

Synchrotron XRF microprobe determination of the Cl/Br ratio in microscopic fluid inclusions in natural quartz: preliminary results

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Based upon the composition of minute saline fluid inclusions in 3.2 billion-year-old quartz that formed beneath the Archean sea floor, the Cl/Br ratio of Archean seawater is hypothesized to have, in the past, been significantly different than that of today [1]. These ancient quartz grains from the Barberton greenstone belt in South Africa were previously analyzed by Channer *et al.* [1] using a crush-leach technique combined with gas and ion chromatography. They determined Cl, Br, and I in fluid inclusion leachates from 27 quartz vein samples and reported an average molar Br/Cl ratio of 3.02×10^{-3} , which corresponds to a Cl/Br weight ratio of 147. Modern seawater has a Cl/Br of 289, twice that of the analyzed Archean seawater.

The crush-leach technique homogenizes fluid inclusion populations within a sample. Synchrotron x-ray fluorescence analysis (SXRF) provides an alternative method that has the added advantage of determining the chemical composition from individual inclusions. For the present study, Cl and Br were determined by SXRF in 20 fluid inclusions from two of the same samples analyzed by Channer *et al.* [1]. In addition, two samples from the modern mid-Atlantic ridge (MAR) and the southwest Indian ridge (SWIR) were studied. Analyses of the Archean samples using SXRF were intended to independently verify the published crush-leach analyses. Furthermore, the MAR and SWIR samples were studied because they should exhibit Cl/Br values identical to that of modern seawater.

Equant inclusions with diameters up to about 10 μm that were located within about 5 μm of the upper surface of doubly polished quartz plates were prepared for the analyses. Measurement of inclusion dimensions and depths was facilitated by an optical spindle stage to ensure accurate absorption corrections. The salinity of each inclusion was determined by measuring the ice melting temperature with a standard fluid inclusion freezing stage. Two types of inclusions were analyzed that belonged to either a low-salinity group (7.02 to 10.24 wt. % NaCl equivalent) or a high-salinity group (≥ 22 wt. % NaCl equivalent). These values agreed with those reported by Channer *et al.* [1].

SXRF analyses were performed at GeoSoilEnviroCARS (GSECARS) sector 13 at the Advanced Photon Source (APS). A beam of approximately 3 μm by 3 μm was produced using Kirkpatrick-Baez optics. Energy was tuned to 15 keV with a channel-cut silica monochromator. The mean Cl/Br weight ratio of the Archean specimens is 161 ($N = 20$, $\sigma = 70$), which is very close to the mean value of Channer *et al.* [1]. In contrast, fluid inclusions in the modern oceanic samples have a mean Cl/Br of 263 ($N = 7$, $\sigma = 168$),

essentially identical to that of modern seawater. For both sets of data, the variance about the means is quite high. Future work is planned to reduce this variance through improved procedures for depth corrections (based upon measured $K\alpha/K\beta$ ratios). Synthetic fluid inclusions of known Cl and Br concentrations will be used to assess the precision of the SXRF technique.

These results are significant because they indicate that the global biogeochemical processes that govern seawater halide chemistry have changed between the Archean and the present. Ultimately, the SXRF determination of Cl/Br in fluid inclusions will be extended to specimens of varying geological age and will provide a history of seawater halide composition. This will allow an examination of the mechanisms of the biogeochemical cycling of seawater halogens.

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Reference

- [1] D.M.DeR. Channer *et al.*, *Earth and Planetary Science Letters*, 325–335 (1997).