A COMBINED CRUSH-LEACH AND SYNCHROTRON X-RAY FLUORESCENCE DETERMINATION OF 3.5 GYR SEAWATER Br/Cl

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Knowing the composition of the Early Archaean (3.5-3.0 Gyr) ocean is of prime importance in the understanding of some major geological processes occurring on the Early Earth (e.g. elemental cycles, formation of the continental crust) as well as to bring constraints to the conditions in which primitive life flourished. Early Archaean hydrothermal systems, such as those occurring in well preserved Barberton (South Africa) and Pilbara (Australia) greenstone belts, offer the opportunity to study the remnants of Archaean seawater and seawater-derived hydrothermal fluids trapped as fluid inclusions. Halide elements can be used as tracers of the seawater composition, since their ratio can be considered to be unaltered by fluid-rocks processes such as seafloor hydrothermalism (You et al, 1994). Bulk fluid analyses have been performed by De Ronde et al. (1997) and Channer et al. (1997) for fluid inclusions in primary quartz from the ca. 3.23 Gyr ironstone pods, Barberton. Reported halide ratios (e.g. $Br/Cl_{(weight\ ratio)} = 6.8 \times 10^{-4}$) are significantly higher than modern-day seawater ($Br/Cl = 3.4 \times 10^{-4}$). Such relative enrichment in heavy halide elements can be interpreted as resulting from a lower extent of Br removal by the burial of organic matter (Channer et al., 1997).

In this work, we present composition estimates for Br, Cl and other elements obtained for fluid inclusions which are thought to be representative of ca. 3.5 Gyr Pilbara halide seawater composition. The Pilbara region in Western Australia is a 3,65 to 2,45 Gyr granite-greenstone terrane which underwent only low-grade metamorphism and minor deformation, making it the oldest and best preserved Archaean terrane, and one of the most suitable site for the study of Early Earth hydrothermal processes and primitive life. Oceanic floor and associated hydrothermal system are particularly well preserved and undeformed around the North Pole Dome, where most our samples come from. Analyzed fluid inclusions come from quartz crystallized inside or in-between pillow basalts. A single population of 5-20 μm large, H2O-NaCl-CaCl2 fluid inclusions represents most of the fluid inclusions observed. These fluid inclusions were analyzed using both bulk fluid (crush-leach) and individual inclusion (SXRF = Synchrotron X-Ray Fluorescence) analytical techniques. Crush-leach analyses were performed by crushing ca. 1g of sample, leaching it with di-ionized water and analyzing the obtained solution by ion chromatography (Banks et al., 2000). Results show that all 5 analyzed samples have a Br/Cl ratio identical to that of modern seawater ($Br/Cl_{PILBARA} = 3.5 \pm 0.3 \times 10^{-4}$). SXRF analyses were performed on beamline ID22 of the European Synchrotron Radiation Facility in Grenoble, France. ID22 setup was enhanced by using a Kirkpatrick-Baez lens, which provided a 3x2 μm^2 spot with 10^{11} photons/sec, and a He chamber to eliminate signal absorption by ambient air. This setup allowed us to drastically reduce acquisition times, over 100 inclusions were analyzed. Correction procedure of X-ray spectra were similar to those used by Ménez et al. (2002), and quartz thickness was calculated using Ka/Kb ratios (Philippot at al., 1998) as well as optical measurements. Concentration estimates were based on microthermometry data as well as on calibration to known-composition synthetic inclusions. Data are still under processing at this moment, but preliminary results show a good agreement with crush-leach results. Complete compositional results for Cl, Na, K, Li, Ca, Br, Rb, Sr, Ba obtained from crush-leach and SXRF data will be presented.

We present here the first report of an Archaean seawater Br/Cl ratio similar to modern seawater value. This result calls for a different composition of the 3.5 Gyr Pilbara seawater than that of Barberton seawater and possibly a reinterpretation of ocean composition history. A hypothetical explanation for such a low Br/Cl value could be that the biological activity, which was thought to occur in the Pilbara and in hydrothermal environments such as around the North Pole Dome 3.5 Gyr ago (Dutkiewicz et al, 1998; Shen, 2001), was intense enough as to fractionate Br with regard to Cl in a similar way as does modern marine biomass.

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