

Experimental Tests of Enhancement of Vapor Diffusion in Topopah Spring Tuff

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ABSTRACT

The potential enhancement of thermally driven water vapor diffusion in Topopah Spring Tuff was investigated using a transient—state thermal conductivity measurement. Thermal conductivity was measured as a function of pressure, temperature, and water content by the method of Parikh et al. (1979), which allows separation of thermal conductivity from thermally induced latent heat transport. The measured thermal conductivity of Topopah Spring Tuff ranged from 0.99 W/mK to 2.07 W/mK and showed an increase with increasing temperature above approximately 40°C. These values are slightly lower than the range of values measured for other samples from the Yucca Mountain, Nevada site (e.g., Nimick, 1990). Enhancement of vapor diffusion in tuff was not observed at any of the investigated combinations of water contents, temperatures, and pressures. The method of Parikh et al. (1979) was subsequently tested on a mixture of quartz sand and 10% kaolinite. A considerable degree of enhancement was observed in the soil for a water saturation of 14%, demonstrating the capability of the method to estimate enhancement of vapor diffusion.

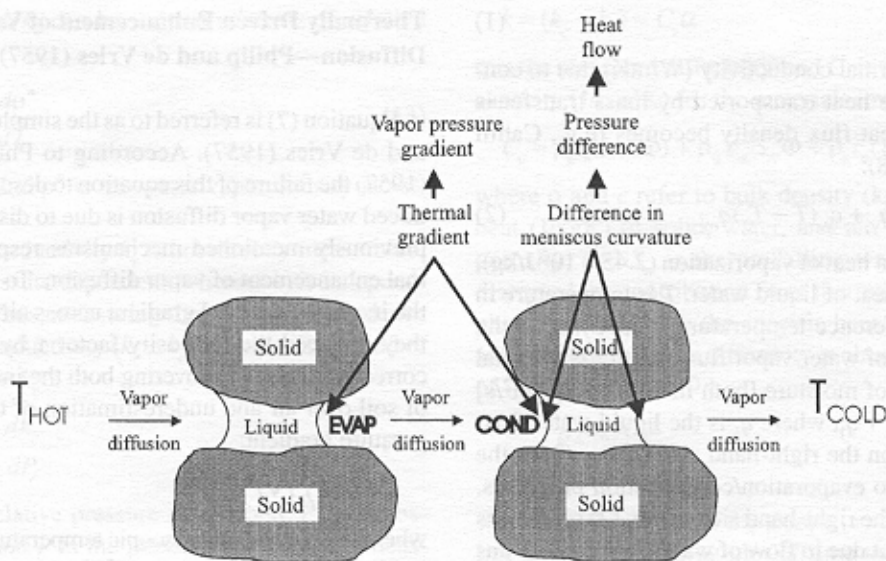


Figure 1. The process of enhancement in the presence of liquid islands.

curvature between the two sides. The evaporation–condensation process repeats itself on the other side of the liquid island, and the result is an enhanced diffusive flux through the medium.

The second enhancement mechanism proposed by Philip and de Vries (1957) relates to the use of an average temperature gradient in Fick's law. The gas-phase thermal conductivity is much less than that in the liquid and solid phases. Therefore, the mean thermal gradient averaged over all three phases is smaller than the temperature gradient across the vapor-filled pores. Water vapor moves primarily through the air spaces, where the higher local thermal gradient provides a driving force for the diffusion of water vapor.

Thus far, the only material for which thermally driven enhanced vapor diffusion has been quantified is soils (Cass et al., 1984). Cass et al. (1984) found various degrees of enhancement for varying water saturations for a sand and a silt loam. Other investigators (Cary and Taylor, 1962; Hopmans and Dane, 1986, and others) have suggested that thermally driven enhancement may be the cause of unexpectedly high thermal conductivities observed for soils. Recently, Ho and Webb (1998) reviewed enhanced vapor diffusion studies and came to the conclusion that, although there is sufficient theoretical basis for enhancement of vapor diffusion, there was no direct evidence to support it. However, in a later publication Webb and Ho (1998) reported both experimental and numerical modeling evidence

of enhancement of vapor diffusion in the absence of a thermal gradient. According to their study, the vapor density gradient, which is driving the enhancement, can be established without the influence of a thermal gradient, for instance due to a concentration gradient. Experiments conducted on various scales showed that enhancement took place as long as a vapor density gradient was present. Regardless of whether the enhancement is driven by temperature or other phenomena, the intent of this study was to investigate the potential for enhancement of vapor diffusion in rocks. Because large temperature gradients will exist in a nuclear waste repository, thermally enhanced vapor diffusion is important for long-term modeling and repository design. Thus, the objective of the present study is to test if thermal enhancement takes place in the welded Topopah Spring Tuff present at Yucca Mountain. To validate our approach, the methodology is tested on a mixture of sand and clay to simulate one of the soils of Cass et al. (1984).

THEORETICAL CONSIDERATIONS

Energy and Mass Equations

Heat or thermal energy transfer by conduction in a fluid or a solid continuum is described by Fourier's law (1822), expressing proportionality between the heat flux density, q_h (W/m^2), and a temperature (T) gradient:

$$q_h = -k_c \nabla T \quad (1)$$

where k_c is the thermal conductivity (W/mK) due to conduction. When the heat transported by mass transfer is considered, the heat flux density becomes (e.g., Cahill and Parlange, 1998):

$$q_h = -k_c \nabla T + Lq_v + c_w(T - T_0)q_m \quad (2)$$

where L is the latent heat of vaporization (2.45×10^6 J/kg), c_w is the specific heat of liquid water, T is temperature in ($^{\circ}\text{C}/\text{m}$), T_0 is a reference temperature ($\sim 25^{\circ}\text{C}$), q_v is the mass flux density of water vapor flux, and q_m is the total mass flux density of moisture [both in units of $\text{kg}/(\text{m}^2/\text{s})$] defined as $q_m = q_v + q_l$, where q_l is the liquid water flux. The second term on the right-hand side of Eq. (2) is the heat transfer due to evaporation/condensation processes. The third term on the right-hand side of Eq. (2) represents the transport of heat due to flow of water between regions of differing temperature. Convective heat transfer is neglected in the present study, as we assume no liquid water flow and the latter term is therefore not further considered:

$$q_h = -k_c \nabla T + Lq_v \quad (3)$$

The vapor flux q_v can be divided into an isothermal part driven by the moisture content gradient and a thermal part driven by the temperature gradient:

$$q_v = -D_\theta \nabla \theta - D_T \nabla T \quad (4)$$

where D_θ and D_T are the respective diffusivities. Fick's law applied to soils can be written as (Cass et al., 1984):

$$q = -a\tau D \nabla \rho \quad (5)$$

where a is the volumetric air-filled porosity, τ is a dimensionless tortuosity factor, D is the diffusion coefficient of water vapor in air (m^2/s), and $\nabla \rho$ is the water vapor density gradient (kg/m^4). If we rewrite Eq. (5) in a form that contains temperature explicitly by transforming the vapor density gradient to an equivalent temperature gradient using $\nabla \rho = d\rho/dT \nabla T$, then the second term on the right-hand side of Eq. (4) becomes:

$$D_T \nabla T = -a\tau D \frac{d\rho}{dT} \nabla T \quad (6)$$

Using only small temperature changes we assume no moisture gradient develops in the sample and the first term on the right side of Eq. (4) can be neglected:

$$q_v = -a\tau D \frac{d\rho}{dT} \nabla T \quad (7)$$

where $a\tau D \frac{d\rho}{dT} = D_T$.

Thermally Driven Enhancement of Vapor Diffusion—Philip and de Vries (1957)

Equation (7) is referred to as the simple theory by Philip and de Vries (1957). According to Philip and de Vries (1957) the failure of this equation to describe thermally induced water vapor diffusion is due to disregard of the two previously mentioned mechanisms responsible for thermal enhancement of vapor diffusion. To take into account the increased thermal gradient across air-filled pore space they replaced the tortuosity factor τ by a dimensionless correction factor (ζ) covering both the increased tortuosity of soil over air and underestimation of the effective temperature gradient:

$$\zeta = (\nabla T)_a / \nabla T \quad (8)$$

where $(\nabla T)_a$ is the microscopic temperature gradient across an air-filled pore (K/m), and ∇T is the same across the soil sample. Series-parallel flow across liquid islands was compensated for by correcting the air-filled porosity term (Cass et al., 1984). The air-filled porosity term a in Eq. (5) is replaced with $a + f(a)\theta$ where

$$f(\theta) = \begin{cases} 1 & \text{if } \dots a \geq a_f \\ a/a_f & \text{if } \dots a < a_f \end{cases} \quad (9)$$

a_f is the air-filled porosity where continuity of water films begin, and θ is the volumetric water content. These correction factors were combined in what is known as the mechanistic enhancement factor η . Equation (7) can then be written as (Cass et al., 1984):

$$q_v = -\eta a\tau D \frac{d\rho}{dT} \nabla T \quad (10)$$

with η accounting for the increase (enhancement) in vapor diffusion compared to that predicted by the simple diffusion theory depicted in Eq. (7). A similar approach was taken by Cary and Taylor (1962), introducing their phenomenological enhancement factor β , which is related to η as $\beta = 0.66 a\eta$.

Using Eq. (10), Eq. (3) can now be written as:

$$q_h = -k_c \nabla T - L\eta a\tau D \frac{d\rho}{dT} \nabla T \quad (11)$$

which can be interpreted as

$$q_h = -(k_c + k_v) \nabla T \quad (12)$$

where k_v is the thermal conductivity resulting from the transfer of latent heat through vapor diffusion and k_c is the previously introduced thermal conductivity due to con-

duction. The term k_v can be written in terms of relative humidity h as:

$$k_v = L\eta\alpha\tau Dh \frac{d\rho^*}{dT} \quad (13)$$

where $h = \rho/\rho^*$, and ρ^* is the water vapor density at saturation.

The thermal conductivity k_v is not directly measurable; however, k_v is pressure dependent, whereas k_c is independent of pressure. Thus, measuring the pressure dependence of the thermal conductivity ($k_v + k_c$) provides a method of separating k_c from k_v :

$$\frac{d(k_c + k_v)}{dP_r} = \frac{dk_v}{dP_r} \quad (14)$$

P_r is reciprocal relative pressure P_0/P , where P_0 is atmospheric pressure and P is the pressure at which the measurement is taken. At infinite pressure the vapor flux and therefore its associated latent heat flux is zero, and thus, $k_v + k_c$ is equal to k_c . Differentiating Eq. (13) with respect to P_r :

$$\frac{dk_v}{dP_r} = Lh\eta\alpha\tau \frac{d\rho^*}{dT} \frac{dD}{dP_r} \quad (15)$$

where the pressure dependence of the water vapor diffusivity can be expressed as (Cass et al., 1984):

$$\frac{dD}{dP_r} = D_0 \left(\frac{T}{T_0} \right)^{1.75} = D_{va} \quad (16)$$

D_0 is the water vapor diffusivity at T_0 , and pressure P , and D_{va} is the binary diffusion coefficient of water vapor in air. Equation (15) then becomes

$$\frac{dk_v}{dP_r} = Lh\eta\alpha\tau \frac{d\rho^*}{dT} D_{va} \quad (17)$$

The only unknown on the right-hand side of Eq. (17) is the mechanistic enhancement factor η ; thus, to quantify the potential enhancement of vapor diffusion according to Philip and de Vries' (1957) theory, knowledge of the pressure dependence of k_v (dk_v/dP_r) is required. A similar expression can be derived for the phenomenological enhancement factor of Cary and Taylor (1962) [see Cass et al. (1984)].

Estimating the Pressure Dependence of k_v

The total thermal conductivity ($k_v + k_c$) can be calculated from the thermal diffusivity as:

$$k = (k_c + k_v) = C_v\alpha \quad (18)$$

α is the measured diffusivity, and C_v is the volumetric heat capacity (J/cm^3K) for the materials involved:

$$C_v = \rho_s c_s (1 - \Phi) + \rho_w c_w S_w \Phi + \rho_a c_a (1 - S_w) \Phi \quad (19)$$

where ρ and c refer to bulk density (kg/m^3) and specific heat (J/kgK) of solid, water, and air, respectively; Φ is porosity; and S_w is the prevailing water saturation. We disregard the contribution from thermal transfer in the air phase, because both the specific heat and the density of air are negligible. The diffusivity is obtained by the method of Parikh et al. (1979):

$$\alpha = \frac{b2.303 r^2}{-X_1^2} \quad (20)$$

where r is the radius of the sample, and b is the slope of a line fitted to a semilog plot of time vs. relative temperature change $T' = (T_2 - T)/(T_2 - T_1)$. The temperatures T_1 and T_2 are the temperatures of the water baths used in the experiment such that $T_2 - T_1$ represents the maximum temperature change. The constant X_1 has a limiting value of 2.405, which is the first positive root of the zeroth order Bessel function (Chung and Jackson, 1954; Parikh et al., 1979; Hopmans and Dane, 1986). As enhancement presumably only takes place at intermediate water contents and possibly only in certain temperature ranges, we measured thermal conductivity as functions of temperature, water content, and pressure.

EXPERIMENTAL DETAILS

A sample core is placed in a water bath, equilibrated at the prevailing temperature and pressure, and then quickly immersed in another water bath of different temperature. The resulting temperature change in the center of the core is monitored with a thermocouple as a function of time. This procedure is repeated for a series of temperatures, pressures, and water contents to measure the thermal conductivity and to estimate the ratio dk_v/dP_r and thus the degree of enhancement under different circumstances. Only small temperature changes are used (approximately 5°C) to keep the thermal gradients relatively small and thus minimize water redistribution in the core [i.e., so the first term on the right side of Eq. (4) can be neglected]. By using two water baths at marginally different temperatures this precaution can be satisfied, and yet thermal conductivities and associated enhancement coefficients can be measured over a wide range of temperatures (e.g., from ambient to 90°C).

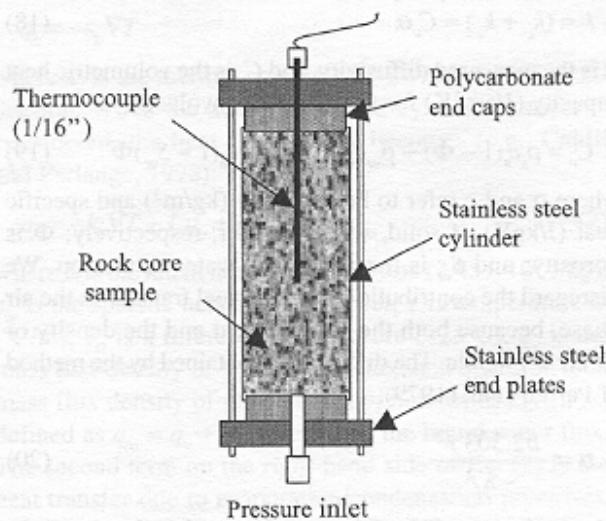


Figure 2. Schematic of the sample holder.

As shown in Fig. 2, a 2.54-cm diameter and 5.08-cm long core sample is mounted in a thin-walled stainless steel cylinder and clamped between steel end plates. Polycarbonate end caps are used at the contact surface between stainless steel and sample core to minimize heat transfer through the end planes. Mixers are used to keep the water moving in the baths and to avoid changes in the water temperature in the immediate vicinity of the sample. To keep evaporation at a minimum and maintain a constant temperature in the water baths, air-filled polyurethane balls covered the water surface. The thermal diffusivity and thus the thermal conductivity are obtained from the transient response of the thermocouples as explained in the section "Estimating the Pressure Dependence of k_v ." An example of a heating and a cooling curve is shown in Fig. 3a. Figure 3b shows the same curve for the thermocouple placed inside the sample (TC1) plotted as relative temperature change (log-scale) vs. time. The latter plot facilitates estimation of the slope factor b used to calculate the diffusivity [Eq. (20)] and thus the thermal conductivity. Once the thermal conductivity is determined the enhancement coefficients can be obtained as described in Eq. (17).

Tuff Sample Preparation

The Topopah Spring Tuff sample analyzed in these experiments originates from the TSw2 thermal/mechanical unit located in the depth range between 211 and 416 m (693–1365 ft) in the Topopah Spring Member of the Paint-

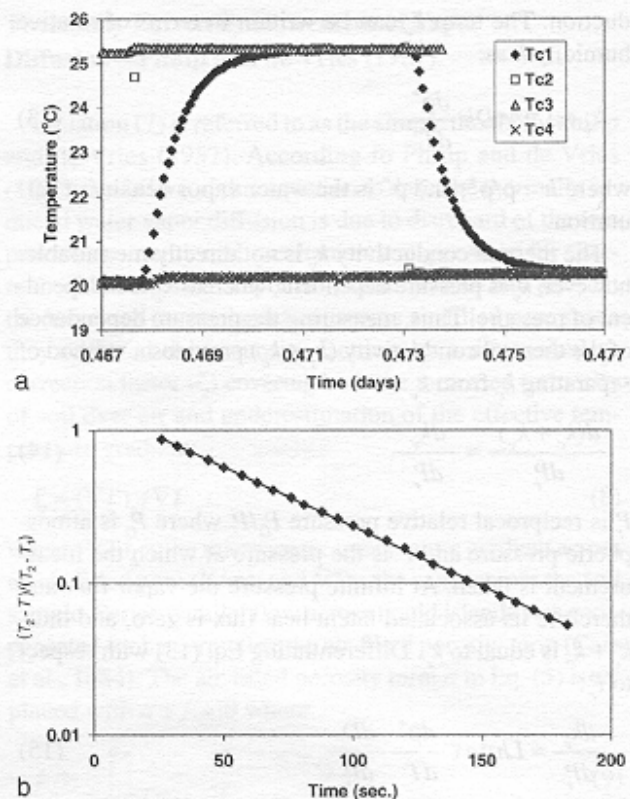


Figure 3. (a) Response of thermocouples during heating and cooling experiment performed on Topopah Spring Tuff. TC1 is the thermocouple placed inside the sample, TC2 is placed immediately on the outside of the cylinder to monitor the boundary condition, and TC3 and TC4 are placed in the two water baths. (b) Semilog plot of time vs. relative temperature change $T' = (T_2 - T)/(T_2 - T_1)$. (T_1 and T_2 are temperatures of water baths used in the experiment such that $T_2 - T_1$ represents the maximum temperature change.) The exponent in the expression for the line fitted to the data is the slope factor b used to calculate the diffusivity [Eq. (20)]. For this experiment performed on Topopah Spring Tuff ($S_w = 0.59$), $y = 1.405e^{-0.018x}$, and $R^2 = 0.9997$.

brush Tuff formation. The TSw2 unit is characterized as welded, devitrified ashflows. The sample consists primarily of quartz and alkali feldspar, and has a bulk density of 2.3 g/cm³ and a porosity of 8.3% determined from wet and dry weights of the sample. Prior to the experiments, a 1.59-mm (1/16-inch) hole was drilled in the center of the core for insertion of a 1.59-mm (1/16-inch) Type J, commercially calibrated thermocouple. A thermocouple was also mounted on the outside of the stainless steel cylinder (in contact with the steel) to monitor the boundary conditions closely.

Wetting of the sample was accomplished by submerging it in a beaker of water. To prevent water from entering the thermocouple hole, the top surface was kept above the water surface. The saturating water was filtered well water (J-13) from the Yucca Mountain site with an electrical conductivity of 266 $\mu\text{S}/\text{cm}$. The sample was weighed intermittently to monitor the increasing saturation and removed when the desired saturation was obtained. Following wetting, the sample was left to equilibrate (to achieve a uniform liquid distribution) for at least 3 days before being mounted in the sample holder for an experimental run. A decrease in saturation was accomplished by placing the sample in a vacuum oven at 35°C until the desired saturation was achieved. At the end of an experimental run, at a specific saturation, the sample was removed and weighed to determine if water was gained or lost. In all cases the saturation remained within 0.065 g of the initial value, corresponding to 0.1% of the average saturation value during the experiment.

Pore pressure was controlled by a pressurized nitrogen source and monitored by a 300-psi pressure transducer. A change in the applied pore pressure was followed by a period of equilibration at the new pressure level before experiments were resumed. Preliminary tests showed that the pressure in the tuff sample equilibrated within approximately 12 h following an imposed change.

Test of the Transient Method on Reference Materials

The method of Parikh et al. (1979) was tested on two reference materials, polycarbonate (Lexan™) and PTFE (Teflon™). The reference materials were machined to fit in the stainless steel cylinder as tightly as the tuff sample. Experiments were carried out the same way as for the rock, except that these materials were dry at all times and pressure was kept at ambient conditions. Additional experiments were carried out on the reference samples without the stainless steel cylinder to confirm that its presence did not affect the measurements. Finally, to verify the

presence of adequate thermal contact between the inserted thermocouple and the test material, some tests were carried out using thermal grease between the two materials. No influence of either stainless steel cylinder or thermal grease was observed in these tests.

As seen in Table 1, the measured thermal conductivities of the reference materials were measured very accurately with an error of only 1.5% and 1.6%. Consecutive measurements showed the method to be repeatable and precise. The reference values of thermal conductivities for these materials were taken from CenBASE/Materials on the World Wide Web (<http://www.centor.com/cbmat/visitors/00456.html>) for Lexan™ and from the homepage of Fietz GmbH, Germany (<http://www.fietz.de/wst1e.htm>) for Teflon™, that is, they were not measured for the actual samples used. The differences between the measurements and the published reference values of 15.3% and 7.8% are therefore not surprising, and our results indicate that the method of Parikh et al. (1979) is adequate for thermal conductivity measurements. Because we are most interested in relative changes in thermal conductivity, the absolute accuracy of the method is less important than the precision. Our method and apparatus are reasonably accurate and very precise, thus appropriate for our study.

RESULTS AND DISCUSSION

Thermal Conductivity of Topopah Spring Tuff

The thermal conductivity of Topopah Spring Tuff was measured for a range of temperatures (22.5, 27.5, 42.5, 57.5, 72.5, 87.5°C), pressures (0–250 psi), and saturations (0.097, 0.20, 0.36, 0.58, 0.76). The temperatures given are average values of the two water baths, that is, the temperature of 87.5°C was obtained by keeping the baths at 85°C and 90°C, respectively. The measurements made at saturations of 0.097, 0.20, 0.36, 0.58, and 0.76 correspond to water contents of 0.008, 0.017, 0.030, 0.048, and 0.063 (cm^3/cm^3) for a sample with a porosity of 0.083 (cm^3/cm^3). Based on propagated errors resulting from

Table 1
Results of test of method on reference materials

	Measured k (W/mK)	Measured error (%)	Reference k (W/mK)	Error (%)	Source of manufacturer's value for k
Lexan™	0.219	1.5	0.19	15.3	www.centor.com/cbmat/visitors/00456.html
Teflon™	0.248	1.6	0.23	7.8	www.fietz.de/wst1e.htm

Table 2

Measured minimum and maximum thermal conductivities for Topopah Spring Tuff

Measured thermal conductivity	$S_w = 0.097$	$S_w = 0.20$	$S_w = 0.36$	$S_w = 0.58$	$S_w = 0.76$
Minimum k (W/mK)	1.02	1.01	0.99	1.00	1.11
Maximum k (W/mK)	1.78	1.77	1.73	1.84	2.07

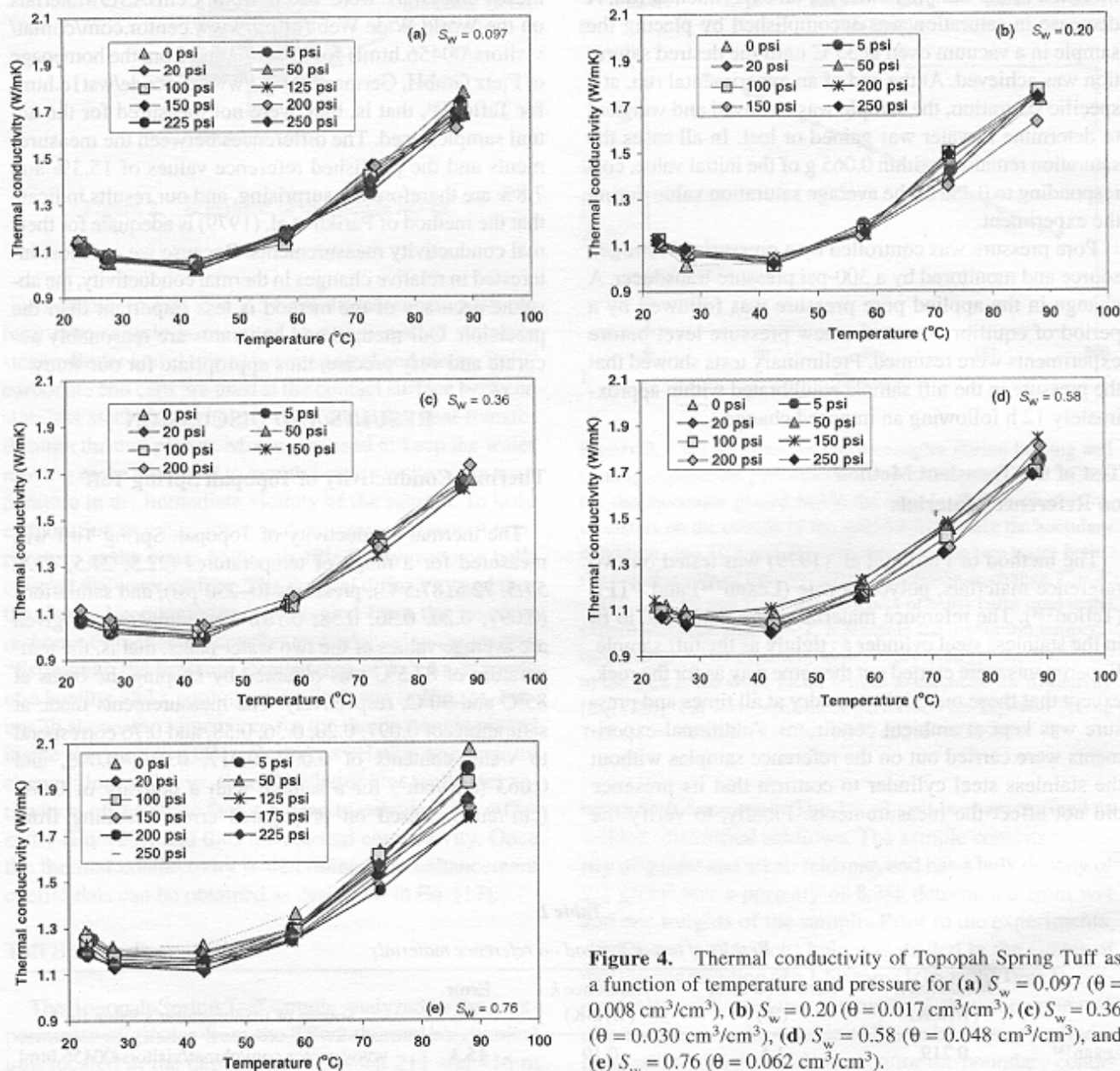


Figure 4. Thermal conductivity of Topopah Spring Tuff as a function of temperature and pressure for (a) $S_w = 0.097$ ($\theta = 0.008 \text{ cm}^3/\text{cm}^3$), (b) $S_w = 0.20$ ($\theta = 0.017 \text{ cm}^3/\text{cm}^3$), (c) $S_w = 0.36$ ($\theta = 0.030 \text{ cm}^3/\text{cm}^3$), (d) $S_w = 0.58$ ($\theta = 0.048 \text{ cm}^3/\text{cm}^3$), and (e) $S_w = 0.76$ ($\theta = 0.062 \text{ cm}^3/\text{cm}^3$).

uncertainty in the heat capacity measurements, weights and volumes of the sample, and error on the estimation of the factor b (slope in log-plot), the estimated error on the thermal conductivity measurements is <3%. The highest and the lowest thermal conductivity measured for each saturation are listed in Table 2. The measured conductivities for these particular water contents vary between 0.99 W/mK and 2.07 W/mK, increasing with increasing temperature above approximately 40°C (Fig. 4a–e), reflecting a similar relationship between specific heat and temperature. The specific heat used for calculating the thermal conductivity was measured by Precision Measurements and Instruments Corporation, Philomath, Oregon (PMIC, 1998) to vary with temperature between 0.810 J/g°C (at 45°C) and 1.430 J/g°C (at 90°C). The thermal conductivity values reported in Fig. 4 are different from those reported for Topopah Spring Tuff (TSw2 unit) by other investigators (e.g., Nimick, 1990). This is largely a result of differences in the measured heat capacity, which is needed to convert thermal diffusivity to thermal conductivity. Before inferences are made regarding the temperature dependence of the thermal conductivity of the partially saturated tuff, additional, more systematic, measurements of the heat capacity need to be performed.

As seen in Fig. 4a–e the temperature dependence is consistent for all pressures between 0 and 250 psi. Generally, slight pressure dependence was observed at the higher saturations, whereas for the lower saturation the curves for the various pressures are almost identical. We measured the maximum thermal conductivity for all saturations to be 2.07 W/mK at a saturation of 0.76 corresponding to a water content of 0.062 (cm^3/cm^3), while the minimum value of 0.99 W/mK was the value measured at a saturation of 0.36 ($0.030 \text{ cm}^3/\text{cm}^3$). In Fig. 5, the thermal conductivity is plotted as a function of saturation at ambient pressure conditions. A small but noticeable increase in thermal conductivity with saturation is observed above approximately 35% saturation for all temperatures. The increase in thermal conductivity above approximately 35% could be due to the availability of bulk water at higher saturations. Recent experiments by Roberts and Lin (1997) on samples from the Topopah Spring member of the Paintbrush Tuff formation (borehole USW G4) showed that from 0% to 15% saturation water is predominantly adsorbed on internal surfaces, between 15% and ~35% saturation water is located in isolated regions, that is, pendular rings and necks. However, above ~35% saturation bulk water exists and is interconnected, thus providing a pathway for thermal transfer.

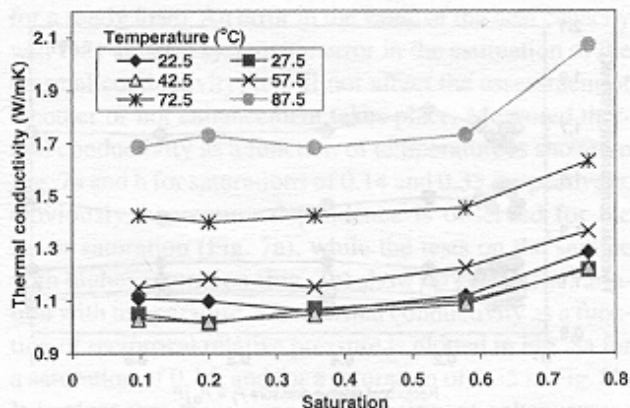


Figure 5. Thermal conductivity as a function of saturation at ambient pressure (0 psi).

In comparison to our measurements, low-temperature (<100°C) thermal conductivity was measured by Nimick (1990) for field samples from the Yucca Mountain Tuff unit TSw2 to be 2.29 W/mK at saturation, 1.66 W/mK air dry, and 1.49 for dry samples. For higher temperatures (>100°C) the thermal conductivity at saturation is 1.59 W/mK. No data are available at partial saturation. Apparently, our measured thermal conductivities are slightly lower than the range of thermal conductivities measured for field samples from the site. The differences in thermal conductivity might be due to a number of factors, including sample heterogeneity (porosity, mineralogy), saturation, and temperature. Also, the values listed by Nimick (1990) have rather large standard deviations, indicating that some of the samples they analyzed had thermal conductivity values similar to those measured in this study. The increase in thermal conductivity with temperature is, however, not evident in the field samples.

Enhancement of Water Vapor Diffusion in Topopah Spring Tuff

The thermal conductivity is plotted as a function of reciprocal relative pressure P_r in Fig. 6a–e to assess the existence of enhancement at the various saturations. A positive slope [$d(k_v + k_c)/dP_r > 0$] in this figure indicates enhancement ($dk_v/dP_r > 0$) as k_c is pressure independent. As seen in Fig. 6a–e all the curves have a zero or negative slope for the various saturations. We note that there is some fluctuation in the data at high pressures (low P_r).

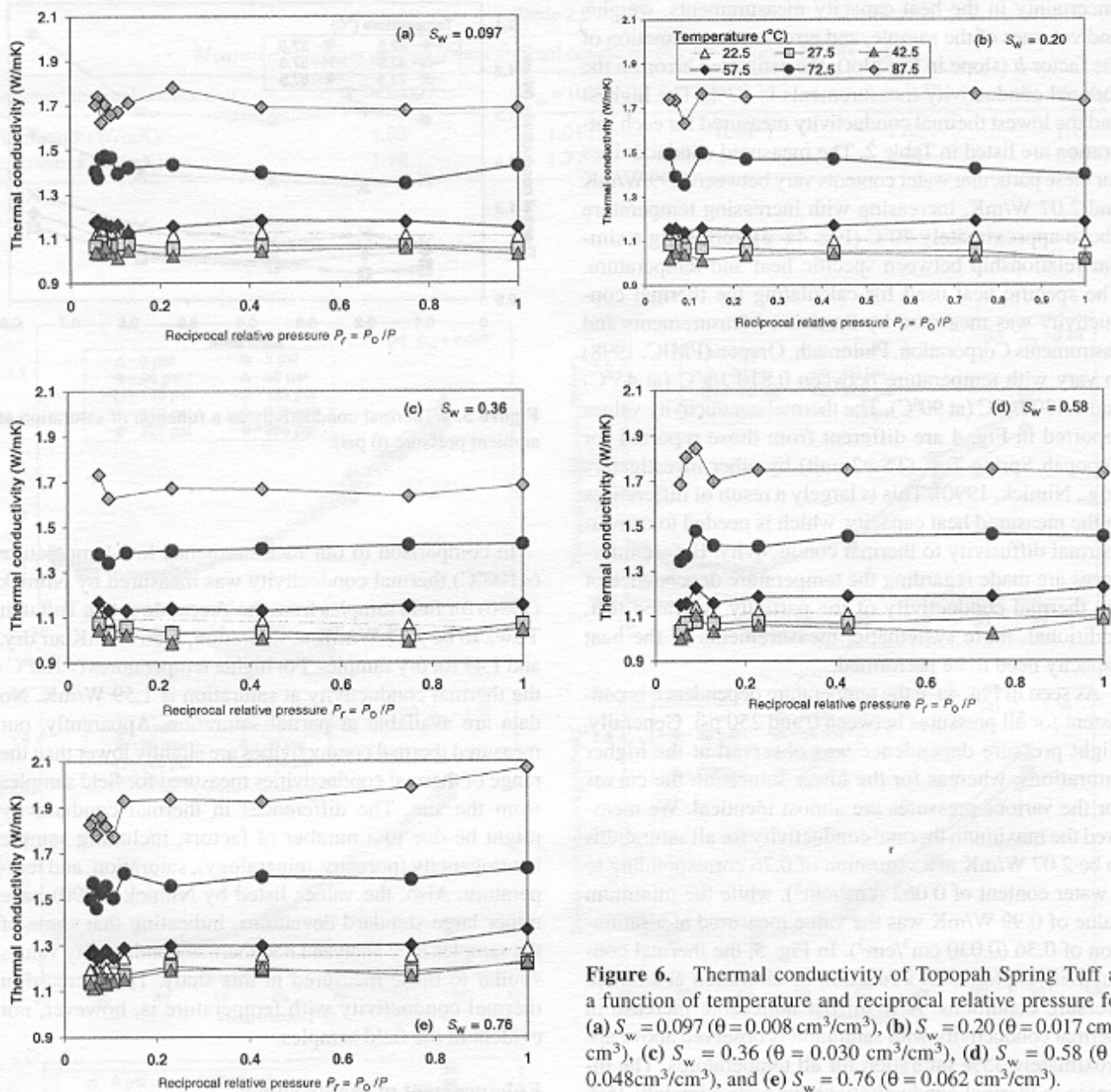


Figure 6. Thermal conductivity of Topopah Spring Tuff as a function of temperature and reciprocal relative pressure for (a) $S_w = 0.097$ ($\theta = 0.008 \text{ cm}^3/\text{cm}^3$), (b) $S_w = 0.20$ ($\theta = 0.017 \text{ cm}^3/\text{cm}^3$), (c) $S_w = 0.36$ ($\theta = 0.030 \text{ cm}^3/\text{cm}^3$), (d) $S_w = 0.58$ ($\theta = 0.048 \text{ cm}^3/\text{cm}^3$), and (e) $S_w = 0.76$ ($\theta = 0.062 \text{ cm}^3/\text{cm}^3$).

This variation was present at all saturations, but did not show a consistent dependence on pressure, that is, it is not possible to derive a positive slope at these high pressures either. Regardless, the fluctuation is observed in a pressure regime beyond the naturally prevailing conditions at the field site. Based on our findings we conclude that the process of enhancement of vapor diffusion is nonexistent or insignificant in this material for the conditions investigated.

Enhancement of Water Vapor Diffusion in a Sand-Clay Mixture

To verify our approach we tested the experimental method (Cass et al., 1984) on a mixture of sand and clay at the same conditions under which Cass et al. (1984) found enhancement. The sand-clay soil was a mixture of 90% 50-mesh quartz sand and 10% kaolinite, resulting in a particle density of 2.65 g/cm^3 . In comparison, the

lysimeter sand of Cass et al. (1984) consisted of 2% clay, 7% silt, and 91% sand with a particle density of 2.82 g/cm³. Two different saturations were tested, 0.35 and 0.14. The mixture was saturated by adding a precalculated amount of water to the dry sand and clay and thoroughly mixing it. The mixture was packed in the sample holder and left to equilibrate for at least 3 days before experiments were performed.

Thermal conductivity was measured on the mixtures for an array of pressures between ambient and 100 psi, and for temperatures between ambient and 60°C. Because of the lack of representative measurements of the heat capacity for this mixed material we used the temperature-dependent expression listed by Hopmans and Dane (1986), Table 2,

for a sandy loam. An error in the value of the heat capacity will only cause a systematic error in the estimation of the thermal conductivity; it will not affect the assessment of whether or not enhancement takes place. Measured thermal conductivity as a function of temperature is shown in Fig. 7a and b for saturations of 0.14 and 0.35, respectively. Obviously, a pressure dependence is observed for the lower saturation (Fig. 7a), while the tests on the sample with higher saturation (Fig. 7b) show no consistent variation with temperature. The thermal conductivity as a function of reciprocal relative pressure is plotted in Fig. 8a for a saturation of 0.14, and for a saturation of 0.35 in Fig. 8b. It is clear that there is no or insignificant enhancement taking place, that is, no well-defined slope at the highest

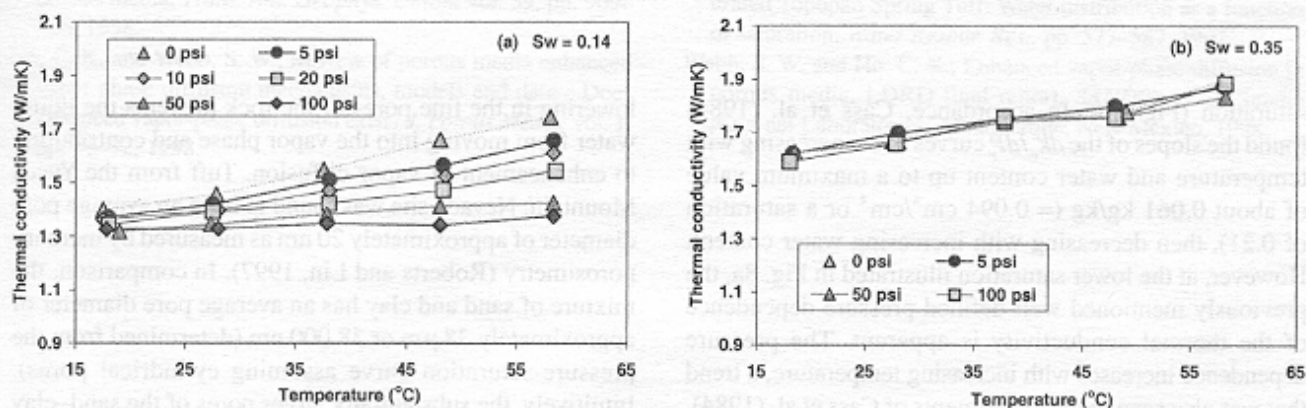


Figure 7. Thermal conductivity of sand-clay mixture as a function of temperature and pressure for (a) $S_w = 0.14$ ($\theta = 0.05 \text{ cm}^3/\text{cm}^3$) and (b) $S_w = 0.35$ ($\theta = 0.12 \text{ cm}^3/\text{cm}^3$).

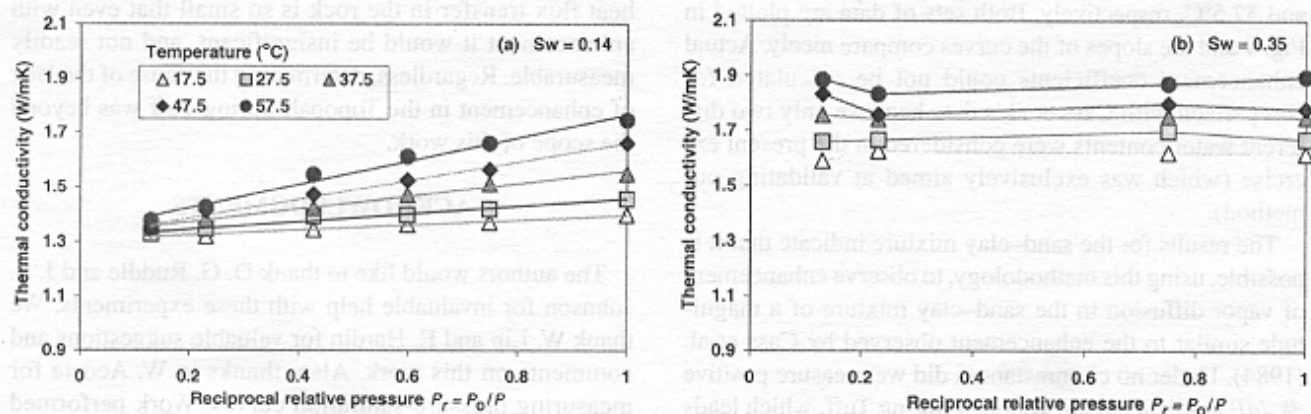


Figure 8. Thermal conductivity of sand-clay mixture as a function of temperature and reciprocal relative pressure for (a) $S_w = 0.14$ ($\theta = 0.05 \text{ cm}^3/\text{cm}^3$), and (b) $S_w = 0.35$ ($\theta = 0.12 \text{ cm}^3/\text{cm}^3$).

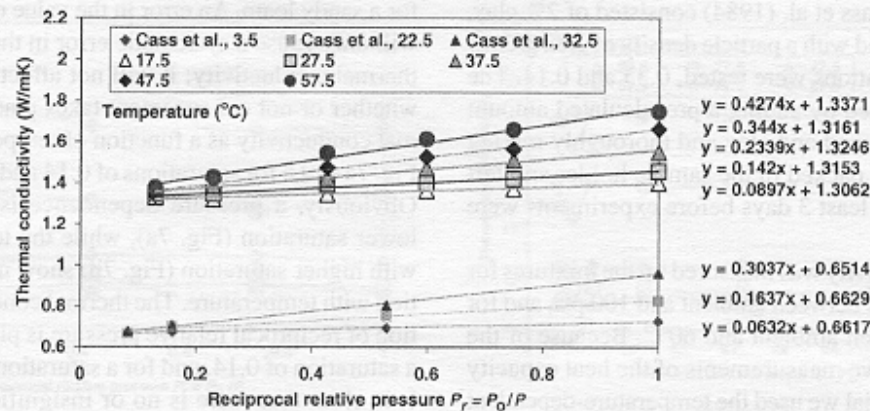


Figure 9. Thermal conductivity as a function of temperature and reciprocal relative pressure for sand–clay mixture at $S_w = 0.14$, and for the lysimeter sand of Cass et al. (1984). The slopes on the right are obtained by curve-fitting lines to the points.

saturation (Fig. 8b). In accordance, Cass et al. (1984) found the slopes of the dk_v/dP_r curves to be increasing with temperature and water content up to a maximum value of about 0.061 kg/kg ($= 0.094 \text{ cm}^3/\text{cm}^3$ or a saturation of 0.21), then decreasing with increasing water content. However, at the lower saturation illustrated in Fig. 8a, the previously mentioned well-defined pressure dependence of the thermal conductivity is apparent. The pressure dependence increases with increasing temperature, a trend that was also seen in the experiments of Cass et al. (1984). Cass et al. found gradients (dk_v/dP_r) to vary between 0.063 and 0.304 W/mK for average temperatures of 3.5°C and 32.5°C, respectively. Our measured gradients for the sand–clay mixture are very similar: They range between 0.090 and 0.427 W/mK for average temperatures of 17.5°C and 57.5°C, respectively. Both sets of data are plotted in Fig. 9 and the slopes of the curves compare nicely. Actual enhancement coefficients could not be calculated for comparison with Cass et al.'s data because only two different water contents were considered in the present exercise (which was exclusively aimed at validating our method).

The results for the sand–clay mixture indicate that it is possible, using this methodology, to observe enhancement of vapor diffusion in the sand–clay mixture of a magnitude similar to the enhancement observed by Cass et al. (1984). Under no circumstances did we measure positive dk_v/dP_r gradients in the Topopah Spring Tuff, which leads us to conclude that enhancement does not take place in the tuff. There are several likely reasons why no enhancement occurs. One possible explanation is that vapor pressure

lowering in the fine pores of the rock prevents the liquid water from moving into the vapor phase and contributing to enhancement of vapor diffusion. Tuff from the Yucca Mountain, Nevada site was found to have an average pore diameter of approximately 20 nm as measured by mercury porosimetry (Roberts and Lin, 1997). In comparison, the mixture of sand and clay has an average pore diameter of approximately 38 μm or 38,000 nm (determined from the pressure-saturation curve assuming cylindrical pores). Intuitively, the substantially larger pores of the sand–clay mixture (or natural soils) are more likely to facilitate vapor diffusion. Also, the pores are better connected in an unconsolidated material, which would promote vapor diffusion and transfer across liquid islands. One could also speculate that the vapor diffusion component of the total heat flux transfer in the rock is so small that even with enhancement it would be insignificant, and not readily measurable. Regardless, determining the cause of the lack of enhancement in the Topopah Spring Tuff was beyond the scope of this work.

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