. Source of Mineralizing Water - In discussion of his inclusion-fluid freezing experiments, which indicate low-salinity to nearly-fresh inclusion fluids, the author makes the point that such waters are compatible with derivation from the regional Paleozoic carbonate aquifer. YMP studies show that such waters are also compatible with present-day unsaturated zone porewaters as well as with the probable compositions of fracture-hosted percolation as inferred from perched water bodies in the UZ.

18. Strontium Isotope Systematics – The author misuses reported Sr isotopic data. The range cited represents a series of very high precision analyses of calcite. These calcite $^{87}Sr/^{86}Sr$ values change as a function of time such that early calcite is much less radiogenic than carbonate aquifer water, and late calcite is more radiogenic. Thus the bulk of the calcite cannot be genetically related to water from the carbonate aquifer. Studies of Devils Hole calcite show that the $^{87}Sr/^{86}Sr$ of calcite deposited from the carbonate aquifer do not change with time.

19. Hydrocarbon Potential – In Section 6.3, Dublyansky cites an unknown reference for hydrocarbon potential (Mattson and others, 1992), and ignores an extensive treatment of the subject by Grow and others, 1994 (IHLRWM proceedings). Those authors (experts on the subject) suggest the possibility of hydrocarbon potential in a narrow zone extending from the Calico Hills to the northeast (away from Yucca Mountain). The authors conclude that "there are sufficient data to conclude that the overall oil and gas potential near Yucca Mountain is low, as previously indicated by Garside and others (1988)". They note that any occurrence would require a favorable structural trap. The YMP has conducted studies that would have identified any obvious structural trap, but not found one. Inasmuch as Dublyansky seems to know little about this subject, he would do well to delete this section. Alternatively, this may represent another example of selective use of information.

Section 7 – Conclusions and Recommendations

This discussion assumes the existence of at least one hydrothermal system that deposited calcite. We would argue that that must first be verified. If substantiated, then careful dating of those portions of calcite hosting elevated temperature inclusions should be determined to assess their significance, if any, to performance assessment. With the exception of He, the isotopic studies that he suggests have been and are being applied to the study of these deposits The results of these studies provide much of the basis for our conclusions that the secondary calcite and opal in the unsaturated zone have formed from downward percolation of meteoric waters during at least the past 8 Ma.

Appendix 1 – Fluid Inclusions in Calcite Samples from the ESF, Nevada Test Site, Nevada" a report assembled by Yuri Dublyansky for the Office of the Attorney General of the State of Nevada.

20. Crushing Experiments – In the discussion of crushing experiments, Dublyansky argues that the less-than-atmospheric pressures he observed must reflect cooling of inclusion gas bubbles trapped from a heated fluid in a saturated zone setting; that they are "... not compatible with a vadose zone setting." This is incorrect. The following mechanism can account for this behavior in the vadose zone. When gas bubbles were trapped to form these all-gas or gas-rich inclusions, they consisted of various gases (air, CO_2, CH_4, etc.), all at atmospheric pressure, including a partial pressure of water vapor corresponding to the vapor pressure of water in the system at the temperature of trapping. On cooling to surface temperature, condensation of this water vapor would decrease internal pressure in the inclusion to <1 atmosphere. Cooling of such an inclusion from 40 to 20°C

would be sufficient to produce significant decrease of internal pressure and an observable decrease in the volume inclusion bubble at the time of crushing.

Furthermore, we would like to know how Dublyansky explains the less-than-atmospheric pressure of all-vapor inclusions formed in a saturated zone setting? Nowhere does he describe a scenario that will yield such inclusions. He presumes saturated conditions, under which any bubble of gas at the time of trapping will be at >atmospheric pressure, depending upon the hydrostatic head. At the depths from which some of his samples were taken, the hydrostatic head could be several atmospheres (if their depositing fluids were actually discharging at the surface), yet the inclusions tested by Dublyansky are now at <1 atmosphere! Condensation of water vapor on cooling from 30-50°C trapping temperatures to surface temperature would decrease the internal pressure somewhat, but would be completely inadequate to cancel out this positive pressure.

21. Volatile Organic Compounds – We find the discussion of organic compounds full of speculation and unconvincing data. The evidence offered for the presence of higher molecular weight hydrocarbons would appear to be very preliminary, with the author admitting that individual peaks could not be resolved due to small sample sizes. To be credible, these experiments should be repeated. The gas chromatographic experiments, which did not face the same sample size restrictions, revealed only lower molecular weight hydrocarbons (methane, ethane, etc.) which in all cases were at concentrations less than 3 ppm. All of these gases are compatible with in situ generation by bacterial degradation of organic compounds (humic and fulvic acids) that could have been carried down by percolating fluids.

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Evaluation

of the Review of "Fluid inclusion studies of samples from Exploratory Studies Facility, Yucca Mountain, Nevada" by Joe Whelan, James Paces, Brian Marshall, Zell Peterman, John Stuckless, Leonid Neymark (USGS) and Edwin Roedder (Harvard University) – compiled by Joe Whelan

by Yuri Dublyansky

I. Comments on the "most serious objections" summarized in the Memorandum from Joe Whelan (USGS) to Dennis Williams (Yucca Mountain Project, DOE)

a. The meaning of the term "hydrothermal". The terms "hydrothermal fluid" or "thermal water" do not have strict definitions, and the perception of these terms strongly depends on the specific field of expertise of the geologist who uses it. For instance, an ore geologist would not consider fluids with a temperature of less than 50-100 ^{o}C as hydrothermal. In hydrology, however, the threshold for thermal water is much lower. For instance, a definition accepted by most European hydrologists calls the water thermal if its temperature *at the orifice* is 4-6 ^{o}C higher than the mean annual temperature of the area. (Schoeller, 1962). In this context the temperatures *in subsurface environments* above those to be expected from normal thermal gradients are also considered hydrothermal (Dublyansky, 1997). Since the results obtained on Yucca Mountain calcites are used to reconstruct the paleo hydrology of the mountain, usage of the "hydrological" meaning of this term is justifiable in my opinion.

However, in order to remove any ambiguity I will explicitly specify in my report that the terms "thermal" and "hydrothermal" are used to refer to waters if they reveal temperatures higher than may be expected at a given depth within the unsaturated zone.

b. Why did the ~75 ^{o}C hydrothermal event not leave its mark on other occurrences? Presently, our knowledge regarding the spatial structure of the ancient hydrothermal system and its development in time are extremely scarce. Therefore, there are many possible reasons why we may be able to see traces of it in some locations and not in others. The statement that "*Such an event should have … affected most of the calcite already present at that time.*" is purely speculative. We do not know the time of calcite deposition, in the first place. Also, fluids with temperature of ~75 ^{o}C would not necessarily affect pre-existing calcites (see my comment 1 – Stretching of Inclusions below).

c. The bulk of calcite is so old that its possible hydrothermal origin is of no consequence to the repository performance. The data and analysis presented in my report are troubling evidence that cast some doubt on the suitability of Yucca Mountain as a repository. This is because of the presence of thermal waters could be very damaging to the integrity of the containment of radioactivity. Since my report is not definitive on the questions of the number, dates and sequence of hydrothermal events, it is not conclusive as to the viability or lack thereof of Yucca Mountain. Therefore I have recommended further detailed study to resolve these issues before a determination of viability is actually made.

Suggestion that "*…the bulk of calcite present, and probably that which hosts the supposed "hydrothermal" fluid inclusions…*" is old represents a speculation on the part of the reviewers which cannot be either proved or disproved using the information now available. The controversy cannot be resolved on this basis. Serious research needs to be carried out before a conclusion can be drawn regarding the age of hydrothermal activity at Yucca Mountain. This is one of the central recommendations of my report.

However, if the calcite from Yucca Mountain subsurface is proved to contain two types of different origin ("old" hydrothermal and "younger" vadose), this would have quite serious implications in terms of the methodology used by DOE to study the origin of the Yucca Mountain minerals. This would indicate that methods used are not capable of discriminating between these two origins. To my knowledge, out of several tens of papers dealing with Yucca Mountain secondary minerals published in the last few years (most of which were authored or co-authored by the reviewers), none concludes or suggests that even part of calcite crusts from the Exploratory Study Facility (ESF) may have formed in a saturated environment from waters with elevated temperatures.

d. Analogy with speleothems. Cave deposits represent not only the closest, but probably the only known natural analog for the origin of the Yucca Mountain calcites as postulated by the reviewers because they are formed from gravitation-driven films of waters. Such a peculiar depositional setting imposes strict constraints on the textures of depositing minerals. These constraints have to do with physics, rather than with geology. If the postulated "descending" origin of the calcite at Yucca Mountain is correct, this calcite should not necessarily "*mimic*" speleothems, but it should comply with the same physical laws (gravitation, surface tension, etc.).

The rates of deposition, chemistry of host rocks, liquid and gas flux rates play in this context a secondary role.

The formation of large euhedral crystals requires a slow uniform supply of matter to the surface of the growing crystal. This, in turn, for most minerals requires a saturated (submerged) environment, a low degree of the fluid super-saturation, and quiet hydrodynamics. Large (up to 1.5 cm) euhedral free-growth crystals, quite common at Yucca Mountain, cannot be formed from thin (typically <1 mm) films of water flowing downward along fissure surfaces. Speleothems are a useful analog, because by studying them we can examine physical mechanisms of mineral growth from film waters. I have not been able to find any reports outside of the publications of DOE scientists on Yucca Mountain of large free-growth calcite crystals forming from film waters.

e. <u>Interpretation and use of isotopic data</u>. The allegation that "*Calculations of the* $\delta^{13}C$ *and* $\delta^{18}O$ *for calcite are based on questionable assumptions and assertions…*" is factually incorrect and misleading. Values of $\delta^{13}C$ and $\delta^{18}O$ in calcite presented in my report were measured, not calculated, and thus cannot be influenced by any assumptions or assertions.

The strontium isotopes were mentioned in my report with the sole purpose of showing that these data do not contradict the "upwelling" model. The quote below represents ALL discussion on $^{87}Sr/^{86}Sr$ that was present in the draft of my report.

> *"Paces et al. (1998) established variations in the* $^{87}Sr/^{86}Sr$ *values across calcite crusts from ESF from about 0.7125 to 0.710. These values match those of the semi-confined Paleozoic carbonate aquifer (0.71175; Peterman et al., 1994) that underlies the modern aquifer beneath Yucca Mountain."*

The numbers in this quote are correct and obtained from cited publications. I do not believe that the quote deserves to be labeled a "gross misuse of the data".

Because the strontium data have no direct bearing on the study's conclusions, it have been omitted from the final version of the report.

f. <u>"Improper" interpretation of crushing results</u>. All-gas inclusions contracting on crushing were interpreted in my report as indication of internal pressures of less than 1 atmosphere and, therefore, incompatible with the vadose zone setting (pressures of 1 atmosphere). This interpretation complies with the generally acknowledged behavior of vadose-zone inclusions, e.g.:

> *"The bubbles trapped in the vadose zone are at one-atmosphere internal pressure (bubble size does not change when sample is crushed)"* (Goldstein and Reinolds, 1994, p. 81)

The criterion of bubbles which do not change their size on crushing is widely used in fluid inclusion studies of diagenetic environments.

The alternative hypothesis that a decrease in internal pressure in a gas-rich inclusion may be caused by the condensation of water vapor in the vacuole was introduced by Roedder et al. (1994), and to my knowledge, it has not been supported by numeric estimates. Some questions regarding this hypothesis are summarized in section 20 of this review. Therefore, the strong statement that "*…when properly interpreted* [the results of crushing experiments] *offer strong evidence that the calcite formed in an unsaturated zone, or vadose, setting*" is not warranted. In addition, the all-gas inclusions in Yucca Mountain calcites have other properties (e.g., chemistry of gases) which make their "unsaturated" interpretation untenable.

II. Comments on the Review of "Fluid inclusion studies of samples from Exploratory Studies Facility, Yucca Mountain, Nevada" by Yuri Dublyansky

1. Stretching of inclusions. The reviewers overlooked the point of the argument that they quoted from my report. When an inclusion homogenizes at comparatively low temperature (e.g., 35 ^oC), it never heterogenizes on cooling to room temperature (i.e., the bubble does not re-nucleate in it). The physical reasons for this failure to nucleate are discussed in detail by Roedder (1984). This means that if my samples containing fluid inclusions with T_h = 35 ^oC were heated to 35 ^oC during sample preparation, these inclusions would homogenize (i.e., they would become one-phase liquid) and I would not be able to see them as two-phase gas-liquid inclusions afterward.

The argument that "*the inclusions in calcite may stretch with as little as 10 degrees of overheating*" is assertive. While it makes sense in theory, because overheating should increase the internal pressure in all-liquid inclusions. I have found, however, it does not work in practice, at least with calcite. For instance, when I tried to stretch inclusions to create a bubble (which is necessary for freezing experiments) I heated my samples (about 15 of them) to 250 ^oC and held them at this temperature for 10-15 min. Even after such significant overheating, most of the all-liquid inclusions did not nucleate bubbles, implying that they did not stretch. In those inclusions that did nucleate bubbles, the latter were typically large with quite irregular liquid-to-vapor ratios from one stretched inclusion to another. Stretching related to overheating, therefore, is easily recognizable. I have incorporated these observations into the final version of my report.

My experiments on stretching can easily be reproduced. I would invite the reviewers to try and manufacture groups of two-phase inclusions that would yield consistent T_h's by means of the heating the all-liquid inclusions in Yucca Mountain samples.

There is no known mechanisms by which groups of inclusions sizes, with similar L:V ratios and T_h varying within a few degrees can be caused by overheating during sample preparation. In fluid inclusion studies, such groups are viewed as the most reliable sources of information (Goldstein and Reinolds, 1994). In my study, careful handling of samples eliminated even gentle heating during preparation; a T_h = 35 ^oC indicates that samples have not been heated over this temperature.

2. "Disturbed" Inclusions. As was discussed above, the two-phase fluid inclusions created by any thermal (overheating) or mechanical impact on the originally one-phase liquid inclusions typically have highly irregular L:V ratios and homogenize at random and generally high temperatures (50-250 ^oC). It is highly unlikely that such processes would create a group of, say, 10 or 20 inclusions with T_h varying within 5-10 degrees of 35-60 ^oC.

There are three samples in the analyzed set (specifically 2217, 2221 and 2224) which reveal some evidence of stretching, expressed as a wider range of measured T_h's. Results obtained on these three samples are less reliable than the data on the rest of samples. Nevertheless, these samples may provide a conservative estimate of the paleo temperature if the higher-temperature part of the measurements is excluded from consideration. By contrast, the remaining 4 samples of the 1998 set of samples and sample SS#85-86 described in Appendix 1 yielded very consistent results. The definition of a "consistent" result is not straightforward. Goldstein and Reinolds (1994) recommend that fluid inclusion associations with 90 % of inclusions homogenizing within a 10-15 ^oC interval should be considered as showing a consistent result (p. 151). For some of my samples (e.g., Fig. 23), data measured on as much as 5 fluid inclusion assemblages fell entirely within 5 ^oC interval!

3. "Tectonic Cavities". Attribution of calcite at the bottoms of cavities uniquely to an unsaturated environment is not warranted. Other explanations are possible.

Firstly, if the calcite in question was formed from films of water flowing along the walls of open fractures, it would be precipitated on both walls: due to the capillary forces and wettening, these films would have to be present on foot walls as well as on hanging walls. This theoretical consideration is confirmed by observations in caves. Gravitation begins to play a significant role and cause asymmetry in film deposits when the films become thick enough (so that the gravity force is compatible to the surface tension and capillary forces). This would require significant amounts of water and high rates of percolation.

Secondly, if calcite on the bottom of a lithophisal cavity was formed from film water, this water should first flow along the ceiling and hanging walls of the cavity and only then reach the floor. The question is: why would calcite deposition begin only when this hypothetical film reached the floor?

Thirdly, comparatively large (up to 1.5 cm) individual crystals do not form from water films. This has to do with basic physics rather than with geology. According to Kendall and Broughton (1978):

> *"Large crystal terminations do not form on the speleothem surface because they form projections that disturb the water flow away from the projections which, as s consequence, are gradually eliminated"* (p. 519).

5. Distribution of T_h. The wish to know the relationship between inclusions and the paragenetic sequence is justifiable, and I am in complete agreement with the reviewer's comment that there is "*…need to describe the fluid inclusion assemblages within a paragenetic context and to then place geochronological constrains on the fluid inclusion assemblages…*", and have expressed a similar point of view in the "Conclusions and Recommendations" of my report.

The reviewers state that: "*…it is impossible to either relate the data to the 9-m.y. history of unsaturated zone calcite deposition, or to assess its significance to site performance*". I agree with the first part of the statement; my data indicate saturated environment of calcite deposition. As I have noted above, I recognize that my current data are inadequate to assess the site performance. This will require much more research (see "Conclusions and Recommendations" in my report). The finding of the saturated environments at Yucca Mountain in the past is, however, a troubling indication, and one that needs to be addressed.

6. Resetting of T_h? This section contains a number of separate questions.

a. *Explanation of all-liquid inclusions*. The most comprehensive explanation of all-liquid inclusions may be found in Edwin Roedder's textbook, "Fluid Inclusions" (1984), in which the section entitled "Failure to Nucleate in Nature", is entirely dedicated to this phenomenon.

> *"The most frequent and obvious example of metastability in inclusions is the failure of some to form a vapor phase (bubble) on cooling. As the bubble is a measure of the differential shrinkage of the liquid and the surrounding crystal host on cooling, inclusions trapped at surface temperature never have bubbles formed in this manner. (*Footnote: *The converse of this statement (i.e., inclusions without bubbles must have formed at surface temperatures) is not generally valid, as detailed below.) … The size at which the division occurs between those inclusions with bubbles and those without, though never precise, is surprisingly consistent for a given sample and varies inversely with the volume of percent of vapor that should be present. … all inclusions larger than 1 μm (and some smaller ones) in minerals formed at high temperatures (≥350 °C) may have bubbles, whereas inclusions as large as 20 μm in some minerals formed near 100 °C seldom show bubbles. Aqueous inclusions formed at 70 °C may be as large as 100 μm and still not nucleate a vapor bubble…"* (p. 292; emphasis by the author).

Subsequent paragraphs in the book contain detailed physical explanation of the phenomena. Rather than paraphrasing it here, I refer the reviewers to the text.

b. *The possibility of "stretching" of inclusions by a late thermal event*. As was discussed above (see comment 1 "Stretching of inclusions"), the susceptibility of fluid inclusions in calcite seems to be significantly over-estimated by the reviewers. In my experiences, overheating to 100-150 °C almost never resulted in the appearance of bubbles in all-liquid inclusions, whereas exposure to higher temperatures sometimes resulted in stretching and partial leakage of inclusions. Therefore exposure of existing early all-liquid inclusions to 70-75 °C due to the ingress of late hot fluids would not necessarily produce stretching.

This is true if these hypothetical all-liquid inclusions were trapped at ambient temperature. However, the all-liquid inclusions may also have been trapped at elevated temperatures and remain all-liquid at room temperature due to the failure to nucleate the bubble (as discussed above). Heating of such inclusions would not produce any excessive internal pressure.

c. *Suggestion to plot ALL the data together*. Plotting together data obtained from different samples, collected from different parts of the tunnel and from different lithological units of tuffs would contradict normal scientific practice.

7. Paragenesis of Fluorite. The reviewers charge that my statement “*Colorless and violet globules of fluorite are associated with latest stages of calcite growth*” is misleading. They support this point by saying that they “*have seen occurrences of fluorite visible through calcite coatings*” and these calcite and fluorite may be millions of years old. They state that they have observed fluorite which was apparently old. On the basis of this observation they conclude that the fluorite, which I observed in other samples is also old.

There general agreement that an old hydrothermal event occurred at Yucca Mountain (the so-called Timber Mountain event, ca. 10-11 Ma). Therefore, minerals deposited before calcite (i.e., paragenetically older) are of lesser interest from the point of view of repository safety. An example of such apparently “old” fluorite may be observed in the ESF at station 52+13. More relevant to the current debate is the fluorite which was deposited simultaneously with or after the calcite at Yucca Mountain. This fluorite may safely be concluded to be as old or younger than the late “portions” of calcite.

In some of my samples I observed fluorite within calcite close to the crystal surface. An example is shown in Fig. 27 of my draft report. Moreover, in sample 2206 (station 76+00.6), minute euhedral crystals of fluorite were deposited on the surface of the calcite and quartz crystals. These observations are provided in the report.

The reviewers remark that “*fluorite does not require high temperature to form*”. Indeed, fluorite is a common low-temperature hydrothermal mineral. For example: “*Fluorite occurs as a typical hydrothermal vein mineral with quartz, barite, calcite, sphalerite, and galena*” (McGraw-Hill Encyclopedia of Geological Sciences, 1988, p. 195).

8. Sample 2217. The claim that the data are “*immaterial to recent unsaturated zone hydrology and therefore to performance assessment*” suggests that the data should be dismissed without further consideration. However, a more correct approach would be to lay the burden of proof on the proponents of the repository site and require them to prove that temperatures measured from

my samples are, indeed, from geologically old part of the calcite and are, therefore, of no concern to the safety of the repository.

10. Paintbrush Fault. The reviewers question the name of fault referred to in my draft report. I re-assert that my study refers to the Paintbrush Fault. There is a present-day thermal anomaly associated with this fault (locally elevated groundwater temperatures detected by Sass et al., 1987) that may indicate "active" character of this fault. However, this is a hypothesis, and there may be other equally valid explanations. However, I reject the reviewers' characterization of this point as an attempt to "*misrepresent geologic information to those unfamiliar with the Yucca Mountain area*".

Section 5. Age of calcite from the ESF.

Paragraph 1. "*The evidence* [of the hydrothermal origin of Yucca Mountain calcites] *remains equivocal at best*". This opinion is at odds with the conclusion by the U.S. Nuclear Waste Technical Review Board:

> *"The fluid inclusion data show that there is little doubt that some of the calcite in the ESF was either formed by, or later exposed to, aqueous fluids at elevated temperatures (at least 72 °C) under different conditions than those present in today's unsaturated environment…"* [1]

Paragraph 2 and Results of SS#45-46. I acknowledge the error of my statement describing the excess of detrital thorium as the cause of the failure of the three analyses. The correct reason is concentrations of thorium too low to allow statistically sound calculations. The samples, as a consequence, were rejected by the program. The error is corrected in final report. Also, more information is provided on sample and procedures, as was suggested by the reviewers, and some technical remarks about number of significant digits for the stated errors were addressed.

The last paragraph on page 4 describes the reviewers' line of reasoning regarding the interpretation of the change of the $^{234}U/^{238}U$ ratios in calcite samples:

> *"We have chosen not to interpret this trend as an indication that the $^{234}U/^{238}U$ composition of the solutions responsible for mineral deposits was changing with time. No substantial changes are seen in either saturated-zone waters, as demonstrated by*

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[1] Letter from Jared L. Cohon, NWTRB Chairman to Lake H. Barrett, Acting Director, Office of Civil Radioactive Waste Management; of July 24, 1998; Attached document entitled "Board Review", p. 4. Available from the NWTRB official web site at http://www.nwtrb.gov

> *Ludwig and others (1992) in their Devils Hole work, nor in the surface environments as demonstrated by our own work with calcite in the region. Instead, we have interpreted this trend, along with other evidence, as indication that growth in these materials is extremely slow…"*

Reviewers used the information on the features of two geologic environments (regional saturated-zone waters and regional surface environments) to make a judgement regarding the features of another geological environment (which is, of fluids responsible for calcite deposition at Yucca Mountain), whose origin is in question. Waters with elevated temperatures which deposited calcite at Yucca Mountain may have little to do with either regional aquifer or surface waters.

The reviewers stress that "*a sample of even small size* [formed in accordance with "continuous" model] *will average older and younger materials and the result will be an intermediate age*". This is correct for all natural geological samples, because virtually any crystal grows through a build-up of molecular layers. Therefore, any sample of a finite size will average multiple growth layers and *any* age obtained through isotopic dating will represent an average over a sampled thickness.

The reviewers complain that I do not acknowledge their hypothesis of "continuous" and slow deposition of the Yucca Mountain calcite[2] (e.g., Paces et al., 1996) and ignore its implications. Indeed, I have quite serious reservations about both "continuous" mode of deposition and the "remarkably constant" 1 to 5 mm per million years deposition rates postulated by the reviewers for Yucca Mountain. I have provided my evaluation of their model in the final version of the report in response to reviewers' comment.

Paragraph 1, page 5. The example calculation, showing how a mixture of two calcite sub-samples with different ages would influence the apparent ^{14}C age is irrelevant since I did not use the ^{14}C dating.

Paragraph 2, page 5. The correct weight of the sample is 4.95 gm (as indicate in final report). The statement: "*the result would clearly be meaningless in terms of dating a specific layer containing two-phase fluid inclusions*" is technically correct but misleading: I never claimed that my result is

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[2] The essence of the model is that the calcite is hypothesized to be deposited as *infinitely thin layers at an extremely low rate* (between 1 and 5 mm per million years; Neymark et al., 1998). The USGS researchers use this model as opposed to the model of episodic/instantaneous growth that envisages formation of layers of a finite thickness which occurs relatively rapidly.

a date on a “specific layer”. This date is obtained on a large sample, some 1 cm thick, and averages ages of this thick layer. Therefore, it applies to a point at 5 mm above the base of the sample in the mean, and needs to be considered as such. The result is internally consistent, and it is difficult to imagine the base of this sample being as old as in the order of 1 million years.

“*The uranium concentration of 0.1396 ppm* [in our sample] *is 5 to 10 times larger than uranium concentration for pure calcite (0.01 to 0.05 ppm)*” First, what is “pure calcite”? Reviewers speculate that the “large” concentration of U measured in my sample is indicative of the presence of opal in our sample and, therefore – of erroneous age. However, when my data are compared with the results published by the reviewers (e.g., Paces et al., 1994), uranium concentrations of 1.1396 are not at all “exotic”. Paces et al. (1996) report that: “*Calcite subsamples without opal … have … U contents* [of] *0.007 to ~0.1 ppm…*” (p. 16). However, this statement misrepresents the reviewer’s own data published in the same report. An excerpt from a table in Paces et al. (1994; Appendix 2, pp. 51-54) is printed below. As shown by these data, concentrations in pure (that is, containing no opal) calcite studied by the reviewers vary from 0.007 to as much as 0.692 (average 0.139). Therefore, there is double misrepresentation of the data: first the reviewers indicated the upper limit of concentration as ~0.1 instead of 0.692 ppm in their report; then they lowered this boundary even more (by a factor of 70!) to 0.01-0.05 ppm in their review of my report. The results of my report are entirely consistent with the original data by Paces et al. (1996)

#	Sample Name	ESF station, m	Occurrence	U conc. (ppm)
1	SPC00504305-U1	579.15	Fracture coating	0.420
2	SPC00509037-U1	625.18	Unclear	0.166
3	HD2005-U1	1710.95	Fracture coating	0.0271
4	ESF1975-U1	1975	Unclear	0.692
5	HD2010-U1	2468.2	Fracture coating	0.0301
6	HD2096-U3	2523	Fracture coating	0.0138
7	HD2011-U1	2568	Fracture coating	0.0070
8	HD2011-U2	2568	Fracture coating	0.0466
9	HD2019-U3	2881	Lithophysae	0.395
10	HD2019-U4	2881	Lithophysae	0.260
11	HD2019-U5	2881	Lithophysae	0.266
12	HD2059-U1	3017.78	Lithophysae	0.185
13	HD2059-U2	3017.78	Lithophysae	0.142
14	HD2059-U7	3017.78	Lithophysae	0.0280
15	HD2059-U8	3017.78	Lithophysae	0.0378
16	DH2100-U3	4029.9	Lithophysae	0.0119
17	HD2111-U1	4861.4	Fracture coating	0.0186
18	HD2111-U2	4861.4	Fracture coating	0.0126
19	HD2114-U1	4986.5	Fracture coating	0.0119
20	HD2115-U1	4988.9	Fracture coating	0.0109
Average				0.139

* There appears to be at least two clusters of data in this set.

Paragraph 3, page 5. We know little about the source of mineral forming fluids at Yucca Mountain. Anomalously high $^{234}U/^{238}U$ ratios in shallow volcanic aquifer are irrelevant, because if this calcite was formed from upwelling deep-seated waters, the latter would have little to do with the shallow aquifer. Waters from deeper Paleozoic carbonate aquifer have closer, but still high uranium activity ratios. This carbonate aquifer at Yucca Mountain was tapped by only one borehole (UE-25 p#1), therefore the knowledge regarding this aquifer is not sufficient. And again, waters upwelling from significant depth may have had quite different isotopic values.

All interpretations of isotopic values contain an inherent uncertainty: one does not know the initial isotopic properties of the source of calcite (or, calcite-depositing waters), therefore one must assume them to have certain values. However, since the major issue is the origin of this calcite (or waters), this leads to circular reasoning: one assume some properties for calcite-depositing fluids and then, on the basis of this assumption infers the origin of these fluids.

Fluid inclusion method, however, is empirical in its nature and is free of this uncertainty. This is the reason why the most successful national programs dealing with geological isolation of nuclear wastes (e.g., those of Canada, Finland, and Sweden) implement integrated studies of isotopes and fluid inclusions to interpret the paleo hydrologic environment. Isotopic methods that are not supported and constrained by fluid inclusion studies do not have enough power of resolution. The absence of adequate fluid inclusion research is a major and most regrettable deficiency of the Yucca Mountain characterization activities.

Last paragraph, page 5. The reviewers misrepresent my data. The temperature interval “*between 25 and 35 ^{o}C*” is not correct: the correct numbers are 30 and 40 ^{o}C (see histogram on sample SS#45-46 in my report). Strictly speaking, the temperatures should be indicated as 30 and 49 ^{o}C, since the class interval in this histogram is 5 ^{o}C. These temperatures, low as they are, are still higher than the temperatures expected in the unsaturated zone at a given depth. On top of that, the fluid inclusion data indicate saturated environment during calcite formation.

Paragraph 4. I am familiar with the reviewer’s results showing that stratigraphically old calcite may be old. In their work, the reviewers consider the Yucca Mountain calcite as monogenic, or formed as a consequence of one single process. Therefore, all ages obtained from growth sequence should be considered as representing different points in the time history of these deposits.

My observations presented in the report are in agreement with the single-origin interpretation. In studied samples, I never observed features indicative of a dramatic change in environments (e.g., from saturated to unsaturated). Part of my samples contained fluid inclusions indicative of the saturated environment and elevated temperatures. Typically, elevated temperatures were measured from the oldest growth zones; inclusions typical of saturated zone, however, persisted throughout the samples. Therefore, an inference that the youngest parts of the calcite reflect the same, saturated, depositional environment but perhaps somewhat lower temperatures is logical. This inference is reinforced by additional evidence, such as textures and stable isotopic profiles, discussed in detail in my report. If my inference is correct, the young ages of calcite reported by the reviewers represent the youngest dates of the existence of the saturated environment in Yucca Mountain at the level of the planned repository. These youthful ages are of concern from the standpoint of the site suitability. Old ages of the micro-stratigraphically early calcite indicate the persistence of a saturated environment in the geologic past.

Summary on the “Age” section. My data on the age of the calcite at Yucca Mountain are by no means conclusive. These results need to be refined through a more fine-scale dating. Future detailed studies must include integrated and concerted research of fluid inclusions, isotopes and ages of calcite samples, as noted in the Conclusions and Recommendations of my report. Similar suggestions nave been made by Dr. Robert Bodnar who reviewed some of my earlier work as a consultant to the U.S. Nuclear Waste Technical Review Board (available from the NWTRB web page at: http://www.nwtrb.gov), and by J. Cline, one of the reviewers of this report.

Section 6 – Discussion

12. Origin of Quartz and Fluorite. The origin of fluorite was briefly discussed earlier (see comment 7). The reviewers invoke a book by Hill and Forti (1997) to argue that fluorite is formed at low temperatures in caves. Fluorite, indeed, has been found in a few caves where it shows indications of low-temperature origin. In most of these cases the exact origin of fluorite is unknown and can be explained through the re-deposition of earlier hydrothermal fluorite veins intersected by caves or found in the vicinity. The presence of these early veins appears to be a necessary prerequisite for low-temperature re-deposition of fluorite. Some occurrences of euhedral quartz have been reported to be formed in a low-temperature environment. Not all of the

occurrences, however, are studied sufficiently, and in some cases interpretations should have been changed after detailed studies:

> *"According to Martin, the formation of theses macro-crystalline quartz speleothems is still going today, and the feeding water is normal subaerial seepage water. However, Stalder and Touray (1970) performed fluid inclusion analyses on these quartz crystals and found that the quartz had grown subaqueously in a fluid rich in methane at temperatures over 200 ^{o}C"* (Hill and Forti, 1997; p. 185)

Conclusions regarding the low-temperature origin of quartz, therefore, need to be approached with caution. While low-temperature deposition of quartz and fluorite is possible in nature, these are not typical low-temperature minerals.

Calcite in vertical flowpaths**.** The strong statement "*…the coarse crystal forms of calcite found in the Yucca Mountain unsaturated zone do not occur along steep flowpaths that would be analogous to water films producing flowstones, but in subhorizontal settings…*(emphasis added)" is incorrect. An example of vertical fracture filled with coarse-crystalline calcite is given in Fig. 1 of my report (station 67+81). Steep-angle fractures or openings hosting crusts of coarse-crystalline calcite may be found in the ESF at stations 01+03; 01+12.7; 10+75.18; 14+72.53; 38+64; 52+13; as well as 0+12.6 and 0+40.5 in Alcove 6. This list is not complete; I cited only locations which I visited and sampled.

Calcite banding**.** Information given in the paper by Whelan et al. (1994) is insufficient to judge that reported "growth banding" observed under cathode excitation represents rhythmic banding typical of speleothems and not growth zoning typical of many crystals. The example shown in Fig. 4-b of Whelan et al. (1994) does not look like speleothemic material.

To my knowledge, cathodoluminescence is used quite rarely to study banding of speleothems, because luminescence under the UV excitation has a much better resolution. The reason is that CL reveals differences in trace element composition, whereas UV luminescence depicts differences in the content of organics (humic material). The latter is typically abundant in speleothems because the calcite-depositing waters seep through soil. My attempts to document banding in my Yucca Mountain samples under the UV excitation have failed.

15. Stable C and O Isotopes of Calcite. The authors agree with my reasoning, but question my data. This can only be resolved by joint repeat analysis of my samples.

"…*we take them* [variations in δ^{13}C and δ^{18}O], *as Dublyansky would suggest, as evidence of meteoric-water percolation fluxes*". From the standpoint of the site suitability, it is of minor concern if some of the Yucca Mountain calcites are proved to be formed by meteoric waters. However, if my isotopic data are correct (which can easily be checked), and the logic is correct (as reviewers have agreed), this will make the "meteoric" origin for my samples untenable. And this will be of concern for site suitability. Since "meteoric" calcite is relatively benign in the context of the site suitability and repository performance, it seems that the energy that has gone into the investigation of this calcite is misplaced. Instead, there needs to be vigorous study of the calcite which may indicate threat to the repository performance.

16. Isotopic Signature of Mineralizing Fluids. "*In fact his argument demonstrates that such water* [that deposited calcite at Yucca Mountain] *is much different than regional ground waters during the past 500,000+ years (e.g., Winograd and others, 1992) although we suspect that that was not his intent*". That was exactly my intent.

The proponents of the "meteoric" concept often argue that since stable isotopic values of the Yucca Mountain calcite cannot be derived from those of the regional ground waters, this calcite was not deposited from regional ground waters. This is logical. However, a subsequent argument that this calcite was derived from soils by descending meteoric waters does not logically follow from the first point. Deep-seated fluids which acquired their isotopic properties from Paleozoic and Proterozoic rocks and up-welled toward the surface would have little to do with shallow waters of regional aquifers.

The isotopic composition of calcite (δ^{18}O and δ^{13}C) deposited from an aqueous fluid critically depends on two parameters: the initial composition of these isotopes in the mineral-forming fluid, and the fractionation coefficients, governing partitioning of isotopes between the fluid and the depositing calcite. The fractionation coefficients are temperature-dependent. Therefore, we have two equations with three unknowns (the isotopic composition of carbon, that of oxygen in mineral-forming fluid, and the temperature).

Fluid inclusion studies provide independent information on the temperature of calcite deposition. This eliminates one of the unknowns and makes it possible to calculate initial values of the mineral-forming fluids. The only other alternative is to assign one of these unknowns with an arbitrary value – a questionable practice.

Calculated values $\delta^{18}O$ and $\delta^{13}C$ for paleo fluids. There was a minor calculation error in numbers for $\delta^{18}O$. Correct values are -4.6 to -6.2 ‰ SMOW. Equations used for calculations are:

$\delta^{18}O_{caclite} - \delta^{18}O_{water} = 2.78(10^6T^{-2}) - 2.89$ (where T is absolute temperature) and

$\delta^{13}C_{water} \cong \delta^{13}C_{calcite} + 2.8$ (at 50 °C) (reflects fractionation between $CaCO_3$ and HCO_3^- in solution).

17. Source of Mineralizing Water. "*…such waters are also compatible with present-day unsaturated zone porewaters as well as with the probable compositions of fracture-hosted percolation…*" The origin of the pore waters is not known with certainty. They may be relics of ancient precipitation, or they could be relics of ancient upwelling fluids. Even less is known regarding the "possible composition of fracture-hosted percolation". From very general consideration (absence of evaporite deposits above the repository horizon), salinities of these waters are expected to be low. However, salinities measured in some inclusions (0.53 to 1.65 wt. % NaCl equiv. or 5.3 to 16.5 g/l) represent what is in hydrology called brackish or slightly saline waters. These concentrations are higher than may be expected for percolating meteoric waters at Yucca Mountain.

19. Hydrocarbon Potential. "*…Dublyansky cites an unknown reference for hydrocarbon potential (Mattson and others, 1992)…*" Two authors of this paper, Steven Mattson and Jean Younker, work for one of the major contractors of the U.S. DOE (Science Application International Corp.). The other two authors, Joel Bergquist and Thomas Bjerstedt represent the U.S. Geological Survey and the U.S. DOE respectively. Their paper was published in Geotimes, a well-known journal published by American Geological Institute.

As far as I understand, the reviewers do not argue with my thesis that aromatic hydrocarbons are not compatible with aerated vadose (unsaturated) zone. Therefore, sedimentary rock underlying Yucca Mountain represent probably the only reasonable source of hydrocarbons in Yucca Mountain calcites. I believe it is clear that in the context of this study, we are interested not in *economic* hydrocarbon potential, but in the potential source of hydrocarbons. Grow et al. (1994) pointed out that:

> *"While much of the Cambrian through Triassic rocks have thermal potential for gas, extensive Late Tertiary faulting at Yucca Mountain suggest that seals might be inadequate for retaining gas."* (p. 1298).

Restricted data available to date indicate that thermal history of Paleozoic carbonaceous rocks under Yucca Mountain was such as to allow organic matter trapped in these sedimentary rocks to be transformed into oil and gas. The only drill hole which penetrated Silurian dolomite under Yucca Mountain (UE25p#1) produced Conodonts having color alteration index, CAI, of 3 (Grow et al., 1994). Such a value is typical of rocks that have reached temperatures of ~180 ^{o}C and is in the range where:

> *"… oil is no longer generated, but in the range where gas is generated and previously generated oil is being converted to gas"* (Grow et al., 1994. p. 1301).

Although the amount of these hydrocarbons in Paleozoic rocks may presently be quite small, they represent a plausible source of tiny amounts of gases trapped in fluid inclusions. Moreover, it should be noted that the fluid inclusions were formed in the geologic past, so that the oil-to-gas ratio yielded by current exploration would not necessarily be relevant to the time of calcite formation.

Section 7 – Conclusions and Recommendations

21. Volatile Organic Compounds. The evidence for the presence of aromatic hydrocarbons may be considered as preliminary in the sense that I am presently unable to identify gases trapped in the inclusions. Nevertheless, it is the best available explanation of observed facts:

a. Luminescence of inclusions under Ar-laser excitation:

> *"Fluid inclusions are generally fluorescent if they contain cyclic or aromatic hydrocarbons or fluorescent daughter minerals"* (Burke, 1994, p. 30) ;

and

b. Decrease in luminescence with increasing time of the Raman signal accumulation, which I interpret as the result of the de-composition of organic molecules under the influence of the heat-energy of the laser beam.

I agree that the results of the gas chromatographic analyses may reflect organic material in calcite (not necessarily derived from fluid inclusions). However, the presence of humic and fulvic acids in studied calcites, suggested by the reviewers, is highly unlikely. These acids cause calcite to fluoresce under the UV-excitation in very characteristic yellowish-brownish colors (which is quite successfully used to identify the most fine-scale rhythmic growth banding in speleothems and to get detailed paleo-climatic records from them; see Shopov, 1997).

In this final section, the reviewers express their opinion that the existence of the hydrothermal system at Yucca Mountain must be verified and, if substantiated, the careful dating needs to be performed in order to assess the significance of the data for the performance of the repository. I agree with these suggestions, which are similar to those presented in the Conclusions and Recommendations of my report.

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Statement of Yuri Dublyansky on

Fluid inclusion studies of samples from the Exploratory Study Facility, Yucca Mountain, Nevada

My name is Yuri Dublyansky, and I am Senior Scientist at the Institute of Geology, Geophysics and Mineralogy of the Siberian Branch of a Russian Academy of Sciences. My field of expertise is fluid inclusions in minerals. I have been studying Yucca Mountain since 1994. Initially I did so as a consultant to the State of Nevada.

According to the current concept a repository is proposed to be constructed within the unsaturated zone of Yucca Mountain that is, in relatively dry rocks, far above the water table. Regulations require that the repository ensures safe containment of radionuclides for at least 10,000 years. Peak radiation doses are expected to occur on far longer time scales. In order to be able to forecast repository performance in the future, we need to carefully understand the geologic history of Yucca Mountain.

The concept of a high-level nuclear waste repository at Yucca Mountain critically relies on the assumption that the repository zone will remain unsaturated during the time period required for protection of the public (on the order of tens of thousands of years). Therefore, an indication that the mountain may have been saturated in the geologic past would be very troubling.

The first doubts regarding the long-term stability of the unsaturated zone at Yucca Mountain were raised as early as 1987 by the DOE Yucca Mountain Project staff geologist J. Szymanski. His hypothesis regarding the possibility of excursions of thermal waters into the currently unsaturated zone was criticized and eventually discarded by a National Research Council Panel in 1992.

The DOE and its contractors remain publicly confident that Yucca Mountain has been unsaturated for millions of years and therefore that the future stability of the unsaturated zone is reasonably assured for the relevant time periods. Specifically, according to the DOE, the unsaturated zone at Yucca Mountain was formed 9-10 million years ago and since that time the water table has never risen more than about 300 feet above its present level (which is 1000 feet below the planned repository horizon). Therefore, any flooding of the repository in the future is deemed unlikely.

A potential stumbling-block for the DOE-endorsed concept was discovered during extensive exploration drilling at Yucca Mountain. Cores recovered from boreholes often contained veinlets of calcite – a mineral which is practically always formed by precipitation from water. These veinlets represented “footprints” of ancient waters that moved inside the mountain in the past. In 1995-1997, when a 5 mile-long tunnel (called Exploratory Study Facility or ESF) was excavated into Yucca Mountain, many more occurrences of secondary minerals became available for study.

DOE researchers interpreted this calcite as being deposited in the unsaturated zone by rain water percolating through interconnected fractures and carrying dissolved calcium carbonate from overlying soils. Calcite was extensively studied in terms of its stable (carbon, oxygen) and radiogenic (strontium, uranium, thorium, lead) isotope compositions to determine its origin. The problem with this methodology is that isotopic methods, on their own, are not capable of distinguishing between different origins of minerals. The only method which can provide unequivocal determination of the origin – the fluid inclusion method – has never been adequately applied in the DOE studies

Fluid inclusions are tiny vacuoles in minerals, filled with the liquids from which minerals grow. If these fluids are trapped and sealed at elevated temperatures, upon cooling to ambient temperature they form tiny bubbles inside them. This stems from the physical properties of liquids and solids: on cooling liquids trapped in the inclusion contract faster than surrounding solid, the pressure in the vacuole decreases and at a certain point homogeneous liquid (e.g., water) splits onto two phases: liquid and vapor. This process is reversible: if we heat such inclusions, the pressure inside will increase and at some temperature, the bubble will disappear and fluid will become homogeneous. This temperature reflects the temperature of the liquid from which the crystal grew. Inclusions in minerals formed at low temperatures (less than ~35-40 ^oC) do not contain bubbles.

In June 1998, I collected samples covering all 5 miles of the ESF tunnel, and in October I conducted a study on the fluid inclusions in them. The report that we release today presents the results of this study.

Examination of calcite samples from the ESF tunnel leads to two principal conclusions:

- the studied calcite was formed by upwelling of water and not from percolation of surface water; and
- the water that entered the Yucca Mountain repository area in the past from below was at elevated temperatures.

The main evidence for these findings is as follows:

1. Many fluid inclusions in samples from the ESF had vapor bubbles formed in them. I obtained about 300 measurements of fluid inclusion temperatures, which indicate temperature of ancient water of 35 to 75 ^oC. Water with such temperature could not have come from surface sources.
2. In a few samples, traces of aromatic hydrocarbons were found in all-gas inclusions. Aromatic hydrocarbons are heavy molecules that could not have originated in surface sources. There is evidence of hydrocarbons (natural gas) in the geologic media beneath Yucca Mountain area. Hence, the trapped hydrocarbons provide supplementary, though at present fragmentary, evidence of upwelling of water into the repository horizon.
3. Veins and crusts at Yucca Mountain contain other minerals in addition to calcite, such as opal, quartz, and minor fluorite. These minerals typically precipitate from warm or hot water. In particular, it is extremely rare for quartz and fluorite to be formed from surface water percolation. Hence, the presence of these minerals is strong evidence of past presence of upwelling warm water in the Yucca Mountain area.
4. Minerals formed in an unsaturated zone, that is, above the water table, are typically deposited in laminated formations consisting of millions of tiny crystals. For example, stalactites in caves are created in this way. By contrast, large perfectly shaped crystals require a saturated environment to form. The calcite at Yucca Mountain often forms perfectly shaped individual crystals up to 1.5 cm in size, clearly indicating that the mountain was, at some time in the past, saturated.

My study also addresses the question of the age of the calcites, though in less detail. The timing of the formation of the calcites is important because it provides evidence of when the area was saturated and hence of the probability of its becoming saturated in the future during the period relevant to repository performance. The findings of my research for the timing of past repository saturation are only tentative and indicative. There are indications that the calcite may have been formed in the recent geologic past (less than one million years ago). This is a very complex and difficult area of work and considerable further research is needed to clarify this crucial question.

The issue addressed by my research has direct and significant bearing on the viability of the site as a potential host for the high-level nuclear waste repository. The critical questions remaining to be resolved are:

- When did the upwelling happen?
- Did it happen as a one-stage process, or did water rise and recede intermittently?
- If the upwelling occurred in pulses, what was the recurrence period of these pulses and what was the duration of each pulse?
- How much water was involved?
- What was the spatial distribution of this upwelling?
- What was the cause of the upwelling?

Only when all these questions have been satisfactorily answered can we address the ultimate question:

- Could the repository become submerged again in the future on time scales comparable to those during which radiation doses could be significant?

Without these answers, any assessment of the site viability will necessarily be incomplete. It is clearly premature at present to declare the site viable.

More data need to be acquired and analyzed in order to assess the implications of the new findings for repository viability. This may be accomplished through concerted efforts of researchers, involving:

a. Detailed fluid inclusion studies in calcite and other minerals from Yucca Mountain. Such studies may provide important information on the spatial structure of the ancient hydrological system;

b. Careful dating of calcite samples hosting fluid inclusions indicating elevated entrapment temperatures, which would constrain timing of ancient hydrothermal system; and

c. Detailed isotopic study of minerals, which could provide important information on the origin of fluids and pattern of fluid migration.

Saturation of the Yucca Mountain repository after burial of highly radioactive waste could cause the waste canisters to corrode far more rapidly than if the mountain remained dry allowing the radioactive materials to be carried away. Because of the great threat to the environment and to human health that would be posed by such a situation, further study is absolutely necessary.