

Magmatic Fluid Inclusions from the Zaldívar Deposit, Northern Chile: The Role of Early Metal-bearing Fluids in a Porphyry Copper System

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Abstract: The occurrence of a distinct type of multi-solid, highly-saline fluid inclusions, hosted in igneous quartz phenocrysts from the Llamó porphyry, in the Zaldívar porphyry copper deposit of northern Chile is documented. Total homogenization of the multi-solid type inclusions occurs at magmatic temperatures (over 750°C), well above the typical temperatures of hydrothermal fluids (less than 600°C) usually recorded in porphyry copper systems. The analysis of this type of fluid inclusions, using a combination of non-destructive microthermometry, Raman and PIXE techniques and the identification of daughter minerals by SEM method, indicates that the trapped fluid was a dense, complex chloride brine in which Cl, Na, K, Fe, Cu, and Mn are dominant. The high chlorine and metal contents indicate that the metals were separated from the crystallizing magma as homogeneous aqueous chloride-rich solutions that represent the primary magmatic fluids exsolved at high temperatures and depth during the crystallization of the parental intrusive.

The multi-solid type inclusion illustrates the mechanism by which ore components are sequestered from the crystallizing parental magma and concentrated in the exsolved magmatic aqueous fluids. These fluids are significant with respect to the origin of porphyry copper deposits, as they are responsible for the first enrichment of metals and represent the precursors of metal-bearing hydrothermal fluids in a porphyry copper system.

Keywords: porphyry copper deposits, fluid inclusions, metal-bearing fluids, magmatic hypersaline fluids, Zaldívar porphyry deposit

1. Introduction

Since the publication of the classical example of magmatic dense saline fluid inclusions by Roedder and Coombs (1967), numerous reports of magmatic hydro-saline inclusions characterized by high homogenization temperatures (>650°C) and extremely high salinities (>65 wt% NaCl equiv.) occurring either in shallow intrusives or intimately associated with magmatic processes, have been published (see reviews in Roedder, 1971, 1992; De Vivo and Frezzotti, 1994; see also Kamenetsky et al., 2004 and references therein). The study of these magmatic remnants has not only provided physical evidence to numerical models and experimental data on the mechanism of generation of exsolved magmatic fluids from upper crustal silicic magmas (e.g. Shinohara, 1994; Webster, 1997), but has also contributed to a better understanding of the mechanisms by which metals could be sequestered from a crystallizing magma, providing evidences for a possible origin and nature of magmatic ore-bearing fluids (e.g. Fournier 1999; Cline 1995; Cloos, 2001).

The study of fluid inclusions has proven to be a use-

ful procedure in constraining the physicochemical parameters of metal-bearing fluids in porphyry copper environments. Most research, however, has concentrated on the early hydrothermal stage, with few studies dedicated to characterize the magmatic ore-bearing fluids. Although the occurrence of magmatic hydrosaline fluid inclusions appear to be a rather common feature in shallow intrusions related to porphyry copper deposits (Roedder, 1971), documentation of this type of inclusions is limited, mostly because they are difficult to recognize in quartz phenocrysts due to the numerous secondary fluid inclusions related to main hydrothermal stages. Despite the fact that there is little information in the literature concerning these multi-solid type of inclusions, the detailed study of magmatic hydrosaline fluid inclusions has demonstrated that they are potential source of key information on the early evolutionary stages of porphyry copper deposits (e.g. Kamenetsky et al., 1999; Ulrich et al., 1999, 2001; Campos et al., 2001; Harris et al., 2003).

In a study of the Zaldívar porphyry copper deposit of northern Chile, Campos et al. (2001) reported a distinct type of highly-saline aqueous fluid inclusions and melt inclusions hosted in igneous quartz phenocrysts. These highly-saline inclusions were named multi-solid (MS)

type because they characteristically contain several soluble solid phases within the cavity. The MS-type inclusions homogenize at temperatures over 750°C, well above the typical values usually found associated with the early and main hydrothermal stages of porphyry copper systems.

The aim of this study is to provide compositional data with the objective to unravel the chemistry of magmatic aqueous fluids trapped as MS-type inclusions. Their significance in the early stages of a porphyry copper system will be discussed, with special attention to the origin of metals and evolution process related to the Zaldívar primary mineralization.

In this study, several non-destructive analytical techniques were employed to qualitatively determine the composition of fluids trapped on individual MS-type fluid inclusions. These techniques include high- and low-temperature microthermometry (heating/quenching and heating/freezing stages, respectively), Raman and PIXE (Proton Induced X-ray Emission) microanalysis. In addition, several inclusions were opened and the residual solids were analyzed by energy dispersive X-ray analysis attached to a scanning electron microscope.

The Zaldívar porphyry copper deposit is located in the Atacama Desert of Northern Chile, approximately 175 km SE of Antofagasta and 5 km north of the giant Escondida deposit (Fig. 1). The deposit is hosted within the Llamo porphyry, a NNE elongated subvolcanic intrusion of granodioritic to dioritic composition (38.7 ± 1.3 Ma; Richards et al., 1999), to which the hypogene mineralization appears to be genetically related. The Llamo porphyry itself intrudes both the Zaldívar porphyry, a subvolcanic rhyolitic unit (290 ± 4 Ma; Richards et al., 1999), and the fine-grained to porphyritic andesites of the Augusta Victoria Formation (66.6 ± 2.2 to 41.2 ± 2.2 Ma; Marinovic et al., 1995).

All igneous quartz phenocrysts investigated in this study belong to the Llamo porphyry, this mineral represents the most suitable mineral to investigate late magmatic evolution, as most phenocrysts contain melt, mineral and fluid inclusions that appear to have been shielded from the effects of hydrothermal alteration (Campos et al., 2001).

2. Types of Fluid Inclusions Hosted in Quartz Phenocrysts from Llamo Porphyry

As described by Campos et al. (2001), aqueous fluid inclusions, like in any porphyry copper deposits, are ubiquitous and usually abundant in all studied igneous quartz phenocrysts from Llamo porphyry. A detailed

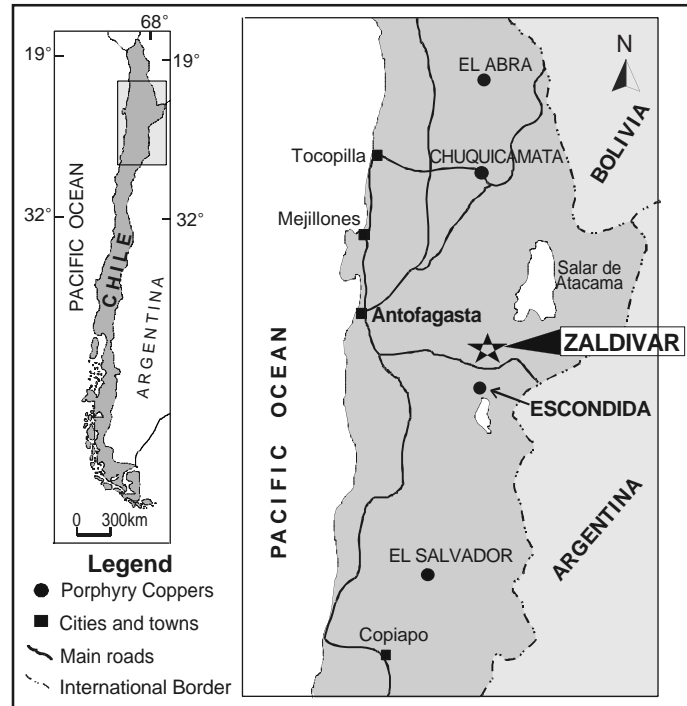


Fig. 1 Location map of the Zaldívar deposit.

examination of fluid inclusions at room temperature, allows the identification of four major types (Fig. 2), described in the following paragraphs.

MS-type are multi-solid inclusions and the main objective of this study, therefore they will be later characterized in detail.

B-type are brine inclusions characterized by an aqueous fluid that represents more than 30 % of the cavity volume; other major components are a gaseous phase and a colorless, well-formed isotropic halite crystal (about 20 and 30 % by volume, respectively). In some inclusions, the NaCl cube accompanies a red to brownish-orange or opaque grain of hematite and/or a rounded crystal of sylvite and less frequently, a semitransparent, tabular or prismatic daughter mineral that may be anhydrite. The morphology of the B-type inclusions is normally round to elongated, always tending to a negative crystal shape.

G-type are low-salinity, low-density, gas-rich inclusions, in which the vapor bubble, that comprises more than 70% of the cavity volume, is frequently surrounded by a thin rim of aqueous fluid. The shape of these inclusions approximates to a negative quartz crystal; however, elongate to irregular-shaped inclusions may also be present.

W-Type are low-salinity, liquid-rich inclusions that contain a small vapor bubble less than 30 % by volume and no daughter minerals, and usually show irregular shape.

No direct coexistence or spatial association is observed

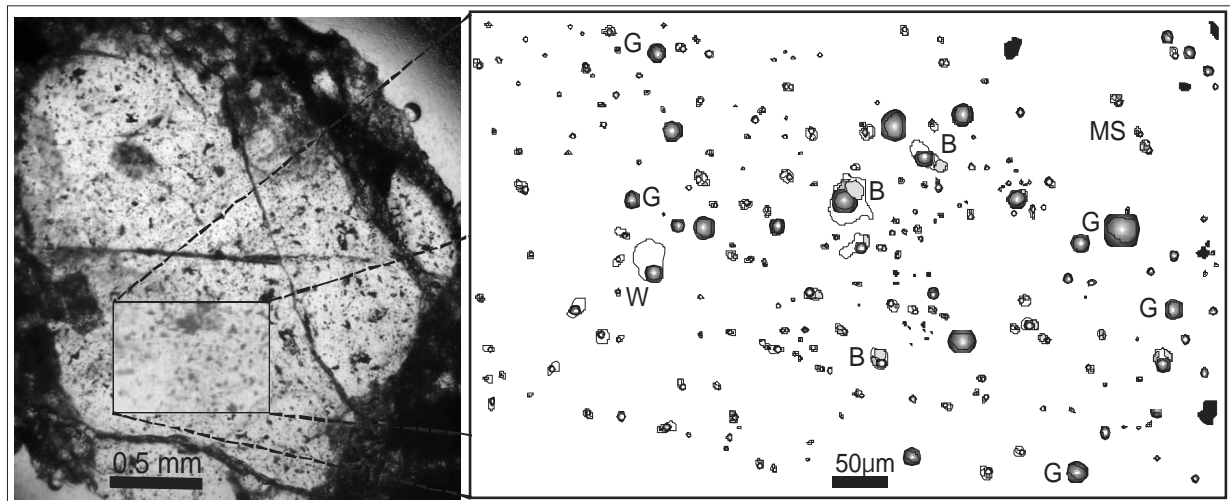


Fig. 2 Quartz phenocrysts from the Llamo porphyry show a dense concentration of different types of aqueous and gaseous fluid inclusions. In the figure a schematic representation for the distribution of various fluid inclusion types is presented. MS: multi-solid, B: brines, G: gas-rich, and W: liquid-rich.

between MS-type inclusions, and the numerous fluid inclusions observed in all of the studied quartz phenocryst that are related to subsequent hydrothermal stages (B-, G- and W-type).

B- and G-types are closely associated and may occur in linear array along traces of growing planes, randomly distributed, or in re-crystallized micro-fractures (pseudosecondary inclusions) within the host. Among these two types, the B-type constitutes about 40 % of all observed inclusions, whereas the G-type are the second most abundant (about 30 %). W-type inclusions are usually aligned on healed micro-fractures planes that frequently cut across the host crystal. Because of their morphology and distribution, they are undoubtedly secondary and represent less than 20 % of all observed inclusions. The distribution of different types of inclusions in a given phenocryst is schematically indicated in Figure 2.

3. Description and Microthermometry of MS-type Inclusions

The MS-type inclusions are not ubiquitous in all studied samples, and their relative abundances varied within phenocrysts of the same sample, usually they are very scarce and restricted to relatively inclusion-free domains in the host crystal. The inclusions are always smaller than 35 μm , possess a characteristic rounded to drop-like shape, and in general are randomly distributed, either iso-

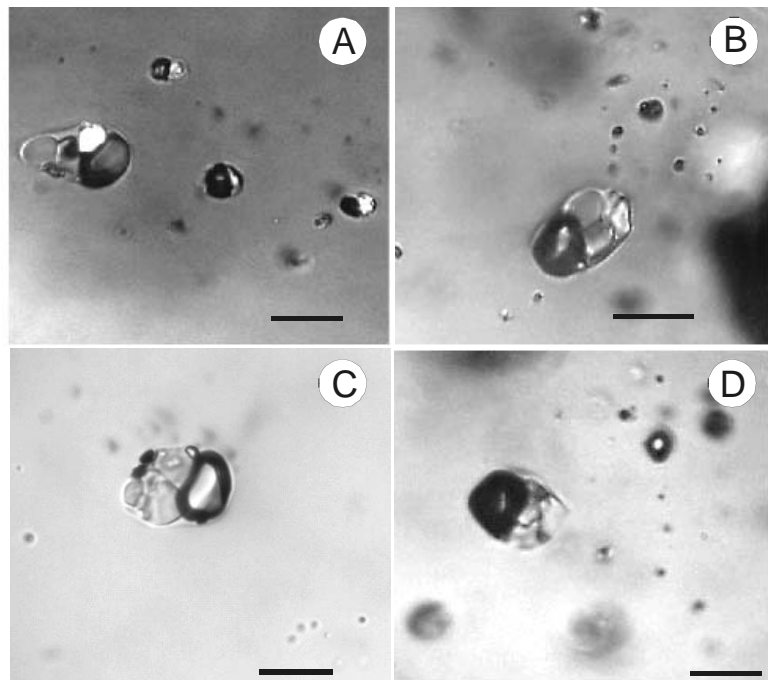


Fig. 3 Set of microphotographs showing general features of MS-type inclusions such as shape, size, and multi-solid content. Scale bar 20 μm .

lated, in clusters of a few inclusions, or more rarely, in trails (Fig. 3-A, B, C and D).

No definitive criterion was observed that could unquestionably indicate that these inclusions are primary or secondary in origin (i.e. inclusions within growth zones or trapped along fracture planes). Nevertheless, MS-type inclusions are interpreted as the earliest inclusions, as they are only found in restricted to discrete domains that contain few inclusions in igneous quartz phenocrysts, show-

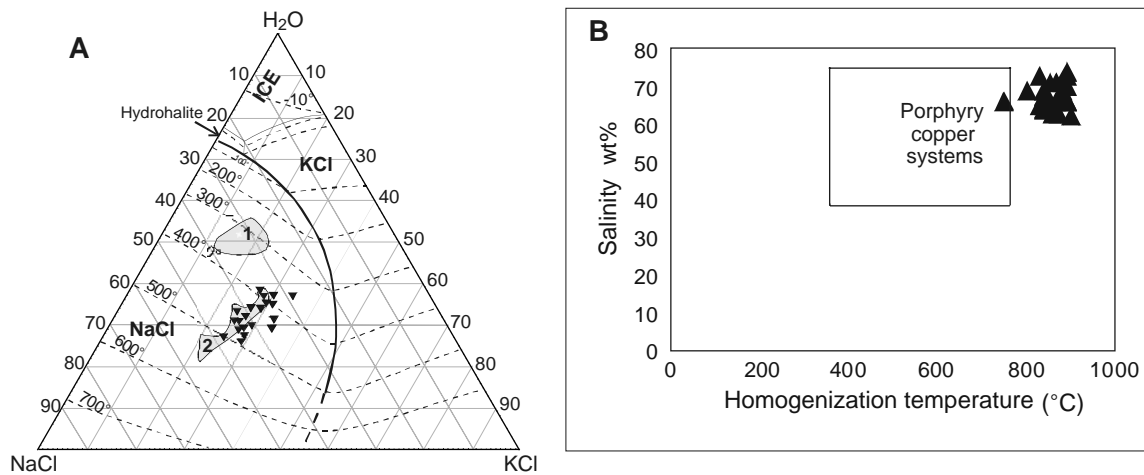


Fig. 4 A) NaCl-KCl-H₂O ternary diagram. Triangles: MS-type inclusions, shaded area 1: fluid inclusions from Bingham Canyon (Moore and Nash, 1974), shaded area 2: fluid inclusions from Granisle-Bell (Wilson et al., 1980). B) Homogenization temperature vs. salinity. Triangles: MS-type fluid inclusions. The box for common porphyry copper systems (Wilkinson, 2001) is somewhat arbitrary and serves only as a reference.

ing no evidence of coexistence or spatial association with other aqueous inclusion types related to subsequent hydrothermal stages.

At room temperature, these inclusions are easily recognized, as the cavity contains several solid phases (at least three translucent solids) and a consistent volume ratio of about 60 % of the cavity volume (Fig. 3-A, B, C and D). The solid phases are all soluble salts, of which two can be easily identified with the petrographic microscope as halite and sylvite (Campos, 2002). The other solid phase, which typically has a greenish-blue color with a high-order birefringence and high positive relief remains unknown. It always occurs as anhedral grains filling the remaining space left between the bubble, halite and sylvite crystals. The bubble has a fairly constant size of approximately 30 % of the total cavity volume, and is normally compressed and deformed by the daughter minerals. The liquid phase always represents the smallest proportion of the total inclusion volume, consisting of less than 10 % of the cavity total volume.

Microthermometric analysis was undertaken on thirty-seven MS-type inclusions using both a Linkam MSTH-600 cooling/heating stage and a Vernatsky type high temperature heating stage at the Vrije Universiteit Amsterdam, while a Linkam MSTH-600 cooling/heating stage and a Linkam TH-1500 high temperature heating stage were used at the Universidad de Concepción. Cooling of single inclusions to -180°C, yielded no phase transitions that would indicate the presence of any gaseous phase other than H₂O (i.e. CO₂, CH₄ or N₂). Furthermore, Raman analyses performed on several MS-type inclusions at the Vrije Universiteit Amsterdam, failed to indicate the presence of any Raman-active species (daughter mineral, polyatomic gas, or polynuclear species in solution). How-

ever, the presence of an iron-rich fluid and/or solid within the inclusions caused the dissolution of at least one of the solid phases, due to the phenomenon of energy absorption as the laser beam hit the inclusion (E. A. J. Burke, pers. comm.).

The solid phases dissolved progressively upon heating with concomitant liquid formation: the unknown crystal between 100 and 160°C, sylvite in the range of 250 to 350°C, and halite within the 377 to 571°C temperature interval. Salinity estimates based on the dissolution temperature of halite and sylvite and the NaCl-KCl-H₂O diagram of Roedder (1971) yield values between 33 to 48 wt % NaCl equivalent, 25 to 34 wt% KCl and a total salinity of the fluid between 63 and 74 wt% (Fig. 4-B). Similar salinity values have been reported for the Granisle and Bell porphyry copper deposits by Wilson et al. (1980). These values are higher than those found in the main hydrothermal stage of such porphyry copper systems as Bingham Canyon deposit (Fig. 4-A).

Homogenization always occurs with the disappearance of the vapor bubble into the liquid phase, at temperatures over 750°C and several with values up to 900°C. The homogenization temperatures of the MS-type inclusions are higher than values usually reported for porphyry copper deposits (Fig. 4-B). Total homogenization (T_H) was only possible using a high-temperature heating stage in which the temperature is measured with a Pt-Pt₉₀Rh₁₀ thermocouple (accuracy ±5°C) calibrated with the melting point of gold (99.9 % purity). The high temperature stage is described in detail by Sobolev et al. (1980) and Campos (2002).

Cooling of the inclusions from the homogenization temperature is characterized by the reappearance of the vapor bubble at 10 to 30°C below the T_H, followed by the

renucleation (in reverse order) of all the dissolved solid phases: first halite, then sylvite and finally the unknown solid phase which crystallized at temperatures below 100° C, in the free space left by the earlier nucleated solids. At room temperature, all the initial phases are present once again in the inclusion.

All microthermometric measurements were repeated at least twice for each inclusion, yielding very consistent and repetitive results (within $\pm 5^\circ\text{C}$). No changes in the original shape of the cavity were observed, thus it is assumed that the inclusions did not stretch upon heating.

A major difference between the MS-type inclusions from the Zaldívar deposit and similar inclusions described in other porphyry copper deposits around the world (Roedder, 1971; Wilson et al., 1980; Eastoe and Eadington, 1986; Pintea, 1993; Ulrich et al., 2001) is that the MS-type inclusions do not coexist with vapor-rich inclusions (Figs. 2 and 3-A, B, C and D). As no evidence of liquid-vapor immiscibility has been observed, the formation of this high-density fluid cannot be explained by boiling of a less saline aqueous fluid, nor the result of heterogeneous trapping. Accordingly, the MS-type fluid represents an early, extremely saline, metal-rich, homogeneous magmatic aqueous fluid exsolved during the crystallization of the parental intrusive, probably following the mechanism proposed by Cline and Bodnar (1991), Cline (1995) and Cloos (2001).

4. PIXE Microanalysis

PIXE microanalysis applied to the study of fluid inclusions provides a good estimate of the composition of the trapped fluids, especially when factors such as the size, depth, and geometry of the inclusion, which are needed to quantify the metal contents, are taken into consideration (e.g. Ryan et al., 1993; Kurosawa et al., 2003). Such factors, however, were not considered in this study. Thus PIXE analysis presented here provides only qualitative results on the fluid inclusion composition. Nevertheless, these results enable us to make important discussion.

Following the microthermometric analysis, quartz grains that host the MS-type inclusions were individually embedded in epoxy resin. Given that the sensitivity of PIXE microanalysis is mainly related to the absorption of X-rays by the overlying quartz, the inclusions

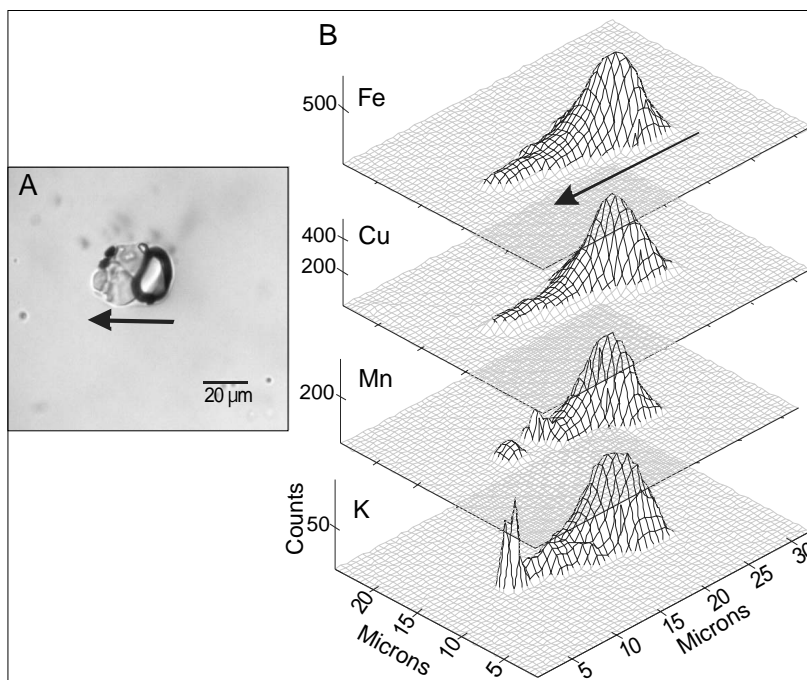


Fig. 5 A) Typical MS-type fluid inclusion at room temperature with the different visible phases. B) X-Y scan of the same inclusion showing the distribution of metals measured by PIXE. Arrow indicates the orientation of the inclusions. Note the lack of metals within the quartz that hosts the inclusion.

were brought close to the surface (less than 10 μm deep) by careful grinding and polishing.

PIXE measurements were undertaken at the Vrije Universiteit Amsterdam, using a 1.7 MV NEC tandem pelletron accelerator attached to a nuclear microprobe (Vis et al., 1993). For this work protons of 3.0 MeV have been used. The microprobe can focus the beam to a final spot size of about 5 μm . Emitted X-rays were detected with a high-purity Ge detector (Ortec-Iglet Co.). All inclusions were analyzed using an irradiation time of 15 minutes. A detailed description of the PIXE at the VUA is given in Vis et al. (1993) and Campos (2002).

All the PIXE microanalyses on MS-type inclusions yielded X-ray emission spectras consisting of a strong Fe peak, followed by lower intensities of Mn, Cu, and Zn (Campos, 2002). The occurrence of strong Cl and K peaks would be expected due to the occurrence of sylvite as a daughter mineral. However, Cl and K intensities were low, and their intensities were strongly dependent on the depth of the inclusions, due to the absorption of the overlying quartz. Moreover, the presence of a halite daughter mineral shows that these inclusions contain high concentrations of Na that cannot be detected with the PIXE probe.

An MS-type inclusion located few microns below the host surface was selected to perform an X-Y scan using the PIXE microbeam in order to investigate the distribu-

tion of metals within the cavity and evaluate any possible contamination from the host crystal (Fig. 5-B). The results demonstrate that the occurrence of metals such as Fe, Cu, and Mn is restricted to the cavity, whereas the host mineral is completely devoid of these elements, thus possible contamination by the host can be ruled out.

During PIXE microanalysis, the heat generated by proton bombardment was sufficient to provoke the dissolution of at least one of the solid phases. The complete re-crystallization of this dissolved solid took several weeks after the PIXE analysis.

A portion of all the MS-type inclusions exposed to the proton microbeam changed from colorless to a pale yellow brown, and the color did not disappear upon heating as reported by Heinrich et al. (1992). This coloring effect may be due to the oxidation of Fe^{2+} by protons (Anderson et al., 1989).

5. SEM and EDX Analyses

To better characterize the solid phases contained within the MS-type inclusions, several inclusions were opened by careful hand-polishing and trying to prevent the dissolution or loss of the daughter crystals, following the procedure described by Campos (2002). Once the inclusions were opened, the remaining solid phases within the cavity were observed with a scanning electron microscope and analyzed using an attached energy dispersive X-ray analysis system. All samples analyzed in the SEM were coated with a carbon film of a standard 25nm thickness deposited in a high vacuum (10^{-3} Pa) chamber by electrically heating a narrow carbon rod.

Using this procedure, it was possible to confirm the occurrence of halite and sylvite as daughter minerals (Fig. 6), but the unknown daughter crystal could not be detected. Given that halite and sylvite crystals were successfully found after the opening procedure, we assume that the third solid phase is not really a solid but probably corresponds to a dense gel-like compound that was lost during the opening or carbon-coating procedure. Furthermore, as the inner walls of the open cavity are usually encrusted with material that contains traces of Fe, Mn, and Cu, the gel-like compound could correspond to a dense hydrous mixture of Fe-Mn-Zn-Cu and Cl.

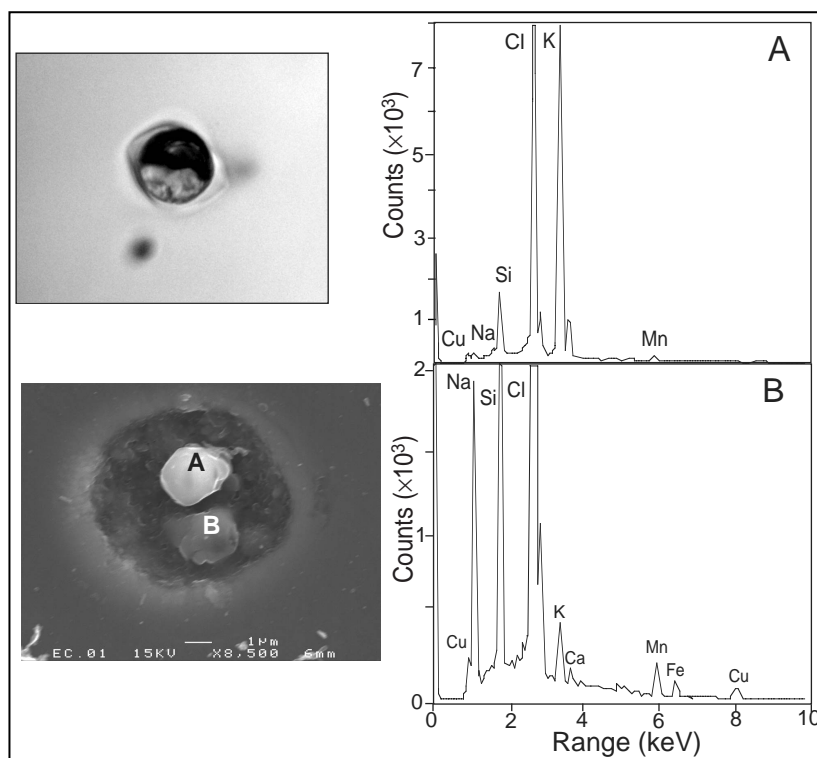


Fig. 6 SEM image and EDS spectra of an opened MS-type fluid inclusion. Picture in the top left corner shows the inclusion before opening.

6. Summary and Discussion

The MS-type inclusions are interpreted as primary fluid inclusions hosted in igneous quartz phenocrysts. They occur mostly isolated or in clusters in relatively inclusion-free areas of the host mineral (Campos et al., 2001). The fluid trapped in these inclusions corresponds to extremely dense saline brine, which at room temperature characteristically contains several soluble solid phases and a very insignificant aqueous phase. In this respect, they resemble the hydrosaline melts described by Roedder (1971).

Non-destructive analyses of individual MS-type inclusions, in combination with the identification of daughter minerals, provide a good qualitative approach to estimate the overall composition of the trapped fluid. The SEM and PIXE results indicate that the fluid corresponds to a dense, chlorine-rich compound, saturated with NaCl and KCl (defined by the occurrence of halite and sylvite crystals), and that also contains several metals including Fe, Cu, and Mn (Fig. 5-B). The fluid would have been exsolved at elevated temperatures (over 750°C), as a highly saline, chlorine- and metal-bearing brine. The best approximation of the bulk salinity of this fluid is over 60 wt% NaCl equivalent, estimated from the dissolution temperature of sylvite and

halite. The origin of this type of fluid has been previously discussed in detail by several authors, concluding that the exsolution of a homogeneous fluid with similar characteristics as the one trapped in the MS-type inclusions would occur at depths of about 6 km or more (Cline and Bodnar, 1991; Cline, 1995; Cloos, 2001).

The estimated temperature, pressure, and composition of the fluid trapped in the MS-type inclusions leads us to conclude that the fluid could represent primary magmatic remnants of the earliest homogeneous aqueous metal-bearing fluid exsolved during the crystallization and that initial water saturation of the Llamo porphyry in the Zaldívar porphyry copper deposit at depth. This fluid would have played a fundamental role in the early concentration of metals in the Zaldívar deposit, being responsible for the extraction of metals from the crystallizing parental magma. The metal extraction process would have been favored by the partitioning of chlorine into the exsolved aqueous phase (Cline and Bodnar, 1991; Cline, 1995; Cloos, 2001). Due to the great affinity of metals to chlorine, they are readily separated from the magma, mainly in the form of hydrosaline chloride-rich compounds. This finding strongly supports the fact that the metals present in the Zaldívar deposit were fundamentally derived from the parental Llamo porphyry.

Following the ideas of Cloos (2001), this highly saline metal-bearing fluid would subsequently rise from depth where it was exsolved from the parent magma and pool beneath the cupola at the top of the solidifying stock. Buoyancy of the accumulated magmatic fluid would cause it to rise diapirically until it reached lower pressure zones (about 1 kbar) where boiling would occur, producing the separation of two immiscible phases, liquid brine and vapor (Roedder and Bodnar, 1997; Heinrich et al., 1999; Ulrich et al., 2001). These later, cooler and less saline fluids (Fig. 4-A and B) are related to the main hydrothermal system that would have been responsible for the widespread alteration and precipitation of metals in the upper portions of the intrusion and surrounding host rocks. In addition, evidence for the existence of this type of fluid has also been reported by Kamenetsky et al. (1999) and Harris et al. (2003) at the Dikini and Bajo de La Alumbrera porphyry copper deposits, respectively.

In conclusion, the fluid trapped in the MS-type inclusions offers an important piece of evidence that strongly supports the evolution of magmatic aqueous fluids in porphyry copper systems as proposed by Cline and Bodnar (1991) and later refined by Cline (1995) and Cloos (2001). At pressures greater than 2 kbar, H₂O saturation occurs after more than 60 % of the melt is crystallized and under these conditions, the initial fluid is a high salinity brine (more than 50 wt% NaCl equiv.),

with metals strongly partitioned into the fluid phase. Further research should be undertaken to better quantitatively characterize the composition of the MS-type inclusions, in order to further evaluate their role in the early evolution of the Zaldívar porphyry copper deposit in particular and porphyry systems in general.

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