STABLE ISOTOPES OF AUTHIGENIC MINERALS IN
VARIABLY-SATURATED FRACTURED TUFF

by

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Nov. 25, 1956
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With admiration and love,
this thesis is dedicated to
my Mother

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TABLE OF CONTENTS

	Page
LIST OF ILLUSTRATIONS.	viii
LIST OF TABLES	x
ABSTRACT	xi
1. INTRODUCTION	1
1.1 Description of Problem	1
1.2 Stable Isotope Determinations.	2
1.3 Previous Work.	5
1.3.1 Effect of Rock-Water Interaction on Isotopic Composition	6
1.3.2 Effect of Temperature on Isotopic Composition	10
1.4 Objectives and Scope of Work	14
2. GENERAL DESCRIPTION OF THE SUPERIOR STUDY AREA	16
2.1 Regional Setting	17
2.2 Climate.	19
2.3 Geology of the Apache Leap Tuff.	20
2.3.1 Description.	20
2.3.2 Structure.	23
2.4 Hydrogeology of the Superior Study Area.	27
2.5 Site Locations	32
3. METHODS AND RESULTS.	35
3.1 Fracture-filling Minerals.	35
3.1.1 Mineral Isolation and Description.	36
3.1.2 Procedure and Results of Isotopic Analysis . .	40
3.2 Rock Matrix Minerals	44
3.2.1 Mineral Isolation and Treatment.	44
3.2.2 Procedure and Results of Isotopic Analysis . .	47
4. DISCUSSION OF RESULTS.	48
4.1 Fracture-filling Minerals.	48
4.1.1 Fracture-filling Quartz.	48
4.1.2 Fracture-filling Calcite	52

TABLE OF CONTENTS--Continued.

	Page
4.2 Rock Matrix Minerals	56
4.2.1 Opal Isolation and the ABFS Treatment.	57
4.2.2 Effect of Heterogeneous Opal Formation on the Oxygen Isotope Composition of Opal. . .	59
4.3 Conditions of Authigenic Mineral Formation	62
4.3.1 Evaporation and Rock-Water Interaction	62
4.3.2 Hydrogeochemical Interpretation of Stable Isotope Ratios.	76
5. SUMMARY AND CONCLUSIONS.	83
APPENDIX A: PROCEDURE AND CORE LOGS OF DRILLING OPERATIONS AT THE APACHE LEAP SITE	86
APPENDIX B: FRACTURE ORIENTATION OF DRILL CORE FROM THE APACHE LEAP SITE	105
APPENDIX C: METHODS OF X-RAY DIFFRACTION AND X-RAY DIFFRACTION PATTERNS.	113
APPENDIX D: PROCEDURE FOR ISOLATION OF OPAL IN ROCK MATRIX SAMPLES	120
REFERENCES	122

LIST OF ILLUSTRATIONS

Figure		Page
1.1	Schematic representation of D/H and ^{18}O correlation of clay minerals and a meteoric water source	8
2.1	Generalized geologic map of the the Superior quadrangle and field site locations	18
2.2	Average monthly precipitation of the study area near Superior, Arizona	21
2.3	Physical characteristics of the Apache Leap tuff	22
2.4	Distribution and inclination of joints intercepted by boreholes at the Apache Leap site	28
2.5	Borehole diagram and 2-dimensional representation of fracture network, Apache Leap site.	33
3.1	XRD patterns of rock matrix opal-c, sample ALS-X2: 18.72	46
4.1	Oxygen isotope composition of fracture-filling quartz versus depth, Apache Leap site	50
4.2	Seasonal temperature profile measured in borehole X3, Apache Leap site,.	51
4.3	Ranges of measured $\delta^{18}\text{O}$ values for fracture-filling quartz and water intersected by lines predicted by equation 4.1 using temperatures of 15 and 25°C.	53
4.4	Ranges of measured $\delta^{18}\text{O}$ values for fracture-filling calcite and water intersected by lines predicted by equation 4.1 using temperatures of 15 and 25°C.	55
4.5	Oxygen isotope composition of rock matrix opal versus depth, Apache Leap site	58
4.6	Oxygen isotope composition of fracture-filling quartz versus fracture inclination, Apache Leap site.	65
4.7	Oxygen isotope composition of low inclination, fracture-filling quartz versus depth, Apache Leap site	66

LIST OF ILLUSTRATIONS--Continued.

Figure		Page
4.8	The $\delta^{18}\text{O}$ predicted for percolating water ($\delta^{18}\text{O}_d$) after alteration of volcanic glass to opal under isotopic equilibrium conditions versus the mole fraction of oxygen in the solid phase.	70
4.9	The $\delta^{18}\text{O}$ of percolating water after alteration versus partial saturation of water for the reaction volcanic glass to opal	73
4.10	Activity of H_4SiO_4 in groundwater samples from the Superior study area.	78
4.11	Isotopic composition of groundwater in the Superior study area compared to the global meteoric water line.	81
B.1	Schematic diagram of fracture plane ellipse.	107
B.2	Geometrical relationships between angled borehole and a normal to a fracture plane	108
B.3	Key triangles of Figure B.1 used in mathematical solution of fracture orientation	109
C.1	XRD patterns of fracture-filling quartz samples, white unit, Apache Leap tuff	115
C.2	XRD pattern of fracture-filling opaline silica sample, white unit, Apache Leap tuff	116
C.3	XRD patterns of fracture-filling calcite associated with other minerals, white unit, Apache Leap tuff	117
C.4	XRD patterns of fracture-filling palygorskite-sepiolite samples, white to brown units, Apache Leap tuff.	118
C.5	XRD patterns of rock matrix opal samples, white unit, Apache Leap tuff	119

LIST OF TABLES

Table	Page
2.1 Average modes and chemical analyses of the Apache Leap tuff in the Superior region.	24
2.2 Parameters and concentration of major ions in water samples collected from wells and springs in the Superior study area.	30
3.1 Results of isotopic analysis of fracture-filling minerals, rock matrix minerals, and associated water in the Apache Leap tuff.	41
A.1 Construction and design details of boreholes at the Apache Leap Site, near Superior, Arizona.	88
A.2 Fracture description and orientation log of Borehole X1, Apache Leap Site, white unit, Apache Leap tuff	90
A.3 Fracture description and orientation log of Borehole X2, Apache Leap Site, white unit, Apache Leap tuff	93
A.4 Fracture description and orientation log of Borehole X3, Apache Leap Site, white unit, Apache Leap tuff	99

ABSTRACT

Identifying stable isotope variation and mineralogical changes in fractured rock may help establish the history of climatic and geomorphological processes that might affect the isolation properties of a waste repository. This study examines the use of the stable isotope ratios of oxygen ($^{18}\text{O}/^{16}\text{O}$) and carbon ($^{13}\text{C}/^{12}\text{C}$) in authigenic minerals as hydrogeochemical tools tracing low-temperature rock-water interaction in variably-saturated fractured tuff. Isotopic compositions of fracture-filling and rock matrix minerals in the Apache Leap tuff, near Superior, Arizona were concordant with geothermal temperatures and in equilibrium with water isotopically similar to present-day meteoric water and groundwater. Oxygen and carbon isotope ratios of fracture-fillings, in unsaturated fractured tuff, displayed an isotopic gradient probably resulting from near-surface isotopic enrichment due to evaporation rather than the effects of rock-water interaction. Oxygen isotope ratios of rock matrix opal samples exhibited an isotopic gradient due to leaching and reprecipitation of silica at depth. Results can be used to further define primary flowpaths and the movement of water in variably-saturated fractured rock.

CHAPTER ONE

INTRODUCTION

The stable isotope ratios of oxygen ($^{18}\text{O}/^{16}\text{O}$), hydrogen (D/H), and carbon ($^{13}\text{C}/^{12}\text{C}$) have been suggested, and used, as hydrogeochemical indicators tracing low-temperature water-rock interactions (Taylor, 1968; Savin, 1980; Longstaffe, 1983). In low-temperature environments, the stable isotope composition of water imparts a diagnostic signature on exchanging solid phases. In turn, this fingerprinting provides information on both the movement and source of water (e.g., meteoric water, connate water) and the physical and chemical processes by which the water may have been modified (e.g., evaporation, dissolution) in a water-rock system. The resulting stable isotope composition of minerals, when formed or altered in situ from the interaction with a particular source of water, provides information on the movement of water through soil and rock. In addition, the oxygen isotope ratios of authigenic minerals (minerals formed in situ) can be used to interpret the temperature of formation, and perhaps more importantly, the timing of alteration.

1.1 Description of the Problem

Identifying mineralogic changes and analyzing isotopic variation may help establish the history of climatic and geomorphological processes that might affect the isolation properties of a waste repository setting in the unsaturated zone. For example, if the

authigenic minerals of a fractured rock at a proposed waste repository depth reflect the strong presence of present-day meteoric water, the risk of off-site contamination may be higher. Similarly, if the authigenic minerals reflect the paleohydrology of a wetter climate, the proposed unsaturated zone may be inadequate as the primary barrier between percolating water and a waste repository, and/or a rising water table and a waste repository if future climates become wetter.

The purpose of this study was to determine if the flux and source of water in a fractured, volcanic ash flow tuff can be examined by identifying authigenic minerals and measuring their component oxygen, and in some samples carbon, stable isotope composition. Oriented core samples from three boreholes (X1, X2, and X3) in a slightly welded, unsaturated zone of the Apache Leap tuff near Superior, Arizona, along with samples from an exploration borehole and a mining shaft that penetrated deeper, more welded, saturated zones of the tuff, were used to assess the hydrologic significance of the variation of stable isotopes in the variably-saturated fractured tuff. If a relationship exists between the stable isotopes of authigenic minerals in tuff and fluxes of water, these variations should prove useful in distinguishing primary flowpaths and interpreting the rate of water movement over long time periods in fractured rock having thick variably-saturated zones of low permeability.

1.2 Stable Isotope Determinations

Isotopes of a particular element have the same number of protons and thus behave similarly in chemical reactions. However, differences

in physical properties of an element arise from the minute differences in mass. Variations in mass cause isotopic fractionation, or isotope ratios of an element in a particular phase or state to be different if a phase change occurs. For example, the ^{18}O to ^{16}O isotope ratio ($^{18}\text{O}/^{16}\text{O}$) of snow will be different from the cloud vapor from which it condensed. These mass difference effects are most pronounced for the lighter elements.

Stable isotope ratios measured on mass spectrometers are reported using differences given in the δ notation in parts per thousand (permil or ‰). Differences between a sample and a standard can be measured far more precisely than absolute values. For example, the δ -value is defined for oxygen as:

$$\delta^{18}\text{O} = \frac{((^{18}\text{O}/^{16}\text{O})_{\text{sample}} - (^{18}\text{O}/^{16}\text{O})_{\text{standard}})}{(^{18}\text{O}/^{16}\text{O})_{\text{standard}}} \times 1000 \quad (1.1)$$

The internationally accepted reference standard for oxygen and hydrogen isotopes is Standard Mean Ocean Water (SMOW) (Craig 1961). For carbon isotopes, the internationally accepted standard is Pee Dee belemnite (PDB). A sample with a $\delta^{18}\text{O}$ value of +10 is enriched in ^{18}O (or is greater in $^{18}\text{O}/^{16}\text{O}$) by 10 per mil, or 1 percent, relative to SMOW. A negative δ -value signifies the sample is depleted in the heavy isotope relative to the standard.

The isotope ratios of D/H (deuterium/hydrogen) and $^{18}\text{O}/^{16}\text{O}$ have wide but systematic variation in fresh water ($\delta^{18}\text{O} = -50$ to 0; $\delta \text{D} = -400$ to 0). The isotopic behavior of most fresh water can be described

by the meteoric water line (Craig, 1961), as:

$$\delta D = 8(\delta^{18}O) + 10 \quad (1.2)$$

This linearity results from evaporation and condensation cycles. As water evaporates, for example, there is preferential removal of the light isotope to the vapor phase causing an enrichment of the heavy isotope in the liquid phase.

The determination of isotopic ratios in hydrogeochemical systems is important if chemical equilibrium exists or if the kinetics of the reaction process are fully understood. Applying the principle of the conservation of mass to isotope fractionation, the isotopic exchange reaction can be described by a temperature-dependent equilibrium constant, normally called the isotopic fractionation factor, α . The isotopic fractionation factor for oxygen between two species, A and B, is given as:

$$\alpha_{A/B} = (^{18}O/^{16}O)_A / (^{18}O/^{16}O)_B \quad (1.3)$$

In terms of quantities measured by mass spectrometry (δ -values) this expression for oxygen isotopes becomes:

$$\alpha_{A/B} = (1000 + \delta^{18}O_A) / (1000 + \delta^{18}O_B) \quad (1.4)$$

As the temperature of a system involving phases A and B decreases, the fractionation factor of the two phases increases. Because the fractionation factor between two phases such as quartz and water is essentially based on temperature, the low temperature formation of quartz will have $\delta^{18}O$ values significantly heavier (enriched in ^{18}O)

than coexisting water, assuming complete equilibrium. To illustrate that silica-water fractionations are large and positive at low temperatures the $\delta^{18}\text{O}$ values of quartz at different temperatures in equilibrium with water of a $\delta^{18}\text{O}$ of 0 per mil are as follows (Friedman and O'Neil, 1977):

	25°C	100°C	250°C	400°C
Quartz	+35 ⁰ /oo	+21 ⁰ /oo	+9 ⁰ /oo	+4 ⁰ /oo

In the absence of chemical alteration, isotopic exchange will only be significant at increased temperatures. At or near the surface of the earth, temperatures are normally low enough so that significant isotopic exchange does not occur between already formed minerals and water. However, isotopic exchange will take place if the mineral undergoes chemical alteration such as dissolution or reprecipitation.

1.3 Previous Work

When water moves through a fractured rock, the body of rock can be considered a dynamic system tending toward isotopic equilibrium with the water. This process, driven by the quantity and chemistry of present or past waters, can cause growth and alteration of mineral assemblages in situ. The isotopic composition of these authigenic minerals are a function of the isotopic composition of the water-rock system and the temperature of the environment. Where isotopic equilibrium between a mineral and water has not been achieved, the

isotopic composition of the mineral will also depend on the nature and extent of isotopic exchange with water.

This section reviews representative research regarding the effects that rock-water interaction and temperature have on isotopic composition. The concepts and references presented in these papers are used in later chapters to interpret the isotopic composition of minerals and suites of minerals found in the rock matrix and fracture zones of the tuff. In turn, information is obtained on the conditions of formation, subsequent alteration, and the environment where the authigenic minerals existed.

1.3.1 Effect of Rock-Water Interaction on Isotopic Composition

Water is one of the most important reservoirs that control the isotopic composition of fractured rock. In extensive, open fracture systems, the ratio of water to fracture surface may be quite high (water in this context meaning the total water that has flowed through a fracture, not the amount present at any instant). When water-rock ratios are high, the isotopic composition of the water imparts a characteristic signature upon precipitating or exchanging solid phases while the change in isotopic composition of the water is normally negligible.

The weathering process generally involves large quantities of meteoric water and high water-rock ratios. Under such conditions the isotopic conditions of the parent rock was shown by Lawrence and Taylor (1972) to have no effect on the alteration weathering products. In a weathering zone, the D/H and $^{18}\text{O}/^{16}\text{O}$ of clay minerals and hydroxides

forming from the alteration of igneous parent rock correlated directly with the systematic variations of D/H and $^{18}\text{O}/^{16}\text{O}$ of corresponding present-day meteoric water (Lawrence and Taylor, 1971).

Figure 1.1 shows the relationship where clay minerals of similar chemical composition, which have equilibrated with different meteoric waters at the same temperature, have characteristic D/H and $^{18}\text{O}/^{16}\text{O}$ ratios that lie along lines parallel to the meteoric water line. At temperature T_1 the isotopic composition of a particular clay mineral lies along a line parallel to isotopic compositions of meteoric water. As temperatures increase, the clay mineral line approaches the meteoric water line ($T_1 < T_2 < T_3$, see section 1.3.2). The dashed lines connect hypothetical isotopic ratios of meteoric water for a specific climate and latitude in equilibrium with clay at different temperatures of formation. For a given area, the similarity between the isotopic composition of authigenic minerals such as clays in the soil zone and the meteoric water indicates that the isotopic composition of the liquid phase (e.g., ambient water), and not the isotopic composition of the solid phase (e.g., parent rock), is the controlling factor in the final isotopic composition of authigenic minerals (Savin, 1980). The close relationship also suggests that authigenic minerals forming from the alteration of the parent rock approach isotopic equilibrium with the environment in which they formed.

As the water-rock ratio decreases, the isotopic composition of the water may be significantly affected. This situation may exist in rocks of low permeability and sedimentary formations with restricted

Figure 1.1. Schematic representation of D/H and $^{18}\text{O}/^{16}\text{O}$ correlation of authigenic clay minerals formed at different temperatures ($T_1 < T_2 < T_3$) and a meteoric water source (after Savin, 1980).

circulation of water (Savin, 1980). Lawrence et al. (1979) have suggested that the downward depletion of ^{18}O in the pore water of deep-sea sediment cores is the result of upward diffusion of water depleted in ^{18}O due to the low temperature alteration of deep layered basalts ($\delta^{18}\text{O}$, +6 to +10) to smectite ($\delta^{18}\text{O}$, +20 to +25). In low permeability rock such as shale, an additional factor affecting the isotopic ratios in the subsurface may be isotopic fractionation due to membrane-filtration of water (Graf et al., 1966; Hitchon and Friedman, 1969).

In volcanic rocks, both the glassy and crystalline portions of the rock exhibit characteristic chemical and isotopic changes when exposed to water (Friedman and Smith, 1958; Friedman et al., 1966). Taylor (1968) found that the $\delta^{18}\text{O}$ values of the glassy component of siliceous flows and tuffs increase as a result of isotopic exchange with meteoric water during hydration. Because the $\delta^{18}\text{O}$ values of the glass become heavier than the water, the glass must be undergoing isotopic exchange with the water, having similar isotopic fractionation to that of silica, in addition to acquiring water.

Similarly, Garlick and Dymond (1970) showed the $\delta^{18}\text{O}$ values of glass shards in deep-sea sediments increase with age due to increased hydration and resulting isotopic exchange between the volcanic glass and ocean water. Pineau et al. (1976) related $^{18}\text{O}/^{16}\text{O}$ ratios of fresh and weathered basalts also as a function of water content. Accordingly, as the water content of the basalt increases so does the alteration of the basalt to low temperature alteration products (e.g., clays and hydroxides). Finding correlation between $\delta^{18}\text{O}$ and water content, the

authors concluded the deep-sea basalts were a mixture of fresh basalt, smectite, and hydrated glass.

Longstaffe (1984) researched authigenic mineral formation and the stable isotope geochemistry of the Milk River aquifer in the Virgelle sandstone of southeastern Alberta. Earlier Schwartz and Muehlenbachs (1979) had theorized young, isotopically lighter groundwater has been displacing older, isotopically heavier formation water in this area. Longstaffe supported this theory by showing the authigenic carbonate and clay minerals in pore-linings and pore-fillings of the Virgelle sandstone have similar isotopic variations of $\delta^{18}\text{O}$ when compared to the isotopic composition of the groundwater. Furthermore, his analysis of the $^{13}\text{C}/^{12}\text{C}$ variation of the calcite pore-fillings revealed consistently low $\delta^{13}\text{C}$ values in the southern recharge area versus more positive $\delta^{13}\text{C}$ values in the northern downgradient area. The low $\delta^{13}\text{C}$ nature of the calcite in the recharge area suggests involvement of organically derived CO_2 . The probable source of such CO_2 is from the infiltration of precipitation through the overlying soil.

1.3.2 Effect of Temperature on Isotopic Composition

The isotopic composition of authigenic minerals displays systematic variations that not only provide insight into the nature of coexisting waters, but also reflect the temperature of final oxygen equilibration. This temperature dependency of isotope fractionation is of particular importance because systematic differences in $\delta^{18}\text{O}$ values of authigenic minerals may be interpreted in terms of an equilibrium

temperature. However, this temperature relationship can only be applied provided that all of the authigenic minerals of a particular zone equilibrated with oxygen from the same water source and that the minerals have not undergone any subsequent recrystallization.

Minerals formed during authigenesis are normally enriched in ^{18}O because they crystallize at low temperatures in isotopic equilibrium with water. The oxygen isotope fractionation for the systems silica-water, carbonate-water, and clay-water are large at low temperatures (Friedman and O'Neill, 1977). Conversely, igneous and metamorphic related minerals have relatively depleted ^{18}O compositions because of higher temperatures of formation. Therefore, authigenic minerals derived from equilibrium precipitation with low ^{18}O , continental meteoric water should have $\delta^{18}\text{O}$ values significantly different than chemically equivalent minerals of detrital origin (e.g., minerals derived and transported from another source area), minerals formed earlier in the diagenesis of the unit from more ^{18}O -rich formation waters, or minerals formed at higher temperatures.

Negligible oxygen isotope exchange occurs between water and minerals at low temperatures, even over tens of millions of years (Savin and Epstein, 1970; Lawrence and Taylor, 1971; Yeh and Savin, 1976). However, at higher temperatures isotopic exchange does become important. Of the common minerals, quartz is most resistant to isotopic exchange subsequent to crystallization and calcite probably the least resistant (Savin, 1980; Clayton, 1959).

The system carbonate-water was observed by Keith and Weber (1964) to exchange oxygen isotopes at low temperatures. They observed

the tendency of limestones to have depleted ^{18}O with increasing geologic age. This is attributed to prolonged exposure to ^{18}O poor meteoric water. During burial metamorphism no oxygen isotope exchange was observed between any size fraction of quartz and water for temperatures up to 170°C (Longstaffe, 1983; Clayton, 1978). However, oxygen isotope exchange can occur during burial metamorphism for clay minerals. Yeh and Savin (1977) observed with increasing depth (e.g., increasing temperature), isotopic exchange increased between clay minerals and water, especially in the finer sized fractions. In the laboratory, O'Neil and Kharaka (1976) observed significant isotopic exchange in clays at temperatures near 300°C for oxygen and 100°C for hydrogen.

Opal varieties (e.g., hydrous silica with cristobalite-like X-ray diffraction patterns), commonly occurring in altered volcanic ash, were studied by Henderson et al. (1971) using X-ray diffractometry (XRD) and oxygen isotope ratios. Low temperature, disordered, authigenic opal (e.g., broad peak at $22.13^{\circ} 2\theta$) isolated from bentonite deposits and soils developed from volcanic ash, had values of +26.0 to 30.0 per mil compared to values of +9.0 to 11.0 per mil for hydrothermal, ordered opal (e.g., sharp XRD peak at $22.13^{\circ} 2\theta$) isolated from vesicles in obsidian. Assuming opal to behave similarly as quartz with regard to oxygen exchange, the enriched ^{18}O authigenic opal indicated a non-igneous origin and could have resulted from formation with meteoric water of an isotopic composition of -10 per mil at 25°C . The lighter oxygen isotope compositions of the opal indicated hydrothermal formation temperatures of 200 to 400°C in equilibrium with latent volcanic waters of typical $\delta^{18}\text{O}$ values of +6 to +10 per mil (Taylor, 1974).

Fallick et al. (1985) examined the hydrogen and oxygen isotope ratios in microcrystalline quartz of agates found in volcanic rocks of Scotland. Agates found in Devonian lavas (410 million years before the present, Myr BP) have isotopic ratios ($^{18}\text{O}/^{16}\text{O}$ of silica and D/H of bound water) distinct from those agates found in Tertiary lavas (62 Myr BP), but correlate well on a linear plot of δD versus $\delta^{18}\text{O}$; the line displaced, but approximately parallel to the line defined by present-day meteoric water. This was interpreted as evidence that interaction with recent waters has been minimal and that the isotopic signatures of the agates were established at the time or soon after formation. Using the measured oxygen and hydrogen isotope ratios, the authors infer the agates of both ages were formed at low temperatures (50°C) from water having a strong meteoric component.

In a similar manner, Shieh and Sutter (1979) utilized oxygen isotope ratios to determine formation conditions of authigenic kaolinite and calcite in vertical fracture-fillings in the Illinois Coal Basin. Using an assumed uniform isotope composition of groundwater, they estimated a temperature range of formation from 13°C to 30°C . No information was given, however, on the depth from which samples were taken to find out how well the calculated temperatures of formation correlated with the present-day geothermal gradient.

The use of oxygen isotope geothermometry has been recently applied by Hearn et al. (1985) on fracture-filling mineral assemblages in the Columbia River basalts of Washington. The oxygen isotope ratios reportedly reflect low temperature authigenesis and yield a thermal gradient concordant with the existing geothermal gradient obtained from

actual borehole temperature measurements (40°C/km). These results, based on oxygen isotopes, suggest the authigenic minerals have isotopically equilibrated with present-day waters. This interpretation allows for an estimation on the timing of alteration, and perhaps more importantly, the recognition that these waters have driven authigenic mineralization in fracture zones to an extensive depth (1400 m) within the basalts.

1.4 Objectives and Scope of Work

The primary objectives of this study were to:

- (1) isotopically analyze authigenic minerals from fractures and in the rock matrix of fractured tuff and determine if the minerals are in isotopic equilibrium with present-day percolating water;
- (2) distinguish primary flowpaths of percolating water by investigating the relationship between fracture orientation and the isotopic ratios of the fracture-filling authigenic minerals; and
- (3) assess the influence that the rock environment has on precipitating authigenic minerals and attempt to determine the timing of alteration related to fluxes of water.

Hydrogeochemical analysis emphasizing these isotopic parameters may lead to information concerning the flux of water in the Apache Leap tuff and determine the applicability of these measurements used as indicators of rock-water interaction in variably-saturated fractured rock. Results may be useful in distinguishing primary flowpaths and

defining the movement of water. In addition, oxygen isotopes of authigenic minerals could indicate conditions of formation and determine the relative influence of deep percolation from a present or a past climate.

CHAPTER TWO

GENERAL DESCRIPTION OF THE SUPERIOR STUDY AREA

Ash flow tuff is a lithified deposit of volcanic ash resulting from the eruption and flow of gaseous and pyroclastic material (nuée ardente). Using the classification of Ross and Smith (1961) the more general term ash flow tuff is used in this paper rather than the terms ignimbrite or welded tuff. In a review of the hydrogeology of ash flow tuff Winograd (1971) wrote:

Ash flow tuffs, silicic pyroclastic rocks commonly mapped as silicic lava flows (rhyolite, dacite, or quartz latite) on many pre- 1960 maps, cover tens of thousands of square miles in the southwestern states and aggregate between 35,000 and 60,000 mi² in the Great Basin alone. In contrast to silicic lava flows but similar to basalts, ash flow tuffs are sheetlike bodies; individual flows have been traced for as much as 100 miles. Welding, the cohesion of molten glassy shards and pumice fragments during emplacement of these rocks, results in significant vertical variations in the physical properties within individual flows. Interstitial porosity and permeability vary from 70 percent and 2 gpd/ft² (gallons per day per foot squared), respectively, in nonwelded portions or zones of ash flows to less than 5 percent porosity and zero permeability in welded zones. Primary and secondary joints spaced several feet apart in nonwelded zones are as close as a fraction of an inch in densely welded zones.

Proposals to use thick unsaturated zones of ash flow tuff such as Yucca Mountain in the Nevada Test Site of the southern Great Basin for high level, radioactive waste disposal has led to studies concerning the isolation properties of tuff (Tien et al., 1985). As a generic field site used to investigate variably-saturated fractured tuff, the Apache Leap tuff in the mining district near Superior, Arizona, was

considered a suitable study location due to the well represented units of welding, previous work done on the geology of the area, and proximity of the Magma Mining Company which made space and equipment available.

2.1 Regional Setting

The Superior study area, near the extreme western edge of the mountains of south-central Arizona, lies between the Superstition mountains to the northwest and the Pinal mountains to the east. The region is characterized by steep hills, narrow canyons, and pinnacles of weathered tuff. The town of Superior, on the eastern edge of an alluvial deposit, is at an elevation of 910 meters (2985 feet). Vegetation in the region consists mainly of mesquite, chaparral, creosote, and oak woodland.

Apache Leap is approximately 1.5 kilometers east of Superior. It is a steep west-facing escarpment of ash flow tuff rising to an elevation of 1433 meters (4700 feet). The ash flow tuff of the region, the Apache Leap tuff, is named after this steep cliff. The dacitic ash flow tuff at one time covered an areal extent of approximately 1000 km² in the Superior region. Presently, this area has an irregular and interrupted distribution of tuff, having been reduced by extensive faulting and erosion to approximately 250 km². Field sites are east of the town of Superior in the Apache Leap tuff; in this area the thick middle Miocene (20 Myr BP) ash flow tuff reaches a maximum thickness exceeding 600 meters (Figure 2.1).

The Salt and Gila Rivers drain flat desert valley west of Superior. Both rivers flow westward out of the mountains to the east.

Figure 2.1. Generalized geologic map of the Superior quadrangle and approximate field site locations (After Peterson, 1968).

The region around Superior is drained by Queen Creek and its tributaries. All streamflow is ephemeral and Queen Creek is a tributary of the Gila River.

2.2 Climate

South-central Arizona has a semi-arid climate. In the Superior region the summer climate is warm, and temperatures average in the eighties (degrees Fahrenheit). High temperatures are usually accompanied by low relative humidities. In winter months the temperature rarely falls below freezing at night and rises into the sixties during the day.

Precipitation in the region occurs predominantly in mid-summer and mid-winter. Greatest amounts of rain fall in the summer, from early July to September, when the state receives moist tropical air from the Gulf of Mexico. When combined with high surface temperatures and orographic lifting this moisture produces short, intense storms. Moderately heavy precipitation may occur in the winter. Rain in the winter is more widespread and less intensive than summer rainfall, and may continue intermittently for several days. Only a small part of winter precipitation falls as snow (Sellers and Hill, 1974).

Average annual precipitation for the town of Superior (elevation 910 m) from 1914 to 1974 was 453.1 mm (17.8 inches). Since 1974 precipitation has also been recorded at the Magma Copper Company's number 9 shaft, three kilometers east of Superior at an elevation of 1270 meters (4165 feet). Average annual precipitation at the number 9 shaft from 1974 to 1984 was 639.6 mm (25.2 inches). For this same

period, the average annual precipitation for the town of Superior was 538.8 mm (21.2 inches), notably higher than the more extensive record. Figure 2.2 shows average monthly precipitation for the two measuring stations from 1974 to 1984. The Apache Leap escarpment and the steep terrain around the weather station at number 9 shaft apparently has an orographic effect on storm systems, more evident in winter months, causing increased precipitation at elevations above the town of Superior.

2.3 Geology of the Apache Leap Tuff

Peterson (1961, 1968) studied the units of the Apache Leap tuff in the region around Superior concluding the deposit is composed of a number of ash flows erupted in rapid enough succession to form an ash flow sheet representing a single cooling unit. This section, unless otherwise noted, is a summary of his comprehensive work.

2.3.1 Description

The Apache Leap tuff is composed of densely-welded to non-welded tuff, and can be divided into five different units based on the degree of welding and flattening of pumice lapilli (Figure 2.3). In the field, despite the thickness of the tuff, vertical sections show the consistent pattern illustrated in Figure 2.3. This pattern indicates that the ash flow tuff most likely cooled as single unit.

On the basis of chemical composition, the tuff is a quartz latite. Although classified as a quartz latite, dacite is more commonly used in reference to the Apache Leap tuff because the units of the tuff include large phenocrysts embedded in a groundmass. The modal analysis

Figure 2.2. Average monthly precipitation of the Superior region, Superior, Arizona for the years 1974-1984.

Figure 2.3. Physical characteristics of the Apache Leap tuff.

of the phenocrysts (ranging in diameter from 0.5 to 3.0 mm) and the crypto- and micro-crystalline groundmass is presented in Table 2.1 for the non- to partially-welded, white unit and the densely-welded, brown unit.

Peterson suggested the proportions of plagioclase, sanidine, and quartz of the white zone may be significantly different and transitional between the underlying, more welded zones and rocks from the source area. The similarities in the chemical composition between the units again supports the view that the entire ash flow sheet was laid down in rapid succession and that it originated from a single magma chamber. Peterson made the following observations of the chemical composition of the tuff: 1) SiO_2 progressively increases upward in the section; 2) Ferric iron is higher and ferrous iron and magnesium are lower in rocks from the upper portions of the ash flow sheet; and 3) Calcium generally declines upward in the section. The trends in ferric and ferrous iron indicate that rocks higher in the section had more time to react with the atmosphere and therefore have a higher oxidation state. Other trends in the chemical composition of the tuff were explained to be a result of escaping gases during the cooling of the ash flow sheet.

2.3.2 Structure

The ash flow tuff in the Superior region, essentially a sheet-like deposit, was laid down on upper Precambrian and Paleozoic rocks of moderate to steep relief. These underlying rocks dip eastward at angles from 30° to 45° while the overlying tuff dips eastward at smaller

Table 2.1. Average Modes and Whole-Rock Chemical Analyses of the Apache Leap Tuff in the Superior Region (after Peterson, 1961).

Modes		Chemistry	
WHITE UNIT (non- to partially-welded tuff), northeast of Kings Crown Peak, Superior quadrangle			
Phenocrysts	41.0	SiO ₂	68.70
plagioclase	67.1	Al ₂ O ₃	16.70
sanidine	7.0	Fe ₂ O ₃	2.70
quartz	14.1	FeO	0.10
biotite	6.2	CaO	2.20
magnetite	3.4	MgO	0.38
hornblende	<u>1.8</u>	Na ₂ O	4.20
	99.6	K ₂ O	3.60
Groundmass ¹	59.0	H ₂ O ⁻	1.40
cristobalite		H ₂ O ⁺	NA ²
K-feldspar		TiO ₂	0.40
quartz		CO ₂	0.05
plagioclase		P ₂ O ₅	0.15
		MnO	<u>0.08</u>
			100.66

Table 2.1.--Continued

Modes		Chemistry	
BROWN UNIT (densely-welded tuff), northeast of Kings Crown Peak, Superior quadrangle			
Phenocrysts	36.8	SiO ₂	67.70
plagioclase	73.7	Al ₂ O ₃	16.30
sanidine	2.2	Fe ₂ O ₃	2.50
quartz	9.9	FeO	0.13
biotite	8.9	CaO	2.50
magnetite	4.3	MgO	0.76
hornblende	<u>0.9</u>	Na ₂ O	4.10
	99.9	K ₂ O	3.60
Groundmass	63.2	H ₂ O ⁻	1.80
cristobalite		H ₂ O ⁺	NA
K-feldspar		TiO ₂	0.43
quartz		CO ₂	0.05
plagioclase		P ₂ O ₅	0.16
		MnO	<u>0.08</u>
			100.11

¹Groundmass minerals were identified using x-ray diffractometry.

²Not analysed.

angles, generally from 15° to 25° . The dips of the tuff are measured using joints that are parallel to flattened pumice lapilli. Assuming the tuff was laid down horizontally and the pumice lapilli were flattened from vertical stresses, the dips of the tuff are a result of tilting after solidification. Also, the difference in dips between the tuff and the underlying older rocks suggests that the structural block of the area began to be tilted before the tuff was laid down and that tilting continued after the tuff had solidified.

The Apache Leap tuff is cut in all zones of welding by a system of nearly vertical joints. In many areas two joint systems intersect each other at angles from 60° to 90° . The joints vary from widely spaced in the less welded units to closely spaced in the densely welded units of the tuff. Commonly the joint systems in outcrop are distinct, and parallel joints in some instances extend continuously for hundreds of meters. The continuity of the joints regionally is interpreted as the joints being of tectonic origin, rather than cooling features of the tuff.

Hammer and Peterson (1968) noted two principal sets of faults in the Superior region. The first and oldest set trends principally east and is mineralized. The younger, second set trends generally north to northwest. Overall, these faults are less mineralized, more dominant and offset the first set of faults and older rocks. Figure 2.1 shows mainly this latter set of faults.

In this report mineralization in fractures was examined primarily in the joint system of the tuff. Joints are defined as fracture planes, usually planar with some secondary mineralization, in

which no evidence of fault movement was recognized after field and laboratory examination. Figure 2.4 shows the distribution and inclination of joints intercepted by drilling in the white unit of the Apache Leap tuff.

A number of fault zones were also evident upon examination of the core samples. However, faults were not sampled as extensively because of low secondary mineralization or low core recovery in fault zones. Faults were identified upon the recognition of: (1) striations and slickensides on fracture planes; (2) brecciated core; and (3) zones of granulation and low core recovery.

2.4 Hydrogeology of the Superior Region

The town of Superior receives water from wells to the east near Florence Junction. The Arizona Department of Water Resources reports that these wells pump from a regional aquifer in basin fill alluvium. Magma Copper Company has a series of tunnels in the older rocks overlain by the Apache Leap tuff. Tunnel levels are almost every 30 meters (100 feet) and range from an elevation of 183 meters (600 feet) Mean Sea Level (MSL) to -183 meters (-600 feet) MSL. The tunnels are well below the variably welded units of tuff. Before closure of Magma Mine in 1986, an average of 450 gallons per minute (gpm) was continuously pumped out of the tunnel system from various pumping stations. Maximum pumping rates (largest 1200 gpm) were after heavy rainfalls and when water flowed in Queen Creek (Walter Martin, Magma Copper Company, personal communication).

Figure 2.4. Inclination and distribution of joints intercepted by boreholes at the Apache Leap site (non- to partially-welded tuff). See Appendix B for an explanation of measurements of fracture orientations.

Previous studies are unknown concerning the hydrogeology of the Apache Leap tuff. American Smelting and Refining Company (ASARCO) has several exploration boreholes in the study area that penetrate the Apache Leap tuff. Some of the boreholes were installed with pumps to fill stock tanks. However, many of the boreholes have permanent caps or obstructions making measurements of water levels impossible. Also, because the exploration boreholes are not cased and extend into the Paleozoic and Precambrian rocks overlain by tuff, altitude of water levels in the Apache Leap tuff are difficult to determine.

The Arizona Department of Water Resources has information on water levels reported by drillers and ASARCO for some of the exploration boreholes in the study area. However, this information could not be verified because the boreholes are presently either capped or obstructed and lithologic logs are either incomplete or confidential. Hence, defining regional water level elevations would be difficult and speculative based on this information. For this report, in conjunction with analyzing isotopic ratios, a reconnaissance study of the quality of water in saturated sections of Apache Leap tuff and water level elevations was performed with the aid of Walt Lockhardt, manager of ASARCO's JI-Ranch. Table 2.2 tabulates the results from the five sampling locations. Generally the groundwater is dominated by calcium, bicarbonate, and sulfate ions and has silica concentrations (reported as SiO_2) typical of volcanic terrain (Hem, 1985). Total dissolved solids of groundwater are highest in the welded unit of the Apache Leap tuff and in the limestone underlying the tuff.

Table 2.2. Parameters and Concentration of Major Ions in Water Samples Collected from Wells and Springs in the Superior Study Area.

Constituents (milligrams per liter)	Sample Identifier ¹				
	QC-PS	WM-ALU	SPR-WU	HOW-BU	HOW-LS
Calcium	50.0	28.2	12.8	69.3	108
Magnesium	12.0	5.15	4.60	8.05	52.0
Sodium	11.0	7.0	13.0	38.5	30.5
Potassium	--	2.61	3.5	0.77	0.42
Alkalinity.	146.0	96.0	46.4	286.4	538.0
Chloride.	6.0	3.52	6.04	12.15	8.28
Sulfate	49.0	25.95	33.35	48.95	98.2
Nitrate	1.5	<0.6	4.47	2.02	<0.6
Fluoride.	0.2	0.45	<0.12	0.42	<0.12
Silica.	--	31.9	33.8	66.3	50.9
TDS	240	135	116	352	640
Ec, μ mhos/cm (field). .	--	240	225	540	860
pH (field).	--	6.5	7.2	7.7	7.9
Temp., °C (field) . . .	--	20	28.5	24.5	26.0
Laboratory ²	ATL	UA	UA	UA	UA

¹Location and description of water sampling locations.

QC-PS: Queen Creek, Pump Station, (D-1-12)36aca, just below old highway tunnel; elevation 939 meters (3080 feet); sampled 12-14-81 by Magma Copper Company.

Table 2.1--Continued.

WM-ALU: Windmill with pump in alluvium and weathered tuff near Hackbery Creek, (D-2-13)8acb. Large outcrops of white unit, Apache Leap tuff in vicinity; land surface elevation 1208 meters (3960 feet), depth to water about 10 meters and total depth of well about 30 meters (reported by rancher); sampled 6-17-86.

SPR-WU: Spring in lower white unit, Apache Leap tuff, (D-1-13)22adb. Sampled from spring box catching water from large fractures of the white unit, about 10 meters up cliff on south side of road; flow out of spring box about 0.25 gpm; elevation of spring box about 1293 meters (4240 feet); sampled 6-17-86.

HOW-BU: Horizontal well in brown unit, Apache Leap tuff, (D-1-13) no section designation. Horizontal well core drilled in a ravine cut in the brown unit, 2 kilometers northeast of Queen Creek pump spring on service road; flow rate about 15 gpm; elevation about 1488 meters (4880 feet); sampled 6-17-86.

HOW-LS: Horizontal well, Paleozoic limestone, stratigraphically below Apache Leap tuff, (D-1-13) no section designation. Well was core drilled in a ravine cut in the limestone, some rhyolite in vicinity, northeast of Queen Creek Spring and about 1 kilometer north on service road from HOW-BU; flow rate about 10 gpm; elevation about 1500 meters (4920 feet); sampled 6-17-86.

²Laboratory analysis: ATL - Arizona Testing Laboratory
UA - University of Arizona Analytical Center

2.5 Site Locations

As noted previously, Figure 2.1 shows the three site locations for sampling authigenic minerals in the fractures and the rock matrix of the tuff. All three of the sites have surface collars set in the white unit of the Apache Leap tuff. Two of the locations, Apache Leap site at an elevation of about 1269 meters (4160 feet) and Magma Mine's shaft number 9 site at an elevation of 1270 meters (4165 feet), are within one kilometer of each other. The third location and highest, ASARCO's AI-2 exploration site at an elevation of about 1452 meters (4760 feet), is about 6 kilometers northeast of the Apache Leap site.

The Apache Leap site, in unsaturated fractured tuff, is on land operated by the U.S. Forest Service. The site was established by the Department of Hydrology and Water Resources of the University of Arizona to study the hydrologic characteristics of unsaturated fractured tuff. The approximate 40 m² area consists of three boreholes (X1, X2, and X3) angled at 45° that were drilled in a vertical plane; the deepest hole, X3, reaches a vertical depth of 33.5 meters below land surface (bls) in the white unit (Figure 2.5).

A major portion of this report uses data obtained from the oriented core taken from the drilling project at the Apache Leap site. Appendix A provides a more complete description of the oriented core drilling and a detailed log describing the core. Appendix B describes the methods used to orient the fracture planes of the joints and faults intersecting the boreholes at the Apache Leap site.

Limited data were also obtained from selected samples of core from the exploration work at Magma Mine's shaft number 9 and ASARCO's

Figure 2.5. Borehole diagram and 2-dimensional representation of fracture network for the Apache Leap site in an unsaturated portion of the white unit, Apache Leap tuff. See Appendix A for description of core and Appendix B for methods of determining fracture orientation.

AI-2 site. The shaft number 9 site before dewatering penetrated saturated tuff, and extends through all the variously welded zones of tuff and into the older, ore-rich rocks overlain by tuff. The total depth of the shaft is about 1465 meters (4800 feet). The AI-2 exploration borehole was reportedly drilled only through tuff to a depth of about 460 meters (1500 feet), and also penetrates saturated tuff.

The static water levels at these latter two field sites are unknown because of dewatering at the shaft number 9 site and a permanent cap on the AI-2 exploration borehole. However, before permanently capping the exploration borehole at ASARCO's AI-2 site, the driller reported the depth to water in the borehole to the Arizona Department of Water Resources as 110 meters (360 feet).

CHAPTER THREE

METHODS AND RESULTS

This chapter describes methods for isolation and isotopic analysis of authigenic fracture and matrix minerals in the Apache Leap tuff, including quartz, opal, calcite and clays. The fracture-filling mineral assemblages in the variably-saturated units of the Apache Leap tuff cover a vertical section of near surface samples in the non- to partially-welded unit of the tuff to a depth of about 430 meters (1400 feet) in the densely-welded unit of the tuff; the samples of the rock matrix extend from the surface to a depth of about 20 meters in the non- to partially-welded portion of the tuff. Data are interpreted in chapter 4.

Methods of x-ray diffractometry (XRD) and XRD patterns of isolated mineral samples are presented in Appendix C. Appendix A has a detailed log of the core samples (Tables A.2, A.3, and A.4) from the Apache Leap site in the white unit of the Apache Leap tuff (non- to partially-welded tuff).

3.1 Fracture-filling Minerals

Fracture-filling samples consisting mostly of quartz with lesser amounts of calcite and opal varieties were isolated from oriented core samples of the Apache Leap site in unsaturated tuff between December 1985 and April 1986 (see Figure 2.5). In May 1986, additional fracture-

filling samples of calcite and clay minerals were isolated from core samples of exploration holes penetrating deeper, more welded and presumably saturated portions of the Apache Leap tuff. These latter samples were collected from Magma Copper Company's core storage facility of their number 9 shaft, drilled in the early 1970's, and from D. W. Peterson's (U.S. Geological Survey) core samples of ASARCO's exploration borehole AI-2, drilled in the late 1970's. In all, the fracture-filling mineral assemblages cover a vertical section of near surface samples in the non- to partially-welded unit of the tuff to a depth of about 430 meters (1400 feet) in the densely welded unit of the tuff.

3.1.1 Mineral Isolation and Description

Quartz, opaline silica and calcite were hand-picked from fracture surfaces and analyzed for purity using XRD methods before stable isotope analysis. Clay minerals were also identified on fracture surfaces but were not isotopically analyzed because of difficulties in isolating the small quantity present. Also, petrographic examination of thin sections cut perpendicular to closed fractures and grain mounts of samples were conducted to investigate the nature of authigenic mineral crystallization.

Quartz. Fracture-filling quartz occurred as patchy, frosted masses on fracture surfaces, had a sometimes platy appearance, and was ubiquitous on fracture surfaces in the shallow portion of the tuff at the Apache Leap site. In association with quartz, opal (hydrous silica with broad, disordered, cristobalite-like XRD peaks) appearing as small (<1 mm), clear, hardened globules was common from the surface to about 5

meters on fracture surfaces and in vugs and cavities of pitted, pumice lapilli in the rock matrix of the tuff. Appendix C, Figure C.1 is an XRD pattern of representative quartz samples and Figure C.2 is a diffraction pattern of an opal sample.

Thin sections of closed fractures (<200 μm) of core samples from the white unit and brown unit of the Apache Leap tuff displayed roughly equidimensional quartz grains with smooth regular boundaries and with slightly different optical orientation. Only a few of these closed fractures could be isolated for petrographic description, and efforts to describe sampled fracture surfaces in thin section were unsuccessful. Grain mounts of hand-picked quartz from fracture surfaces were anhedral with essentially no poikilitopic texture; most samples of fracture-filling quartz similarly examined had parallel to subparallel striations. Also in grain mounts, some quartz samples appeared pitted with possible fluid inclusions however, this possibility is difficult to confirm because of problems isolating samples of fracture-filling quartz in thin section.

In mineral mounts, opaline silica appeared clear, rounded, and with fine lamellae that sometimes terminated anhedral to subhedral quartz crystals. The presence of opaline silica associated with quartz on fractures suggests recrystallization, and although all samples were examined optically in grain mounts before isotopic analysis, the possibility cannot be dismissed that some of the fracture-filling quartz has been recrystallized (see Chapter 4). Suspect samples, especially near-surface samples where opal was prevalent in fractures, were

examined by XRD methods for amorphous quartz that characteristically broadens cristobalite peaks (see Appendix C, Figure C.2) and were not isotopically analyzed as fracture-filling quartz if amorphous quartz were found to be present.

Calcite. In welded, saturated tuff, calcite was commonly observed and usually chalky white, forming powdery massive coatings on fracture surfaces. However, deeper calcite samples, below a depth of 250 meters, were subhedral, translucent and as large as 1 centimeter. In the unsaturated, less welded white unit, fracture-filling calcite was uncommon, sometimes stained reddish brown, and normally only identifiable using XRD methods (Figure C.3). Calcite was noted, however, in a fracture sample at 15.32 meters depth as cloudy subhedral crystals with lengths of 1 to 4 mm.

Petrographically, calcite was identified using staining methods in some of the isolated closed fractures of the non- to partially-welded white unit and densely-welded brown unit of the tuff. In addition to fractures, authigenic calcite was also identified surrounding embayed quartz and feldspar crystals of the rock matrix in some thin sections of the white unit. Crystal boundaries were regular, uniform, and nearly equidimensional; crystal sizes displayed no gradational changes from fracture walls to the center of fractures. In polarized light, optical orientations were slightly different for individual crystals.

Clay Minerals. Associated with fracture-filling quartz and calcite were clay minerals of the smectite group and of the fibrous clay mineral group palygorskite-sepiolite. Notably absent were fracture-filling minerals from the zeolite group. Because of problems isolating

smectite samples and unavailable isotopic data on palygorskite-sepiolite, isotopic ratios of these clay minerals were not determined.

Montmorillonite and mixed layered illite-montmorillonite of the smectite clay group were identified throughout the white unit of the tuff. Identification was made by glycolation and subsequent expansion of the d-spacing from the 15Å peak to the 17Å on XRD patterns. Other clays of the smectite group had minor peaks on XRD patterns but were not identified for this study. Attempts were made to isolate the smectite clays from other fracture-filling minerals using ultrasonic disaggregation in distilled water after removal of the carbonate according to the procedure of Jackson (1969). However, difficulties were continuously encountered in obtaining a significant quantity for isotopic analysis and isolating samples without contamination of quartz and traces of feldspar.

Magnesium-rich palygorskite-sepiolite of the fibrous clay mineral group was identified on fracture surfaces of mainly faults at depths between 60 meters and 350 meters in variably-welded tuff (white to brown units). The clay normally formed scaly aggregates on fracture surfaces with a silky luster. Calcite and smectite commonly were associated with palygorskite-sepiolite. Identification was made using XRD patterns (characteristic peaks at 10.5Å and 12Å, Figure C.4) and behavior of the XRD peaks when samples of palygorskite-sepiolite were treated with hydrochloric acid (Nathan, 1968). Isotopic data of the mineral-water relationship for palygorskite-sepiolite is unknown and isotopic ratios were not analyzed for this report.

3.1.2 Procedure and Results of Isotopic Analysis

For oxygen isotope analysis, the mineral samples of fracture-filling quartz were crushed with an agate mortar and pestle and passed through a 200 mesh (75 μm). Approximately 100 mg of sample was then treated with 3N HCl to remove any trace carbonates. Oxygen isotope compositions of the quartz samples were then analyzed in three 25 mg aliquots using ClF_3 to eventually liberate CO_2 gas according to the techniques of Borthwick and Harmon (1982) and Clayton and Mayeda (1963). Results of oxygen isotope analysis are presented in Table 3.1 for fracture-filling quartz samples. Analyses were performed by the Stable Isotope Laboratory Institute for the Study of Earth and Man of Southern Methodist University, Dallas, Texas. Oxygen isotope ratios for fracture-filling quartz are reported in the δ -notation in per mil deviations from SMOW; also reported is the variation of replicate samples and the number of determinations. The variation from replicate oxygen isotope analyses of a National Bureau Standard glass was about 0.12 ‰. Repeatability of analyses of some silica samples had a slightly higher uncertainty and may be attributable to incomplete removal of non-structural water during the evacuation process and traces of feldspar impurities before isotopic analysis.

Calcite samples from fractures were powdered with an agate mortar and pestle to pass through a 200 mesh sieve and reacted with anhydrous phosphoric acid to produce CO_2 gas for oxygen and carbon isotope compositions after the technique described by McCrea (1950). Results of oxygen and carbon isotope analysis are also presented in Table 3.1 for samples of fracture-filling calcite. Analyses were

Table 3.1. Results of Isotopic Analysis of Fracture-filling Minerals, Rock Matrix Minerals, and Associated Water in the Apache Leap Tuff.

Sample	Sample Identifier ¹	Isotopic Ratio ²	
Quartz (fracture-filling)		$\delta^{18}\text{O}$ (SMOW)	
	ALS-X1: 2.93	28.51±0.30 (3)	
	ALS-X1: 3.06	30.66±0.09 (3)	
	ALS-X2: 3.66	29.59±0.25 (3)	
	ALS-X1: 6.31	29.55	
	ALS-X2: 14.11	29.23	
	ALS-X2: 15.32	28.62±0.00 (2)	
	ALS-X2: 15.90	29.02	
	ALS-X3: 24.37	28.69±0.08 (3)	
	ALS-X3: 25.43	28.11±0.27 (3)	
Calcite (fracture-filling)		$\delta^{18}\text{O}$ (SMOW)	$\delta^{13}\text{C}$ (PDB)
	ALS-X1: 3.08	23.81±0.20 (2)	-9.31±0.13 (2)
	ALS-X2: 15.32	19.47	-9.57
	SHAFT9:213.50	17.77	-11.15
	SHAFT9:274.50	15.04	-9.73
	AS-AI2:334.00	14.20	-9.61
	AS-AI2:396.50	14.68	-6.62

Table 3.1--Continued

Sample	Sample Identifier ¹	Isotopic Ratio	
Opal (rock matrix)		$\delta^{18}\text{O}$ (SMOW)	
	ALS-X1: 0.0	18.63	
	ALS-X1: 0.75	20.54	
	ALS-X1: 2.84	20.73 $\pm$ 0.09 (2)	
	ALS-X1: 11.39	23.84	
	ALS-X2-2T: 18.72	25.96	
	ALS-X2-1T: 18.72	25.53	
	ALS-X2-NT: 18.72	10.71	
Whole Rock (rock matrix)		$\delta^{18}\text{O}$ (SMOW)	
	ALS-X2-WR: 18.72	10.82 $\pm$ 0.02 (2)	
Water ³		$\delta^{18}\text{O}$ (SMOW)	δD (SMOW)
	WM-ALU	-8.29	-62.05
	SPR-WU	-10.09 $\pm$ 0.01	-66.49 $\pm$ 0.78
	HOW-BU	-9.93	-68.16
	HOW-LS	-9.93	-67.53

¹Sample identifier indicating sampling location, borehole, and vertical depth below land surface in meters (ALS = Apache Leap site; SHAFT9 = Magma Mine exploration shaft nine; AS-AI2 = ASARCO exploration borehole AI-2). See Appendix A for descriptions of Apache Leap site samples.

Table 3.1--Continued

²Variation given where appropriate. Number of determinations in parentheses.

³Water samples were collected on 06-17-86, see Table 2.2 for description of water sampling locations.

performed by the Laboratory of Isotope Geochemistry of the University of Arizona, Tucson, Arizona. Isotopic compositions are reported in the δ notation for fracture-filling calcite in per mil deviations from SMOW for oxygen and from PDB for carbon. Variation from replicate oxygen and carbon isotope analyses of a standard carbonate was 0.25 ‰. Repeatability of calcite samples was within this range.

3.2 Rock Matrix Minerals

Opal varieties were also isolated from core samples of the Apache Leap site in the unsaturated, non- to partially-welded white unit of the Apache Leap tuff between February 1986 and April 1986 (see Figure 2.5). These samples of the rock matrix extended from the surface to a depth of about 20 meters (65 feet) at the Apache Leap site, where significant weathering and alteration of the rock matrix of the tuff was most apparent. In this shallow portion of the unit, the authigenic opal varieties were expected to be more variable in isotopic composition and therefore yield more information than deeper, less weathered portions of the rock matrix of the tuff.

3.2.1 Isolation and Treatment

Varieties of opal were isolated from the rock matrix by selective chemical dissolution of the other mineral components in HCl, NaOH, and H_2SiF_6 (ABFS) using the technique of Henderson et al. (1972). This treatment is commonly used and known not to affect the isotopic composition of opal. The ABFS treatment was preceded by sufficient crushing of 1 kg samples of drill core with no natural fractures in a carbide mill to a sample fraction between 88 μm and 149 μm . Opal

varieties were then separated from quartz and feldspars using heavy liquid at a specific gravity of 2.38 (see Appendix D).

Petrographically, the isolated opal samples appeared as spongy textured, anhedral masses with very weak birefringence. The purity of the opal isolates after ABFS treatment was established by analysis of XRD patterns (Figure C.5).

Based on the XRD patterns and according to the classification of Jones and Segnit (1971) and the observations of Henderson et al. (1971), the varieties of opal found after dissolving feldspar impurities were opal-c and opal-ct (e.g., low cristobalite with tridymite stacking), characteristic alteration minerals of weathering volcanic deposits. The varieties are distinguished by ordering of the cristobalite structure; opal-c has a more ordered structure than opal-ct. According to Florke (1955) disordering appears temperature related and is accomplished by formation of opal with periodic interstratification of SiO_2 tetrahedral layers having a tridymite structure causing an increase and broadening in the $d(101)$ reflection. Untreated rock matrix samples of a specific gravity less than 2.38 showed a progressive shift in the $d(101)$ reflection from $4.02 \text{ \AA}$ at the surface of the Apache Leap site to $4.06 \text{ \AA}$ at about 20 meters with a corresponding broadened peak. This characteristic change was attributed to increasing disordered opal concentrations in the rock matrix of the tuff with depth.

Figure 3.1 shows a series of XRD patterns for sample ALS-X2:18.72 (notation represents sampling site, borehole identifier and vertical distance below land surface) before and after selectively dissolving feldspar impurities. The bottom pattern (A) shows the

Figure 3.1. XRD patterns of rock matrix opal, sample ALS-X2:18.72, before and after selectively dissolving feldspar impurities using ABFS technique. Cr, Q, and F identify diffraction peaks of cristobalite, quartz, and feldspar.

untreated sample after heavy liquid separation with strong feldspar peaks. The middle pattern (B) shows diminished feldspar peaks after one 3-day treatment using the ABFS technique. The top XRD pattern (C) shows the sample after two 3-day treatments using the ABFS technique, removing feldspar impurities. Characteristic opal peaks after ABFS treatment showing cristobalite structure, Figure 3.1 and Figure C.5, are at 22.13° , 28.54° , 31.55° , and 36.16° 2θ (4.02 , 3.13 , 2.84 , and 2.48 Å).

3.2.2 Procedure and Results of Isotopic Analysis

Using the same technique and method of reporting as previously described for oxygen isotope compositions of fracture-filling quartz samples, oxygen isotopes were determined for opal-c and whole rock samples from selected intervals of the rock matrix from the surface to about 20 meters in the slightly welded unit of the Apache Leap tuff. Results of oxygen isotope analysis for opal and whole rock samples are presented in Table 3.1. Oxygen isotope ratios for rock matrix sample ALS-X2:18.72 show the effect of feldspar impurities causing lighter isotope compositions (see Figure 3.1).

CHAPTER FOUR

DISCUSSION OF RESULTS

This chapter discusses the results of stable isotope measurements for authigenic minerals in fractures and the rock matrix of the Apache Leap tuff. The isotope ratios of fracture-filling samples quartz and calcite are first discussed, followed by a discussion of the isotope ratios of rock matrix samples of opal varieties. Also, based on the isotope evidence and authigenic mineral assemblages, analyses are presented on the possible geochemical interactions of water movement in fractures and the rock matrix of the tuff and the conditions of authigenic mineral formation.

4.1 Fracture-filling Minerals

Quartz, the dominant fracture-filling mineral found in the drill core from the Apache Leap site, non- to partially-welded unit of the Apache Leap tuff, was analyzed for oxygen isotope composition. Also analyzed for oxygen isotope composition, as well as stable carbon isotope composition, was fracture-filling calcite found in fracture-filling samples from the Apache Leap site, and in deeper, more welded portions of the tuff from Magma Mine's shaft number nine and ASARCO's exploration borehole AI-2.

4.1.1 Fracture-filling Quartz

The enriched ^{18}O compositions of fracture-filling quartz at the Apache Leap site (Table 3.1) indicate a low temperature origin. Figure

4.1 is plot of $\delta^{18}\text{O}$ versus depth. The data show little scatter and $\delta^{18}\text{O}$ values possibly decreasing with depth. However, deeper samples are needed to test this hypothesis. The mean $\delta^{18}\text{O}$ value is 29.11 per mil; the range of $\delta^{18}\text{O}$ values is 2.55 per mil with extremes at a vertical depth of 3.06 m (30.66 per mil) and 25.43 meters (28.11 per mil).

Oxygen isotope fractionation between quartz and water is large at low temperatures. Using experimental results for such fractionation as a function of temperature, Clayton et al. (1972) extrapolated their data to temperatures below 200°C by the equation:

$$1000 \ln \alpha_{q/w} = 3.38(10^6 T^{-2}) - 3.40 \quad (4.1)$$

where

$\alpha_{q/w}$ = fractionation factor for quartz-water exchange,
and

T = temperature (K).

Figure 4.2 shows temperature profiles of the Apache Leap site to a depth of more than 20 meters measured in winter and summer months. A fluctuation of over 10°C is apparent near the surface of the rock profile due to seasonal cooling and heating. However, below about 10 meters, the temperature profile is consistent and exhibits little fluctuation from seasonal effects. Using equation 4.1, geothermal temperatures of 15 to 25°C, and the mean $\delta^{18}\text{O}$ value for fracture-filling quartz of 29.11 per mil, the computed equilibrium $\delta^{18}\text{O}$ value for water is -9 to -6 per mil.

This range of values (-9 to -6 per mil) is slightly heavier than the oxygen isotope composition of groundwater in the Superior area which

Figure 4.1. Oxygen isotope composition of fracture-filling quartz versus depth, Apache Leap site. Line represents a linear regression analysis ($\delta^{18}\text{O}_{\text{qtz}} = 0.06y + 29.8$, $r = 0.66$).

Figure 4.2. Seasonal temperature gradient measured in borehole X3, Apache Leap site.

is -8 to -10 per mil based on the water samples collected in June, 1986 (Table 3.1). However, the computed $\delta^{18}\text{O}$ values are within the range of the present-day oxygen isotope composition of meteoric water at similar elevations for southeastern Arizona (Smalley, 1980; Merz, 1985; and Strauss, in progress). Figure 4.3 is a plot of these relationships.

4.1.2 Fracture-filling Calcite

The stable isotope data for fracture-filling calcite (Table 3.1) represent samples from the Apache Leap site in non- to partially-welded tuff, Magma Mine's shaft number 9 in welded tuff, and ASARCO's exploration borehole AI-2 in densely welded tuff. Of the six calcite samples, two samples were from unsaturated tuff (Apache Leap site, non- to partially-welded tuff), and the remainder were from saturated tuff.

Oxygen Isotope Data. The enriched ^{18}O compositions for the calcite samples (Table 3.1) indicate a low temperature origin. The range of $\delta^{18}\text{O}$ values is 8.87 per mil, and the data trends toward less enriched ^{18}O compositions with increasing depth. The extremes occur at a vertical depth of 3.08 m (23.81 per mil) and 274.50 meters (15.04 per mil).

The samples from the Apache Leap site in unsaturated tuff have an average $\delta^{18}\text{O}$ composition of 21.64 per mil. Using the following equation relating the temperature of calcite formation (O'Neil et al., 1969):

$$1000 \ln \alpha_{\text{C/W}} = 2.78(10^6 T^{-2}) - 2.89 \quad (4.2)$$

Figure 4.3. Ranges of measured $\delta^{18}\text{O}$ values for fracture-filling quartz and water intersected by lines predicted by equation 4.1 using temperatures of 15 and 25°C. Δ 's represent range of $\delta^{18}\text{O}_{\text{water}}$ values (-9 to -6 per mil) in unsaturated tuff predicted by equation 4.1 using an average $\delta^{18}\text{O}_{\text{qtz}}$ value (29.11 per mil) from Apache Leap site samples and temperatures of 15 and 25°C

where

and $\alpha_{c/w}$ = fractionation factor for calcite-water exchange,

T = temperature (K),

with the ambient temperature of 15 to 25°C, the computed $\delta^{18}O$ value for water assuming isotopic equilibrium with calcite is -9 to -7 per mil. This range of values is again similar to present-day $\delta^{18}O$ compositions of meteoric water in the region, but slightly heavier than groundwater in the Superior study area.

The remaining four calcite samples from deeper, more welded, saturated portions of the tuff have lighter $\delta^{18}O$ compositions. Using equation 4.2, oxygen isotope data of sample SHAFT9:213.5 (17.77 per mil) and a temperature of formation of 29°C (temperature assuming a geothermal gradient of 0.04°C per meter) the calculated $\delta^{18}O$ of water in isotopic equilibrium with calcite would be -9.9 per mil. This value is within the range of oxygen isotopic composition measured for groundwater in the tuff (samples SPR-WU and HW-BU) and indicates calcite is probably an equilibrium phase in fractures of the tuff at this depth. Fracture-filling calcite samples below the depth of sample SHAFT9:213.5 may represent equilibrium phases with groundwater as light as -12.4 per mil. Figure 4.4 plots the oxygen isotope relationship of fracture-filling calcite in unsaturated and saturated tuff as a function water.

Carbon Isotope Data. The carbon isotope composition of calcite is controlled by several factors: 1) $\delta^{13}C$ value of carbon dioxide gas in equilibrium with bicarbonate and carbonate ions in solution; 2) temperature and ultimately the isotopic fractionation between carbon

Figure 4.4. Ranges of measured $\delta^{18}\text{O}$ values for fracture-filling calcite and water intersected by lines predicted by equation 4.2 using temperatures of 15, 25 and 35°C. Δ 's represent range of $\delta^{18}\text{O}_{\text{water}}$ values (-9 to -7 per mil) in unsaturated tuff predicted by equation 4.2 using an average $\delta^{18}\text{O}_{\text{calcite}}$ value (29.11 per mil) from Apache Leap site samples and temperatures of 15 and 25°C. +, o represent range of $\delta^{18}\text{O}_{\text{water}}$ values (-9.9 to -12.4 per mil) in saturated tuff predicted by equation 4.2 using $\delta^{18}\text{O}_{\text{calcite}}$ values from SHAFT9:213.5 (17.77 per mil, 29°C) and AS-A12:334.0 (14.2 permil, 34°C).

dioxide gas and bicarbonate and carbonate ions in solution and solid calcium carbonate; and 3) pH and other chemical properties of the system that may have an influence on bicarbonate and carbonate ions in solution (Deines et al., 1974).

The $\delta^{13}\text{C}$ values of fracture-filling calcite have an average composition of -9.33 per mil (PDB) and range from -6.62 to -11.15 per mil (Table 3.1). The depleted ^{13}C data indicate that carbon was biogenically derived. Emrich et al. (1970) gave the fractionation factor for calcium carbonate-carbon dioxide gas in the carbonate equilibria system at 20°C as:

$$\alpha_{\text{CaCO}_3/\text{CO}_2} = (\delta^{13}\text{C}_{\text{CaCO}_3} + 1000) / (\delta^{13}\text{C}_{\text{CO}_2} + 1000) \quad (4.3)$$

$$= 1.01017.$$

Using the average measured $\delta^{13}\text{C}$ composition of calcite, the isotopic composition of CO_2 gas in equilibrium with calcite is about -19 per mil (PDB). The relative depletion of the ^{13}C component of CO_2 gas is probably attributable to oxidation of organic debris and respiration of plants.

4.2 Rock Matrix Minerals

Rock matrix samples of opal from the Apache Leap tuff were isolated and analyzed for oxygen isotope composition using non-fractured core samples from the drilling operation at the Apache Leap site (Table 3.1). The rock matrix samples of opal extended from the surface to a depth of about 20 meters. In this interval, significant weathering and

alteration of the tuff was apparent (see drill core logs, Table A.2, A.3, and A.4).

Figure 4.5 is a plot of the $\delta^{18}\text{O}$ composition of opal versus depth. The data show a trend toward enriched ^{18}O with depth. The range of $\delta^{18}\text{O}$ values is 6.90 per mil. Extremes occur for samples at the surface (18.63 per mil) and at the deepest sample depth of 18.72 meters (25.53 per mil).

4.2.1 Opal Isolation and the ABFS Treatment

Selective dissolution of feldspar from opal varieties by ABFS treatment is commonly used and known not to affect the oxygen isotope composition (Syers et al., 1968; Chapman et al., 1969; Henderson et al., 1971; and Henderson et al., 1972).

The isotopic gradient observed in the oxygen isotope composition of rock matrix opal cannot be attributed to feldspar contamination of opal samples because isolation procedures and isotopic measurement of opal sample ALS-X2:18.72 exclude this possibility. After one treatment using the ABFS technique for opal isolation, the sample still showed feldspar contamination, but only a slightly less enriched oxygen isotope composition compared to the same sample after undergoing two ABFS treatments (Table 3.1 and Figure 3.1). After each ABFS treatment, XRD patterns of opal samples were routinely performed to guard against significant contamination problems (Figure C.5). Also, if contamination was the cause of the large range between oxygen isotope compositions of opal samples, the data would show more scatter rather than the apparent smooth, linear trend with depth.

Figure 4.5. Oxygen isotope composition of rock matrix samples of opal versus depth, Apache Leap site. Line represents a linear regression analysis ($\delta^{18}\text{O}_{\text{opal}} = -0.35y + 19.6$, $r = -0.96$).

4.2.2 Effect of Heterogenous Opal Formation on the Oxygen Isotope Composition of Opal

More probable causes for the isotopic gradient for the samples of opal are past and present alteration reactions of minerals and volcanic glass in the tuff resulting in heterogeneous forms of opal in the rock matrix. Early in the cooling history of the tuff and/or under present weathering conditions, possible reactions include the alteration of volcanic tuff to silica polymorphs, smectite, and zeolites (Pettijohn, 1975). Hence the oxygen isotope gradient could be a result of a heterogeneous mixture of both lower temperature and higher temperature forms of opal.

Alteration of Volcanic Glass. The non-welded to densely-welded units of the Apache Leap tuff have undergone devitrification, a distinctive characteristic of ash-flow tuffs whereby the metastable glassy portion of the rock crystallizes to fine-grained feldspars and silica polymorphs (cristobalite, opal varieties, and minor amounts of tridymite). The metastable character of these silica polymorphs causes the minerals to invert to quartz, the stable polymorph of silica. However, the kinetics of alteration are slow. The groundmass of Cretaceous tuffs and older studied by Ross and Smith (1961) consisted of fine-grained quartz, but metastable silica polymorphs were dominant in the groundmass of Tertiary tuffs and younger.

Devitrification of ash-flow tuff occurs over a wide temperature range and probably begins sometime after compaction and welding of the glass shards. Lofgren (1971) experimentally produced devitrification products and textures in volcanic glass using pure and alkali-rich water

in the temperature and pressure ranges of 240° to 700°C and 0.5 to 4.0 kilobars. Taylor (1968) used the stable isotopes of oxygen and hydrogen to show that the alteration of volcanic glass can also be promoted by hydration from meteoric water at surficial temperatures. Further support of low temperature alteration of volcanic glass has been reported by Gruner (1940) and Henderson et al. (1971) who found evidence of metastable silica polymorphs only in altered volcanic ash deposits (bentonites). The slow but eventual conversion of the metastable silica polymorphs to stable quartz was indicated by the observation that only quartz existed in Cretaceous and older bentonites.

Formation of Opal Varieties. X-ray examination of rock matrix samples from the Apache Leap site indicated the most characteristic rock matrix minerals were alkali feldspars and low cristobalite with tridymite stacking. According to the classification of Jones and Segnit (1971), these forms of cristobalite are hydrous silica classified as opal-c and opal-ct. Distinction between the two forms is made by the disordering of the low cristobalite structure by differing amounts of tridymite which forms an integral part of the opal structure. The development of the tridymite structure in the opal, as proposed by Florke (1955), is due to incorporation of cations into the low cristobalite form.

Similar forms of opal from Eocene, altered, volcanic ash in Texas were analyzed for oxygen isotopes by Henderson et al. (1971) and considered on that basis to be of low temperature origin (25°C in the presence of water of $\delta^{18}\text{O} = +10$ per mil). These same authors also analyzed other opal samples from isolated vesicles in obsidian and

concluded they were of high temperature origin (200° to 600°C in hydrothermal water with $\delta^{18}\text{O}$ compositions in the range of +6 to +10 per mil). In their study, x-ray diffraction patterns of both forms of opal had similar but distinguishable d(101) peaks. The increased and broadened d(101) spacing observed for the low temperature forms of opal reflected a more disordered crystal structure (see Figure C.2).

A similar relationship was found by Murata et al. (1977) in the d(101) peaks of ordered and disordered opal in the Monterey shale of California. However, based on nearly identical $\delta^{18}\text{O}$ values, both forms indicated low temperature formation (50°C). A progressive sharpening and a shift toward smaller d(101) spacings of opal with increasing burial depth and temperature without change in oxygen isotope composition was interpreted by them to represent solid state ordering of the crystal structure.

The rock matrix samples of opal from the Apache Leap site have $\delta^{18}\text{O}$ values ranging from 18.63 per mil at the surface to 25.53 per mil at a depth of 18.72 meters. In addition to the trend in isotopic values, X-ray diffraction patterns of untreated opal show a trend toward more disordered opal with depth (4.02 Å at the surface to 4.06 Å at a depth of 18.72 meters).

Both of these trends are supportive of heterogeneous forms of opal in the rock matrix of the non- to partially-welded tuff at the Apache Leap site, with the lower temperature, more disordered form of cristobalite becoming increasingly dominant with depth. This form of opal, with enriched ^{18}O compositions, is more consistent with formation in equilibrium with present-day water and temperature. Conversely, opal

from higher in the profile represents a more ordered form (e.g., opal-c), and the lower $\delta^{18}\text{O}$ values indicate a higher temperature of formation and/or isotopic equilibrium with isotopically heavier water. This formation of opal may have been a devitrification product of the tuff due to cooling and latent hydrothermal activity early in the history of the Apache Leap tuff.

Logs of the drill core from the Apache Leap site indicate solution near the surface, evidenced by pitting and increased porosity, particularly in areas of pumice lapilli of the tuff near the surface. The logs also indicate reprecipitation of silica at depth. These observations suggest the tuff (volcanic glass, plagioclase feldspar and perhaps opal-c) has been leached near the surface due to the downward flux of percolating water freeing silica and cations which have been redeposited and concentrated with depth as disordered opal and clay.

4.3 Conditions of Authigenic Mineral Formation

This section discusses the possible geochemical relationships, based on the isotopic data of fracture-filling and rock matrix minerals, of the flux of water and conditions of authigenic mineral formation in the variably-saturated portions of the Apache Leap tuff.

4.3.1 Evaporation and Rock-Water Interaction

Isotopic gradients in percolating water have been observed as a result of evaporation and rock-water interaction (Barnes and Allison, 1983; Lawrence et al., 1979). Because of difficulty extracting water directly from the unsaturated tuff at the Apache Leap site, isotopic gradients of percolating water in fractures and the rock matrix were

examined indirectly by measuring the stable isotope composition of related fracture-filling and rock matrix minerals.

Evaporation. Evaporation causes a preferential removal of ^{16}O relative to ^{18}O near an evaporating surface resulting in isotopically heavier water compared to the initial isotopic composition. Allison et al. (1983) noted in the first few meters of soil profiles as much as a five per mil increase in $\delta^{18}\text{O}$ of percolating water resulting from evaporation in a semi-arid climate. Below this depth the isotopic composition of percolating water was only 1 to 2 per mil heavier than local precipitation. Oxygen and hydrogen isotope data from these greater depths (3 to 15 meters) in four soil profiles of different lithologies plotted on a line and were displaced slightly to the right and parallel to the local meteoric water line.

In the same study, Allison et al. proposed the isotopic gradient of percolating water in a soil profile of semi-arid areas was due to evaporation effects and mixing of isotopically distinct water. The composition of the local meteoric water was first enriched in heavier isotopes from near-surface evaporation. Subsequently, this enriched ^{18}O water was displaced downward and mixed by the next recharge event. The amount of displacement from the local meteoric water line was determined by a balance between the amount of near-surface enrichment due to evaporation and subsequent dilution due to precipitation events. Ultimately a relationship then existed between the amount of isotopic displacement and the recharge rate at a particular site.

To investigate the effects of evaporation and rock-water interactions in fractures of unsaturated tuff, fracture-filling quartz

(discussed in Section 4.1.1 and represented in Figure 4.1) was sampled in fractures of varying inclination to investigate any systematic variation of oxygen isotope ratios (Figure 4.6). The notation in parentheses in Figure 4.6 represents the borehole and vertical distance in meters below land surface. No consistent change of $\delta^{18}\text{O}$ was noted with change of fracture inclination. However, the $\delta^{18}\text{O}$ values of high inclination fracture samples show less variation (range of 28.51 to 29.55 per mil) than low inclination fracture samples (range of 28.11 to 30.66 per mil).

Figure 4.7 is a plot of the $\delta^{18}\text{O}$ values of low inclination fracture-filling quartz versus depth and shows a trend toward lighter values with depth. Using equation 4.1 and an average temperature of 20°C, this trend corresponds to about a 2 per mil difference in the predicted isotopic composition of water in low inclination fractures. The most likely interpretation is that this difference results from isotopically heavier water near the surface and isotopically lighter water at depth.

Such a change in the isotopic composition of the water at the Apache Leap site could have been brought about by evaporation effects preferentially removing the lighter isotope of percolating water in near-surface, low inclination fractures that have not drained as rapidly as high inclination, more continuous fractures. Similar to the model proposed by Allison et al. (1983), subsequent precipitation events would then have displaced and mixed this isotopically enriched parcel of water

Figure 4.6. Oxygen isotope composition of fracture-filling quartz versus fracture inclination, Apache Leap site. Numbers following borehole identifiers are sample depths.

Figure 4.7. Oxygen isotope composition of low inclination, fracture-filling quartz versus depth, Apache Leap site. Line represents a linear regression analysis ($\delta^{18}\text{O}_{\text{qtz}} = 0.1y + 30.55$, $r = 0.94$).

in the profile resulting in the observed isotopic gradient of the $\delta^{18}\text{O}$ composition of authgenically derived fracture-filling quartz. This explanation and use of equation 4.1 under isothermal conditions is based on an average of the seasonal temperature gradients seen in the first six meters of the rock profile at the Apache Leap site (Figure 4.2). With the exception of sample ALS-X1:2.93 which has a $\delta^{18}\text{O}$ composition signifying equilibrium with less enriched ^{18}O water (e.g. not influenced by evaporation), high inclination, fracture-filling quartz also show a similar, but less pronounced $\delta^{18}\text{O}$ gradient.

The relative difference between the oxygen isotope ratios from the Apache Leap site for the two calcite samples (Table 3.1) also fits this pattern. Sample ALS-X1:3.08 is from a low inclination fracture. Using equation 4.2, an equilibrium temperature of 20°C and the measured isotope composition of this sample, the calculated value for coexisting water is -5.9 per mil, similar to the calculated value for coexisting fracture-filling quartz at a similar depth (-5.7 per mil, sample ALS-X1:3.06 using equation 4.1). The significance of the calcite isotopic ratios is uncertain due to the limited number of samples, and more sampling is needed of fracture-filling calcite to investigate the apparent trend of depleted ^{18}O calcite with fracture orientation and depth.

Rock-Water Interaction. Depending on the ambient temperature and the initial oxygen isotope compositions of water and rock, a decrease or increase in the $\delta^{18}\text{O}$ composition of water could also arise from the alteration of volcanic rock and glass (Lawrence et al., 1975).

As discussed in chapter 1, the magnitude of the shift in the water depends on the ratio of water to rock in addition to temperature and initial isotopic composition. If the effective ratio of water to rock is high (e.g. total amount of water that has passed through a rock rather than the amount present at any one instant), any shift in $\delta^{18}\text{O}$ in the water is likely to be negligible. However, if the water content of the rock is low due to low porosities or dry conditions, the effective water-rock ratio will be low and noticeable isotopic shifts in the water may occur.

Lawrence et al. (1975) showed that rock-water interactions below 20°C can decrease the $\delta^{18}\text{O}$ composition of water as a result of the alteration of volcanic ash to smectite and the recrystallization of biogenic silica to chert in seawater. The core logs from the Apache Leap site (Tables A.2, A.3, and A.3) indicate pumice lapilli in the first 20 meters showed extreme pitting reflecting silica dissolution. In addition, ubiquitous authigenic silica formation was observed in fractures throughout the profile of tuff along with minor amounts of smectite. Other reactions such as alteration of the tuff to zeolites were not observed at the Apache Leap site.

Following the study of Lawrence et al. (1975), the material balance equation can be used to investigate the change in the $\delta^{18}\text{O}$ of percolating water controlled by the alteration reaction of volcanic glass to opal at the Apache Leap site. The approach assumes equilibration of all the recrystallized solids with the percolating water in a closed system. Initial conditions which must be known or

estimated are the mole fraction of oxygen in the solid phase (x_1), the oxygen isotope composition of the whole rock (δl_a), and the oxygen isotope composition of the percolating water (δl_b), and the isotopic fractionation factor between the authigenic mineral and the equilibrated percolating water ($\alpha_{c/d}$). By combining the material balance equation:

$$x_1 \delta l_a + (1 - x_1) \delta l_b = x_1 \delta l_c + (1 - x_1) \delta l_d, \quad (4.4)$$

with the isotope fractionation equation:

$$\alpha_{c/d} = (1000 + \delta l_c) / (1000 + \delta l_d), \quad (4.5)$$

the final oxygen isotope composition of the authigenic mineral (δl_c), and the percolating water (δl_d) can be calculated:

$$\delta l_d = \frac{x_1 \delta l_a + (1 - x_1) \delta l_b - 1000 x_1 (\alpha_{c/d} - 1)}{x_1 (\alpha_{c/d} - 1) + 1}, \quad (4.6)$$

$$\delta l_c = 1000 (\alpha_{c/d} - 1) + (\alpha_{c/d}) (\delta l_d). \quad (4.7)$$

The mole fraction of oxygen in the solid phase (x_1) is the proportion of total oxygen within the system (rock plus water) that resides in the rock phase. The isotopic fractionation factor between the alteration phase and the fluid during authigenesis ($\alpha_{c/d}$) is a function of temperature as described in Section 1.2 and Equation 1.3.

Figure 4.8 illustrates the variation of the $\delta l^{18}O$ of water (δl_d) as a function of fixed values of the mole fraction of oxygen in volcanic glass (x_1). Using equation 4.6, the three lines represent the

Figure 4.8. The del^{18}O predicted for percolating water (del_d) after alteration of volcanic glass to opal under isotopic equilibrium conditions versus the mole fraction of oxygen in the solid phase. The initial del^{18}O for volcanic glass is assumed to be +10 per mil.

reaction of volcanic glass altered to silica at temperatures of 30°, 20°, and 10°. The oxygen isotope composition of the volcanic glass ($\delta_{\text{a}} = +10$ per mil) is representative of the $\delta^{18}\text{O}$ composition of unaltered glass given in Taylor (1968) and is similar to the whole rock value of sample ALS-X2-WR:18.72 (10.82 per mil). The initial oxygen isotope composition of water is assumed to have a $\delta^{18}\text{O}$ value of -8 per mil (δ_{b}), similar to the meteoric water in the region and the calculated value of percolating water in fractures of the tuff from isotope data of fracture-filling minerals. Values of $\alpha_{\text{c/d}}$ were taken from Friedman and O'Neil (1977) for silica-water fractionation and were verified by isotopic data reported by Henderson et al. (1971). Note that for a medium of uniform porosity, the displacement of the δ_{d} value from the initial isotopic composition of water ($\delta_{\text{b}} = -8$ per mil) is a measure of the water-rock ratio. Hence, the ^{18}O depletion of water will increase as x_1 increases, or as the water-rock ratio (w/r) decreases:

$$w/r = (1 - x_1) / x_1 \quad (4.7)$$

A modification of the material balance equation expresses the change in δ_{d} as a direct function of the degree of saturation of the tuff. Again, assuming complete isotopic equilibrium of silica and water, the amount of saturated pore space can be expressed as:

$$\text{Partial Saturation} = x_{\text{a}} / (1 - x_1) \quad (4.8)$$

The mole fraction of oxygen in the fluid phase for partial saturation

becomes:

$$(1 - x_1)' = x_a / (x_a + x_1), \text{ and} \quad (4.9)$$

$$x_1' = 1 - (1 - x_1)' \quad (4.10)$$

where $x_a \leq (1 - x_1)$.

Using equations 4.7 and 4.9 after determining a value of x_a from equation 4.8, Figure 4.9 is a plot of δl_d (oxygen isotope composition of water after alteration) as a function of saturation for boundary condition values of x_1 of 0.05 and 0.1. The plot is based on the assumptions that initial isotope composition of water is -8 per mil (δl_b), δl_b of volcanic glass is +10 per mil, and temperature of equilibration is 20°C. Note that as the oxygen reservoir of the pore fluid decreases (due to partial saturation), the influence of the oxygen isotope reservoir of the solid phase (volcanic glass) on δl_d becomes increasingly important.

In the rock matrix of the tuff, assuming homogeneous, low temperature formation of opal in equilibrium with present-day meteoric water and temperatures at the Apache Leap site, the oxygen isotope data indicate substantial depletion of ^{18}O at near-surface depths (0 to 3 meters). Using equation 4.1 for silica-water fractionation, this change corresponds to an isotopic composition of water in the rock matrix of -17 to -15 per mil. Compared to the isotopic composition of water calculated for percolating water in fractures (using the isotope data of fracture-filling minerals), this is a shift of oxygen isotope composition of water in the rock matrix of -6 to -8 per mil. At a depth

Figure 4.9. The $\delta^{18}\text{O}$ of percolating water (δ_d) after alteration versus saturation of water for the reaction volcanic glass to opal. The initial isotope composition is assumed to be -8 per mil for water and +10 per mil for volcanic glass. Temperature of equilibration is 20°C.

of about 20 meters (opal sample ALS-X2: 18.72), the difference is less and corresponds to a shift of about -3 per mil compared to calculated values of water in equilibrium with fracture-filling minerals.

Using the rock-water relationship in the mass balance approach for a closed system, the oxygen isotope data of rock matrix samples of opal from the Apache Leap site indicate rock-water interactions to be more significant at the surface to near-surface than at depth (20 meters). This trend in the oxygen isotope profile of opal is consistent with increasing volumetric water content of the tuff with increasing depth. However, assuming that alteration and isotopic exchange are similar for quartz formation, the heavier isotopic composition of fracture-filling quartz in shallow, low inclination fractures cannot be accounted for by the same explanation of rock-water interaction. Still the kinetics of quartz formation are slower, and this does not disprove the hypothesis that the $\delta^{18}\text{O}$ values of opal may be controlled by water saturation of the tuff.

The conceptual relationship between water-rock ratios and oxygen isotope ratios illustrates how a gradient of volumetric water content in unsaturated tuff at the Apache Leap site may explain the observed isotopic gradient in the $\delta^{18}\text{O}$ values of rock matrix samples of opal. Using the simplified closed system approach, the isotopic compositions represent maximum estimates of degree of saturation. Because of the higher density of fracturing near the surface at the Apache Leap site, especially near borehole X1 where rock matrix samples were located, infiltration through fractures rather than through the rock matrix may

dominate in this part of the tuff. Also, increased evaporation causes decreased water-rock ratios near the surface.

More quantitative determinations of the relationship between water content and oxygen isotope composition of opal in the tuff at the Apache Leap site is beyond the scope of this study. The conceptual model discussed above approached the rock-water relationship as a closed system, a convenient but inappropriate description for shallow conditions. Effects of evaporation must also be considered, and would necessarily cause an isotopic gradient in the opposite direction of the observed trend assuming homogeneous, present-day formation of opal in the rock matrix of the tuff. Also, from the argument presented in Section 4.2.2, the oxygen isotope ratios of rock matrix samples opal did not appear to reflect homogeneous, low-temperature assemblages. Finally, contrary to the conclusion of decreased water-rock ratios in the matrix of the tuff needed for describing the observed isotopic gradient, information from the core logs indicated porosity decreases from the surface to about 20 meters. The higher near-surface porosity was reflected in the dissolution of pumice lapilli apparently resulting from the flux of percolating water in the rock matrix. Below a depth of about 15 meters, the tuff was less altered, the rock matrix was more competent and pumice lapilli were less pitted.

Data for volumetric water contents of the tuff versus depth or percentages of volcanic glass in the tuff were not available for this study. However, using the conceptual model for rock-water interaction in unsaturated tuff and assuming the volcanic glass percentages to be constant based on Peterson's (1961) description of the Apache Leap tuff,

deeper rock matrix sampling of opal and corresponding oxygen isotope measurements below 20 meters may indicate the regularity of the volumetric water content in unsaturated, fractured tuff versus depth. Additional rock matrix samples of opal and corresponding oxygen isotope measurements at discrete intervals from a fracture wall may also prove to have a relationship with water content.

4.3.2 Hydrogeochemical Interpretation of Stable Isotope Ratios

Stable isotope evidence of the low temperature formation of quartz in fractures and increasing disordered opal concentrations at depth in the rock matrix indicates significant dissolution-precipitation of silica at the Apache Leap site in the shallow profile of tuff. Below about 30 meters, quartz precipitation in fractures is less frequent and fracture-filling clay is more common. Based on stable isotopes, calcite in the saturated portion of tuff is also of low temperature origin. However, assuming isotopic equilibrium and using preliminary chemistry and isotope data of groundwater in the study area, precipitation of calcite in deep fractures was influenced by water isotopically and chemically distinct from the water in the more shallow portion of the tuff.

Dissolution and Precipitation of Silica. The solubility of silica increases with increasing pH and is also controlled by the size and degree of crystallinity of the solid and by temperature and pressure (Stumm and Morgan, 1981).

The solubility of quartz (diameter 100 μm) at 25°C and atmospheric pressure is about 6 milligrams per liter (mg/l), reported as

SiO_2 (Morey et al., 1962). Fournier and Rowe (1962) reported the solubility of cristobalite to be 27 mg/l at 25°C and 94 mg/l at 84°C. Morey et al, (1964) reported the solubility of amorphous silica to be 115 mg/l at 25°C. The solubility of opal-c, opal-ct and other silica species are inferred to lie between the solubilities of cristobalite and amorphous quartz (Kastner, 1979).

The rate of crystallization of quartz is slow in low temperature ranges and the solubility of amorphous silica is normally considered the upper limit of dissolved aqueous silica. Kinetics of dissolution and precipitation of silica from 0° to 300°C were studied by Rimstidt and Barnes (1980). Experimental and field work by Henne (1982) and White and Claasan (1979) with volcanic tuff of Rainier Mesa, Nevada suggests that percolating water could acquire its dissolved silica as quickly as 3 months (33 mg/l) from the dissolution of volcanic glass and feldspars. Rate expressions from these studies generally show an inverse relation between residence time of water and available surface of the dissolving silicate in order to attain a given silica concentration in the water.

Groundwater samples from the Superior study area (Table 2.2) have more dissolved silica than the quartz equilibrium value but less than the amorphous silica value (Figure 4.10). In the unsaturated zone, McQueen and Miller (1972) showed that percolating water can have solute concentrations significantly higher than the underlying groundwater. At the Apache Leap site, the near-surface portion of the profile of tuff showed evidence of leaching, and precipitation of silica polymorphs in fractures and in the rock matrix at depth. Oxygen isotope ratios of authigenic silica polymorphs support this interpretation reflecting low

Figure 4.10. Activity of H_4SiO_4 in groundwater samples from the Superior study area (diagram and solubility of silica species at 25°C after Lindsay, 1979). Solid lines represent solubility relationships of different forms of silica. See Table 2.2 for description of sampling locations.

temperature mineral precipitation in equilibrium with percolating water enriched in ^{18}O probably due to the effects of evaporation. A possible mechanism, modified from a study by Helgeson et al. (1969), to explain the dissolution-precipitation of silica is localized changes in pH of percolating water and the weathering of silicates in the shallow profile of tuff at the Apache Leap site. With dissolution of volcanic glass and plagioclase feldspar, the pH of percolating water increases due to the reaction of hydrogen with silica and the subsequent leaching of cations into solution. As an example, the equilibrium reaction of silica can be expressed:

Also the weathering expression of plagioclase feldspar can be written as:

Hence percolating water becomes more basic and dissolved silica concentrations increase. Silica concentrations would be further increased by evaporation at the site as would poor drainage in the area (i.e., increase residence time of water). Later influxes of percolating water, changes in the partial pressure of CO_2 in the soil gas, and evaporation could cause precipitation of saturated dissolved silica as silica polymorphs and clay minerals. At depth in the profile of tuff, leaching became less dramatic and silica concentrations using this model would not be significant enough for precipitation of opal and quartz.

When the major ion data of groundwater samples (Table 2.2) was plotted on mineral stability diagrams, equilibrium with clay minerals (kaolinite, and Na- and Ca-smectite) controlled the silica concentrations in saturated portions of the tuff. This was also evidenced in core samples.

Deep Percolation. The isotopic composition of fracture-filling calcite samples in deeper, more welded, and presumably saturated tuff suggests groundwater is more depleted in ^{18}O compared to percolating water at the Apache Leap site. Preliminary results of the isotopic composition of groundwater in the tuff (Table 3.1) also show water depleted in ^{18}O compared to the calculated values of percolating water at the Apache Leap site, but plot close to the meteoric water line (Figure 4.11). The oxygen isotope data of groundwater samples are within the range of calculated values for isotopic equilibrium with fracture-filling calcite. In agreement with this isotopic data, the preliminary results of the chemistry of groundwater samples, when plotted on a mineral stability diagram, also indicated chemical saturation with respect to calcite.

Gat (1971) summarized mechanisms that can cause variations in isotopic compositions of precipitation as compared to that of groundwater. The following mechanisms may be responsible for the variation in $\delta^{18}\text{O}$ compositions between percolating water in the shallow, unsaturated portion of tuff at the Apache Leap site and groundwater in deeper, saturated portions of the tuff in the Superior study area:

Figure 4.11. Isotopic composition of groundwater in the Superior study area compared to global meteoric water line of Craig, 1961. See Table 2.2 for description of water sampling locations.

- 1) recharge that occurred in past periods of different climate when the isotopic composition of precipitation was different from that at the present;
- 2) present-day meteoric water recharging from different elevations mixing with groundwater; and
- 3) isotopic fractionation processes resulting from differential recharge water movement through the unsaturated zone and/or the saturated zone due to evaporation and rock-water interaction.

The stable isotope composition of fracture-filling and rock matrix minerals in the variably-saturated tuff indicate low temperature, authigenic mineral formation related to an environment similar to present-day conditions. At the Apache Leap site, mineral formation in fractures is consistent with water slightly enriched in ^{18}O probably due to evaporation, relative to water in deeper portions of the tuff. Although analyses of groundwater are preliminary, the isotopic data show little variation and suggest a trend toward lighter values with depth (i.e., shallowest sample most enriched due to evaporation while deeper samples reflect unmodified meteoric values). The shallowest groundwater sample, from a depth of about 30 meters in alluvium and weathered tuff (sample WM-ALU, Table 3.1), shows the closest similarity to calculated oxygen isotope compositions of percolating water based on stable isotopes of authigenic minerals in unsaturated tuff. From these observations, deep percolating water may possibly recharge saturated tuff rather quickly, most likely through large, high inclination fractures, without undergoing significant evaporation.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

Precipitation, percolating water, and groundwater of a particular area may have distinct isotopic tags. The usefulness of isotope measurements along pathways of water movement is that inferences may be drawn about hydrologic sources. This study has shown that from rock where water may be difficult to extract directly such as unsaturated tuff, conclusions can be made concerning the source and flux of water by measuring the stable isotope composition of authigenic minerals formed in equilibrium with the percolating ground water.

The isotopic compositions of fracture-filling and rock matrix minerals in variably-saturated tuff near Superior, Arizona, are concordant with the existing geothermal gradient and in equilibrium with percolating water isotopically similar to present-day precipitation and groundwater. The oxygen isotope compositions of fracture-filling quartz and calcite at the Apache Leap site, in unsaturated fractured tuff, display an isotopic gradient most pronounced in low inclination fractures. The gradient most likely results from near-surface, isotopic enrichment in recharging water due to evaporation rather than from the effects of rock-water interaction. Less variation was observed in the oxygen isotope composition of quartz in high inclination fractures.

Based on the oxygen isotope data of fracture-filling and rock matrix quartz and opal, the rock matrix of unsaturated tuff at the

Apache Leap site has been leached near the surface by the downward flux of chemically undersaturated percolating water, freeing silica and cations which were redeposited at depth as opal having a disordered low cristobalite form. Some quartz was also precipitated in the deeper fractures. Hydrogeochemically silica precipitation would have required a component of percolating water to have undergone a combination of a pH and a dissolved silica change compared to the measured values of pH and dissolved silica in groundwater samples. The chemistry of groundwater samples and analysis of deep core samples of tuff indicated precipitation of clay minerals controlling silica concentrations in saturated portions of the tuff.

From the stable isotope data and the indication of high water-rock ratios, recharge from precipitation and through fractures at the Apache Leap site has extended to a depth of at least 25 meters. In deeper, saturated portions of the tuff, the oxygen isotope data of authigenic, fracture-filling calcite indicated equilibrium conditions with groundwater. Groundwater chemistry data also indicated saturation with respect to calcite. However, oxygen isotope data of groundwater in the saturated portion of tuff was isotopically lighter than oxygen isotope values calculated for percolating water in the unsaturated tuff. Recharge to saturated tuff may have been fast considering these observations, and most likely occurred through extensive, high inclination fractures without undergoing significant evaporation.

Stable isotopes of oriented fracture-filling samples and rock matrix samples of variably-saturated tuff have been shown by this study to be a useful hydrogeochemical indicator tracing low temperature rock-

water interaction. However, samples from more extensive and deeper portions of the tuff would be needed in order to better interpret the isotopic profiles of authigenic minerals and to show how they relate to the isotopic composition of deep percolating water. Also needed would be data concerning the seasonal variations of isotopic compositions of meteoric water and surface runoff to better understand the extent and influence seasonal recharge had on precipitating authigenic minerals.

A thorough analysis of groundwater and of surface water and precipitation for chemical and isotopic properties could further delineate the relative component of recharge to the aquifer. Used in conjunction with the results from this study of the chemical and isotopic composition of authigenic minerals, this information would lead to more quantitative relationships between groundwater conditions and unsaturated zone properties and flow conditions in fractured rock.

APPENDIX A

PROCEDURE AND CORE LOGS OF DRILLING OPERATION AT THE APACHE LEAP SITE

The design of the Apache Leap site near Superior, Arizona is shown in Figure 2.7. The boreholes, drilled in September 1985, are inclined at an angle of 45° and are offset from each other by a vertical distance of 10 meters. The boreholes vary in length from 18.3 meters for the uppermost (X1), to 46.6 for the lowermost (X3), with the intermediate borehole (X2) having a length of 32.6 meters. This design allows for the monitoring of fluid and solute flow in both the horizontal and vertical directions. To determine the alignment of the boreholes, a down-hole gyroscope was used with an automatic camera (Eastman Whipstock Co., Long Beach, CA). The photographs of the gyroscope at selected depths indicate that the total displacement of the borehole from design specifications ($262^\circ/45^\circ$) amounted to less than 3° vertically and 2° horizontally (Table A.1).

The construction of the three boreholes in the non- to partially-welded tuff at the Apache Leap site was contracted to Muncy Drilling Inc., Phoenix, Arizona. The drilling procedure used Longyear manufactured surface set HQ oversized diamond-core bits (10.2 cm) and a stabilizer equivalent to the borehole diameter to hold the hole straight. The core drill, a Longyear model 38, had a 0.6 meter hydraulic head stroke powered by a 3-53 Detroit diesel engine. The equipment also had steel derricks for 6.1 meter pulls using a wire-line hoist. The unit, capable of drilling vertical or angle holes, had a depth rating of 580 meters using NQ wire-line drill rods. The drilling operation used water supplied by a 535 Bean pump with a maximum delivering capacity of 35 gallons per minute.

Table A.1. Construction and design details of boreholes at the Apache Leap site, near Superior, Arizona.

Borehole	Diameter	Total Length	Bearing/Plunge/Borehole Length ¹
X1	15.2 cm (0-0.9 m) ² 10.2 cm (0.9-18.3 m)	18.4 m	261°/45°SW/4.6 m 260°/45°SW/18.0 m
X2	15.2 cm (0-0.9 m) ² 10.2 cm (0.9-32.6 m)	32.6 m	262°/46°SW/4.6 m 262°/48°SW/31.7 m
X3	15.2 cm (0-0.9 m) ² 10.2 cm (0.9-12.8 m) 9.9 cm (12.8-46.6 m) ³	46.6 m	262°/45°SW/4.6 m 262°/46°SW/23.3 m 262°/47°SW/45.7 m

¹Design specifications required boreholes to have a bearing and plunge of 262°/45°. These data are from a borehole survey taken at selected borehole lengths using a down-hole gyroscope.

²A steel casing with an inside diameter of 12.7 cm and 1.25 m long was emplaced from land surface to a borehole length of approximately 0.9 meters to maintain the integrity of the borehole wall near land surface. Values in parentheses are distances along the inclined borehole where these diameters exist.

³Due to excessive bit wear when drilling borehole X3, at a borehole length of 13 meters a new bit with a slightly smaller diameter (9.9 cm) was used to drill to the total borehole length of 46.6 meters.

The two shallowest boreholes (X1 and X2) were drilled using a specially made HQ oversized diamond bit, 10.2 centimeters in diameter, and a standard HQ core barrel, 1.5 meters long and 6.5 centimeters in diameter. The deepest borehole (X3) was drilled to a borehole length of 13 meters with these same specifications. However, due to excessive wearing of the bit, a standard HQ oversized bit 9.9 centimeters in diameter was used to drill the remaining 33.6 meters. The HQ size drilling was selected to minimize breakage of the core in the core barrel and thus to preserve fracture orientation. Core recovery for the three boreholes averaged over 95 percent.

Scribed cores with a diameter of 6.4 centimeters were obtained from the boreholes. The scribing tool (Allied Machine Works, Phoenix, Arizona) that was used to preserve core orientation provided an orientation mark every 3.1 meters on the core. The cores, once logged in the laboratory, provided information regarding the location and orientation of fractures within the boreholes, and of the composition and occurrence of fracture-filling minerals. A description of the cores and fractures from the three boreholes, along with orientation data of the fracture planes, is presented in Tables A.2, A.3, and A.4.

Table A.2. Fracture Description and Orientation Log of Borehole X1,
Apache Leap Site, White Unit, Apache Leap tuff.

Fracture Distance from Surface along Borehole (m)	Fracture Distance from Surface Vertically (m)	Orientation of Fracture ¹		Description of Fracture Surface
		Strike	Dip	
1.77	1.25	345°	75°	Subplanar, open. No secondary mineralization; fracture possibly induced by drilling.
4.15	2.93	352°	85°	Very planar, open. Orange-red staining with patches of dark brown smectite. Ubiquitous, white, translucent, subhedral to anhedral quartz forms a crust on fracture surface. Sampled fracture-filling quartz for oxygen isotope ratio.
4.33	3.06	215°	12°	As above. Rock matrix appears porous, most notably in areas of pumice lapilli; core breaks frequently near areas of dense pumice lapilli. Sampled fracture-filling quartz for oxygen isotope ratio. Sampled for thin section.
4.36	3.08	346°	73°	As above. Also with trace calcite. Sampled fracture-filling calcite for oxygen isotope ratio.

Table A.2.--Continued

Fracture description and orientation log of
Borehole X1.

Fracture Distance from Surface along Borehole (m)	Fracture Distance from Surface Vertically (m)	Orientation of Fracture ¹		Description of Fracture Surface
		Strike	Dip	
4.63	3.27	329°	76°	As above. Orange-red staining forms rinds on fracture surface.
4.79	3.39	336°	84°	Planar, open. Less weathered; anhedral quartz forms crust on fracture surface.
5.73	4.05	326°	82°	Planar, closed. Orange-red stained unidentified carbonate.
6.92	4.89	359°	75°	Planar, open. Trace of anhedral, platy quartz on fracture surface.
7.13	5.04	358°	69°	Subplanar, open, possibly induced. Trace of patchy masses of anhedral quartz, fracture surface less weathered.
8.93	6.31	031°	48°	Very planar, open. Ubiquitous quartz forms crusty patches on fracture surface.

Table A.2.--Continued

Fracture description and orientation log of
Borehole X1.

Fracture Distance from Surface along Borehole (m)	Fracture Distance from Surface Vertically (m)	Orientation of Fracture ¹		Description of Fracture Surface
		Strike	Dip	
9.78	6.92	035°	64°	Planar, open. Less weathering; trace of patchy masses of anhedral quartz. Below this borehole length rock appears less porous, more competent, and breaks less frequently in areas of dense pumice lapilli.
Total Borehole Length 18.44 (m).				
No observed fractures in core of borehole X1 below 6.92 (m).				

¹See Appendix B for method of determining fracture orientation.

Table A.3. Fracture Description and Orientation Log of Borehole X2,
Apache Leap Site, White Unit, Apache Leap tuff.

Fracture Distance from Surface along Borehole (m)	Fracture Distance from Surface Vertically (m)	Orientation of Fracture ¹		Description of Fracture Surface
		Strike	Dip	
1.77	1.25	359°	82°	Planar, open. Some frosted white, anhedral quartz. Trace slickensides on reddish brown, lustrous, unidentified clay. Sampled for thin section.
2.32	1.64	300°	56°	Planar, open. Ubiquitous quartz and opaline silica. Quartz is frosted white and anhedral; opaline silica is clear and globular, sometimes "sitting" on pedestals in pitted pumice lapilli.
2.38	1.68 ²			Very subplanar, partially closed, no orientation possible. Secondary mineralization as above.
2.47	1.75	359°	85°	Planar, open. Some patchy masses of anhedral quartz.
3.63	2.57 ²			Very subplanar, partially closed, no orientation possible. Fracture possibly induced. Ubiquitous quartz and opaline silica in pumice lapilli.
3.69	2.61 ²			As above. Rock matrix is porous and very friable in areas of dense, pitted pumice lapilli.

Table A.3.--Continued

Fracture description and orientation log of
Borehole X2.

Fracture Distance from Surface along Borehole (m)	Fracture Distance from Surface Vertically (m)	Orientation of Fracture ¹		Description of Fracture Surface
		Strike	Dip	
3.75	2.65 ²			As above.
4.85	3.43	191°	17°	Subplanar, open. Possibly induced. Secondary mineralization as above.
5.18	3.66	354°	84°	Planar, open. Ubiquitous, patchy masses of anhedral quartz forms crust on fracture surface. Fracture-filling quartz sampled for oxygen isotope ratio. Sampled for thin section.
6.07	4.29 ²			Very subplanar, partially closed, no orientation possible. Platy, crust-like quartz forms in jagged fracture and surrounds lithic fragment.
8.50	6.01 ²			Very subplanar, partially closed. No orientation possible because of high core breakage near fracture. Ubiquitous, anhedral, platy quartz on core fragments of fracture surface.
9.45	6.68	347°	78°	Planar, open. Secondary mineralization as above. Also trace calcite. Sampled for thin section.

Table A.3.--ContinuedFracture description and orientation log of
Borehole X2.

Fracture Distance from Surface along Borehole (m)	Fracture Distance from Surface Vertically (m)	Orientation ¹ of Fracture		Description of Fracture Surface
		Strike	Dip	
10.67-12.19	7.54-8.62	low core recovery		Core barrel mismatch. Numerous core breaks in areas of dense pumice lapilli.
13.38	9.46	331°	75°	Planar, open. Patchy masses of translucent, platy quartz. Masses of quartz sometimes pitted.
13.56	9.59	342°	59°	As above. Sampled for thin section. Driller estimates about 200 gallons of water lost in drilling from surface to vertical depth of 10 meters.
15.48	10.95	020°	17°	Very planar, open. Fault; slickensides on reddish brown to gray unidentified clay. Pumice lapilli indistinct, normally stained reddish brown and pitted.
15.51	10.97	020°	17°	As above. At borehole length 16.25 m core breaks near large lithic fragment. Platy, frosted quartz on core fragments near break.
18.68	13.21	032°	47°	Subplanar, open. Trace of anhedral, platy, frosted quartz. Masses of quartz sometimes pitted.

Table A.3.--Continued

Fracture description and orientation log of
Borehole X2.

Fracture Distance from Surface along Borehole (m)	Fracture Distance from Surface Vertically (m)	Orientation of Fracture ¹		Description of Fracture Surface
		Strike	Dip	
19.96	14.11	327°	89°	Subplanar, open. Secondary mineralization as above. Fracture-filling quartz sampled for oxygen isotope ratio.
21.03	14.87	334°	67°	Planar, open. Anhedral, frosted white quartz forms crusted patches.
21.67	15.32	016°	30°	Subplanar, partially closed. Cloudy subhedral calcite (1 to 4 mm) and anhedral quartz fill fracture. Fracture-filling quartz and calcite sampled for isotope ratios.
22.49	15.90	347°	79°	Subplanar, open. Ubiquitous quartz and trace calcite, both platy, anhedral, and form crusts on fracture surface. Fracture-filling quartz sampled for oxygen isotope ratio.
24.78	17.52	339°	76°	Planar, closed. Anhedral, frosted white quartz forms patchy crusts. Core becoming more competent, breaks less frequently.

Table A.3.--Continued

Fracture description and orientation log of
Borehole X2.

Fracture Distance from Surface along Borehole (m)	Fracture Distance from Surface Vertically (m)	Orientation of Fracture ¹		Description of Fracture Surface
		Strike	Dip	
28.47	20.13	303°	60°	Subplanar, closed. Anhedral quartz and calcite fill fracture. Pumice lapilli more distinct, equidimensional, largest 5 cm. Sampled for thin section.
28.56	20.19 ²			Very subplanar, closed. Subhedral to anhedral quartz fills fracture, trace calcite.
28.65	20.26	044°	63°	Subplanar, open. Anhedral quartz and trace calcite. Sampled for thin section.
29.23	20.67	318°	78°	Subplanar, closed. Trace quartz filling fracture.
29.38	20.77	003°	72°	Subplanar, partially closed. Trace quartz.
Total Borehole length 32.61 (m). ³				
No observed fractures in core of borehole X2 after 29.38 (m).				

¹See Appendix B for methods of determining fracture orientation.

²No orientation possible either due to very subplanar fracture or high degree of mineralization closing fracture or loss of orientation due to drilling.

Table A.3.--Continued

Fracture description and orientation log of
Borehole X2.

³Driller estimates total water loss drilling borehole X2 was about 800 gallons. Total drilling time was about nine hours.

Table A.4. Fracture Description and Orientation Log of Borehole X3, Apache Leap Site, White Unit, Apache Leap Tuff.

Fracture Distance from Surface along Borehole (m)	Fracture Distance from Surface Vertically (m)	Orientation of Fracture ¹		Description of Fracture Surface
		Strike	Dip	
1.62	1.15 ²			Planar, open. Lost orientation. Ubiquitous, orange-red staining on fracture surface. Trace anhedral quartz and opaline silica. Rock matrix porous, friable, and breaks frequently in areas of dense, pitted pumice lapilli.
2.74	1.94 ²			As above.
4.15	2.93	356°	74°	Subplanar, open. Core badly broken and friable, orientation may be erroneous. Ubiquitous, opaline silica and anhedral to subhedral, platy quartz in pitted pumice lapilli.
4.66	3.30	338°	14°	As above.
5.52	3.90 ²			As above. Lost orientation.
7.01	4.96	019°	06°	As above. Orientation good.
7.01-7.62	4.96-5.39	low core recovery		Core badly broken, lost orientation. Ubiquitous, opaline silica and anhedral to subhedral quartz.

Table A.4.--Continued

Fracture description and orientation log of
Borehole X3.

Fracture Distance from Surface along Borehole (m)	Fracture Distance from Surface Vertically (m)	Orientation of Fracture ¹		Description of Fracture Surface
		Strike	Dip	
7.62	5.39 ²			As above.
7.62-8.53	5.39-6.03	low core recovery		As above. Driller estimates about 250 gallons of water lost in drilling from surface to a vertical depth of 6 meters.
8.84	6.24	005°	79°	Subplanar, open, core badly broken. Some anhedral quartz and opaline silica on fracture surface and in pitted pumice lapilli. trace brownish red, powdery clay.
9.02	6.38	337°	76°	Planar, open. Ubiquitous masses of platy quartz, some subhedral. Trace orange-red, lustrous unidentified clay.
10.12	7.16	020°	73°	Planar, possibly induced. No secondary mineralization. Less weathered.
12.44	8.80	332	83°	Planar, partially closed. Masses of platy quartz, some subhedral.

Table A.4.--Continued

Fracture description and orientation log of
Borehole X3.

Fracture Distance from Surface along Borehole (m)	Fracture Distance from Surface Vertically (m)	Orientation of Fracture ¹		Description of Fracture Surface
		Strike	Dip	
13.32	9.42	343°	76°	Planar, open. Ubiquitous, patchy masses of platy anhedral quartz. Core becoming less deeply pitted in areas of pumice lapilli, breaks less frequently when removed from core barrel.
15.85	11.21	336°	66°	As above.
18.62	13.17	011°	67°	Planar, open. Possible fault; some slickensides on reddish brown, lustrous, unidentified clay. Trace patchy masses of anhedral quartz.
18.90	13.36	006°	71°	Planar, partially closed. Some patchy masses of platy quartz. Fracture plane almost parallel to above.
21.03	14.87	334°	71°	Planar, open. Trace reddish brown, powdery unidentified clay.
25.60	18.10	010°	67°	Planar, open. Ubiquitous patches of platy anhedral quartz. Pumice lapilli in rock matrix indistinct, some stained reddish brown.

Table A.4.--Continued

Fracture description and orientation log of
Borehole X3.

Fracture Distance from Surface along Borehole (m)	Fracture Distance from Surface Vertically (m)	Orientation of Fracture ¹		Description of Fracture Surface
		Strike	Dip	
25.73	18.19	336°	66°	Planar, open. Some patches of platy anhedral to subhedral quartz, trace brownish red, unidentified clay. Fracture plane almost orthogonal to above.
28.68	20.28	008°	74°	Planar, open. Some masses of platy quartz. Pumice lapilli becoming more distinct, less pitted.
29.66	20.97	329°	72°	Planar, open. Possibly induced by drilling. Trace quartz.
29.81	21.08	011°	66°	Very planar, partially closed. Anhedral, translucent masses of platy quartz forms crust.
30.54	21.60	312°	87°	Planar, open. Fault; slickensides on reddish brown, lustrous, unidentified clay.
30.60	21.64	336°	78°	Planar, open. Masses of platy, anhedral quartz.
31.09	21.98	328°	66°	Subplanar, open. Possibly induced. Trace anhedral quartz near pumice lapilli.

Table A.4.--Continued

Fracture description and orientation log of
Borehole X3.

Fracture Distance from Surface along Borehole (m)	Fracture Distance from Surface Vertically (m)	Orientation of Fracture ¹		Description of Fracture Surface
		Strike	Dip	
31.58	22.33	336°	64°	Subplanar, open. Patchy masses of anhedral quartz.
31.91-32.52	22.57-23.00	low core recovery		Core badly broken, no orientation possible. Planar to subplanar fracture with trace slickensides. Ubiquitous, platy, anhedral quartz.
32.95	23.30	332°	85°	Subplanar, partially closed. Patches of anhedral quartz.
33.65	23.79	337°	82°	Subplanar, open. Trace of platy quartz.
34.47	24.37	339°	87°	Very planar, open. Some patchy masses of platy quartz. Sampled quartz for oxygen isotope ratio.
34.60	24.47	342°	72°	As above.
35.14	24.85	324°	81°	Planar, open. Some patchy masses of anhedral quartz. Also trace reddish brown, unidentified clay.
35.23	24.91	323°	80°	As above.
35.97	25.43	316°	36°	As above. Trace slickensides. Sampled fracture-filling quartz for oxygen isotope ratio.

Table A.4.--Continued

Fracture description and orientation log of
Borehole X3.

Fracture Distance from Surface along Borehole (m)	Fracture Distance from Surface Vertically (m)	Orientation of Fracture ¹		Description of Fracture Surface
		Strike	Dip	
42.25	29.88	052°	55°	Subplanar, closed. Some calcite associated with reddish brown unidentified clay fill fracture in layers. White, equidimensional (as large as 5 cm) pumice lapilli becoming very distinct.
42.64	30.15	309	86°	Planar, open. Trace platy, anhedral quartz associated with reddish brown, lustrous clay.
46.30	32.74 ²			Subplanar, closed. Mostly calcite filling fracture. Pumice lapilli nearly equidimensional; outside boundary usually rimmed by reddish brown staining. Sampled for thin section.

Total borehole length 46.64 (m).

No observed fractures in core of
borehole X3 after 46.30 (m).

¹See Appendix B for methods of determining fracture orientation.

²No orientation possible either due to very subplanar fracture or high degree of mineralization closing fracture or loss of orientation due to drilling.

APPENDIX B

FRACTURE ORIENTATION OF DRILL CORE FROM THE APACHE LEAP SITE

The absolute orientations of fractures in the drill core from the Apache Leap site were determined by measurement of two angles:

- 1) the angle between the fracture plane and core axis; and
- 2) the angle between the major axis of the elliptical trace of the fracture plane and the scribe line, measured on the circumference of the core (see Figure B.1).

A scribing tool oriented the core while it was being drilled by etching the first piece of core in a run before drilling commenced. The apparent angles of the fracture surfaces were measured in the laboratory using a goniometer for drill core.

Mathematical, graphical, and mechanical methods for correcting apparent dips of fractures in oriented drill core taken from angled boreholes have been described by Zimmer (1963), McClellan (1948), and Johnson (1939). Using these studies, the orientations of fractures in the drill core from the Apache Leap site were determined using a combination of mechanical and mathematical techniques. A graphical technique using a stereonet was used to verify the results (Goodman, 1976). Basically, the concept requires imagining the borehole in a vertical position when the observed angles are measured for a fracture plane intersecting the core. The borehole is then tilted into its true position and the resulting true dip and strike are calculated.

In Figure B.2, the fracture plane passes through the origin of the coordinates, and at the origin the line OP represents a normal to the fracture plane. Triangles constructed for a mathematical solution, shown in Figure B.3, have key angles defined as follows:

δ = direction of dip;

Figure B.1. Schematic diagram of fracture plane ellipse.

Figure B.3. Key triangles for mathematical solution of fracture orientation in an angled borehole.

δ = amount of total dip (vertical);

β = dip component in XZ plane; and

ϕ = the complement of the angle between the axis of tilt
and the fracture plane normal.

As the borehole is tilted, ϕ remains constant and β varies by the amount of tilt. A goniometer, constructed after Goodman (1976) for drill core, was used to measure the two apparent angles of γ and δ . The final values of true azimuthal and dip angles were calculated using the mathematical technique described below.

Curtis (1939) expressed four equations using the above relationships:

$$\cos \delta = \cos \beta \cos \phi \quad (\text{B.1})$$

$$\sin \phi = \sin \gamma \sin \delta \quad (\text{B.2})$$

$$\tan \beta = \tan \delta \cos \gamma \quad (\text{B.3})$$

$$\tan \phi = \tan \gamma \sin \beta \quad (\text{B.4})$$

These equations express any four variables in terms of two of the others. By measuring the dip in the drill core (δ_1) and the direction of dip (γ_1), the parameters ϕ_1 and β_1 can be calculated using equations B.2 and B.3. Here the variables with subscript 1 designate values before tilting and those with subscript 2 designate after tilting the borehole into its true position. After the borehole is tilted, ϕ_1 remains constant, and β_1 becomes:

$$\beta_2 = \beta_1 + \Delta \quad (\text{B.5})$$

where:

Δ = amount of tilt of the borehole from the vertical.
The values of δ_2 (true dip) and γ_2 (true direction of dip) are

then calculated from equations B.1 and B.4, using the value of β_2 . As an example, assume:

- 1) azimuthal bearing and plunge of borehole = $262^\circ/45^\circ$;
- 2) measured dip of fracture plane in core, $\beta_1 = 30^\circ$; and
- 3) measured direction of observed dip of fracture plane, $\gamma_1 = 11^\circ$.

Values for the true strike and dip of the fracture plane intersecting the core can then be found as follows:

- 1) find β_1 ,

$$\tan \beta_1 = \tan \delta_1 \cos \gamma_1,$$

$$\beta_1 = 30^\circ;$$
- 2) find ϕ ,

$$\tan \phi = \tan \gamma_1 \sin \beta_1,$$

$$= 6^\circ;$$
- 3) find β_2 ,

$$\beta_2 = \beta_1 + \Delta,$$

$$\beta_2 = 75^\circ;$$
- 4) find γ_2 ,

$$\tan \gamma_2 = \tan \phi / \sin \beta_2,$$

$$\gamma_2 = 7^\circ; \text{ and}$$
- 5) find δ_2 ,

$$\tan \delta_2 = \tan \beta_2 / \cos \gamma_2,$$

$$\delta_2 = 75^\circ.$$

The true strike of the fracture plane is determined from γ_2 (7°).

Because γ_1 is measured counter-clockwise from the direction of borehole

deflection, the direction of the true dip must be measured from γ_1 in the same direction. The true dip direction is then 257° ; the value of the true strike is $\pm 90^\circ$, or 345° . The true strike and dip of this example is N15W/75SW, or equivalently $345^\circ/75^\circ$, using the azimuthal bearing for strike and the right-hand rule directed downward for dip.

Zimmer (1963) used the above geometry, expressing the equations as:

$$\begin{aligned}\Sigma &= \tan^{-1} ((\cos \gamma_1 \sin \Delta + \tan \delta_1 \cos \Delta) / \sin \gamma_1); \\ \delta_2 &= \cot^{-1} (\tan \Delta / (\sin \tan^{-1} (\cos \gamma_1 \tan \Delta + \tan \delta_1 / \sin \gamma_1 \tan \Delta)) \\ &\quad + \cot^{-1} (\tan \delta_1 / \sin \tan^{-1} (\cos \gamma_1 \tan \delta_1 \\ &\quad + \tan \Delta / \sin \gamma_1 \tan \delta_1))); \end{aligned}$$

where:

Σ = strike $\pm$ azimuth of borehole axis;

δ_2 = dip of the fracture plane and the horizontal plane perpendicular to the strike;

Δ = inclination of the borehole from the horizontal;

δ_1 = vertical angle between the major axis of the fracture plane ellipse and a normal to the fracture plane (see Figure B.1); and

γ_1 = azimuthal angle between the lower axis of the fracture plane ellipse and the scribe line.

The fracture plane data from the Apache Leap site were analyzed for true orientations using these latter equations for Σ and δ_2 . Results are presented in the fracture description and orientation logs of the drill core from the Apache Leap site, Tables A.2, A.3, and A.4.

APPENDIX C

METHODS OF X-RAY DIFFRACTOMETRY AND X-RAY DIFFRACTION PATTERNS OF SAMPLES

This appendix presents x-ray diffraction (XRD) patterns of fracture-filling and rock matrix minerals used to verify the purity of the samples before analysis of stable isotopic ratios (Figures D.1 to D.5). For x-ray analysis a mineral sample was finely ground in an agate mortar and pestle, dispersed with anhydrous isopropyl alcohol on a glass slide, and allowed to air dry. A Siemens diffractometer was used with graphite monochromatic filtered CuK alpha radiation equipped with a 0.15° detector slit and 1° diffractometer beam. The samples were normally scanned at 2° per minute and at 10^3 impulses per second over a range of 3° to 70° 2-theta.

Figure C.1. XRD patterns of representative samples of fracture-filling quartz, white unit, Apache Leap tuff. Q identifies diffraction peaks of quartz.

Figure C.2. XRD pattern of fracture-filling opal, white unit, Apache Leap tuff.
Q identifies diffraction peaks of quartz.

Figure C.3. XRD pattern of fracture-filling calcite associated with other minerals, white unit, Apache Leap tuff. Cl, Q, F, and Cr identify diffraction peaks of calcite, quartz, feldspar, and cristobalite.

Figure C.4. XRD patterns of fracture-filling of palygorskite-sepiolite, white to brown units, Apache Leap tuff. P-S identify diffraction peak of palygorskite-sepiolite.

Figure C.5. XRD patterns of rock matrix opal samples, white unit, Apache Leap tuff. Cr identifies diffraction peaks of cristobalite.

APPENDIX D

PROCEDURE FOR ISOLATION OF OPAL IN ROCK MATRIX SAMPLES OF TUFF

Crush approximately 1 kg of rock in a carbide mill and sieve a sample fraction between 100 to 170 mesh (88 μm to 149 μm) to yield about 300 g.

Heavy Liquid Separation

1. Wash sample to remove rock dust and dry at 80°C overnight prior to heavy liquid separation.
2. Transfer about 100 g of sample to a tetrabromomethane and acetone mixture at a specific gravity of 2.38.
3. Separate float (<2.38) fraction and wash with acetone to remove all traces of tetrabromomethane.
4. XRD for purity, and repeat steps 2 and 3 if quartz is present. If glass is present repeat at a specific gravity of 2.30.

Acid-Base Hydrofluorosilicic Acid (ABFS) Treatment

1. Crush and sieve about 300 mg of sample to pass through a 325 mesh (<50 μm).
2. Clean sample ultrasonically in 6N HCl 3 times or until extract is colorless; wash three times with water.
3. Boil in 0.5N NaOH for 2.5 minutes with a ratio of 1 ml of NaOH per milligram of residue; wash with water.
4. Wash three times with 3N HCl; 3 times with water.
5. Treat about 150 mg of sample with 30 percent H_2SiF_6 for 3 days at 20°C to remove feldspars.
6. XRD for purity, repeat step 5 if feldspar impurities are present.

Adapted from Henderson et al. (1972).

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