Silicon, sulphur and carbon behaviour during core/mantle segregation

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Experiments

Silicon-rich iron alloys have been reacted with silicates and carbonates at 20-25 GPa and 1800-2200°C. The experiments were carried out in multi-anvil high-pressure systems in Bayreuth (Germany) and Clermont Ferrand (France). Oxygen fugacity relative to iron/wüstite equilibrium was estimated a posteriori by analyzing metal and silicate phases.

Silicon incorporation in metal

A major interest of these new compositional data is that they were obtained by using silicon rich metal alloys as starting materials. This allowed to investigate very low oxygen fugacities : at four log units below the iron/wustite (IW) buffer, silicates were found in equilibrium with Si-rich metallic alloys, up to 17wt% of Si in Fe at 20 GPa and 2200°C. From these experiments, we calculate that Earth forming materials in a reduced state comparable to that of enstatite chondrites would incorporate up to 10wt% of Si in metal during core segregation.

Behaviour of sulphur

Similar experiments performed in sulphur-bearing systems showed that Fe-Si-S metals were segregated into two immiscible silicon-rich and sulpur-rich melts. This immiscibility behaviour known at low pressures thus persists at much deeper conditions. MgS was observed in these experiments. We show that the presence of silicon in the metal alloy is required to allow the formation of MgS. We propose that the formation of MgS might be responsible for the low bulk S content of the Earth.

Behaviour of carbon

Reaction of Fe-Si alloys with $FeCO_3$ siderite yielded the formation of 20-30 µm sized diamonds embedded in the metal phase. This shows that at 20 GPa and 1800°C, silicon is more reducing than carbon. This property might be significant for establishing the CO_2/reduced carbon balance in the early Earth as well as for constraining the maximum amount of carbon in the Earth's core.

The oceanic Mo cycle over the past 60Ma

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Dissolved ocean Molybdenum shows a substantial fractionation of 1 permil per mass unit relative to oxic marine sediments. This offset has been constant for the past 60 Ma. With an increasing number of data on Mo isotope fractionation (Siebert et al., 2001, Barling et al., 2001, McManus et al., 2002) the geochemical cycle of Mo in the recent oceans becomes traceable. Here new data on ocean Mo sources and sinks are presented that were determined using a Nu Instruments MC-ICP-MS and double spike techniques (Siebert et al., 2001, external standard reproducibility below 0.1 permil (2s.d.) on ^{98}Mo/^{95}Mo). Given the long (800ka) residence time Mo in the oceans, Mo isotopes are homogenous. Data are presented in permil relative to Mean Ocean water Mo (MOMO) for the ^{98}Mo/^{95}Mo ratio, which is +2.3 permil relative to an in-house Johnson Mattey ICP standard solution.

Mo sources: Two granites (+ mild acid leaches), seven volcanic rocks and two clastic sediments show a narrow range of compositions (-2.0 to -2.3 permil relative to MOMO). These data indicate that fractionation by chemical weathering and magmatic processes is insignificant on global scale and they should therefore represent the composition of dissolved input to the oceans and of the average continental crust.

Oxic Mo sinks: Pelagic sediments and six Fe-Mn crust surface layers show lighter compositions (-2.7 and -2.9 permil and -2.7 to -3.1 permil, respectively).

Suboxic Mo sinks: The balancing heavy Mo is found in recent suboxic sediments from open ocean basins which display more variable values of -0.7 to -1.6 permil.

Mo seawater histories: Two depth profiles through thick sections of Fe-Mn crusts yield uniform Mo isotope compositions throughout the entire 60 Ma (average of -3.2 and -2.9 permil, time resolution is limited by the 800 ka Mo residence time). Steep gradients for Mo concentrations and the large isotope offset from seawater Mo preclude post-depositional homogenisation or infiltration of Mo.

Implications: The constant and uniform isotope offset between oxic sediments and seawater suggests an equilibrium fractionation process. We propose this occurs between (dominant) MoO_4^{2-} and (minor) $Mo(OH)_6$ species, of which the latter can be scavenged.

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