Archean to Paleoproterozoic seawater halogen ratios recorded by fluid inclusions in chert and hydrothermal quartz

RAY BURGESS1,*,‡, SARAH L. GOLDSMITH1, HIROCHIKA SUMINO2, JAMIE D. GIMOUR1, BERNARD MARTY3, MAGALI PUJOL3‡, and KURT O. KONHAUSER4

1Department of Earth and Environmental Sciences, University of Manchester, Manchester, M13 9PL, U.K.
2Department of Basic Science, Graduate School of Arts and Sciences, University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo, 153-0041, Japan
3Centre de recherches pétrographiques et géochimiques, CNRS, Université de Lorraine, 15, rue Notre-Dame-des-Pauvres, 54500 Vandoeuvre-lés-Nancy, France
4Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta T6G 2E3, Canada

ABSTRACT

Past changes in the halogen composition of seawater are anticipated based on the differing behavior of chlorine and bromine that are strongly partitioned into seawater, relative to iodine, which is extremely depleted in modern seawater and enriched in marine sediments due to biological uptake. Here we assess the use of chert, a chemical sediment that precipitated throughout the Precambrian, as a proxy for halide ratios in ancient seawater. We determine a set of criteria that can be used to assess the primary nature of halogens and show that ancient seawater Br/Cl and I/Cl ratios can be resolved in chert samples from the 2.5 Ga Dales Gorge Member of the Brockman Banded Iron Formation, Hamersley Group, Western Australia. The values determined of Br/Cl ~2 × 10⁻³ M and I/Cl ~30 × 10⁻⁶ M are comparable to fluid inclusions in hydrothermal quartz from the 3.5 Ga North Pole area, Pilbara Craton, Western Australia, that were the subject of previous reconstructions of ancient ocean salinity and atmospheric isotopic composition. While the similar Br/Cl and I/Cl values indicate no substantial change in the ocean halide system over the interval 2.5–3.5 Ga, compared to modern seawater, the ancient ocean was enriched in Br and I relative to Cl. The I/Cl value is intermediate between bulk Earth (assumed chondritic) and the modern seawater ratio, which can be explained by a smaller organic reservoir because this is the major control on marine iodine at the present day. Br/Cl ratios are about 30% higher than both modern seawater and contemporary seafloor hydrothermal systems, perhaps indicating a stronger mantle buffering of seawater halogens during the Archean.

Keywords: Halogen, argon isotopes, seawater salinity, chert, banded iron formation, ocean chemistry; Halogens in Planetary Systems

INTRODUCTION

There have been relatively few studies of halogens in the Archean oceans, and no reliable record of seawater halogen evolution has been compiled. In particular, past salinity changes in the oceans are largely unconstrained, and the biologically controlled evolution of the iodine cycle remains unknown. Previous studies have analyzed fluid inclusions to determine halogen ratios in Precambrian seawater. However several factors have hampered the interpretation of these results for understanding the halogen composition of the early oceans, including: the challenges of delimiting primary seawater composition in mixed hydrothermal fluids formed during seawater-basalt interaction processes; possible overprinting during later metamorphic and deformation events; and the analytical difficulties of determining low halogen concentrations, especially for least-abundant iodine.

The limited halogen data that exist are mainly derived from fluids associated with volcanic-sedimentary successions. This includes mid-Archean (~3.2 Ga) ironstone pods, and silicified komatitites and sediments from the Barberton Greenstone Belt, Kapvaal, South Africa (Channer et al. 1997; de Ronde et al. 1997; Farber et al. 2015); hydrothermal quartz in metabasalts from the ~3.4 Ga North Pole area, Pilbara, Western Australia (Foriel et al. 2004); and volcanic-related quartz veins and pods in the Paleoproterozoic (2.22 Ga) Ongeluk Formation, Kapvaal, South Africa (Gutzmer et al. 2003).

Fluid inclusions in quartz veins hosted in ironstone pods from Barberton have chemical compositions that approximately match modern seawater, except for higher Br/Cl and I/Cl (de Ronde et al. 1997; Channer et al. 1997). These fluids may have been trapped fluids from seafloor hydrothermal vent systems (de Ronde et al. 1997), however both their age and origin is contested (de Ronde et al. 2004; Lowe and Byerly 2004), leading to uncertainty for their use in reconstructing early ocean chemistry (Lowe and Byerly 2003, 2007; Hren et al. 2006).

Crush-leach analysis of fluid inclusions in chert and quartz veins in komatitites from Barberton yielded Br/Cl and I/Cl much...