Micro-scale oxygen isotopic variation in 1.9 Ga Gunflint cherts: New constraints on their paleo-environnemental significance

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Precambrian sedimentary cherts have the potential to preserve a record of O and Si isotopic composition ($\delta^{18}O$ and $\delta^{30}Si$) of seawater and may give access to oceanic paleo-temperatures (Knauth and Lowe, 1973 ; Robert & Chaussidon, 2006). However, bulk $\delta^{18}O$ of individual cherts at a given age show a typical 3-4‰ range (Knauth, 2005) which complicates paleo-temperatures reconstruction. In addition, some cherts may be of hydrothermal origin and $\delta^{18}O$-values may be altered by metamorphic fluids. We looked for µm- scale $\delta^{18}O$ variations in the 1.9 Ga old Gunflint iron-formation (Canada), which contains among the least metamorphosed precambrian cherts, in order to (1) constrain their origin and (2) to assess their preservation.

Four cherts samples, containing different types of silica (microcrystalline quartz, drusy quartz, megaquartz, and quartz veins) and minor carbonates (siderite and ankerite), hematite and pyrite, were analysed (> 100 spots per sample) by multicollector CAMECA ims 1270 ion microprobe, with an external reproductibility on quartz standards of 0.31‰ (1 σ, n=22).

The four Gunflint cherts show (i) large megaquartz with $\delta^{18}O$ 10-12‰ lower than microcrystalline quartz, (ii) a typical 3-5 ‰ $\delta^{18}O$ range for microcrystalline quartz and (iii) quartz veins with $\delta^{18}O$ 5-7‰ lower than microcrystalline quartz. The variation in the proportion of the differences types of silica appears to explain bulk variations (i.e. sample 4 0f 06/30/84 ; bulk = 22.75‰, $\delta^{18}O$ calculated from modal proportions of silica = 23.18‰). Considering microcrystalline quartz only, a $\delta^{18}O$ range from 0‰ to 3‰ higher than previous bulk $\delta^{18}O$ (Winter and Knauth, 1991) is found, which would correspond to a difference of temperature of 0-15°C. This approach may allow to better constrain oceanic paleo-temperatures in the Precambrian.

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Iron isotope fractionation during hydrothermal ore deposition and alteration

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Iron isotopes fractionate during hydrothermal processes. Therefore, the Fe isotope composition of ore-forming minerals characterizes either iron sources or fluid histories. 51 samples of iron ores and iron mineral separates from the Schwarzwald region, southwest Germany, were analyzed for their iron isotope composition using multicollector ICP-MS. Further, the ore-forming and ore-altering processes were quantitatively modeled using reaction path calculations.

The Schwarzwald mining district hosts mineralizations that formed discontinuously over almost 300 Ma of hydrothermal activity. Primary hematite, siderite and sulfides formed from mixing of meteoric fluids with deeper crustal brines. Later, these minerals were partly dissolved and oxidized, and secondary hematite, goethite and iron arsenates were precipitated.

Two types of alteration products formed: (1) primary and high-temperature secondary Fe minerals formed between 120 and 300 °C, and (2) low-temperature secondary Fe minerals formed under supergene conditions (<100 °C). Measured iron isotope compositions are variable and cover a range in $\delta^{56}Fe$ between -2.3‰ and +1.3‰. Primary hematite ($\delta^{56}Fe$: -0.5 to +0.5‰) precipitated by mixing oxidizing surface waters with a hydrothermal fluid that contained moderately light Fe ($\delta^{56}Fe$: -0.5‰) leached from the crystalline basement. Occasional input of CO_2-rich waters resulted in precipitation of isotopically light siderite ($\delta^{56}Fe$: 1.4 to 0.7‰). The difference between hematite and siderite is compatible with published Fe isotope fractionation factors. The observed range in isotopic compositions can be accounted for by variable fractions of Fe precipitating from the fluid. Therefore, both fluid processes and mass balance can be inferred from Fe isotopes.

Supergene weathering of siderite by oxidizing surface waters led to replacement of isotopically light primary siderite by similarly light secondary hematite and goethite, respectively. Because this replacement entails quantitative transfer of iron from precursor mineral to product, no significant isotope fractionation is produced. Hence, Fe isotopes potentially serve to identify precursors in ore alteration products.

This iron isotope study illustrates the potential of the new technique in deciphering ore formation and alteration processes. Isotope ratios are dependent on and characteristic of fluid and precipitation histories. Therefore, they are less suitable to provide information on Fe sources. However, it will be possible to unravel the physico-chemical processes leading to the formation, dissolution and redeposition of ores in great detail.