Stagnant-lid tectonics in early Earth revealed by ^{142}Nd variations in late Archean rocks

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The progressive μ^{142}Nd decrease in early Archean rocks from +20 to 0 between 3.9 to 3.6 billions years (Gyr), with rocks younger than 3.5 Gyr showing no μ^{142}Nd anomalies, is thought to indicate the efficient remixing of the first primitive crust into the Archaean convecting mantle that ultimately produce a well-mixed present-day convecting mantle with μ^{142}Nd = 0 [1]. The implied long mixing time of ~1 Gyr from the Hadean to Archaean for the whole mantle is paradoxical on several levels. This is much longer than the rapid mixing time (<100 Myr) inferred for the Archean due to vigorous mantle convection related to Earth's hotter thermal regime [2], and similar to the mixing time inferred for the present-day Earth's mantle [3].

Here we report a resolvable positive ^{142}Nd anomaly of μ^{142}Nd = +7 ± 3 ppm relative to the modern convecting mantle in a 2.7 Gyr old tholeiitic lava flow from the Abitibi Greenstone Belt in the Canadian Craton. Our result effectively extends the early Archean convective mixing time to ~1.8 Gyr, i.e. even longer than present-day mantle mixing timescale [3], despite a more vigorous convection expected in the Archean. Different hypotheses have been examined to explain such a protracted mixing in the Archean, such as mantle overturn, two-layer convection or the existence of a dense layer at the bottom of the mantle. We postulate that the requirement of a delayed mixing in a strongly convective mantle is best explained by long periods of stasis in the global plate system, with scarce episodes of subduction throughout the Hadean and Archean [4].

Our numerical model confirms that in absence of continuous plate tectonics, the convective mantle mixing is relatively inefficient in erasing the chemical heterogeneities inherited from the primordial differentiation of the early Earth. This constrains the tectonic regime of the Hadean and Archean to a stagnant-lid regime with episodic subduction. In this case, the timing for the onset of continuous modern plate tectonics can only occur shortly before or after 2.7 Gyr.

[1] Bennett et al. (2007) *Science* **318**: 1907-1910. [2] Coltice and Schmalzl (2006) *GRL* **33**: L23304. [3] Kellogg and Turcotte (1990) *JGR* **95**: 421-432. [4] O'Neill et al. (2007) *EPSL* **262**: 552-562.

The effect of aqueous organic ligands on forsterite dissolution rates

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Forsterite is an abundant mineral which reacts exothermically with CO2 to form secondary minerals including carbonates. As such it is viewed as the most promising source material for the divalent metals required for mineral carbonation [1]. Mineral carbonation could potentially be accelerated if catalyses that accelerate forsterite dissolution can be identified. This study was initiated to determine if common aqueous organic ligands can accelerate forsterite dissolution rates. Aqueous organic species have long been considered as potential catalyses for enhancing silicate mineral dissolution rates (e.g. [2], [3]).

Forsterite dissolution rates were measured at 25 ºC in 10-2 M NaCl using mixed-flow reactors as a function of pH and concentration of 13 organic ligands (acetate, alginate, oxalate, Na-glutamate, citrate, EDTA, L-glutamic, humic, malic, malonic salicylic, tartaric and L-aspartic). Stoichiometric dissolution was observed. Selected measured dissolution rates as a function of organic ligand concentration is presented in figure 1.

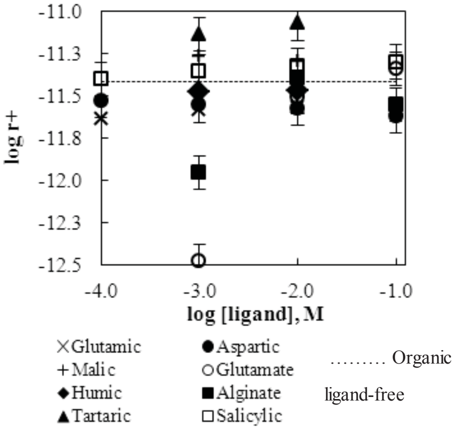

Figure 1: Summary of pH 3 olivine steady-state dissolution rates as a function of ligand concentration.

As depicted in Fig. 1, aqueous organic ligands in general have weak effects on pH 3 forsterite dissolution rates. Humic, salicylic and aspartic acid have no detectable effect on these rates, while the tartaric and malic acid decreases these rates.

Overall, results of this study demonstrate that organic ligand do not affect sufficiently forsterite dissolution rates at mildly acidic conditions. As these pH conditions likely to be characteristic of the fluids at carbon storage sites due high CO2 pressure carbon storage, it seems likely that organic additives will not accelerate substantially forsterite carbonation.

[1] Oelkers et al. (2008) *Elements*, **4,** 333-337.
[3] Pokrovsky et al. (2009) *Am. J. Sci.* **309**, 731-772.
[4] Wolff-Boenisch et al. (2011) *Geochim. Cosmochim. Act.* **75**, 5510-5525.