

Seawater as the common Si source for both Archean BIF and cherts: insights from silicon isotopes

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In an attempt to bring new insights into the identification of the silicon source(s) of Archean BIF, we compare silicon isotopic compositions of Si-rich mesobands of BIF and S-cherts ranging in age from 3.25 Ga to 2.5 Ga. We observe a progressive temporal 0.6‰ increase in $\delta^{30}\text{Si}$ signatures of Si-rich mesobands of BIF from $-1.80 \pm 0.62\%$ at 3.25 Ga to $-1.18 \pm 0.37\%$ at 2.5 Ga. Interestingly, this trend is parallel to the increasing $\delta^{30}\text{Si}$ trend recorded in cherts [1, 2, 3]. The common gradual change in the Si isotopic composition through time suggests that both Si-deposits had a main common Si-conveyor: the seawater. However, the comparison of both trends also reveals a systematic 1.5‰ difference between the two parallel trends where the BIF trend is the light one. We suggest here that such systematic 1.5‰ difference is most likely related to the respective genetic process that gave rise to both types of Si-rich deposits: a high to low-temperature geothermal seawater circulation for cherts [4] and a Si adsorption onto Fe-oxyhydroxides for BIF in which Si-rich mesobands are of diagenetic origin [5].

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[2] Van den Boorn *et al.* (2007) *Geology* **35**, 939-942.

[3] Van den Boorn *et al.* (2010) *Geochim. Cosmochim. Acta* **74**, 1077-1103. [4] Abraham *et al.* (2011) *Earth Planet. Sci. Lett.* **301**, 222-230. [5] Delvigne *et al.* (2012) *Earth Planet. Sci. Lett.* **355-356**, 109-118.

Earthworms produce highly stable amorphous calcium carbonate

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Many species of earthworm secrete granules of calcium carbonate. The earthworms *Lumbricus terrestris* and *L. rubellus* are the main granule producers in European soils. The granules begin as micron-scale spherulites of amorphous calcium carbonate within the earthworm's calciferous glands. These spherulites agglomerate and crystallise prior to secretion of granules up to 2 mm in diameter into the digestive tract and, ultimately, into the soil. The secreted granules are predominantly calcite but may contain aragonite, vaterite and amorphous calcium carbonate [1, 2, 3].

Granules subsampled from granule sets recovered from a range of chemically distinct soils and stored dry for over two years since their production contained between 2 and 14 % amorphous calcium carbonate and had elevated relative concentrations of glutamic acid / glutamine (Glx). After a further two year period amorphous calcium carbonate concentrations measured on further subsamples of these granule sets lay in the range 0 – 13 %; the relative amino acid composition of the granules was investigated by reverse-phase HPLC. No significant relationship was found between granule elemental composition and amorphous calcium carbonate content nor between the amorphous calcium carbonate contents determined after two and four years.

We ascribe the lack of relationships to the compositional heterogeneity of the granules and are currently performing spatially explicit analysis of the granules using Fourier transform infrared spectroscopy, electron microprobe analysis and electron backscattered diffraction. Controls on amorphous calcium carbonate stability will be discussed.

[1] Lee *et al.* (2007) *Geology* **36** 943-946. [2] Fraser *et al.* (2011) *Geochimica et Cosmochimica Acta* **75** 2544-2556. [3] Brinza *et al.* doi: 10.1016/j.gca.2013.03.011