



## Determination of the origin of Precambrian cherts from their silicon isotopic compositions and trace elements concentrations

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Precambrian cherts considered as sedimentary rocks, are often used as a proxy of paleo-environmental conditions of the Early Earth, especially for the reconstruction of oceanic paleo-temperatures<sup>1,2</sup> from their oxygen isotopic compositions. Cherts are made of different forms of silica (microquartz, megaquartz, fibrous quartz and quartz vein). The origin of these rocks is still highly debated though they are key to constrain paleo-environmental conditions of the Early Earth. The various possible origins include (i) direct precipitation of quartz from hydrothermal fluids of various origins, (ii) silicification of volcanoclastic deposits or (iii) diagenetic transformation of silica-rich precursors (e. g. water-rich amorphous silica) precipitated directly from seawater. Trace elements concentrations (B, Na, Mg, Al, K, Ca, Ti, Fe) and silicon isotopic compositions ( $\delta^{30}\text{Si}$ ) can be used as proxies of the origin of cherts because their variations reflect changes in, i.e., the nature of the precursors of cherts or the composition of the hydrothermal or diagenetic fluids.

Trace elements ( $^{11}\text{B}$ ,  $^{23}\text{Na}$ ,  $^{24}\text{Mg}$ ,  $^{27}\text{Al}$ ,  $^{39}\text{K}$ ,  $^{42}\text{Ca}$ ,  $^{48}\text{Ti}$ ,  $^{54}\text{Fe}$ ) concentrations were measured in situ (spot size  $\approx 25\ \mu\text{m}$ ) in quartz with an ims 3f ion microprobe. The external precision was determined on glass standards and was better than  $\sim 1\%$  for Mg, Al, and Ca,  $\sim 2\%$  for K,  $\sim 5\%$  for Ti and Fe and  $\sim 10\%$  for B and Na.  $\delta^{30}\text{Si}$  values were measured in situ (spot size  $\approx 25\ \mu\text{m}$ ) in quartz with the Nancy CAMECA ims 1270 multi-collector ion microprobe (CRPG-CNRS in Nancy) in six well documented Precambrian cherts, three from the Gunflint Iron formation (1.88 Ga, Canada), one from the Dresser Formation (3.45 Ga, Australia) and two from Onverwacht Group (3.4 Ga, South Africa). The external reproducibility on quartz standard was of  $\pm 0.3\text{‰}$  ( $1\ \sigma$ ,  $n=45$ ) for  $\delta^{30}\text{Si}$  values.

Archean cherts show strong correlations between  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{K}_2\text{O}$  and  $\text{MgO}$  and  $\text{CaO}$ , while Proterozoic cherts show different correlations between  $\text{MgO}$  and  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{K}_2\text{O}$  and strong correlation between  $\text{TiO}_2$  and  $\text{FeO}$ , as previously shown<sup>3</sup>. These correlations allow to evidence (for part of the samples) silicification of volcanoclastic deposits as one process of chert formation. The systematic of  $\delta^{30}\text{Si}$  values and trace element concentrations can be understood as reflecting the presence among our set of chert samples of three different end-members characterized by quartz of three different origins: quartz derived from a precursor precipitated from seawater, hydrothermal deposits and volcanoclastic deposits silicification (strongly negative  $\delta^{30}\text{Si}$  for hydrothermal silica and  $\delta^{30}\text{Si} \approx 0\text{‰}$  for volcanoclastic deposits). Archean cherts formed by diagenetic transformation of amorphous silica precipitated from seawater (as indicated by their trace elements systematic) show negative  $\delta^{30}\text{Si}$  values (between  $-1.3\text{‰}$  to  $-0.2\text{‰}$ ) while Phanerozoic cherts of the same origin have positive  $\delta^{30}\text{Si}$  values (between  $+0.4\text{‰}$  to  $+1.8\text{‰}$ ). The different  $\delta^{30}\text{Si}$  values of quartz derived from direct precipitation from seawater between the Gunflint chert sample and the chert from the Dresser formation can be used to reconstruct the silicon isotopic signature of ancient seawater at 1.88 Ga and at 3.5 Ga and to demonstrate that it has changed significantly ( $\approx 2$  to  $3\text{‰}$  increase during the Precambrian).

<sup>1</sup> Knauth C. P. & Lowe D. R. (1978) *Earth Planet. Sci. Lett.* **41**, 209-222.

<sup>2</sup> Marin J. et al. (2010) *Geochim. Cosmochim. Acta* **74**, 116-130.

<sup>3</sup> Sugitani K. (1992) *Precamb. Res.* **57**, 21-47.