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$^{40}Ar/^{39}Ar$ DATING OF ALUNITE FROM THE PUEBLO VIEJO GOLD-SILVER DISTRICT, DOMINICAN REPUBLIC*

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Abstract

New $^{40}Ar/^{39}Ar$ ages for alunite from the Moore and Monte Negro deposits in the Pueblo Viejo district, as well as from a newly discovered alunite-bearing zone on Loma la Cuaba west of the known deposits, are reported here. The ages range from about 80 to 40 Ma, with closely adjacent samples exhibiting very different ages. Interpretation of these results in the context of estimated closure temperatures for alunite and the geologic and tectonic evolution of Hispaniola does not lead to a simple conclusion about the age of mineralization. The simplest interpretation, that mineralization was caused by a buried Late Cretaceous (~80 Ma) intrusion, is complicated by lack of intrusions of this age in the area and absence of alteration in overlying limestone. The alternative interpretation, that mineralization was formed during Early Cretaceous (~110 Ma) magmatism and that the $^{40}Ar/^{39}Ar$ ages were completely reset by Late Cretaceous thrusting, is complicated by a lack of information on the timing and thermal effects of thrusting in central Hispaniola. Alunite studies have yielded similar unclear results in other pre-Cenozoic ore systems, notably those of the Lachlan fold belt in Australia.

Introduction

Resolving the controversy about the age of the Pueblo Viejo district in the Dominican Republic (Sillitoe et al., 2006, 2007; Muntean et al., 2007) is important because knowledge of the age of this giant high-sulfidation epithermal deposit will clarify its relationship to the tectonic and petrologic evolution of its host magmatic arc, help explain some of its unusual geologic and mineralogical characteristics, and improve geologic models used to explore for similar deposits (Hedenquist et al., 2000; Simmons et al., 2005). On one side of the controversy are those who consider mineralization to be essentially coeval with the Early Cretaceous Los Ranchos Formation that hosts ore (Bowin, 1966; Kesler et al., 1981; Sillitoe and Bonham, 1984; Muntean et al., 1990; Mueller et al., 2008). On the other side of the controversy are those who consider the district to be the product of a Late Cretaceous magmatic-hydrothermal event that overprinted the Los Ranchos Formation (Redwood et al., 2006; Sillitoe et al., 2006).

One of the key minerals in the controversy is alunite, which is an important constituent of the advanced argillic hydrothermal alteration assemblage at Pueblo Viejo and a common subject of isotopic (K-Ar and $^{40}Ar/^{39}Ar$) age measurements (e.g., Itaya et al., 1996). Surprisingly, to date only two samples of alunite from Pueblo Viejo have been dated. The results, 66.0 and 77.0 Ma (Kesler et al., 1981; Kesler, 1998, respectively) were inconclusive and have added to the controversy.

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*Supplementary material for this paper is available at <http://economicgeology.org/>

**Alphabetical listing of authors reflects uniform contributions to the work and lack of unanimity on significance of data.

In this contribution, we present results of $^{40}Ar/^{39}Ar$ analyses of alunite samples from drill core from gold-silver ore in the Pueblo Viejo district as well as alunite-bearing outcrop samples from a newly discovered zone outside the area of known mineralization in the district. Unfortunately, our results do not provide a clear answer. Our data demonstrate a complex thermal history for the Pueblo Viejo region characterized by partial to total loss of radiogenic argon in the hydrothermal alunite. Resolution of the controversy will likely require a better understanding of other key minerals in the advanced argillic assemblage, such as pyrophyllite, and analyses in other isotopic systems.

Geologic Setting of Samples Analyzed in this Study

The Pueblo Viejo district, with reserves in 2010 of about 23.7 million ounces (Moz) of gold (http://www.barrick.com/GlobalOperations/NorthAmerica/PuebloViejoProject/default.aspx), is one of the largest high-sulfidation epithermal gold-silver deposits in the world. It is located in the Dominican Republic, which shares the island of Hispaniola with Haiti (Fig. 1). As discussed in more detail later in this report, central Hispaniola consists largely of fault-bounded strips of Cretaceous volcanic and sedimentary rocks that have undergone several periods of magmatic activity and deformation, including thrusting (Fig. 2). Mineralization at Pueblo Viejo occupies the upper part of one of the oldest volcanic units in this sequence, the Lower Cretaceous Los Ranchos Formation (Fig. 3).

Alunite samples analyzed in this study come from two areas: the main mineralized system in the Pueblo Viejo district, which is defined by the Moore and Monte Negro deposits, and a newly discovered alunite-bearing zone in the western part of the district on Loma la Cuaba (Figs. 3, 4). Alunite in

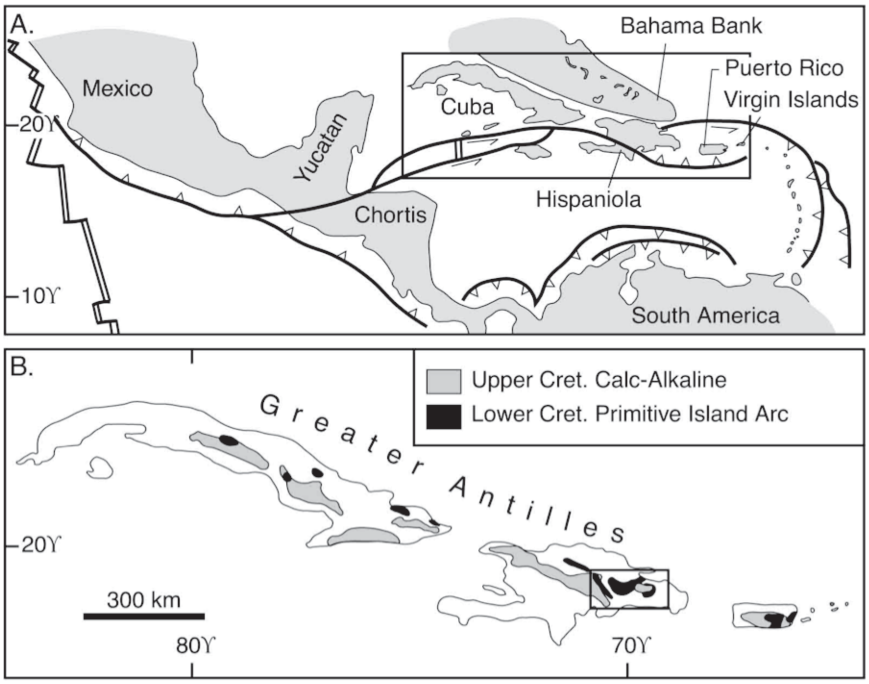

FIG. 1. A. Present plate tectonic setting of the Caribbean region showing location of Hispaniola, which is shared by Haiti on the west and the Dominican Republic on the east. B. Distribution of Lower and Upper Cretaceous volcanic and intrusive rocks in the Greater Antilles. Rectangle shows location of Figure 2.

the Moore and Monte Negro deposits is found largely at the deepest levels of the mineralized zone, well below the zone of weathering, and is clearly hypogene in origin (Kesler et al., 1981, Fig. 3; Muntean et al., 1990, Fig. 4). The interpretation of a hypogene origin for the alunite is supported by its sulfur isotope composition and the fact that it coexists with pyrite and quartz and is replaced locally by diaspore, pyrophyllite, kaolinite, and sparse sericite (Muntean et al., 1990; Fig. 5). The main alteration minerals in the upper parts of the deposits are kaolinite and quartz, which are replaced

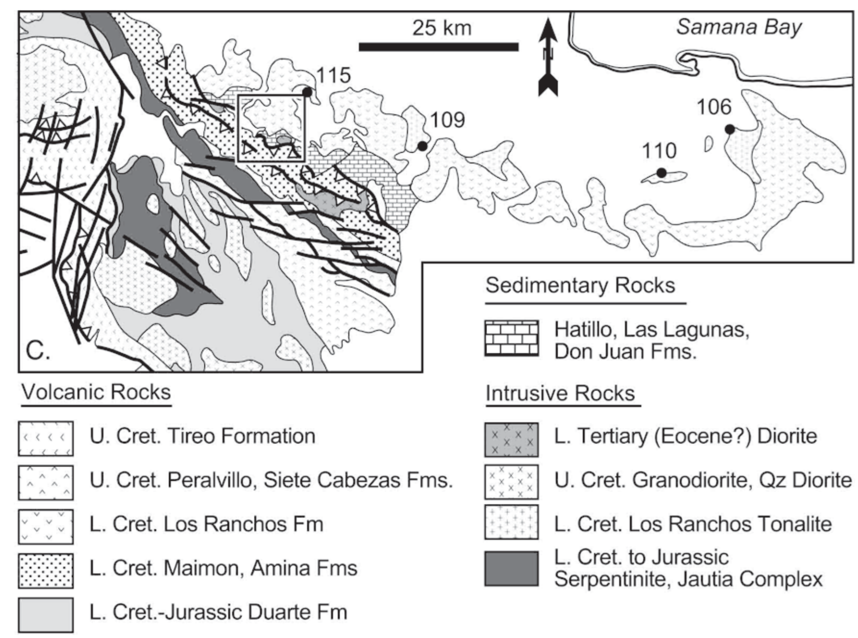

FIG. 2. Geologic map of the Central Cordillera of the Dominican Republic (modified from Escuder Viruete et al., 2002), showing the regional geologic setting of the Los Ranchos Formation and the Pueblo Viejo district. Numbers beside black dots in the Los Ranchos Formation are ages measured on zircons in tonalite intrusions from Kesler et al. (2005) and Escuder-Viruete et al. (2006b). Rectangle shows location of Figure 3.

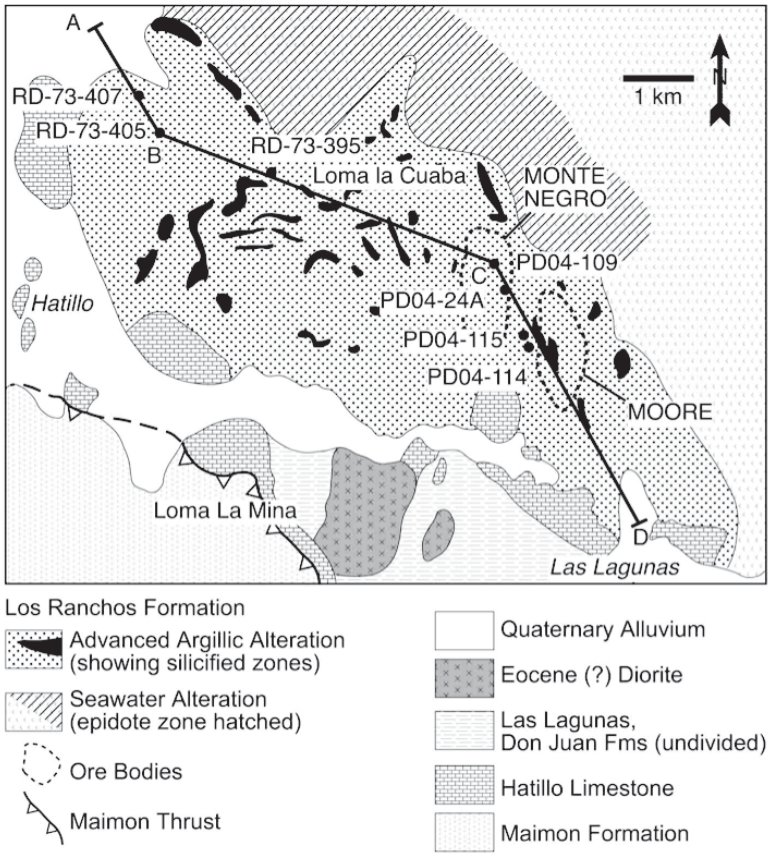

FIG. 3. Geologic map of the southern part of the Los Ranchos Formation and adjacent rocks, showing location of Moore and Monte Negro, the largest deposits in the Pueblo Viejo district, as well as samples analyzed in this study. Cross section along line A-B-C-D is shown in Figure 4.

partly or completely in many places by pyrophyllite and grade farther upward into intensely silicified rocks at the top of the deposits.

The Moore and Monte Negro deposits form part of a large zone of advanced argillic alteration that extends westward onto Loma la Cuaba (Fig. 3) where massive, stratiform layers of silica are enclosed within foliated rock consisting largely of quartz and pyrophyllite with local areas containing alunite. Both the stratiform bodies of silica and the enclosing foliated rock dip to the southwest parallel to regional structural trends. These alunite-hosting rocks have undergone weathering that

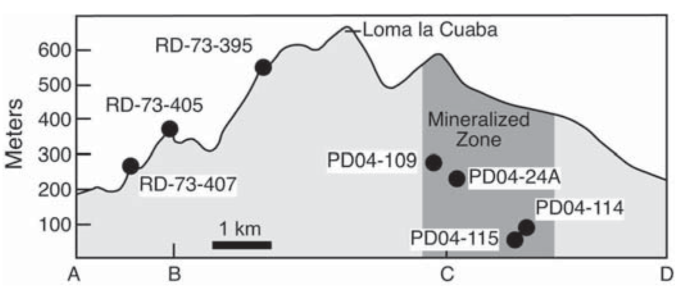

FIG. 4. Cross section through the Pueblo Viejo district, showing the relative location of samples analyzed in this study and the relationship between alunite-bearing zones in the Moore-Monte Negro area and Loma la Cuaba. Shaded zone shows the projection downward of the limits of gold mineralization in the Monte Negro-Moore deposits.

removed pyrite but are otherwise similar in mineralogy to those in the Moore and Monte Negro deposits.

Alunite from the Moore and Monte Negro deposits

Alunite was selected from drill core in the Moore and Monte Negro deposits (Fig. 3) with guidance from an infrared spectrometric survey conducted by Placer Dome Inc. in 2004 and 2005 (C. Tarnocai, writ. commun.). Consistent with previous observations (Kesler et al., 1981), samples with the highest concentration of alunite were found along a deep northwest-southeast–trending core zone of alteration that connects the two deposits. Seven samples from four separate drill holes (PD04-109, PD-04-024, PD04-114 and PD04-115) were selected for separation of alunite. Average grades of the drill core intervals from which the samples were collected are low (0.25–1 or 2 g/t Au) with the exception of PD04-115 (265 and 266 m), which averaged 2 to 3 g/t Au. Alunite in these samples forms disseminated white to light pink, fine-grained (<0.5 mm) masses, veinlets, and breccia matrix (Fig. 5). To test consistency of analytical results, pairs of closely spaced samples were collected from three drill holes, including PD04-115 at depths of 266 and 265 m, PD04-24A at depths of 102.1 and 109.7 m, and PD04-109 at depths of 143.4 and 145.8 m. Individual samples in these pairs have similar mineralogical, structural, and geochemical characteristics.

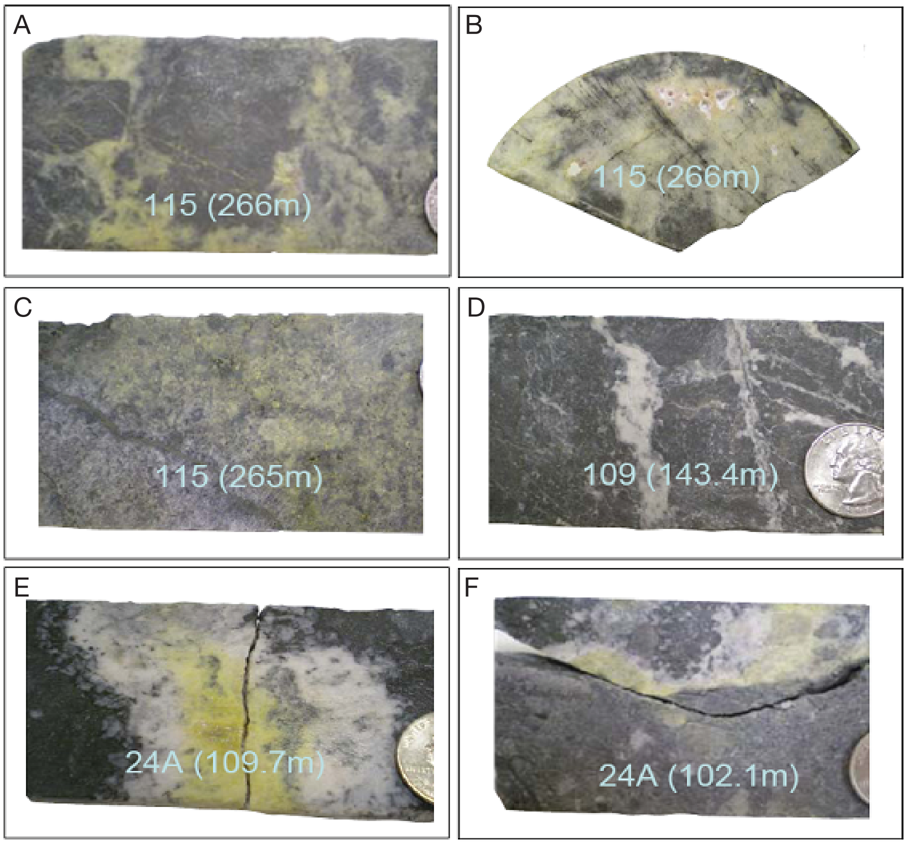

FIG. 5. Photos of alunite-bearing drill core from the Moore and Monte Negro orebodies at Pueblo Viejo used for Ar-Ar analyses. Numbers identify drill hole and depths (in parenthesis) from which samples were obtained. Alunite is the dominant mineral, together with quartz and minor to trace amounts of pyrophyllite, illite, anhydrite, and kaolinite, in the light-colored domains of the drill core. Yellow stain is a patina developed in the drill core box from weathering of fine-grained pyrite in sample. Photo B shows microdrilling pits used to extract pure (pink) alunite for analysis.

Alunite from Loma la Cuaba

Alunite that was analyzed from Loma la Cuaba comes from a zone of advanced argillic alteration located about 3 to 5 km west of Monte Negro (Fig. 3). The zone is represented in this study by three samples (RD-73-395, RD-73-405, and RD-73-407) collected along a northwest-trending ridge that extends downward for about 300 m from the summit of Loma la Cuaba toward the Hatillo Limestone (originally mapped as Las Canas Limestone by Bowin, 1966). The range of elevations on Loma la Cuaba that contain alunite is approximately the same as that of the main ore zones in the mine area (Fig. 4).

All of the samples consist largely of quartz with various combinations of pyrophyllite, kaolinite, alunite, and diaspore, and minor topaz and limonite pseudomorphs after pyrite. Samples RD-73-395 and RD-73-407 are strongly sheared and foliated parallel to regional trends. Foliation in sample RD-73-407 is due to numerous, narrow shear zones containing pyrophyllite and alunite, whereas foliation in RD-73-395 is due to parallel alignment of fine-grained alunite crystals that are disseminated throughout the rock (Fig. 6). Alunite in both samples forms lenses containing several grains that might originally have been a single grain. Sample RD-73-405 lacks foliation and consists of enclaves containing coarse-grained (1–0.5 mm) alunite, diaspore, and iron oxide pseudomorphs after pyrite (Fig. 6) that are surrounded by massive quartz and minor kaolinite. The juxtaposition of quartz and diaspore, which are not stable together under hydrothermal conditions, is probably due to shearing (Hemley et al., 1980). The mineralogical composition and preshearing textures of these rocks are similar to those found in the deep, alunite-bearing cores of the Moore and Monte Negro deposits. Their presence to the west of the main deposits suggests that similar rock might underlie the top of Loma la Cuaba, which separates the newly discovered area from the ore deposits (Fig. 3).

Analytical Methods and Results

Alunite mineral separates from the Moore and Monte Negro deposits were prepared by drilling out alunite-rich areas and handpicking under a binocular microscope to remove impurity minerals. Visual inspection indicated that impurity minerals made up about 5 to 10 percent of the separates. X-ray diffraction analyses indicate that the mineral separates were composed largely of alunite and quartz, with minor to trace amounts of pyrophyllite, illite, anhydrite, and/or kaolinite. Samples from Moore and Monte Negro were analyzed at the University of Nevada, Las Vegas, where they were wrapped in pure Al foil and irradiated in the TRIGA type reactor at the Nuclear Science Center of Texas A&M University. During analysis multiple grains were step-heated in a resistance furnace. Alunite samples from Loma la

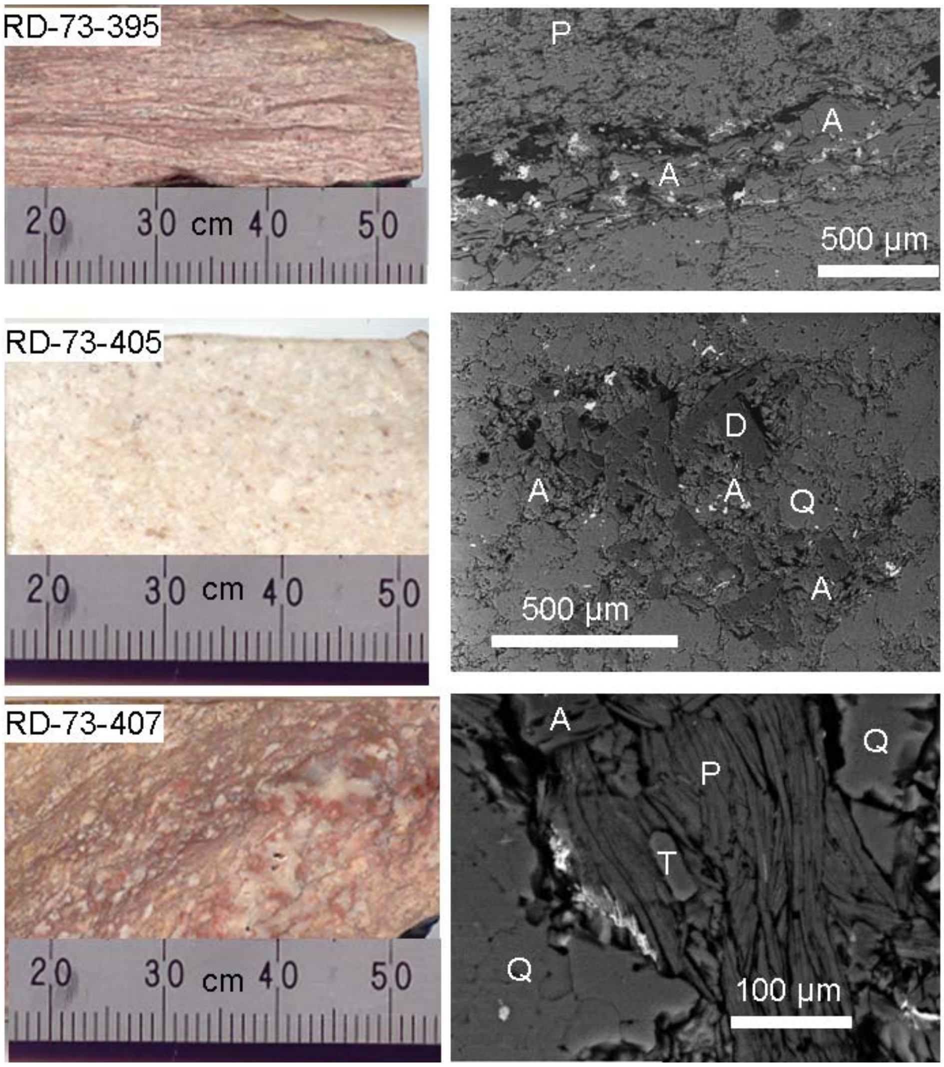

FIG. 6. Photos and SEM images of alunite-bearing samples from Loma la Cuaba used for Ar-Ar analyses. A = alunite, D = diaspore, P = pyrophyllite, Q = quartz, T = topaz.

Cuaba were prepared by drilling out areas of thin section chips that were observed to be especially alunite rich in optical examination of the thin section from each chip. In most cases, alunite constituted about 30 vol percent of the area that was drilled out, with the remainder consisting largely of quartz, with minor pyrophyllite and diaspore. Alunite-rich chips measuring a few millimeters in diameter from this material were wrapped in pure Al foil and irradiated at the McMaster Nuclear Reactor at McMaster University in Hamilton, Ontario, and analyzed at the University of Michigan. Age spectra were derived from individual grains by step-heating using a continuous argon-ion laser. All analytical data are reported at the confidence level of 1s (standard deviation). See Appendix 1 for details of the analytical procedures.

$^{40}Ar/^{39}Ar$ spectra from the alunites range from simple to very complex (Table 1, Fig. 7; additional data are provided in App. 1, which contains tables of analytical results for both laboratories, as Supplementary Tables 1 and 2, as well as spectra for samples not shown in Fig. 7 and isochron plots for selected samples). In the simplest spectra, three or more gas fractions comprising more than 50 percent of the total gas yield a good plateau. These include PD04-24A-102.1 (74.2 ± 0.9 Ma), PD04-114-175 (46.1 ± 0.3 Ma), PD04-115-265 (73.0 ± 1.1 Ma), and PD04-115-266 (42.1 ± 1.1 Ma) from the Moore-Monte Negro mineralized zone. In the case of Loma la Cuaba samples, four different aliquots of each of the three samples were analyzed. For RD-73-407, plateau ages of 47.3 ± 0.3, 45.8 ± 1.1, 50.0 ± 2.2, and 53.4 ± 0.4 Ma were determined from all four aliquots. For RD-73-405, plateau ages of 55.6 ± 3.3, 56.0 ± 2.6, and 69.0 ± 3.7 Ma could be determined from three of the aliquots. For RD-73-395, only one aliquot yielded a plateau age (66.1 ± 4.6 Ma). Representative age spectra from Moore-Monte Negro and Loma la Cuaba are shown in Fig. 7a-c and Fig. 7d-f, respectively. Both areas yield ages ranging from ~70 to 80 Ma to ~45 Ma (Table 1), with age spectra that give good plateaus (Fig. 7a, b, e, and f) or that are significantly disturbed (e.g., Fig. 7c). The generally coarse grained nature of the samples argues against recoil being a significant issue in these spectra; however, it should be noted that identification of this phenomenon is ambiguous when

TABLE 1. Summary of Ar-Ar Ages Used in This Study (all quoted errors are 1σ)

Sample no.	Run	alteration zone	Mineral	Plateau (alunite) or retention (illite) Age (Ma)	1σ	Total gas Age (Ma)	1σ	Note[1]
PD04-115-266		Moore	Alunite	42.1	1.1	44.0	1.1	1
PD04-115-265		Moore	Alunite	73.0	1.1	71.1	1.1	1
PD04-24A-102.1		Monte Negro	Alunite	74.2	0.9	72.4	0.8	1
PD04-24A-109.7		Monte Negro	Alunite			78.8	0.3	1
PD04-114-175		Moore	Alunite	46.1	0.3	45.9	0.3	1
PD04-109-143.4		Monte Negro	Alunite			47.8	0.3	1
PD04-109-145.8		Monte Negro	Alunite			75.2	0.4	1
RD-73-405	a	Loma La Cuaba	Alunite			58.9	1.5	2
	b			55.6	1.3	56.3	3.3	
	c			69.0	3.7	157.7	6.8	
	d			56.0	2.6	52.6	6.0	
RD-73-407	a	Loma La Cuaba	Alunite	47.3	0.3	50.0	1.0	2
	b			53.4	0.4	53.1	1.4	
	d			45.7	1.1	45.7	2.4	
	e			50.0	2.2	51.6	4.3	
RD-73-395	a	Loma La Cuaba	Alunite	66.1	4.6	88.2	13.1	2
	b					52.0	2.9	
	c					61.0	0.3	
	e					71.2	0.7	
DDH-168-44		Moore	illite	58.3	0.7	49.1	0.7	3
DDH-170-176	a	Monte Negro	Alunite			77.0	0.3	4
	b					77.7	0.6	
DDH-177-205		Moore	Alunite			66.0	0.8	5

[1] Note: 1 = analyses performed at the University of Nevada, Las Vegas (see Supplementary Table 1 for additional information; 2 = analyses performed at the University of Michigan (see Supplementary Table 2 for additional information; 3 = illite analysis performed at the University of Michigan and reported in Kesler et al. (2005); 4 = analysis from Kesler (1998) performed at Ohio State University; 5 = analysis from Kesler et al. (2005) performed at Ohio State University

the diluting mineral is quartz, which does not produce any identifying Ar isotope.

A remarkable feature of these age spectra is their extreme variability. Even for samples separated by only a few millimeters or centimeters there is a large variability in ages, and separate aliquots of the same sample also give significantly different ages. The Loma la Cuaba samples were each derived from single clumps of alunite and/or quartz that measured ~1 to 2 mm in diameter, whereas the Moore-Monte Negro samples were aggregates of multiple grains. Even these multigrain aggregates show a wide range of ages. For instance PD04-115-265 and PD04-115-266 (Fig. 7a, b, respectively) are only 1 m apart in the same drill core, and yet their ages span the complete range seen in this study. The range of ages of the Moore-Monte Negro samples were more than an order of magnitude larger than the ages of the samples from Loma la Cuaba and might have generated even greater variability if they had been analyzed at a finer scale.

Two additional features can be seen in the age spectra. First, some high apparent ages correspond to Cl-rich fluid inclusions that degassed at low temperature (Fig. 7c-e). Age spectra for several other samples show elevated Ca/K and Cl/K ratios in the high-temperature region that reflect the presence of a retentive phase (Fig. 7a, d, and especially e). It is difficult to explain these high ages as due to ^{39}Ar recoil, which would tend to make the ages younger, or as incorporation of "excess Ar," because that would tend to come out at a lower temperature. In addition, some of these retentive phases yield ages that are unusually old relative to rocks in the Greater Antilles, especially 719 ± 14 Ma from RD-73-405 on Loma la Cuaba and 317 ± 11 Ma from DDH-115-226 at Monte Negro. If these old ages reflect detrital components in the protolith for these altered rocks, the protoliths were sedimentary or volcaniclastic rather than purely volcanic, a potentially important point in the debate about the origin of these highly altered rocks.

^{40}Ar/^{39}Ar analyses for Pueblo Viejo alunite from this study (Table 1) and previous efforts are shown separately for the Moore, Monte Negro, and Loma la Cuaba zones as both plateau and total-fusion ages (Fig. 8). In most cases, the plateau and total-fusion gas ages are very similar. Alunite ages from the Moore and Monte Negro deposits from this study define a bimodal population with clusters at 42 to 48 and 71 to 79 Ma. Combined with the alunite ages from Loma la Cuaba, the dataset provides a broadly even spread of ages between ~40 and ~80 Ma, and no ages younger than 42 Maor older than 79 Ma.

The wide range of ages cannot be ascribed to mixtures of two different K-bearing phases. All samples were characterized by either X-ray (Monte Negro, Moore) or SEM (Loma la Cuaba) and the only abundant K-bearing phase is alunite. Illite is present in trace amounts in a few samples, but its abundance is too small to account for the range of ages or spectra, especially in view of its lower content of potassium. There is also no relationship between the presence of trace illite and the spectra that were observed. Thus, the variability of results

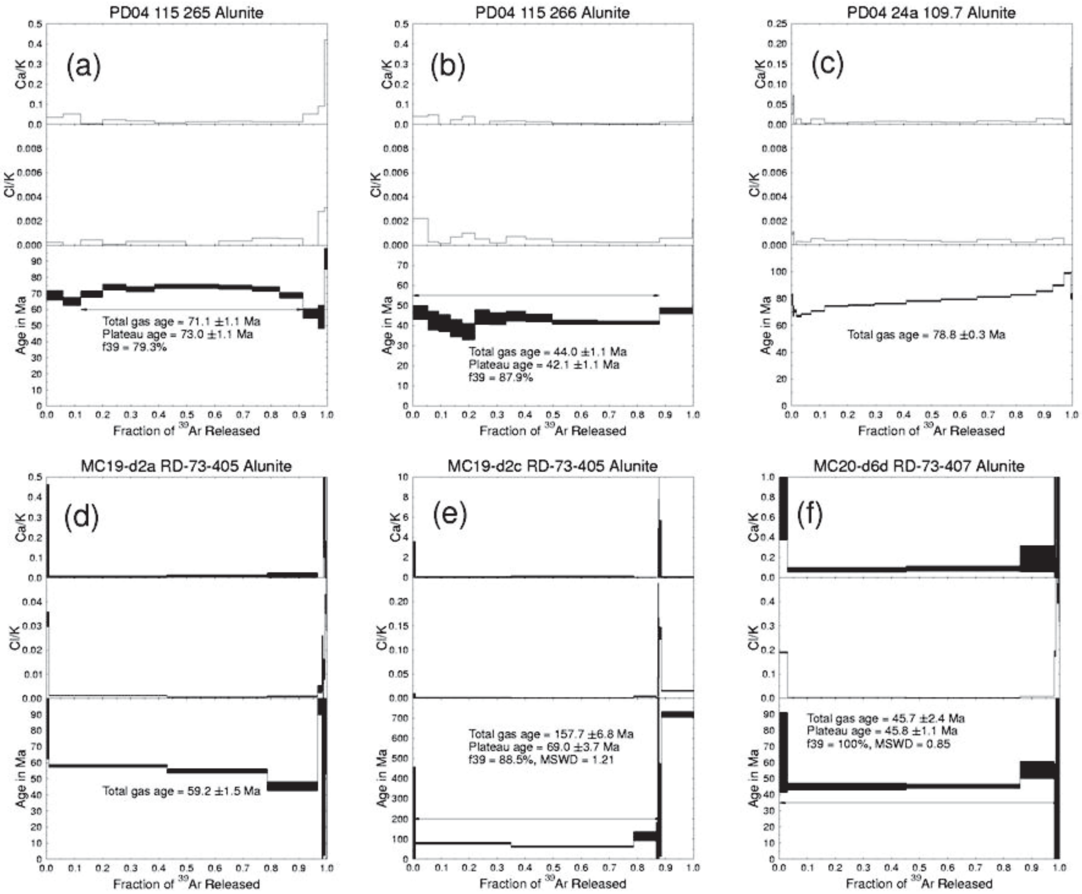

Figure 7. Age, Ca/K and Cl/K spectra for samples from Monte Negro (a, b, and c) and Loma La Cuaba (d, e, and f). Cl/K and Ca/K values from Monte Negro do not have error estimates and only their calculated values are shown. Otherwise, error boxes are ±1 .

appears to reflect the actual $^{40}Ar/^{39}Ar$ geochemistry of the alunite, with individual alunite crystals or crystal groups yielding different ages. Sample PD04-24a-109.7 (Fig. 7c) is particularly interesting in this respect because it appears to show a range of ages from ~65 to ~90 Ma.

Interpretation of the Results

It is unrealistic and highly unlikely that the range of alunite ages from ~40 to ~80 Ma (Fig. 8) represents a 40-m.y. period during which alunite continuously formed. Instead, it probably reflects the closure of Ar diffusion in different alunite samples during a complex thermal evolution for the Pueblo Viejo region. Interpretation of the number of thermal events involved in this evolution depends on the closure temperatures of alunite and how they relate to the tectonic history of Hispaniola.

Closure temperatures and indicated number of thermal events

Estimation of closure temperatures in minerals requires the assumption of sphere, infinite cylinder, or infinite slab geometry. For the Pueblo Viejo alunites, a spherical shape is most appropriate based on the dimensions of crystals seen in thin section (Fig. 6). Closure temperatures for alunite have been estimated previously by Itaya et al. (1996) and Love et al. (1998). Based on the measured argon diffusion parameters for alunite and data for sample DL-198 of Love et al. (1998), we can estimate an activation E of 90.4 kcal/mol and a frequency factor D_0/a^2 of 2.756×10^{21} s^{-1} using a spherical geometry. There is some ambiguity as to the grain size of the samples in the Love et al. (1998) study. If one assumes a diameter of 100 μm, the value of D_0 would be 6.89×10^{16} cm^2/s, but a diameter of 1 mm would yield a value for D_0 of 6.89×10^{18} cm^2/s. Our alunite samples typically had diameters of ~100 μm, but the coarsest samples reached ~1 mm and with generally equant shapes that are best modeled as a sphere. Assuming the first value of D_0, and a diameter of 100 μm, estimated blocking temperatures for our alunite samples would be 268°or 283°C for cooling rates of 10 or 100°C/Ma, respectively. Using the second value of D_0, the estimated blocking temperature would be 241° and 254°C for cooling rates 10° and 100°C/Ma, respectively. Assuming a diameter of 1 mm for our samples increases the estimated blocking temperatures. For the first value of D_0, blocking temperature estimates are 299° and 316°C for cooling rates of 10° and 100°C/Ma, respectively, and for the second D_0 value, these estimates are 268° and 283°C for cooling rates of 10° and 100°C/Ma. We therefore estimate a blocking temperature for

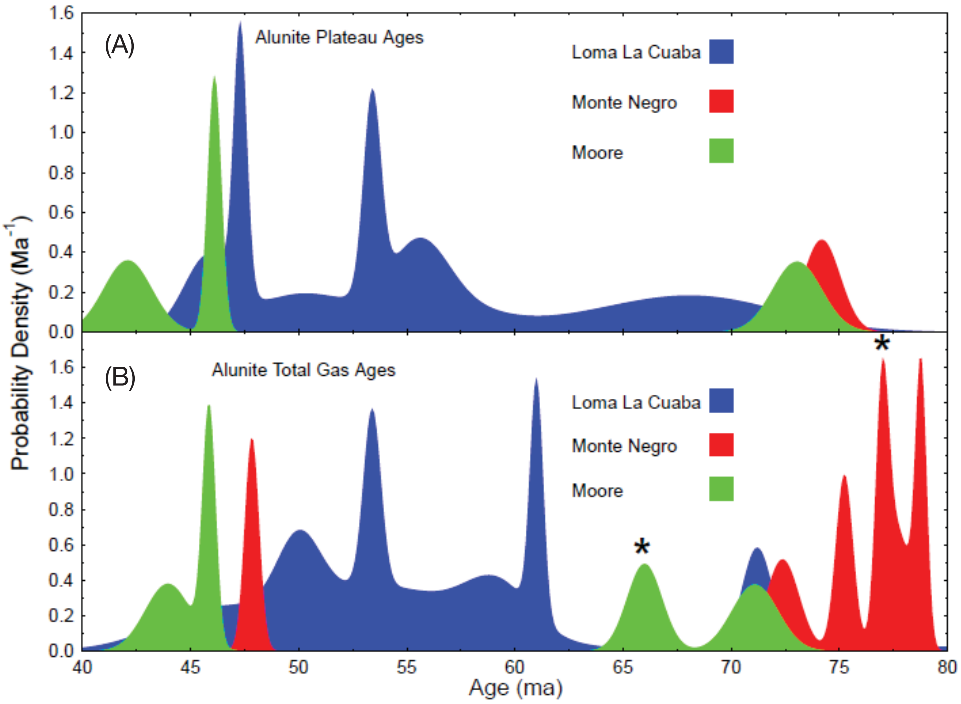

FIG. 8. Plot of all alunite Ar-Ar and K-Ar ages considered in this study. This histogram is in the form of a plot of individual probability distributions for each age determination, so that the area under each measured age distribution is 1, a characteristic that is shared with more conventional histograms, but in this case the effect of variable measurement precision can be accounted for. Asterisks indicate previously published alunite ages from Kesler (1998) and Kesler et al. (1981).

our alunite samples to be ~300°C or less, even for a fast cooling rate of about 100°C/m.y., which would be typical of epithermal environments.

Use of alunite closure temperatures in interpretation of the Pueblo Viejo $^{40}Ar/^{39}Ar$ ages is complicated by the lack of a strong clustering of alunite ages into discrete groups with respect to location or geologic features. Alunite samples collected within even meters to centimeters of one another yield different ages. One possible explanation for this is that the cooling history of the region involved at least one and possibly several later heating events that formed or reset minerals locally, possibly along veinlets that are not obvious in the altered rock.

Earlier K-Ar and $^{40}Ar/^{39}Ar$ analyses support the interpretation of a complex thermal history for the region. Nelson (2000) reported K-Ar ages of 46.1±1.2 and 63.1±1.7 Ma for impure concentrates of sericite and feldspar, respectively, and 32.5 Ma for feldspar in dikes that cut the Pueblo Viejo orebodies and were interpreted to be postore in age. Kesler et al. (2005) reported a $^{40}Ar/^{39}Ar$ age of 58 Ma for illite from the Moore ore body. Using the model age spectra of Hall et al. (2000), this illite age spectrum is best interpreted as representing a single age population for which the retention age model is most appropriate; therefore, 58 Ma probably represents the Ar closure age for illite in the Moore deposit. Unfortunately, the wide range in estimated diffusion parameters for muscovite (Robbins, 1972; Hames and Bowring, 1994; Harrison et al., 2009) yields possible closure temperatures over a range of about 200°C for likely grain sizes (Parry et al., 2001).

The closure temperatures estimated here for alunite are either comparable to or lower than those for illite, especially if we use the Harrison et al. (2009) diffusion parameters. Because the illite age is younger than many of the alunite ages, this difference in closure temperature requires that there was at least one episode of illite formation after the main Ar-blocking time for alunite at ~80 Ma, but prior to the final exhumation and/or cooling event that marks the end of argon loss at ~40 to 45 Ma. This is consistent with the observation of illite replacing alunite at Monte Negro (Muntean et al., 1990). Resetting of alunite during this illite event was not so severe as to either completely outgas all of the alunite, or to outgas some of the unusually old, possibly detrital, phases in the alunite. The high variability of ages over a very broad range of length scales suggests that Ar retention was determined largely by local factors and that the alunite was probably close to its Ar closure temperature at the time of the later disturbing event.

Relationship of isotopic ages to geologic evolution of Hispaniola

Two major features of the geologic evolution of Hispaniola, volcanic-intrusive activity and deformation, might have played a role in the formation or resetting of alunite at Pueblo Viejo. The first stage of arc magmatism in Hispaniola involved Early Cretaceous southwest-directed subduction, which formed volcanic rocks of the Rio Verde, Maimon, Amina, and Los Ranchos Formations on a basement of sea floor probably related to the Duarte Formation and Loma Caribe Peridotite-Serpentinite Complex (Fig. 3; Escuder Viruete et al., 2010). During this time, tonalite intrusions with U-Pb isotope ages (on zircons) of 106 to 115 Ma were emplaced along the entire extent of the Los Ranchos Formation from Cotui eastward through Cevicos to Sabana Grande (Fig. 2; Kesler et al., 2005; Escuder-Viruete et al., 2006b). One tonalite intrusion of this age at Cotui directly underlies the Pueblo Viejo district and has been linked to mineralization by those favoring an Early Cretaceous age (Kesler et al., 2005).

Subsequent Late Cretaceous arc magmatism, which formed the Tireo, Peralvillo South and North, and Siete Cabezas Formations (Fig. 2), continued intermittently until the end of the Campanian (about 72 Ma; Escuder-Viruete et al., 2007, 2008). This magmatism shifted location with time but was focused mainly to the west of the Los Ranchos Formation in the central and western parts of the Cordillera Central. It produced a wide zone of granodiorite and quartz diorite intrusions, most of which range in age from 87 to 80 Ma (Kesler et al., 1991). These are the right age to account for the suggested Late Cretaceous formation of Pueblo Viejo mineralization (Sillitoe et al., 2007), although their outcrop belt does not extend as far east as the Pueblo Viejo district (Fig. 2).

The final phases of arc magmatic activity formed the mid-Eocene Loma Caballero tuffs and Eocene(?) diorites (Bowin, 1966), which are near the Pueblo Viejo district. The diorite stocks, in particular, intrude Hatillo Limestone within a few hundred meters of Pueblo Viejo and could have supported hydrothermal systems that circulated through the ore deposits. This hydrothermal circulation almost certainly produced the youngest, mid-Cenozoic ages reported here.

Deformation of the Pueblo Viejo region, which was widespread during Cretaceous and later plate reorganization in the northern Caribbean (Escuder-Viruete et al., 2006a; Garcia-Casco et al., 2008; Krebs et al., 2008), could have reset ages. Early Cretaceous and older volcanic-sedimentary rocks (Amina, Maimon, Rio Verde Formations) and coeval sea floor and mantle (Duarte and Loma Caribe Peridotite-Serpentinite Complexes) in the Cordillera Central are exposed in long thin belts that have undergone variable degrees of northeastward thrust displacement toward the Los Ranchos Formation and the Pueblo Viejo district (Fig. 2). Confirmation that the Los Ranchos Formation participated in the thrusting is seen in its uppermost part on Loma la Cuaba, which is strongly foliated parallel to the regional structural trend. Postmineral, east-verging thrusts were mapped in the Los Ranchos Formation throughout the mine area.

The age of this deformation, and its relationship to the age of alunite at Pueblo Viejo, is the subject of continuing study. Draper et al. (1996) described intense, mylonitic penetrative deformation in the Maimon-Amina Formations and lesser penetrative deformation in the upper, pyrophyllite-rich part of the Los Ranchos Formation around Pueblo Viejo. Lack of similar deformation in the overlying Hatillo Limestone led Draper et al. (1996) to conclude that the regional thrusting event took place before deposition of the Hatillo Limestone, probably at about 110 m.y. This Early Cretaceous age for thrusting is supported by $^{40}Ar/^{39}Ar$ ages of 110 m.y. for metamorphic rocks in the Rio Verde Complex, which occupies a thrust sheet just west of Pueblo Viejo (Escuder-Viruete et al., 2009, 2010). If this interpretation is correct, then mineralization took place before 110 m.y. because pyrophyllite-bearing rocks are strongly foliated.

However, Los Ranchos Formation rocks below the pyrophyllite-rich upper part are unfoliated. Thus, an alternative interpretation of the field relationships is that the contact between the Hatillo and Los Ranchos is a depositional surface, probably an unconformity, as suggested by Kesler et al. (1981) and Sillitoe et al. (2006), and that deformation foliated only the weakest part of the Los Ranchos Formation (and similar, phyllosilicate-rich parts of the Maimon and Amina Formations) and that this event did not generate foliation in the overlying Hatillo Formation or underlying Los Ranchos volcanic rocks, which contained much smaller amounts of phyllosilicates. If so, our ages of ~70 to 80 Ma for foliated pyrophyllite-bearing rocks in the upper Los Ranchos Formation could represent the age of regional thrusting and metamorphism. Thrusting of this age could have reset older (110 m.y.) alunite ages only through thermal effects, and the thermal effects of Late Cretaceous thrust sheets varied greatly from place to place. Assemblages up to granulite facies in the Rio Verde Complex tens of kilometers west of Pueblo Viejo (Fig. 2) are thought to reflect emplacement of an overlying thrust sheet consisting of hot peridotitic mantle (Escuder-Viruete et al., 2002). The northeastward extension of this thrusting might account for metamorphism of the Maimon Formation immediately southwest of the Pueblo Viejo area, and structurally above it, at temperatures of 300° to 350°C (Escuder-Viruete et al., 2002, Figs. 6, 7).

The only possible evidence that temperatures of this magnitude might have affected the Pueblo Viejo area is seen in widespread paragenetically late pyrophyllite, which crops out over an area of about 30 km^2 in the top of the Los Ranchos Formation (Loma la Cuaba). This pyrophyllite is much more widespread than gold and replaces kaolinite far beyond the central areas of most intense mineralization (Muntean et al., 1990). Widespread, paragenetically late pyrophyllite of this type has not been described in other high-sulfidation epithermal deposits, and its unusual location as well as great extent might be the result of a metamorphic overprint on an original kaolinite-quartz alteration assemblage. Reaction between kaolinite and quartz to form pyrophyllite occurs at 260°C at pressures along the liquid-vapor curve of water and increases to 273°C at 1 kbar and about 300°C at 3 kbars (Hemley et al. 1980), which might have been adequate to reset older 110 Ma $^{40}Ar/^{39}Ar$ ages.

The final stages of deformation in the arc took place during early Cenozoic collision of the Greater Antilles with the Bahama platform (Fig. 2), which resulted in oblique offset along preexisting structures (Garcia-Casco et al., 2008). The younger (~40–45 Ma) alunite ages, which coincide with the last phase of arc activity in Hispaniola as noted above, also overlap the beginning of this collision event. The Hatillo thrust, which carries the Maimon Formation over the mid-Eocene Loma Caballero Formation, formed at this time and led to major strike-slip faulting and uplift in the Oligocene, all of which could have contributed to resetting of ages ascribed above to the Eocene(?) diorites.

Comparison to other districts

Although alunite has been analyzed by $^{40}Ar/^{39}Ar$ methods in only a few pre-Cenozoic deposits, many of these ages do not agree with simple interpretations of their host geology. For instance, at Toodogone, $^{40}Ar/^{39}Ar$ ages of alunite in a large alteration zone are about 190 Ma, older than most other isotopic ages (Diakow et al., 1991), whereas at Tapajos, alunite ages of 1869 to 1846 Ma are considerably younger than mineralization (Juliani et al., 2005; Landis et al., 2005). In the El Peñon district, alunite from two areas yielded ages that both precede and follow mineralization in the main El Peñon veins (Warren et al., 2008) and at Fanshan, alunite mineralization is 10 to 20 m.y. younger than host volcanic rocks (Shengli et al., 1998).

Even where alunite has yielded an age that could be related to its geologic environment, interpretation of its relationship to mineralization is controversial. The best example of this is at Temora and Peak Hill in the Lachlan fold belt, where alunite yields Early Devonian $^{40}Ar/^{39}Ar$ ages of 405 to 417 Ma (Perkins et al., 1995). Here, Allibone (1995, 1998) described foliated, pyrophyllite-rich alteration that overprints nonfoliated, quartz-kaolinite-alunite-pyrite alteration and argued that mineralization coincided with Early Devonian deformation. In contrast, Thompson et al. (1986) and Masterman et al. (2002) described pyrophyllite that was locally intergrown with quartz and kaolinite and argued that mineralization formed before Early Devonian deformation. In the first case, alunite represents the age of mineralization and deformation, whereas in the second case it represents only the age of deformation.

None of these geologic situations is exactly similar to Pueblo Viejo. They do show, however, that $^{40}Ar/^{39}Ar$ ages of alunite in many areas tend to complicate rather than simplify reconstructions of hydrothermal events.

Conclusions

This report was written by a group of authors with different opinions about the age of mineralization at Pueblo Viejo. Unfortunately, the data presented here did not compel us toward a consensus. Some authors favor the simplest interpretation, which is that the 80 to 40 Ma spread of ages reflects a Late Cretaceous age of mineralization for Pueblo Viejo, probably around 80 Ma, which was followed by thermal resetting from deformation and/or magmatism in the Eocene, probably around 40 Ma. Other authors favor the interpretation that Pueblo Viejo formed at ~110 Ma during Los Ranchos magmatism and that thermal and chemical effects of later deformation and thrusting account for the total lack of ^{40}Ar-^{39}Ar ages older than about 80 Ma. However, ages and thermal effects of this thrusting are not well understood and regional pyrophyllite is the only evidence that temperatures related to thrusting might have been high enough to cause the necessary resetting. The main conclusion, on which all authors have converged, is that $^{40}Ar/^{39}Ar$ geochemistry has not yet conclusively resolved the current debate about the age of Pueblo Viejo mineralization.

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APPENDIX 1

Analytical Procedures

Detail of the analytical procedures for alunite samples measured at the University of Nevada, Las Vegas

Samples were wrapped in pure Al foil and irradiated for 14 h in the D3 position on the core edge (fuel rods on three sides, moderator on the fourth side) of the 1MW TRIGA type reactor at the Nuclear Science Center at Texas A&M University. Correction factors for interfering neutron reactions on K and Ca were determined by repeated analysis of K glass and CaF_2 fragments. Measured $(^{40}Ar/^{39}Ar)_K$ values were 0.0002 (±150%). Ca correction factors were $(^{36}Ar/^{37}Ar)Ca = 3.134$ (±7.09%) × 10^{-4} and $(^{39}Ar/^{37}Ar)Ca = 7.357$ (±9.92%) × 10^{-4}. J factors were determined by fusion of four to five individual crystals of neutron fluence monitors which gave reproducibilities of 0.13 to 0.58 percent at each standard position. Irradiated crystals together with CaF_2 and K glass fragments were placed in a Cu sample tray in a high vacuum extraction line and were fused using a 20-W CO_2 laser. Samples analyzed by the step-heating furnace method utilized a double vacuum resistance furnace similar to the Staudacher et al. (1978) design. Reactive gases were removed by three GP-50 SAES getters prior to being admitted to a MAP 215-50 mass spectrometer by expansion. Mass spectrometer discrimination and sensitivity was monitored by repeated analysis of atmospheric argon aliquots from an online pipette system. Measured $^{40}Ar/^{36}Ar$ ratios were 285.62 ± 0.41 percent during this work; thus a discrimination correction of 1.03462 (4 AMU) was applied to measured isotope ratios. The sensitivity of the mass spectrometer was ~6 × 10^{-17} mol mV^{-1} with the multiplier operated at a gain of 52 over the Faraday. Line blanks averaged 3.36 mV for mass 40 and 0.01 mV for mass 36 for laser fusion analyses and 33.36 mV for mass 40 and 0.08 mV for mass 36 for furnace-heating analyses. Discrimination, sensitivity, and blanks were relatively constant over the period of data collection. Computer automated operation of the sample stage, laser, extraction line, and mass spectrometer as well as final data reduction and age calculations were done using LabSPEC software written by B. Idleman (Lehigh University). An age of 27.9 Ma (Steven et al., 1967; Cebula et al., 1986) was used for the Fish Canyon tuff sanidine flux monitor in calculating ages for samples.

Details of the analytical procedure for alunite samples measured at the University of Michigan

Samples were wrapped in pure Al foil and irradiated for 20 h at location 5C at the McMaster Nuclear Reactor at McMaster University in Hamilton, Ontario, in irradiation packages mc19 (sample packet d2) and mc20 (sample packets d6 and d7). Standard hornblende MMhb-1 was used as a neutron-fluence monitor with an assumed K-Ar age of 520.4 Ma (Samson and Alexander, 1987). Samples were incrementally heated with a Coherent Innova 5 W continuous argon-ion laser until complete fusion was achieved. Ar isotopes were measured using a VG1200S mass spectrometer with a source operating at 150 A total emission and equipped with a Daly detector operating in analog mode. Fusion system blanks were run every five fusion steps and blank levels from argon masses 36 through 40 (~2 × 10^{-14}, ~4 × 10^{-14}, ~1 × 10^{-14}, ~2 × 10^{-14}, and 2 × 10^{-12} ccSTP) were subtracted from sample gas fractions. Corrections were also made for the decay of ^{37}Ar and ^{39}Ar, as well as interfering nucleogenic reactions from K, Ca, and Cl and production of ^{36}Ar from the decay of ^{36}Cl. For $^{40}Ar/^{39}Ar$ analyses a plateau segment consists of three or more contiguous gas fractions having analytically indistinguishable ages (i.e., all plateau steps overlap in age at $\pm 2\sigma$ analytical error) and comprising a significant portion of the total gas released (typically >50%). Total gas (integrated) ages were calculated by weighting by the amount of ^{39}Ar released, whereas plateau ages were weighted by the inverse of the variance. For each sample inverse isochron diagrams were examined to check for the effects of excess argon. Reliable isochrons were based on the MSWD criteria of Wendt and Carl (1991) and, as for plateaus, must comprise contiguous steps and a significant fraction of the total gas released.