1 **Noble gas and halogen constraints on fluid sources in iron oxide-copper-gold mineralization: Mantoverde and La**
2 **Candelaria, northern Chile**

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Abstract

The noble gas (Ar, Kr, Xe) and halogen (Cl, Br, I) composition of fluid inclusions in hydrothermal quartz and calcite related to the hypogene iron oxide-copper-gold (IOCG) mineralization at Mantoverde and Candelaria, Chile, have been investigated to provide new insights of fluid and salinity sources in Andean IOCG deposits. A combination of mechanical extraction by crushing and thermal decrepitation methods were applied and collectively indicate that fluid inclusions with salinities ranging from 3.4 up to 64 wt. % NaCl equivalent have molar Br/Cl and I/Cl ratios of between 0.5×10^{-3} and 3.0×10^{-3} and I/Cl of between 8×10^{-6} and 25×10^{-6} in the majority of samples, with maximum values of 5.2×10^{-3} obtained for Br/Cl and 64×10^{-6} for I/Cl in fluid inclusions within individual samples. The fluid inclusions have age-corrected $^{40}\text{Ar}/^{36}\text{Ar}$ ratios ranging from the atmospheric value of 296 up to 490 ± 45 , indicating the presence of crustal or mantle derived excess ^{40}Ar in the fluid inclusions of most samples. The fluid inclusions have $^{84}\text{Kr}/^{36}\text{Ar}$ and $^{130}\text{Xe}/^{36}\text{Ar}$ ratios intermediate of air and air-saturated water. However, $^{40}\text{Ar}/^{36}\text{Ar}$ is not correlated with either $^{84}\text{Kr}/^{36}\text{Ar}$ or $^{130}\text{Xe}/^{36}\text{Ar}$, and the fluid inclusion ^{36}Ar concentrations of $0.2\text{--}3.5 \times 10^{-10}$ mol/g (calculated from measured Cl/ ^{36}Ar and thermometric salinity measurements) extend below the seawater value of 0.34×10^{-10} mol/g, suggesting that contamination with modern air is a minor artefact. The range of fluid inclusion Br/Cl and I/Cl ratios overlap those previously documented for the mantle and magmatic-hydrothermal ore deposits, and the fluids unusually low ^{36}Ar concentration is consistent with the involvement of magmatic-hydrothermal fluids. Input of additional non-magmatic fluid components is suggested by the spread in Br/Cl and I/Cl to values characteristic of bittern brine sedimentary formation waters and near atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$. These data are compatible with mixing of magmatic-hydrothermal fluids and evaporated seawater, which was modified by interaction with back-arc basin sediments as the major control on ore formation. Low Br/Cl ($< 0.5 \times 10^{-3}$) and I/Cl ($< 5.0 \times 10^{-6}$) values that would provide evidence for evaporite dissolution as an important source of fluid salinity were not detected.

Introduction

The nature of hydrothermal fluids involved in the formation of iron oxide copper-gold (IOCG) deposits has been fiercely debated because the hypersaline fluids required for efficient transport of metals and sulfur that form the sulfide ores could have originated from either magmatic or evaporitic sources (Barton and Johnson 1996; Pollard 2000; Chen 2013). Halogen and/or combined noble gas (Ar, Kr and Xe) and halogen (Cl, Br and I) analyses have proven useful for tracing fluid sources in a variety of ore deposits including IOCG's in

Canada, Australia and Scandinavia (Kendrick et al. 2006a; Kendrick et al. 2007; Fisher and Kendrick 2008; Smith et al. 2013). These data can help to identify processes such as fluid mixing, dissolution of evaporites, or hydrothermal boiling because halogens have distinctive abundance ratios and noble gases have distinctive isotopic ratios in these different reservoirs and noble gas elemental ratios are fractionated by boiling (Böhlke and Irving 1992; Kendrick et al. 2001a). In this contribution, we present new noble gas and halogen data for fluid inclusions in ore-related quartz and post-ore calcite from the hypogene zone of Mantoverde and selected quartz samples from the Candelaria deposit and discuss the implications of these and previously published microthermometric data (Rabbia et al. 1996; Marschik et al. 1997; Marschik and Fontboté 2001a; Rieger et al. 2012) for the genesis of IOCG deposits.

Mantoverde and Candelaria-Punta del Cobre are the two economically most significant IOCG districts in the Atacama Region of northern Chile that exhibit typical features of this deposit class including complex high salinity fluid inclusions, such that they provide an excellent case study for evaluating the sources of these fluids in IOCG systems (Vila et al 1996; Marschik and Fontboté 2001a; Rieger et al. 2010 and 2012). Mantoverde is located in the Coastal Cordillera about 100 km north of Copiapó (Fig. 1). In 2013, the mine produced around 56,800 tonnes of cathode copper (AngloAmerican 2014). At the end of 2011, it had proven and probable leachable supergene oxide-ore reserves of 42.7 Mt at 0.58% Cu and 45.4 Mt at 0.26 % Cu (AngloAmerican 2012) plus an estimated resource of 440 Mt at 0.56% Cu and 0.12 g/t Au in hypogene sulfides (Rieger et al. 2010).

The Candelaria mine is located about 15 km south of Copiapó (Fig. 1). It started production in 1993. In 2013, the mine produced mineral concentrates with around 111,100 tonnes of recoverable copper. Proven and probable reserves at the end of 2013 were 281 Mt at 0.58 % Cu and 0.14 g/t Au (Freeport-McMoran 2014). At Candelaria, Fe-pellets are produced from IOCG ores or magnetite-rich flotation tailings, respectively. In 2011, the magnetite plant processed 28.65 Mt at 8.4 % Fe (CAP Minería 2012).

Recent studies have suggested that mixing of hydrothermal fluids of magmatic and non-magmatic origins could have played an important role in mineralization processes in these Chilean IOCG districts (Vila et al. 1996; Cornejo et al. 2000; Marschik and Fontboté 2001a; Benavides et al. 2007; Rieger et al. 2010, 2012). However, the nature and significance of the non-magmatic fluid component has been controversial. Based on fluid inclusion salinities, Vila et al. (1996) suggested input of meteoric water in the Mantoverde district. In contrast, based on an interpreted paragenetic sequence and limited sulfur isotope data, Benavides et al. (2007) suggested seawater-derived sulfate introduced by either seawater or a fluid that dissolved evaporites is required for Cu mineralization at Mantoverde and probably in other Andean IOCG deposits. This interpretation was disputed by Rieger et al. (2010) and Rieger et al. (2012), who presented a detailed paragenetic study on the Mantoverde mineralization, additional sulfur isotope data on pyrite and chalcopyrite, microthermometric and stable-isotope data (O, C) on hydrothermal gangue minerals (quartz, calcite, and K-feldspar). These authors suggest a predominantly magmatic–

hydrothermal fluid component during the main stages of iron oxide and sulfide mineralization in the Mantoverde district. Marschik et al. (2000) and Marschik and Fontboté (2001a) came to similar conclusions for the Candelaria-Punta del Cobre district, based on similar stable isotope and microthermometric data. Mathur et al. (2002) determined initial $^{187}\text{Os}/^{188}\text{Os}$ ratios of ore minerals from Candelaria and magmatic magnetite from nearby Early Cretaceous granitoid plutons, which suggest a common Os source for the IOCG mineralization and the plutons. The age relationships in the Candelaria-Punta del Cobre district are consistent with a genetic link between the mineralization and metaluminous, shoshonitic (high-K) quartz–monzonite porphyry and/or monzodiorite intrusions (Marschik and Söllner 2006).

Chiaradia et al. (2006) presented Br/Cl ratios and Sr isotope ratios of quartz-hosted fluid inclusions in South American IOCG deposits, among them were samples of the Candelaria deposit. They determined molar Br/Cl ratios of 0.80×10^{-3} and 0.89×10^{-3} and initial Sr isotope ratios of 0.70535 and 0.70564 (Chiaradia et al. 2006). These Br/Cl values are much lower than seawater (1.54 ± 0.02 ; McCaffrey et al. 1986) and fall into the range documented for magmatic-hydrothermal fluids (Kendrick et al. 2001a; Banks et al. 2000). However, the initial Sr isotope ratios are higher than those of the nearby Early Cretaceous plutonic rocks ($^{87}\text{Sr}/^{86}\text{Sr}_{\text{initial}}$ of 0.70307–0.70323; Marschik et al. 2003a) and coeval volcanic rocks ($^{87}\text{Sr}/^{86}\text{Sr}_{\text{initial}}$ of ~ 0.7036 ; Morata and Aguirre 2003), which indicates that the ore forming components had multiple sources and is consistent with mixing magmatic-hydrothermal and basinal fluids (Chiaradia et al. 2006).

Geological Framework

The IOCG ores at Mantoverde formed around 119 Ma (K-Ar ages of hydrothermal sericite of 121 ± 3 and 117 ± 3 Ma; Vila et al. 1996) and around 115 Ma at Candelaria-Punta del Cobre (Re-Os molybdenite ages of 114.2 ± 0.6 Ma and 115.2 ± 0.6 Ma; Mathur et al. 2002; $^{40}\text{Ar}/^{39}\text{Ar}$ biotite age 114.9 ± 1 Ma, Marschik et al. 1997), respectively. The geological record of the Atacama Region indicates juvenile aqueous fluids, sedimentary formation waters, meteoric waters, seawater and/or evaporitic brines could all have potentially been involved in mineralization at 115–119 Ma. Jurassic-Early Cretaceous magmatism produced plutons in the Coastal Cordillera of the Atacama Region including gabbro, (monzo)diorite, tonalite, granodiorite to quartz monzonite rocks (Scheuber and Andriessen 1990; Marschik et al. 2003a; Marschik and Söllner 2006). These plutons formed in an arc/back-arc environment, related to the eastward subduction of the Pacific plate under the South American continent and they show similar geochemical characteristics suggesting a

common subduction fluid-modified mantle source without significant crustal contamination (McNutt et al. 1975; Berg and Baumann 1985; Brown 1988; Marschik et al. 2003a; Lucassen et al. 2006). The plutons intrude volcanic and volcanoclastic rocks at Mantoverde, which are correlated with the Jurassic La Negra Formation (Lara and Godoy 1998). In the Candelaria-Punta del Cobre district, they are in contact with volcanic and volcanoclastic rocks of the Early Cretaceous Punta del Cobre Formation and the overlying marine back-arc sediments of Chañarillo Group (Marschik and Fontboté 2001b). Marine conditions prevailed in the back-arc region south and east of Copiapó until late Aptian (Pérez et al. 1990). Then a change in the tectonic regime towards transpressional conditions resulted in back-arc basin inversion and marked uplift in the arc region, coeval with pluton emplacement and the mineralization in the Candelaria-Punta del Cobre district (Marschik and Fontboté 2001a; Marschik and Söllner 2006). Paleoclimatic reconstructions suggest arid to semi-arid conditions in the region since the Mesozoic (Suarez and Bell 1987; Hartley et al. 2005). Evaporites occur within Upper Triassic to Lower Cretaceous sequences in the Atacama Region (Suarez and Bell 1987; Hopper and Correa 2000), which could provide sulfates and/or chlorine to crustal fluids (Mathur et al. 2002). Some of these evaporites may represent continental playa lake deposits or coastal saline lakes (Suarez and Bell 1987) and could have potentially been an important source of residual brines (which have high Br/Cl).

The structural framework is complex and dominated by the Atacama Fault Zone (AFZ). The AFZ is a north to south trending major strike-slip fault system that accommodates parts of the crustal deformation in the Coastal Cordillera of northern Chile, which is caused by the oblique subduction of the Pacific plate. It has been active since Jurassic times and controlled the intrusion of Jurassic-Cretaceous plutons and dikes (Scheuber and Andriessen 1990; Brown et al. 1993; Scheuber et al. 1995; Dallmeyer et al. 1996; Taylor et al. 1998). The Mantoverde district is a structural block between the central and eastern branches of the AFZ (Vila et al. 1996; Rieger et al. 2010). However, NNW to NW-trending faults are of major importance for the IOCG mineralization. They control most of the ores in both, the Mantoverde and the Candelaria-Punta del Cobre districts and are the main fluid conduits in less permeable massive igneous rocks (Marschik and Fontboté 2001a; Rieger et al. 2010). Conglomerates and coarse epiclastic rocks are important hosts for sub-concordant ore lenses particularly in Candelaria-Punta del Cobre district. These originally highly permeable volcanoclastic units, formed in the Neocomian Atacama back-arc basin, could have been important reservoirs for seawater-derived fluids, which may have experienced evaporation and prolonged interaction with basinal sediments. The presence of saline fluids in the volcanoclastic rock units at Candelaria is consistent with the exceptional widespread and voluminous zones of Na(-Ca) and propylitic alteration (Marschik et al. 2000; Marschik et al. 2003b), the high permeabilities expected at the shallow level of mineralization (< 3 km; Marschik et al. 2001a), and the paleoclimatic conditions in the region (Suarez and Bell 1987; Hartley et al. 2005).

Alteration and Mineralization

Alteration in the Mantoverde district is characterized by intense K-metasomatism, silicification, carbonatization (veining and/or pervasive), and lacks the intense Na and/or Ca component to alteration seen in the Candelaria-Punta del Cobre district (Marschik and Fontboté 2001a). Calcite veins and pervasive carbonatization are common at shallow levels in the Punta del Cobre district, but is poorly developed in the Candelaria deposit.

The IOCG systems in the Mantoverde and Candelaria-Punta del Cobre districts are zoned: copper and gold are associated with hematite at shallow levels or locations distal relative to the inferred fluid conduits, and magnetite occurs at depth or in the proximal parts of the hydrothermal system (Marschik and Fontboté 2001a; Rieger et al. 2010). The mineralization can be subdivided into three hydrothermal stages (Marschik et al. 2001a; Rieger et al. 2010 and 2012): 1) an early Iron-Oxide Stage, with magnetite at depth, forming at temperatures of > 400 °C, and hematite at shallow levels and/or laterally to the main fluid conduits, at lower temperatures and possibly under more oxidized conditions; 2) a Sulfide Stage at $\sim 350 - 250$ °C, in which the main Cu and gold mineralization took place; and 3) a late stage at < 250 °C, which is characterized by abundant calcite and minor or trace amounts of hematite and sulfides. Fluid inclusions in hydrothermal quartz and calcite from Mantoverde and in hydrothermal quartz from Candelaria are dominated by several similar types of aqueous inclusion (Rieger et al. 2012; Marschik and Fontboté 2001a): Type I inclusions are complex fluid-vapor bearing inclusions with two or three solid phases (Fig. 2a); Type II inclusions are fluid-vapor inclusions with one solid phase (Fig. 2b); Type III inclusions are liquid dominated two phase fluid-vapor inclusions. In addition, a group of small (< 3 μm) vapor-only inclusions, which occur along crystal growth zones or crystal fractures, have been identified in hydrothermal quartz from Mantoverde. This volumetrically minor fluid inclusion type commonly does not show clear genetic relationships with liquid-rich high-salinity inclusions present elsewhere in the host minerals and suggests that boiling was limited (Rieger et al. 2012). Solid phases in the complex Type I inclusions include halite and one or two of the following phases: an unidentified greenish semitransparent salt (probably iron chloride), magnetite or hematite, and an unidentified green mineral (probably chlorite). A flaky, orange mineral, which is most likely pyrosmallite, is present in some Type I fluid inclusions in Candelaria quartz (Fig. 2c). Salinities of Type I inclusions may reach close to 64 wt. % $\text{NaCl}_{\text{equiv}}$. (Rieger et al. 2012). Halite-bearing Type II inclusions have salinities up to 46 wt. % $\text{NaCl}_{\text{equiv}}$. (Rieger et al. 2012) and Type III inclusions with no visible daughter minerals have salinities of < 30 wt. %

NaCl_{equiv.}. Type II inclusions dominate the vein samples selected from both Mantoverde and Candelaria, with a higher proportion of Type I inclusions at Mantoverde.

Samples and Analytical Methods

Fluid inclusions in a total of 10 samples of hydrothermal gangue minerals from the Mantoverde and Candelaria IOCG deposits have been analysed for halogens (Cl, Br, I) and isotopes of Ar, Kr and Xe. Six quartz and two calcite samples were selected from key positions in the paragenetic sequence of the IOCG mineralization in the Mantoverde district (Rieger et al. 2012; see appendix), and two quartz samples (PC98014; PC99093) were selected from the center of the Candelaria ore body. The provenance of the Mantoverde samples and their trapped fluid inclusions, except MV07473, have been described previously in Rieger et al. (2012). Descriptions of samples MV07473, which contains significant feldspar as well as quartz, PC98014, and PC99093 are given in the appendix.

Sample aliquots comprising sub-mm sized chips were irradiated in position 5c of the McMaster Nuclear Reactor, Canada, on two occasions. Samples included in Irradiation UM#42 of 50 hrs on the 24/08/2010 received 10^{19} neutrons cm^{-2} with a thermal/fast ratio of 2.4; and samples included in UM#48 of 30 hours on the 15/12/2011 received 10^{19} neutrons cm^{-2} with a thermal/fast ratio of 2.7 (Tab. 1). Naturally occurring noble gas isotopes and irradiation-produced noble gas proxy isotopes for K, Ca, Cl, Br and I ($^{39}\text{Ar}_\text{K}$, $^{37}\text{Ar}_\text{Ca}$, $^{38}\text{Ar}_\text{Cl}$, $^{80}\text{Kr}_\text{Br}$ and $^{128}\text{Xe}_\text{I}$) were extracted from the samples by two complementary techniques: 1) Each sample was crushed 2 or 3 times in vacuum, which releases noble gases from fluid inclusions. 2) Previously uncrushed quartz samples, and a crushed aliquot of MV07215, were then analysed by stepped heating with typical steps of 300, 500, 700, 1200, 1400 and 1600 °C. Stepped heating releases gases from fluid inclusions and isotopes of argon (e.g. K-derived ^{39}Ar and radiogenic ^{40}Ar) from K-bearing mineral impurities present in the sample matrix or from accidentally trapped micas within the fluid inclusions (Kendrick et al. 2006a). The extracted gases were purified and isotopic compositions analysed with the MAP-215 noble gas mass spectrometer at the University of Melbourne. Noble gas proxy isotopes were converted to K, Ca, Cl, Br and I abundances on the basis of $^{39}\text{Ar}/\text{K}$, $^{37}\text{Ar}/\text{Ca}$, $^{38}\text{Ar}/\text{Cl}$, $^{80}\text{Kr}/\text{Br}$ and $^{128}\text{Xe}/\text{I}$ production ratios monitored with the $^{40}\text{Ar}/^{39}\text{Ar}$ flux monitor Hb3Gr and scapolite halogen standards. The method is an extension of the $^{40}\text{Ar}/^{39}\text{Ar}$ methodology (Böhlke and Irwin 1992) and has been described in detail by Kendrick (2012) and Kendrick et al. (2006a and 2013). Typical blank corrections amounted to less than 1-5% for Ar isotopes and blanks were below the detection limit for Kr and Xe.

Results

The noble gas and halogen compositions measured by *in-vacuo* crushing, which breaks open fluid inclusions, and stepped heating, which releases noble gases from both the fluid inclusions and mineral impurities, are summarized in Figures 3-6 and Tables 1 and 2. Firstly, the abundances of ^{40}Ar , ^{36}Ar , K and Cl measured in a gram of quartz, together with the measured K/Cl, $^{40}\text{Ar}/^{36}\text{Ar}$ and apparent $^{40}\text{Ar}/^{39}\text{Ar}$ ages calculated for each sample from $^{40}\text{Ar}^*/^{39}\text{Ar}$ ratios, are summarized in Table 1 ($^{40}\text{Ar}^* = ^{40}\text{Ar}_{\text{total}} - ^{40}\text{Ar}_{\text{atmospheric}} = ^{40}\text{Ar}_{\text{total}} - 295.5 \times ^{36}\text{Ar}$; note that $^{40}\text{Ar}^*/^{39}\text{Ar}$ is proportional to $^{40}\text{Ar}^*/\text{K}$; McDougall and Harrison 1999). Each sample contains noble gases dominantly in fluid inclusions and K and $^{40}\text{Ar}^*$ variably distributed between fluid inclusions and minerals impurities. Each sample is represented by two lines in Table 1 that show the total gas released from fluid inclusions by 2-3 crushing experiments and the total gas released by fusing uncrushed quartz samples at 1600 °C (Table 1). In contrast, Table 2 presents the data considered most representative of the fluid inclusions in the samples at the time of trapping, obtained mainly by *in-vacuo* crushing. The fluid inclusions ^{36}Ar concentration (per gram of water) has been estimated from the maximum measured Cl/ ^{36}Ar ratio and fluid inclusion salinities of 38 wt. % $\text{NaCl}_{\text{equiv}}$ for quartz-hosted fluid inclusions, and 34 wt. % $\text{NaCl}_{\text{equiv}}$ for calcite-hosted fluid inclusions (Table 2). The salinities have been obtained from microthermometric experiments and petrographic observations (Rieger et al. 2012; Fig. 2), and the maximum Cl/ ^{36}Ar ratio measured for each sample was used to minimise the possible influence of modern air contaminants (Turner and Bannon 1992; Kendrick et al. 2005), which if present, would serve to increase the apparent ^{36}Ar concentration of the fluid inclusions. The fluid inclusion initial $^{40}\text{Ar}/^{36}\text{Ar}$ values have been corrected for post-entrapment production of radiogenic ^{40}Ar , based on the measured K abundance and mineralization ages of 119 Ma and 115 Ma for Mantoverde and Candelaria, respectively (Table 2). Note that the age-corrected $^{40}\text{Ar}/^{36}\text{Ar}$ ($^{40}\text{Ar}/^{36}\text{Ar}_{\text{initial}}$) values (Table 2) are only slightly lower than the values measured by crushing (Table 1), and that this correction therefore does not influence interpretation of the fluid inclusion data below (Table 2).

The data in Table 1 show the amount of ^{36}Ar released by *in-vacuo* crushing and stepped heating are broadly similar, but that stepped heating releases between 3 and 180 times more K-derived ^{39}Ar than *in-vacuo* crushing. Furthermore, *in-vacuo* crushing yields K/Cl ratios of 0.03-0.12 for the majority of samples that are realistic for Na-Ca brine inclusions (Fig. 2), but higher values are always measured by stepped heating with maximums of 1 to 83 in samples MV 07264, MV 07473, and MV 07491 providing evidence for

significant contamination with K-bearing mineral impurities (e.g. Fig. 3; Table 1), because charge balance requires any saline fluid dominated by the Cl anion has $(K+Na+Ca+Fe)/Cl \sim 1$, therefore K/Cl must be $\ll 1$.

The apparent $^{40}Ar/^{39}Ar$ ages obtained by *in-vacuo* crushing vary from 271 Ma to 1550 Ma, which exceed the estimated mineralization ages of 115-119 Ma (Vila et al. 1996; Mathur et al. 2002) in every case and provide evidence for the presence of crust- or mantle-derived excess ^{40}Ar in the fluid inclusions (Fig. 3; Tables 1 and 2). In contrast, the apparent ages of 56 to 104 Ma obtained by stepped heating samples MV 07264, MV 07473, and MV 07491 are significantly younger than the mineralization ages, indicating ^{40}Ar -loss from the mineral impurities that dominate the Ar budget of these samples (Fig. 3; Table 1).

Initial $^{40}Ar/^{36}Ar$ ratios that are representative of the fluid inclusions at the time of trapping cannot be calculated for the stepped-heating analyses of samples MV 07264, MV 07473, and MV 07491, where ^{40}Ar has been lost from mineral impurities. However, because *in-vacuo* crushing breaks open fluid inclusions without efficiently releasing K-derived ^{39}Ar or radiogenic ^{40}Ar from mineral impurities, initial $^{40}Ar/^{36}Ar$ ratios representative of the fluid inclusions can still be calculated from the *in-vacuo* crushing data for these samples (Table 2). All the samples yield age-corrected ‘initial’ $^{40}Ar/^{36}Ar$ ratios from close to the atmospheric value of 296 to a maximum of 490 ± 45 (Table 2). The age-corrected values obtained by *in-vacuo* crushing are within 4% of the measured values for all the samples (cf. Tables 1 and 2) and similar age-corrected $^{40}Ar/^{36}Ar$ ratios are obtained by total fusion of samples MV 07399, MV 07215, PC 98014 and PC 99093 (Table 1). This demonstrates all the samples contain a high proportion of atmospheric and excess argon and that the age-correction is reliable for all the samples investigated (cf Tables 1 and 2).

The fluid inclusion $^{84}Kr/^{36}Ar$ and $^{130}Xe/^{36}Ar$ ratios obtained by *in-vacuo* crushing vary from close to the air values of 0.0207 and 0.000113, respectively, up to values of 0.033 and 0.000364 that are in the range of air-saturated waters such as 25 °C seawater or bittern brines (Fig. 4a; Table 2), but the fluid inclusions $^{40}Ar/^{36}Ar$ ratio is not correlated with either $^{84}Kr/^{36}Ar$ or $^{130}Xe/^{36}Ar$ (Fig. 4b). The estimated concentration of ^{36}Ar in the fluid inclusions varies from a minimum of 0.16×10^{-10} mol/g in sample MV 07393, that is about half the 25 °C seawater value of 0.34×10^{-10} mol/g (Table 2), up to a maximum of 3.5×10^{-10} mol/g that is more typical of crustal fluids trapped in fluid inclusions (Kendrick and Burnard 2013).

Finally, the molar halogen abundance ratios measured by *in-vacuo* crushing range from 1.4×10^{-3} to 5.2×10^{-3} for Br/Cl and from 15×10^{-6} to 34×10^{-6} for I/Cl (Table 2). In comparison the Br/Cl and I/Cl values obtained by stepped heating are 20-50% lower than the crushing values for most samples, with exceptions for the I/Cl ratios in samples MV 07399 and MV 07473 (Fig. 5; Table 2). The discrepancy between the two extraction techniques is greater than the variation between individual crushes or individual heating steps

in the range 200-1400 °C; however, high Br/Cl values were also obtained in the 1600 °C heating step for some of the samples (Fig. 6).

Discussion

Fluid inclusion halogen ratios

The Br/Cl and I/Cl ratios obtained by *in-vacuo* crushing are higher than those determined from stepped heating (Fig. 5; Table 2) indicating, that compared to *in-vacuo* crushing, stepped heating releases Cl-derived $^{38}\text{Ar}_{\text{Cl}}$ more efficiently than the noble gas proxies for Br and I (Table 2; Kendrick et al. 2001b). Two possible explanations for the lower Br/Cl measured by stepped heating are release of $^{38}\text{Ar}_{\text{Cl}}$ from mineral impurities in the samples (e.g. Fig. 3) or perhaps that $^{38}\text{Ar}_{\text{Cl}}$ is retained in daughter minerals during *in-vacuo* crushing (Kendrick et al. 2001b). If the latter were true, it would imply that the halogen abundance ratios measured by stepped heating are most representative of the fluid inclusions (Table 2). However, a difference in halogen ratios between *in-vacuo* crushing and stepped heating is not always observed in samples containing fluid inclusions with daughter minerals (Fisher and Kendrick 2008) and it has now been observed in samples containing only low salinity fluid inclusions, suggesting it is unrelated to the presence of daughter minerals.

The $^{40}\text{Ar}/^{39}\text{Ar}$ age data and K/Cl systematics of the current samples demonstrate the presence of K-bearing mineral impurities in some of the samples of this study (e.g. Fig. 3). Chlorine data are not available for K-bearing alteration minerals from the Mantoverde or Candelaria-Punta del Cobre districts. However, amphibole and mica in analogous styles of alteration in the Cloncurry District of NE Australia contain 100's to 1000's of ppm Cl and have average K/Cl ratios of 3 ± 1 and 21 ± 11 , respectively, with a minimum K/Cl of 0.1 reported for amphibole (Marshall and Oliver 2006). The relative importance of K- and/or Cl-bearing mineral impurities can be evaluated quantitatively based on the data in Table 1.

Sample MV 07473 with the highest measured K concentration of 636×10^{-6} mol/g (equivalent to 2.5 wt. % K) is estimated to contain 10-20 vol. % feldspar. Assuming this feldspar together with minor phyllosilicate impurities have a combined K/Cl ratio of 400, and all K in the sample was hosted by minerals and not fluid inclusions, the minerals would have contributed 21% of the total $^{38}\text{Ar}_{\text{Cl}}$ (Cl) released by stepped heating this sample. In contrast, sample MV 07215 contains just 1.4×10^{-6} mol/g K (equivalent to 53 ppm K) that indicates very minor contamination with <0.05 vol. % K minerals. The importance of this mineral impurity for halogen measurement depends on its K/Cl ratio; if the contaminant had a K/Cl ratio of 1, it could have contributed up to 27 % of the total Cl released by stepped heating, which would explain the discrepancy between the *in-vacuo* crushing and

stepped-heating data for this sample (Table 2).

These calculations suggest that stepped heating is likely to yield Br/Cl and I/Cl ratios that are lower than the fluid inclusions true values and that the stepped heating data should therefore be interpreted as providing a lower limit for the fluid inclusions Br/Cl or I/Cl (Table 2). In contrast, unless significant $^{38}\text{Ar}_{\text{Cl}}$ is retained within daughter minerals, which seems unlikely based on the low retentivity of noble gases in micron-sized daughter minerals, and the measurement of anomalously low Br/Cl ratios in samples containing fluid inclusions without daughter minerals, the *in-vacuo* crushing analyses can be considered as most representative of the fluid inclusions actual Br/Cl and I/Cl ratios.

Significance of apparent ages

All the samples contain excess ^{40}Ar in fluid inclusions, which results in fluid inclusions released by *in-vacuo* crushing having $^{40}\text{Ar}/^{36}\text{Ar}$ ratios above the atmospheric value (Table 2) and anomalously high $^{40}\text{Ar}/^{39}\text{Ar}$ ages (Fig. 3; Table 1). In contrast, total fusion of samples MV 07264, MV 07473, and MV 07491 gave ages of 56-104 Ma (e.g. Fig. 3), which are younger than the estimated mineralization age of 119 Ma by varying amounts (Table 1). These variable and low apparent ages are interpreted to be the result of very low closure temperatures of micron-sized mineral impurities in samples MV 07264 and MV 07491, and K-feldspar in sample MV 07473. The implication is that ^{40}Ar has been lost from the mineral impurities in these samples and the ages do not have geological significance (see Kendrick et al. 2006b), however, it is important to note that these anomalously young apparent ages do not require the integrity of fluid inclusions, assumed to have been trapped during mineralization at 115-119 Ma, to have been compromised. The fluid inclusions have unknown closure temperatures, but are more retentive to ^{40}Ar than mineral impurities because they are hosted by large grains of quartz or calcite and there is an activation energy that does not favour diffusion of noble gases from the fluid inclusions into the host mineral, which is required for ^{40}Ar loss to occur.

One potential artefact that could have exerted a minor influence on the initial $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of these samples is that ^{40}Ar lost from the mineral impurities could have entered the fluid inclusions. However, the uniformity of the initial $^{40}\text{Ar}/^{36}\text{Ar}$ ratios in all the samples investigated, irrespective of K content (Tables 1 and 2), suggests this was a minor process and the initial $^{40}\text{Ar}/^{36}\text{Ar}$ ratios summarized in Table 2 can be taken as representative of the fluid inclusions in every sample.

Fluid sources and salinity

The I/Cl ratios and the lowest Br/Cl ratios obtained by *in-vacuo* crushing, that are considered representative of brine inclusions in our samples (Fig. 2), overlap the fields defined for

the mantle by mid-ocean ridge glasses (Kendrick et al. 2013; Jambon et al. 1990; Schilling et al. 1978) and magmatic-hydrothermal fluids from Phanerozoic porphyry copper deposits (Irving and Roedder 1995; Kendrick et al. 2001a; Fig. 5). In contrast, the highest Br/Cl ratios extend significantly above this range to values that are typical of 'bittern brine' sedimentary formation waters (Fig. 5; Worden 1996). Bittern brine sedimentary formation waters form by sub-aerial evaporation of seawater beyond the point of halite saturation and the brines acquire high Br/Cl ratios because Br is excluded from the halite lattice (Zharebstova and Volkova 1966). In addition, bittern brines may acquire elevated I/Cl ratios, if they interact with organic-rich sedimentary rocks in the subsurface (Kendrick et al. 2011a).

The fluid inclusions in our samples have extremely variable salinities, ranging from near seawater values (i.e. 3.5 wt. % salts) up to 64 wt. % $\text{NaCl}_{\text{equiv.}}$. Magmatic fluids can have similarly variable salinities of ~2 to 80 wt. % $\text{NaCl}_{\text{equiv.}}$, depending on the relative rates at which a magma outgases H_2O and Cl (Cline and Bodnar 1992), but halite-saturated bittern brine sedimentary formation waters are restricted to salinities of ~30 wt. % salt, which is the saturation point of salt in water at surface conditions (Zharebstova and Volkova 1966).

Taken together the Br/Cl, I/Cl and salinity data are consistent with mixing halogens from multiple sources including magmatic hydrothermal fluids and 'bittern brine' sedimentary formation waters (Fig. 5) and they preclude dissolution of halite-bearing evaporites as the major source of salinity (Fig. 5). However, the halogen data do not preclude evaporites as a minor source of solutes because bittern brines with very high Br/Cl ratios of up to 11×10^{-3} could dissolve substantial halite and retain Br/Cl above the seawater value (Fig. 5). Furthermore input of low salinity surface fluids could help explain some of the previously documented variation in fluid inclusion salinity.

The noble gas systematics of the fluid inclusions provide further evidence for the involvement of surface-derived fluids because the fluid inclusion $^{40}\text{Ar}/^{36}\text{Ar}$ values are all between the modern atmospheric value of 296 (Nier 1950) and a relatively low value of ~490 (Table 2), and the fluid inclusions have $^{84}\text{Kr}/^{36}\text{Ar}$ and $^{130}\text{Xe}/^{36}\text{Ar}$ that are intermediate of air and air-saturated water (Fig. 4). The relatively minor excess ^{40}Ar component could have been introduced by either magmatic-hydrothermal fluids or acquired in the subsurface. Magmatic-hydrothermal fluids are usually assumed to have high $^{40}\text{Ar}/^{36}\text{Ar}$ ratios with values of up to 3000 reported for porphyry copper deposit fluid inclusions (Hu et al. 1998, 2004; Irwin and Roedder 1995; Kendrick et al. 2001a). However, magmatic-hydrothermal fluids are likely to have variable and often low concentrations of noble gas that could result from either hydrothermal boiling or the relative rates of H_2O , Cl and ^{36}Ar degassed from a magma, which also results in the variable salinities of magmatic fluids (Cline and Bodnar 1992; Irwin and Roedder 1995; Kendrick et al. 2001a). A consequence of the low noble gas concentration in magmatic-hydrothermal fluids is that magmatic $^{40}\text{Ar}/^{36}\text{Ar}$, $^{84}\text{Kr}/^{36}\text{Ar}$ and $^{130}\text{Xe}/^{36}\text{Ar}$ signatures could be quickly overprinted by fluid-rock interaction or mixing between crustal fluids. For example, a $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of 3000 in a magmatic-

hydrothermal fluid with sufficiently low ^{36}Ar concentration (e.g. $<0.1 \times 10^{-10}$ mol/g) could theoretically be reduced to the range of $^{40}\text{Ar}/^{36}\text{Ar}$ observed in the IOCG fluid inclusions (300-500) by mixing with a 20% portion of ^{36}Ar -rich surface-derived brine (Fig. 7). Unfortunately we have insufficient isotope data to prove this model or quantify the relative portions or compositions of our interpreted fluid end-members and Fig. 7 is therefore intended only to illustrate how mixing would affect the fluid signatures. However, we consider the apparently low ^{36}Ar concentrations, which are lower than in air-saturated waters, in fluid inclusions in samples MV 08264 and MV 07393 to be consistent with the involvement of magmatic-hydrothermal fluids in ore genesis in these South American IOCG deposits (Table 2). This interpretation is consistent with the halogen data (Fig. 5) and the generally high concentration of ^{36}Ar in most crustal fluids preserved in fluid inclusions: the only fluid inclusions previously found to have lower than air-saturated water ^{36}Ar concentrations were from porphyry copper deposits (Kendrick and Burnard 2013).

Finally, it should be noted that vapor-rich inclusions have a low abundance in the IOCG deposits of this study compared to porphyry copper systems, and where present they do commonly not preserve a clear genetic relationship with liquid-rich high-salinity fluid inclusions (Rieger et al. 2012). This suggests that hydrothermal boiling was not a significant process at the level of mineralization in the Chilean IOCG systems (Rieger et al. 2012). However, recurrent short-lived boiling events may have occurred due to pressure drops related to veining or brecciation, and could have generated the vapor inclusions seen in some Mantoverde samples. Phase separation can contribute to the range of ^{36}Ar concentrations in the fluid inclusions (Table 2), because noble gases partition into the vapor phase during boiling potentially leading to low ^{36}Ar concentrations in residual brines and apparently high ^{36}Ar concentrations in some of the samples that trap vapor-rich inclusions. If the variation in ^{36}Ar concentration is partly explained by hydrothermal boiling, fractionation of noble gas elemental ratios, as observed in fluid inclusions of porphyry copper deposits (Kendrick et al. 2001a), could be expected, because Kr and Xe have a higher solubility in aqueous fluids than Ar (Smith and Kennedy 1983). However, fractionated $^{84}\text{Kr}/^{36}\text{Ar}$ and $^{130}\text{Xe}/^{36}\text{Ar}$ ratios are not detected in the fluid inclusions of this study (Fig. 4), which is consistent with a minor role of boiling and mixing with surface-derived formation waters.

Comparison with fluids in other IOCG districts

Iron oxide Cu-Au deposits from around the world are associated with variably saline NaCl-CaCl fluid inclusions similar to those described as typical of the Mantoverde and Candelaria deposits (Fig. 2; Fu et al. 2003; Hunt et al. 2005; Marshall and Oliver 2007; Oliver et al. 2004; Torresi et al 2012). The Br and Cl systematics of these fluid inclusions and related fluid inclusions associated with regional alteration have been investigated by a number of techniques including PIXE, ion chromatography and laser ablation ICP-MS

(Baker et al. 2008; Gillen 2010; Smith et al. 2013; Chiaradia et al. 2006). In addition, the combined Cl, Br, I and noble gas systematics of similar fluid inclusions have been investigated in Australian and Canadian deposits using the same technique that has been applied in this study (Kendrick et al. 2006a and b; 2007; 2008a and b; 2011b). In every case these techniques have yielded similar results suggesting IOCG fluids contain components derived from multiple sources (Williams et al. 2010).

In most cases fluid inclusion Br/Cl ratios are variable and extend from the magmatic-hydrothermal field to lower values that are consistent with the involvement of evaporites (Baker et al. 2008; Kendrick et al. 2007; 2008a and b; Smith et al. 2013). The data from the Cloncurry district of Australia are particularly interesting because several deposits formed prior to or contemporaneously with a regionally extensive A-type batholith have been investigated (Baker et al. 2008; Kendrick et al. 2007; Fisher and Kendrick, 2008; Kendrick et al. 2011b). In addition, because the regional A-type granite was sourced by melting Paleoproterozoic basement rocks, the magmatic fluids exsolved from these magmas have distinctively high $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of $>30,000$ (Kendrick et al. 2011b). The studies from this region have shown Br/Cl and I/Cl co-vary with $^{40}\text{Ar}/^{36}\text{Ar}$ in the Ernest Henry deposit, where the fluid inclusions with the most magmatic Br/Cl and I/Cl ratios also have the highest $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of $\sim 30,000$, and fluid inclusions with low Br/Cl and I/Cl ratios of closer to halite have $^{40}\text{Ar}/^{36}\text{Ar}$ of <1000 that is closer to the atmospheric value (Kendrick et al. 2007). These data have been interpreted as providing strong evidence for the involvement of magmatic-hydrothermal fluids sourced from the A-type magmas in the Ernest Henry deposit (Kendrick et al. 2007, 2011b). However, evidence for similar aqueous magmatic fluids are lacking from deposits in the south of the district, and deposits that formed prior to intrusion of the regional batholiths. Furthermore, the magmatic noble gas signature is associated with CO_2 fluid inclusions in areas of un-mineralized regional Na-Ca alteration (Fisher and Kendrick 2008; Kendrick et al. 2011b). Taken together these data have been interpreted as indicating mineralization and related alteration at ~ 1525 Ma occurred in a magmatic regime, but magmatic-hydrothermal fluids were not the most important ingredient required for mineralization (Kendrick et al. 2011b).

The Mantoverde and Candelaria IOCG districts share many of the attributes reported for fluid inclusions in IOCG deposits previously, such as variable salinity and halogen systematics that require multiple sources of salinity. However, they differ with respect to the relative abundances of vapor-only or CO_2 bearing fluid inclusions, which are much less common than in Cloncurry, and they also lack Br/Cl and I/Cl ratios of less than 0.5×10^{-3} and 5×10^{-6} , respectively, that would provide strong evidence for the involvement of evaporites (Fig. 4). Furthermore, they have a more homogenous noble gas signature dominated by atmospheric argon that could result partly from mineralization occurring at a shallow crustal levels of < 3 km at Mantoverde and Candelaria, compared to a suggested depth of 6-10 km for the Cloncurry IOCG deposits in Australia (Kendrick et al. 2011b), that would imply greater surface connectivity and infiltration of surface waters. In contrast, magmatic noble gas signatures would potentially be better preserved at the deeper crustal

levels of the Cloncurry deposits.

Conclusions

Fluid inclusions in hydrothermal gangue minerals from the Mantoverde and Candelaria-Punta del Cobre IOCG districts have variable Br/Cl and I/Cl signatures that extend from the mantle field, defined with mid-ocean ridge glasses and magmatic-hydrothermal fluids, to values characteristic of bittern-brine sedimentary-formation waters. Extremely low Br/Cl ($< 0.5 \times 10^{-3}$) and I/Cl ($< 5.0 \times 10^{-6}$) values that would provide evidence for the involvement of evaporites, and have been reported from other IOCG deposits, were not detected. The fluid inclusions have low $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of < 500 that are relatively close to the atmospheric value, and $^{84}\text{Kr}/^{36}\text{Ar}$ and $^{130}\text{Xe}/^{36}\text{Ar}$ ratios intermediate of air and air-saturated waters. These data are compatible with mixing of magmatic-hydrothermal fluids and evaporated seawater, which was modified by interaction with back-arc basin sediments, as the major control on ore formation. The data preclude halite-dissolution as the dominant source of fluid salinity.

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Table captions

Table 1. Summary of ^{40}Ar - ^{39}Ar data for fluid inclusions and mineral impurities in quartz and calcite samples (1σ uncertainties)

Table 2. Fluid inclusion noble gas and halogen data summary (all ratios are molar; 1σ uncertainties)

Figure captions

Figure 1. Location and geological map of the Mantoverde and Candelaria-Punta del Cobre districts.

447

448 Figure 2. Photomicrographs of fluid and mineral inclusions in vein quartz from the Candelaria mine. a) Complex aqueous Type 1 fluid inclusions with a vapor bubble, a halite cube,
 449 and colorless transparent salt crystals of unknown composition; b) Aqueous Type 2 fluid inclusions with a vapor bubble and a halite cube; c) Translucent orange or reddish mineral
 450 inclusion (pyrosmallite) in quartz. These mineral inclusions may occur also within Type 1 fluid inclusions.

451

452 Figure 3. Typical $^{40}\text{Ar}/^{39}\text{Ar}$ systematics of the samples in this study are illustrated by age spectra for sample MV 07491. Note that the stepped heating data (blue) yield K/Cl ratios of
 453 >1 that are characteristic of mineral impurities rather than Na-Ca-K-Cl brines, but the *in-vacuo* crushing data yield K/Cl of 0.2-0.5 that are reasonable for fluid inclusions. The
 454 stepped heating data define a plateau age of 106 ± 2 Ma that is significantly younger than the estimated mineralization age of 119 Ma. In contrast, the fluid inclusions broken open
 455 by *in-vacuo* crushing have $^{40}\text{Ar}/^{39}\text{Ar}$ apparent ages of much greater than the mineralization age reflecting the presence of excess ^{40}Ar trapped in the fluid inclusions (see text).

456

457 Figure 4. Noble gas signature of fluid inclusions. a) $^{130}\text{Xe}/^{36}\text{Ar}$ versus $^{84}\text{Kr}/^{36}\text{Ar}$, and b) $^{130}\text{Xe}/^{36}\text{Ar}$ versus $^{40}\text{Ar}/^{36}\text{Ar}$. Air-saturated water (ASW) reference values of meteoric water at
 458 0°C and seawater at 25°C from Ozima and Podosek (2002) and of bittern brine based on 26 wt. % NaCl brine at 29°C and 1 atm pressure from Smith and Kennedy (1983). Note
 459 that total values are shown.

460

461 Figure 5. *In-vacuo* crushing and stepped-heating total fusion halogen data relative to compositional fields of seawater, evaporated seawater trajectory (SET), halite, basalts, and I-
 462 type magmatic fluids (basalts of Kendrick et al. 2012a and b, and unpublished data; other reference fields based on values from various authors compiled by Kendrick and Burnard
 463 2013). The calculated weighted total of sample MV07215 is shown (see text for explanation).

464

465 Figure 6. Stepped-heating experiments of quartz over a temperature range of 300 to 1600°C : a) Br/Cl ratios b) I/Cl ratios.

466

467 Figure 7. Schematic diagram illustrating the effect of mixing a magmatic-hydrothermal fluid (m) with $^{40}\text{Ar}/^{36}\text{Ar}$ of 3000 with a surface-derived fluid (s). If the two fluids have equal

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468 ^{36}Ar concentration (s/m = 1) the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of the mixture is linearly related to the proportions of the two components. However, if the magmatic fluids have low ^{36}Ar
469 concentrations relative to the surface fluids, as observed in porphyry copper fluid inclusions (Irwin and Roedder 1995; Kendrick et al. 2001a), the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of the magmatic
470 fluid can be overprinted by a relatively small proportion of surface derived water. The compositions of the two end-members are poorly defined in this study, but the hypothetical
471 magmatic fluid must have $^{40}\text{Ar}/^{36}\text{Ar}$ of >490 and ^{36}Ar concentration of $<0.16 \times 10^{-10}$ mol/g, which are respectively the highest and lowest values measured in sample MV 07393
472 (Table 2).
473

Table 1.

Sample/mineral/irradiation	Mass (mg)	Ext.	^{40}Ar $\times 10^{12}$ mol/g	^{36}Ar $\times 10^{15}$ mol/g	K $\times 10^6$ mol/g	Cl $\times 10^6$ mol/g	K/Cl	% $^{40}\text{Ar}^*$	$^{40}\text{Ar}/^{36}\text{Ar}_{\text{measured}}$	Apparent age (Ma)
				<u>total release</u>	<u>total release</u>					
<i>Mantoverde</i>										
MV 07215	96.4	Cr	9.52	32.2	0.11	1.81	0.062 ± 0.004	0	295 ± 7	nd
Qtz/UM#42	79.7	TF*	44.2	143	2.71	10.1	0.268 ± 0.002	4.3	309 ± 7	101 ± 48
MV 07264	33.6	Cr	13.3	39	0.36	4.56	0.079 ± 0.003	13	342 ± 30	599 ± 364
Qtz/UM#42	41.2	TF	29.1	68.3	14.9	14.8	1.01 ± 0.01	31	426 ± 21	84 ± 10
MV 07393	44.4	Cr	27.6	76.3	1.1	13.2	0.083 ± 0.001	18	362 ± 7	561 ± 57
Qtz/UM#42	83.6	TF	28.6	59.7	4.95	27.8	0.178 ± 0.001	38	478 ± 16	291 ± 18
MV 07399	31.7	Cr	507	1670	1.13	9.19	0.12 ± 0.01	2.4	303 ± 1	1167 ± 212
Qtz/UM#48	102.5	TF	688	2182	30.3	40.5	0.75 ± 0.01	6.1	315 ± 1	193 ± 6
MV 07473	103	Cr	98.1	308	3.53	4.47	0.789 ± 0.008	7.2	319 ± 1	271 ± 8
Qtz/UM#42	93	TF	373	411	636	7.68	83 ± 2	67	908 ± 5	56 ± 1
MV 07491	44.8	Cr	54.2	172	1.28	3.96	0.32 ± 0.01	6.0	315 ± 3	339 ± 56
Qtz/UM#42	60.9	TF	147	174	129	11.6	11.2 ± 0.1	65	849 ± 18	104 ± 2
MV 07329 Cte/UM#48	112	Cr	38.6	122	0.20	6.02	0.033 ± 0.002	6.3	316 ± 3	1255 ± 252
MV 07490 Cte/UM#48	103.7	Cr	57.4	177	0.41	10.9	0.037 ± 0.001	8.6	324 ± 3	1236 ± 150

Candelaria

PC 98014	48.3	Cr	49.1	170	0.52	4.38	0.118 ± 0.006	0	289 ± 4	nd
Qtz/UM#48	52.5	TF	41.1	126	6.78	11.3	0.60 ± 0.01	9.3	326 ± 17	81 ± 40
PC 99093	42.4	Cr	93.6	286	0.51	8.36	0.061 ± 0.004	9.6	328 ± 5	1601 ± 388
Qtz/UM#48	82.7	TF	101	289	1.40	15.73	0.089 ± 0.004	15	348 ± 3	1117 ± 96

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Abbreviations: Ext. = extraction method, Cr = in-vacuo crushing, TF = total fusion (calculated for uncrushed samples except TF, which indicates the sum of the gas released by crushing and fusion of crushed sample), nd = not determined. $^{40}\text{Ar}^* = ^{40}\text{Ar}_{\text{total}} - ^{40}\text{Ar}_{\text{atmospheric}} = ^{40}\text{Ar}_{\text{total}} - 296 \times ^{36}\text{Ar}$

Table 2.

Sample/mineral/irradiation	Mass (mg)	Ext.	NaCl _{equiv.} wt. %	Br/Cl ×10 ⁻³	I/Cl ×10 ⁻⁶	K/Cl	Cl/ ³⁶ Ar ×10 ⁶	³⁶ Ar mol/g ×10 ⁻¹⁰	⁴⁰ Ar/ ³⁶ Ar _{initial}	⁸⁴ Kr/ ³⁶ Ar	¹³⁰ Xe/ ³⁶ Ar	
			mean	total	total	total	max	min	total	max	max	max
<i>Mantoverde</i>												
MV 07215	96.4	Cr	38	2.39 ± 0.03	15.8 ± 0.3	0.062 ± 0.004	78 ± 6	0.83	292 ± 7	302 ± 6	0.021 ± 0.001	0.00022 ± 0.00005
Qtz/UM#42	79.7	TF*	38	1.75 ± 0.02	10.6 ± 0.1							
MV 07264	33.6	Cr	38	2.35 ± 0.03	15.4 ± 0.3	0.079 ± 0.003	287 ± 123	0.23	334 ± 29	354 ± 49	0.030 ± 0.004	0.00022 ± 0.00006
Qtz/UM#42	41.2	TF	38	1.97 ± 0.02	8.0 ± 0.2							
MV 07393	44.4	Cr	38	2.30 ± 0.03	16.3 ± 0.3	0.083 ± 0.001	394 ± 36	0.16	349 ± 7	490 ± 45	0.033 ± 0.003	0.00021 ± 0.00002
Qtz/UM#42	83.6	TF	38	1.51 ± 0.02	10.4 ± 0.2							

MV 07399	31.7	Cr	38	1.67 ± 0.01	19.6 ± 0.9	0.12 ± 0.01	18.8 ± 0.1	3.5	303 ± 1	306 ± 1	0.024 ± 0.001	0.00016 ± 0.00003
Qtz/UM#48	102.5	TF	38	1.01 ± 0.01	22.9 ± 0.5							
MV 07473	103	Cr	38	1.35 ± 0.02	23.4 ± 0.4	0.789 ± 0.009	20.6 ± 0.1	3.2	309 ± 1	317 ± 1	0.020 ± 0.002	0.000106 ± 0.000003
Qtz/UM#42	93	TF	38	1.25 ± 0.08	64 ± 1							
MV 07491	44.8	Cr	38	2.05 ± 0.02	17.5 ± 0.3	0.32 ± 0.01	43 ± 2	1.5	308 ± 3	340 ± 17	0.022 ± 0.001	0.000128 ± 0.00004
Qtz/UM#42	60.9	TF	38	1.67 ± 0.01	12.6 ± 0.2							
MV 07329	112	Cr	34	1.92 ± 0.02	16.1 ± 0.2	0.033 ± 0.002	86 ± 10	0.7	315 ± 3	326 ± 11	0.026 ± 0.003	0.00021 ± 0.00007
Cte/UM#48												
MV 07490	103.7	Cr	34	2.03 ± 0.02	18.4 ± 0.3	0.037 ± 0.001	105 ± 5	0.6	322 ± 3	371 ± 18	0.029 ± 0.002	0.000213 ± 0.000009
Cte/UM#48												
<i>Candelaria</i>												
PC 98014	48.3	Cr	38	2.17 ± 0.02	24.4 ± 0.4	0.118 ± 0.006	44 ± 2	1.5	286 ± 4	318 ± 16	0.022 ± 0.001	0.00016 ± 0.00001
Qtz/UM#48	52.5	TF	38	1.44 ± 0.01	13.1 ± 0.2							

PC 99093	42.4	Cr	38	5.16 ± 0.06	34.4 ± 0.6	0.061 ± 0.004	58 ± 3	1.1	326 ± 5	361 ± 19	0.027 ± 0.002	0.00017 ± 0.00003
Qtz/UM#48	82.7	TF	38	2.81± 0.03	17.8± 0.3							
Reference values	Seawater 25 °C		3.5	1.5	0.8	0.02		0.34		296	0.0359	0.00035
	Air									296	0.021	0.00011

1) Abbreviations: Ext. = extraction method, Cr = in-vacuo crushing, TF = total fusion (calculated for uncrushed samples except TF, which indicates the sum of the gas released by crushing and fusion of crushed sample).

2) The average salinity is estimated for the samples fluid inclusion assemblage from microthermometric measurements and petrographic observations (cf. Fig. 2).

3) The initial $^{40}\text{Ar}/^{36}\text{Ar}$ is calculated based on mineralization ages of 119 Ma for Mantoverde and 115 Ma for Candelaria is within 4 % of the measured value (cf. Table 2).

4) Note that the ^{36}Ar concentration in this table is estimated for a gram of fluid inclusion water, whereas concentrations are per gram of quartz in Table 1 (see text).

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