SYNCHROTRON X-RAY FLUORESCENCE MICROPROBE DETERMINATION OF HALIDES IN NATURAL AND SYNTHETIC AQUEOUS FLUID INCLUSIONS: ANALYTICAL PROTOCOL FOR LOW-SALINITY INCLUSIONS. J. C. Gray¹, D. A. Vanko¹, R. J. Bodnar², S. R. Sutton³, and A. Lanzirotti³,

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Introduction: Aqueous chloride and bromide are significant geochemical tracers for a number of geological processes. Because aqueous fluid inclusions in quartz are common and they preserve a record of past geological fluids, we are developing a protocol for the determination of halides in both natural and synthetic fluid inclusions. This approach uses the synchrotron X-ray fluorescence microprobe (SXRFM), a technique that is uniquely suited to non-destructive investigations of fluid inclusions.

Analytical Protocol: Previous SXRFM studies have been successful in analyzing Cl and Br in high-concentration brine inclusions [1], but the determination of these elements is particularly difficult in low-salinity fluid inclusions. The characteristic X-rays from Cl are strongly absorbed at even modest depths within the host mineral (>5 µm). Br X-rays are not radically absorbed, but Br is typically present at concentrations 200–300 times lower than Cl. Opportunities to analyze Cl and Br are improving as more powerful synchrotron facilities become available and as earlier facilities are upgraded. We have performed initial experiments at the National Synchrotron Light Source at Brookhaven National Laboratory (beamline X26A) and at the Advanced Photon Source, Argonne National Laboratory (beamline ID-13). Both SXRF microprobes provide monochromatic X-rays focused with Kirkpatrick-Baez mirrors. However, the flux density of X-rays at ID-13, emanating from an insertion device, is about three orders of magnitude higher than that from the bending magnet source at X26A.

The protocol for analyzing both Cl and Br involves a two-step approach that optimizes the production of fluorescent X-rays by using two different exciting energies. Br is determined using an exciting energy of 13.7 keV, just above the critical excitation energy of 13.468 keV, and Cl is determined using a more appropriate exciting energy of 6 keV (the critical excitation energy for Cl is 2.819 keV). In order to co-register or correlate the two experiments, an intermediate-Z element that is excited by both the 6 keV and the 13.7 keV beam is needed. We use about 15000 ppm I in synthetic inclusions for this purpose, and can use Ca, Mn, or Fe in natural fluid inclusions.

Quantification of the X-ray spectra requires knowledge of the differential absorption of Cl and Br X-rays by the thickness of host material. This is accomplished by monitoring the differential absorption of the two K-lines of the intermediate-Z element (I in the case of the synthetic inclusions), following the procedure outlined in reference [2].

Results: Synthetic fluid inclusions have been made using three Cl/Br ratios of 500, 250, and 50. The three fluids also contain about 15000 ppm I as an internal, intermediate-Z standard. The total salinity of each fluid is 3.5 wt. %, chosen to approximate seawater as well as numerous low-salinity aqueous fluids from ore deposits.

Characteristic X-rays from Cl and Br were detected in spectra collected both at NSLS and at APS, with the latter spectra containing much stronger signals due to the more intense exciting beam. Analysis of the spectra indicates that the SXRFM technique will be suitable for determining Cl/Br in low-salinity aqueous fluid inclusions.

Future Applications: Fluid inclusions of seawater salinity and provenance are common in quartz veins from sub-seafloor hydrothermal systems. As long as processes that partition Br from Cl have not occurred (e.g., phase separation, halite growth), the modified-seawater inclusions should preserve the Cl/Br 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 modern seawater [3]. Thus, SXRFM determinations on the Archean fluid inclusions and on modern oceanic samples will be used to test the crush-leach results. Future research on samples of varying geologic age, and perhaps in different host minerals such as halite [4] or marine carbonate cements may extend our knowledge of oceanic Cl/Br through time.

References: