From: English Pearcy
Sent: Thursday, April 06, 2006 11:26 AM
To: James Myers
Subject: hydrothermal upwelling summary
Attachments: Musgrove-YM-thermal_hist.wpd

Jim,

See below and attached.

English

-----Original Message-----
From: MaryLynn Musgrove [mailto:mmusgrove@cnwra.swri.edu]
Sent: Wednesday, April 05, 2006 5:42 PM
To: English Pearcy
Cc: John Stamatakos
Subject:

English,

As I'm rapidly running out of time here I think it prudent to send you what I have so far with respect to the "Syzmanski theory" as it has come to be know. I personally have taken to calling it the "Szymanski hypothesis" or the "thermal upwelling hypothesis", simply because by the scientific method a theory has much more credence than a hypothesis, and indicates some level of confirmatory testing and support.

Attached is a draft document that largely summarizes this history of this topic, provides background on the relevant milestones, so to speak, that have marked its 20 or so year history (e.g., reviews by the NAS and the NWTRB), details some of the most current topics of debate (which are the ones likely to be perhaps be revisited, or continue, during review of a license application), some recommendations, and an annotated bibliography.

I'll bring you a hardcopy tomorrow, along with a hefty stack of papers and documents –and if you've got suggestions that I can incorporate in the next couple of days, please let me know. I'd also be quite interested in discussing possibly ideas of getting a summary like this out in the literature, if relevant. I also apologize that I haven't properly proofed this, but wanted to get something to you sooner rather than later. I should have time to go thru it before I depart on Friday.

I regret that I haven't made nearly as much progress on this project as I'd hoped to. What I've done is far more summary than evaluation and the recommendations are on the thin side. But, I sincerely hope that what is here will be useful to whomever may picking up this topic in the future, given its long history and the wealth of information associated with it. The references list on the attached file is annotated (though only partly so) –I found, given the numerous publications on the topic, a brief review of what relevance a reference may have to be helpful.

In a nutshell, there are some new/continuing issues --they largely revolve around fluid inclusion data (Whelan et al., 2002 and Wilson et al., 2003) , as well as the origin of the Class B faults (Gray et al, 2005), which all document the existence of higher temperatures than might be expected under meteoric conditions. The "catch" with respect to this data is the age control. The results of Whelan et al. (2002) and Wilson et al. (2003) construct a paragenetic sequence which suggests that higher temperatures occurred "early" in the geologic history of the site and are not relevant for the Quaternary. The results of Gray et al. (2005) that suggest higher temperatures have no temporal control at all. Dublyansky and associates have argued that evidence of higher temperatures supports a thermal upwelling hypothesis, but this is not necessarily true if the geologic history of the site can account for these early higher temperatures. But, even based on the ages determined by Wilson et al. (2003) for the early (or oldest) secondary minerals, the timing is still challenging to account for a seemingly necessary source of heat millions of years beyond the tuff formation. All of the continuing issues may be minor if everything suggesting high temperatures is v. old and occurred shortly after the tuffs formed. An aspect of much of the geochronology that is not really focused on is that age constraints are largely on associated opals, rather than directly on calcites themselves. Thus, the ages are MINIMUM ages –based on the v. slow growth rates of the opals, the calcites could be considerably older.

There are a number of other issues, certainly more minor but which may still come up again, that I haven't unfortunately had time to address at all. These include topics such as Sr/Ca ratios in the calcites, fluid inclusion gases chemistry, presence of hydrocarbons in fluid inclusions, and the existence of fluorite and strontianite in the secondary mineral assemblages. These are all brought up in Dublyansky et al. (2004) and (2005), which are responses to Whelan et al. (2002) and Wilson et al., (2003).

I am of course happy to answer any questions on this, undertake revisions as deemed necessary, or help in any way I can with this matter in the future. Regardless of all of the issues it has caused for the Yucca Mountain Project, it is scientifically extremely interesting, and I've very much enjoyed working on it. Please don't hesitate to contact me about it.

Cheers,
MaryLynn

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A Review of Secondary Mineralization and the Thermal History at Yucca Mountain, Nevada: Implications for Paleohydrology

M. Musgrove

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San Antonio, TX

April 2006

Outline

1. Introduction
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1. Introduction

Yucca Mountain in southern Nevada is currently under evaluation as the location for a potential high level nuclear waste repository. Water flow through the future repository is an important control governing the supply of water reaching the waste packages. Water flow is a likely mechanism for transporting radionuclides to the groundwater and potentially impacting population in the surrounding area. An understanding of the hydrogeology of the system provides a fundamental basis for assessing water flow, and is crucial for placing constraints on the future behavior of the repository.

Yucca Mountain is composed of approximately 500-700 meters of Miocene aged volcanic tuffs.

The proposed repository will be located approximately 200-300 meters above the current water table and 200-300 meters below the land surface. Water moving through the unsaturated zone in the past left behind deposits of secondary minerals, largely calcite and silica, in lithophysal cavities in the vadose zone, in fractures in the tuffs, and at the surface. Physical, chemical, and isotopic characteristics of these secondary minerals provide insight into their origin, timing, setting, and conditions of formation, which in turn reveal conditions of paleohydrology. There has been a long debate over the origin of these secondary minerals, which has significant implications for the behavior of the potential repository in response to natural fluid flux processes it may be expected to encounter in its lifetime.

The secondary minerals and thermal history of Yucca Mountain have been studied for many years and are complex and multifaceted topics. While many aspects are well documented and understood, other aspects of the importance, interpretation and potential scenarios indicated by the science behind this topic remain matters of ongoing scientific debate. Described herein are the background and evolution of this topic, and a brief summary of potentially unresolved and/or remaining potential issues that may be revisited during review of a license application. With 20+ years of intensive and evolving study on this topic, this is by no means meant to serve as a comprehensive review and it is likely that not all relevant work and literature on the topic is included herein. The goal of this effort, nonetheless, is to provide sufficient information to support future efforts to address in more thorough detail specific issues that may be contended or revisited during review of a license application. Also included and imbedded in the References section is an annotated summary of much of the relevant literature.

2. Early Investigations of Unsaturated Zone Secondary Minerals: Meteoric Deposition or Thermal Upwelling Waters?

In 1982 Congress passed the Nuclear Waste Policy Act, which requires the federal government to develop a geologic repository for the permanent disposal of high level radioactive wastes and spent nuclear fuel from nuclear power plants. In 1983, the Department of Energy (DOE) Office of Civilian Radioactive Waste Management (OCRWM) was established, and initially began studying three potential sites for a waste disposal facility, one of which was Yucca Mountain. In 1987 Congress passed the Nuclear Waste Policy Amendments Act which directed the DOE to focus its efforts exclusively on Yucca Mountain. During development of the Yucca Mountain site characterization plan (DOE, 1988), which established the basis for extensive scientific and engineering investigations of the area, a DOE staff scientist suggested that in the recent geologic past the groundwater had risen by hundreds of meters, and that this type of event could happen again in the repository lifetime (Szymanski, 1989). Such a groundwater rise could flood the repository and provide a pathway for migration of radionuclides from the site. The Szymanski hypothesis, as it has come to be known based on the name of the DOE employee proposing the argument, suggests that the groundwater rise is driven by a repetitive process of interacting crustal stresses and tectonic activity leading to earthquake induced pumping of deep hydrothermal waters to much higher levels (Broad et al., 1990). The hypothesis is based not on specific tectonic evidence for such processes occurring, but rather on interpretations of the origin, timing, and conditions of formation of secondary minerals in the unsaturated zone, which, based on the Szymanski hypothesis formed from associated upwelling waters.

The alternative and more generally accepted hypothesis for secondary mineral formation is that they precipitated from downward flowing meteoric waters in the unsaturated zone. It is on the interpretation of data detailing the secondary mineralization in the unsaturated zone that the debate between these two hypotheses has hinged. If the secondary minerals were formed by upwelling thermal groundwater this lends credence to the Szymanski hypothesis and suggests that a mechanism may exist for raising the water table hundreds of meters as it has operated in the past. If the secondary minerals were formed by downward percolating meteoric waters then this negates the evidence Szymanski (1989) cites as documentation for the hypothesis of upwelling waters. It should be noted, however, that evidence that may support an interpretation that the secondary minerals were formed by upwelling thermal waters does not necessarily provide a geological reasonable mechanism to drive such a processes. Evaluation of Szymanski's proposed theory of "seismic pumping" has largely been secondary to the interpretation of data supporting meteoric sources vs. upwelling sources of fluid. Scientists familiar with the region, however, have been generally skeptical of earthquakes producing shifts in the water table of the scale necessary to substantiate a water table rise of hundreds of meters (e.g., see discussion in Marshall, 1991).

The early debate about secondary mineralization (i.e., mid-late 1980s through early 1990s) focused on the origin of calcite and opaline silica fracture fill deposits in an exploratory pit excavated across the Bow Ridge fault on Yucca Mountain (Trench 14). Trench 14 was initially excavated to evaluate the nature and frequency of Quaternary movement on the fault (Taylor and Huckins, 1995), but subsequent questions were raised about the secondary mineral deposits revealed in the trench. The secondary mineral deposits are thick, well-layered, and well-indurated, and were proposed to resemble vein cements and travertine deposits that are commonly associated with surface-discharging springs (Quade and Cerling, 1990). The deposits are also contiguous with slope-parallel calcretes that are typically attributed to a pedogenic origin (Whelan et al., 2004). The vertical veins in Trench 14 have uranium-series ages of 228,000 to >400,000 years (Stuckless et al., 1991 and references cited therein). Trench 14 is located about 150 meters above the repository level. Thus, if spring deposits formed at this level, it would suggest that a much higher water table existed at some point in the past when the deposits formed.

3. National Academy of Sciences Report (1992)

The theory of upwelling hydrothermal fluids that periodically rise above the water table and inundated the unsaturated zone, as proposed initially by Jerry Szymanski and furthered by Yuri Dublyansky and others, was reviewed in detail by the National Academy of Sciences' National Research Council (NAS/NRC) in 1992. The NAS/NRC established the Panel on Coupled Hydrologic/ Tectonic/ Hydrothermal Systems at Yucca Mountain, Nevada to evaluate 1) if the water table had been raised in the geologically recent past to the level of the proposed repository, and 2) if it is likely that it will happen within the 10,000 year period covered by regulation of the potential site. The panel evaluated Szymanski's report, reviewed relevant and contributory literature, "interviewed or consulted with scientists involved in field and laboratory investigations", and spent time in the field led by "scientists on both sides of the controversy." The panel looked at multiple potential lines of evidence including soils, springs, textural and morphological evidence, geochemical and isotopic data for near-surface and sub-surface fracture fillings, breccias cemented by carbonates or carbonate/silica, and surficial, surface-parallel deposits of carbonate and silica. Numerous studies of the geochemistry, geology, and hydrology of the fault and Trench 14 secondary minerals as well as studies of their regional hydrologic context were available to facilitate the Panel's review (e.g., Stuckless et al., 1991; Quade and Cerling, 1990; Szabo and Kyser, 1990; Winograd et al., 1988; Benson and Klieforth, 1989; Whelan and Stuckless, 1990).

The Panel's conclusions with respect to point #1 ("has it happened?"), were unequivocal and in summary state that "there is no evidence to support the assertion that the water table has risen periodically hundreds of meters from deep within the crust. In fact, the evidence strongly supports a surface-process origin from rainwater for the vein and surface parallel carbonate and carbonate-silica deposits throughout the Yucca Mountain area." The panel further concluded that none of the evidence put forth to support upwelling groundwater in and around Yucca Mountain "could be reasonably attributed to that process." Many are "classic examples of arid soil characteristics recognized world-wide."

With respect to point #2 ("can it happen?") the Panel independently considered possible mechanisms by which a significant rise in the water table could be achieved: increased rainfall, volcanic intrusion, and earthquakes. The Panel's concluded that these mechanisms offer varying degrees of concern, and proposed recommendations to better constrain these concerns. For the modeling results available at the time, which the Panel considered overly conservative, they nonetheless concluded that climate change and its impacts on rainfall is a mechanism that has the potential to affect a large rise in the water table. As a result, they recommended further efforts to better consider precipitation changes and associated hydrologic changes. With respect to volcanic intrusions, the Panel concluded they are a low probability risk. Specifically relevant for the Szymanski hypothesis, the Panel concluded that earthquake induced seismic pumping raising water to the repository level is unlikely, though large uncertainties supported continued efforts at site characterization. In evaluating evidence from historic earthquakes around the globe, the Panel concluded that "the magnitude of the water table changes for these earthquakes is consistent with modeling results and, therefore, provides further evidence that earthquake strain release mechanisms (or 'seismic pumping') are inadequate to pose a threat to the unsaturated zone location of the proposed repository." Additionally, "various earthquake models have been used to analyze the response of the water table to stress changes in the crust resulting from earthquakes. It appears that water table rises of more than a few tens of meters are unlikely." Finally, the Panel recommended ongoing work to better understand the local hydrologic system, the nature of the steep hydraulic gradient to the north of the proposed repository, connections with the underlying Paleozoic carbonate aquifer, and the appointment of a site characterization science coordinator.

4. Nuclear Waste Technical Review Board Evaluation (1998)

After the 1992 NAS/NRC report, the U.S. Nuclear Waste Technical Review Board (NWTRB) noted that they would consider reviewing any new data or modifications that may be presented in the future on the origin of secondary mineralization. Subsequent research efforts continued to address the geochemical, isotopic, geologic, and hydrologic characteristics of the Trench 14 and fault deposits, and to evaluate their regional context (e.g., Bish and Aronson, 1993; DOE, 1993; Dublyansky and Reutsky, 1995; Dublyansky and Szymanski, 1996; Dublyansky et al., 1996; Hill et al., 1995; Ingraham et al., 1991; Paces et al., 1996; Quade et al., 1995; Stuckless et al., 1998; Szabo et al., 1994; Taylor and Huckins, 1995; Vaniman et al., 1994; Vaniman and Chipera, 1996). Additionally, Dublyansky (1998) and Dyblyansky et al. (1998) identified two-phase fluid inclusions in mineral crusts from fractures and cavities in the Exploratory Studies Facility (ESF), indicative of higher temperatures of formation.

In 1998, in response to these developments and new materials submitted subsequent to the 1992 NAS/NRC report, the NWTRB decided to further evaluate the issue. The new materials included 11 reports and publications submitted by J. Szymanski (a mixture of peer-reviewed published documents and unpublished reports by various authors) and 3 reports submitted by the State of Nevada Attorney General's office. The reports focused on proposed evidence for two main topics: ongoing intermittent hydrothermal activity and large earthquake-induced changes in the water table at Yucca Mountain. The review involved detailed evaluation and input from the board members as well as four outside qualified scientists, previously unaffiliated with the Yucca Mountain project. The outside scientists were charged to review the new material submitted to the NWTRB along wirh several other reports, rather than to duplicate efforts of the 1992 NAS/NRC Panel. The scientists were charged with four questions, which were then integrated for a final evaluation by the NWTRB. The questions were: "1) Are there significant new data and interpretations since the 1992 NAS/NRC report?; 2) What is the quality of these data and interpretations?; 3) How much credence do these data and interpretations lend to the hypothesis of ongoing, intermittent hydrothermal activity and large earthquake-induced changes in the water table at Yucca Mountain?; and 4) If these data and interpretations significantly affect the conclusions of the 1992 NAS report, how can the issue be resolved?" (http://www.nwtrb.gov/reports/98summ2.pdf).

In their 1998 report (available at http://www.nwtrb.gov/reports/reports.html), the NWTRB concluded that there was, subsequent to the NAS/NRC report, new material to be considered. They further concluded, however, that the new material was of varying significance and did not make a credible case for an assertion of ongoing intermittent hydrothermal activity or a likelihood for large earthquake-induced changes in the water table at Yucca Mountain. They conclude that the new material did not significantly affect the conclusions of the 1992 NAS/NRC report. The new data was generally considered to be of good quality, but issue was taken with much of the data interpretation and with an insufficient documentation of important details necessary to properly interpret the data. The NWTRB specifically called out numerous questionable interpretations, such as "very tenuous fits of lines to scattered small data sets.......in Hill and others (1995), Dublyansky (1995), Dublyansky and Szymanski (1996) and Szymanski and Dublyansky (1996)." The NWTRB, recognized several potential areas to continue to further evaluate the hypotheses of ongoing intermittent hydrothermal activity and large earthquake-induced changes in the water table, but they viewed such research as a low priority due to a lack of any substantive evidence to support either hypothesis.

A potential exception to this conclusion by the NWTRB centered around measurements on fluid inclusions in secondary mineral deposits which indicate the presence of elevated temperature fluids (e.g., at least 72°C) at some point in the past in the vicinity of the proposed repository. The significance of this fluid inclusion data for the question at hand depends on when the inclusions formed: "If the limited, poorly documented, and indirect estimates of young ages (less than 100,000 years) quoted by Hill et al. (1995) and Dublyansky and Reutsky (1995) are correct, this could led credence to the hypotheses of ongoing, intermittent hydrothermal activity at Yucca Mountain. On the other hand, if the ages of the calcites are shown to be around 10,000,000 years or older, the presence of fluids at elevated temperatures could be associated with volcanic events related to the original formation of Yucca Mountain and would have no bearing on the hypothesis of ongoing hydrothermal activity" (NWTRB, 1998). Based on this uncertainty, the NWTRB recommended constraining the ages of fluid inclusions via a joint program between federal and State of Nevada scientists, which would reduce opportunity for disagreements associated with sample collection and handling.

5. Recent Efforts (Post NWTRB Evaluation)

Based on the NWTRB's recommendations, the DOE initiated parallel studies of the secondary mineral deposits by the University of Nevada Las Vegas (UNLV), the U. S. Geological Survey (USGS) and the State of Nevada's Nuclear Waste Project Office (represented by Y. Dublyansky). Samples were collected by the UNLV group, who provided polished sections of each sample to the USGS and the State of Nevada (represented by Y. Dublyansky), thus, independent analyses could be performed on the sample sample set for comparison (Wilson and Cline, 2005). Results of efforts by both the UNLV and USGS studies confirmed the fluid inclusion temperatures reported by Dublyansky. The results of these studies also described in detail the distribution, textures, petrography, and geochemistry of secondary minerals in fractures and lithophysal cavities, and developed a geochronologically constrained mineral pargagenesis (e.g., Paces et al., 2001; Whelan et al., 2002; Wilson et al., 2003). These efforts, which are described in more detail below, conclude based on a variety of types of data sources that the secondary minerals are consistent with formation by descending meteoric water. As noted in Whelan et al. (2004) "to date, the results of the Nevada Nuclear Waste Project Office studies have not been published, nor has the theory of the upwelling hydrothermal fluids been presented as a comprehensive and testable hypothesis in the peer-reviewed literature." Dublyansky and others, however, as detailed below, have responded with comments to the results of both the UNLV and USGS studies (Dublyansky et al., 2004; 2005). Their comments clearly indicate that they do not accept the interpretation of the UNLV and USGS studies as credible, and they continue to support a model of secondary mineralization by thermal upwelling fluids.

The USGS and UNLV study results are summarized in Whelan et al. (2002) and Wilson et al. (2003), and work cited therein. An additional recent effort with direct bearing on the current status of understanding for secondary mineralization at Yucca Mountain is Gray et al. (2005). These three studies are summarized below.

Whelan et al. (2002)

Whelan et al. (2002) presents the results of the USGS parallel study of secondary mineral deposits from the ESF and EWCD, building on previous results. The authors describes in detail the distribution, morphology, texture, and mineralogy of the deposits and establish a paragenetic sequence of early (ending between 6 and 8 Ma), intermediate, and late (beginning about 3-4 Ma) stages of formation (Whelan et al., 2002; Whelan and Moscati, 1998). Although deposits displaying the complete paragenetic sequence are rare, the sequence is nonetheless consistent with the deposits found. Most early-stage and some intermediate stage calcite formed at temperatures of 35 to 85°C, where as late stage calcite (deposited since 3-4 Ma) formed at temperatures <30°C. Stable carbon and oxygen isotope data, and ^{230}Th/U and ^{235}U/^{207}Pb ages of fracture and cavity hosted calcite and silica support the paragenetic sequence interpretation (based on data from Whelan et al., 1998; Neymark et al., 2002; and Paces et al., 2001). Calcites exhibit a large range in stable isotope values and exhibit a trend of decreasing δ^{13}C and increasing δ^{18}O values through time. The authors discuss upwelling versus percolation-driven deposition models for formation of the secondary minerals and conclude, consistent with the previous studies that this work builds on, that they are consistent with deposition from descending meteoric waters. They further conclude that fluid inclusion temperatures also reflect the paragenetic sequence, with elevated fluid inclusion temperatures restricted largely to early stage mineral deposits, and with no elevated temperatures reported from late-stage calcite (i.e., 2-4 Ma). They propose that warmer depositional temperatures in the past, as reflected in elevated fluid inclusion temperatures in early stage minerals reflect prolonged thermal input to the unsaturated zone from ongoing regional magmatic activity. Whelan et al. (2002) consider that the sporadic and limited (<10%) distribution of the deposits as some of the most compelling evidence arguing against the upwelling thermal water hypothesis. Mineral coatings are large limited to fracture footwalls and lithophysae floors, indicative of a gravity control (Paces et al., 1998, 1999, 2001), and are largely restricted from cavity ceilings and cavity and fracture walls.

Wilson et al. (2003)

Similarly to Whelan et al. (2002) this work builds on previous studies in characterizing secondary mineral deposits from fractures and lithophysal cavities. These results are based on 155 samples collected from the ESF and repository block cross drift (ECRB) tunnels, and are focused on determining the temperatures of fluids that deposited secondary minerals, as well as the extent and timing of fluid flow, in particular with respect to elevated temperature fluids. In order to address this broader topic, the authors further constrain the generalized paragenetic sequence detailed by Whelan et al. (2002), integrating petrology with electron probe microanalyses and C and O isotopic data. The authors detail the occurrence of fluid inclusions, associated fluid temperatures and salinities, and include 41 U-Pb and U-series ages on 18 samples of opal and chalcedony. Wilson et al. (2003) establish the most detailed and constrained picture yet offered as to the nature and timing of fluid inclusions. Significant results include the following: Based on the distribution and limited occurrence of secondary minerals, the authors concur with Whelan et al. (2002) that secondary mineral formation is consistent with a vadose zone origin and is inconsistent with formation under saturated conditions. Age constraints indicate that two-phase fluid inclusions, associated with elevated temperature fluids occur in the oldest secondary minerals, that is, older than at least 5.32 Ma (± 0.02 Ma). It should be emphasized that these ages are not directly on the calcites containing the two-phase inclusions but rather on opals and chalcedonies that are paragenetically younger. As such, the interpretation that two-phase inclusions occur in samples >5.32 Ma in age represents a MINIMUM age and the inclusions may be older than 5.32 Ma. It should also be noted, however, that ages collectively indicate that the two-phase inclusions are also younger than 9.06 Ma (± 0.08 Ma). Two-phase fluid inclusions are minor overall, but are more abundant in the lithophysal cavity zone and eastern part of the ECRB and mostly occur in calcite. Their distribution indicates that elevated temperature fluids accessed most of the site, and their salinity is consistently low. Only all-liquid inclusions, associated with formation at ambient temperatures, were associated with both the intermediate and youngest phase minerals. These results indicate that elevated temperature fluids occurred only prior to 5 Ma, and not at all during the Quaternary. These results consistently indicate that the highest temperature fluids were present early in the history of the site and that they record a unidirectional cooling trend with time. This paper also presents a good overview of previous work addressing the geologic background, petrography, paragenesis, and chemical composition of secondary minerals, stable isotope data, fluid inclusion studies, and U-Pb and U-series dating. Data from secondary mineral occurrences in fractures result in similar age constraints on two-phase fluid inclusions, although results indicate that such inclusions are older than 4.00 Ma (±1.46 Ma), and younger than 9.06 Ma (± 0.08 Ma). Within analytical uncertainty, fractures yield the same age range for two-phase fluid inclusions associated with higher temperature fluids.

The paragenetic sequence of Wilson et al. (2003); which is in broad agreement with the work of Whelan et al. (2002), is summarized as follows:

1) Early to early-intermediate secondary minerals (9.06 to >6.29 Ma), >50ºC.
2) Early-intermediate secondary minerals (6.29 to 5.32 Ma), 35-45ºC.
3) Late intermediate secondary minerals (5.32 to ~2.9 Ma), < 35 ºC.
4) Late Mg-enriched growth zoned calcite (~2.9 Ma to present), < 35 ºC.

Gray et al. (2005)

Gray et al. (2005) present field and microstructural analysis of faults that distinguishes four distinct fault zones (Classes A-D). Classes A, C, and D are genetically related and represent progressive fault deformation resulting from increasing displacement and response of the welded tuffs. Class B fault zones, however, are of an unusual style "in which faults of generally minor displacement are heavily mineralized with blocky calcite." The significance of these faults is in these secondary minerals, which are distinct from other secondary minerals in lithophysal cavities and fractures. The Class B fault mineralization exhibit textures indicative of formation in a fluid saturated environment (specifically poikilotopic and drusy textures, coarse sparry or mosaic calcite). The poikilotopic calcite contains two-phase fluid inclusions and abundant deformation twins, the thickness of which is proposed to correlate with the temperature of deformation (as described by Ferrill, 1991 and 1998; Burkhard, 1993). Applying this methodology to Class B fault rocks suggests that deformation twinning occurred at relatively elevated temperatures (>170º). The timing of this mineral formation, however, is relatively unconstrained and the relevance of the Class B fault mineralization to the issue at hand likely hinges on the timing of formation. The texture of the Class B calcite matrix suggests it occurred rapidly and is, thus, synkinematic. Poikilotopic textures, however, are generally attributed to slow growth or recystallization – they are interpreted by Gray et al. (2005) to represent recrystallization that also was synkinematic (textures indicate recryrstallization and abundant deformation twins suggest synkinematic formation). The Class B faults also contain rare veins, which are partially or entirely filled with relatively strain-free calcite, and are thus interpreted to be postkinematic and to have formed at some later time. The textures of these veins (drusy) are also suggestive of saturated conditions. These veins currently are undated and have no chronologic control.

In summary, the Class B fault mineralization history is complex and polygenetic, but suggests at least some mineral formation under warm saturated conditions. If the Class B fault zone textures formed shortly after caldera eruptions and deposition of the tuffs (15-11 Ma) then the mineralization likely resulted from associated volcanic-geothermal activity circulating hot fluids, and subsequent cooling of the calderas. While there is no evidence to suggest that the faults are young (in fact, textures suggest they are recrystallization cements and that recrystallization was synkinematic with faulting), age constraints would resolve their timing and formation history. Additionally, age constraints on the secondary cross-cutting veins would also help constrain the timing and hydrologic importance of these features.

6. Potential Continuing Issues

Opponents of a metoric origin for secondary minerals have, in recent work, distilled their arguments to address specific matters of contention regarding a meteoric origin, which they consider to be a combination of problematic models, missing interpretations, and biased interpretations and selective use of information (Dyblyansky et al., 2004). It is possible and perhaps likely that some or all of these issues may be revisited during the licence application process. Note, however, that the issues are largely with respect to data interpretation, rather than with data itself. Opponents of the meteoric origin theory present varying degrees of counterargument for these issues, ranging from detailed alternative interpretations of data, to simply taking issue with aspects of the meteoric origin interpretation (without, in my opinion, necessarily presenting a viable alternative interpretation that is strongly supportive of a non-meteoric origin). These current issues are summarized as follows based on discussions presented in Dublyansky et al. (2003, 2004, 2005), and Dublyansky and Smirnov (2005), and are each discussed below in more detail:

1. Salinity of paleowaters
2. Carbon isotope enrichment of early basal calcites
3. Stable isotope compositions of paleowaters
4. Source of heat for higher-temperature fluid inclusions
5. Secondary mineral textures, distribution, and growth
6. Mg zonation in late calcites

6.1 Salinity of Paleowaters

Values for the salinities of fluid inclusion waters are as high as 2.71 wt% NaCl equivalent (that is up to 2700 ppm NaCl equivalent), with the majority indicating a salinity range of 0.71 to 1.57 wt% NaCl equivalent (that is 710 to 1570 ppm NaCl equivalent; Wilson et al., 2003). Salinity values are based on ice melting temperatures and Wilson et al. (2003) note that trace CO_2 in the fluid may contribute to freezing point depression and yield higher apparent salinity values. Dublyansky et al (2005) consider salinity values based on these measurements to be very high, inconsistent with current pore water and surface water salinities, and thus not compatible with a dilute meteoric water origin. As noted in both Wilson and Cline (2005) and Marshall et al., (2005), evaporation is a likely process that will affect fluid inclusion salinities (as well as isotopic compositions). As secondary minerals precipitate and evaporation occurs, the remaining, increasingly saline water is trapped in fluid inclusions. As noted in Wilson and Cline (2005) this process is observable in other localities, such as cave pools at Carlsbad Caverns, New Mexico, where evaporation increased salinity 10-fold (Ingraham et al., 1991). The model for secondary mineral precipitation proposed by Whelan et al. (2002) calls on evaporation as the major process driving mineral precipitation. Evaporation is also required to precipitate opaline silica (Marshall et al., 2003; Marshall et al., 2005). In summary, higher salinity values would be expected in fluid inclusions from slow-growing calcite. A review of salinity data from fluid inclusions in other studies, and inferences about paleosalinity of precipitating fluids and their enviroments may provide further insight into this topic.

6.2 Carbon Isotope Enrichment of Early Basal Calcites

Carbon and oxygen isotope data from Wilson et al. (2003) show a consistent trend of decreasing $\delta^{13}C$ (from +9.5 to -8.5‰) along with increasing $\delta^{18}O$ values (from +5.2 to +22.1‰) that occurs from paragenetically older (early) calcite to younger Mg-enriched growth-zoned calcite. Carbon isotope values that are geochronologically constrained by $^{207}Pb/^{235}U$ ages on chalcedony or opal show a quite steady decrease through time from early, intermediate, and late stages of secondary mineral deposition (Whelan et al., 2002; Whelan, 2004). The data, however, is not sufficiently distinct to determine deposition stage of secondary minerals from stable isotope values; plots of $\delta^{18}O$ vs $\delta^{13}C$ suggest that isotopic values for different morphologically distinct types of intermediate and late calcite overlap in value.

Whelan et al. (2002) state that "unsaturated zone minerals (Whelan et al., 1994; Paces et al., 2001) and fluids (Thorstenson et al., 1998; Yang et al., 1998) at Yucca Mountain have isotopic properties and chemical signatures consistent with meteoric water interacting with the overlying soils during infiltration." Dublyansky et al. (2004), however, take issue with this statement in discussing $\delta^{13}C$ values. They suggest that, based on sources of carbon to the meteoric environment at Yucca Mountain, calcite forming in isotopic equilibrium should have $\delta^{13}C$ values between -11 and +1‰ (e.g., sources of atmospheric CO_2 with a pre-industrial value of -6‰; calcareous surface deposits with values between -8 and -3‰ (DOE, 1993); measured soil CO_2 and gaseous CO_2 from the vadose zone ranging from -9 to -26‰ (Thorstenson et al., 1989; McConnaughey et al., 1994)).

The high-$\delta^{13}C$ values measured for early calcites are unusual for vadose zone conditions. Dublyansky et al. (2001) initially noted that "since there could be many different sources of carbon in mineral-forming fluids at Yucca Mountain (e.g., Paleozoic carbonates, deep-seated CO_2, Soil CO_2, hydrocarbons, etc.), genetic interpretation of the carbon isotopic record in the Yucca Mountain calcites is problematic." Results from Wilson et al. (2003) suggest that higher than average homogenization temperatures in part of the ESF of 75 to 81°C are consistent with the suggestion by Paces et al. (1997) that calcite with low $\delta^{18}O$ values (and correspondingly high $\delta^{13}C$ values) formed from higher temperature fluids. Dublyansky et al. (2004) suggest that $\delta^{13}C$ values greater than +1‰ constitute almost half of the isotopic record. It should be clarified, however, that the high-$\delta^{13}C$ values (up to +9.5‰) occur almost exclusively in basal calcites that formed early in the paragenetic sequence (Wilson et al., 2003), which is also indicative that they formed under higher temperatures and correspondingly associate conditions. Wilson and Cline note that for non-basal calcites, that is, the Mg-enriched calcites that formed during the Pleistocene, $\delta^{13}C$ values are indicative of surficial sources and are consistent with surface pedogenic carbonates (Wilson and Cline, 2005; Paces et al., 1997; Whelan et al., 2002).

The high $\delta^{13}C$ values measured in basal calcites are problematic with respect to their environment of formation, and most likely require interaction with a ^{13}C -depleted component, such as CH_4 (the presence of which has been identified in fluid inclusion gases; see Roedder et al., 1994; Dublyansky et al., 1996). Such conditions would be indicative of anaerobic conditions existing in the unsaturated zone. Dublyansky et al. (2005) argue that such high $\delta^{13}C$ values are incompatible with meteoric precipitation and point to anaerobic mechanisms known to produce ^{13}C-enriched calcite as support for a deep-seated provenance consistent with thermal upwelling waters. Whelan et al. (2003b) suggest that widespread conditions existed in the unsaturated zone during the time of early stage secondary mineral precipitation, which, coupled with higher temperatures of 40-70°C (methanogenic bacteria are thermophillic) were conducive for bacterial methanogenesis to occur. Vadose zone conditions today are sufficiently oxygenated to preclude methanogenesis (Dublyansky et al., 2005; Fabryka-Martin, 2000). Whelan et al. (2004), however, agree that methanogenic bacterial reduction of CO_2 could account for the high measured $\delta^{13}C$ values (Hacklet et al., 1996; Grossman, 2002;) and propose that anoxic conditions in the unsaturated zone are not necessarily implausible (Newman et al., 1996). A study by Newman et al. (1997) suggested that anoxic conditions and microbially induced precipitation of vadose-zone calcites may occur in fractures of the Bandelier Tuff Formation in New Mexico. Fluid inclusion gases measured in this study include CH_4. Newman et al. (1996) analyzed fluid inclusions in a variety of nonmarine calcites and documented distinct differences between pedogenic calcites and those formed in water-saturated conditions: high CH_4 contents and low oxygen contents suggested that anaerobic conditions were present.

Nonetheless, such heavy $\delta^{13}C$ values as those measured at Yucca Mountain (up to +9.5‰) have not been commonly measured in pedogenic calcites. Improved development of a model for high $\delta^{13}C$ values to occur in early stage calcites via anaerobic and methanogenic conditions would be helpful to resolve this issue.

6.3 Stable isotope compositions of paleowaters

Stable isotope compositions of secondary minerals are a topic of longstanding study at Yucca Mountain. Quade and Cerling (1990) compared carbon and oxygen isotopic data for carbonates from Trench 14 with data for carbonates in modern desert soils (formed from pedogenic processes and younger than 7,000 years0. Their results were supportive that the carbonates from Trench 14 are pedogenic in origin.

The NAS/NRC (1992) panel evaluated stable isotope evidence via a comparison of stable isotope values for the Trench 14 and Busted Butte carbonates with modern groundwaters in the Yucca Mountain region (Benson and Klieforth, 1989). This comparison indicated that the calcites did not precipitate from modern groundwaters. Although the possibility exists that modern groundwaters may be different from paleogroundwaters that precipitated the cements, regional data for paleogroundwater compositions suggest that even with climatically induced variations, groundwater stable isotope composition has not varied significantly enough to account for stable isotope values of the secondary minerals (Winograd et al, 1989; Szabo and Kyser, 1990).

Subsequent to the NAS/NRC report, new stable isotope data on secondary minerals were examined by the NWTRB (1998). A thorough review of the stable isotope data by Dr. J. Valley (University of Wisconsin - Madison) provided no new data "that adds credence to the hypothesis of on-going hydrothermal activity" (NWTRB, 1998). In his letter to the NWTRB (included in NWTRB, 1998) Dr. Valley does note, however, that the carbonate cements in drill cores were precipitated by fluids that are not well understood and warrant further study. He also called attention to poorly constrained stable isotope gradients in surface carbonate deposits, that *if substantiated* (italics from NWTRB, 1998), would be permissive of possible ongoing hydrothermal activity, and recommended further study of these possible gradients (as presented in Dublyansky and Szymanski, 1996, and Szymanski and Dublyansky, 1996b).

Additional, more recent stable isotope data was discussed by Whelan et al. (2002) and Wilson et al. (2003) - inverse with $\delta^{13}C$ values, $\delta^{18}O$ values of secondary mineral calcite samples generally increase with decreasing relative age. Early calcite $\delta^{18}O$ values were interpreted to have formed from fluids with elevated temperatures of 50-80°C, consistent with the paragenetic sequence, and later values are compatible with local meteoric water (Wilson et al., 2003; Paces et al., 1997; Whelan et al., 2002). Wilson et al. (2003) also presented several (n=3) δD compositions for fluid inclusion waters (for one intermediate calcite and two young Mg-enriched calcite) to assess if a magmatic fluid component could be identified. They concluded, based on the low δD values, that no magmatic fluid was present and that the values deviated only slightly from the meteoric water line, indicative of a meteoric origin. Dublyansky et al. (2005) take issue with this interpretation: they calculate corresponding $\delta^{18}O_{H2O}$ values, plot the $\delta^{18}O$ and δD values, and argue that the results plot well to the right of the meteoric water line, consistent with thermal waters, such as modern thermal waters of Nevada and California. They refer to a more detailed discussion in Dublyansky and Smirnov (2003).

Wilson and Cline (2005) question the appropriateness of the calculations of Dublyansky et al. (2005), which must assume equilibrium conditions between H2O and calcite, arguing that equilibrium was unlikely. A further argument presented by Wilson and Cline (2005) suggests that even if the calculations of Dublyansky et al. (2005) are correct, overlap with thermal fluids is not necessarily problematic, given their own meteoric origin as well as consideration of the small number of samples, and potential errors associated with the analyses and calculations.

6.4 Source of heat for higher-temperature fluid inclusions

Recent evidence of higher than ambient temperature fluid inclusions leads directly to a question of the potential source of heat. Wilson et al. (2003) do not discuss in detail the potential source of heat necessary to create the conditions for vadose zone temperatures indicated by the two-phase fluid inclusions. They note that "elevated temperatures within the sequence could be expected for a few million years following intrusion of the Timber Mountain Caldera at around 10 Ma" and that temperatures indicate the sequence was above current ambient temperatures "for a considerable time after tuff deposition (12.7 Ma) and intrusion of the Timber Mountain Caldera (10 Ma)". They suggest that infiltrating meteoric waters percolated into the warm tuff sequence (>50°C) and precipitated the secondary minerals. Both Wilson et al. (2003) and Whelan et al. (2004) clarify that the distribution of two-phase fluid inclusions suggest that the highest temperatures were restricted to the north and are not spatially distributed across the site. Marshall and Whelan (2000) initially proposed that variations in Sr and O isotopic compositions of secondary calcites indicated a gradual cooling trend. As discussed in Marshall et al. (2005), Marshall and Whelan (2001) proposed a thermal model (as developed by Wohletz et al., 1999 for a magma system in Italy) that "links the slow cooling of the unsaturated zone at Yucca Mountain to the cooling magma body beneath the Timber Mountain caldera complex...............The driving mechanism is dissipation of a large amount of thermal energy emplaced at shallow crustal levels via magmatic processes."

The results of Wilson and Cline (2005) demonstrated that fluids were heated before 6 Ma based on paragenetic and geochronologic constraints and that no fluids of elevated temperatures were present at Yucca Mountain during the Quaternary period. Dublyansky et al. (2005), however, question the emplacement of the Timber Mountain caldera as a viable source of energy sufficient to heat waters percolating in the vadose zone to such high temperatures and/or to potentially sustain this heating for a period of several million years. From the standpoint of heat transfer, they do not accept conductive heating as a viable explanation, arguing that a magma chamber some 8-10 km away and 5 km deeper than the study area cannot yield sufficient heat transfer (Dublyansky and Smirnov, 2005). Part of their opposing argument, however calls upon a paleo-temperature field proposed by Dublyansky and Smirnov (2005) and Dublyansky et al. (2005), which they consider demonstrates an east-west paleotemperature gradient. This would be inconsistent with a heat source located to the north of Yucca Mountain, such as Timber Mountain. Wilson and Cline (2005) and Marshall et al. (2005), however, point out that this proposed temperature gradient is misleading because it contains a subset of available data which are temporally unrelated and therefore cannot represent a temperature gradient at any one point in time.

The highest fluid inclusion temperatures were found near the north portal of the Exploratory Studies Facility in some of the oldest secondary minerals (Wilson and Cline, 2005). This is broadly consistent with the Timber Mountain caldera theory (located to the north), as well as data which suggests temperatures declined relatively uniformly across the site (Wilson et al. 2003). Some of the highest temperature calcite may be associated with transient fumarolic activity that occurred early in the site's history, which has been identified in the Paintbrush Group (Whelan et al., 2004; e.g., Peterman et al., 1996; Holt, 2002). This, along with deposition of later tuffs are potential explanations for early higher temperatures (Sonnenthal et al., 2005). Wilson et al. (2004) note that an absence of bleaching or elevated-temperature secondary minerals on the Bow Ridge fault suggests that faulting (~11.6 Ma) postdates the highest-temperature secondary mineral deposition.

The question of the heat source for higher fluid inclusion temperatures is problematic and is one that may be expected to be revisited during review for a license application. In recent correspondence with B. Leslie of the NRC (email of 8/8/05), Y. Dublyansky restates his interpretation that the USGS thermal model envisaging conductive heating of the vadose zone of Yucca Mountain by a magma body emplaced under Timber Mountain caldera is unlikely. He proposes a formal evaluation, noting that Bechtel SAIC (2004) documented that the thermal model "does not work", and includes his own (partial) evaluation of the model (the copy received by CNWRA from B. Leslie is included with other Y. Dublyansky materials and appears incomplete). The USGS model argument is based on application of an independent model to the Yucca Mountain area and the sole publication addressing the model is a meeting abstract. The Bechtel SAIC report referred to by Y. Dublyansky is Appendix H, of Technical Basis Document No. 2 (unsaturated zone flow), which confirms that "the time-temperature trajectory does not match that predicted by the Marshall and Whelan (2001) Timber Mountain thermal history simulations during the early stages of the Yucca Mountain thermal history." Marshall and Whelan's (2001) results "indicated that to produce long-lived thermal perturbations for the near-surface (0-500 m) environment, it is necessary to maintain a high-temperature magma chamber throughout the duration of large-scale volcanic activity at Timber Mountain (15-11 Ma)." (Bechtel SAIC, 2004). Bechtel SAIC (2004) documents that "between 10 and 6 Ma, the magnitude and duration of heating predicted....are less than those recorded by fluid inclusion and stable isotopic data." They conclude that "while the thermal model simulations of Marshall and Whelan......do not predict a thermal event that is a prolonged and pronounced as that recorded by secondary minerals at Yucca Mountain, their general model provides a mechanism to account for the presence of elevated temperatures between 10 and 6 Ma." However, "extending the period of magmatic heating beyond 11 Ma for the Marshall and Whelan simulations would result in higher predicted temperatures over a longer time span." The model does, however, agree well with the mineralogy temperature record for the last 5 Ma which shows a cooling from values of about 30-40°C to values of about 20-25°C. Bechtel SAIC (2004) proposes several scenarios that might possibly account for enhanced early heating of Yucca Mountain to resolve the thermal source inconsistencies with the Marshall and Whelan (2001) model, including sustained magmatism postdating volcanic activity, magmatic intrusions closer to Yucca Mountain, lateral subsurface outflow of hydrothermal fluids from the Timber Mountain area, and removal of additional overburden. These scenarios require further investigation.

6.5 Secondary mineral textures, distribution, and growth

Within the first 10-15 meters below the surface at Yucca Mountain, fractures are commonly coated with mixtures of secondary minerals which are similar to pedogenic calcrete in the overlying soils, and are consistent with meteoric precipitation (Whelan et al., 2002 and references cited therein). Below these initial depths, secondary minerals are found in open fractures and lithophysal cavities. Their grain sizes increase, forming coarse, sparry growths of calcite, with layers and masses of silica minerals and also with minor amounts of fluorite, zeolites, and clays (Whelan et al., 2002). Whelan et al. (2002) propose a depositional model to account for distinctive features, though notes that calcites from Yucca Mountain display a number of distinctive textural features that are not apparent in descriptions of other independent environments. Distinctive textures include freestanding calcite blades, late stage calcite overgrowths and opal at the tips of blades, and possible dissolution of calcite at the base of the deposits.

Dublyansky et al (2004 and 2005) introduce a number of questions and issues with respect to mineral textures and growth, as well as their distribution. They question the nature of calcite crystal morphologies and textures and take issue with the proposal of Whelan et al (2002) that the secondary minerals precipitated from thin water films. Dublyansky et al. (2004, 2005) argue that this model “seems implausible”, thin water films cannot physically form the types of crystals present at Yucca Mountain, that there are no independent examples of mineral formation that form from the surface tension mechanism proposed, and that the mechanism is not valid. Dublyansky et al. (2004) state that “large euhedral calcite and quartz crystals may only form in a submerged state from slightly supersaturated fluid”; they cite Kendall and Broughton (1978) to assert that crystals formed through a mechanism of water films (that is, speleothems), always have very small sizes. Dublyansky et al. (2004) also asserts that an absence of meniscus textures, expected in a formational environment with “rugged” substratum such as the surface of lithophysal cavities, argues against formation by water films.

It is incorrect, however, that all speleothems exhibit small crystal sizes as suggested by Dublyansky et al. (2004). Many studies of cave spelothems have documented large calcite crystals, which are also composed of fine, numerous (and chemically distinct) growth layers. Much work has been done in the last 10-20 years to understand speleothem formation and the physics of speleothem growth (e.g., Dreybrodt, 1999), which is extremely complex and still incompletely understood. While the physics of secondary mineral formation and textures in karst cave environments may not yet be completely understood (a very different hydrologic setting than a semi-arid silicic volcanic one), this does not necessarily provide, as argued by

Dublyansky et al. (2004), “a strong indication supporting the argument against crystallization in the vadose-zone environment.” Applying this same criteria, proponents of the thermal upwelling hypothesis have not provided a strong basis detailing the formation of these same textures in a saturated zone environment. In response to Dublyansky et al. (2004), Whelan et al. (2004) implemented a 3 month experiment testing the mechanism of capillary film flow on calcite and silica coatings by placing the bases of several samples in calcite-saturated $CuSO_4$ and dilute uranine solutions. The results demonstrated that solutions were drawn up several centimeters between intergrown mineral blades, with precipitates forming at the top of calcite blades (Whelan et al., 2004). These results are consistent with the model of Whelan et al. (2002).

Whelan et al. (2002) and Wilson et al. (2003) both note that secondary minerals occurrences are largely on floors of lithophysal cavities and fractures. There are however also occasional occurrences of calcite found as scattered patches or small pendants on cavity ceilings, but there are no “bathtub rings” of deposition on cavity walls or completely lined cavity interiors (Whelan et al., 2002). The secondary minerals are also a relative minor occurrence in the unsaturated zone. Greater than 90% of the open spaces at Yucca Mountain have no secondary minerals, and cavities and fractures with secondary minerals are commonly intersected or surrounded by barren fractures and/or cavities (Whelan et al., 2002; Wilson et al., 2003). Furthermore, less than 6% of fractures longer than 1 m are mineralized (Whelan et al., 2002). Whelan et al. (2004) state that all of these features are “considered to be incompatible with mineral deposition in a saturate zone environment”, both with respect to abundance of deposits as well as their distribution and morphology. Dublyansky et al. (2004) argue that “gravity-asymmetry” is not necessarily unique to the vadose zone (providing several examples of studies demonstrating upward growing crystals in saturated environments), and proposes an alternative scenario where crystals form rapidly from supersaturated solution (e.g., driven by an abrupt onset of CO_2 degassing), settle to the cavity floor and become nuclei for further (upward-facing) crystal growth. Whelan et al. (2004) counter that for this scenario to have occurred several features would be expected that are not observed, such as, 1) crystals settling out on greater than the 10% of observed openings, 2) mineral coatings covering all upward facing surfaces of openings, rather than partially as observed, and 3) evenly distributed coatings of late-stage opal. Additionally, there is little if any opal deposited in gaps between calcite blades, and it is present commonly as isolated hemispheres at the tips of blades (Whelan et al., 2004). The very long growth rates of the opals (determined by Paces et al., 2000, 2004), indicating single, millimeter-diameter opal hemispheres formed over greater than a million years would suggest very long periods of saturation in the geologic past. This scenario seems to be inconsistent with the features of mineral textures and growth, as well as a seismic pumping mechanism for producing thermal upwelling. Supporters of this hypothesis have not, to my knowledge, yet provided a geologic model demonstrating a mechanism to sustain periodic and long-lasting upwelling episodes of thermal waters.

The nature of this debate over features of secondary mineral textures and formation is largely a result of differing interpretations of the same features. The physics of mineral growth is extremely complex and poorly understood in many environments and examples of many variable types of mineral formation exist in different settings. The large majority of the data, however, seems to better and more simply support a model of meteoric precipitation.

6.6 Mg zonation in late calcites

The majority of the intermediate stage and almost all late stage outermost calcite, as documented by the paragenetic mineral sequence of Wilson et al. (2003), is Mg-enriched, which provide a useful "stratigraphic marker". Wilson et al. (2003) discuss a variety of possible sources of Mg and concluded that the growth zoning plausibly could be accounted for by paleoclimatic/paleohydrologic variability impacting changes in the Mg/Ca ratios of the precipitating fluid. Dublyansky et al. (2003) comment that "their argumentation in support of this assertion is incoherent" and that calling on external (climate-related fluctuations) is "nonunique".

There are many examples of climatic and or hydrologically controlled Mg/Ca variations in both fluids and/or resulting calcites (e.g. speleothems) that have been documented in other groundwater systems (e.g., Plummer, 1977; BarMatthews et al., 1991; Roberts, 1998; Fairchild et al., 2000; Musgrove and Banner, 2004). Dublyansky's comments on this topic appear to largely serve to criticize the argument of Wilson et al. (2003) without providing a counter-argument against climatic induced changes in hydrologic functioning, nor offering an explanation as to how Mg-enrichment in calcites may support a thermal upwelling hypothesis, except to note that oscillatory zoning in calcite may develop in a growing mineral regardless of changes in the precipitating solution (citing Wang and Merino, 1992).

7. Summary of Current Understanding and Recommendations

In recent years, three primary research groups have extensively studied the vadose zone cements from the Yucca Mountain region: 1) researchers at UNLV (The University of Nevada at Las Vegas), 2) researchers with the U.S. Geological Survey (USGS), and 3) Y. Dublyansky and colleagues from the Russian Academy of Sciences, working largely with the State of Nevada.

As discussed in Whelan et al. (2002) initial efforts to characterize the secondary mineralization included evaluation of approximately 700 samples from drill cores, which included samples from both the unsaturated and saturated zone. After the ESF and EWCD were constructed an additional ~300 samples were collected (defined by stations at 100 m intervals). Subsequently, detailed work by the USGS and UNLV jointly collected an additional approximately 150 samples from the ESF and EWCD specifically for fluid inclusion studies, which were sampled and handled to preserve the fluid inclusion record (Whelan et al., 2002).

Numerous studies have provided compelling integrated evidence that the unsaturated zone secondary minerals in fractures and cavities formed from meteoric water (Whelan et al., 2002; Wilson et al., 2003, and many others). This body of work is supported by two independent reviews by the NAS/NRC (1992) and the NWTRB (1998). Nonetheless, an alternative scenario that attributes the deposits to warm upwelling hydrothermal waters continues to be considered viable by a small group of researchers (e.g., see Dublyansky and Szymanski, 1996; Dublyansky and Smirnov, 2005; Dublyansky et al., 2003, 2004, 2005; Hill et al., 1995) This hypothesis has received renewed attention in recent years due to the presence of fluid inclusions in secondary minerals that suggest formation at high depositional temperatures (e.g., Hill and Dublyansky, 1999; Stuckless et al., 1998). As discussed herein, the current debate is largely focused on specifics of the interpretation of the data regarding these secondary minerals, supporting either a meteoric origin, or a thermal upwelling water origin. The timing of formation of these secondary minerals is crucial to this debate.

Wilson et al. (2003) document two-phase fluid inclusions that formed at warm temperatures (up to 83°C, though generally 45-60°C) between 5.32 (±0.02) and 9.06 (± 0.08) Ma, with the warmest temperatures (>50°C) associated with inclusions >6.29 (± 0.30 Ma). These ages determinations are constrained paragenetically by ages on associated opals and chalcedonies rather than by age constraints directly on the calcites containing the fluid inclusions, and they thus represent minimum ages. Further geochronology directly on the inclusion bearing calcites would better constrain the timing of the presence of warm fluids.

Age constraints on Class B type fault calcites (textures of which are suggestive of formation under warm saturated conditions), and cross-cutting calcite veins detailed in Gray et al. (2005) are necessary to evaluate the potential hydrologic importance of these features. While there is no evidence to suggest that the faults are young (in fact, textures suggest they are recrystallization cements and that recrystallization was synkinematic with faulting), age constraints would resolve their timing and formation history. If fluid inclusions are available from the Class B fault calcites, homogenization temperatures would also help constrain temperature data determined from twin thicknesses. Bechtel SAIC (2004; Appendix H) note that Wilson et al. (2003) also studied Class B fault calcite and measured homogenization temperatures of 43 to 59°C for fluid inclusions on untwinned calcite from the ESF. These temperatures are considerably lower than those determined by the calcite twinning. Further analyses and geochronology may help resolve this apparent discrepancy. Bechtel SAIC (2004; Appendix H) notes that the USGS is currently conducting additional age dating and evaluation of fluid inclusion homogenization temperatures in twinned calcite from Class B faults (Bechtel SAIC, 2004b).

How best to approach geochronology on these calcites, however, is problematic. Previous geochronologic studies of secondary minerals have noted that the fracture and cavity calcites do not lend themselves to U-Pb dating, and have instead applied U-Pb methodologies to associated opals. If the Class B fault calcites are synkinematic with faulting, they will likely exceed the datable age range for U-series dating methodologies (back to ~350,000 years, although the ^{238}U - ^{234}U pair can provide maximum age information up to about 1 Ma, if isotopic equilibrium is observed). Ages older than about 1 Ma cannot be determined by U-series methodologies. The

U-series method, however, can confirm that samples exceed a maximum age of 1 Ma, although this may be of limited value in attempting to ascertain ages between 5 and 10 Ma.

As noted in an earlier internal memo from J. Stamatakos to B. Leslie and P. Justus of the NRC (Jan. 4, 1999) apatite fission track analysis on apatite grains from the tuffs at Yucca Mountain will provide not just age constraints on the tuffs but also a subclosure temperature thermal history extending from closure temperature to the present. This cooling history may provide some perspective on thermochronometry and thermochronology, but unfortunately cannot provide direct information on the secondary minerals.

With respect to the most recent stable isotope discussions of Dublyansky et al. (2005) and Wilson and Cline (2005), both of which are responses to Wilson et al. (2003), it is problematic to base strong conclusions on only three samples. The calculations of Dublyansky et al. (2005) require assumptions that cannot be verified (e.g., equilibrium precipitation) and the comparison with thermal waters is likely not valid. Even so, this comparison does not account for the processes that could potentially control such stable isotope values based on the thermal upwelling hypothesis.

The USGS model argument for a heat source based on conductive heating via a magma body under Timber Mountain caldera is based on application of an independent model to the Yucca Mountain area. The sole publication addressing the model is a meeting abstract. Better constraints on the potential source and transfer of heat in the region at the time of elevated temperature secondary mineral formation, as well as presentation of results in the peer-reviewed literature for evaluation and review are important consideration for resolving questions of the source of heat responsible for early and intermediate stage secondary minerals.

The high $\delta^{13}C$ values observed in early stage secondary minerals remain problematic. Improved development of a model for high $\delta^{13}C$ values to occur in early stage calcites via anaerobic and methanogenic conditions would be helpful to resolve this issue.

There are also other potential issues, not discussed herein, which would benefit from further investigation and potentially contribute to understanding the origin and history of secondary minerals at Yucca Mountain. These include topics such as Sr/Ca ratios in the calcite, fluid inclusion gases chemistry, multiphase inclusions, the presence of hydrocarbons in fluid inclusions, and existence of fluorite and strontianite in the secondary mineral assemblages.

In arguing against a meteoric origin model, Dublyansky et al. (2004) state that "a failure to explain an observed feature will invalidate the model. Furthermore, a failure to provide rational models for all relevant observed features will invalidate the concept. By contrast, a consistency between observed features and their respective models with the concept does not constitute and automatic validation of the latter. Validation requires compliance with two additional conditions: (a) the model describing the feature must be unique and unequivocal (.i.e.,no alternative explanation is possible for the feature) and (b) the model (and, thus, the feature) must be incompatible with any competing concept." In their conclusions, Dublyansky et al. (2004) state that "it is the author's opinion that Whelan et al. (2002) failed to develop a comprehensible and defensible concept as an alternative to the hydrothermal upwelling concept." Presumably, the burden of this same argument should apply to the proponents of the thermal upwelling hypothesis. However, Independent reviews and current understanding of this subject suggest that this burden remains unmet. Furthermore, as noted earlier, evidence that may support an interpretation that the secondary minerals were formed by upwelling thermal waters does not in and of itself provide a geological reasonable mechanism to drive such a processes, or provide any geologically constrained details of such a mechanism, such as when seismic pumping occurred in the past, or how frequent such cyclical events may or may have occurred.

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Bish, D. L., and Aronson, J. L., 1993, Paleogeothermal and paleohydrologic conditions in silicic tuff from Yucca Mountain, Nevada, Clays and Clay Minerals, v. 41, p. 148-161.

> Clay minerals (predominantly interstratified I/S) suggest that rocks at depth at northern end of Yucca Mountain were altered early in their history (10.0 to 11 mya; to temperatures of 275°C, 200°C, and less than 100°C for three respective wells) and that no significant hydrothermal alteration has occurred since Timber Mountain (~10.7 ma). This data documents a decreasing temperature gradient away from the Timber Mountain caldera and are consistent with Timber Mountain moat volcanism as the major and last source of hydrothermal alteration.

Broad, W., J., 1990, A Mountain of Trouble, New York Times Magazine, Nov. 18, sec. 6, p.37.

DOE (U. S. Department of Energy), 1988, Site Characterization Plan: Yucca Mountain Site, Nevada Research and Development Area, Nevada, Office of Civilian Radioactive Waste Management, Washington, D. C., DOW/RW 0199.

DOE (U. S. Department of Energy), 1993, Report on the origin of calcite-silica deposits at Trench 14 and Busted Butte and methodologies used to determine their origin, YPM193-11-R.

Denniston, R. F., Shearer, C. K., Layne, G. D., and Vaniman, D. T., 1997, SIMS analyses of minor and trave element distributions in fracture calcite from Yucca Mountain, Nevada, USA, Geochimica et Cosmochimica Acta, v. 61, p. 1803-1818.

> Study of chemical composition of calcite. Shows that unsaturated zone calcite is depleted in Mn, which is similar to samples from the soil zone, and distinguishes unsaturated zone calcite from Mn-enriched calcite in the deeper calcite alteration zone.

Dreybrodt, W., 1999, Chemical kinetics, speleothem growth and decline, Boreas, v. 28, p. 347-356.

Dublyansky, Y. V., 1995, Stable isotope composition of carbonates exposed in trenches at the Stagecoach Road fault, Report submitted to Nevada NWPO.

> Report considered by NWTRB in their 1998 report. Not readily available for review.

Dublyansky, Y. V., 1998, Fluid inclusion studies of samples from the Exploratory Study Facility, Yucca Mountain, Nevada, Research Report, Institute for Energy and Environment, available at http://www.ieer.org/reports/yucca/summrec.html .

Dublyansky, Y. V., 2002, Extreme crystal-scale variability of d13C in hydrothermal calcite from Yucca Mountain, Nevada, Geochimica et Cosmochimica Acta, v. 66, Supplement 1, p. A198.

Goldschmidt Conference abstract.

Dublyansky, Y. V., Ford, D., and Reutski, V., 2001, Traces of epigenetic hydrothermal activity at Yucca Mountain, Nevada: preliminary data on the fluid inclusion and stable isotope evidence, Chemical Geology, v. 173, p. 125-149.

Argues that calcite-opal-quartz crusts from the unsaturated zone of Yucca Mountain were formed by hydrothermal fluids in a saturated/phreatic environment based largely on fluid inclusion studies and formation temperatures.

Dublyansky, Y. V., and Lapin, B., 1995, Bedrock tuffs, mosaic breccias and young volcanic rocks at Yucca Mountain, Nevada, Report submitted to Nevada NWPO.

Report considered by NWTRB in their 1998 report. Not readily available for review.

Dublyansky, Y. V., and Reutsky, V. N., 1995, Preliminary data on fluid inclusions in epigenetic minerals from tunnel excavated under Yucca Mountain, Report submitted to Nevada NWPO.

One of the documents submitted to the U.S. Nuclear Waste Technical Review Board by the State of Nevada Attorney General's office for consideration in the Board's 1998 review of new information (subsequent to the NAS/NRC 1992 report) regarding hypotheses for ongoing intermittent hydrothermal activity and large earthquake-induced changes in the water table at Yucca Mountain. The report is cited in the Board's review, but not currently readily available from Nevada NWPO.

Dublyansky, Y. V., Smirnov, S. Z., and Shugurova, N., 1996, Fluid inclusions in calcite from the Yucca Mountain exploratory tunnel, in, Brown, P. E., and Hagemann, S. G. (eds.), Program and Abstracts, 6yh Biennial Pan American Conference on Research on Fluid Inclusions, May 30-June 1, 1996, University of Wisconsin Department of Geology, Madison, WI, p. 38-39.

First reference (as far as I can ascertain) to higher temperature data for fluid inclusions. Not readily available for review.

Dublyansky, Y. V.,and Smirnov, S. Z., 2003, Review of the report "Thermochronological evolution of calcite formation at the potential Yucca Mountain repository site, Nevada, Publishing House SB RAS, Novosibirsk.

Report cited by Dublyansky et al. (2005). Transmitted to the NWTRB, as documented on their website (http://www.nwtrb.gov/corr/corr.html) by Harry W. Swainston on Oct. 27, 2003, although the report itself is not readily available for review.. The NWTRB response letter of Feb. 24, 2004 from Richard Parizek notes that after reviewing the report, "the Board sees nothing that would alter the Board's previous conclusion that the evidence presented does not make a credible case for the hypothesis of ongoing, intermittent hydrothermal activity at Yucca Mountain."

Dublyansky, Y. V., and Smirnov, S. Z.,2005, Commentary: Assessment of past infiltration fluxes through Yucca Mountain on the basis of the secondary mineral record - is it a viable methodology?", Journal of Contaminant Hydrology, v. 77, p. 209-217.

Argues that the methodology of two papers that attempt to assess past volumes of seepage and infiltration fluxes through the vadose zone of Yucca Mountain based on modeling of the spatial distribution of secondary calcite is not viable. The two papers are Marshall et al. (2003) and Xu et al. (2003). Dublyansky and Smirnov first argue that the thermal boundary conditions used in both papers correspond with modern vadose-zone temperatures and do not reflect temperatures of the mineral forming fluids as based on results of fluid inclusion studies. Their second and main point, is that they take issue with the fundamental premise of two papers,

which is based on a model of secondary mineral deposition via seepage of meteoric water, hypothesizing instead that secondary minerals formed from hydrothermal solutions, and thus Marshall et al. (2003) and Zu et al. (2003) are based on an inadequate phenomenological model that does not explain mineralogical and geochemical data. Note: Fig. 1 is the same as Fig. 1 in Dublyansky et al. (2005); see comment in Wilson and Cline (2005).

Dublyansky, Y. V., Smirnov, S. Z., and Pashenko, S. E., 2003, Identification of the deep-seated component in paleo fluids circulated through a potential nuclear waste disposal site: Yucca Mountain, Nevada, USA, Journal of Geochemical Exploration, v. 78-79, p. 39-43.

Argues for invasion of deep-seated thermal fluids into the vadose zone along the permeable fault zone and for resulting unidirectional evolution of cooling groundwaters from reducing to oxidizing based on factors such as 1) mineralogy, 2) stable isotopes, 3) fluid inclusion temperatures, 4) chemistry of inclusion-trapped gases, and 5) geochronology and heat flow constraints.

Dublyansky, Y. V., Smirnov, S. Z., and Palyanova, G. P., 2004, Comment on: "Physical and stable-isotope evidence for formation of secondary calcite and silica in the unsaturated zone, Yucca Mountain, Nevada" by J. F. Whelan, J. B. Paces, and Z. E. Peterman, Applied Geochemistry, v. 19, p. 1865-1877.

Presents arguments dissenting from the conclusions of Whelan et al (2002), and supporting an alternative upwelling process of deep-seated waters into the vadose zone based on problematic models for the morphology of calcite crystals, fluid inclusions including paleothermometry, liquid-to-vapor ratios and two-phase inclusions, mineralogy and mineral textures, d13C and d18O values, 5) chemistry of gases trapped in fluid inclusions, and gravity asymmetry. The authors group these topics as problematic models, missing interpretations, or biased interpretations and selective use of information.

Dublyansky, Y. V., Smirnov, S. Z.,and Pashenko, S. E., 2005, Comment on "Origin, timing, and temperature of secondary calcite-silica mineral formation at Yucca Mountain, Nevada" by N. S. F. Wilson, J. S. Cline, and Y. V. Amelin, Geochimica et Cosmochimica Acta, v. 69, p. 4387-4390.

Evaluates Wilson et al. (2003) and argues that the proposed phenomenological model is not supported based on multiple issues: 1) temperatures field of paleowaters, 2) source of heat to paleowaters, 3) stable isotope composition of paleowaters, 4) salinity of paleowaters, 5) ^{13}C enrichment in calcite, 6) secondary mineral textures, and 7) Mg zonation in secondary minerals. Note that Fig. 1 in Dyblyansky et al. is the same as Fig. 1 in Dublyansky and Smirnov (2005); see comment on this figure in Wilson and Cline (2005).

Dublyansky, Y. V., and Szymanski, J. S., 1996, Carbonate deposits at Yucca Mountain (Nevada, USA) and the problem of high-level nuclear waste disposal, Chemistry for Sustainable Development, v. 4, p. 14-161.

Presents arguments for a hypogene origin of epigenetic calcite-opal veins and slope carbonates, with a particular focus on stable isotope compositions (δ^{18}O and δ^{13}C); argues that the comparative approach used by supporters of a pedogenic cement origin is inappropriate and erroneous; argues instead that an analysis of stable isotope trends suggests that during the last 400-500 ka the groundwater level under Yucca Mountain has undergone multiple and frequent large-amplitude upward fluctuations of hydrothermal waters.

Dyblyansky, Y., Szymanski, J., Chepizhko, A., Lapin, B.,and Reutsky, V., 1998, Geological history of Yucca Mountain (Nevada) and the problem of a high-level nuclear waste repository, in, Stenhouse, M., and Kirko, V., eds., Defense Nuclear Waste Disposal in Russia, NATO Series, Kluwere Academic, p. 279-292.

Evans, N. J., Wilson, N. S. F., Cline, J. S., McInnes, B. I. A.,and Byrne, J., 2005, Fluorite (U-Th)/He thermochronology: Constraints on the low temperature history of Yucca Mountain, Nevada, Applied Geochemistry, v. 20, p. 1099-1105.

Based on fluorite thermochronometry authors conclude that fluorite precipitated from warm fluids (65-80°C) approximately 8-10 Ma; they suggest that 9.7 Ma is the last period of hydrothermal fluid activity in the area (although uncertainties may result in that age being closer to 8 Ma).

Fabryka-Martin, J., 2000, Analysis of geochemical data for the unsaturated zone, ANL-NBS-HS-000017, Rev. 00, Office of the Civilian Radioactive Waste Management, U.S. DOE, 284 p.

Fairchild, I. J., Borsato, A., Tooth, A. F., Frisia, S., Hawkesworth, C. J., Huang, Y. M., McDermott, F., and Spiro, B., 2000, Controls on trace element (Sr-Mg) compositions of carbonate cave waters: implications for speleothem climate records

Feng, X., Faiia, A. M., WoldeGabriel, G., Aronson, J. L., Poage, M. A., and Chamberlain, C. P., 1999, Oxygen isotope studies of illite/smectite and clinoptilolite from Yucca Mountain: implications for paleohydrologic conditions, Earth and Planetary Science Letters, v. 171, p. 95-106.

Gascoyne, M., Miller, N. H., and Neymark, L. A., 2002, Uranium-series disequilibrium in tuffs from Yucca Mountain, Nevada as evidence of pore-fluid flow over the last million years, Applied Geochemistry, v. 17, p. 781-792.

U-series analyses on tuffs from the Exploratory Studies Facility and the Cross Drift tunnels indicated a depletion on 234U, likely a result of leaching by pore-fluids (note: analyses are by alpha spectrometry, though verified for several samples by TIMS). Authors conclude that similar ratios for fractured samples vs. unfractured samples suggest that pore fluids move equally through fractured and unfractured rocks. However, fracture walls may have a thin zone of greater disturbance, indicating higher flow through fractures. As the authors admittedly did not investigate this, their conclusion is only conjecture and unsubstantiated.

Gray, M. B., Stamatakos, J. A., Ferrill, D. A., and Evans, M. A., 2005, Fault-zone deformation in welded tuffs at Yucca Mountain, Nevada, USA, Journal of Structural Geology, v. 27, p. 1873-1891.

Presents field and microstructural analysis of faults that distinguishes four distinct fault zones (Classes A-D). Classes A, C, and D are genetically related and represent progressive fault deformation resulting from increasing displacement and response of the welded tuffs. Class B fault zones, however, are a unique and unusual style "in which faults of generally minor displacement are heavily mineralized with blocky calcite." The significance of these faults is in these secondary minerals, which are distinct from other secondary minerals (in lithophysal cavities and frractures). The Class B fault mineralization exhibit textures indicative of formation in a fluid saturated environment. The poikilotopic calcite contains abundant deformation twins, the thickness of which is believed to correlate with the temperature of deformation (as described by Ferrill, 1991 and 1998; Burkhard, 1993) and suggests that deformation twinning occurred at relatively elevated temperatures (>170º). The Class B faults also contain rare veins, which are partially or entirely filled with relatively strain-free calcite, and are thus interpreted to be postkinematic and to have formed at some later time. Both the Class B fault zone calcites and the secondary cross-cutting veins are undated with, currently, no constraints on the timing of their formation.

Grossman, E. L., 2002, Stable carbon isotopes as indicators of microbial activity in aquifers, in, Christon, J. H. (Ed.), Manual of Environmental Microbiology, ASM Press, Washington, DC, p. 728-742.

Hackley, K. C., Liu, C. L., and Coleman, D. D., 1996, Environmental isotopic characteristics of landfill leachates and gases, Ground Water, v. 34, p. 827-836.

Hay, R. L., Pexton, R. E., Teague, t. T.,and Kyser, T. K., 1986, Spring-related carbonate rocks, Mg clays, and associated minerals in Pliocene deposits of the Amargosa Desert, Nevada and California, Geological Society of America Bulletin, v. 97, p. 1488-1503.

Hill, C. A., Dublyansky, Y. V., Harmon, R. S., and Schluter, C. M., 1995, Overview of calcite/opal deposits at or near the proposed high-level nuclear waste site, Yucca Mountain, Nevada, USA: pedogenic, hypogene, or both?, Environmental Geology, v. 26, pp. 69-88.

> Reexamines the origin of calcite/opal deposits at Yucca Mountain and argues that some of the data may support both a hypogene and pedogenic origin, but questions the pedogenic origin,and instead proposes that Sr, C, and O isotope data, fluid inclusion data, and other data favor a hypogene interpretation. Hypothesizes that the secondary mineral deposits precipitated from warm, CO2 rich water that episodically upwelled along faults, then, upon reaching the surface also then formed pedogenic deposits. As an aside, in the opinion of this writer, Hill et al. arguments for Sr isotope values supporting interaction with deep Precambrian sources is simply not substantiated by the data. The authors themselves indicated that lead isotope data is equivocal and indeterminant, but then call on ascending water as a plausible scenario.

Hill, C. A., and Dublyansky, Y. V., 1999, Response to Stuckless and others (1988) on" Paces Overview of calcite/opal deposits at or near the proposed high-level nuclear waste site, Yucca Mountain, Nevada, USA: pedogenic, hypogene, or both, Evironmental Geology, v. 38 p. 77-81.

> Brief response to Stuckless et al. (1998) rebuttal of Hill et al. (1995), which addresses only major issues (rather than a detailed rebuttal of points noted by Stuckless et al.), and examines some new data. Hill and Dublyansky further argue that in their original paper they were constrained by "suggestive" data vs. "definite" data (i.e., data which is equivocal for interpretation, vs. data which can only be explained by one model), and that subsequent new data further argues for a hypogene origin (e.g., fluid inclusion temperatures, aromatic hydrocarbon gases in fluid inclusions, and stable isotope gradients in slope deposits).

Holt, E. W., 2002, $^{18}O/^{16}O$ evidence for an early, short-lived (~10 yr), fumarolic event in the Topopah Spring Tuff near the proposed high-level nuclear waste repository within Yucca Mountain, Nevada, USA, Earth and Planetary Science Letters, v. 201, p. 559-573.

> Oxygen isotope data supports theory that prominent zone of hydrothermal alteration directly atop the Topopah Spriing Tuff in the Exploratory Studies Facility tunnel is a result of fumarolic activity. Data suggest it was short-lived (~10-25 years) and high temperature (500°C). Preservation of this type of event, with a fragile fingerprint, suggests that the upper part of this ash-flow sheet has not experiences any subsequent metoric-hydrothermal activity.

Ingraham, N. L., Lyles, B. F., Jacobson, R. L., and Hess, J. W., 1991, Stable isotopic study of precipitation and spring discharge in southern Nevada, Journal of Hydrology, v. 125, p. 243-258.

Johnson, T. M., and DePaulo, D. J., 1994, Interpretation of isotopic data in groundwater-rock systems: Model development and application to Sr isotope data from Yucca Mountain, Water Resources Research, v. 30, p. 1571-1587.

Presents results of Sr isotope modeling of calcite fracture fillings and tuffs at Yucca Mountain and concludes that the model does not allow for conclusive evidence either for or against past high water-table conditions and upwelling waters.

Levy, S. S., and O'Neil, J. R., 1989, Moderate-temperature zeolitic alteration in a cooling pyroclastic deposit, Chemical Geology, v. 76, p. 321-326.

Ludwig, K. R., and Paces, J. B., 2002, Uranium-series dating of pedogenic silica and carbonate, Crater Flat, Nevada, Geochimica et Cosmochimica Acta, v. 66, p. 487-506.

Ludwig, K. R., Simmons, K. R., Szabo, B. J., Winograd, I. J., Landwehr, J. M., Riggs, A. C., and Hoffman, R. J., 1992, Mass-spectrometric 230Th-234Th-238U dating of the Devils Hole calcite vein, Science, v. 258, p. 284-287.

Presents details of uranium series geochronology for the ~500,000 year (566 ka to ~60ka) vein calcite deposited from groundwater at Devils Hole, Ash Meadows, Nevada. Replicate analyses are used to validate geochronology and the suite of ages are very self-consistent.

Marshall, E., 1991, The geopolitics of nuclear waste, Science, v. 251, p. 864-867.

"News and Comment" overview of Szymanski hypothesis and debate surrounding it. Discusses current status (as of the time in 1991) of the debate as being focused on carbonates and opal veins from the exploratory pit known as Trench 14. The article notes that Szymanski's hypothesis had not received much support from peer review evaluations by 1) a group of experts retained by the State of Nevada, or 2) A panel of federal scientists chaired by William Dudley, Jr., of the USGS. A thorough review by a NAS panel is underway and due out by the end of the year (1991).

Marshall, D., 2000, Isotope geochemistry of calcite coatings and they thermal history of the unsaturated zone at Yucca Mountain, Nevada, Geological Society of America Abstract with Program, available at http://rock.geosociety.org/absindex/annual/2000/51463.htm .

Marshall, B. D., Neymark, L. A., and Peterman, Z. E., 2003, Estimation of past seepage volumes from calcite distribution in the Topopah Spring Tuff, Yucca Mountain, Nevada, Journal of Contaminant Hydrology, v. 62-63, p. 237-347.

Use calcite distribution to estimate past seepage volumes in the Topopah Spring Tuff at Yucca Mountain. Measurements of calcite and opal coatings in the Exploratory Studies Facility (ESF) tunnel are used to estimate secondary mineral deposition. The authors estimate the volume of water required to precipitate measured volumes of calcite and determine a range of 0.005 to 5 liters/year (median and 95th percentile, respectively).

Marshall, B. D., Neymark, L. A., and Peterman, Z. E., 2005, Reply to "Commentary: Assessment of past infiltration fluxes through Yucca Mountain on the basis of the secondary mineral record - is it a viable methodology?", by Y. V. Dublyansky and S. Z. Smirnov, Journal of Contaminant Hydrology, v. 77, p. 219-224.

A response to Dublyansky and Smirnov (2005) comments on Marshall et al. (2003). Dublyansky and Smirnov (2005) take issue with the fundamental premise of Marshall et al. (2003) that secondary mineral deposition at Yucca Mountain occurred via seepage of meteoric water (Also see Sonnenthal et al., 2005). Marshall et al. (2005) note that Dublyansky and Smirnov's comments reflect a longstanding debate and require consideration of other work to reply. With respect to thermal gradients, Marshall et al. acknowledge that their model does not account for past thermal gradients, but that the use of a larger thermal gradient does not significantly alter their results. They further note that Dublyansky and Smirnov's argument against meteoric secondary mineral deposition is not specifically relevant to their calculation of past water seepage. Regardless, they raise issues with Dublyansky and Smirnov's arguments, stating that they "use select evidence to support their hypothesis" and note where these issues have been previously addressed and elsewhere discussed.

Marshall, B. D. and Whelan, J. F., 2000, Isotope Geochemistry of Calcite Coatings and the Thermal History of the Unsaturated Zone at Yucca Mountain, Nevada, Geological Society of America Abstracts with Programs, Boulder Colorado, v. 32, p. A-259.

GSA abstract that applies Sr and O isotopic data to suggest a gradual cooling trend for the region.

Marshall, B. D., and Whelan, J. F., 2001, Simulating the thermal history of the unsaturated zone at Yucca Mountain, Nevada, Geological Society of America Abstracts with Programs, Boulder Colorado, v 33, p. A-375, available at: http://gsa.confex.com/gsa/2001AM/finalprogram/abstract_26407.htm .

GSA abstract that is the primary reference for the USGS thermal model of conductive heat transport via a magma body under Timber Mountain caldera; based on model initially developed by Wohletz et al. (1999) for the Phlegraean magmatic system in Italy.

McConnaughey, T. A., Whelan, J. F., Wicklan, K. P., Moscati, R. J., 1994, Isotopic studies of yucca Mountain soil fluids and carbonate pedogenesis, in, Proceedings of the 2nd Annual International Meeting on High level Radioactive Waste Management, American Nuclear Society, La Grange Park, IL, p. 2584-2589.

Monger, H. C., and Adams, H. P., 1996, Micromorphology of calcite-silica deposits, Yucca Mountain, Nevada, Soil Science Society of America Journal, v. 60, p. 519-530.

Musgrove, M., and Banner, J. L., 2004, Controls on the spatial and temporal variability of vadose dripwater geochemistry: Edwards aquifer, Central Texas, Geochimica et Cosmochimica Acta, v. 68, p. 1007-1020.

National Academy of Sciences (NAS), 1992, Ground water at Yucca Mountain: How high can it rise?, Final Report of the Panel on Coupled Hydrologic/Tectonic/Hydrothermal Systems at Yucca Mountain, National Academy Press, 242 p., available at http://www.nap.edu/catalog/2013.html.

Report of the Panel established by the NAS/NRC in response to concerns about the Szymanski hypothesis "to evaluate 1) if the water table had been raised in the geologically recent past to the level of the proposed" repository, "and 2) if it is likely that it will happen in the manner described in the DOE staff scientist's report within the 10,000 year period covered by the regulations" (pg. 2). The panel evaluated Szymanski's report, reviewed relevant and contributory literature, "interviewed or consulted with scientists involved in field and laboratory investigations", and spent time in the field led by "scientists on both sides o the controversy" (pg. 2). The panel looked at multiple potential lines of evidence including soils, springs, textural and morphological evidence, breccias, and isotopic data. They concluded, with respect to point #1, above, that "there is no evidence to support the assertion that the water table has risen periodically hundreds of meters from deep within the crust. In fact, the evidence strongly supports a surface-process origin from rainwater for the vein and surface parallel carbonate and carbonate-silica deposits throughout the Yucca Mountain area" (pg.5.).

Newman, B. D., Campbell, A. R., Norman, D. I., and Ringelberg, D. B., 1997, A model for microbially induced precipitation of vadose-zone calcites in fractures at Los Alamos, New Mexico, USA, Geochmica et Cosmochimica Acta, v. 61, p. 1783-1792.

Newman, B. D., Norman, D. I., Gundimeda, M., Levy, S. S., 1996, Understanding the genesis of nonmarine calcie deposits through quadrupole mass spectrometric analysis of fluid inclusion gases, Chemical Geology, v. 132, p. 205-213.

Neymark, L. A., Amelin, Y. V., and Paces, J. B., 2000, ^{206}Pb-^{230}Th-^{238}U and ^{207}Pb-^{235}U geochronology of Quaternary opal, Yucca Mountain, Nevada, Geochimica et Cosmochimica Acta, v. 64, p. 2913-2928.

Neymark, L. A., Amelin, Y. V., Paces, J. B., and Pterman, Z. E., 2002, U-Pb ages of secondary silica at Yucca Mountain, Nevada: implications for the paleohydrology of the unsaturated zone, Applied Geochemistry, v. 17, p. 709-734.

Neymark, L. A., and Paces, J. B., 2000, Consequences of slow growth for ^{230}Th/U dating of Quaternary opals, Yucca Mountain, NV, USA, Chemical Geology, v. 164, p. 143-160.

> Presents conceptual model of continuous secondary mineral growth at slow constant rate of <5 mm/m.y.

Neymark, L. A., Paces, J. B., Marshall, B. D., Peterman, Z. E., and Whelan, J. F., 2005 Geochemical and C, O, Sr, and U-series isotopic evidence for the meteoric origin of calcrete at Solitario Wash, Crater Flat, Nevada, USA, Environmental Geology, v. 48, p. 450-465.

Nuclear Waste Technical Review Board (NWTRB), 1998, Review on hydrothermal activity, available at http://www.nwtrb.gov/reports/review1.pdf, 15 p., and http://www.nwtrb.gov/reports/review2.pdf, 46 p.

Paces, J. B., Ludwig, K. R., Peterman, Z. E., and Neymark, L. A., 2002, ^{234}U/^{238}U evidence for local recharge and patterns of groundwater flow in the vicinity of Yucca Mountain, Nevada, USA, Applied Geochemistry, v. 17, p. 751-779.

> Results suggest that the Tertiary volcanic aquifer beneath the central part of Yucca Mountain is isolated from N-S regional groundwater flow, and that saturated zone groundwater beneath Yucca Mountain is dominated by local recharge rather than regional flow. Discusses streamflows associated with rainfall events with ^{234}U/^{238}U values similar to initial values in pedogenic deposits, and progressive increases in initial ^{234}U/^{238}U values in secondary minerals with increasing depth.

Paces, J. B., Neymark, L. A., Marshall, B. D., Whelan, J. F., and Peterman, Z. E., 1996, Ages and origins of calcite and opal in the Exploratory Studies Facility Tunnel, Yucca Mountain, Nevada, U. S. Geological Survey - Yucca Mountain Project Branch, 1996 Milestone Report 3GQH450M.

Paces, J. B., Neymark, L. A., Marshall, B. D., Whelan, J. F., and Peterman, Z. E., 1998, Inferences from Yucca Mountain UZ hydrology from secondary minerals, in, Proceedings of the

8th International Conference on High level Radioactive Waste Management, Las Vegas, NV, American Nuclear Society, LaGrange Park, IL, p. 36-39.

Paces, J. B., Neymark, L. A., Persing, H. M., Wooden, J. L., 2000, Demonstrating slow growth rates in opal from Yucca Mountain, Nevada, using microdigestion and ion-probe uranium-series dating, Geological Society of America Abstracts with Programs, Boulder Colorado, v 32, p. A-259.

Paces, J. B., Neymark, L. A., Whelan, J. F., and Peterman, Z. E., 1999, Characteristics of unsaturated-zone fracture flow interpreted from calcite and opal deposits at Yucca Mountain, Nevada, Abstr., Eos, Transactions , American Geophysical Union, v. 80, p. S4.

Paces, J. B., Neymark, L. A., Marshall, B. D., Whelan, J. F., and Peterman, Z. E., 2001, Ages and origins of calcite and opal in the Exploratory Studies Facility Tunnel, Yucca Mountain, Nevada, U. S. Geological Survey Water Resources Investigations Report 01-4049.

Paces, J. B., Neymark, L. A., Wooden, J. L., and Persing, H. M., 2004, Improved spatial resolution for U-series dating of opal at Yucca Mountain, Nevada, USA, using ion-microprobe and microdigestion methods, Geochimica et Cosmochimica Acta, v. 68, p. 1591-1606.

> Details improved resolution of U-series dating on opals. Results suggest that secondary mineral (opal) growth rates may correlated with changes in climate, with faster growth during wetter and cooler climates (glacial maximum), slower growth during transition climates, and no growth during dry warm climates (e.g., modern).

Paces, J. B., Whelan, J. F., Peterman, Z. E., Marshall, B. D., and Neymark, L. A., 2000, Formation of calcite and silica from percolations in a hydrologically unsaturated setting, Yucca Mountain, Nevada, Geological Society of America Abstract with Program, available at http://rock.geosociety.org/absindex/annual/2000/51360.htm .

Peterman, Z. E., Spengler, R. W., Singer, F. R., and Dickerson, R. P., 1996, Geochemistry of outcrop samples from the Raven Canyon and Paintbrush Canyon reference sections, Yucca Mountain, Nevada, U. S. Geological Survey Open-File Report 94-550.

> Identifies fumarolic activity.

Plummer, L. N., 1977, Defining reactions and mass-transfer in part of Floridan aquifer, Water Resources Research, v. 13, p. 801-812.

Quade, J., and Cerling, T. E., 1990, Stable isotopic evidence for a pedogenic origin of carbonates in Trench 14 near Yucca Mountain, Nevada, Science, v. 250, p. 1549-1552.

> Compares carbon and oxygen isotopic data for carbonates from Trench 14 at Yucca Mountain with data for carbonates in modern desert soils, which have formed from pedogenic processes and are younger than 7000 years old (to best establish the relationship between the carbonates and modern rainfall and vegetation). Results are supportive that the hypogenic minerals from Trench 14 are pedogenic in origin.

Quade, J., Mifflin, M. D., Pratt, W. L., McCoy, W., and Burckle, L., 1995, Fossil spring deposits in the southern Great Basin and their implications for changes in water-table levels near Yucca Mountain, Nevada, during Quaternary time, Geological Society of America Bulletin, v. 107, p. 213-230.

Roberts, M. S., Smart, P. L.,and Baker, A., 1998, Annual trace element variations in a Holocene speleothem, Earth and Planetary Science Letters, v. 154, p. 237-246.

Roedder, E., Whelan, J. F., and Vaniman, D. T., 1994, Fluid inclusion homogenization and crushing studies of calcite veins from Yucca Mountain, Nevada, tuffs, in Proceedings of the 5th International Conference on High level Radioactive Waste Management, Las Vegas, NV, March 22-26, 1994, American Nuclear Society, LaGrange Park, IL, p. 1854-1860.

Smirnov, S., Dublyansky, Y., Mel'Gunov, M., and Mel'Gunova, E., 2002, REE geochemistry of the fluorite from Yucca Mountain, USA: fingerprinting multiple sources of matter in hydrothermal fluids, Geochimica et Cosmochimica Acta, v. 66, Supplement 1, p. A721
.
Sonnenthal, E., Xu, T., and Bodvarsson, G., 2005, Reply to "Commentary: Assessment of past infiltration fluxes through Yucca Mountain on the basis of the secondary mineral record - is it a viable methodology?", by Y. V. Dublyansky and S. Z. Smirnov, Journal of Contaminant Hydrology, v. 77, p. 225-231.

A response to Dublyansky and Smirnov (2005) comments on Xu et al. (2003). Dublyansky and Smirnov (2005) take issue with the fundamental premise of Xu et al. (2003) that secondary mineral deposition at Yucca Mountain occurred via seepage of meteoric water (also see Marshall et al., 2005). The authors address Dublyansky and Smirnov's comments on the issue of inappropriate boundary conditions by showing results of a sensitivity simulation approximating the temperature history inferred from fluid inclusions. Results for modeled calcite abundances are similar to earlier results. The authors conclude that a better treatment of the thermal evolution of the unsaturated zone (not available at the time of the original work) does not change the conclusions of Zu et al. (2003).

Stuckless, J. S., Marshall, B. D., Vaniman, D. T., Dudley, W. W., Peterman, Z. E., Paces, J. B., Whelan, J. F., Taylor, E. M., Forester, R. M., and O'Leary, D.W., 1998, Comments on "Overview of calcite/opal deposits at or near the proposed high-level nuclear waste site, Yucca Mountain, Nevada, USA: pedogenic, hypogene, or both" by C. A., Hill, Dublyansky, Y. V., Harmon, R. S., and Schluter, C. M., Environmental Geology, v. 34, p. 60-78.

Rebuttal paper to Hill et al. (1995) that argues, with numerous specific examples that "the paper contains several misstatements of fact, some important omissions of pertinent and readily available information, and some misleading generalizations that together bias the reader toward the erroneous conclusion that the hypogene model remains viable" The aurhors instead note that if error and selective data use is eliminated, that a hypogene model is untenable.

Stuckless, J. S., Peterman, Z. E., and Muhs, D. R., 1991, U and Sr isotopes in ground water and calcite, Yucca Mountain, Nevada: Evidence against upwelling water, Science, v. 254, p. 551-554.

Evaluates strontium and uranium isotopic compositions of hydrogenic calcite deposits in fault zones (specifically Trench 14 as well as deposits at Busted Butte) at Yucca Mountain. The authors compare compositions of the hydrogenic deposits with groundwater compositions in the two aquifers underlying Yucca Mountain (the Tertiary aquifer and the deeper Paleozoic carbonate aquifer) as possible source waters. If the deposits were formed from upwelling waters associated with these deeper groundwaters then it is plausible that there would be geochemical similarities between the hydrogenic deposits and the groundwaters. The authors conclude that the hydrogenic calcites did not precipitate from deeper groundwater and are consistent with a surficial meteoric water origin.

Szabo, B. J., Kolesar, P. T., Riggs, A. C., Winograd, I. J., and Ludwig, K. R., 1994, Paleoclimate inferences from a 120,000-yr calcite record of water-table fluctuation in Browns Room of Devils Hole, Nevada, Quaternary Research, v. 41, p. 59-69.

Uses petrography and morphology of calcites, combined with uranium-series dating to infer water table fluctuations in Devils Hole and for the Ash Meadows groundwater basin by extension. They compare the fluctuations in Browns Room (up to about +9m above current level) with independent records paleoclimate records for the Great Basin. They proposed that wetter episodes of climate over the last 100,000 years is the dominant control on paleowater-table fluctuations where wetter climate causes the flow system to transmit more water, with a resulting water table rise.

Szabo, B. J., and Kyser, T. K., 1990, Ages and stable-isotope compositions of secondary calcite and opal in drill cores from Tertiary volcanic rocks of the Yucca Mountain area, Nevada, Geological Society of America Bulletin, v. 102, p. 1714-1719.

Uses uranium-series dating to infer episodes of calcite deposition in the unsaturated zone during recharge events over the last 400 ka, and proposes that episodes of major calcite deposition occurred at 28, 170, and 280 ka. This work supports the argument that calcite deposition in the unsaturated zone may be an ongoing process that occurs during pluvial (wet) cycles.

Szymanski, J. S., 1989, Conceptual considerations of the Yucca Mountain ground water system with special emphasis on the adequacy of this system to accommodate a high-level nuclear waste repository, unpublished DOE report.

Initial Szymanski report detailing theory of periodic thermal upwelling waters; not readily accessible or available for review.

Szymanski, J. S., and Dublyansky, Y. V., 1996, Stable isotope gradients in slope calcretes at Yucca Mountain, Nevada: evidence for the involvement of carbonic gases in the hydrothermal discharges. Abstract submitted to 1995 Geological Society of America meeting and report submitted to Nevada NWPO.

Report considered by NWTRB in their 1998 report. Not readily available for review.

Szymanski, J. S.,and Dublyansky, Y. V., 1996b, Stable isotope gradients in slope calcretes at Yucca Mountain, Nevada, Report submitted to NWPO, Part 6 of TRAC-NA Final Report, Research conducted during FY ‘92 through FY’95, Technology and Resource Assesment Corporation, North America, Boulder, CO.

Szymanski, J., Pashenko, S., and Dublyansky, Y., 2000, Early thermal history of the Yucca Mountain, Nevada, USA, Geological Society of America Abstract with Program, available at http://rock.geosociety.org/absindex/annual/2000/51664.htm .

Taylor, E. M., and Huckins, H. E., 1995, Lithology, fault displacement, and origin of secondary calcium carbonate and opaline silica at trenches 14 and 14D on the Bow Ridge Fault at Exile Hill, Nye County, Nevada, U. S. Geological Survey Open File Report, 93-477.

> Investigates trench 14 (provided very detailed discussion of characteristics of Trench 14) with the initial goal of studying nature and frequency of Quaternary movement on the Bow Ridge Fault, but focusing on the origin of secondary minerals. Authors conclude, based on physical, chemical, mineralogical, biologic, petrographic, and isotopic data that they are characteristic of an environment of formation with descending water, rather than ascending water.

Thorstenson, D. C., Weeks, E; P., Haas, Busenberg, E., Plummer, L. N., and Peters, C. A., 1998, Chemistry of unsaturated zone gases sampled in open boreholes at the crest of Yucca Mountain, Nevada: data and basic concepts of chemical and physical processes in the mountain, Water Resources Research, v. 34, p. 1507-1529.

Vaniman, D. T., and Chipera, S. J., 1996, Paleotransport of lanthanides and strontium recorded in calcite compositions from tuffs at Yucca Mountain, Nevada, USA, Geochimica et Cosmochimica Acta, v. 60, p. 4417-4433..

> Uses lanthanide chemistry to distinguish two distinct depositional environments in the tuffs at Yucca Mountain as well as an intermediate “barren zone” where calcites are rare – an upper system in which Ce is oxidized and a deep carbonate-altered system. Calcites from these two environments have different origins. In the upper unsaturated zone the calcite has largely surface origins. A “barren zone” straddles the water table. In this zone mixing of surface and subsurface sources of calcite may occur and calcites that are present may show evidence of dissolution. Deeper in the saturated zone, distinctive Mn calcites reflect an origin by deeper sources.

Vaniman, D. T., Chipera, S. J., and Bish, D. L., 1994, Pedogenesis of siliceous calcretes at Yucca Mountain, Nevada, Geoderma, v. 63, p. 1-17.

> Describes use of mineralogy, geochemistry, and fungal microfossils to assess pedogenic vs. non-pedogenic origins for vadose zone siliceous calcretes, specifically those found in Trench 14. Discusses lack of field features such as tufa dams and rimstone pools, which would be evidence of deposition from surface discharge and flow. Presence of calcified filaments, needle-fiber calcites, and related fungal microfossils all suggest a pedogenic origin. Addresses question of accumulation of calcites and opals, responding to suggestion by Archambeau and Price (1991) that gradual pedogenic accumulation cannot account for amount of observed calcite and opal in Trench 14 - concludes that calcite could have accumulated over time span between 4 million and 240,000 years, which is considerably less than the age of the wall-rock tuffs.

Vaniman, D. T., Chipera, S. J., Bish, D. L., Carey, J. W., and Levy, S. S. , 2001, Quantification of unsaturated-zone alteration and cation exchange in zeolitized tuffs at Yucca Mountain, Nevada, USA, Geochimica et Cosmochimica Acta, v. 65, p. 3409-3433.

> Discusses zeolitized horizons in unsaturated zone and draws several relevant conclusions. Zeolite and alkaline-earth occurrences in the 4 drill holes studied consistently indicate downward flow into zeolitized horizons and

argue against any significant upward flow. The abundances of Ca, Mg, and Sr accumulated in the zeolitized horizon allow for most of the excess alkaline-earth elements accumulated in the zeolites to be sourced from eolian carbonate sources (based on moderate dust accumulation rates), which supports a downward migrating flow pathway.

Wang, J.S., 2002, Scientific Notebooks Referenced in AMR U0035, Calibrated Properties Model, MDL-NBS-HS-000003 REV 01, Memorandum from J.S. Wang (BSC) to File, October 25, 2002, with attachments. ACC: MOL.20021107.0287.

Cited in note under Xu et al. (2003).

Wang, Y., and Merino, E., 1992, Dynamic model of oscillatory zoning of trace elements in calcite: Double layer, inhibition and self-organization, Geochmicia et Cosmochimica Acta, v. 56, p. 587-596.

Whelan, J. F., 2004, Secondary mineral deposits and evidence of past seismicity and heating of the proposed repository horizon at Yucca Mountain, Nevada, U. S. Geological Survey Water-Resources Investigations report 03-4321, 12 p.

Looks at secondary minerals from Yucca Mountain for evidence of past seismicity and heating of the unsaturated zone. Discusses 3 stages for the post-eruptive thermal history: early, intermediate, and late states based on a combination of isotopic, fluid inclusion, and geochronologic data (also see Whelan et al., 2002; and Wilson et al., 2003). Based on U-Pb ages and depositional temperatures determined from fluid inclusion homogenization temperatures, secondary calcites show systematic trends of decreasing formation temperature with younger age, as well as decreasing δ^{13}C and increasing δ^{18}O values with younger age. Early stage calcites were deposited up to about 8 ma with depositional temperatures of 50-90°C, and also include fragments of tuff; "Depositional temperatures then slowly decreased during the intermediate state to present-day ambient temperatures of 20-25°C, which have prevailed for the past 2-4 million years........through deposition of the late-stage minerals".

Whelan, J. F., and Moscati, R. J., Allerton, S. B. M., and Marshall, B. D., 1998, Applications of isotope geochemistry to the reconstruction of Yucca Mountain paleohydrology - status of investigations: June 1996, U. S. Geological Survey Open-File Report 98-83.

Whelan, J. F., and Moscati, R. J., 1998, 9 M.Y. record of southern Nevada climate from Yucca Mountain secondary minerals, in Proceedings of the 8th International Conference on High level Radioactive Waste Management, American Nuclear Society, LaGrange Park, IL, p. 12-15.

Whelan, J. F., Neymark, L. A., Roedder, E., Moscati, R. J., 2003, Thermochronologyof secondary minerals from the Yucca Mountain unsaturated zone, in Proceedings of the 10th International Conference on High level Radioactive Waste Management, Las Vegas, NV, March 30-April 2, 2003, American Nuclear Society, LaGrange Park, IL, p. 357-366.

Whelan, J. F., Neymark, L. A.,Moscati, R. J., 2003b, Evidence from secondary calcite d13C values of unsaturated-zone depositional conditions and past climate at Yucca Mountain, Nevada, Geological Society of America Abstracts with Programs, Boulder Colorado, v. 35, p. 23, available at: http://gsa.confex.com/gsa/2003AM/finalprogram/abstract_61597.htm .

Introduces hypothesis of anaerobic conditions and bacterial methanogenesis in the unsaturated zone to account for early stage calcite secondary minerals with high $\delta^{13}C$ values (up to +.1‰). Attributes subsequent $\delta^{13}C$ values to climate change and changes in the C3-C4 plant communities.

Whelan, J. F., Paces, J. B., and Peterman, Z. E., 2002, Physical and stable-isotope evidence for formation of secondary calcite and silica in the unsaturated zone, Yucca Mountain, Nevada, Applied Geochemistry, v. 17, p. 735-750.

Builds on previous studies characterizing secondary mineral deposits of predominantly calcite and silica from fractures and lithophysal cavities in the welded tuffs. This paper describes the deposits and their distribution and establishes a paragenetic sequence of early, intermediate, and late stages of formation. Although deposits displaying the complete paragenetic sequence are rare, the sequence is nonetheless consistent with the deposits found. Stable carbon and oxygen isotope data support the paragenetic sequence interpretation. Calcites exhibit a large range in stable isotope values and exhibit a trend of decreasing $\delta^{13}C$ and increasing $\delta^{18}O$ values through time. The authors discuss upwelling versus percolation-driven deposition models for formation of the secondary minerals and conclude, consistent with the previous studies that this work builds on, based on texture, mineralogy, distribution, and paragenetic sequences that they are consistent with deposition from descending percolating waters. They further conclude that fluid inclusion temperatures also reflect the paragenetic sequence, with elevated fluid inclusion temperatures restricted largely to early stage mineral deposits with none reported from late-stage calcite (i.e., 2-4 Ma). They propose that warmer depositional temperatures in the past, as reflected in elevated fluid inclusion temperatures in early stage minerals reflect prolonged thermal input to the unsaturated zone from ongoing regional magmatic activity.

Whelan, J. F., Paces, J. B., Peterman, Z. E., Marshall, B. D., and Neymark, L. A., 2004, Reply to the comment on “Physical and stable-isotope evidence for formation of secondary calcite and silica in the unsaturated zone, Yucca Mountain, Nevada”, by Y. V. Dublyansky, S. E. Smirnov and G. P. Palyanova, Applied Geochemistry, v. 19, p. 1879-1889.

Detailed response to the critical comments of Dublyansky et al. (2004) on Whelan et al. (2002), grouped into 3 categories: 1) distribution, morphology, textures, and growth of the secondary minerals; 2) fluid inclusion evidence; and 3) fluid geochemistry. Also presents a very thorough and clear overview of the long history and major components of this longstanding debate.

Whelan, J. F.,and Stuckless, J. S., 1990, Reconnaissance $\delta^{13}C$and $\delta^{18}O$ data from Trench 14, Busted Butte, and drill hole G-4, Yucca Mountain, Nevada Test Site, Proceedings of the 2nd International Conference on High level Radioactive Waste Management, American Nuclear Society, LaGrange Park, IL, p. 930-933.

Whelan, J. F., Vaniman, D. T., Stuckless, J. S., Moscati, R. J., 1994, Paleoclimatic and paleohydrologic records from secondary calcite - Yucca Mountain, Nevada, in, Proceedings of the 5th International Conference on High level Radioactive Waste Management, Las Vegas, NV, May 22-26, American Nuclear Society, LaGrange Park, IL, Vol. 4, p. 2738-2745.

Wholetz, K., Civetta, L., and Orsi, G., 1999, Thermal evolution of the Phlegraean magmatic system, Journal of Volcanology and Geothermal Research, v. 91, p. 381-414.

Thermal conductive heat model developed for a system in Italy; applied to heat transport at Yucca Mountain by Marshall and Whelan (2001).

Wilson, N. S. F., Cline, J. S., and Amelin, Y. V., 2003, Origin, timing, and temperature of secondary calcite-silica mineral formation at Yucca Mountain, Nevada, Geochimica et Cosmochimica Acta, v. 67, p. 1145-1176.

Petrographic and paragenetic study of 155 secondary minerals samples and associated fluid inclusions from the Exploratory Studies Facility and repository block cross drift tunnels at Yucca Mountain to determine the temperatures of fluids from which the minerals formed, and the extent and timing of elevated temperature fluid flow through the site. Results document paragenetic relationships and age control to constrain multiple generations of different cement formation, with later cements forming at cooler temperatures. The proposed paragenetic sequence is:1) Early to early-intermediate secondary minerals (>5.32 Ma), >50ºC initially, later 35-45ºC; 2) Late intermediate secondary minerals (5.32 to ~2.9 Ma), < 35 ºC; 3) Late Mg-enriched growth zoned calcite (~2.9 Ma to present), < 35 ºC.

Wilson, N. S. F., and Cline, J. S. K., 2005, Reply to comment on "Origin, timing, and temperature of secondary calcite-silica mineral formation at Yucca Mountain, Nevada" by Y. V. Dublyansky, S. Z. Smirnov,and G. P. Palyanova, Geochimica et Cosmochimica Acta, v. 69, p. 4391-4395.

Rebuts the comments of Dublyansky et al. (2005) and notes that the conclusions of Wilson et al., (2003) "have been accepted by the State of Nevada Nuclear Waste Project Office, the DOE, and the NWTRB, which 'considers this issue resolved...' ". Wilson and Cline address each of Dublyansky et al. 7 points with counter arguments and conclude that the data is not consistent with Dublyansky et al. hypothesis of hydrothermal fluids flooding the repository.

Winograd, I. J., Szabo, B. J., Coplen, T. B.,and Riggs, A. C., 1988, A 250,000-year climatic record from Great Basin vein calcite: Implications for Milankovitch Theory, Science, v. 242, p. 1275-1280.

Presents a continuous record of oxygen isotope variations in vein calcite deposited from groundwater at Devils Hole, an open fault zone at Ash Meadows, Nevada between 50 and 310 ka (dated by uranium-series). The detailed oxygen isotope record is interpreted to represent changes in climate, and parallels marine and ice core records of paleoclimate with, however, some discrepancies in timing of climate transitions. Relative constant initial ^{234}U/^{238}U values for the calcite are also similar to values for modern spring waters, which suggests well-homogenized and relatively chemically constant (with respect to U-series geochemistry) waters moving through the large drainage basin over the last 300 ka.

Winograd, I. J., Coplen, T. B., Landwehr, J. M., Riggs, A. C., Ludwig, K .R., Szabo, B. J., Kolesar, P. T., and Revesz, K. M., 1992, Continuous 500,000-year climate record from vein calcite in Devils Hole, Nevada, Science, v. 258, p. 255-260.

Presents a continuous record of oxygen isotope variations in vein calcite deposited from groundwater at Devils Hole, an open fault zone at Ash Meadows, Nevada over the last 500,000 years (566 ka to ~60ka as dated by uranium-series). This is a second and longer core than that detailed in Winograd et al. (1988). Uranium-series geochronology is detailed separately in Ludwig et al. (1992).

Xu, T., and Pruess, K., 1998, Coupled modeling of non-isothermal multi-phase flow, solute transport and reactive chemistry in porous and fractured media: 1. Model development and validation, Lawrence Berkeley National Laboratory Report BLNL-42050, Berkeley, California.

Cited in note under Xu et al. (2003).

Xu, T., and Pruess, K., 2001, Modeling multiphase non-isothermal fluid flow and reactive geochemical transport in variably saturated fractured rocks: 1. Methodology, American Journal of Science, v. 301, p. 16-33.

Cited in note under Xu et al. (2003).

Xu, T., Sonnenthal, E., and Bodvarsson, G., 2003, A reaction-transport model for calcite precipitation and evaluation of infiltration fluxes in unsaturated fractured rock, Journal of Contaminant Hydrology, v. 64, p. 113-127.

Investigates relationship between measured calcite abundances in fractures and lithophysal cavities at Yucca Mountain and percolation flux using reactive transport modeling. Modeling for calcite deposition under different infiltraton conditions was performed using the multiphase non-isothermal reactivetransport model TOUGHREACT (Xu and Pruess, 1998, 2001). A dual-permeability approach is used for fractures and matrix interaction. Three infiltration rates were modeled - a base-case rate of 5.92 mm/year and bounding rates of 2 and 20 mm/year. Over the 2-20 mm/year infiltration rates, the simulations match well with measured data from WT-24 well cuttings. The base-case infiltration rate of 5.92 mm/year provides the closest match to the data and may represent the long-term mean infiltration rate for this location. The simulations dependence on infiltration rate decreases at higher rates. Note that it is currently unclear where the 5.92 mm/year value originates: Xu et al. (2003) cite Ahlers and Lui (2000) whenpresenting the value for their base-case scenario. However, a review of Ahlers and Lui (2000) does not readily reveal the source of the 5.92 mm/year value; their table 6-5 lists a base-case area-averaged infiltration rate for borehole WT-24 of 5.50 mm/year and further cites Wang (2002) as the table source.

Yang, I. C., Yu, P., Rattray, G. W., Ferarese, J. S., Ryan, J. N., 1998, Hydrochemical investigations in characterizing the unsaturated zone at Yucca Mountain, Nevada, U. S. Geological Survey Open-File Report 98-4132.