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Supergene destruction of a hydrothermal replacement alunite deposit at Big Rock Candy Mountain, Utah: mineralogy, spectroscopic remote sensing, stable-isotope, and argon-age evidences

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Abstract

Big Rock Candy Mountain is a prominent center of variegated altered volcanic rocks in west-central Utah. It consists of the eroded remnants of a hypogene alunite deposit that, at ~21 Ma, replaced intermediate-composition lava flows. The alunite formed in steam-heated conditions above the upwelling limb of a convection cell that was one of at least six spaced at 3- to 4-km intervals around the margin of a monzonite stock. Big Rock Candy Mountain is horizontally zoned outward from an alunite core to respective kaolinite, dickite, and propylite envelopes. The altered rocks are also vertically zoned from a lower pyrite–propylite assemblage upward through assemblages successively dominated by hypogene alunite, jarosite, and hematite, to a flooded silica cap. This hydrothermal assemblage is undergoing natural destruction in a steep canyon downcut by the Sevier River in Marysvale Canyon. Integrated geological, mineralogical, spectroscopic remote sensing using AVIRIS data, Ar radiometric, and stable isotopic studies trace the hypogene origin and supergene destruction of the deposit and permit distinction of primary (hydrothermal) and secondary (weathering) processes. This destruction has led to the formation of widespread supergene gypsum in cross-cutting fractures and as surficial crusts, and to natrojarosite, that gives the mountain its buff coloration along ridges facing the canyon. A small spring, Lemonade Spring, with a pH of 2.6 and containing Ca, Mg, Si, Al, Fe, Mn, Cl, and SO₄, also occurs near the bottom of the canyon. The ⁴⁰Ar/³⁹Ar age (21.32±0.07 Ma) of the alunite is similar to that for other replacement alunites at Marysvale. However, the age spectrum contains evidence of a 6.6-Ma thermal event that can be related to the tectonic activity responsible for the uplift that led to the downcutting of Big Rock Candy Mountain by the Sevier River. This ~6.6 Ma event also is present in the age spectrum of supergene natrojarosite forming today, and probably dates the beginning of supergene alteration at Big Rock Candy Mountain. The δ³⁴S value (11.9‰) of alunite is similar to those for replacement alunite from other deposits in the Marysvale volcanic field. The δ³⁴S values of natrojarosite (0.7‰ to −1.2‰)

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are similar to those for aqueous sulfate in Lemonade Spring, but are larger than those in pyrite (0.4‰ to −4.7‰). The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ values of gypsum show an excellent correlation, with values ranging from 15.2‰ to −5.2‰ and 7‰ to −8.2‰, respectively. The stable-isotope data indicate that the aqueous sulfate for gypsum is a mixture derived from the dissolution of hypogene gypsum and alunite, and from the supergene oxidation of pyrite. The aqueous sulfate for the natrojarosite, however, is derived largely from the supergene oxidation of pyrite, with a minor contribution from the dissolution of alunite and gypsum. The exceptional detailed spectral mapping capabilities of AVIRIS led to the recognition of a small amount of jarosite that is probably the top of the steam-heated system that produced the primary hypogene alteration at Big Rock Candy Mountain. Published by Elsevier B.V.

Keywords: Supergene; Alunite; Stable isotopes; Natrojarosite; Jarosite; Marysvale

1. Introduction and previous work

Oh the buzzin' of the bees, In the cigarette trees, Near the soda water fountain, At the Lemonade Springs, Where the bluebird sings, On the Big Rock Candy Mountain

The chorus of a hobo song written by Harry “Haywire Mac” McClintock and popularized by Burl Ives in the 1930s called attention to a prominent

yellow, brown, and white hill of altered rock (Fig. 1) in west-central Utah. Located along the Sevier River in Marysvale Canyon, Big Rock Candy Mountain (Fig. 2) is on a scenic route to Zion and Bryce Canyon national parks. Tourists have long stopped to admire the sight and to drink from Lemonade Spring, a mineral-rich spring that emanates from the base of the hill and has been rumored to have healing powers. Today, motorists who venture south from the newly constructed Interstate 70 are still rewarded with the

Fig. 1. Big Rock Candy Mountain, Utah, is a prominent center of hydrothermally altered and surficially weathered andesitic to dacitic lava flows, volcanic breccias, and tuffs. The buff color is due to the presence of natrojarosite and kaolinite that form by modern surficial oxidation of hydrothermally introduced pyrite; the white, subhorizontal layer that crops out at the top of the hill is 21 Ma replacement alunite. View is looking south along U.S. Highway 89.

Fig. 2. Index map showing the location of Big Rock Candy Mountain, the spatial relation between replacement alunite cells and similar age quartz monzonite plutons, and calderas within the Marysville volcanic field.

sights of the variegated volcanic rocks, old mining districts, and historic, small towns within the Marysville volcanic field.

Hydrothermally altered volcanic centers containing replacement alunite are widespread in the Marysville volcanic field. These replacement centers, discussed by Cunningham et al. (1984), Rye et al. (1992), and Rye and Alpers (1997), have been shown to have a classical steam-heated origin. The Big Rock Candy Mountain center is unique in that exposure of its lower parts by downcutting of the Sevier River has led to intense supergene alteration and the formation of abundant natrojarosite and gypsum. A low-temperature spring emanating from the mountain also has a low pH and a composition typical of solutions that produce natrojarosite. The mountain was not studied earlier by Cunningham et al. (1984) but was assumed to have had an origin similar to that of the other replacement alunite centers at Marysville. The current study integrates mineralogy, remote-sensing spectroscopy (AVIRIS), stable isotopes, and Ar radiometric ages to

show that the hypogene history of Big Rock Candy Mountain is indeed similar to that of the other replacement alunite deposits at Marysville, but that it has a subsequent supergene evolution caused by the downcutting of the Sevier River, that led to its present unique mineral assemblage and appearance.

Alunite at Big Rock Candy Mountain occurs mainly as a subhorizontal layer near the top of the cliff that forms the canyon wall (Fig. 1). The mineral was first recognized in the Marysville volcanic field in 1910 (Butler and Gale, 1912), and the first published analysis of alunite from Big Rock Candy Mountain was in 1938 (Callaghan, 1938). Paul Kerr and his students, in the course of investigating uranium deposits near Marysville, published the first geological description of Big Rock Candy Mountain (Green, 1954; Kerr et al., 1957). Eardley and Beutner (1934) described the geomorphology of the pediments and faults near Marysville Canyon. The area was included in geological maps at various scales including Callaghan and Parker (1962; 1:62,500), Steven and Cunningham (1979; 1:24,000), Cunningham et al. (1983; 1:50,000), and Rowley et al. (2001; 1:100,000). The area has recently been used as a natural laboratory for evaluating high spectral and spatial resolution remotely sensed mapping of alteration mineralogy by the NASA Airborne Visible/Infrared Imaging Spectrometer (AVIRIS; Vane, 1987). The Marysville volcanic field and Tushar Mountains were chosen for the remote-sensing experiments because of the excellent geological base that is available in the Marysville volcanic field, the extensive suite of well-exposed, hydrothermally altered rocks, and the abundance of past local mining activity for precious metals, base metals, and uranium, which have spurred interest both in mineral exploration and in environmental studies.

2. Geological setting

Geological mapping of the Marysville volcanic field has shown that the host rocks of Big Rock Candy Mountain are part of a stratovolcano that is centered northwest of the Monroe Peak caldera and is well exposed in Marysville Canyon (Fig. 2). The volcano consists of andesitic to dacitic lava flows, lahars, volcanic breccias, and local tuffs that mostly are propylitically altered. They are part of the Bullion

Canyon Volcanics Formation. This volcano is older than 27 Ma because the Three Creeks Tuff Member of that age (Steven et al., 1979) unconformably overlies it approximately 3.5 km northwest of Big Rock Candy Mountain (Cunningham et al., 1983; Rowley et al., 2001). Patches of late Tertiary sands and gravels of the Sevier River Formation locally overlie the stratovolcano. The Sevier River flows in a serpentine path through Marysvale Canyon, following prominent incised meanders, as can be seen in Fig. 2. Northeast, across the river from Big Rock Candy Mountain, is a small rhyolite lava flow called the Rhyolite of Big Star (Cunningham et al., 1983) that has been dated at about 14 Ma (Bassett et al., 1963) and overlies the Big Star alteration center.

Many of the spatial and geological relationships of alteration-mineral assemblages at Big Rock Candy Mountain can be seen in Fig. 1 and in the AVIRIS data discussed below. The alunite is present mostly in a subhorizontal layer, approximately 10 m thick, located at the top of the cliff face shown in Fig. 1. AVIRIS data also show that patches of jarosite and superjacent hematite-rich rock overlie the alunite and extend to the high point of the ridge. The alunitic layer is tuffaceous and extends back into the hill. Natrojarosite, along with associated minor kaolinite and goethite, makes up the soft, yellow-colored material that covers the sides of the cliff (Fig. 1) and constitutes most of the face of the hill. The natrojarosite is most abundant at the base, where it has washed downslope and accumulated. Pyrite-bearing, dark lava flows and associated volcanic breccias are the dark brown areas in Fig. 1. The natrojarosite forms by weathering oxidation of pyrite and alteration of the host lava flows and is transitional to them. Gypsum, as transparent crystals (selenite), occurs in late fractures that cut pyrite-bearing lava flows, and is ubiquitous across all alteration zones at Big Rock Candy Mountain; gypsum is forming today as evaporation crusts on weathering surfaces, is common in colluvium at the base of the mountain, and is present as an efflorescent crust near the uppermost part of the section of altered rocks. Kaolinite is associated with the natrojarosite, and montmorillonite is associated with the dark, relatively unaltered, volcanic rocks.

Lemonade Spring is a small spring located behind the motel and is the only active spring on the mountain. The spring emanates from a small stream

valley cut in variably altered lava flows. When sampled in September 2000, it was flowing at about 2 L min⁻¹. The measured pH was 2.6 and the temperature, although not measured, was probably near 20 °C. The spring was not effervescing. In August 2001, the spring was almost dry and the surrounding runoff area contained evaporate crusts of secondary minerals discussed later.

2.1. Replacement alunite deposits

Marysvale is widely known for its replacement and vein-type alunite deposits. During World War I, alunite from both types of deposits was mined at Marysvale as a source for potash, and during World War II, shortages of bauxite resulted in renewed exploration and development of alunite for alumina (Callaghan, 1973). Cunningham et al. (1984) recognized that the principal, bulk-tonnage alunite deposits replace similar-aged, intermediate-composition lava flows and tuffs in an approximately equally spaced pattern around the perimeter of similar-aged quartz monzonite stocks (Fig. 2). Cunningham et al. (1984) also showed with geologic mapping, and stable and radiogenic isotopes studies, that the alunite deposits formed at the paleoground surface, are bowl-shaped, zoned laterally as well as vertically, and are cut by hydrothermal explosion breccias that flare upwards. The deposits formed within propylitically altered equivalent rocks, and are located above pyrite-bearing zones. The alunite deposits are zoned upward from alunite to scattered jarosite, to hematite, to replacement or “flooded” silica, to remnants of possible sinter. They are zoned outward from alunite to kaolinite. Recent studies by Rockwell et al. (2001) have shown that dickite is locally present between the kaolinite and propylite and that fracture-controlled areas of pyrophyllite are locally present. Cunningham et al. (1984) interpreted the data to indicate that the heat associated with the intrusion of the stocks established vertical meteoric water convection cells adjacent to the perimeter of the stock that entrained H₂S from the magma and scavenged sedimentary sulfate from Mesozoic evaporates underlying the volcanic field. The alunite deposits were interpreted to form above the upwelling limb of a convection cell, which interacted with atmospheric oxygen near the ground surface (Cunningham et al., 1984). Replacement

alunite and jarosite both formed from sulfuric acid produced by the oxidation of H_2S in a steam-heated environment (Rye et al., 1992; Rye and Alpers, 1997). The Big Rock Candy Mountain deposit was considered to be similar to the other replacement alunite deposits because its location fit the spatial pattern; however, the mineralogy is different, isotopic data had not been collected and, because of the downcutting by the Sevier River, the appearance and post-depositional supergene evolution were known to be strikingly different from the other Marysville alteration centers.

3. Sample collection and analysis

Samples were collected from the variety of altered rocks at Big Rock Candy Mountain to identify the alteration mineralogy and to provide appropriate material for stable-isotope and geochronological studies. Alunite (M956) was collected from the subhorizontal layer that crops out at the top of the cliff (Fig. 1). The natrojarosite samples (M972A and M977) were collected from the central area of the cliff, about one-quarter of the way up. The jarosite sample (M984) was collected above the alunite. Barite (M986B) was collected from the top of the yellow cliff, just below the alunite. Gypsum (M958, M978, M979, M980, M981, M986, and M987) was collected from the dry washes beneath the cliff, from veins along the base of the cliff, and from near the top of the cliff. The gypsum that was collected from the dry washes (M958, M978, M979) was selenite crystals up to 10 cm long; they were float samples in the colluvium. The other gypsum samples were collected in place. Pyrite (M957, M976, M980, M981, and M983) also was collected along the face of the cliff, about one-quarter of the way up, from relatively unaltered rocks in close proximity to the natrojarosite.

3.1. Mineralogical and geochemical analysis

Minerals were identified using X-ray diffraction (XRD), chemical, and optical procedures. Several kilograms of alunite were crushed, pulverized, and split with diluted heavy liquids and magnetic separators to concentrate the alunite. The resulting fractions were monitored by XRD to optimize the concentration. An XGEN-400 XRD diffractometer operating

at 45 kV and 40 Ma with copper radiation was used for XRD determinations. Natrojarosite was microwave acid digested (CEM cooperation) with double distilled nitric acid followed by hydrofluoric acid. The solution was then evaporated to dryness (to remove the HF) on a hot plate and brought up to volume in 1% nitric acid. Major cations were measured by Direct Current Plasma (DCP-OES, ARL Spectraspan IV with ADAM data acquisition software v 2.0), and trace metals by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Perkin Elmer Elan 4000). An acid blank and reference material were carried through the digestion procedure. Recovery of the digested material ranged between 95% and 96%.

3.2. $^{40}\text{Ar}/^{39}\text{Ar}$ analysis

An alunite sample and a natrojarosite sample were analyzed using $^{40}\text{Ar}/^{39}\text{Ar}$ age-spectrum dating techniques to determine their age and thermal history. The samples were prepared using standard mineral separation techniques to a purity of about 99%, with the primary impurities being inseparable kaolinite and quartz. The samples were then irradiated in the central thimble facility of the USGS TRIGA reactor (Dalrymple et al., 1981) in Denver, CO. Sanidine FCT-3 from the Fish Canyon Tuff, dated at 27.79 Ma (Kunk et al., 1985; Cebula et al., 1986), was used as the neutron flux monitor. Corrections for the production of interfering Ar isotopes produced during the irradiation were the values reported by Dalrymple et al. (1981) and Roddick (1983). Corrections for mass-spectrometer discrimination were determined using repeat measurements of atmospheric Ar. The decay constants used were those reported by Steiger and Jäger (1977). The age determinations were performed using a fully automated double-vacuum furnace, similar in design to the one described by Staudacher et al. (1978), and a cleanup system that are attached to an automated VG 1200 b mass spectrometer. The samples were degassed in a stepwise manner. Prior to its admission to the mass spectrometer, the gas was cleaned by using two Saes getters, one operated at room temperature and the other at 400 °C. The Ar was then analyzed in five analytical cycles, and the individual Ar peaks were linearly regressed to T_0 , the time of admission of the gas to the mass spectrometer. Procedural blanks were subtracted from

the analytical results of each analysis prior to the data reduction that was done using an updated version of ArAr* (Haugerud and Kunk, 1988).

3.3. Stable isotopes

Techniques developed by Wasserman et al. (1992) were used to prepare samples to determine δD , $\delta^{18}O_{SO_4}$, $\delta^{18}O_{OH}$ in alunite, jarosite, and natrojarosite by conventional spectrometry. The δD of water was determined by conventional mass spectrometer on samples from Lemonade Spring and on water extracted from heating gypsum to 100 °C in a vacuum by the zinc shot technique (Coleman et al., 1982). The $\delta^{18}O$ of water from Lemonade Spring was determined by the CO_2 -equilibration technique modified from Epstein and Mayeda (1953). The $\delta^{34}S$ analyses of pyrite, alunite, jarosite, and natrojarosite were made by continuous flow mass spectrometer techniques (Fry et al., 1992; Kester et al., 2001), as were $\delta^{18}O$ and $\delta^{34}S$ analyses of gypsum after removal of hydration water by heating in a vacuum. Stable-isotope values are reported in the δ notation as permil (‰). The oxygen and hydrogen isotopic compositions are reported relative to Vienna Standard Mean Ocean Water (VSMOW), and the sulfur isotopic compositions are reported relative to Vienna Cañon Diablo Trolite (VCDT). Analytical uncertainty for $\delta^{18}O$, δD , and $\delta^{34}S$ analyses are $\pm 0.2\text{‰}$, $\pm 3\text{‰}$, and $\pm 0.2\text{‰}$, respectively.

3.4. AVIRIS and imaging spectroscopy

High-resolution, low-altitude, digital imaging spectroscopy data of the Big Rock Candy Mountain area were acquired with the AVIRIS sensor in 1999. These data measure reflectance characteristics of the ground surface in 224 discrete spectral bands over the 0.35–2.50- μm region of the electromagnetic spectrum. Analysis of these data can be used to construct detailed maps of mineral species, water, vegetation, and man-made materials. Specialized software (Clark and Swayze, 1995; Rockwell, 2002) quantitatively compared the spectrum of every pixel of AVIRIS data to reflectance spectra from a published spectral library to identify materials on the ground surface. The airborne survey was performed with a Twin Otter aircraft flown at 5320 m altitude (MSL). These

AVIRIS data have an effective ground resolution of 2–3 m per pixel. Mineral maps, generated by analysis of the AVIRIS data, were superimposed on USGS Digital Elevation Models of the area to identify vertical and horizontal patterns of mineralogical zonation associated with the hydrothermal alteration. It should be emphasized that the AVIRIS data are so good at discriminating small amounts of alteration minerals that we had to go back and recheck the geology. In one example, the AVIRIS recognized jarosite that composed less than 5% of rocks on a small (approximately 5 m²) ridge that we sampled.

Rock samples collected from the mountain were characterized both in the field and the laboratory by using a portable spectrometer; this instrument also measures reflectance characteristics over the 0.35–2.50- μm spectral region. The laboratory spectra were compared with reference spectra from a published spectral library for the purposes of mineral identification.

4. Results

4.1. Mineralogical identification

Alunite $[KAl_3(SO_4)_2(OH)_6]$ and jarosite $[KFe_3(SO_4)_2(OH)_6]$ differ in the amount of mutual substitution of Al^{+3} for Fe^{+3} . Alunite and natroalunite $[NaAl_3(SO_4)_2(OH)_6]$, as well as jarosite and natrojarosite $[NaFe_3(SO_4)_2(OH)_6]$, form complete solid solutions having mutual substitutions of Na for K. Alunite is widely recognized to be either hypogene or supergene, whereas jarosite is generally considered as a supergene mineral. However, hypogene replacement jarosite was recognized in an upward sequence of jarosite, hematite and silica overlying the replacement alunite at the Yellow Jacket deposit at Marysville (Fig. 6, Cunningham et al., 1984). Hypogene jarosite is interpreted at Big Rock Candy Mountain (as noted below) and has been recognized elsewhere around the world (Dutriz and Jambor, 2000; Lueth et al., this volume).

Natrojarosite at Big Rock Candy Mountain was identified by XRD and shown by ICP-MS analysis (Table 1) to have a mole fraction (K/(K+Na)) of about 0.1. This is the first time natrojarosite has been reported from the Marysville volcanic field, and it is

Table 1

DCP and ICP-MS analyses of natrojarosite and jarosite from Big Rock Candy Mountain, Utah

M972A natrojarosite			M984(2) jarosite			M984(4) jarosite			M972A natrojarosite			M972A natrojarosite			M972A natrojarosite			M972A natrojarosite		
Element	($\mu\text{g g}^{-1}$)		($\mu\text{g g}^{-1}$)			($\mu\text{g g}^{-1}$)			Element	($\mu\text{g g}^{-1}$)		Element	($\mu\text{g g}^{-1}$)		Element	($\mu\text{g g}^{-1}$)		Element	($\mu\text{g g}^{-1}$)	
Ca	600	3600			4100			Ag	<5		Eu	<5		Nb	26		Sm	2.6		
Mg	400	670			1075			As	<5		Ga	10		Nd	13		Sn	17		
Na	56,400	7800			19,900			Au	<5		Gd	<5		Ni	<5		Ta	25		
K	10,500	62,000			57,000			B	125		Ge	<5		P	<30		Th	<5		
Sr	1300	1100			500			Ba	2800		Hf	18		Pb	<5		Tl	<5		
Si	330	3250			9900			Be	<5		Hg	<5		Pd	<5		U	<5		
Al	4100	2650			4250			Bi	<5		In	<5		Pt	<5		V	<5		
Fe	48,0000	27,0000			32,3000			Ce	25		Ir	<5		Rb	37		W	<5		
Mn	55	48			50			Co	<5		La	10		Ru	<5		Y	<5		
SO ₄	210,000							Cr	16		Li	110		Sb	<5		Yb	<5		
K/Na	0.19	8			2.9			Cs	<5		Mn	26		Sc	<5		Zn	115		
								Cu	110		Mo	325		Se	<5		Zr	16		

M972A supergene natrojarosite from base of cliff; M984(2) and (4) supergene jarosite near-float from above alunite. Analyst: Terry Councill.

this mineral that gives the mountain its buff coloration. The relatively low K content of the mineral was also confirmed by the analysis for $^{40}\text{Ar}/^{39}\text{Ar}$ dating. Table 1 shows that the natrojarosite sample contained minor Al, Ba, and Sr. The mineral structure and chemistry of the jarosite group of minerals is known for its ability to accommodate metals and various other elements. This sample contains an appreciable amount of Mo (325 ppm), Zn (115 ppm), and Cu (110 ppm). The XRD pattern shows traces of quartz present. Float samples of jarosite (mole fraction (K/(K+Na)) of about 0.6 to 0.8) from above the basal alunite layer were analyzed and their results are in Table 1. XRD data showed that the alunite is the K-rich variety (Cunningham and Hall, 1976) and is similar in composition to the other replacement alunite deposits of the Marysville volcanic field. The unaltered remnants of Bullion Canyon lava flows at Big Rock Candy Mountain (the dark brown areas in Fig. 1) locally contain albite, epidote, chlorite, calcite, montmorillonite, and pyrite.

A chemical analysis was made of water collected in September 2000 at Lemonade Spring. The analysis shows the spring is sulfate-dominated with elevated levels of rare-earth elements and metals. The pH measured at the spring was 2.6. The analysis of Lemonade Spring can be used to assess the equilibrium state of the spring relative to jarosite and other minerals observed at the site through the use of the equilibrium geochemical program PHREEQC (Parkhurst and Appelo, 1999). The WATEQ4F database

was used for the calculations, which includes thermodynamic data for potassium jarosite, sodium jarosite, hydronium jarosite, and a potassium-rich jarosite solid solution (Alpers et al., 1989; Ball and Nordstrom, 1991). Modeling results indicate that even under suboxic conditions (<1 mg L⁻¹ dissolved oxygen), Lemonade Spring is significantly supersaturated with respect to all jarosite phases included in the database. In addition, modeling indicates that the spring is supersaturated with respect to alunite, and saturated with respect to gypsum, ferrihydrite, and amorphous silica (Robert Seal, personal communication, 2004).

4.2. $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra

Results of the $^{40}\text{Ar}/^{39}\text{Ar}$ dating of alunite and natrojarosite are given in Tables 2 and 3 and shown in Fig. 3. Replacement alunite sample M956 was degassed in 35 steps in an effort to quantify what was expected to be a diffusive-loss, age-spectrum pattern. Its spectrum (Table 2, Fig. 3a) has a minimum apparent age of 6.6 Ma in the 653 °C step. The apparent ages then climb to a maximum of 21.3 Ma in the 760 °C step, with about 90% of the ^{39}Ar in the sample released. The only deviation in this smooth climb is a low age in the 700 °C step that reflects electronic problems in the analytical equipment. Between 705 and 1250 °C, the apparent age falls to a low of 12.2 Ma before climbing to 27.4 Ma. Apparent K/Ca ratios climb in a fairly constant way from 99 in the 650 °C step to >3000 in the 770 °C

Table 2

Data for $^{40}\text{Ar}/^{39}\text{Ar}$ dates for replacement alunite sample M956 from Big Rock Candy Mountain, Utah

Temperature (°C)	% ^{39}Ar of total	Radiogenic yield	Moles $^{39}\text{Ar}_\text{K}$ ($\times 10^{-12}$)	$^{40}\text{Ar}^*/$ $^{39}\text{Ar}_\text{K}$	K/Ca	K/Cl	Apparent Age (Ma) and Precision (1σ)	
650	0.1	28.6	0.066566	0.904	48.4	99	7.97	0.70
653	0.2	29.0	0.082740	0.752	45.9	125	6.63	0.65
656	0.2	36.9	0.085221	0.876	37.2	148	7.72	0.65
660	0.2	41.3	0.103749	0.903	47.7	173	7.96	0.60
663	0.3	48.6	0.125830	0.991	42.8	197	8.73	0.37
666	0.3	53.7	0.143023	1.035	44.9	226	9.12	0.48
670	0.4	58.1	0.181971	1.095	45.2	248	9.64	0.27
672	0.4	62.9	0.212469	1.186	44.8	281	10.44	0.27
675	0.6	67.3	0.269498	1.314	41.3	294	11.57	0.30
680	0.8	76.1	0.398409	1.502	50.9	351	13.21	0.23
685	1.1	81.0	0.528240	1.669	56.0	384	14.67	0.08
690	1.4	85.6	0.689520	1.806	54.4	441	15.88	0.09
695	1.8	88.6	0.857039	1.920	56.9	461	16.88	0.07
700	0.3	79.0	0.163212	1.768	60.2	346	15.55	0.20
705	3.0	91.9	1.432288	1.996	68.0	580	17.54	0.05
710	3.3	92.9	1.598853	2.071	67.6	560	18.20	0.05
715	4.5	94.1	2.168002	2.134	68.7	659	18.75	0.04
720	5.1	95.0	2.430445	2.191	68.8	650	19.24	0.04
725	6.3	95.5	2.985085	2.242	72.2	761	19.69	0.02
730	7.7	96.1	3.692665	2.298	74.8	944	20.18	0.04
735	8.9	96.5	4.228935	2.336	77.6	970	20.51	0.02
740	9.9	96.7	4.710203	2.363	80.7	1036	20.75	0.02
745	12.4	97.3	5.900382	2.393	86.6	1237	21.01	0.01
750	8.5	97.6	4.078400	2.411	90.9	1761	21.17	0.04
760	11.9	98.0	5.703795	2.429	91.7	2495	21.32	0.04
770	7.2	97.7	3.421039	2.383	96.4	3146	20.92	0.04
780	0.8	79.4	0.381313	2.132	67.2	581	18.73	0.13
790	0.4	71.5	0.199420	1.941	51.3	417	17.06	0.20
800	0.3	62.8	0.132857	1.787	41.9	287	15.71	0.59
825	0.2	40.4	0.099833	1.383	33.5	143	12.17	0.75
850	0.2	35.6	0.100736	1.566	30.6	86	13.77	0.78
875	0.2	39.4	0.096574	1.589	29.0	90	13.98	0.62
900	0.2	38.4	0.090172	1.641	24.2	83	14.43	0.59
1000	0.3	32.2	0.131559	2.456	17.2	54	21.56	0.33
1250	0.5	9.4	0.245223	3.121	10.5	12	27.35	0.75
Total gas no Plateau	100	93.2	47.735266	2.250	77.8	1272	19.76	

Ages calculated assuming an initial $^{40}\text{Ar}/^{36}\text{Ar}=295.5\pm 0$. Ages of individual steps do not include error in the irradiation parameter J ; $J=0.004895\pm 0.25\%$ Sample wt.=0.2501 g. No error is calculated for the total gas age. $^{39}\text{Ar}_\text{K}$ gas quantities are $\text{mol}\times 10^{-12}$.

step, and then drop off sharply through the 1250 °C step. The high-temperature drop in the K/Ca ratios corresponds with the abrupt decrease in apparent age in the last 3–4% of the ^{39}Ar released from the sample. We suggest that the cause of this high-temperature age variation may be due to contaminants in the sample and with contained internal Ar recoil during irradiation. Although Ar recoil effects are usually seen at lower temperatures in an age spectrum, the alunite degassed at very low temperatures (90% of the ^{39}Ar

was degassed by 760 °C) relative to other minerals. Thus, we interpret the 21.32 ± 0.07 Ma apparent age of the 760 °C step to be a minimum apparent age (includes the uncertainty in the irradiation parameter J) of formation of the alunite, and the 6.6 ± 0.7 Ma age of the 653 °C step to be a maximum for a thermal event that partly reset this sample.

Natrojarosite sample M972A also degassed at low temperatures (Table 3, Fig. 3b). Because of the low content of K and the young apparent ages, it was not

Table 3

Data for $^{40}\text{Ar}/^{39}\text{Ar}$ dates for natrojarosite sample M972A from Big Rock Candy Mountain

Temperature (°C)	% ^{39}Ar of total	Radiogenic yield	Moles $^{39}\text{Ar}_K$ ($\times 10^{-12}$)	$^{40}\text{Ar}^*/^{39}\text{Ar}_K$	K/Ca	K/Cl	Apparent age (Ma) and precision (1 σ)	
500	0.9	−1.2	0.026098	−0.566	7.0	25	−4.99	2.85
550	3.5	0.3	0.103006	0.050	7.6	85	0.44	1.02
600	10.2	−0.3	0.299445	−0.011	8.2	293	−0.10	0.39
625	11.8	−2.8	0.345558	−0.110	8.0	286	−0.97	0.44
650	29.4	2.6	0.859098	0.200	10.3	199	1.76	0.39
675	28.4	2.9	0.828949	0.143	12.3	267	1.26	0.31
700	10.8	5.5	0.315627	0.376	10.2	157	3.31	0.38
725	2.3	6.3	0.067333	0.578	8.9	77	5.08	1.44
750	1.5	3.1	0.045125	0.282	7.3	66	2.48	2.09
800	1.1	7.1	0.033465	0.768	4.6	40	6.74	2.32
Total gas	100	2.1	2.923704	0.149	10.1	222	1.31	

Ages calculated assuming an initial $^{40}\text{Ar}/^{36}\text{Ar}=295.5\pm 0$. All precision estimates are at the one sigma level. Ages of individual steps do not include error in the irradiation parameter J . No error is calculated for the total gas age. $^{39}\text{Ar}_K$ gas quantities are in $\text{mol}\times 10^{-12}$. Natrojarosite $J=0.004877\pm 0.25\%$, Sample wt.=0.1076 g.

possible to obtain as detailed an age spectrum for this sample, and the results have large analytical errors. For gas released between 500 and 625 °C, the apparent ages are negative and (or) overlap with zero age, suggesting that some of the natrojarosite in this sample is modern. From 650 to 800 °C, the apparent ages climb to a maximum of 6.7 ± 2.3 Ma. We interpret this apparent age to represent a minimum for the beginning of formation of the natrojarosite. This age is indistinguishable from the minimum age of 6.6 ± 0.7 Ma from the alunite, suggesting that the partial resetting of the alunite and the formation of the

natrojarosite were caused by the same event. The modern ages in the early portion of the natrojarosite age spectrum suggest that the mineral is still in the process of forming today.

4.3. Stable isotopes

The stable-isotope data from Big Rock Candy Mountain (Table 4, Fig. 4) show that there are significant differences in the isotopic composition of the sulfates that can be used to constrain the sources of components and the processes by which the minerals

Fig. 3. (a) $^{40}\text{Ar}/^{39}\text{Ar}$ age spectrum for replacement alunite of Big Rock Candy Mountain. Apparent age is 21.3 Ma, modified by a thermal event at about 6.6 Ma. (b) $^{40}\text{Ar}/^{39}\text{Ar}$ age spectrum for surficial natrojarosite from Big Rock Candy Mountain. The age is interpreted to be partly modern but with mixed older natrojarosite back to about 6.7 Ma.

Table 4
Big Rock Candy Mountain stable-isotope data

Sample	Mineral	δD	$\delta^{34}S$	$\delta^{18}O_{OH}$	$\delta^{18}SO_4$
M956	Alunite ^a	−112	11.9	3.9	10.8
M972A	Natrojar	−126	0.7		
M972A	Natrojar ^b	−123	−1.2	−1.9	7.3
M977	Natrojar ^c		−0.7	−5.8	1.7
M984(2)	Jarosite		−7.7		3.3
M984(2) dup	Jarosite		−7.3		
M984(4)	Jarosite		−7.1		4.2
M986B	Barite		8.6		3.3
M978	Gypsum ^d	−133	13.4		5.1
M958	Gypsum		15.2		6
M958F	Gypsum		14.1		7
M979A 1	Gypsum		13		2.1
M979A dup	Gypsum		15.2		
M979A pdr	Gypsum		14.5		−0.8
M980B 1	Gypsum		8.1		
M980B 1 pdr	Gypsum		7		1.2
M981B 1	Gypsum		8.4		
M981B 2	Gypsum		9		1.8
M986A 1	Gypsum		2.2		0
M986A 2	Gypsum		8.5		2.7
M987A solid 1	Gypsum		−5.2		−8.2
M987A 2	Gypsum		0.9		0.9
M957	Pyrite		−4.3		
M976A	Pyrite		−4.7		
M976B	Pyrite		−2.8		
M980A	Pyrite		−2.7		
M981A	Pyrite		−2.3		
M983	Pyrite		0.4		
M974	LemSpr	−95	0.1		−3.6

Natrojar=natrojarosite; LemSpr=Lemonade Spring.

^a δD_{H_2O} calc.=−108; $\delta^{18}O_{H_2O}$ calc.=−8.5; T_{SO_4-OH} =100 °C.

^b δD_{H_2O} calc.=−75; $\delta^{18}O_{H_2O}$ calc.=−11.4; $\delta^{18}O_{total}$ =6.5.

^c $\delta^{18}O_{H_2O}$ calc.=−13.9.

^d δD_{H_2O} calc.=−118.

formed. The $\delta^{18}O$ vs. $\delta^{34}S$ values in Fig. 4a for gypsum show a positive correlation, with $\delta^{34}S$ values ranging from 15.2‰ to −5.2‰ and $\delta^{18}O_{SO_4}$ values ranging from 7.0‰ to −8.2‰. The selenite crystals that were collected as float in the colluvium (M958, M978, M979) have distinctly smaller $\delta^{34}S$ and $\delta^{18}O_{SO_4}$ than the rest of the gypsum samples. Conversely, the gypsum collected near the top of the cliff (M986, M987) contain large $\delta^{34}S$ and $\delta^{18}O_{SO_4}$ values, and the samples collected near the base of the cliff (M980, M981) contain intermediate values.

The data for the aqueous sulfate from Lemonade Spring fall on the gypsum trend. The $\delta^{34}S$ values for alunite (11.9‰) and natrojarosite (0.7 to −1.2‰)

differ from each other and are at the extreme range of those for gypsum. The $\delta^{18}O_{SO_4}$ values for alunite (10.8‰) and natrojarosite (9.5‰ to 1.7‰) are larger than those for gypsum having similar $\delta^{34}S$ values. The $\delta^{34}S$ value of 11.9‰ from the replacement alunite (sample M956) is within the range (11.5–15.4‰) of alunite sulfur measured on the other replacement alunite deposits in the Marysvale volcanic field, as well as within the range (11.9–16.7‰) of nearby Permian-to-Jurassic evaporite deposits that likely underlie the volcanic field (Cunningham et al., 1984).

Oxygen isotopic fractionation between sulfate and hydroxyl sites in alunite is temperature-dependent, thereby allowing the depositional temperature of steam-heated, replacement alunite to be constrained (Rye et al., 1992). The results for M956 of 100 °C are commensurate with the temperatures of 90 to 160 °C from the other replacement alunites at Marysvale. These temperatures are typical for steam-heated alunite (Rye et al., 1992; Ebert and Rye, 1997). Pyrite has variable $\delta^{34}S$ values of −4.7‰ to −2.8‰ that, except for one sample, are lower than the $\delta^{34}S$ values of natrojarosite from the Big Rock Candy Mountain (−1.2‰ to 0.7‰; Table 4 and Fig. 4a). Furthermore, the $\delta^{34}S$ values of pyrite from the entire district (mostly −15.3‰ to −5.4‰; Cunningham et al., 1984) are lower than the $\delta^{34}S$ of natrojarosite. The $\delta^{34}S$ value of SO_4 in Lemonade Spring (0.1‰) is also within the range of values for natrojarosites. The jarosite found higher on the canyon wall, above the basal alunite, has a $\delta^{34}S$ (−7.0‰) lower than the values for pyrite and natrojarosite at Big Rock Candy Mountain. It also has a $\delta^{18}O_{SO_4}$ of 3.3‰ to 4.2‰, which is in the range of values for natrojarosite at the mountain. As will be discussed, the combination of geology, mineralogy and the low $\delta^{34}S$ and large $\delta^{18}O_{SO_4}$ values for the jarosite indicates that the jarosite is most likely related to the oxidation of H_2S at the top of the system that produced the primary hydrothermal alteration at Big Rock Candy Mountain such as occurred in the Yellow Jacket replacement deposit at Marysvale (Cunningham et al., 1984; Rye and Alpers, 1997). The composition of water in fluids that is calculated from δD and $\delta^{18}O_{OH}$ of natrojarosite (Table 4 and Fig. 4b) show that the natrojarosite-forming fluid, water from Lemonade Spring, and presumably the gypsum parental fluid plot on or near the meteoric water line (MWL), but with different

Fig. 4. (a) $\delta^{34}\text{S}$ vs. $\delta^{18}\text{O}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{OH}}$ of alunite and natrojarosite, $\delta^{34}\text{S}$ vs. $\delta^{18}\text{O}_{\text{SO}_4}$ of gypsum and barite, $\delta^{34}\text{S}$ vs. $\delta^{18}\text{O}$ of SO_4^{2-} in Lemonade Spring, and $\delta^{34}\text{S}$ of pyrite from Big Rock Candy Mountain. (b) δD vs. $\delta^{18}\text{O}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{OH}}$ of alunite, natrojarosite, δD vs. $\delta^{18}\text{O}_{\text{SO}_4}$ of gypsum, and δD vs. $\delta^{18}\text{O}$ of water from Lemonade Spring at Big Rock Candy Mountain. Fluid in equilibrium with alunite calculated from equation of Stoffregen et al. (1994) using 100 °C indicated by $\delta^{18}\text{O}_{\text{SO}_4}$ –OH data in Table 4; fluid in equilibrium with jarosite calculated from $\delta^{18}\text{O}_{\text{OH}}$ values and equations of Rye and Stoffregen (1995) and typical supergene temperatures of 20 to 80 °C. SJSF is the Supergene Jarosite Sulfate Field, and SJOZ is the Supergene Jarosite OH Zone (Rye and Alpers, 1997).

$\delta\text{D}_{\text{H}_2\text{O}}$ values. Big Rock Candy Mountain alunite parental fluids plot to the right of the MWL, as do the fluids for the other hydrothermal replacement alunite and jarosite samples at Marysvale (Rye et al., 1992; Rye and Alpers, 1997).

4.4. Laboratory and imaging spectroscopy

The distribution of surficial clay, carbonate, sulfate, mica, and iron-bearing minerals was mapped using low-altitude AVIRIS data of the Big Rock Candy Mountain area (Fig. 5a,b). For orientation, the Sevier River traverses the center of the map, the curved stripe just to its left is Utah Highway 89, and the black and yellow area on Fig. 5b that is marked with the letter “P” is the prominent yellow-colored cliff shown in Fig. 1.

A simplified map of alteration zones, shown at the lower right of 5a, was interpreted from the AVIRIS mineral maps (Fig. 5a,b). The mineral map consists of color-coded mineralogical information from Fig. 5a and b, overlaid on a grayscale image backdrop of the area. The color codes correspond to the spectrally dominant mineral or mineral assemblage identified in that pixel. The legend for color codes for clays, carbonates, sulfates, and micas shown in Fig. 5a is in Fig. 6 and the corresponding legend for iron-bearing minerals shown in Fig. 5b is in Fig. 7.

The assignment of the dominant mineral on the alteration map (Fig. 5a) was field checked with a portable spectrometer and samples were confirmed with XRD analyses. AVIRIS uses reflected sunlight so it is sensitive to materials at the ground surface and does not penetrate the ground. A qualitative measure of the modal abundance of minerals in an area is indicated by the amount of colored pixels in an area. The minerals whose areal distributions are shown on this map are characterized by vibrational spectral absorption features in the 1.4–2.5- μm spectral region. Pixels that appear in greyscale on the map are the ones in which water, vegetation, and (or) man-made materials were mapped. The dark patches on the slopes of hillsides are shadowed areas from which little or no reflected sunlight was measured by AVIRIS. The area east of the river, characterized by abundant green-colored pixels, is part of a propylitically altered quartz monzonite stock. Calcite, epidote, and chlorite are the spectrally dominant minerals in these pyrite-poor altered intrusive rocks (see legend in Fig. 6).

Big Rock Candy Mountain is immediately west of Highway 89, and is marked on the mineral map by the conspicuous exposures of argillically and propylitically altered rocks. The pyrite-bearing, propylitically altered Bullion Canyon lava flows exposed on the eastern and northern flanks of the mountain that are

Fig. 5. (a) High-resolution, low-altitude AVIRIS data from Big Rock Candy Mountain showing the spatial distribution of surface clay, sulfate, and mica alteration minerals. The map of alteration zones reflects the dominant mineralogy within an area. Location of the transect for the topographic profiles in Figs. 6 and 7 is shown. (b) High-resolution, low-altitude AVIRIS data from Big Rock Candy Mountain showing the spatial distribution of surface Fe-bearing alteration minerals. The map of alteration zones reflects the dominant mineralogy within an area. Location of the transect for the topographic profiles in Figs. 6 and 7 is shown.

Fig. 6. Surface clay–sulfate–mica mineralogy along the topographic profile of the NE–SW-trending transect of Big Rock Candy Mountain.

Fig. 7. Distribution of surface Fe-bearing minerals along the topographic profile of the NE–SW-trending transect of Big Rock Candy Mountain.

altering to natrojarosite have been marked with the letter P in Fig. 5a and b. The area is marked by three dominant mineral assemblages on the map: a mixture of natrojarosite, illite, clay, and gypsum shown in orange, a mixture of illite with kaolinite shown in

light green, and a mixture of kaolinite with montmorillonite/smectite shown in dark blue-green. On the iron-bearing minerals map (Fig. 5b), the area is shown in yellow that corresponds to fine-grained jarosite. The relatively large area marked by the letter A

(Fig. 5a) and enclosing red and yellow pixels is dominantly the subhorizontal 21.3 Ma replacement alunite that is visible in Fig. 1. The area to the southwest is at higher elevations and is dominated by kaolinite or dickite. The map of alteration zones (Fig. 5a) integrates the pixels in an area and classifies it according to the dominant mineralogy.

The transect line for the topographic profiles extends from the Sevier River on the NE, across the highway, up the prominent face of the mountain (Fig. 1), to higher elevations to the SW. Cross-sections along this transect were constructed with two complimentary suites of color-coded, dominant surface minerals; Fig. 6 shows the surface distribution of clay–carbonate–sulfate–mica minerals and Fig. 7 shows the corresponding distribution of iron-bearing minerals. They document the distribution of propylitically altered rocks on the face of Big Rock Candy Mountain and the overlying zone of replacement alunite. The overlying and adjacent areas are dominated by kaolinite and a ridge of quartz–dickite. To the SW at higher elevation is a small area of propylitically altered rocks with a patch of alunite at the highest elevation. Fig. 7 shows the surface Fe-bearing mineralogy, including jarosite. It distinguishes, on a spectral basis, two groups of jarosite and hematite, a fine-grained variety and a coarse-grained variety. The AVIRIS mapping confirms the spatial juxtaposition of fine-grained jarosite with the propylitically altered lava flows in the cliff face of Big Rock Candy Mountain. The AVIRIS map of iron minerals (Fig. 5b) and its transect (Fig. 7) show that there are small patches of coarse-grained jarosite, beneath a zone of coarse-grained hematite at the highest elevation, that correspond to the position of the uppermost alunite. This is probably the dissected remnants of a slightly older deposit formed at slightly higher elevation.

5. Discussion

Jarosite and alunite (as well as their natro-end-member varieties) form under different conditions, with jarosite requiring considerably higher Fe^{3+} activity and a lower pH for its formation (Stoffregen, 1993). The extreme conditions for jarosite stability generally limit the formation of the mineral to the vadose zone, where high $f\text{O}_2$ and low pH values of the

solutions can result from the presence of abundant atmospheric oxygen. Alunite, in contrast, forms at or below the water table where pH and $f\text{O}_2$ are somewhat more buffered by reaction with wallrocks. This difference applies whether the minerals form in a steam-heated hydrothermal environment from aqueous sulfate produced by the oxidation of H_2S , or in a supergene environment from the oxidation of pyrite (Rye et al., 1992; Rye and Alpers, 1997). Geological, geochronological, and isotopic evidence indicates that the alunite at Big Rock Candy Mountain formed at or slightly before 21.3 Ma as part of the hydrologic system that formed the other deposits of replacement alunite around the periphery of similar aged plutons. The age, chemistry, position relative to the central pluton, and stable isotopes for all of the deposits are almost the same. By analogy, we interpret the alunite at Big Rock Candy Mountain to have formed near the top of the upwelling limb of a hydrothermal convection cell at or below the paleo water table. The position of the 23 Ma ground surface is indicated by the basal contact of the 23 Ma Osiris Tuff that was erupted from the Monroe Peak caldera at approximately the same time (Fig. 2; Rowley et al., 1994). The base of this tuff, along with the paleoground surface marked by the 19 Ma tuff from the Red Hills caldera, is close to the present-day valley floor. The flooded silica cap, the uppermost part of the Big Rock Candy Mountain deposit (Fig. 8), has been erosionally removed except for parts that remain as float on the ridges above the alunite. The small patches of alunite, hematite, jarosite (including sample M984) and propylite located at higher elevations are interpreted to be the remnants of the top of the system.

The excellent exposures through the vertical section at Big Rock Candy Mountain, together with the spectral capabilities of AVIRIS, the use of $^{40}\text{Ar}/^{39}\text{Ar}$ dating, and advances in understanding of the processes in modern geothermal systems, have resulted in the creation of an improved genetic model for steam-heated, replacement-alunite deposits, as well as a genetic model for their natural destruction during dissection and oxidation. As shown in Fig. 8, the upward vertical succession of mineral assemblages is pyrite-bearing, chlorite, epidote, calcite propylitic assemblage, massive replacement alunite, replacement jarosite, hematite, to a flooded silica cap that is cut by hydrothermal breccia pipes. The lateral zoning from

Fig. 8. Genetic model of steam-heated, replacement-alunite deposits, showing the distribution of alteration minerals and proximity to the paleo-ground surface and paleo-water table, and location of the present surface of supergene alteration (fine dashed line).

the center outward is alunite, kaolinite, and locally dickite, to a distal propylitic zone. When the pyrite in the sulfidized andesite in the deepest part of the deposit is exposed by erosion, it weathers to a natrojarosite–kaolinite assemblage that tends to accumulate on ridges containing the most altered rock and in soil at the base of the mountain.

The mineralogical zoning provides insight into the processes that formed these deposits. The abundant pyrite beneath the alunite at Big Rock Candy Mountain was formed in the unoxidized part of a 21.3 Ma upward-flowing limb of a convection cell by the reaction of H₂S in the limb with the Fe released during propylitic alteration of the host rocks. The oxidation of this H₂S by atmospheric oxygen produced the aqueous sulfate that led to alunite formation. The large $\delta^{34}\text{S}$ values of the alunite probably indicate that the aqueous sulfate (formed from the oxidation of H₂S) underwent exchange with streaming H₂S prior to precipitation as alunite (Rye et al., 1992; Ebert and Rye, 1997). The heavier sulfate was formed

with increased time and temperature as the system approached isotopic equilibrium. A component of aqueous sulfate may have also been derived from evaporites by convection cells established during pluton penetration through the evaporites beneath the volcanic field, and this component may have initially been deposited as isotopically heavy, crystalline hypogene gypsum, such as that observed at the Yellow Jacket deposit (Cunningham et al., 1984). The H₂S for the underlying isotopically light pyrite could have been derived from sedimentary sulfate via thermochemical reduction, a magma, or sedimentary sulfide. The range of low $\delta^{34}\text{S}$ values for the H₂S may reflect variable exchange with evaporite sulfate in the deep part of the hydrothermal system (cf., Lueth et al., this volume). Disseminated barite (M986B; Table 4) is present just below the alunite layer. Barite is typically precipitated by the mixing of sulfate-rich and dilute water (Holland and Malinin, 1979). The spatial distribution of barite, its relation to the overlying alunite, and its $\delta^{34}\text{S}$ value of 8.6‰, indicate that the

barite formed from isotopically heavy sulfate in the hydrothermal fluids and mixed with meteoric water (probably containing sulfate from the oxidation of isotopically lighter H_2S).

The range in $\delta^{34}\text{S}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ values in gypsum, high in the selenite float crystals in the dry washes, low near the top of the cliff, and intermediate near the base of the cliff, appears to reflect both origin and age of the gypsum. The low isotopic values near the top may indicate that the gypsum there is the youngest and is forming today where relatively rapid erosion of the host rocks exposes light pyrite to recent oxidation. The higher values lower in the cliff probably reflect mixing of the light, young sulfate from above with heavier sulfate from either hypogene gypsum deeper in the deposit or dissolved from the hypogene alunite, or both. The highest isotopic values, found in the selenite, may indicate the source was principally high $\delta^{34}\text{S}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ from relatively old, hypogene gypsum that is present mainly deep in the system, is now being exposed, and produces large selenite crystals that survive their erosional journey of only tens of meters in a slurry of yellow mud at the base of the cliff.

The geological, geochronological, and isotopic evidence indicates that the natrojarosite at Big Rock Candy Mountain formed in a supergene environment from the aqueous sulfate produced by the oxidation of pyrite. This natrojarosite forms in the most altered rock and commonly accumulates in elevated areas along ridges and at the base of the mountain rather than in stream drainages, where it would be easily flushed by storm runoff. The supergene natrojarosite and sulfate in Lemonade Spring have similar $\delta^{34}\text{S}$ values. Lemonade Spring did not appear to be precipitating natrojarosite in September 2000, when flow was 2 L min^{-1} , but when flow was a small trickle, clear to yellowish brown crusts were deposited that XRD and the portable spectrometer indicated to be a mixture of copiapite, epsomite, and alunogen. Upon drying, the crusts changed color and began to decompose and disintegrate. The composition of the spring is probably similar to that of the supergene fluids responsible for the formation of natrojarosite as the mountain eroded. In support of this, the chemistry of Lemonade Spring (Table 5) shows enrichment in some of the same elements observed in the natrojarosite. The slightly larger $\delta^{34}\text{S}$ value for the natrojarosite than that of the

Table 5

Chemical analysis of lemonade spring, big rock candy mountain

Element	mg L ⁻¹	Trace metals	$\mu\text{g L}^{-1}$	Trace metals	$\mu\text{g L}^{-1}$
Ca	550	Ag	<1	Nd	240
Mg	1000	As	6	Ni	600
Na	110	Au	<1	Os	<1
K	1.8	B	<1	P	560
Sr	2.11	Ba	<1	Pb	<1
Si	80	Be	41	Pd	<1
Al	750	Bi	<1	Pr	42
Fe	375	Ce	200	Pt	<1
Mn	85	Cd	15	Rb	34
HCO ₃	<1	Co	1350	Re	<1
Cl	425	Cr	14	Ru	<1
SO ₄	10000	Cs	<1	Rh	<1
F	<0.1	Cu	820	Sb	<1
Br	<0.1	Dy	105	Sc	19
NO ₃	<0.1	Er	42	Se	<1
PO ₄	<0.1	Eu	38	Sm	90
		Ga	<1	Sn	<1
pH	2.6	Gd	130	Ta	<1
	meq	Ge	<1	Tb	20
Cations	214.53	Hf	<1	Te	<1
Anions	220.19	Hg	<1	Th	<1
%Error	-1.30	Ho	18	Tl	<1
		I	<1	Tm	4.9
		In	<1	U	<1
		Ir	<1	V	<1
		La	50	W	<1
		Li	520	Y	510
		Lu	3.4	Yb	27
		Mo	<1	Zn	6300
		Nb	<1	Zr	<1

Trace metals by ICP-MS scan mode; major cations by DCP-AES. Major anions by IC. Precision $\pm 15\%$ except for REE, which are $\pm 5\%$.

source pyrite may reflect addition of isotopically heavy sulfate derived from the dissolution of alunite and gypsum. This possibility is supported by the observation that gypsum has an isotopic composition compatible with a source of aqueous sulfate in common with alunite. The large $\delta^{18}\text{O}_{\text{SO}_4}$ values for natrojarosite relative to gypsum with similar $\delta^{34}\text{S}$ values (Fig. 4a) reflect the different hydrogeochemistry of the minerals (Rye et al., 1992). The larger $\delta^{18}\text{O}_{\text{SO}_4}$ values for natrojarosite may indicate a greater component of atmospheric oxygen versus water-derived oxygen in the parental aqueous sulfate or a greater degree of oxygen-isotope exchange between the aqueous sulfate and water. This latter would not be surprising considering the fact that natrojarosite forms from fluids that have lower pH that more readily allow for

oxygen-isotope exchange between aqueous sulfate and water than the more neutral fluids for gypsum.

The jarosite that overlies alunite on Big Rock Candy Mountain was discovered by AVIRIS. The presence of this “coarse-grained” jarosite is shown in the area of the resistant quartz–dickite ridge on Fig. 7. The jarosite occurs as nearly in-place float in an area of about 15 m². The jarosite makes up a few percent of 10-cm chips that form a somewhat silicified float whose abundance is not more than a few chips per square meter. The presence of this jarosite adds a complication to the Big Rock Candy Mountain story. The $\delta^{34}\text{S}$ values of the jarosite are lower than any observed for pyrite on Big Rock Candy Mountain, but not lower than the -15.3‰ to 5.1‰ values previously observed for the Marysville volcanic field (Cunningham et al., 1984) and the textural appearance is that of dried, silicified mud in contrast to the microcrystalline texture of alunite. The stable-isotope data alone for this jarosite do not distinguish a hypogene from supergene origin. However, the combination of geological occurrence, texture, silicic nature of the float, and $\delta^{18}\text{O}_{\text{SO}_4}$ values are most consistent with a formation from the oxidation of H_2S at the top of the Big Rock Candy Mountain deposit at 21 Ma.

Lemonade Spring is modern groundwater and has a δD of -95‰ . This water is probably derived from recharge by melting snow high on the mountain, and may have a δD value typical of average meteoric groundwater in the area today. The δD value of the spring water is about 20‰ higher than that of the gypsum parental fluid, and is about 20‰ lower than that of the natrojarosite parental fluid. This difference suggests that there have been seasonal variations in the precipitation of different minerals, or secular changes in the δD of meteoric water over the time period of downcutting by the Sevier River. Analysis of water from Lemonade Spring (Table 5) shows it to be sulfate-dominated, with elevated levels of rare-earth elements and metals. The water contains 171 ppm SiO_2 , which would be in equilibrium with amorphous silica at about 58°C (Fournier and Potter, 1982). Modeling results indicate that Lemonade Spring is significantly supersaturated with respect to alunite, potassium jarosite, sodium jarosite, hydronium jarosite, and a potassium-rich jarosite solid solution and saturated with respect to gypsum, ferrihydrite, and amorphous silica (Robert Seal, personal communication, 2004).

The calculated $\delta\text{D}_{\text{H}_2\text{O}}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values of the fluid responsible for the 21.3 Ma alunite are similar to those of present-day meteoric water (Fig. 4b) but are shifted to larger values of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ due to oxygen isotopic exchange of the parental fluids with the host rocks. This ^{18}O shift is observed in the fluids of all of the replacement alunite at Marysville (Rye et al., 1992). Apparently the isotopic composition of meteoric water has not changed much in 21.3 m.y.

The erosional history of the Sevier River and basin-range extension played a major part in the supergene evolution of Big Rock Candy Mountain. Atop the stratovolcano that is the host for Big Rock Candy Mountain and Marysville Canyon to the north are scattered patches of Miocene sands and gravels (Cunningham et al., 1983). These are remnants of the Sevier River Formation (Callaghan, 1938) that buried the replacement-alunite deposits and protected them from erosion. Basin-range extension began in a mild way in the Marysville area at about 21–23 Ma. The Sevier River Formation was deposited in gently downwarped basins, and continued accumulating predominantly fluvial sediments until early Pleistocene time (Steven et al., 1979). The main episode of basin-range faulting in the Marysville area was between about 5 and 8 Ma (Steven et al., 1979; Rowley et al., 1994). Most probably, the coincidence of timing of the 6.6 Ma heating event seen in the alunite data (Fig. 3a), the trace of 6.7 Ma data in the natrojarosite (Fig. 3b), and the 5–8 Ma period of basin-range uplift and extension were related events. With the onset of rapid extension and crustal thinning, the upper crustal rocks were heated, and numerous rhyolite domes, flows, and basalt flows were erupted (Rowley et al., 1994). The area was uplifted and the Sevier River, which had been meandering on the Sevier River Formation, cut downward and entrenched its meanders into the hard rocks beneath to form Marysville Canyon. In doing so, the river exposed and began eroding the replacement-alunite alteration assemblage and the underlying pyrite-bearing rocks at Big Rock Candy Mountain. The sulfur and oxygen isotopic data indicate the deportment of the aqueous sulfate from the dissolution of hypogene gypsum and (or) alunite, as well as a significant contribution from the oxidation of pyrite, into the gypsum now present and forming all over the mountain. The requisite Ca for the formation of hypogene gypsum was derived from

propylitically altered andesites, which form a concentric halo around the feeder zone for the replacement-alunite center (Fig. 5). The supergene alteration of these same andesites during the oxidation of pyrite continues to supply Ca for gypsum precipitation. In contrast, the natrojarosite forms from aqueous sulfate derived from the oxidation of pyrite, with a minor contribution of sulfate from the dissolution of alunite and gypsum. The small occurrence of jarosite with hematite and silica above Big Rock Candy Mountain is probably near the top of the original replacement alunite deposit.

6. Conclusions

Big Rock Candy Mountain provides a unique opportunity to study a three-dimensional exposure of a classic steam-heated replacement alunite deposit and to trace its development and destruction through time. The addition of high-resolution AVIRIS mapping capability for the identification and distribution of altered rocks offered the opportunity to bring together geological, mineralogical, and stable-isotope geochemistry with synergistic results. Big Rock Candy Mountain is the dissected remnant of a 21.3 Ma hydrothermal system that formed a replacement-alunite deposit much like others in the Marysvale volcanic field, but the uniqueness is that the base is well exposed, in marked contrast to the other deposits. Big Rock Candy Mountain is zoned vertically upward from a pyrite-bearing, propylitic assemblage, to alunite, with minor barite, and with the presumed jarosite, hematite, and silica cap mostly removed by erosion. The mountain is zoned laterally from alunite outward to kaolinite, to dickite, and to a propylitic assemblage. The deposit is interpreted to have formed above the upwelling limb of a hydrothermal convection cell, near the paleo ground surface, with alternating deposition of silica, hydrothermal explosions, and introduction of atmospheric oxygen that oxidized hot H₂S to form sulfuric acid. The acid, in turn, reacted with the host rocks to form alunite and kaolinite below the water table and the upward sequence of jarosite, hematite, and silica above it. Below the zone of oxidation, the andesites were propylitized and sulfidized. Big Rock Candy Mountain was buried and protected by sands and gravels

until rapid uplift of the Eastern Basin and Range at about 7.0 Ma caused the Sevier River to cut and expose the pyrite-bearing, deeper part of the system. These pyrite-bearing dacite lava flows are being oxidized and are forming gypsum, and the natrojarosite and kaolinite that give the buff color to the cliff, by reaction with acid waters like those occurring in Lemonade Spring.

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