Solid inclusions of halite in quartz: evidence for the halite trend

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Abstract

Compositions of fluid inclusions containing halite and sylvite daughter minerals can define a linear trend of decreasing salinity when plotted in the NaCl±KCl±H₂O ternary system. This is termed the Halite Trend, and is attributed to halite precipitation from the fluid before trapping. Salt crystals observed in vein quartz crystals from mineralized zones in the Capitan Mountains, NM, USA, using an electron microprobe are evidence of halite precipitation causing the halite trend. The crystals (observed on both polished and broken sample surfaces) are often euhedral and enclosed in quartz with little suggestion of associated fluid cavities. Based on the textural evidence, these salt crystals are interpreted as solid inclusions that were trapped during the growth of quartz. Given halite-saturated fluids, trapping of heterogeneous (liquid + halite) fluid inclusions is possible, leading to the potential to overestimate the fluid inclusion salinities. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

High-salinity fluid inclusions have been documented in many ore deposits, particularly those thought to have been deposited from magmatic fluids. It is typical for these inclusions to contain daughter minerals; the most common of which are halite and sylvite. The microthermometric behavior of these inclusions can be divided into two general groups; those that show final homogenization by vapor disappearance and those that homogenize by halite disappearance. With inclusions that homogenize by halite disappearance, it is possible that the fluids were saturated in halite at the time of trapping. In the NaCl–KCl–H₂O ternary system, inclusion compositions from some deposits plot in linear trends of decreasing salinity. This was termed the “Halite Trend” (Erwood et al., 1979) and explained as a trend caused by halite precipitation from the fluid prior to trapping. The extension of the trend intersects the NaCl–KCl binary at some composition near, but not at, the NaCl apex signifying that the precipitating phase was a K-bearing halite.

The halite trend (Fig. 1) was first described for the Naica deposit (Erwood et al., 1979) and was then identified by Cloke and Kesler (1979) in other deposits including Panguna (Eastoe, 1978) and Granisle–Bell (Wilson, 1978) and has also been noted in the Capitan pluton (Campbell et al., 1995).
Evidence for the halite trend from fluid inclusion microthermometry at Capitan is similar to that seen from the previously described deposits; a linear array of inclusion compositions trending to lower salinities (Fig. 2). The microthermometric evidence for halite precipitation (as shown in Fig. 2) is supported by fluid inclusion chemistry, which shows that as the salinity decreases by 50%, the Br/Cl ratio doubles (Campbell et al., 1995). Halite tends to exclude bromine when it is crystallizing, so one would expect the residual fluid to show an increasing Br/Cl ratio as the salinity drops due to halite precipitation. Halite precipitation has also been suggested as a possible explanation for the trends seen in the halogen compositions in fluid inclusions from the porphyry deposit at Bingham, UT (Irwin and Roedder, 1995).

If the cause of the halite trend is precipitation of the halite from the fluid, then one would expect to see halite as part of the paragenetic mineral assemblage. Even though most halite crystals would likely be dissolved away at some time after deposition, some may remain preserved as solid inclusions in vein minerals. This point was raised in a very detailed study of the chemical composition of halite trend fluid inclusions from the Granisle porphyry Cu deposit in British Columbia (Quan et al., 1987), which concluded that the geochemical variation is consistent with halite precipitation. However, they noted that “The major problem facing proposals of halite subtraction is the absence of solitary halite inclusions.” It is remarkable that none of the deposits from which the halite trend has been reported are known to contain halite solids. In fact, the only occurrence of solid inclusions of halite is reported in quartz from a metamorphic terrain (Trommsdorff et al., 1985). In this study, we present evidence for the occurrence of solid inclusions of halite in hydrothermal vein quartz from Capitan Pluton, NM.

2. Geologic background

The Capitan Mountains, in Southeastern New Mexico, USA, are the topographic expression of the 28.3 ± 0.1 Ma Capitan granitic pluton (Campbell et al., 1994). This pluton has an exposed area of approximately 35 × 8 km², and is part of the alkaline Lincoln county porphyry belt (Allen and McLemore, 1991). The pluton has been tilted up in the east and eroded such that roof pendants are still exposed on the western end. A number of small U–Th–REE vein deposits are hosted by the granite on the west end, generally located in the brittle fractured outer carapace of the pluton. The veins containing quartz,

Fig. 2. Fluid inclusions from the Capitan Pluton showing the halite trend. Fields A and B are type 1 inclusions in quartz and fluorite, respectively, fields C and D are type 2 inclusions in quartz and fluorite, respectively. Note that the intersection of the trend with the NaCl–KCl binary indicates that the precipitating phase would have the composition NaCl₉₀. Figure modified from Campbell et al. (1995).
fluorite, adularia, hematite, calcite, titanite, and allanite are interpreted to have formed from magmatic fluids based on the high salinity fluid inclusions (up to 80 wt.% NaCl), homogenization temperatures of...

Fig. 3. Typical type 1 inclusion in quartz from the MTE prospect hosted by the Capitan pluton. Inclusion is approximately 100-μm long.

Fig. 4. SE image of fluid inclusion in a broken sample from the MTE prospect, Capitan Mountains. Element mapping confirms that the largest daughter mineral is halite.
500°C to 600°C (often by halite dissolution), hydrogen and oxygen isotope compositions (Campbell et al., 1995), and timing of vein mineralization relative to pluton cooling (Campbell et al., 1994). The movement of mineralizing fluids from the crystallizing magma up through the partially crystalline melt has been documented and is thought to have been facilitated by interconnected porosity within the granite (Dunbar et al., 1996).

Samples in the present study come from two of the many Th–U–REE prospects in the Capitan Mountains. The CMX sample is clear quartz from a 2-cm wide vein cutting the granite. The MTE sample is clear quartz intergrown with adularia from a breccia zone in the granite. It occurs with smoky quartz, allanite and titanite.

3. Previous fluid inclusion studies

Previous studies of the Capitan pluton have investigated the fluid inclusions in vein quartz and fluorite (Campbell et al., 1995) and igneous quartz (Ratajeski and Campbell, 1994). One of the most striking features of the mineralization is the high salinity of the inclusion fluid and virtual absence of later low temperature and low salinity fluids. Campbell et al. (1995) described four types of fluid inclusions from the vein mineralization.

Type 1 inclusions (Fig. 3) are multiphase inclusions with liquid (l), vapor (v), halite (h), sylvite (s) and three or more other daughter minerals that homogenize by either halite or vapor disappearance from 400°C to greater than 600°C. Bulk salinities range from 65 to 83 wt.% NaCl + KCl. Some of the other daughter minerals have been identified as anhydrite, hematite and carbonate. Type 1 inclusions are the dominant type in quartz, and account for over 90% of the inclusions in quartz from the MTE and CMX prospects.

Type 2 inclusions contain liquid, vapor, halite, sylvite and 0–2 other daughters. They generally homogenize by halite disappearance from 340°C to 480°C and have bulk salinities from 52 to 70 wt.%

![BSE image of broken sample from the MTE prospect, Capitan mountains. Large halite daughter mineral is sitting in an opened fluid inclusion cavity.](image)
Fig. 6. BSE image of broken sample from the CMX prospect, Capitan mountains. Crusty material is interpreted to have been deposited from fluid escaping the inclusion. Insert shows typical hopper crystals that comprise the crust.
NaCl + KCl. Type 1 and type 2 inclusions define the halite trend on Fig. 2. Inclusion type 3 (liquid + vapor + halite) and type 4 (liquid + vapor) are lower in salinity and homogenization temperature and account for a low percentage of the inclusions in quartz.

4. Analytical methods

Images shown in this paper were obtained with a Cameca SX-100 microprobe operated at an accelerating voltage of 15 kV. Three types of images are presented. Backscattered electron (BSE) images reflect mean atomic number and are useful for differentiating phases. Secondary electron (SE) images portray the surface topography. Element maps were obtained by setting a wavelength dispersive spectrometer to detect and map the distribution of X-rays generated by specific elements, to show spatial distribution of element concentration. BSE images and element maps were obtained at 10–20 na beam currents, whereas SE images were obtained using lower beam currents.

Samples were prepared with both polished and broken surfaces. Initially, polished samples were made to search for inclusions of potassium-bearing silicate phases, and the polish was accomplished using diamond powder suspended in water. Even though one would expect this preparation technique to result in the dissolution of some salts, we did find halite in these samples. To minimize salt dissolution, two sample preparation techniques were used to maximize the chance of preserving salt crystals. First, two samples were cut and polished using oil instead of water. Tests with oil showed no salt dissolution. Second, samples were simply broken. This was accomplished by scoring the perimeter of a

Fig. 7. BSE image of broken sample from the MTE prospect, Capitan mountains. The euhedral halite crystal has no obvious fluid inclusion cavity.
large crystal with a saw and fracturing along a plane. The uneven broken surface of quartz crystals caused some X-rays to be blocked from one or more spectrometers, resulting in an incomplete image of element distribution. Wherever possible, X-ray images were collected with two spectrometers, and images were superimposed in order to produce the final images shown in this paper. Because of the microprobe spectrometer configuration, Na X-ray images were particularly affected by spectrometer shadowing, and it was not possible to collect complimentary images using multiple spectrometers. Due to this unavoidable analytical difficulty, some of the Na images presented in this paper appear incomplete. All samples were carbon coated prior to analysis, and care was taken not to disturb broken surfaces prior to carbon coating.

5. Solid inclusions

Halite inclusions in quartz were not recognized with the petrographic microscope. However, examination of hydrothermal quartz crystals using the electron microprobe revealed solid inclusions containing some combination of Na, K and Cl.

5.1. Broken surfaces

Opened fluid inclusions were more abundant on broken surfaces than solid inclusions. In some open fluid inclusions, multiple daughter minerals are visible, located in obvious cavities (Fig. 4). The crystals are typically subhedral. These inclusions look very similar to fluid inclusions seen with the microscope in doubly polished thick sections (Fig. 3). Element maps of Na, K, and Cl identify the largest crystals as halite and sylvite. Iron, calcium and sulfur were also detected in some solids, corresponding well with the daughter minerals previously identified such as hematite, carbonate, and anhydrite. In another case, a single euhedral halite crystal occurs in an obvious cavity. The cavity is substantially larger than the halite crystal and has smooth rounded walls as would be expected from a fluid inclusion cavity (Fig. 5).
Note the small amount of precipitation around the cavity implying that some fluid has escaped from the cavity. Other open inclusion cavities are surrounded by abundant, fine-grained, crusty material. This is composed of small, individual-hopper shaped crystals (Fig. 6). This texture is interpreted to result from rapid precipitation of halite from the inclusion fluid as it escapes from the inclusion.

We also observed some halite crystals are not associated with any obvious inclusion cavity (Fig. 7). In this image, a euhedral crystal is surrounded by quartz, with only a small hint of an accompanying cavity. One of the most compelling images is of a broken halite crystal surrounded by quartz that appears to be a mold of the crystal shape of the halite (Fig. 8). This implies that a euhedral halite crystal formed first, and then quartz grew around it. An alternative explanation is that the salt is mimicking the shape of a negative crystal-shaped fluid inclusion, but negative crystal-shaped inclusions have not been observed in the fluid inclusions studied to date.

5.2. Polished surfaces

On the polished surfaces, open and empty inclusion cavities are obvious. A few still contain small daughter minerals, but others have presumably fallen out or have been dissolved. Images from both the MTE and CMX prospects show well-formed crystals of halite embedded in quartz with little evidence of fluid inclusion cavities such as Fig. 9. This is a multigranular aggregate of euhedral halite crystals surrounded by quartz with no evidence of an inclusion cavity. It is very unlikely that these could be from a fluid inclusion because a fluid inclusion should contain only one crystal of halite.

Larger solid inclusions of halite were observed in the samples of quartz that were polished without water. Fig. 10 shows a tabular solid imbedded in quartz. This shape is what would be expected if a cube was oriented with its (110) direction approximately parallel to the plane of the section. In that case, this inclusion would represent a cube approxi-

![Fig. 9. BSE image of a polished sample from the CMX prospect Capitan mountains. Multigranular aggregate of halite cubes embedded in quartz. Dark line is the edge of the sample.](image-url)
Fig. 10. BSE and SE images of MTE quartz polished without water. The solid halite completely fills the cavity in quartz. The Cl and Na elements maps (see text for details) confirm that halite is the only mineral present.

approximately 40 μm on a side. The SE image shows the solid to be in direct contact with the quartz along all edges and that the inclusion is slightly recessed with respect to the host, which is probably a polishing artifact because halite is softer than quartz. Because the inclusion is slightly recessed, the earlier-mentioned shadowing problem was very apparent in surface X-ray element maps. For Cl this was overcome by collecting Cl maps on two spectrometers situated opposite each other. The resulting images were combined to yield Fig. 10C. The Na element map (Fig. 10D) could only be collected on one spectrometer and shows the shadowing problem. A map of K distribution (not shown) revealed very low concentrations of K.

Fig. 11 shows the utility of using both BSE and SE images. In BSE, there appears to be some empty area around the solid inclusion. However, in SE, it is obvious that the solid extends to the walls of the quartz cavity. This is confirmed by the Cl element map showing that Cl is present in the entire cavity. This map was composed of two superimposed images as described for Fig. 10. The Na distribution (not shown) matches Cl distribution. Interestingly, almost all the K is found (with Cl) around the margin of the halite, this might represent sylvite exsolved from an original mixed salt composition.

5.3. Halite compositions

Quantitative analyses were performed on halite crystals on the polished sample surfaces. This type of analysis is difficult due the high volatility of Na in
Fig. 11. BSE and SE images of MTE quartz polished without water (11a,b). Although in the BSE image there appears to be an empty cavity around the halite, the SE image shows this to be an imaging edge effect. The Cl distribution (11c) is matched by the Na distribution (not shown) confirming the solid to be halite. The K distribution (11d) shows small crystals of sylvite concentrated along the edge of the halite. These may represent K exsolved from the halite during cooling.

either the chosen analytical conditions, analytical totals for some analyses were as low as 65%, probably due to a combination of non-flat sample morphology (causing some X-rays to be blocked and absorbed by the host crystal), Na volatilization, and overlap onto the host quartz crystal. Due to these problems, only analyses in which the cation ratio of (Na + K) was equal to Cl were accepted as part of the data set.

Images were collected from all crystals that were analyzed. From these images the solid was classified as either a solid inclusion, a precipitate, or of undetermined origin. The compositions of the salts and their interpreted origin are shown in Fig. 12. Compositions cluster in four general ranges; NaCl-rich,
KCl-rich, NaCl$_{90}$, and sub-equal quantities of NaCl and KCl.

6. Discussion

The electron microprobe images of vein quartz from the MTE and CMX prospects in the Capitan Mountains document the existence of solid crystals of halite enclosed in quartz. Many of the salt crystals are in direct contact with quartz on all sides and show no evidence of a surrounding cavity that could be interpreted as a host fluid inclusion. In contrast, many obvious fluid inclusions, both full of daughter minerals and empty, were observed in the same samples. The simplest interpretation for the origin of these salt crystals is that they are solid inclusions trapped by quartz crystallizing from an aqueous fluid that was saturated with respect to halite. This interpretation is consistent with the observation from the fluid inclusion microthermometry that many of the fluid inclusions homogenize by halite disappearance (Campbell et al., 1995).

Other origins for the solid inclusions can be hypothesized. One could argue that these apparent solid inclusions are daughter minerals in long narrow fluid inclusions that have been polished (or broken) perpendicular to the long axis of the inclusion. The best evidence against this hypothesis is that many of the solids are euhedral cubic crystals completely surrounded by quartz. If the salt crystals grew to fill a fluid inclusion, it might be in contact with the walls of the inclusion cavity, but the salt would mimic the shape of the cavity, which would be unlikely to have a square cross-section. In addition, some solid inclusions occur as multigranular clusters. Fluid inclusions typically contain only a single crystal of each daughter phase, rather than clusters of each phase. Another hypothesis is that these salt crystals were left behind as their host fluid inclusion migrated away. This hypothesis is harder to discredit on a textural basis because the result would have the same textural feature; isolated solid inclusions of halite in quartz. However, we did not find halite solid inclusions clustered with solid inclusions of the other minerals such as anhydrite and hematite, which occur as daughter minerals in the fluid inclusions. Although the occurrence of solid inclusions of sylvite is supporting evidence for this hypothesis, they can also be explained resulting from exsolution during cooling (see below).
The chemical compositions of the salts plot in several groups along the NaCl–KCl binary (Fig. 12). A population of solids with compositions around 80–90 mol% NaCl corresponds to the composition of the precipitating halite indicated by the halite trend (Fig. 2). This is also the composition indicated by the solvus for halite forming at 400°C to 500°C (Sterner et al., 1988). Compositions of nearly pure halite and sylvite presumably represent exsolution from the original 80% NaCl composition. The greater range of sylvite compositions is consistent with the asymmetric solvus allowing more Na than K in halite (Sterner et al., 1988). This type of exsolution was noted by Tromsdorff et al. (1985) who found paired compositions which plot along the solvus indicating that exsolution occurred during cooling. It has been experimentally observed that halite and sylvite continually recrystallize to maintain chemical equilibrium during heating and cooling measurements in fluid inclusions (Sterner et al., 1988). From the composition distribution in Fig. 12, it appears that some solid inclusions have reequilibrated, whereas others have not. Reequilibration is supported by textural evidence in Fig. 11 in which a fairly pure NaCl solid inclusion is surrounded by small crystals of KCl. Reequilibration of solid inclusions may be related to whether or not any liquid was trapped with the solid. A thin film of liquid trapped around a solid inclusion could facilitate reequilibration, whereas a dry solid inclusion would be more likely to retain its original composition. End-member halite and sylvite compositions might also result from trapping at temperatures below 400°C, where expansion of the solvus allows less solid solution. Compositions of salts formed by evaporation of fluid due to decrepitation of inclusions exhibit a wide range including some intermediate compositions as expected from the known bulk composition of the fluid.

6.1. Implications

The presence of solid inclusions of halite in quartz implies that the mineralizing fluid was saturated with respect to halite at the time of crystal growth. This provides a constraint on pressure that is analogous to that provided by inclusions from a boiling fluid assuming that the homogenization temperature is equal to the trapping temperature. Thus, no pressure correction is necessary. In this case, the constraint is given by the position on the liquid + halite isochore. Unfortunately, for the NaCl–H2O system, these isochors are known only up to 40 wt.% NaCl (Bodnar, 1994).

A heterogeneous (liquid + solid) fluid also permits heterogeneous trapping. Inclusions that trapped liquid + halite would yield artificially high halite dissolution temperatures. This results in over-estimates of salinity, as well pressure over-estimates. This can be significant given the steep slope of the (liquid + halite) isochore (Bodnar, 1994). Consider the heating path for an inclusion containing liquid + vapor + halite which homogenizes by halite disappearance. The inclusion will move along the three phase curve until the vapor disappears. Then, the inclusion will move up along the liquid + halite isochore until the halite homogenizes. Inclusions that contain trapped halite will have to be heated past their true trapping temperature to reach homogenization. Given the steep slopes of the liquid + vapor isochore, the apparently high homogenization temperatures will result in substantially higher minimum pressures. Consider the liquid + halite isochore for a 40 wt.% NaCl solution which Bodnar (1994) determined to have a slope of 20 to 25 bar/°C. For inclusions from Capitan quartz, which have a halite dissolution temperature 100°C higher than vapor homogenization (Campbell et al., 1995), this would yield a minimum pressure of 2.25 kbar. Campbell et al. (1995) discussed that this is geologically unreasonably high. They discounted this calculation as being in error due to approximating the complex chemical composition of the inclusion fluid with the simple system NaCl–H2O. However, more realistically, this could be attributed to heterogeneous trapping.

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