X-ray Fluo-microscopy and Analysis

First Direct Observation of Brine Droplets and Solid Inclusions in Accreted Ice from the Sub-glacial Lake Vostok (Antarctica)

The largest sub-glacial lake (14,000 km^2) discovered by a radio-echo survey under the Antarctic ice cap is covered by 3,750 m of ice and underlies the Russian station of Vostok where a 3620 m deep ice core has been recovered. Ice coring has been stopped 130 m above the lake surface, in ice formed by the refreezing of lake water at the bottom of the glacier. Although made of large ice crystals of very high crystalline quality, accretion ice contains many visible inclusions and large amounts of soluble species (sulphate salts and NaCl) [1]. The origin of these impurities is puzzling and information on their composition and location is essential for the understanding of the lake's environment and mechanisms driving ice formation and aging process.

We present here data obtained by X-ray fluorescence at beamline **ID21**. The microprobe was set at 4.5 keV for 2D mapping of elements lighter than Ca. A specific experiment was carried out for sulphur species, tuning the excitation energy to around 2.5 keV. The shift in energy produced a clear distinction between sulphur present as sulphide (S^{II-}, 2.470 keV), sulphite (S^{IV}, 2.478 keV) and sulphate (S^{VI}, 2.482 keV) [2,3]. The cryosystem allowed the temperature of the sample holder to be kept stable and close to -140°C. The cell containing the ice sample was tightly closed by a film of "ultralene"®, making it possible to study the upper 50 µm of samples for several hours under high vacuum (2 x 10^{-5} kPa) conditions without any visual change of the ice surface. In this experiment, the plastic film was mechanically fastened to the top of the cell to avoid chlorine contamination from glue.

Four accretion ice samples containing visible inclusions and one grain boundary have been studied. A very large inclusion was carefully investigated (**Figure 1**).This inclusion was a very large aggregate of various particles including sulphur compounds, alumino-silicates and other silicate species, and relatively large carbonates. Several smaller dark aggregates showing rather similar composition were found inside ice crystals, while the grain boundary structure contained only very few particles per µm. One aggregate was studied for sulphur speciation, showing that reduced sulphur species were present along with sulphate salts.

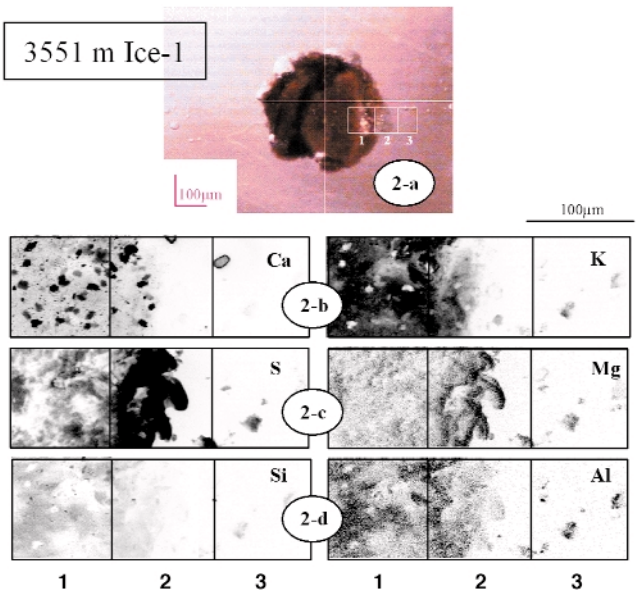

Fig. 1: Elemental maps of three contiguous areas of a very large solid inclusion (600 µm) at 3551 m. Beam energy was focused at 4.5 keV. Probe size was 1 x 1 $µm^2$. The highest concentration of the total area represented in elemental mapping is automatically scaled to black.

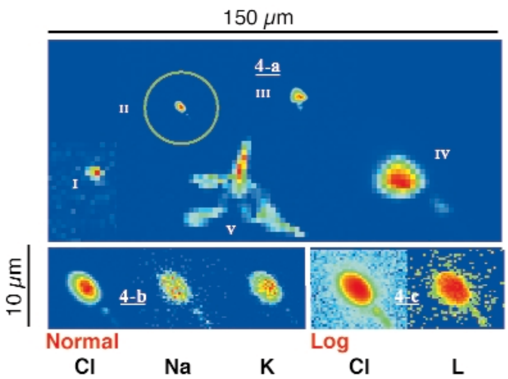

Fig. 2: Brine inclusions at 3551 m. Five colourless oblong objects were observed over an area of 200 x 200 $µm^2$, with apparent diameter varying from ~ 3 to ~ 15 µm. Object V exploded during the scan. Probe size ranged from 0.3 x 0.5 $µm^2$ (II and III) to 1 x 1 $µm^2$ (I, IV and V). The intensity scale extends from dark blue to red.

Chlorine was almost exclusively detected in colourless micrometer-sized structures (**Figure 2**), which are very likely to be brine micro-pockets entrapped in the ice lattice. A rough estimate of their salinity leads to a value (1.5%) significantly higher than the maximum salinity calculated for the main lake [1]. At the temperature prevailing in accreted ice (-3°C), brine should remain in a liquid state. During drilling, the outer pressure decreases from 30 to 0.1 MPa and ice cores are cooled to about -50°C. The relaxation and the freezing of water droplets can initiate ice cracks along crystallographic planes, which could explain the shape and orientation of bubble extensions clearly visible in Figure 2c. The freezing of brine droplets could also lead to concentration gradients as observed in brine bubbles (Figure 2b), solute

exclusion occurring at the ice water interface during the freezing process.

This work is, to our knowledge, the first direct observation of well-preserved liquid microstructures along with other solid and complex objects in ice. Accretion ice from lake Vostok contains solid particles initially boosted by saline water in frazil slush. Single crystals that growing once the ice is accreted may keep large solid aggregates as well as haline droplets inside the ice lattice. The structure and composition of solid inclusions linked to the high salinity of brine droplets provide new arguments for the occurrence, under lake Vostok, of saline water pulses through a deeper sulphur rich sedimentary reservoir.

References

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Modern Composition of 3,500 Million-year-old Seawater: Implications for Life on the Primitive Earth

There are two fundamental requirements for life as we know it, liquid water and organic polymers, such as nucleic acids and proteins. At about 4.4 to 4.0 billion years (Gyr), the Earth may have been cool enough for the presence of extensive oceans for long periods. Life on Earth dates from before about 3.8 Gyr, and is likely to have gone through one or more hot-ocean environments. Only hyperthermophiles (microorganisms optimally living in water at 80–110°C) would have survived. Early hyperthermophile life probably developed near hydrothermal systems including 'black smokers' (**Figure 1a**). It would have had access to redox contrast between a more oxidised atmosphere–ocean system and the more reduced fluids emanating from mantle-derived magmas. Sulphur offers the best opportunities. With water present in the air, volcanic SO_2 would have been oxidised to sulphate. Dissolved in water, sulphate would provide oxidation power for organisms to react against reduced species in hydrothermal fluids, such as H_2S and CH_4. Considering that sulphate-reducing

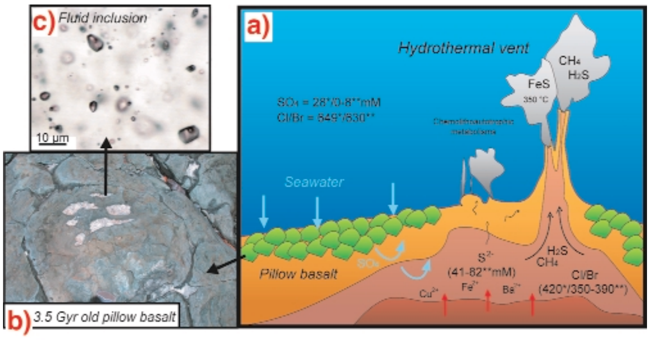

Fig. 1: (a) Hydrothermal system on the seafloor showing the main fluid pathways and elemental distribution patterns. * refers to modern day values, whereas ** corresponds to element concentration estimates in "North Pole" Archaean fluids. (b) Archaean pillow basalt. (c) Fluid inclusions in intrapillow quartz pods.

microbes had evolved by 3.5 Gyr ago, the poorly-fractionated Early Archaean sedimentary sulphides have been attributed to either biological sulphate reduction in a fully anoxic ocean containing little sulphate (< 200 µM to 1 mM) or to intense biological sulphate reduction at sulphate oceanic concentrations not much different from today's (28 mM). Clearly, the oxidation state and composition of the Archaean ocean and atmosphere remains essentially unconstrained.

Insights into the composition of Archaean seawater and hydrothermal fluids can be obtained by direct analysis of fluid inclusions preserved in Archaean hydrothermal systems. Here, we investigated a suite of quartz pods preserved in basaltic pillow lavas (Figure 1b) that formed during oceanic hydrothermal alteration of the 3.5 Gyr North Pole formation. The pods contain myriad fluid inclusions (Figure 1c), which were analysed individually using synchrotron radiation X-ray microfluorescence (µ-SR-XRF) . The main advantages of the µ-SR-XRF technique reside in its non-destructive character, high spatial resolution, multi-element analytical capability and high sensitivity. Hence, µ-SR-XRF can analyse small, diluted individual fluid inclusions, discriminate distinct inclusion populations trapped in a single crystal and provide information about complex histories of fluid circulations.

Calculated model composition yielded a bulk fluid salinity of four-times the present-day value reflecting a typical modern-day seawater evaporation trend in a shallow marine, closed basin environment. Individual fluid inclusion analysis using µ-SR-XRF revealed the presence of three fluid populations (**Figure 2**): a metal-depleted fluid, a Ba-rich and S-depleted fluid, and a Fe–S-rich end-member. The Cl/Br ratio of metal-depleted fluid inclusions (630) is similar to the modern seawater value (649; Figure 1a). In contrast, Ba- and Fe-rich brines have Cl/Br ratios (350 and 390) close to the bulk Earth value (420), hence arguing for a hydrothermal origin of these fluids. The metal depleted fluid displays