

Vein carbonates in the low sulfidation epithermal Au-Ag District of El Peñón, II Región, Chile: environment of formation and exploration implications

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ABSTRACT

Carbonate minerals are common gangue minerals in the low sulfidation epithermal Au-Ag District of El Peñón, II Región, Chile. They can be subdivided into two principal groups on the basis of the paragenetic relationships. Paragenetically early carbonates occur together with quartz and sulfide minerals in banded veins and are closely associated with precious metal mineralization. These carbonates are compositionally complex, consisting of calcite, finely intermixed with ankerite, kutnohorite, rhodochrosite and dolomite, but also contain up to 0.8 wt% PbCO_3 and up to 4.1 wt% ZnCO_3 . In contrast, the paragenetically late carbonates are relatively pure calcite, although dolomite has been recognized locally. Late calcites contain less than 3.5 wt% MnCO_3 , less than 0.5 wt% ZnCO_3 and less than 2.7 wt% FeCO_3 and are also distinct from the early carbonates in that they exhibit moderate to intense red fluorescence under short-wave ultraviolet light. The red fluorescence color is likely related to moderate Mn contents in calcite, combined with trace amounts of Pb, but low Fe and Mg concentrations. Late carbonates are interpreted to have precipitated from CO_2 -rich steam-heated fluids and are not directly associated with ore. $\delta^{18}\text{O}$ compositions of both, early and late carbonates generally range between 21.1 and 14.1‰ relative to the Standard Mean Ocean Water (VSMOW). However, two samples of late calcite yielded $\delta^{18}\text{O}$ values of 3 and 5‰, respectively. The calculated composition of water in equilibrium with calcite at the estimated temperature of deposition of 230°C yielded $\delta^{18}\text{O}$ values between 6 and 13‰, but negative values of -3.1 and -5.1‰ for two samples of late calcite. Although the low $\delta^{18}\text{O}$ values for two of the late calcites and oxygen isotopic data of vein quartz from earlier studies suggest precipitation from a meteoric fluid, the heavy isotopic signature of most carbonates indicates that the mineralizing fluid was overall heterogeneous. $\delta^{13}\text{C}$ values range between -8.9‰ and +1.5‰ relative to the Pee Dee Belemnite (VPDB) standard and are consistent with a meteoric or magmatic origin, in some samples probably with a minor contribution of organic carbon. Periodic involvement of a fluid with a strong magmatic component or, alternatively, meteoric water which has undergone extensive evaporation probably played an important role in the hydrothermal system. The complex stable isotope signature of El Peñón is interpreted as indicative for arid climatic conditions as a meteoric origin of the fluid is not as evident as in similar deposits emplaced in more pluvial regions.

Key words: Epithermal, Low sulfidation, Carbonates, Ultraviolet fluorescence, Stable isotopes, El Peñón, Chile.

RESUMEN

Carbonatos en vetas en el distrito epitermal de baja sulfuración de El Peñón, II Región, Chile: ambiente de formación e implicancias para la exploración. En el distrito epitermal de Au-Ag de baja sulfuración de El Peñón, II Región, Chile, los carbonatos son minerales de ganga comunes. Estos minerales pueden ser subdivididos en dos grupos principales sobre la base de sus relaciones paragenéticas. Carbonatos paragenéticamente tempranos se encuentran junto a cuarzo y sulfuros en vetas bandeadas y están estrechamente asociados con la mineralización de metales preciosos. Estos carbonatos son composicionalmente complejos, consistiendo en calcita entrecrecida con ankerita, kutnohorita, rhodocrosita y dolomita, pero también contienen hasta 0,8% en peso de PbCO_3 y hasta 4,1% en peso de ZnCO_3 . En contraste, los carbonatos paragenéticamente tardíos son calcita relativamente pura, aunque localmente también se ha reconocido dolomita. Las calcitas tardías contienen menos de 3,5% en peso MnCO_3 , menos de 0,5% en peso de ZnCO_3 y menos de 2,7% en peso de FeCO_3 y también son distintas a los carbonatos tempranos en que se caracterizan por una fluorescencia roja moderada a intensa bajo luz ultravioleta de onda corta. El color rojo de fluorescencia bajo luz ultravioleta probablemente está relacionado con contenidos en algún porcentaje de Mn, combinado con trazas de Pb y bajos contenidos de Fe. Los carbonatos tardíos se interpretan como precipitados de fluidos ricos en CO_2 condensados de vapor ('steam-heated') y no tienen relación directa con la mena. Las composiciones de $\delta^{18}\text{O}$ de carbonatos, tanto tempranos como tardíos, varían entre 21,1 y 14,1‰ relativo al estándar VSMOW 'Standard Mean Ocean Water'. Sin embargo, dos muestras de calcita tardía arrojan valores de $\delta^{18}\text{O}$ de 3 y 5‰. Los valores calculados para la composición de agua en equilibrio con calcita en las temperaturas estimadas de precipitación de 230°C entregan valores de $\delta^{18}\text{O}$ entre 6 y 13‰ pero valores negativos de -3,1 y -5,1‰ para dos muestras de calcita tardía. A pesar de que el valor bajo de $\delta^{18}\text{O}$ de algunas calcitas tardías y datos isotópicos para cuarzo en vetas de estudios anteriores, sugieren precipitación desde un fluido meteórico, la signatura isotópica pesada de la mayoría de las muestras de carbonato indican que el fluido en general ha sido heterogéneo. Los valores de $\delta^{13}\text{C}$ varían entre -8,9‰ y +1,5‰ relativo al estándar VPDB 'Pee Dee Belemnite' son consistentes con un origen meteórico o magmático, en algunas muestras probablemente con una contribución menor de carbono orgánico. Un aporte periódico de fluido con un importante componente magmático o, alternativamente, agua meteórica que ha sufrido extensa evaporación probablemente jugó un rol importante en el sistema hidrotermal. Los isótopos estables en carbonatos en El Peñón se interpretan como evidencia de condiciones climáticas áridas, ya que el origen meteórico del fluido no está tan bien definido como en yacimientos epitermales similares en regiones más pluviales.

Palabras claves: Epitermal, Baja sulfuración, Carbonatos, Fluorescencia ultravioleta, Isótopos estables, El Peñón, Chile.

INTRODUCTION

Carbonates are common gangue minerals in low sulfidation epithermal deposits (*e.g.*, Cooke and Simmons, 2000; Simmons *et al.*, 2005). They may occur in the wall rock as part of the alteration assemblage, or as gangue in veins or breccias hosting the mineralization. Carbonates in veins may grow as tabular crystals, commonly replaced in part by quartz (lattice texture), banded quartz-carbonate veins or, alternatively as late open space infill (Simmons *et al.*, 2000, 2005). Thus, carbonate occurrence and textures are varied and provide constraints on the depositional environment within epithermal districts. The lattice texture is widely interpreted as evidence for fluid boiling and is normally found close to the mineralized zone (Cooke and Simmons, 2000; Simmons *et al.*,

2005); similarly the carbonate which occurs together with quartz and/or chalcedony in banded colloform-crustiform veins is spatially related to mineralization. In turn, the late, commonly coarse calcite filling open space has been demonstrated to have been precipitated from steam-heated meteoric waters, rich in CO_2 (Simmons *et al.*, 2000). The latter type of carbonate is therefore not directly related to precious metal deposition.

Due to the different possible associations with ore, a characterization of carbonates present in low sulfidation epithermal prospects may help focussing exploration efforts. This is particularly valid for the El Peñón district of northern Chile, located near the eastern margin of the Central Depression, some 165 km southeast of Antofa-

gasta. The El Peñón Au-Ag deposit (>4.5 Moz Au; >70 Moz Ag), owned and operated by Meridian Gold Corporation, is considered a typical low sulfidation epithermal Au-Ag deposit (Warren *et al.*, 2004). The volcanic rocks and epithermal veins are not well exposed due to a cover of an evaporitic crust essentially consisting of nitrate cemented gravel typically found throughout northern Chile and commonly referred to as 'caliche' in the region (cf. international usage of the term which describes carbonate cemented soil). Geological mapping of the district is to a large part based on the distribution of clasts in the float (Zuluaga, 2004; Warren *et al.*, 2004). Quartz-carbonate vein material is also commonly found in the float and knowing the origin

of the carbonate in such clasts will help establishing exploration guidelines for non-outcropping veins.

In this study, we present the results of vein-carbonate characterization in the El Peñón district. Along with observations under short-wave ultraviolet light, geochemical data, including carbon and oxygen stable isotopes from a limited number of samples are presented. The results yield new insights into the origin of the fluids from which the carbonate minerals precipitated. This study also demonstrates the possible use of ultraviolet fluorescence as an inexpensive tool for future exploration in the El Peñón district or areas with similar geological characteristics.

GEOLOGICAL SETTING OF EL PEÑÓN

The El Peñón deposit is located within a north-south trending belt of epithermal deposits of Paleocene age (Sillitoe 1991; Fig. 1), within the Central Depression of northern Chile. The deposit is hosted by late Upper Paleocene to Lower Eocene subaerial rhyolitic flows and domes, overlying Upper Cretaceous and Paleocene andesite and dacite flows (Fig. 1; Zuluaga, 2004; Warren *et al.*, 2004). The Cretaceous and Paleocene belt of volcanic rocks are confined to the Central Depression, here only approximately 20 km wide (Arancibia *et al.*, 2006a). Recent geochronology (Arancibia *et al.*, 2006a) yields

$^{40}\text{Ar}/^{39}\text{Ar}$ ages of 54.5 ± 0.6 Ma for the rhyolitic dome complex hosting the veins; an age range from 53.1 ± 0.5 to 51.0 ± 0.6 Ma for vein-adularia; and broadly coincident K-Ar ages for late dacitic to rhyodacitic domes. $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology on supergene alunite and Mn-oxides indicates that oxidation of the El Peñón deposit occurred between ~27 and ~14 Ma, but continued with less intensity until ca. 9 Ma (Arancibia *et al.*, 2006b). A change from arid to hyper arid climate in the Late Miocene is held responsible for the cessation of supergene processes (Arancibia *et al.*, 2006b; Rech *et al.*, 2006).

ALTERATION AND MINERALIZATION

The following description of the El Peñón epithermal system is summarized from Warren *et al.* (2004). The Au-Ag mineralization is hosted by at least four distinct, steeply dipping N to NE striking veins (Fig. 1) emplaced in pre-existing normal faults. The gold-silver mineralization is restricted to banded quartz±adularia veins, hydrothermal breccias and minor quartz stockwork. Veins are normally 0.5 to 4 m, but locally up to 20 m wide. Veinlets up to 10 cm in thickness with similar gangue mineralogy occur commonly within

10 m of the principal veins. Primary sulfide ore minerals include pyrite, chalcopyrite, galena, sphalerite, and electrum which typically account for less than 3% of the vein material. The primary sulfide minerals were oxidized locally as deep as 400 m below the actual surface and principal ore minerals in the oxidized zones are electrum, gold, silver and acanthite. The veins exhibit textures typical for low sulfidation epithermal deposits including banded, colloform-crustiform, massive, brecciated and lattice textures.

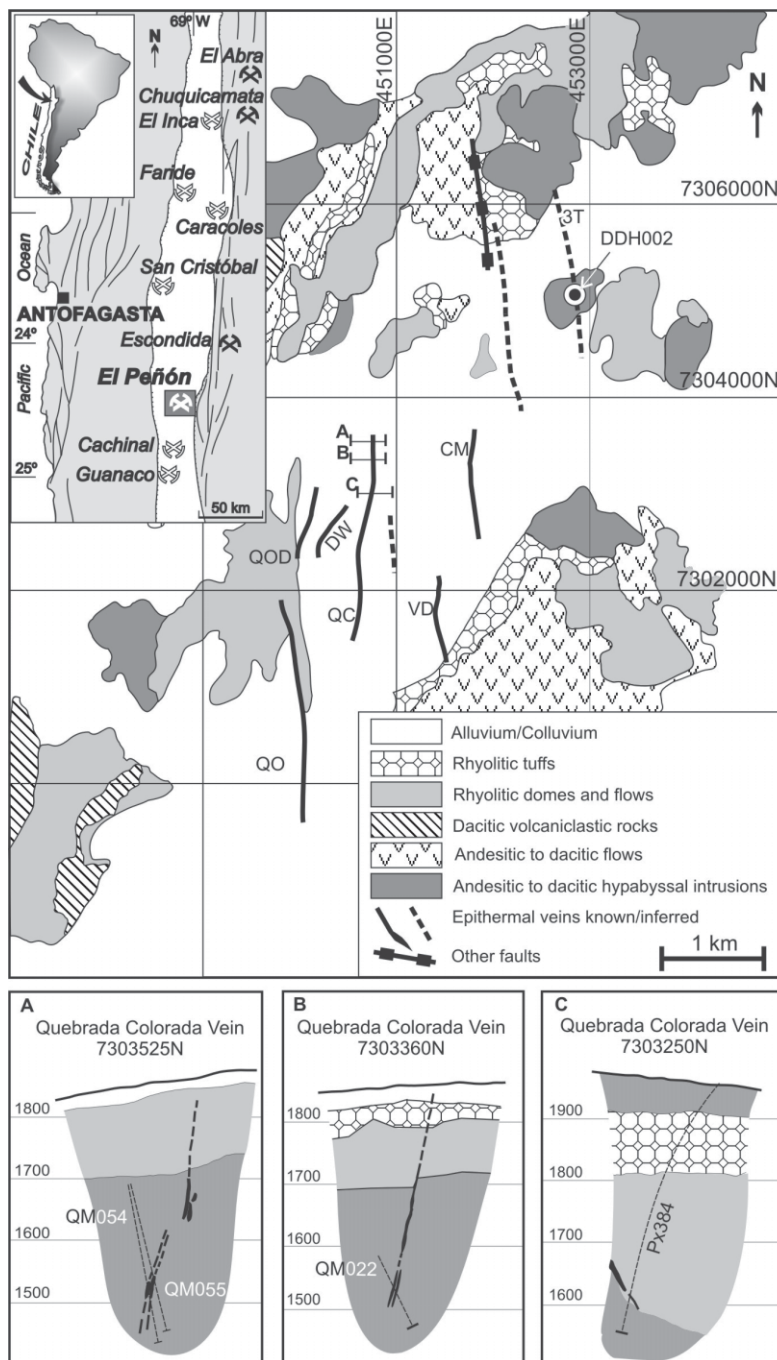


FIG. 1. Location map, simplified geological map, and cross-sections of the El Peñón area. The inset in the upper left corner shows the location of El Peñón and selected other ore deposits of Northern Chile. Escondida, Chuquicamata and El Abra are porphyry copper deposits whereas the other deposits are precious metal and polymetallic vein deposits, mostly of epithermal type. Geological information taken from Zuluaga (2004) and unpublished maps of Meridian Gold Corp. The surface projections of the steeply dipping veins are indicated. Abbreviations: **QO**: Quebrada Orito vein; **QOD**: Quebrada Orito vein, Diablada section; **DW**: Discovery Wash vein; **QC**: Quebrada Colorada vein; **CM**: Cerro Martillo vein; **VD**: Veta dorada vein; **3T**: Tres Tontos prospect. The sample location of surface sample DDH-002 is indicated. The cross-sections **A**, **B** and **C** shown at the bottom of the figure are indicated on the map as well. The samples were taken at or within 15 m of the intersection of drillholes with the veins shown in the cross-sections (the drillholes are indicated with their respective numbers).

Wall-rock alteration is dominated by quartz-adularia-illite±disseminated pyrite in the rhyolitic rocks in the immediate vicinity of the veins, grading into more smectite-rich and low quartz-adularia

assemblages at distances of more than ~10 m from the vein (Warren *et al.*, 2004). Dacitic rocks present chlorite and calcite, as well as illite/smectite in the alteration assemblage.

OCCURRENCE OF CARBONATES IN THE VEINS OF EL PEÑÓN

Carbonate minerals have generally been tested in the field using dilute HCl and calcite has been found to be present in most samples. X-ray diffraction identified principally calcite, in some samples mixed with lesser amounts of ankerite, dolomite, rhodochrosite and kutnohorite. Carbonates most commonly occur as gangue in the main mineralized veins as well as fracture infill within a few meters from the principal veins. Fine-grained calcite mixed with lesser dolomite, kutnohorite and ankerite are commonly found in banded to massive veins, overgrown or partially replaced by quartz ('early carbonate' hereafter). Lattice texture is mostly preserved as pseudomorphs of quartz after calcite, but the latter is locally still preserved. Calcite, locally together with minor amounts of rhodochrosite and/or dolomite, also occurs as late open space infill, overgrowing drusy quartz or as late stage veinlets cutting earlier banded quartz or

quartz-carbonate veins ('late calcite' hereafter). Late calcite is also present as massive calcite±quartz veins up to 50 cm wide, featuring individual calcite crystals of up to 6 cm in diameter (see also Warren *et al.*, 2004). The carbonates found in the float or in exploration trenches on the surface can on textural grounds commonly be assigned to the latter type, but examples of probable early calcite have also been observed at the Tres Tontos prospect (Fig. 1). Vein carbonates within or near known mineralized veins are mostly hosted by dacitic rather than rhyolitic host rocks, but carbonate bearing veins also occur in rhyolitic wall rock. Within the currently mined mineralized structures, carbonates are commonly found at depths greater than 250 m. Above this level supergene oxidation of pyrite probably has generated sufficient acid to dissolve a large part of the vein carbonates.

CHEMISTRY OF THE CARBONATES AT EL PEÑÓN

Eight carbonate samples from diamond drill holes, complemented by one calcite sample from the float on the surface were analyzed in the laboratories of the Universidad Católica del Norte, Antofagasta, Chile for carbonate compositions (Table 1, Fig. 2). Additionally, one limestone sample from the El Profeta Formation (Chong, 1973) collected some 15 km east of El Peñón was analyzed for comparison. The chemical analyses of the carbonates are aimed to identifying differences in compositions of carbonates from different evolutionary stages and are compared to the fluorescence colors of the carbonate minerals observed under ultraviolet light (Fig. 3). The fluorescence under ultraviolet light has widely been used for almost a century in the prospecting for scheelite (*e.g.*, Greenwood, 1943), but is only occasionally applied to carbonate minerals in the context of

mineral exploration (*e.g.*, Escalante *et al.*, 2006). Under short-wave ultraviolet light (UV; 254 nm wavelength) and in absence of other light sources, calcite crystals can present fluorescent colors varying from pale blue over red and yellow to greenish, but may also lack fluorescence (*e.g.*, Chang *et al.*, 1996). The fluorescence colors are attributed to minor trace element contents such as Mn, Pb, Zn and REE or defects in the crystal structure whereas in calcites with elevated contents of Mg or Fe the fluorescence under UV light is suppressed (Gies, 1975).

In addition, a total of 17 samples, including all of those for which the carbonate compositions were determined, were analyzed for stable oxygen and carbon isotopes. The data provide constraints for the nature of the fluids from which the carbonate precipitated.

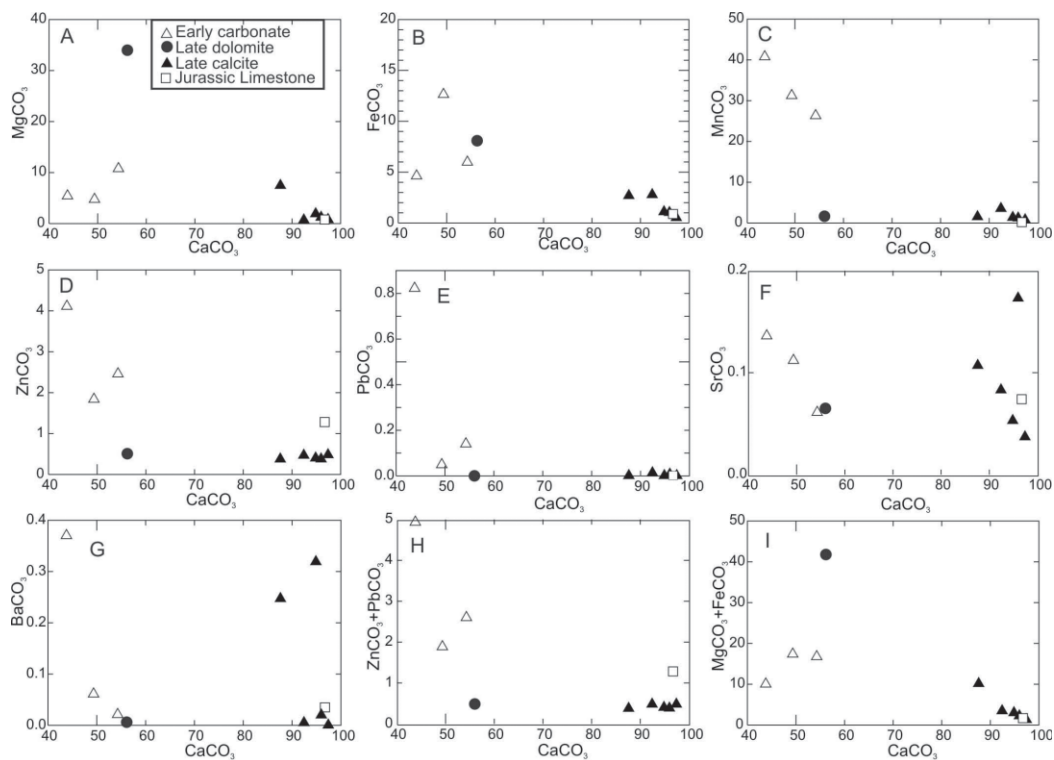


FIG. 2. Variation diagrams showing the compositions of carbonate minerals from the El Peñón district. For analytical data see table 1. Note that all late carbonates have low Mn, Pb and Zn, and with the exception of late dolomite, also low Mg and Fe contents compared to early carbonates. Jurassic limestone sample is from the El Profeta Formation (Chong, 1973).

TABLE 1. GEOCHEMICAL ANALYSES OF SELECTED CARBONATE SAMPLES.

Sample	CaCO ₃	MgCO ₃	FeCO ₃	MnCO ₃	ZnCO ₃	PbCO ₃	SrCO ₃	BaCO ₃	Total	Norm.	Fluorescence
Early carbonates											
QM54-170.27 (1)	43.78	5.41	4.62	40.76	4.11	0.822	0.136	0.370	100	1.39	None
QM54-170.27 (2)	54.27	10.76	5.97	26.31	2.46	0.140	0.061	0.021	100	1.86	None
QM-54-175	49.34	4.73	12.63	31.24	1.84	0.049	0.112	0.061	100	2.04	None
Late calcite											
Px384-405 (1)	94.87	1.90	1.09	1.36	0.40	0.001	0.053	0.319	100	1.10	Intense red
Px384-405 (2)	97.41	0.78	0.52	0.77	0.48	0.001	0.037	0.000	100	1.19	Intense red
QM022-156	92.43	0.69	2.77	3.54	0.47	0.013	0.083	0.005	100	1.10	Intense red
QV004-91.78	87.61	7.46	2.68	1.52	0.37	0.001	0.107	0.247	100	1.09	Moderate red
DDH-002	95.98	1.21	1.02	1.21	0.38	0.007	0.173	0.020	100	1.09	Intense red
Late dolomite											
QM-53-10.2	56.12	33.55	8.02	1.75	0.49	0.001	0.065	0.004	100	1.03	None
El Profeta limestone											
4TB03	96.73	0.80	0.88	0.20	1.28	0.0005	0.074	0.035	100	1.21	None

Numbers in parentheses indicate analyses performed on different carbonate material from the same rock sample. Data expressed as carbonate wt% and the values have been normalized to 100% (normalization factors indicated). Sample numbers coincide with the drill-core sampled. See table 2 for location sample TB03.

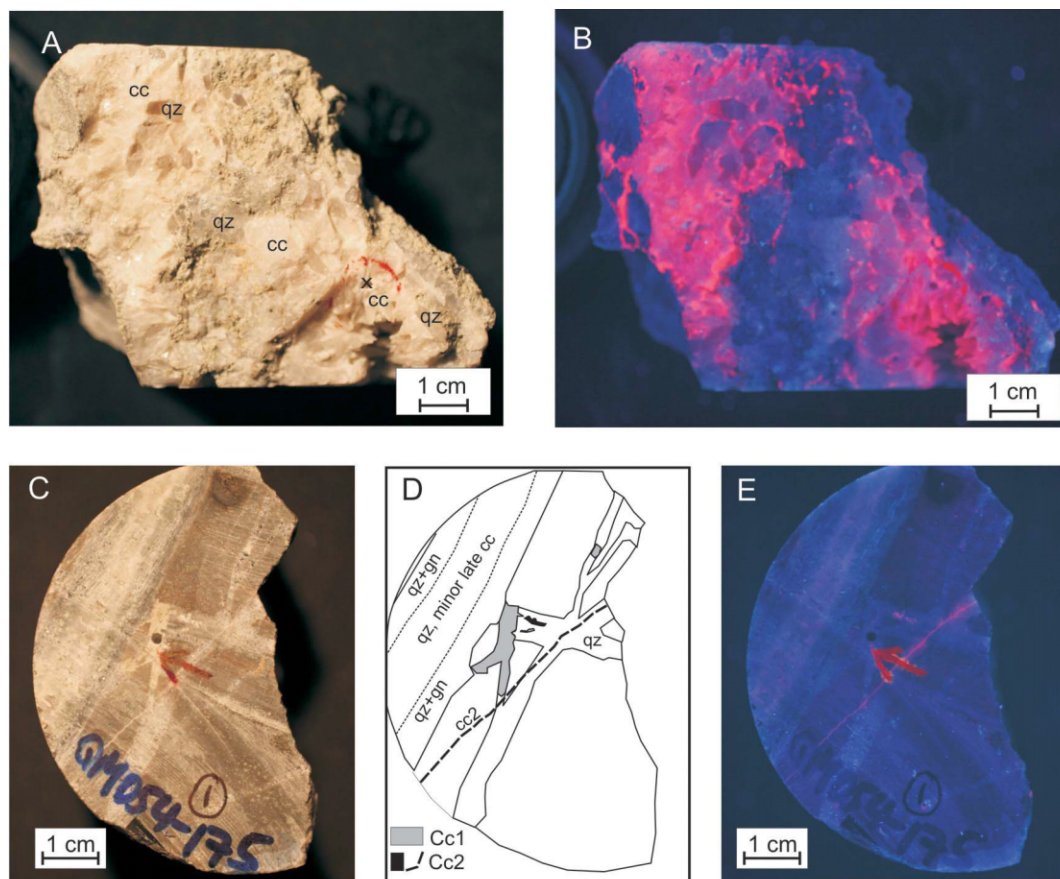


FIG. 3. Examples of vein carbonates and their fluorescence color under short wave ultraviolet light (254 nm wavelength). **A.** Sample QM022-156.2 under natural light. Euhedral quartz crystals (qz: white to grey) are overgrown by white-creamy colored calcite (cc). Open space still remains (lower right). The red circle and x indicate the location where the sample for stable isotope analysis was taken; **B.** Sample QM022-156.2 under short-wave UV light. Note the moderate to intense red fluorescence of calcite; **C.** Sample QM054-175, under natural light, exhibiting several generations of carbonate and banded quartz±sulfide±carbonate veins. Red arrow indicates sample location for stable isotope and geochemical analysis; **D.** Drawing of sample QM054-175 indicating vein generations and cross-cutting relationships (gn: galena); **E.** Sample QM 054 -175 under short wave ultraviolet light. Note the red fluorescing late carbonate veinlet cutting earlier generations of quartz±carbonate veins.

ANALYTICAL PROCEDURES

CARBONATE COMPOSITIONS

Amounts of between 0.017 to 0.057 g of material have been drilled out from the samples using a Dremel micro-drill tool. Care has been taken to select carbonate material as pure as possible, but in some cases up to 50 wt% quartz and other insoluble mineral grains were incorporated. To the extracted samples, 25 ml of deionised water and 2 ml of concentrated hydrochloric acid were added.

The solutions obtained were heated to approximately 80°C on a heating plate and subsequently diluted to 50 ml. It is assumed that during this procedure only carbonates were dissolved in some samples leaving a significant insoluble silicate fraction. The solutions obtained were analyzed for Ca, Mg, Fe, Mn, Zn, Pb, Sr and Ba by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The analytical data were normalized to 100% for better comparison and are presented as

carbonate wt% (Table 1). This data processing was necessary because the insoluble fraction was not analyzed, but is part of the weight considered for percent calculations before normalization. The analytical results show, however, that the majority of the samples contained less than 18 wt% insoluble material (Table 1), mostly quartz, but from two fine-grained banded calcite-quartz veins up to 50 wt% of the material was insoluble.

STABLE ISOTOPES

Fourteen samples from diamond drill cores, complemented by one sample of late calcite from the surface were analyzed for stable oxygen and carbon isotopes (Table 2). Additionally, two limestone samples taken from the Jurassic El Profeta Formation, were analyzed for comparison. The

analyses were carried out at the Pacific Centre for Isotope Geochemical Research (PCIGR) at the University of British Columbia, Vancouver, Canada. Carbonate samples were analysed using a Gas Bench connected to a Finnigan Delta Plus XL mass spectrometer. Between 150 and 300 µg of crushed sample material was placed in the bottom of a clean exetainer, and sealed with a piercable septum. After flushing the exetainer with helium for 5 minutes, 7 drops of 99% phosphoric acid were introduced and then left to equilibrate at 72°C for an hour. Subsequently the CO₂ gas produced was sampled and analyzed. The sample run consists of 5 aliquots of reference CO₂ gas of known composition, 10 aliquots of sample gas, and one final aliquot of reference gas. In-house rock standards were distributed throughout the samples in the gas bench after every eight samples.

TABLE 2. STABLE ISOTOPE DATA OF CARBONATES FROM THE EL PEÑÓN DISTRICT.

Sample	δ ¹³ C ‰	std dev	δ ¹⁸ O ‰	std dev	δ ¹⁸ O‰ 230°C	Depth (m)	vein/location	Fluorescence
El Profeta limestone								
4TB02	-0.82	0.14	22.88	0.17		0	470.324/7315.756	None
4TB03	0.49	0.07	25.97	0.09		0	470.338/7315.695	None
Early carbonate								
PX384-398.70	1.43	0.09	18.10	0.12	10.01	359	Quebrada Colorada	None
QM054 178.9 (1)	-2.09	0.21	18.12	0.32	10.03	337	Quebrada Colorada	None
QM054-178.9 (2)	-3.15	0.10	14.73	0.12	6.64	337	Quebrada Colorada	None
QM054-170.27	-1.31	0.08	15.85	0.13	7.76	325	Quebrada Colorada	None
QM054-175 (1)	-4.36	0.05	14.89	0.03	6.80	334	Quebrada Colorada	None
QM054-175 (2)	-8.87	0.10	17.41	0.07	9.32	334	Quebrada Colorada	None
QM055-101.40	1.53	0.08	16.84	0.15	8.75	259	Quebrada Colorada	None
QD005-197.8	0.71	0.09	20.27	0.13	12.18	400	Quebrada Orito	None
QD005-233	0.84	0.05	21.10	0.11	13.01	426	Quebrada Orito	None
Late calcite								
PX384-405	-4.37	0.08	4.97	0.13	-3.12	370	Quebrada Colorada	Intense red
QM022-156.2	0.24	0.06	14.10	0.13	6.01	303	Quebrada Colorada	Intense red
QV004-91.78 (1)	1.00	0.08	17.92	0.09	9.83	325	Quebrada Orito	Moderate red
QV004-91.78 (2)	1.37	0.07	16.59	0.12	8.50	325	Quebrada Orito	Moderate red
QM054-173	-1.70	0.06	16.30	0.12	8.21	331	Quebrada Colorada	Intense red
ICI336-45-61.3	-1.89	0.04	16.05	0.09	7.96	260	Quebrada Colorada	Moderate red
DDH-002	-3.11	0.10	2.96	0.14	-5.13	0	452.794/7305.103	Intense red
Late dolomite								
QM053-10.20	-0.59	0.11	18.48	0.13	10.39	220	Quebrada Colorada	None

Numbers in parentheses indicate analyses performed on different carbonate material from the same rock sample. δ¹³C values are given as per mil relative to the VPDB standard, whereas the δ¹⁸O values are given relative to the VSMOW standard. Sample numbers coincide with the drill-core sampled. UTM zone 19S coordinates (PSAD56 datum) for samples taken at surface are given.

Measured $^{18}\text{O}/^{16}\text{O}$ ratios were corrected for fractionation between phosphoric acid and calcite following the procedure of Das Sharma *et al.* (2002), and were adjusted for machine fractionation using a factor calculated from repeated analyses of internal UBC standards BN 13, BN 83-2, H6M, which are calibrated against two international standards, NBS

18 and NBS 19. The final results $\delta^{13}\text{C}$ (VPDB) and $\delta^{18}\text{O}$ (VSMOW) were corrected to VPDB and VSMOW based on an average of multiple analyses of NBS 18 and 19. The standard deviation on the average analyses of NBS 18 and 19 is < 0.1 per mil at the 2 sigma level for both $\delta^{13}\text{C}$ (VPDB) and $\delta^{18}\text{O}$ (VSMOW).

ANALYTICAL RESULTS

COMPOSITIONAL VARIATIONS

The samples analyzed for carbonate compositions can be separated into two groups based on their calcite content (values given as wt% and ppm). Samples with high calcite contents (87-97.5%), but low FeCO_3 ($< 2.8\%$), MgCO_3 ($< 2\%$, except sample QV004-91.87 with 7.46%), PbCO_3 ($< 130\text{ppm}$), ZnCO_3 ($< 0.49\%$), as well as MnCO_3 contents between 0.78-3.5% are characteristic for late stage carbonates (Fig. 2). Sample QV004-91.87 represents coarse white calcite overgrowing fine-grained yellowish calcite, the latter coexisting with sphalerite. Thus, the high Mg content of this sample may be explained by contamination with early, yellowish magnesian-calcite. An exception to the general rule is sample QM-53-10.2 which corresponds to paragenetically late dolomite. This sample contains 33.53% MgCO_3 , 8.02% FeCO_3 , but similar to the other late carbonates, low MnCO_3 , PbCO_3 and ZnCO_3 contents. In contrast, early carbonates, representing the second group, exhibit calcite contents of only 43 to 54.3%, combined with elevated FeCO_3 (4.6-12.7%), MnCO_3 (25-41%), MgCO_3 (4.7-10.8%), PbCO_3 (491-8218 ppm) and ZnCO_3 (1.8-4.11%) concentrations (Fig. 2, Table 1). The content of SrCO_3 and BaCO_3 for both groups does not show any correlation with calcite content. The Jurassic limestone exhibits concentrations similar overall to those of the late calcite, but has with only 0.2% a distinctly lower Mn carbonate content, but at 1.28% a relatively high Zn carbonate concentration. Although the limestone analyzed is an apparently unaltered oolitic limestone, the unusually high Zn content may be a distal feature of polymetallic vein mineralization which has been observed in the wider area from where the limestone has been sampled (S. Matthews, personal communication, 2006).

ULTRAVIOLET (UV) FLUORESCENCE OBSERVATIONS

The carbonates of El Peñón have been characterized under short-wave UV light in dark rooms and can be assigned to two principal groups, based on their fluorescence under UV light. Late stage carbonate is most commonly calcite which typically presents moderate to intense red fluorescence, the intensity of which varies with crystal zoning (Fig. 3). However, locally paragenetically late dolomite which does not exhibit fluorescence has been observed (sample QM053-10.20). Contrastingly, early carbonate is characterized by a complete lack or barely detectable fluorescence in yellowish-greenish or reddish colors (Fig. 3). The use of UV light combined with XRD on samples from El Peñón also led to the identification of scheelite, present as late stage mineral in the Quebrada Colorado vein.

STABLE ISOTOPE COMPOSITIONS

The limestones of the El Profeta Formation present isotopic values typical for marine carbonates ($\delta^{18}\text{O} = +22.9$ and $+26\text{‰}$, $\delta^{13}\text{C} = -0.8$ and $+0.5\text{‰}$) with no indication for hydrothermal isotopic signatures, whereas the values of $\delta^{18}\text{O}$ of the majority of the early as well as late calcites from El Peñón are isotopically somewhat lighter (between $+14.1$ and $+21.1\text{‰}$) (Fig. 4). However, the sample from the surface (DDH-002) and one sample of late calcite from the Quebrada Colorado vein (PX384-405) have a distinctly lighter oxygen isotopic signature of $+2.96\text{‰}$ and $+4.97\text{‰}$, respectively. The corresponding isotopic composition of water in equilibrium with calcite was calculated for 230°C using the fractionation factors between calcite or dolomite and water given in Friedman and O'Neil (1977).

Because no microthermometric data are available for fluid inclusions in carbonate minerals, the temperature of 230°C was inferred from fluid inclusion data from vein quartz (Warren *et al.*, 2004) and represents the lower end of the temperature range for the Au-Ag mineralization at El Peñón (Warren *et al.*, 2004). Equilibrium water $\delta^{18}\text{O}$ compositions fall between +6‰ and +13.1‰, the only exception being the samples DDH-002 and PX384-405 which have values of -5.1‰ and -3.1‰ respectively (Fig. 4, Table 2).

Most of the carbonates analyzed fall in the range of $\delta^{13}\text{C}$ values between -2.1‰ and +1.53‰, albeit three samples of early carbonates exhibit distinctly more negative values between -8.9‰ and -3.15‰. Relatively low $\delta^{13}\text{C}$ values are also characteristic for those late calcite which have low $\delta^{18}\text{O}$ values ($\delta^{13}\text{C} = -3.1‰$ for DDH-002, and -4.3‰ for PX384-405). Within the dataset there is no apparent overall correlation of oxygen or carbon isotopic compositions with distance from mineralized veins or depth below surface.

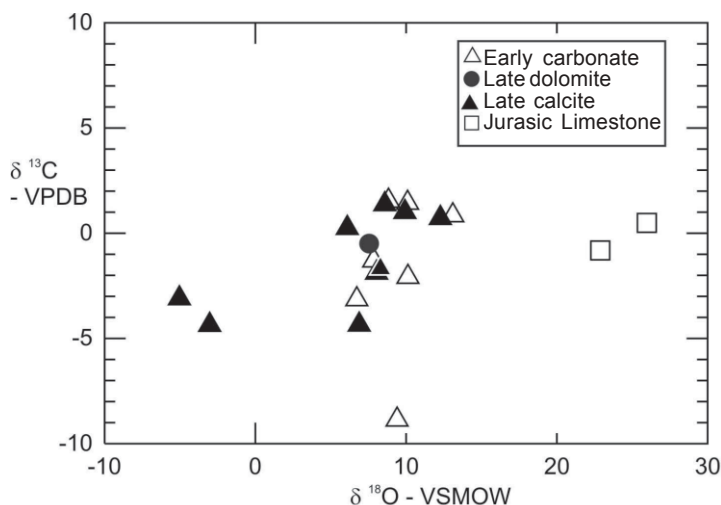


FIG. 4. Stable carbon and oxygen isotope compositions calculated for fluids in equilibrium with carbonates from the El Peñón district. The values of $\delta^{18}\text{O}$ are given relative to the VSMOW standard and represent water compositions in equilibrium with calcite or dolomite at 230°C, calculated using the fractionation factors compiled in Friedman and O'Neil (1977). Two samples of Jurassic limestone from the El Profeta Formation (Chong, 1973) are shown for comparison.

DISCUSSION

GEOCHEMISTRY AND FLUORESCENCE COLOR

The fluorescence color of calcite is a function of defects or trace elements in the crystalline structure (Gies, 1975). Red colors are generally believed to be indicative for Mn contents between 1-15 mole percent, combined with trace contents of Pb (Gies, 1975; Chang *et al.*, 1996). The paragenetically late stage calcites exhibiting moderate and strong red fluorescence colors from El Peñón contain between 0.77 and 3.54 wt% MnCO_3 , but low MgCO_3 and FeCO_3 as well as low Pb and Zn contents. In contrast, the non fluorescing early stage carbonate samples have much higher Mn, Mg, Fe, Pb and Zn carbonate contents combined with less than 60% calcite. The lack of fluorescence can probably be attributed to the high Fe and Mg contents in the calcite structure

or could be an indication that calcite is a relatively minor constituent of the early carbonate material. Thus, in the El Peñón district intense red fluorescence is most likely related to MnCO_3 contents between 0.7 and 3.6% in otherwise relatively pure calcite samples. Complementing other exploration techniques, the UV fluorescence color of carbonate minerals in the El Peñón district and other areas in the Paleocene epithermal belt of northern Chile is a potential low cost exploration tool which can routinely be applied for the classification of vein carbonate samples and identification of carbonate material most likely spatially associated with mineralization. Fluorescence colors of carbonate minerals have been proved to be useful tools for research and exploration in the context of carbonate rock hosted deposits in Central Perú (Escalante *et al.*, 2006).

Paragenetically early carbonates contain large amounts of Fe, Mn, Mg, Pb and Zn, whereas late carbonates consist largely of calcite with minor Mn, but generally low Fe, Mg, Pb and Zn contents. The carbonate compositions of the main stage of hydrothermal activity reflect the generally high concentrations of metals typically abundant in epithermal fluids. These early carbonates probably precipitated from fluids with higher temperatures as the more pure late carbonates as the incorporation of ions other than Ca is a function of temperature (Chang *et al.*, 1996). In the waning stages of the hydrothermal activity, the concentration of these elements decreased dramatically, which is reflected in the relatively pure late stage calcites present throughout the district. It also is probable that the fluid temperatures were lower during the late stages of hydrothermal activity but direct evidence is lacking. Abundant massive white calcite cross-cutting the mineralization has been studied at the Golden Cross epithermal system in New Zealand, where this type of calcite has been inferred to have precipitated from steam-heated fluids in the waning stages of hydrothermal activity (Simmons *et al.*, 2000). The composition, commonly coarse grained nature and paragenetic relationships of the late calcite at El Peñón are similar to the calcites precipitated from steam-heated waters at Golden Cross (Simmons *et al.*, 2000).

STABLE ISOTOPE DATA

The stable isotopes provide constraints on the nature of fluids from which the carbonates precipitated. The ore fluids of low sulfidation epithermal deposits are typically dominated by meteoric water characterized by variably negative $\delta^{18}\text{O}$ values (*e.g.*, Cooke and Simmons, 2000; Simmons *et al.*, 2000; Simmons *et al.*, 2005). However, at El Peñón, the majority of the $\delta^{18}\text{O}$ values for water in equilibrium with calcite calculated at temperatures of 230–260°C (Warren *et al.*, 2004) lie between +6 and +13‰ and are thus significantly heavier than expected. Only two samples of late calcite have oxygen isotope compositions consistent with meteoric water. The isotopic data of carbonates obtained in this study contrast with the oxygen isotope compositions of quartz from three samples of the Quebrada Colorada vein reported by Warren (2005). The data of Warren (2005) suggest that the

quartz precipitated from meteoric waters with $\delta^{18}\text{O}$ between -1.3‰ and -4.9‰ (calculated for 230°C), *i.e.*, values similar to those for the two late calcite samples from this study. However, all other carbonate samples analyzed in this study have significantly heavier isotope compositions in which early and late carbonates cannot be distinguished. The origin of the heavy carbonate isotope compositions is somewhat difficult to understand and we favor a model in which extensive surface-near evaporation of meteoric water generated ^{18}O enriched waters with a high content of dissolved carbonate. This enriched meteoric fluid was incorporated periodically in the hydrothermal cycle and may have led to increased calcite precipitation. An alternative explanation for heavy oxygen signatures would be an oxygen source from magmatic CO_2 in the carbonates. CO_2 would have been contributed periodically to the otherwise meteoric water dominated hydrothermal system and isotopic equilibration between H_2O and CO_2 was not attained prior to carbonate precipitation. In contrast, partial or complete isotopic exchange between meteoric fluids and the host volcanic rocks, while a possible cause for heavy oxygen isotopic signature, cannot explain the discrepancy between quartz and carbonate isotopic composition and we therefore discard this explanation. We also discard low temperature isotopic re-equilibration of carbonate minerals. Although this may lead to overestimated $\delta^{18}\text{O}$ values when calculated at 230°C, it does not explain the fact that not all samples were affected by this process.

A juvenile magmatic component is also suggested by strontium isotopic data (unpublished data, S. Matthews, 2006) and consistent with documented magmatic activity coeval with the mineralization in the district (Arancibia *et al.*, 2006a). The discrepancy between quartz and carbonate isotopic compositions may be due to fluctuations in the overall fluid budget. Carbonate precipitation may have been enhanced after periods of increased surface evaporation or, alternatively due to magmatic fluid flashing. Although low sulfidation epithermal systems are most commonly dominated by meteoric fluids (Simmons *et al.*, 2005), significant magmatic contributions have also been reported (*e.g.*, Faure *et al.*, 2002). An important difference between El Peñón and other low sulfidation deposits such as Golden Cross (New Zealand) or Hishikari (Japan) is the climate at the time of

mineralization. The climate in northern Chile is characterized by its aridity which likely has dominated as far back as the Late Jurassic or even Triassic (Hartley *et al.*, 2005; Clarke, 2005). Ground water of meteoric origin was subject to strong evaporation and probably replaced much slower than at Golden Cross or Hishikari where the climate is more pluvial. Thus, periods of strong surface evaporation or pulses of magmatic degassing may have a considerable effect on the overall oxygen isotopic composition.

The relatively restricted range of $\delta^{13}\text{C}$ values between -2.1‰ and $+1.53\text{‰}$ for most samples indicates that carbon originating from organic

matter did not play a significant role in the ore fluid. The compositional range is consistent with a magmatic origin or from interaction of the fluid with arc magmatic rocks. However, three samples of early carbonates exhibit distinctly more negative values between -8.9‰ and -3.15‰ . These negative values may indicate an origin from a relatively reduced magma or a component of organic carbon (see Faure, 1986). The slightly negative $\delta^{13}\text{C}$ values of the two calcite samples exhibiting also low $\delta^{18}\text{O}$ values are consistent with values expected for meteoric water, possibly characterized by minor organic carbon (see Faure, 1986).

CONCLUDING REMARKS

The carbonate minerals present in the veins at El Peñón can, on the basis of their fluorescence color under UV light, be distinguished into two groups. Paragenetically early carbonate minerals have no or only weak fluorescence whereas paragenetically late carbonates exhibit moderate to intense red fluorescence colors. The fluorescence is controlled by the carbonate composition and is strongest in relatively pure calcites with Mn carbonate contents of in the range of up to a few percent combined with traces of Pb. Thus, the UV fluorescence may serve as an exploration tool for classifying vein carbonate material found throughout the district in the float. Fluorescing calcites have a less direct relationship with epithermal mineralization and are probably of steam-heated origin, whereas non-fluorescing carbonate minerals are more directly related to mineralization.

The oxygen isotope values of both early and late carbonate minerals at El Peñón are in general significantly heavier than expected for low sulfidation epithermal systems and distinct from those obtained for vein quartz in earlier studies. The unusually heavy oxygen isotope signatures of carbonates may be explained by fluctuations in the fluid budget. Unusually heavy $\delta^{18}\text{O}$ values can be explained by periods of extensive surface evaporation and bicarbonate enrichment of meteoric water or, alternatively, by magmatic CO_2 episodically contributed to the hydrothermal system. Unlike in other epithermal districts around the world where the climate is more pluvial, the arid climate of northern Chile favored the generation of isotopically heavy fluids by strong evaporation and/or restricted dilution of magmatic CO_2 in the ore fluid.

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