Low sulphate concentration and biological control of Cl/Br ratio in the 3.5 billion years old ocean

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The composition of ancient oceans may hold critical information about the evolution of Earth's life and atmosphere:
- **Cl/Br** ratio may be used to **trace biological activity** in the sea,
- **seawater sulfate** (SO_4^{2-}) **concentration is linked to atmospheric oxygen** concentration (through oxydative weathering of land S^{2+}).

Previous estimates of the Cl/Br composition of 2.2-3.2 billion years old (Gyr) seawater from the Kapvaal Craton, South Africa, suggest that bioproductivity was low and Cl/Br ratio controlled by geological processes only [1,2]. **Whether the atmosphere contained O_2 between the time of Earth's formation 4.6 Gyr ago and 2 Gyr ago is intensly debated**. Conflicting models argue that oxygen concentration was either similar to the present atmospheric level (PAL)[3], or was very low <1% PAL[4].

Here, we present a micro-Synchrotron Radiation X-Ray Fluorescence (µSR-XRF) analysis of **fluid inclusions representative of the composition of 3.5 Gyr old seawater** from North Pole, Pilbara Craton, Australia. Cl/Br ratio as well as sulphate concentration in North Pole seawater were calculated.

Results

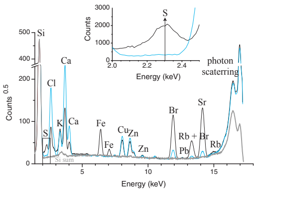

Figure 2: µSR-XRF spectra of metal-depleted (blue) and Fe-rich (black) fluid inclusions and inclusion-free quartz (gray). Insert is a magnification around sulfur peak energy (arrow).

	S	Cl	K	Mn	Fe	Br	Ba	Cl/Br
crush-leach								
Pi 01-21	39	2280	60	1.0	19.7	3.7	2.1	619
Pi 02-39	13	2258	61	8.5	14.0	3.3	6.3	687
µSXRF								
hydrothermal fluid								
Fe-rich (12)	41-82 (3)	1857	274	0.26	8.94	4.72	2.32	442
Ba-rich (6)		1666	644	0.66	0.56	4.79	8.38	346
North Pole seawater endmember								
Pi01-21 (7)		2458	53	0.10	0.27	3.82	1.10	632
Pi02-39/1 (16)		1756	36	0.24	0.28	2.47	0.84	701
Pi02-39/2 (14)	< 7,2-15 (4)	2347	62	0.13	0.06	3.67	0.37	682
Pi02-39/3 (14)	< 5,4-6,9 (2)	2213	53	0.13	0.40	3.91	0.84	609
modern seawater	28.2	550	9.7	5.5E-07	9.9E-07	0.85	1.5E-04	649

Table 1: Crush-leach bulk fluid composition of 2 intrapillow quartz (Pi01-21 and Pi02-39). Average of µSR-XRF results for all Fe-rich and Ba-rich inclusions in both samples and for metal-depleted inclusions in 4 quartz chips. Number of inclusions in each case is in parenthesis.

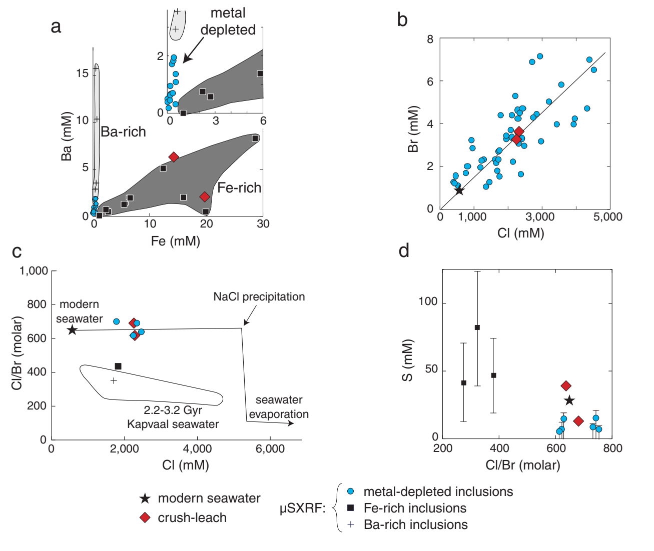

Figure 4 Details of µ-SXRF and crush-leach results.

µSR-XRF results reveal the presence of **three fluid populations**: a metal-depleted fluid, a Ba-rich phase and a Fe-rich end-member (Fig. 4a). **Metal-depleted fluid Inclusions have a Cl/Br ratio** (660) **similar to modern seawater value** (649) (Fig. 4b) and **their origin is almost certainly "North Pole seawater"**. High Cl concentration (ca. 4 x present-day value) reflects a typical modern-day seawater evaporation trend (Fig. 4c). By contrast, **Ba- and Fe-rich fluids have Cl/Br ratio** (346-442) **not different from bulk Earth value** (420) and, considering their metal-rich character, **are best interpreted in terms of hydrothermal fluids**.

Sulphur content ranges between 41 and 82 mM in the Fe-rich hydrothermal inclusions, but was not detected in seawater inclusions and Ba-bearing inclusions (Fig. 4d). Sulphur detection limits calculated using Cl concentrations as an internal standard indicate that the **sulphur content of North Pole seawater must have been lower than about 8 mM**. By contrast, crush-leach results yielded sulphur concentrations higher (39 mM) and lower (13 mM) than modern seawater value (28 mM), which likely reflects different degrees of mixing between North Pole seawater and Fe-rich hydrothermal fluids.

Samples

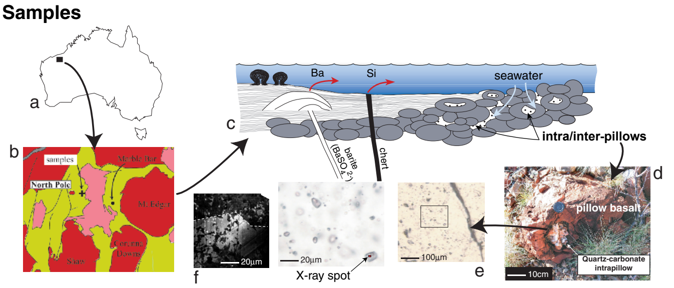

Figure 1: sample location and description.

North Pole, Pilbara Craton, Western Australia (Fig. 1a,b), is the best preserved Archaean (2.5 to 4.0 Gyr ago) terrain on Earth. It is a shallow seawater basin, exposed to 2 types of hydrothermal vents releasing Ba-rich and Si-rich fluids (Fig. 1c). Inside and in-between pillow basalts (volcanic rocks formed on the seafloor), we found quartz and carbonate crystals (Fig. 1d). These intrapillow quartz are formed by shallow infiltration of seawater through the top of the seafloor (Fig. 1c). Intrapillow quartz contain fluid inclusions (Fig. 1e) which may have recorded seawater composition. Fluid inclusions are tiny bubbles (5-20 µm here) of liquid/gas trapped by crystals during their growth. Luminescence imaging of quartz grains (Fig. 1f) reveals a complex texture of brecciated quartz fragments reflecting episodic hydrofracturation and sealing. However, optical observation did not allow us to identify different populations of inclusions linked to different fluid trapping events.

Methods

The **bulk fluid** content of intrapillow quartz was analyzed by **crush-leach** [5] (Table 1). This method results in the mixing of different fluids which may be present in a single sample. **Fluid inclusions were analyzed individually by µSR-XRF** at the µ-fluorescence, µ-imaging and µ-diffraction beamline (ID22) of the European Synchrotron Radiation Facility (ESRF). Fig. 2 shows a schematic view of the beamline.

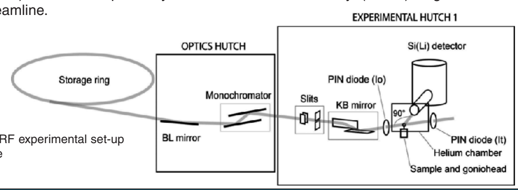

Figure 2: µSR-XRF experimental set-up at ID22 beamline

Conclusion

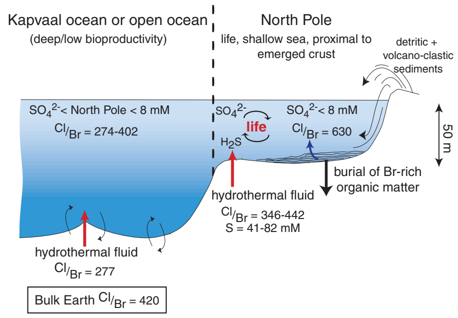

Figure 5: Comparison of models for North Pole 3.5 Gyr old and Kapvaal 2.2-3.2 Gyr seawaters. In both cases, Br-rich hydrothermal fluid is supplied. At North Pole, the sedimentary flux was high, life existed [6] and the water body was small. In these conditions, Br can be removed by burial of Br-rich organic matter and resulting seawater is at higher Cl/Br (present-day level at North Pole). Mantle control and/or water-rock interaction dominate the halogen geochemistry in a Kapvaal setting in absence of significant bioproductivity [1,2]. Sulphate concentration is well below present level at North Pole and may be even lower in a more open setting.

The difference between North Pole seawater (660) and hydrothermal fluids Cl/Br composition (346-442) calls for a balancing process to maintain high seawater Cl/Br. Modern organic matter is strongly enriched in heavy halogens (Cl/Br =1). **A rapid burial of organic matter could partition Br into sediments leading to a Br-depleted seawater** and Br-enriched sediments. At North Pole, conditions were most favorable for this process to take place (Fig. 5). Cl/Br value therefore suggest that **biological activity was high at North Pole** and it controlled seawater Cl/Br composition.

On the basis of geological arguments, we suggest that S^{2+} is the most likely sulphur species in the Fe-rich vent fluids whereas SO_4^{2-} probably predominated in North Pole seawater. Isotopic evidences for bacterial sulfate reduction suggest that **North Pole basin was exceptionally sulphate-rich compared to the rest of the Archaean ocean [6]**. Therefore, the sulphate content of North Pole seawater (<8mM) must be regarded as a maximum value for the Archaean. This implies that the early Archaean ocean as a whole must have been dramatically depleted in sulphate. **Our results represent the first direct evidence of a sulphate-poor marine reservoir during the early Archaean, reflecting unarguably the low oxygen concentration of Earth's primitive atmosphere.**

References:
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