The relationship between subduction zone redox budget and arc magma fertility

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A number of lines of evidence point to a causal link between oxidised slab-derived fluids, oxidised sub-arc mantle, and the formation of economic concentrations of metals such as Cu and Au that require oxidised magmas. However, trace element evidence from V/Sc ratios suggests that sub-arc mantle is no more oxidised than mantle elsewhere.

A simple analytical model is applied to constrain the evolution of sub-arc mantle oxidation state as a function of redox-budget fluxes from the subducting slab. Influential variables include the solubility of Fe^{3+} and SO_4^{2-} in slab-derived fluids, the geometry of the infiltration of slab-derived fluids in sub-arc mantle, the coupling between slab-derived and arc-output redox budgets, and the concentration of redox-buffering elements such as Fe and S in the sub-arc mantle.

Plausible Archean and Proterozoic redox budget fluxes would not have created oxidised sub-arc mantle. Phanerozoic redox budget fluxes, on the other hand, which are dominated by the sulfate component, could have increased sub-arc fO_2 by up to three $\log_{10}$ units. The results are generally consistent with the proposed elevated fO_2 for sub-arc mantle but do not explain V/Sc results.

Increases in sub-arc mantle fO_2 are favoured by focussed fluid infiltration and magma generation, weak coupling between slab and arc-output redox budgets, and restricted redox-buffering in the sub-arc mantle. Fertile arc segments for ore deposits associated with oxidised magmas require fluid chemistry and pressure-temperature gradients that enhance Fe^{3+} and SO_4^{2-} solubility in aqueous and silica-rich fluids, tectonic stress regimes that favour focussed transfer of components into the sub-arc mantle, and a relatively weak redox buffer for the sub-arc mantle. The paucity of Cu and Au deposits associated with oxidised magmas in the Precambrian may be explained as a consequence of a lack of subducted oxidised material, rather than simply as a consequence of preservation potential. Additionally, the reduced nature of subducted material in the Precambrian may have caused S and metal enrichment in the sub-arc mantle.

Coffinitization of uraninite – A review and discussion of observations on different scales

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Coffinite ($USiO_4 \bullet nH_2O$) is a common secondary mineral in uranium ores, observed to replace uraninite in reponse to alteration of uraninite in a reducing environment [1]. This process is often referred to as coffinitization. However, it has proven difficult to synthesize coffinite in the laboratory, and in nature, coffinite is commonly very finegrained, resulting in a lack of experimental data concerning thermodynamic properties for coffinite [2,3]. As is noted by [2], the there are natural, coarse-grained coffinite crystals available from the Grants uranium region. However, it is also observed by [4] that there exists intermediate solid solutions in the system thorite–xenotime–zircon–coffinite and that in natural samples, moderate to strong deviation from perfect stoichiometry is commonplace.

In a recent attempt to synthesize coffinite [3], aqueous U was added to a Si-rich solution under controlled conditions to form a green gel subsequently heated for a few days in condition-controlled autoclave. This produced coffinite but only as a nanocrystalline mixture between coffinite and UO_2. Another experiment investigated the hydrothermal alteration of pellets of UO_2 in groundwater spiked with $CaCl_2$, $NaHCO_3$ and Na_2SiO_3[5]. At the end of the experiment (180 °C, c. 40 days, reducing environment) about 25% of the pellet surface was covered with a phase with a U:Si element ratio of 1:1. However, it was not possible to identify this material as coffinite by XRD.

In spite of these experimental difficulties, coffinite is a widespread alteration product of uraninite. This review aims to elucidate the spatial relationships between coffinite and uraninite as seen on different scales with different methods. The mechanism of uraninite alteration in natural, reducing, Si-rich environments is discussed and some new arguments put forward, involving the effect of impurities, defects, and grain size. Coffinitization is discussed in terms of solid-fluid interaction.

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