A Phanerozoic increase in arc rock oxidation state

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Arc volcanic rocks are typically oxidized vs. MORB (Carmichael, 1991, *CMP*). Two explanations for this are: (1) primary arc and MORB magmas have the same fO_2, but arc magmas are oxidized during ascent and/or eruption (e.g., Lee et al., 2010, *Nature*) or (2) incorporation of an oxidized slab component into the mantle wedge increases the fO_2 of primary arc magma sources (e.g., Cottrell and Kelly, 2009, *Science*). Deep-ocean oxygenation from 540-420 Ma has been proposed to have increased $Fe^{3+}/\Sigma Fe$ ratios of ancient submarine basalts (Stolper and Keller, 2018, *Nature*). If arc rocks are oxidized due to the subduction of oxidized material, then this increase in oceanic crust oxidation state may have caused an increase in source magma fO_2 and thus $Fe^{3+}/\Sigma Fe$ ratios of Phanerozoic vs. Precambrian arc rocks.

To test this, we compiled whole-rock $Fe^{3+}/\Sigma Fe$ ratios of arc rocks from the past 2500 myr (1106 measurements, 41 localities). Subaerially erupted rocks were excluded to avoid samples potentially affected by atmospheric oxidation. We show that whole-rock $Fe^{3+}/\Sigma Fe$ analyses are comparable to μ-XANES measurements on glasses (e.g., Cottrell and Kelly, 2009, *Science*) from the same localities.

We observe an increase in $Fe^{3+}/\Sigma Fe$ of 0.13 (± 0.03, 1σ) in <420 Ma vs. Precambrian arc rocks. This increase occurs in both extrusive (0.09 ± 0.03 [1 s.e.]) and intrusive (0.15 ± 0.05 [1 s.e.]) rocks. This similarity indicates that potential oxidative alteration of Phanerozoic extrusive rocks by dissolved O_2 did not cause the increase in arc rock $Fe^{3+}/\Sigma Fe$ ratios. We also show that differences in rock MgO and SiO_2 contents do not control the observed $Fe^{3+}/\Sigma Fe$ record.

We propose that the observed Phanerozoic increase in $Fe^{3+}/\Sigma Fe$ ratios of arc rocks is due to an increase in the oxidation state of subducted oceanic crust caused in turn by the Phanerozoic oxygenation of the deep ocean. It then follows that arc rocks are oxidized due to incorporation of oxidized subducted slab material into the source region of arc magmas and that this oxidation either began or increased significantly in the Phanerozoic. Finally, this work provides an example where changes in the geochemistry of surface biogeochemical cycles (specifically the O_2 content of the deep oceans) can have a measurable impact on the geochemistry of magmas deep in the Earth's interior.