Mantle-crust fractionation of the platinum-group elements

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We use new sulfide melt/silicate melt partition coefficients ~ 10^6 to develop a fully constrained model of PGE behavior during melting to predict the abundances of PGE in mantle-derived magmas and their restites, including mid-ocean ridge basalts, continental picrites, and the parental magmas of the Bushveld Complex of South Africa. Our model constrains mid-ocean ridge basalt (MORB) to be the products of pooled low and high degree fractional melts. A significant control on PGE fractionation in mantle-derived magmas is exerted by residual alloy or platinum group minerals in their source. Within-plate picrites are pooled products of larger degrees of fractional melting in columnar melting regimes. At low pressures (e.g., MORB genesis) the mantle residual to partial melting retains primitive mantle inter-element ratios and abundances of PGE until sulfide has been completely dissolved but then evolves to extremely high Pt/Pd and low Pd/Ir because Pt and Ir alloys form in the restite. During melting at high pressure to form picrites or komatiites Ir alloy continues to appear as a restite phase but Pt alloy is no longer stable due to the large effect of pressure on fS2, which causes large increases in alloy solubility. Magmas parental to the Bushveld Complex of South Africa appear to be partial melts of mantle that has previously been melted to the point of total sulfide exhaustion at low pressure, closely resembling mantle xenoliths of the Kaapvaal craton. Using the new extremely large D^{sul}_{PGE} the the Merensky Reef and UG2 Pt deposits of the Bushveld Complex can be modeled as the result of sulfide saturation due to mixing of magmas with unremarkable PGE contents, obviating the need to postulate anomalously PGE-rich parent magmas or hydrothermal inputs to the deposits.

An extraterrestrial cause for the Silicate Earth's Nb paradox?

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Although both elements are considered lithophile, the silicate Earth exhibits a marked Nb deficit relative to its geochemical twin Ta, when compared to chondrites [1]. This feature is commonly referred to as "terretrial Nb paradox". Many explanations for this paradox that favour the presence of hidden silicate reservoirs cannot explain the observation that the Early Archean silicate Earth was already depleted in Nb. This would leave core formation at high pressures in a reduced early Earth as the only viable explanation for the terrestrial Nb paradox [2].

In a combined geochemical and experimental study, we investigated, whether low pressure metal segregation on small planetesimal precursors can also account for the Nb deficit. We performed high precision measurements of HFSE concentrations employing isotope dilution and ion exchange separation on representative groups of iron meteorites, their sulfide inclusions and achondrites. This protocol avoids molecular interferences on many HFSE, in particular for iron meteorites and sulfides rich in transition metals. Our results indicate that reduced achondrites exhibit strongly subchondritic Nb/Ta (as low as 1), whereas more oxidised achondrites (e.g., eucrites) exhibit near chondritic Nb/Ta. As expected, iron meteorites exhibit extremely low Nb-Ta concentrations (<1 ppb), whereas Nb can be strongly enriched relative to other HFSEs in sulfides (to ppm levels).

To simulate metal-sulfide segregation on small planetesimals, we performed experiments at ~1300ºC and 10 kbar using a piston cylinder apparatus. Measured sulfide-silicate partition coefficients for Nb are ca. 2 orders of magnitude higher than for Ta. At fO_2 lower than IW-3, Nb becomes chalcophile while Ta remains lithophile, and the silicate melt is thus depleted in Nb, as found in our study for more reduced achondrites.

Collectively, our results reveal that Nb may be sequestered into planetesimal cores at low pressures and low fO_2, provided that immiscibile sulfide and metal liquids were segregated. Therefore, the silicate Earth's Nb deficit may be a feature inherited from differentiated planetesimals that did not fully equilibrate with the proto-Earth upon their accretion.

[1]Münker *et al.* (2003) *Science* **301**, 84-87 [2] Wade & Wood (2001) *Nature* **409**, 75-78.

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