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Journal of Contaminant Hydrology 77 (2005) 219–224
JOURNAL OF Contaminant Hydrology
www.elsevier.com/locate/jconhyd

Discussion

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

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1. Introduction

Many of the comments by Dublyansky and Smirnov (2005) on Marshall et al. (2003) reflect a longstanding debate over the origin of secondary calcite and opal deposits found in cavities and on fracture surfaces at Yucca Mountain, Nevada, site of a proposed high-level nuclear waste repository (US Department of Energy, 2001). These comments require consideration of data and interpretations beyond the scope of Marshall et al. (2003). Dublyansky et al. (2004) and Dublyansky et al. (2005) also have commented on papers published by Whelan et al. (2002) and Wilson et al. (2003), and we will refer to the replies to those comments (Whelan et al., 2004; Wilson and Cline, 2005) in addressing the comments that go beyond the scope of Marshall et al. (2003).

DOIs of linked articles: 10.1016/j.jconhyd.2005.01.003, 10.1016/j.jconhyd.2005.01.005.
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doi:10.1016/j.jconhyd.2005.01.002

2. Discussion

In Section 2 Dublyansky and Smirnov (2005) discuss the thermal boundary conditions used by Marshall et al. (2003) to calculate seepage in the unsaturated zone (UZ) at Yucca Mountain. Marshall et al. (2003) estimated past seepage volumes based on calcite volumes and amounts of water required to precipitate calcite in the UZ. Six values for the water/calcite volume ratio (V_w/V_{cc}) were calculated. Only one of these calculations used an equilibrium thermodynamic model that depended on the thermal gradient (the present-day thermal gradient was used). As Dublyansky and Smirnov (2005) point out, the thermal gradient in the UZ at Yucca Mountain decreased as a function of time, requiring complete models of past UZ mineral deposition to include a time-derivative of the thermal gradient. Marshall et al. (2003) did not employ a changing thermal gradient for two reasons. First, geochronological studies of the calcite and opal coatings indicate uniform (within a factor of 5 to 10) long-term average mineral growth rates over the last 10 m.y. (Neymark et al., 2002; Paces et al., 2004). Second, the goal of Marshall et al. (2003) was to provide a methodology for estimating future seepage of water using the present-day thermal gradient.

Although the V_w/V_{cc} calculated from equilibrium modeling will vary with temperature, other parameters also may have changed over the 10 Ma history of secondary mineral deposition at Yucca Mountain. For example, early in the history of the UZ, pCO_2 (partial pressure of CO_2) may have been greater due to decarbonation reactions occurring in the deeply buried carbonate rocks. Also, at higher thermal gradients, evaporation rates would be greater, reducing the downward moisture flux. New simulations varying all of these parameters have been conducted (Table 1), and none of the resulting V_w/V_{cc} values are outside the range given in Marshall et al. (2003). For example, changing only the thermal gradient from 20 to 150 °C/km results in an estimate of V_w/V_{cc} in the Topopah Spring Tuff of 2.7×10^5, as compared to 3.7×10^5 for 20 °C/km. However, this simulation predicts silica dissolution in the Topopah Spring Tuff. Increasing the evaporation to 20% per model step stabilizes silica but reduces the V_w/V_{cc} to 1.7×10^5. If pCO_2 is raised to 0.9% in the Topopah Spring Tuff to simulate CO_2 streaming through the UZ during the waning stages of volcanic activity (Farrar et al., 1995), V_w/V_{cc} is 9.8×10^4.

All of the additional simulations using the greater thermal gradient during the early history of the UZ require less water to precipitate calcite. If the calcite deposition rate

Table 1
Equilibrium thermodynamic model results for Topopah Spring Tuff[a]

Input parameter			Model calculation
Geothermal gradient (°C/km)	pCO_2 (%)	Fraction of water remaining	V_w/V_{cc}
20	0.09	0.09	3.7×10^5
150	0.09	0.09	2.7×10^5
150	0.09	0.08	1.7×10^5
150	0.9	0.08	9.8×10^4

[a] Results shown for average of 6 depths (100 to 300 m) in borehole USW UZ-1.

was constant during the entire UZ history, the implication is that water seepage is higher in the present-day than during the early thermal history. However, these variations in V_w/V_{cc} (Table 1) are relatively small compared to the overall range of estimates of V_w/V_{cc} (1.4×10^5 to 10^6) given in Marshall et al. (2003). Thus, although the boundary conditions used by Marshall et al. (2003) for modeling the total accumulation of calcite did not account for the past thermal gradient, the use of a larger thermal gradient for the portion of the calcite formed during the slow cooling of the UZ does not significantly change the results nor affect the conclusions of Marshall et al. (2003).

Section 3 of the comment by Dublyansky and Smirnov (2005) concerns the deposition model applied by Marshall et al. (2003) to the secondary mineral deposits at Yucca Mountain. Dublyansky and Smirnov (2005) use selected evidence to support their hypothesis that calcite and other secondary minerals at Yucca Mountain form from hydrothermal solutions. Although none of this discussion is specifically relevant to the calculation of past water seepage presented in Marshall et al. (2003), issues raised in the comment are discussed below and in replies by Whelan et al. (2004) and Wilson and Cline (2005) to similar comments by the same authors.

The first part of Section 3 of Dublyansky and Smirnov (2005) concerns the highest temperatures of deposition obtained for some calcite within the shallower part of the UZ at Yucca Mountain, and modeling of the thermal history. In brief, there is evidence that at least some of the highest temperature calcite is associated with transient fumarolic activity (Whelan et al., 2004). Therefore, local deposition temperatures derived from this fumarolic calcite cannot be used to depict the geothermal gradient for the region. These highest temperatures of deposition are explained in Marshall and Whelan (2001) with a thermal model (developed by Wohletz et al., 1999) that links the slow cooling of the UZ at Yucca Mountain to the cooling magma body beneath the Timber Mountain caldera complex. Matching the modeled thermal history to the observations at Yucca Mountain requires assumptions regarding such parameters as the erosional history and the spatial and temporal extent of hydrothermal activity in the saturated zone. The driving mechanism is dissipation of a large amount of thermal energy emplaced at shallow crustal levels via magmatic processes. Dublyansky and Smirnov (2005) present no viable alternative thermal history model.

Figure 1 of Dublyansky and Smirnov (2005) contains a cross-section and map showing maximum temperatures obtained from fluid inclusions. Although Dublyansky and Smirnov (2005) state that temperatures used to construct the contours correspond to early stages of mineral deposition, geochronologic evidence indicates that the timing for this deposition may extend from the age of the Topopah Spring Tuff (12.8 Ma; Sawyer et al., 1994) to approximately 6 Ma (Neymark et al., 2001; Whelan et al., 2003; Wilson et al., 2003). Therefore, the map and cross-section do not represent a point in time and the apparent gradients shown likely are artifacts of the incomplete record of calcite precipitation and (or) the incomplete preservation of two-phase fluid inclusions. Depictions of paleo-thermal gradients such as these would require more detailed geochronology to constrain the times of calcite deposition. Dublyansky and Smirnov (2005) did not use isotopic paleo-temperature information determined for the late-stage calcite (past 2 to 4 m.y.), which is devoid of 2-phase fluid inclusions suitable for temperature determinations. Temperatures of late-stage calcite deposition derived from oxygen isotopes (Whelan et al., 2002) slightly increase with depth below surface in agreement with the modern geothermal gradient and a meteoric origin of seepage.

The final points (numbered 1 to 4) in Section 3 of Dublyansky and Smirnov (2005) concern chemical and isotopic compositions reported elsewhere; and not discussed in Marshall et al. (2003). Point 1 discusses salinity measurements on fluid inclusions; these salinities are larger than the salinities measured in pore water extracted from the volcanic rocks (~700 ppm; Peterman and Marshall, 2002). However, the pore water extracted from rock core represents matrix water; water traversing the fracture network has not been sampled nor has water been observed in any undisturbed openings. Evaporation of water as it moves down fractures and into open cavities is expected in the UZ. In addition, the equilibrium thermodynamic model presented in Marshall et al. (2003) shows that evaporation is required to precipitate opaline silica. Thus salinities of fluid inclusions from slow-growing calcite deposited in open cavities should be higher than those of pore water. Evaporation also is the likely explanation for the apparent shift in isotopic composition of fluid inclusion waters off the meteoric water line (point 2 in Dublyansky and Smirnov, 2005; Wilson and Cline, 2005).

Points 3 and 4 in Dublyansky and Smirnov (2005) have been raised in previous comments on conceptual models of UZ mineral formation (Dublyansky et al., 2004). The validity of these points has been discussed elsewhere (Whelan et al., 2004; Wilson and Cline, 2005) and is not revisited in this reply.

3. Conclusion

In contrast to the views expressed by Dublyansky and Smirnov (2005), the preponderance of data obtained on the secondary calcite and opal from the UZ at Yucca Mountain indicates precipitation from meteoric water modified to a minor extent by water–rock interaction. These extensive data sets are presented in numerous publications (Paces et al., 2001, 2004; Neymark et al., 2002; Whelan et al., 2002, 2004; Wilson et al., 2003), and were not the subject of the paper by Marshall et al. (2003). The alternative hypothesis of precipitation from hydrothermal waters (Dublyansky and Smirnov, 2005) is not consistent with calcite and opal distributions, mineral textures, or geochemical data, as discussed in Whelan et al. (2004).

Dublyansky and Smirnov (2005) correctly point out that the early stages of mineral deposition occurred at temperatures higher than those assumed in the equilibrium thermodynamic model of Marshall et al. (2003) used to estimate water volumes required to precipitate calcite in the UZ at Yucca Mountain. However, consideration of larger thermal gradients during early depositional conditions does not change the overall ratio of water/calcite derived in the calculations. The conclusions of Marshall et al. (2003) regarding the volumes of water that are required to account for calcite deposited within open fractures and cavities at Yucca Mountain are not affected by the comments of Dublyansky and Smirnov (2005), and these estimates of past seepage may be useful indicators of future seepage into man-made openings.

Acknowledgements

This work was prepared in cooperation with the U.S. Department of Energy under Interagency Agreement DE-AI08-97NV12033. Technical reviews by D. Parkhurst and J. Paces improved the clarity of the paper.

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