

SXRF Microprobe Determination of Cl/Br in Synthetic Quartz-hosted Fluid Inclusions of Low Salinity

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Introduction

Aqueous fluid inclusions in quartz preserve a record of past geologic fluids and are relatively common. Fluid inclusions of seawater salinity and provenance are common in quartz veins from sub-seafloor hydrothermal systems. Aqueous chloride and bromide are significant tracers of geologic processes. Therefore, we have developed an analytic method for the determination of halides in fluid inclusions. One possible application is to explore variation in the chemistry of seawater. As long as modified-seawater inclusions from sub-seafloor hydrothermal systems have not been subjected to processes that partition Br from Cl (e.g., phase separation, halite growth), they should preserve the Cl/Br ratio of the parent seawater. This line of reasoning, applied to some Archean inclusions analyzed by a bulk crush-leach technique, has been used to infer that Archean seawater had a different Cl/Br ratio than does modern seawater [1].

The application of synchrotron x-ray fluorescence (SXRF) is well established for determining most of the common aqueous components of fluid inclusions [2-8]. Furthermore, previous SXRF investigations have succeeded in determining Cl and Br in high-salinity brine inclusions [9]. However, the analysis of low-salinity inclusions, in which halide concentrations may be less than 100 ppm, is highly problematic. Soft Cl characteristic x-rays are strongly absorbed at even modest depths (<5 μm) within the host mineral, typically quartz [10]. Although Br x-rays are not absorbed as strongly as are Cl x-rays, Br is typically present in concentrations 200-300 times lower than Cl. However, the increased brilliance of third-generation synchrotrons such as the APS affords an opportunity to achieve the required analytical sensitivity. This method uses an α/β fluorescence pair to determine empirically the effective absorption properties of each inclusion. It also employs a two-energy analytical approach to optimize fluorescence of Cl and Br.

Methods and Materials

Synthetic Fluid Inclusion Samples

Three fluids were prepared with Cl/Br weight ratios that would bracket the values expected in natural samples

(Cl/Br = 50, 250, and 500). The solutions were prepared by using NaCl, NaBr, and NaI. Salinity was maintained at seawater salinity (S) of 3.5 wt.%. Iodine was added to each fluid, keeping Cl/Br and S at the required values. Synthetic fluid inclusions were prepared by using inclusion-free Brazilian quartz as the host mineral, by following the technique of Bodnar and Sterner [11]. Doubly polished chips were cut from the resulting synthetic inclusion-bearing quartz, and suitable inclusions were optically selected for SXRF microprobe analysis. Nominal depths of each inclusion were determined optically by using a spindle stage [12]. Although inclusions of all sizes and geometries were selected for analysis, only inclusions within 10 μm of the surface were chosen because of the strong absorption effects of quartz.

X-ray Microprobe Analysis

Analyses were performed at beamline 13-ID at the APS, which uses an undulator x-ray source and a cryogenically cooled Si(111) monochromator. Monochromatic x-rays were microfocussed by using Kirkpatrick-Baez (KB) mirrors [13]. The sample was placed in a sample holder at 45° to the incident beam. X-ray fluorescence spectra were then acquired with a Canberra 16-element, germanium, energy-dispersive array detector placed 90° to the beam. A closed-circuit video camera attached to a microscope was used to target inclusions. To reduce interference from Ar when measuring Cl, the entire array of sample holder, microscope, and detector assembly was covered in a He-filled polyethylene tent. A 33- μm Kapton[®] filter was used to reduce the x-ray intensities of silicon, the dominant element fluoresced, which lessened detector dead time and peak pileup.

Because of the wide separation of the x-ray K absorption edges of Cl and Br, we maximized the production of both Cl and Br K x-rays by using two different excitation energies. Br was determined by using an excitation energy of 13.7 keV (i.e., just above the K absorption energy of 13.474 keV). The choice of this energy was a compromise between the need to use energy high enough for the Br Ka peak to be off the Compton scattering peak tail and the need to use energy low enough for the escape peak from the elastic scattering peak to fall

below the iodine lines. Cl, which has a K-absorption-edge energy of 2.819 keV, was determined by using an excitation energy of 6 keV. Both of these excitation energies are greater than the L absorption edges of I (5.188 keV for L₁ to 4.557 keV for L₃ absorption edges); therefore, I was fluoresced in both experiments, allowing correlation of the two spectra for each inclusion. Cl/I was obtained from the 6-keV spectrum and Br/I from the 13.7-keV spectrum from a single inclusion; the ratio of these yielded the Cl/Br that we sought.

Self-absorption, mass attenuation, and scattering effects that occur within the inclusion were calculated by using a modified version of the NRLXRF program [14]. NRLXRF also accounts for x-ray absorption effects between the detector and the inclusion. Although it is possible to specify the thickness of the quartz absorber above the fluid inclusion, we chose to handle that correction separately because the detector array geometry differs from the 45° geometry assumed by NRLXRF. Instead, we used the two monochromatic energies and specified the standard 45° experiment geometry typical of one-detector experiments. We also modeled the self-absorption for each of the three solution compositions. Output results are sensitivity values used to adjust peak intensities to account for these attenuating effects.

Results

The empirical depth correction for absorption by the quartz host was performed by monitoring the hardening of the L α /L β ratio of I (K α /K β ratios could be used for lighter elements in natural inclusions). For a zero thickness value in these calculations, the I L α /L β ratio was measured in a sample of thin potassium iodide crystals precipitated onto a silica slide. Since the I L β ₁ and L β ₃ peaks overlap, these were summed in calculations involving an I L β value. The Cl/Br ratio is extremely sensitive to the I L α /L β ratio for the zero thickness correction; a change of only 0.03 unit resulted in a 15% change in the Cl/Br. We used an average of the zero thickness value 1.3514.

Additional corrections were applied to adjust for the geometry of the 16-element detector array, since only the center detector in the array is actually at a 45° angle to the sample surface. Variation in minimum and maximum peak intensities for geometry-corrected depth was filtered by using a weighted average of the inclusion depth. I L α intensities (the strongest peak) were used as the weighting factor. This depth-weighted average thickness was then used to correct for x-ray hardening by the quartz host and to correct Cl and Br intensities.

Discussion

Cl/Br is sensitive to calculated inclusion depth; Cl/Br increases significantly at depths below 15 μ m. Eliminating data from inclusions at depths greater than

15 μ m resulted in a linear trend with a good correlation ($R^2 = 0.927$) of the average of all Cl/Br determinations but a large spread at 1 σ . The average Cl/Br ratios for the three sets of synthetic fluid inclusions were 22, 251, and 357. This could indicate that fractionation occurred during manufacture of the synthetic inclusions [3].

A significant source of variation of Cl/Br may also be the inclusion geometry, which is also hardest to quantify. NRLXRF and linear and mass attenuation calculations assume that incident and fluoresced x-rays travel through a series of parallel and infinitely wide layers. These assumptions are dramatically distant from the reality of fluid inclusion geometry in which each fluid inclusion shape, thickness, and orientation is unique.

This method should prove useful in the determination of Cl/Br in natural inclusions, although the natural inclusions most likely will not contain I to use as an internal standard. However, Fe, Mn, and Ca are quite common in natural fluid inclusions; any of these could be used as the standard if the appropriate adjustments are made for excitation energy. The two-energy scheme presented here could also extend the range of SXRF microprobe analysis of fluid inclusions to the nondestructive analysis of individual inclusions in which the elements of interest have a wide variation in the x-ray cross section, as long as an element in the inclusions is fluoresced in the two spectra. The modified depth correction procedure is sufficient to correct for x-ray hardening with inclusion depth.

Thus, SXRF microprobe determinations on the Archean fluid inclusions and on modern oceanic samples can be used to test the crush-leach results.

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