

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

**RAY BURGESS^{1,*}, SARAH L. GOLDSMITH¹, HIROCHIKA SUMINO², JAMIE D. GILMOUR¹, BERNARD MARTY³,
MAGALI PUJOL^{3,†}, 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-lès-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 $\sim 2 \times 10^{-3}$ M and I/Cl $\sim 30 \times 10^{-6}$ 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 2.5–3.5Ga, 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