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Transient calcite fracture fillings in a welded tuff, Snowshoe Mountain, Colorado

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Abstract

The core from two boreholes (13.1 and 19.2 m depth) drilled 500 m apart in the fractured, welded tuff near the summit of the Snowshoe Mountain, Colorado (47°30′N, 106°55′W) had unique petrographic and hydrodynamic properties. Borehole SM-4 had highly variable annual water levels, in contrast to SM-1a, whose water level remained near the land surface. Core samples from both boreholes ($n = 10$ and 11) were examined petrographically in thin sections impregnated with epoxy containing rhodamine to mark the pore system features, and were analyzed for matrix porosity and permeability. Core from the borehole sampling the vadose zone was characterized by open fractures with enhanced porosity around phenocrysts due to chemical weathering. Fractures within the borehole sampling the phreatic zone were mineralized with calcite and had porosity characteristics similar to unweathered and unfractured rock. At the top of the phreatic zone petrography indicates that calcite is dissolving, thereby changing the hydrogeochemical character of the rock (i.e. permeability, porosity, reactive surface area, and mineralogy). Radiocarbon ages and C and O stable isotopes indicate that calcite mineralization occurred about 30 to 40 ka ago and that there was more than one mineralization event. Results of this study also provide some relationships between primary porosity development from 3 types of fracture in a welded tuff. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Causes of calcite mineralization, its distribution on a pore scale up to a reservoir scale and stability within fractured bedrock are of great interest in many subdisciplines of geology. In the oil and gas industry the origin and dissolution of calcite is important because it can cause barriers to fluid flows in reservoirs (Winter et al., 1995), whereas calcite dissolution may be important in enhancing the internal porosity required for reservoirs (Taylor, 1979). Weathering of calcite-filled fractures in granitic rocks may be an important source of Ca^{2+} in alpine watersheds, even though the relative volume of calcite may be small (Mast et al., 1990). At the proposed Yucca Mountain nuclear waste storage site in south-central Nevada the study of internal porosity and fracture permeability in welded tuff bedrock has important implications for site feasibility (Winograd, 1981). At Yucca Mountain there is concern about secondary minerals, including calcite in fractures

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in the tuff bedrock, because of the implications regarding hydrologic history and their effects on groundwater pathways (Quade and Cerling, 1990).

Because reaction kinetics of calcite growth and dissolution may be relatively fast and strongly dependent on fluctuating variables (such as pH, temperature, Ca concentration, and P_{CO_2}), it is commonly difficult to say with any certainty whether calcite fracture filling material in a particular location is stable, forming, or dissolving. Mineral dissolution and precipitation processes in aquifers are commonly inferred from water chemistry using mass balance, equilibrium thermodynamics or geostatistics, without direct petrographic evidence (Drever, 1997). Calculations of calcite saturation index (log[ion activity product/solubility product]) from groundwater may also provide ambiguous information pertaining to actual calcite precipitation or dissolution processes, due to the presence of natural kinetic inhibitors in groundwater.

In this study the authors present direct petrographic and hydrologic data from boreholes and examine the influence of calcite mineralization and rock weathering on rock hydraulic characteristics. Also illustrated are the transience of lithohydraulic properties, due to dis-

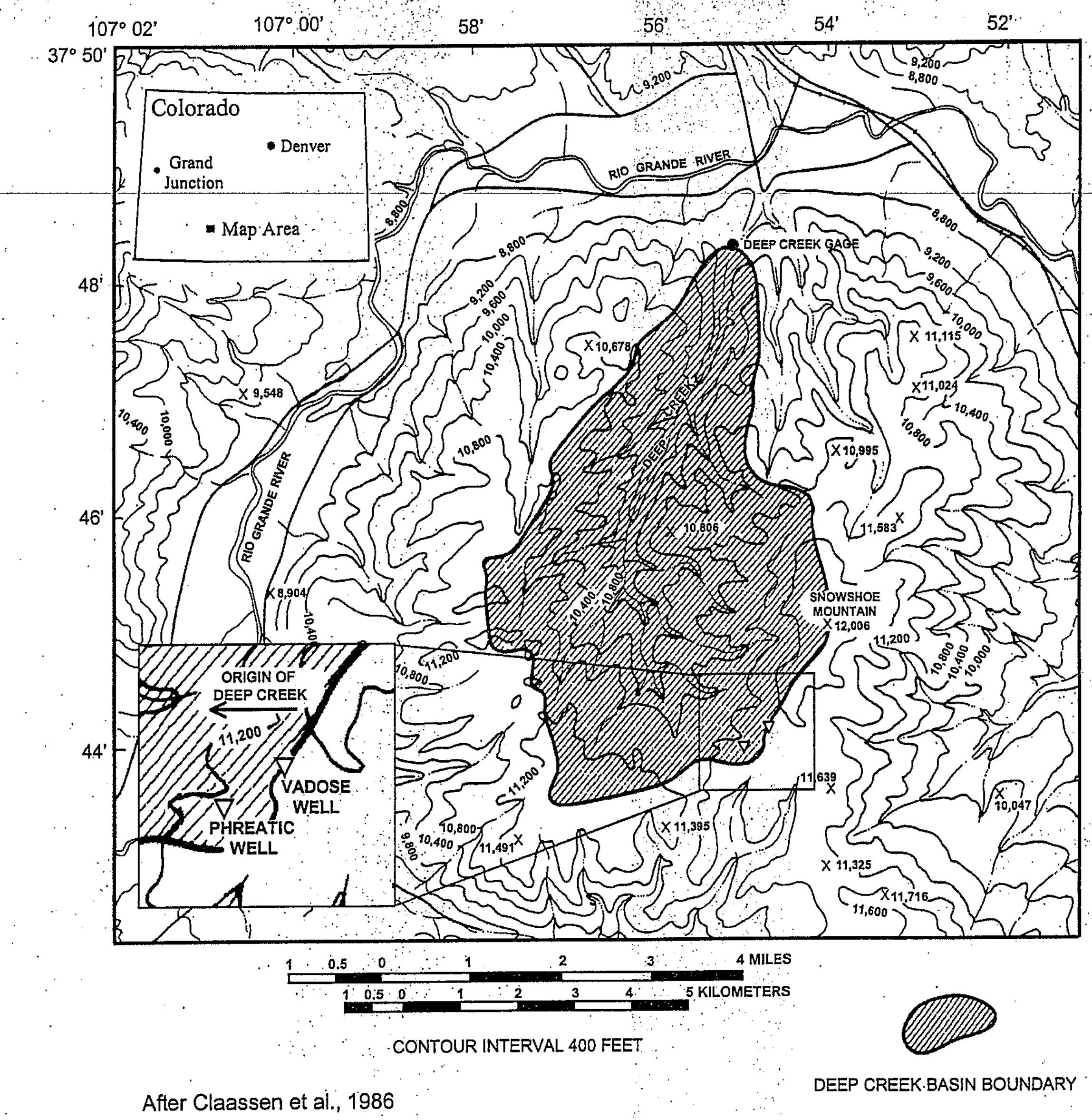

Fig. 1. Location map for Snowshoe Mountain, the borehole sites and the Deep Creek drainage area.

solution of calcite in fractures and the resulting re-opening of high-permeability pathways and enhancement of intragranular porosity.

2. Materials and methods

2.1. Fractured tuff aquifer on Snowshoe Mountain

The focus of the study is core from two boreholes with different hydrologic characteristics near the top of Snowshoe Mountain in the San Juan Mountains of southwest Colorado (Fig. 1). The boreholes were completed with ungrouted 38 mm PVC pipe with no screened intervals (open only at the bottom), so that the waters sampled were composites from the entire borehole. The sites are in a subalpine environment at an elevation of approximately 3475 m, at the head of the recharge area for Deep Creek, a tributary to the upper Rio Grande. Soil depths range from 0.0–1.0 m and the mean annual air temperature is 1.3°C. Mean annual precipitation is about 53 cm much of which is in the form of snowfall (Bates and Henry, 1928). Snow accumulation usually begins in November, after soils are frozen and is typically shallow enough (0–2 m) that soils and shallow colluvium remain frozen until late in the Spring (Hoch et al., 1999).

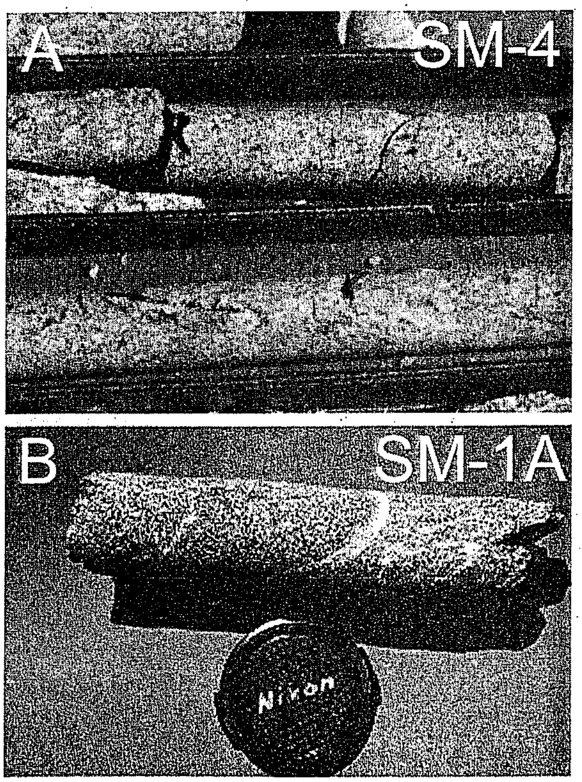

Fig. 2. Comparison of core from (A) borehole SM-4 and (B) borehole SM-1a. The SM-4 borehole core is characterized by open fractures, whereas the SM-1a fractures are typically filled with calcite (white veins). Core diameter is 38 mm.

Snowshoe Mountain is the topographic expression of a well-preserved resurgent dome of the 26.5 Ma Creede caldera complex (Steven and Lipman, 1976). It is made up of texturally variable, but geochemically homogeneous augite–biotite quartz latite welded tuff (Bates and Henry, 1928; Claassen et al., 1983). The relatively low permeability of the matrix of the welded tuff is resistant to deep penetrative chemical weathering, but near-surface weathering of interstitial glass and augite occurs in colluvium exposed by mechanical processes (Hoch et al., 1999). The host rock contains high angle fractures spaced from 10 cm to 1 m apart, that are related to the north to a south trending keystone graben system along Deep Creek (Steven, 1963). Fracture gaps range from 2 mm across to a few microns and are variably mineralized with calcite, mixed dioctahedral and trioctahedral smectite clays (as weathering products of glass and augite, respectively), and less-common Ca–Al zeolite. These macroscopic fractures in the SM-1a borehole are commonly filled with calcite, whereas these same types of fractures in the SM-4 borehole contain no calcite (Fig. 2). Zones of high permeability occur in core from borehole SM-1a near the bottom (19.2 m depth). This zone may be related to the primary bedding features of the tuff and is probably a significant facilitator of groundwater flow.

Elevations and hydrologic features of the two boreholes in this study are summarized in Table 1. Briefly, in borehole SM-4 the water level varies from below the bottom of the borehole during the base-flow season (fall, early winter) to the top of the borehole during the spring snow melt. In contrast, borehole SM-1a has a water level that is quite constant throughout the year, remaining nearly full and varying only a few meters in depth from the top of the casing (Hoch, 1997).

2.2. Petrography

Petrography was done on thin sections impregnated with epoxy containing rhodamine that fluoresces under an Hg vapor lamp (Soeder, 1990) allowing one to see pore system features optically and provide petrologic context for measured hydrologic parameters. Thin sections were prepared from the same core samples used for porosity and permeability measurements. Modal mineralogy, fracture occurrence, and areas of enhanced porosity were determined by counting a 300 point grid on an approximately 20 × 20 mm area on each slide using a mechanical stage and petrographic microscope. The presence of "intragranular porosity" was noted when the microscope crosshairs were located on areas in which the epoxy had penetrated. Selected thin sections were also viewed with a scanning electron microscope, equipped with an energy dispersive X-ray spectrometer to identify fracture minerals and to see zonation in calcite. Attempts were made at analyzing fluid inclusions in calcite with no success, due to the highly friable nature of the mineral. All thin sections studied were similar in primary mineral assemblage and texture.

2.3. Core porosity and permeability

Matrix total porosity and absolute permeability were measured for core samples selected at roughly 1.5 m intervals. Samples that were too friable or had large (> several mm) fractures were not analyzed, as they tend to break when sleeve pressure is applied during core test measurements. Matrix porosity is the volume of interconnected pore space that can be filled with He. Porosity can provide an indication of chemical weathering in the tuff matrix. Permeabilities were measured by forcing N_2 gas along the core axis, i.e., vertical permeability, with a confining sleeve pressure of 2.8×10^6 Pa. Absolute permeability is a measure of flow of a single phase through interconnected pore network. The permeability measurements were used to infer the feasibility of water movement in the rock samples.

2.4. Isotopic characteristics of calcite fracture fillings

Stable isotope values for C and O were obtained for calcite from 3 depths in the borehole SM-1a (one sample in triplicate); radiocarbon (^{14}C) ages were determined for calcite from 3 depths (one in duplicate) (Table 2).

3. Results

Phenocrysts (~50% of the rock) were dominantly plagioclase (~40% by volume), with lesser quartz, sanidine, augite and biotite. The matrix was dominantly quartz and sanidine with traces of interstitial glass. See Reddy et al. (1994) for details of whole rock petrography and Hoch et al. (1999) for further discussion of the interstitial glass.

Three types of fractures were defined in the core:

Type 1 fractures: within phenocrysts (mm scale length).
Type 2 fractures: between phenocrysts, but within core boundaries (cm scale length).
Type 3 fractures: larger fractures that cross-cut entire core samples (> cm scale length).

Measurement of the width of type 1 and 2 fractures was impossible with the optical microscope because the widths are much thinner than the 30 μm thick thin section and they do not penetrate the surface of the samples perfectly normal to the thin section surface. Based on size, Reddy et al. (1994) defined 3 populations of pore diameters in Snowshoe Mountain tuff using Hg intrusion porosimetry: 0.02–0.2, 0.2–10 and 10–100 μm. Type 1 and 2 fractures are probably the source of the 0.2–10 μm pores, whereas type 3 fractures are larger than pores measured by porosimetry. The smallest pores are related to intergranular features within the rock matrix that are too small to be resolved with the light microscope. This microporosity is likely related to the dissolution of interstitial glass or volume loss associated with recrystallization of glass to quartz polymorphs such as chalcedony.

Two major matrix features were defined petrographically: weathered matrix, i.e. exhibiting enhanced porosity, and unweathered matrix. Weathered matrix was most often observed in the proximity of types 2 and 3 open fractures in the SM-4 borehole. Weathering features include the presence of high-birefringence clay minerals (Fig. 3(A)), penetration of epoxy in the partially-dissolved matrix (Fig. 3(B)), and dissolution of pyroxene (Fig. 3(C)). Unweathered matrix showed no signs of mineral dissolution or alteration and no penetration of rhodamine dye (Fig. 3(D)). Differences between rock in the predominantly phreatic (SM-1a) and vadose (SM-4) zones observed on the microscopic scale were similar to differences observed on the hand-sample scale (Fig. 2). In general, borehole SM-4 was characterized by open fractures variably lined with clay minerals and exhibiting signs of penetrative

Table 1
Borehole depths and hydrologic characteristics

Site name	Elevation (m)	Comments
Borehole SM-4	3487	13.1 m depth, water level varies annually from top of borehole to completely empty. Short water residence time in upper borehole
Borehole SM-1a	3475	19.2 m depth, water level only slightly variable, near surface throughout the year

Table 2
Isotopic analyses of calcite fracture fillings from phreatic core

Sample ID	Borehole depth (meters from top of casing)	$\delta^{18}O_{VSMOW}$ (‰)	$\delta^{13}C_{PDB}$ (‰)	^{14}C age (ka)
WSU laboratory				
SMT-CC	16.1	25.3 ± 0.2	−4.3 ± 0.2	
SMT-CC2	16.1	15.8 ± 0.2	−4.2 ± 0.2	
SMT-CC3	6.7	17.7 ± 0.2	−8.1 ± 0.2	
SMT-CC4	12.0	16.3 ± 0.2	−4.7 ± 0.2	
SMT-CC6	16.1	16.1 ± 0.2	−3.5 ± 0.2	
Arizona AMS				
SM-1a-21	6.4		−8.7[a]	39.1 ± 1.2
SM-1a-47	14.3		−5.6[a]	30.1 ± 0.5
ETH-Zurich				
SM-1a-47′	14.3			46.4 ± 1.6
SM-1a-52′9″	16.1			39.1[a]

[a] Errors were not reported.

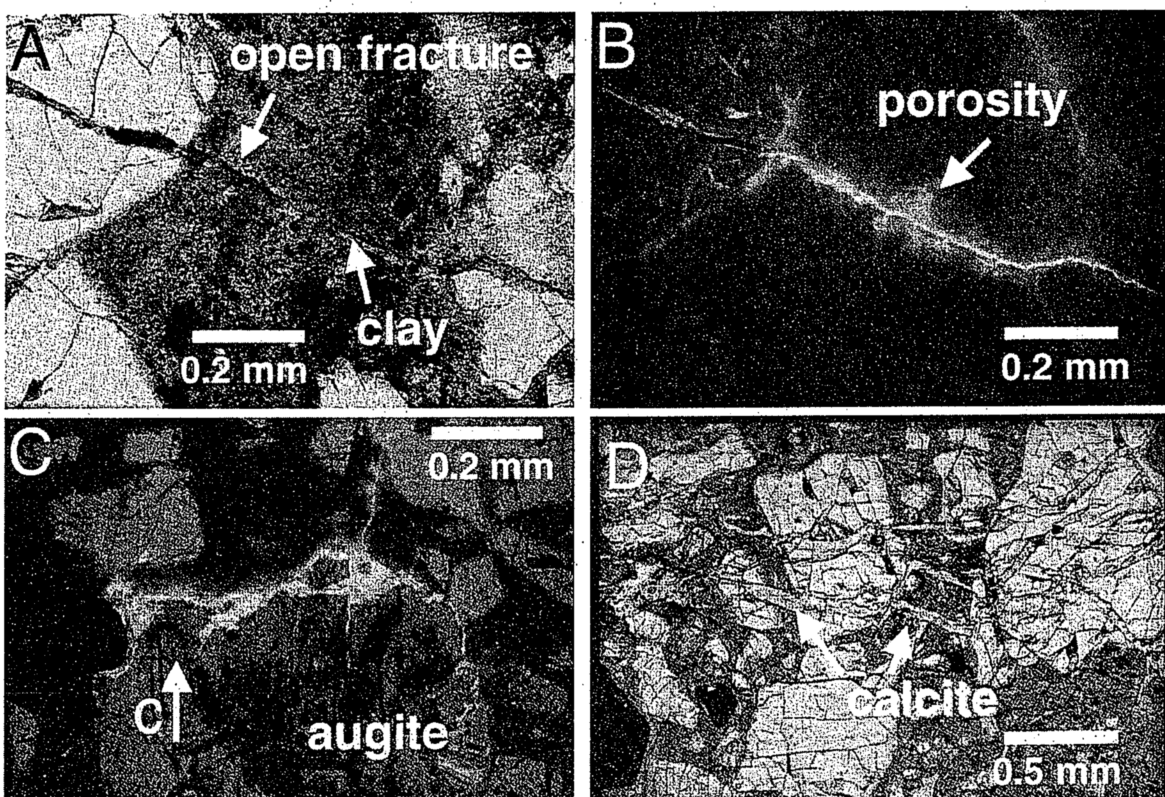

Fig. 3. Comparison between weathered (A, B, C) and unweathered (D) features in core from Snowshoe Mountain. (A) Borehole SM-4, 3.8 m depth; type 3 fracture containing some clay and cross-cutting both matrix and phenocrysts (plane-polarized, transmitted light); (B) same as A, only with Hg vapor lamp reflected light; areas of porosity fluoresce orange. Note penetration of porosity into the rock matrix; (C) vadose zone SM-4, 2.4 m depth; figure showing enhanced porosity along type 2 fractures, crystal boundaries and type 1 fractures in augite, note preferential dissolution at termination of augite C-axis; (D) borehole SM-1a, 10.4 m depth; calcite-filled type 1 and 2 microfractures cross-cutting phenocrysts and matrix, with occluded permeability or porosity (i.e. no fluorescence under Hg-vapor lamp) (plane-polarized, transmitted light).

weathering. Isolated occurrences of Ca-zeolite and gypsum were also observed in borehole SM-4 fractures, along with matrix weathering features. The zeolite is probably related to glass weathering, whereas gypsum may be related to infiltration of Ca^{2+} and SO_4^{2-}-rich precipitation during the dry summer or fall seasons. Both minerals were associated with zones of enhanced weathering and permeability, as shown by the rhodamine dye penetration.

Fracture surfaces in the lower two thirds of the SM-1a borehole were mostly unweathered, because calcite has effectively filled the fractures and minimized reaction of water with the matrix (Fig. 3(D)) down to about 18 m depth. Calcite in smaller, type 2 fractures ($<\sim$0.2 mm fracture gap) was unzoned, suggesting it formed in one episode, whereas complex zoning was observed in calcite in larger type 3 fractures. In one of the larger (0.5 mm gap) calcite-filled fractures studied in detail (SM-1a, 16.1 m depth), it was observed that the walls of the fracture were lined with several layers of calcite separated by zones rich in organic material, which may inhibit calcite dissolution, just as it inhibits crystal growth. Chemical zonation (variable Mg abundance) was also observed using X-ray imaging. In contrast, the deepest sample studied in the SM-1a borehole (19.2 m depth) contained type 3 fractures that were either unfilled by secondary minerals or contained clays with no calcite.

Between the endmembers of open, weathered fractures in borehole SM-4 and prevalent calcite-cemented, unweathered fractures in borehole SM-1a, petrographic textures were observed indicating that calcite is currently being dissolved in the upper 1/3 of borehole SM-1a; in Fig. 4, calcite "islands" in the middle of the

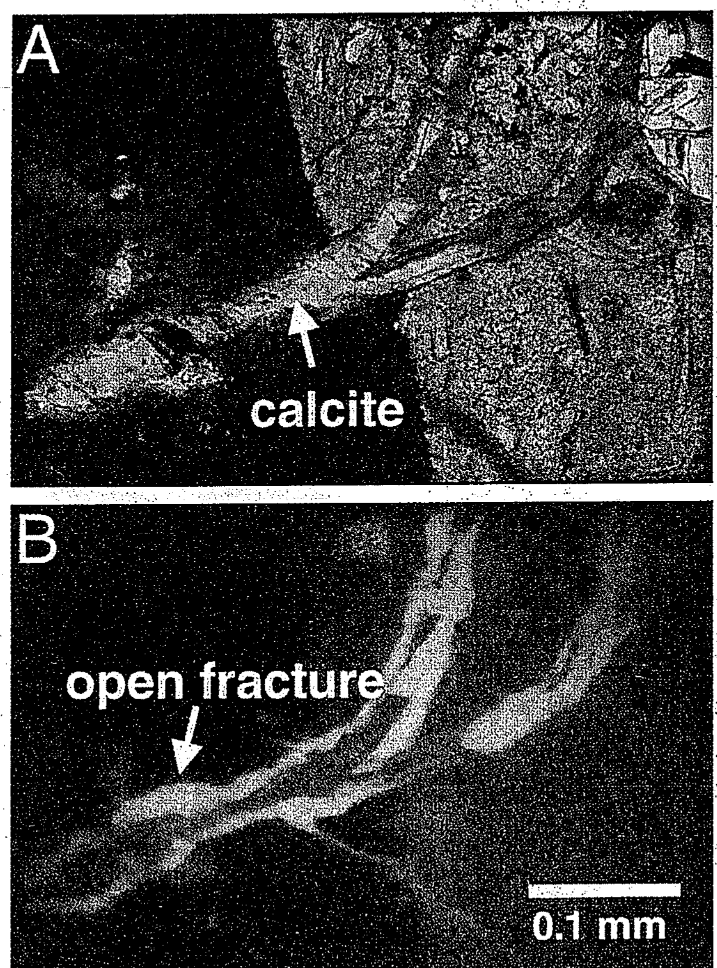

Fig. 4. Borehole SM-1a, 6.4 m depth, calcite partially dissolved out of a type 1 fracture. (A) Fracture cross-cuts both amphibole phenocryst (dark mineral on left) and matrix. Calcite in the center of the fracture is surrounded by open space represented by the violet-colored epoxy (plane-polarized, transmitted light); (B) same field as A, orange fluorescence under Hg-vapor lamp shows extent of minor enhanced porosity near the open fracture.

fracture are surrounded by epoxy from the impregnation/thin section process. Weathering of matrix material around partially-dissolved calcite is absent, in contrast to open fractures of borehole SM-4, indicating very late-stage calcite dissolution. This is consistent with the observation that all waters analyzed by Hoch (1997) on Snowshoe Mountain (precipitation, boreholes, springs and creeks) were undersaturated with respect to $CaCO_3$ phases.

Regolith core samples have experienced the most weathering, and have porosities that range from 3.5 to 7%. Porosity measurements in the borehole SM-4 range from 1 to 2.8%, with the exception of 3 of the 10 samples that had porosities of 4.0, 6.9 and 19.2%. The sample from 8.4 m depth, with a porosity of 19.2% was extensively weathered. Higher measured porosity could also be seen petrographically. Borehole SM-1a core with calcite-filled fractures (lower 2/3 of borehole) had porosities ranging from 1.0 to 3.3% (Fig. 5). Core near the top of the borehole that contained open fractures had porosities from 1.7 to 2.8%, indicating weathering of the matrix was not as extensive as in the SM-4 borehole (Fig. 5).

Permeability varied in both boreholes from less than 0.001 millidarcy (md) to 0.195 md with the exception of the sample with the highest porosity which had a permeability of 0.518 md. Permeability was strongly dependent on the presence of microscopic fractures, some of which were too volumetrically insignificant to be recorded by the point counting method. Hence, a correlation between petrographically-determined "% open fracture" and permeability is not seen in Fig. 5, but these open and unaltered microscopic fractures may cause 100-fold variations in measured permeability. Microfractures within phenocrysts are not a result of drilling. They are likely a result of natural processes such as high pressure at grain boundaries due to tectonism, cooling or unroofing by erosion. Macrofractures are also natural and their frequency is an indication of the severity of local tectonism. Some macrofractures had slickensides from local rock faulting.

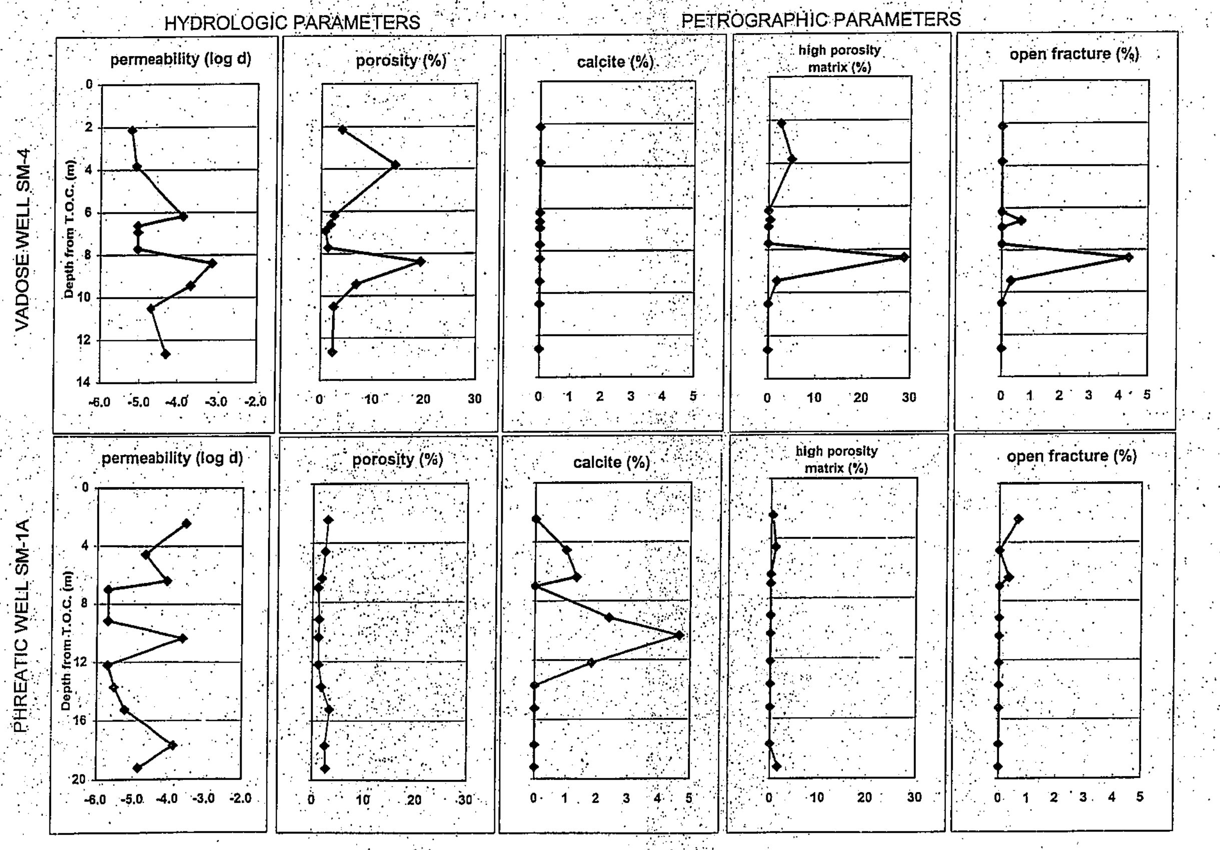

Fig. 5. Comparison of measured hydrologic parameters and petrographic features for the boreholes studied. Note that permeability, porosity and high porosity matrix (a surrogate for chemical weathering) are correlative for the vadose borehole, but not for the phreatic borehole because calcite fills large fractures and impedes alteration by groundwater. (T.O.C. is the top of the casing.)

Calcite from borehole SM-1a $\delta^{18}O$ normalized to VSMOW ranged from 15.8 to 25.3‰. The 25.3‰ value was from a sample analyzed in triplicate with the other two values of 15.8 and 16.1‰, indicating isotopic variability from multiple mineralization episodes within a single fracture location. $\delta^{13}C$ measurements ranged from −3.5 to −8.1‰ (normalized to PDB standard) with better internal consistency among the triplicate samples. Radiocarbon dating yielded ages ranging from 46 to 30 ka within calcite obtained from the same location in the core (Table 2). The ability to obtain ^{14}C ages shows that some fraction of the calcite in the veins formed more recently than hydrothermal activity or saline lake deposition in the early history of Snowshoe Mountain (over 20 Ma ago). Stable O isotope signatures of present ground waters fall within the rather narrow range of −13.5 to −15‰, normalized to VSMOW, whereas $\delta^{13}C$ values in present-day surface waters and ground waters have a much more broad range (−25 to −5‰$_{PDB}$; D. Halm, USGS, unpublished isotopic data).

4. Discussion

4.1. Calcite fracture fillings as barriers to fluid flow

Porosity in core samples from borehole SM-1a was consistently low, even though the abundance of calcite-filled fractures was variable (Fig. 5). Petrographically, calcite-filled fractures were not impregnated with epoxy, indicating that the calcite mineralization inhibited water movement and weathering. In locations with such tightly mineralized fractures, recharge to the deeper aquifer by meteoric water may be strongly impeded or completely inhibited by fracture-filling calcite.

4.2. Calcite-absent fractures and rock weathering

Enhanced porosity due to weathering associated with type 1 and 2 fractures was only observed in samples exhibiting enhanced permeability in the form of open, type 3 fractures, or type 3 fractures filled with expandable clay, gypsum or zeolite (Fig. 3(A)–(C)). The petrographic relationship between secondary minerals other than calcite and weathering features indicate that these minerals formed during or after weathering within the fracture surfaces and that clays and zeolite are poor inhibitors of water movement in this system. Bedrock with large type 3 fractures, as sampled by borehole SM-4, may serve as recharge zones to the deeper aquifer. Calcite dissolution features observed in the upper part of Borehole SM-1a illustrate that the impermeable calcite barriers are transient.

4.3. Origin and stability of calcite fracture fillings

Although the calcite filling type 3 fractures resulted from multiple mineralization events, radiocarbon ages suggest that calcite formation was not entirely related to the 25.1 Ma hydrothermal system associated with the Creede epithermal Zn–Pb–Ag deposit (Bethke et al., 1976) or with Lake Creede, a caldera moat that surrounded Snowshoe Mountain during the Oligocene epoch (Larsen and Crossey, 1996). Some, or most of the calcite mineralization occurred more recently, during the late Pleistocene, probably from percolating groundwater. If present-day groundwater isotopic values (−15 to −13.5‰ $\delta^{18}O$) are used to calculate temperatures of formation of the calcite fracture fillings (Friedman and O'Neil, 1977), formation temperatures are obtained which are slightly warmer (6–14°C) than present day (1.3°C), but not hydrothermal. Given that we are currently leaving an ice age and the mean annual temperature on Snowshoe Mountain is now near freezing, the temperature during the last 40 ka probably was not much colder. The fact that slightly warmer temperatures of formation were calculated may be due to the composite nature of the samples or the isotope fractionation model itself. Regardless of the reason for the discrepancy the calcite probably precipitated from lower-temperature meteoric waters, rather than hydrothermal waters associated with the Creede caldera.

Chemical mechanisms for calcite precipitation may have included processes that increased pH of solution (by CO_2 outgassing, for example), or that directly increased concentrations of Ca^{2+} by weathering of primary silicate materials, and/or evaporation associated with seasonal variations in temperature and precipitation. Outgassing of CO_2 from infiltrating waters may have increased pH and also caused the large variation in $\delta^{13}C$ values observed. Organic C present in some calcite cements in fractures supports an infiltrating soil water source for the calcite-forming waters.

Dilute, low-pH, infiltrating ground waters are more effective in weathering the most reactive rock phases than the more equilibrated, older ground waters. Interstitial glass and augite are orders of magnitude more susceptible to dissolution than quartz and feldspar, especially on freshly created fracture surfaces (Hoch et al., 1999). Weathering the glass releases cations (mainly K^+ and Ca^{2+}), produces alkalinity and increases pH. Augite is weathered, initially, by a rapid exchange of Ca^{2+} for protons, which also produces alkalinity, raises pH and most significantly, increases Ca^{2+} concentrations. Mixing of dilute infiltrating waters that have gained Ca^{2+} by weathering fresh surfaces of augite with deeper, more alkaline groundwater may have led to high calcite supersaturation conditions and subsequent precipitation.

4.4. Present-day calcite dissolution

Petrographic observations and water chemistry indicate that calcite fracture fillings, at least in the upper few feet, of the SM-1a borehole are presently dissolving. Such fracture fillings may or may not have existed in the borehole SM-4. Near surface calcite dissolution in borehole SM-1a is related to the proximity and accessibility of dilute infiltrating waters and active mechanical denudation of the land surface. The calcite in the fracture fillings probably formed earlier from waters subjected to subsurface processes discussed above, but present-day geologic and geochemical conditions render the mineral unstable.

4.5. Implications of calcite cement to long-term hydrodynamics and geochemistry

The groundwater system near the summit of Snowshoe Mountain is dynamic and affected by the presence or absence of calcite mineralization in rock fractures. Chemical conditions that once produced calcite fracture fillings are not detected in borehole and spring waters. Carbon ages obtained from calcite deposited in fractures in borehole SM-1a do not support recent calcite precipitation. Though ages are probably derived from composites of layers in the calcite cemented type 3 fractures, they illustrate the fact that precipitation and dissolution processes have been operating intermittently for tens of thousands of years. At present, it can be seen petrographically that calcite cements are dissolving in the borehole SM-1a and are completely absent in SM-4. Once calcite-cemented fractures reopen, weathering within the rock ensues, enhancing the porosity and reactive character of the rock. In terms of geologic time, these changes may be very rapid and the present hydrologic state of the system should be considered in one of many possible stages of change.

5. Conclusions

The boreholes considered in this report sample a lithologically uniform bedrock subjected to a variety of post emplacement hydrologic and geochemical processes. In borehole SM-4 where calcite fracture fillings are absent, infiltrating water aggressively dissolves reactive phases from the rock, further enhancing porosity by enlarging fractures or removing elements from phenocrysts, increasing permeability and reactive surface area. In borehole SM-1a, calcite fracture fillings block water transport and associated weathering reactions in most of the sampled rock. Observations in the near-surface of borehole SM-1a suggest, however, that these calcite fracture fillings are currently being dissolved by waters infiltrating from the land surface. The processes of $CaCO_3$ precipitation, dissolution, and resulting modifications to the hydrologic character of the bedrock have all occurred approximately within the past 40 ka. These observations on the scale of thin sections, core measurements, and aquifer chemistry provide insight for processes in the hydrologic system of a welded tuff in an alpine environment.

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