Boletín de la Sociedad Geológica Mexicana
Volumen 67, núm. 2, 2015, p. 349-355

Short Note

Geochronology of Mexican mineral deposits. II: Veta Madre and Sierra epithermal vein systems, Guanajuato district

Juan José Martínez-Reyes[1,2], Antoni Camprubí[3,*], I. Tonguç Uysal[4], Alexander Iriondo[5], Eduardo González-Partida[5]

[1] Departamento de Ingeniería en Minas, Metalurgia y Geología, Universidad de Guanajuato. Ex-Hacienda de San Matías s/n, Fracc. San Javier, 36025 Guanajuato, Gto., Mexico.
[2] Programa de Posgrado en Ciencias de la Tierra, Universidad Nacional Autónoma de México. Blvd. Juriquilla 3001, 76230 Querétaro, Qro., Mexico.
[3] Instituto de Geología, Universidad Nacional Autónoma de México. Ciudad Universitaria, 04510 México, D.F., Mexico.
[4] Geothermal Energy Centre of Excellence, University of Queensland. Brisbane St Lucia, QLD 4072, Australia.
[5] Centro de Geociencias, Universidad Nacional Autónoma de México. Boulevard Juriquilla 3001, 76230 Querétaro, Qro., Mexico.

[*] camprubitaga@gmail.com

Abstract

This paper presents two new high-resolution geochronological determinations for the epithermal deposits in the World-class Guanajuato mining district, in central Mexico. These are a Rb-Sr isochron age in illite at 28.47 ± 0.55 Ma for the Villalpando and San Juan de Dios low sulfidation veins of the Sierra group of veins, and a $^{40}Ar/^{39}Ar$ plateau age in adularia ("valencianite") at 30.20 ± 0.17 Ma for the La Valenciana ore shoot of the famous Veta Madre intermediate sulfidation vein. These determinations have greater accuracy, precision and trueness than the preexisting K-Ar determinations for similar adularia samples. The accuracy of such determinations supports the idea of a diachronic emplacement of intermediate and low sulfidation deposits in this district, the former being older than the latter, similar to other epithermal deposits in Mexico. Also, the ~2 m.yr. span between the Veta Madre and Sierra groups of epithermal veins is in agreement with other case studies, regardless of the size of the deposit.

Keywords: Guanajuato, Mexico, epithermal deposits, intermediate sulfidation, low sulfidation, Rb-Sr ages, illite, Ar/Ar ages, adularia.

Resumen

En este trabajo se presentan dos nuevas determinaciones geocronológicas de alta resolución para los depósitos epitermales del distrito minero de clase mundial de Guanajuato, en México central. Éstas son de una edad de isocrona Rb-Sr en illita de 28.47 ± 0.55 Ma de las vetas de baja sulfuración Villalpando y San Juan de Dios del sistema de la Sierra, y una edad de meseta $^{40}Ar/^{39}Ar$ *en adularia ("valencianita") de 30.20 ± 0.17 Ma de la zona mineralizada de La Valenciana en la famosa Veta Madre, de sulfuración intermedia. Estas determinaciones tienen mayor exactitud, precisión y fidelidad que las determinaciones K-Ar preexistentes para muestras de adularia similares. La exactitud de las determinaciones en este trabajo apoya la idea de un emplazamiento diacrónico entre los depósitos de sulfuración intermedia y baja de este distrito, siendo los primeros de ellos más antiguos que los segundos, de forma similar a otros depósitos epitermales en México. Adicionalmente, el rango de ~2 m.a. entre la formación de la Veta Madre y el grupo de vetas epitermales de la Sierra es congruente con otros casos de estudio, independientemente del tamaño de los depósitos.*

Palabras clave: Guanajuato, México, depósitos epitermales, sulfuración intermedia, sulfuración baja, edades Rb-Sr, ilita, edades Ar/Ar, adularia.

1. Introduction

The Guanajuato mining district (homonymous state, central Mexico) has been historically one of the largest silver producers in Mexico. Such endowment comes from polymetallic or Au-Ag epithermal deposits that have been extensively mined since the 16th century. The mineral wealth from these deposits was estimated in 40 Mt at 850 g/t Ag and 4 g/t Au, plus significant concentrations in Pb and Zn (Albinson *et al*., 2001). These deposits are basically intermediate to low sulfidation epithermal veins and stockworks, in which intermediate sulfidation mineral assemblages, when present, occupy the deepest portions of mineralized structures (or "type B", according to Camprubí and Albinson, 2006, 2007). In fact, the different groups of mineralized structures cluster into dominantly intermediate or low sulfidation veins. Such clusters are named, west to east, as the La Luz system, the Veta Madre (which can be translated as "Mother Lode"), and the Sierra system (Figure 1), also known as El Cubo system. The large Veta Madre vein is dominantly an intermediate sulfidation vein (Camprubí and Albinson, 2006, 2007), whereas the La Luz and Sierra systems are, at their presently known exposures, low sulfidation sets of veins (Abeyta, 2003; Devlin and Hansen, 2009).

Previous studies in this area that are related at some extent with the formation of epithermal deposits deal with regional geological or structural aspects (Gross, 1975; Lapierre *et al*., 1992; Randall *et al*., 1994; Loriga, 1999; Aranda-Gómez *et al*., 2003) or with the mineralogy, the characteristics of mineralizing fluids and depositional environment of such deposits (Petruk and Owens, 1974; Gross, 1975; Buchanan, 1981; Mango *et al*., 1991, 2014; Abeyta, 2003; Orozco-Villaseñor, 2010; Moncada and Bodnar, 2012; Moncada *et al*., 2012). For a comprehensive succinct review of the geology of the Guanajuato district, see Moncada *et al*. (2012). The felsic to intermediate magmatism and structural features that occurred between 37 and 27 Ma are commonly invoked as the likeliest setting that allowed the epithermal deposits in Guanajuato to form (Godchaux *et al*., 2003). However, the window for the formation of such deposits appears to be narrower than the time span mentioned above in association with hypabissal magmatic activity of the Sierra Madre Occidental silicic large igneous province (SLIP) in this region as volcanism ceased. Thus, Taylor (1971, in Randall *et al*., 1994), Gross (1975), and Saldaña-Alba (1991) reported K-Ar ages in adularia for the epithermal mineralization in the Veta Madre and the Sierra groups of veins between 30.7 and 27.0 Ma (Oligocene). Such ages correspond to the seemingly most productive metallogenic period in Mexico, especially with regard to epithermal deposits (see Figures 8 and 13 in Camprubí, 2013). Such period followed the climax of ignimbrite volcanism in the Sierra Madre Occidental silicic large igneous province (SLIP) before its magmatism waned and migrated southwards into the Trans-Mexican Volcanic Belt, and reshaping the regional distribution of epithermal deposits (Camprubí *et al*., 2003; Camprubí, 2013).

In this paper, we aim to contribute with high-resolution dating for the Veta Madre vein, and the Villalpando and San Juan de Dios veins (the latter two, within the Sierra group of veins) of the Guanajuato district. In addition, this district poses a good opportunity to evaluate in which degree of synchronicity intermediate and low sulfidation epithermal deposits may occur in a given area.

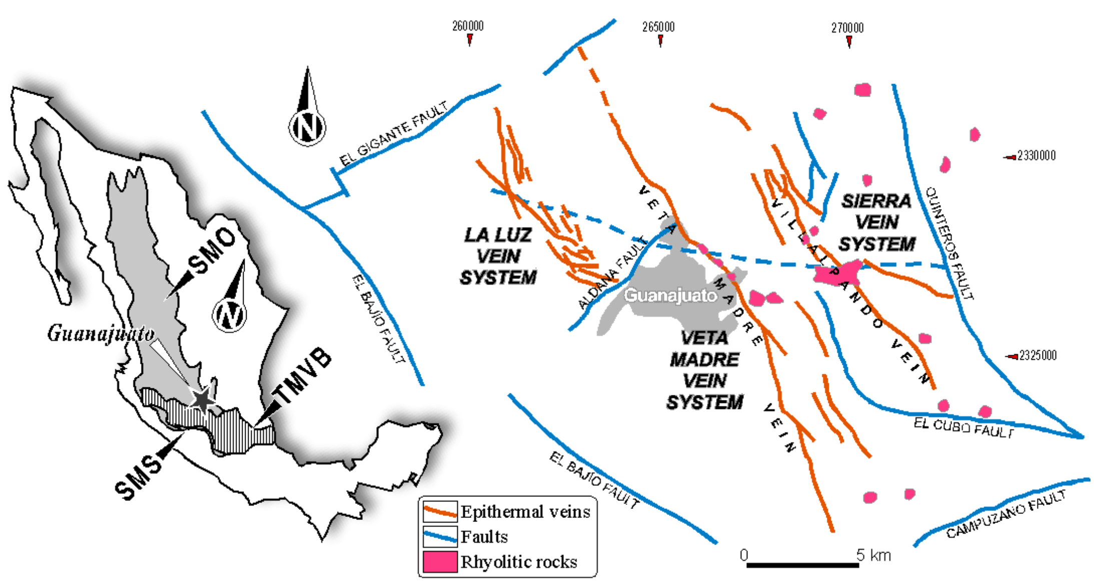

Figure 1. Map of the Guanajuato mining district, with the main epithermal veins and other significant geological structures; modified from Randall *et al*. (1994). The La Luz and Sierra systems are basically constituted by low sulfidation mineralization whereas most of the Veta Madre system belongs to the intermediate sulfidation type. The rhyolitic rocks shown in the map are those that are most likely to have ages similar to those of epithermal deposits. Key: SMO = Sierra Madre Occidental, SMS = Sierra Madre del Sur, TMVB = Trans-Mexican Volcanic Belt.

2. Material and Methods

2.1. Rb-Sr dating of illite from the Villalpando and San Juan de Dios veins (Sierra system)

Clay mineral analyses were conducted by XRD on clay separates (< 2 μm). The XRD analyses were carried out on a Bruker Advance MK III X-Ray diffractometer with Bragg-Brentano geometry and CuKα radiation, operated at 40 kV and 30 mA at a scanning rate of 1 °2θ/min and 0.05 °/step. Samples were prepared for clay-fraction separation by gently hand-crushing the rocks to sand size to avoid artificially reducing grain size of detrital/primary mineral components. Samples were then disaggregated in distilled water using an ultrasonic bath. Different clay size fractions (2 – 1, < 1, 2 – 0.5 and < 0.5 μm) were obtained by centrifugation, and the decanted suspensions were placed on a glass slide. To ensure no detrital contamination, samples were centrifugally separated and rigorously analyzed with XRD. Samples showing contamination with detrital K-feldspar were discarded from analysis. Following XRD analysis of air-dried samples, the oriented clay-aggregate mounts were placed in an ethylene–glycol atmosphere at 30 – 40 °C overnight prior to additional XRD analyses. However, the XRD 001 peak position of the illite does not change after ethylene glycol treatment, which is indicative of the absence of smectite clays.

For the Rb–Sr dating, illitic clay separates were leached for 15 minutes at room temperature in 1 N distilled HCl (Clauer *et al*., 1993). Leachate and residue were separated by centrifuging. The residue was rinsed repeatedly with milli-Q water, dried and reweighed. Clay separates were analyzed in two separate batches. Leachate, residue, and untreated samples were dissolved in a mixture of distilled HF and HNO_3 and measured by Thermo X-series 1 quadrupole ICP–MS with precision better than 0.5 % (1σ). The Sr-enriched fraction was separated using cation exchange resins. Sr isotopic ratios were measured on a VG Sector-54 thermal ionization mass spectrometer (TIMS) in the Radiogenic Isotope Laboratory at the University of Queensland (Australia). Sr was loaded in TaF5 and 0.1 N H_3PO_4 on a tantalum or tungsten single filament. Sr isotopic ratios were corrected for mass discrimination using $^{86}Sr/^{88}Sr$ = 0.1194. Long-term (6 years) reproducibility of statically measured NBS SRM 987 (2σ; n = 442) is 0.710249 ± 28. More recent dynamically measured SRM 987 had $^{86}Sr/^{88}Sr$ ratios of 0.710222 ± 20 (2σ; n = 140). Rb–Sr isochron ages were calculated using the ISOPLOT program (Ludwig, 2003).

For this study, we selected samples of pervasively altered rhyolitic rocks (Figure 2): two of them came from fresh outcrops adjacent to the Villalpando vein, and one sample came from underground exposures of the San Juan de Dios vein. In both cases, they were obtained from phyllic alteration assemblages. The samples of the Villalpando vein consist of illite and smectite (not mixed-layered illite-smectite), whereas the sample from the San Juan de Dios vein consists of pure illite. The samples thus used for Rb–Sr geochronology yielded an isochron age at 28.47 ± 0.55 Ma. These results are presented in Table 1 and Figure 3.

Figure 2. Images of the samples dated in this study. Up: Sample from pervasive phyllic alteration adjacent to the Villalpando vein, Sierra system; notice the green hue due to the abundance of illite. Down: Adularia sample ("valencianite") from the La Valenciana ore shoot of the Veta Madre system.

2.2. $^{40}Ar/^{39}Ar$ dating of adularia from the La Valenciana shoot (Veta Madre vein)

A pure mineral separate of adularia (Figure 2) from crustiform vein material (mostly quartz) from the La Valenciana ore shoot in the Veta Madre vein (central part of the Guanajuato district) was dated by $^{40}Ar/^{39}Ar$ geochronology (Figure 4 and Table 2). A large adularia crystal was torn to pieces that ranged in size from 250 to 180 μm and then were separated using heavy liquids and hand picking to a purity of > 99 %. The resulting sample was washed in acetone, alcohol, and deionized water in an ultrasonic cleaner to remove dust and then re-sieved by hand using a 180 μm sieve.

Aliquots of the adularia sample (~20 mg) were packaged in copper capsules and sealed under vacuum in quartz tubes. The sample aliquots were then irradiated in package number KD52 for 20 hours in the central thimble facility at the TRIGA reactor (GSTR) at the U.S. Geological Survey in Denver, Colorado. The monitor mineral used in the package was Fish Canyon Tuff sanidine (FCT-3) with an age of 27.79 Ma (Kunk *et al*., 1985; Cebula *et al*., 1986) relative to MMhb-1 with an age of 519.4 ± 2.5 Ma (Alexander *et al*.,

Table 1. Rb–Sr data of illite samples from phyllic alteration associated with the Villalpando and San Juan de Dios veins.

Sample Name	Size fraction (μm)	Rb (ppm)	Sr (ppm)	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$	±2σ
AR186	<2U	462	154	8.73	0.707941	0.000008
AR186	2-1U	1112	234	13.73	0.709353	0.000010
AR186	2-1L	6.37	199	0.0927	0.705238	0.000012
AR186	1-0.5U	1171	246	13.75	0.70937	0.000010
AR186	1-0.5L	7.38	212	0.101	0.705227	0.000010
AR186	0.5-0.2U	1174	262	13.16	0.70912	0.000010
AR186	0.5-0.2L	6.95	219	0.0918	0.705225	0.000012
AR186	<0.2L	12.7	435	0.0847	0.705215	0.000010
AR186	<0.2R	1113	33.5	96.32	0.733155	0.000012
AR165	<2U	693	1020	1.966	0.705741	0.000014
AR160	<2U	690	411	4.868	0.706221	0.000012

Key: U = untreated, R = residue, L = leachate.

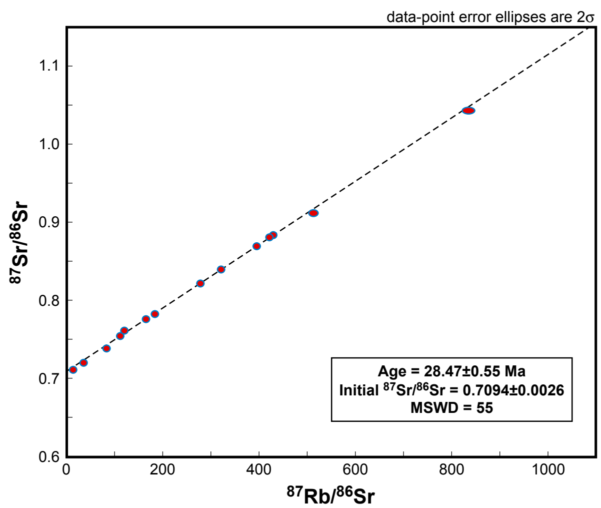

Figure 3. Rb-Sr isochron for the dated illite samples from phyllic alteration assemblages adjacent to the Villalpando and San Juan de Dios veins, Sierra system, eastern part of the Guanajuato mining district.

1978; Dalrymple *et al*., 1981). The type of container and the geometry of the sample and standards were similar to that described by Snee *et al*. (1988).

The adularia sample was analyzed at the U.S. Geological Survey Thermochronology lab in Denver (Colorado, USA), using the $^{40}Ar/^{39}Ar$ step-heating method (from 600º to 1500 ºC; Table 2) and a VG Isotopes 1200B mass spectrometer fitted with an electron multiplier. For additional information on the analytical procedure see Kunk *et al*. (2001). The analyzed sample corresponds to a “classical” collector’s specimen of large and saddle-shaped drusy adularia crystals —or “valencianite”— that are characteristic of this specific location. This sample yielded a $^{40}Ar/^{39}Ar$ plateau age at 30.20 ± 0.17 Ma.

3. Discussion and conclusions

Two ages were obtained in this study for epithermal deposits at the Guanajuato district: (1) Rb-Sr isochron age (Figure 3) at 28.47 ± 0.55 Ma for the Villalpando and San Juan de Dios low sulfidation veins of the Sierra system (eastern part of the district), and (2) an $^{40}Ar/^{39}Ar$ plateau age (Figure 4) at 30.20 ± 0.17 Ma for the La Valenciana ore shoot of the Veta Madre intermediate sulfidation vein (central part of the district). Such ages fall within the range of K-Ar ages reported by Gross (1975), Saldaña-Alba (1991) and Randall *et al*. (1994) for the Veta Madre vein (between 30.7 and 27.0 Ma; Table 3). These ages were obtained in the same type of adularia samples as the one used in this study, from the same location (“valencianite” from the La Valenciana ore shoot). Therefore, the $^{40}Ar/^{39}Ar$ plateau age in this study has higher accuracy, precision and trueness than preexisting K-Ar determinations. Similar characteristics can be assumed for the Rb-Sr isochron age in illite for the veins at the Sierra system, as the reliability of this method has been consistently validated (*e.g*., Middleton *et al*., 2015). Differences in age of ~2 m.yr. from various hydrothermal mineral assemblages of other Mexican epithermal deposits have also been found through high-resolution dating techniques. Such feature occurs regardless of the size of the deposits, whether they are relatively small (Temascaltepec, State of México; Camprubí *et al*., 2003) or giant deposits (Fresnillo, Zacatecas; Velador *et al*., 2010). As it is the case of the Guanajuato district, the Fresnillo and Temascaltepec deposits contain both intermediate and low sulfidation mineralization, although the former is dominantly an intermediate sulfidation deposit and the latter is dominantly a low sulfidation deposit (see Figure 14 in Camprubí and Albinson, 2007). Also, the difference in age between epithermal deposits and the Chichíndaro rhyolitic dome (dated at 32.0 ± 1.0

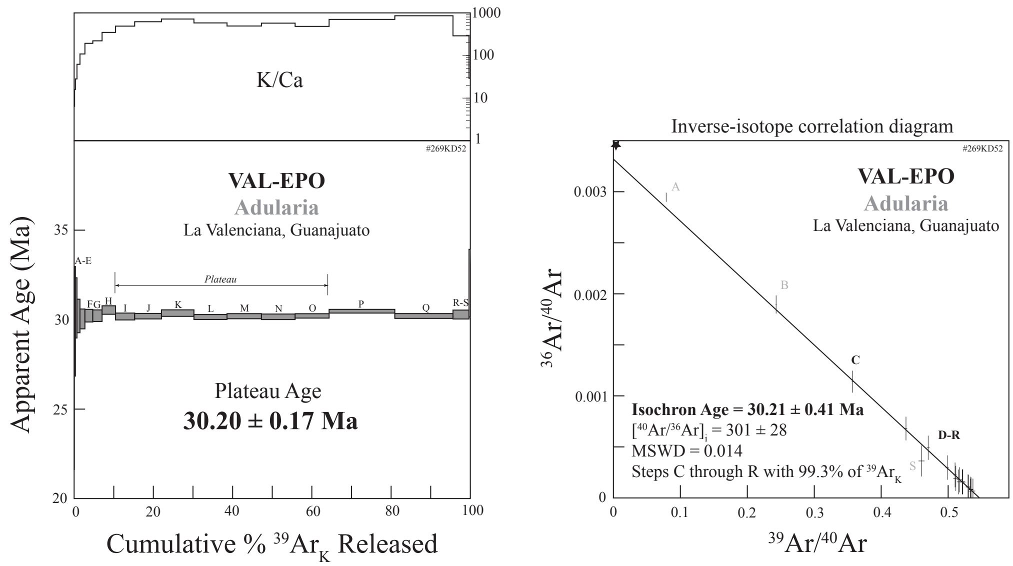

Figure 4. $^{40}Ar/^{39}Ar$ age spectrum and isochron for the VAL-EPO adularia sample ("valencianite") from the La Valenciana ore shoot of the Veta Madre system, central part of the Guanajuato mining district.

Table 2. $^{40}Ar/^{39}Ar$ step-heating data for an adularia sample of the La Valenciana ore shoot, Veta Madre vein system, Guanajuato district.

Step	Temp. °C	$\%^{39}Ar$ of total	Radiogenic Yield (%)	$^{39}Ar_k$ (moles x 10^{-12})	$^{40}Ar^{*}/^{39}Ar_k$	Apparent K/Ca	Apparent K/Cl	Apparent Age (Ma)	Error (Ma)
VAL-EPO	***Adularia***	*J = 0.009234 ± 0.5%*	*wt = 20.7 mg*	*#269KD52*					
A	600	0.1	12.9	0.0070	1.643	6	49	27.16	± 2.77
B	650	0.2	44.0	0.0132	1.810	16	236	29.91	± 1.53
C	700	0.4	66.3	0.0249	1.856	28	484	30.66	± 0.84
D	750	0.8	79.9	0.0481	1.828	62	812	30.20	± 0.47
E	800	1.3	85.5	0.0788	1.818	109	1735	30.04	± 0.28
F	850	2.0	91.2	0.1248	1.830	193	3687	30.22	± 0.18
G	900	2.3	93.3	0.1470	1.829	221	6870	30.22	± 0.16
H	950	3.4	95.4	0.2148	1.849	348	12681	30.54	± 0.12
I	1000	4.8	96.9	0.3036	1.827	489	0	**30.17**	**± 0.10**
J	1050	6.8	97.6	0.4257	1.828	621	498181	**30.19**	**± 0.08**
K	1100	8.2	98.0	0.5163	1.838	718	235927	**30.36**	**± 0.09**
L	1150	8.3	98.0	0.5251	1.825	583	0	**30.15**	**± 0.07**
M	1200	8.7	96.8	0.5479	1.828	492	1234	**30.19**	**± 0.07**
N	1250	8.5	97.5	0.5349	1.826	573	18267	**30.16**	**± 0.08**
O	1300	8.6	95.3	0.5397	1.829	482	14693	**30.21**	**± 0.06**
P	1350	16.6	94.3	1.0442	1.845	703	14466	30.47	± 0.05
Q	1400	14.7	95.4	0.9247	1.828	857	0	30.20	± 0.07
R	1450	4.0	94.8	0.2538	1.833	290	0	30.29	± 0.12
S	1500	0.3	89.3	0.0215	1.941	29	2922	32.04	± 0.94
Total Gas		100	95.4	6.2959	1.832	583	59058	30.27	
		53.89% of gas on plateau in 1000 through 1300°C steps			**Plateau Age = 30.20 ± 0.17 Ma**				

Ages calculated assuming an initial $^{40}Ar/^{36}Ar = 295.5 \pm 0$.
All precision estimates are at the one sigma level of precision.
Ages of individual steps do not include error in the irradiation parameter J.
No error is calculated for the total gas age.

Ma; Gross, 1975) —which is the youngest volcanic rock prior to the emplacement of epithermal deposits— spans 1 to 3 m.yr. The latter is comparable to similar age gaps in other intermediate to low sulfidation epithermal deposits in Mexico (namely, Fresnillo, Pachuca-Real del Monte, Tayoltita and Temascaltepec; Lang *et al*., 1988; McKee *et al*., 1992; Enríquez and Rivera, 2001; Camprubí *et al*., 2003; Camprubí and Albinson, 2007; Velador *et al*., 2010), whereas such gaps are significantly shorter for high sulfidation deposits (La Caridad Antigua; Valencia *et al*., 2005, 2008).

The precision of both sets of ages in this study suggests that the sets of veins whence these were obtained are actually diachronic. This could imply that intermediate

Table 3. Ages of epithermal deposits in the Guanajuato district obtained for this study, and relevant ages from previous studies.

Sample	Mineral	Description and location	Coordinates	Method	Age ± 2σ (Ma)	Sources
VV-81	Illite and smectite	Phyllic alteration adjacent to the Villalpando vein (low sulfidation), Sierra system	21° 01' 18.84" N 101° 11' 5.22" W			
VV-85	Illite and smectite	Phyllic alteration adjacent to the Villalpando vein (low sulfidation), Sierra system	21° 01' 20.02" N 101° 11' 7.21" W			
VV-123	Illite and smectite	Phyllic alteration adjacent to the Villalpando vein (low sulfidation), Sierra system	21° 01' 31.29" N 101° 11' 35.60" W	Rb-Sr (isochron age)	28.47 ± 0.55 *	This study
SJD-49	Illite	Phyllic alteration adjacent to the San Juan de Dios vein (low sulfidation), Sierra system	21° 01' 24.84" N 101° 10' 41.42" W			
SJD-50	Illite	Phyllic alteration adjacent to the San Juan de Dios vein (low sulfidation), Sierra system	21° 01' 25.81" N 101° 10' 41.43" W			
VAL-EPO	Adularia	Vein material from the La Valenciana ore shoot (intermediate to low sulfidation), Veta Madre vein	21º 02' 23.71" N 101º 15' 42.12" W	$^{40}Ar/^{39}Ar$ (plateau age)	30.20 ± 0.17 §	This study
	Adularia	Vein material from the Peregrina mine (low sulfidation), Sierra system		K-Ar	30.7 ± 3.0 to 28.3 ± 5.0 *	Gross (1975)
	Adularia	Vein material from the Torres, Rayas and Sirena mines (intermediate sulfidation), Veta Madre vein		K-Ar	28.4 ± 4.0 to 27.4 ± 4.0 §	Taylor (1971)
	Whole rock	Chichíndaro rhyolitic dome		K-Ar	32.0 ± 1.0	Gross (1975)

Key: Symbols (* and §) denote those ages that correspond to the same hydrothermal events.

sulfidation veins of the Veta Madre system are slightly, albeit significantly, older than low sulfidation veins of the Sierra system. Such feature is in accordance with the common observation in Mexican epithermal deposits in which, when occurring in the same deposit, intermediate sulfidation mineralization normally predates low sulfidation mineralization. Such systematic behavior can be observed both at the scale of a single mineralized structure and at a district scale, as it is also the case of the Zacatecas district (see Camprubí and Albinson, 2007). Further validation for a systematic chronology of low and intermediate sulfidation ores may have relevant consequences in the exploration for epithermal deposits in which the presence of both low and intermediate sulfidation mineralization is plausible. For instance, although it will remain as a matter for speculation, it might be possible that the La Luz or Sierra systems contain significant intermediate sulfidation ores below the known extent of their low sulfidation ores, whether these occur with some spatial continuity or not (that is, "stacked" in the sense employed by Camprubí and Albinson, 2007).

Acknowledgments

This study was financed by means of the CONACYT grant number 155662. We thank Yeu-xing Feng and Ai Duc Nguyen for their help with analytical work and technical assistance to perform Rb-Sr and trace element analyses. Special thanks go to Turgay Demir for his assistance during sample preparation. The authors also wish to thank Michael Kunk for providing access and guidance to perform the $^{40}Ar/^{39}Ar$ geochronology studies at the U.S. Geological Survey Thermochronology Lab in Denver, Colorado. The age determinations in this study were first mentioned by Camprubí (2013). Formal reviews were conducted by José María González-Jiménez and Enrique Merino Martínez, whose comments helped to improve this paper.

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Manuscript received: February 16, 2015.
Corrected manuscript received: March, 23, 2015.
Manuscript accepted: March 25, 2015.