

## Carbon-driven oxidation of the sub-arc mantle in the early Earth

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The oxygen fugacity ( $fO_2$ ) of the sub-arc mantle has controlled the availability of ore-forming elements to magmatic arcs and the speciation of volcanic gases emitted into the atmosphere since the onset of plate tectonics. Fluids generated from dehydration of subducted lithologies transfer oxidation potential inherited from sea water – crust interaction into the mantle wedge overlying subducting slabs, where arc magmas are generated. Sulfate is considered the main oxidant in slab fluids and because the production of abundant sulfate in oceanic crust is directly tied to an oxygenated atmosphere, the oxidation of the mantle is considered to begin only ~510 Ma ago after the Great Oxidation Event (GOE) [1]. However, there are other redox sensitive elements abundant in subducted lithologies that are also mobile in slab fluids, such as carbon. The  $fO_2$  of shallow upper mantle can be high enough for carbonate to be stable; however, there are no data on the  $fO_2$  of depleted sub-arc mantle at the greater depths where the metasomatic alteration by slab fluids primarily takes place. Here we show that at pressure higher than ~3 GPa graphite/diamond is stable in depleted sub-arc mantle. As such,  $CO_2$  in infiltrating fluids will be reduced to graphite/diamond during fluid-rock interaction. This reaction provides an electron sink ( $C^{4+} + 4e^- = C^0$ ), where each mole of  $CO_2$  reduced can oxidize 4 moles of ferrous iron in mantle silicates (e.g.  $CO_{2fluid} + 4FeO_{silicate} = C_{diamond/graphite} + 2Fe_2O_{3silicate}$ ) resulting in an increase in  $fO_2$  of the silicate mantle. Unlike sulfate, carbonate precipitation in subducted lithologies does not require an oxygenate atmosphere, and it was already active in the early Archean [2]. We show that plausible  $CO_2$  fluxes for the Precambrian Earth could have driven oxidation of the sub-arc mantle close to values recorded in modern subduction zones. Therefore, the arc magmatic system and associated volcanic gasses emitted into the atmosphere may have been more oxidized than previously thought during the Proterozoic and possibly Archean.

[1] Evans and Tomkins 2011, *EPSL* 308, 401-409 [2] Nakamura and Kato 2004, *GCA* 68, 4595-4618