The sulphate cycle in subduction zones: Another clue to the Great Oxidation Event?

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Arc lavas are more oxidised compared to mid ocean ridge lavas [1]. This is commonly explained by the addition of hydrous slab-derived agents to the mantle source of arc lavas The resulting $f\text{O}_2$ of the sub-arc mantle is also in the range where the S valence state in silicate melts change from S^{2-} to S^{6+}. From the observation that the $\text{S}^{6+}/\text{S}^{2-}$ equilibrium in silicate melts is a function of the molar Fe/S it has been suggested that the addition of SO_4^{2-} by Fe-poor slab melts may be the oxidising agent in subduction zones [2].

Here we present results from S K-edge XANES and $\text{Fe}^{3+}/\text{Fe}^{2+}$ determinations by EPMA on melt inclusions (MI's) and their host chromite in mantle xenoliths from Avacha and Ritter arc volcanoes, respectively in Kamchatka (Russia) and the West Bismarck Arc (Papua New Guinea). The composition of the MI's varies and includes high-Ca boninites that testify for the addition of a slab-derived agent. S^{6+} is always present in the sub-arc mantle MI's and increased $\text{Fe}^{3+}/\Sigma\text{Fe}$ in the adjacent chromites bear evidence for a redox exchange reaction between S and Fe in the form of $\text{SO}_4^{2-} + 8\text{FeO} = \text{S}^{2-} + 4\text{Fe}_2\text{O}_3$. Such reaction can explain the observed increase of $\text{Fe}^{3+}/\text{Fe}^{2+}$ in arc lavas and of the $f\text{O}_2$ within the mantle wedge.

We propose that the onset of SO_4^{2-} cycling in subduction zones coincides with the Great Oxidation Event (GOE) at the Archean-Proterozoic boundary ~2.5 Ga ago. At that time, the composition of the continental crust switched from reduced TTG rocks to more oxidised calc-alkaline series [3]. TTG is generated by relatively hot shallow melting of S-poor oceanic crust producing S^{2-}-bearing melts with high molar Fe/S. Deeper, colder and S-enriched slab melts, as involved in the generation of the calc-alkaline crust, have low Fe/S promoting the liberation of S^{6+} from the slab. SO_4^{2-} from slab melts are able to i) reduce the amount of O_2 consumed during weathering of the continental crust and ii) release O_2 during volcanic SO_2 emissions both of which contribute to the oxygenation of the atmosphere during the GOE.

[1] Evans et al. (2012) *Geology* **40**, 783 [2] Klimm et al. (2012) *Chem Geol* **322-323**, 250 [3] Keller & Schoene (2012) *Nature* **485**, 490