New metal-silicate partition coefficients and constraints on core composition and oxygen fugacity during Earth accretion

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High-pressure metal-silicate partitioning experiments demonstrate that the mantle contents of some moderately siderophile elements (Ni, Co, P, W, Mo, V) are consistent with core-mantle equilibration at high pressures and high temperatures (e.g. [1-4]). This conclusion is one of the bases for the magma ocean theory, in which molten core materials segregate through a largely molten silicate mantle. To constrain further such theory, one should ask whether these conditions of core formation are consistent with the mantle contents of other elements.

We present the results of new partitioning experiments between molten metal and silicate melt for a series of elements regarded as refractory lithophile and moderately siderophile and volatile. These include Si, Ti, Ni, Cr, Mn, Ga, Nb, Ta, Cu and Zn. Our new data obtained at 3.6 and 7.7. GPa and between 1850 and 2200 °C are combined with literature data to parameterize the individual effects of oxygen fugacity, temperature, pressure and composition on partitioning.

From the derived parameterization, we predict that the silicate Earth abundances of the elements mentioned above and V, Co, P and W are best explained if core formation took place under increasing conditions of oxygen fugacity, with final conditions near IW-2. From our estimate of the most likely oxygen fugacity path during accretion, we predict that the core contains about 10 times more Cu than the Silicate Earth as well as a smaller but significant portion of the Earth's Zn, Ga, Nb, Ta, Mn and Cr. Furthermore, our predictions show that the core should contain some Si and at least a small amount of Ti. Finally, our results suggest that in addition to volatilization, core formation would contribute to the depletion of Ga, Cr, Mn and Zn in the silicate Earth. At present, the uncertainties of our parameterization are too large to predict whether the Nb/Ta ratio of the core is superchondritic. Additional experiments are underway to constrain further our predictions.

References

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Biogenic mineral dissolution and transformation of arsenopyrite

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Arsenopyrite (AsSFe) is one of the most important natural sources of Arsenic on Earth. In oxic environments, such as highly weathered soils or surficial seawater, microorganisms and higher plants produce biogenic ligands such as siderophores to mobilize Fe that otherwise would be unavailable. We conducted batch-dissolution experiments for arsenopyrite in the presence of desferrioxamine (DFO-B), a common siderophore ligand, at pH 5. Arsenopyrite specimens (0.149-0.1mm) from mines from Panasqueira, Portugal, were used for this study. Detected concentrations of Fe, As, and Pb were 0.3, 0.26, and 0.13 µM (CV < 5%), or ca. 0.06, 0.13, and 0.01 μ M (CV < 2%), in the presence of DFO-B or water only, respectively (t < 100 h). The effectiveness of DFO-B for releasing Pb was found to be almost three times higher than that for releasing Fe. These results cannot be accounted for by sizeto-charge considerations prevailing in metal complexation by DFO-B only. Elemental sample enrichment as evidenced by EDX analysis support the idea the Fe-S subunit bond energy is limiting for Fe release, while likely, the mechanism(s) of dissolution for Pb is independent and occurs concurrently to than that for Fe and As. Coupling between redox-induced elemental transformations and the formation of small-particle size secondary minerals will be discussed.