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Core formation in the presence of various C–H–O volatile species

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Abstract—The impact of various mixtures of CO₂, H₂O, H₂, and CH₄ upon Fe, Ni, Co, W, Ge, P, and Mo partitioning between silicate and metal alloy liquids was evaluated experimentally at 1400°C and 10 kb in graphite. The effects observed are consistent with the control expected from redox-driven transfer between metal and silicate liquids. Oxidation moves these metals to the silicate liquid. Oxidizing C–O–H or C–O vapors generated by decomposition of either brucite or magnesite or both have a stronger, opposite effect on element distribution than the reducing C–H vapors generated by anthracene decomposition. Special effects associated with particular volatile and siderophile elements were largely unobserved. Individual C–O–H species involved in the redox equilibria are not so important as their redox effect, except for phosphorous which responds differently to CO₂- and H₂O-inspired vapors. An analysis of the redox effects of several M/MO_x equilibria confirm the presence of large departures from ideality in the solutions involved.

Oxidants might be quite potent in remediating some of the excesses in the siderophile element chemistry of the mantle. Because little special effect for any volatile species is observed, siderophile elements should respond in a coherent manner regardless of which volatile species is the immediate cause of the redox transfer. In consequence, oxidizing the system with any of the plausible volatile agents we have investigated to make Ni or Ge or Mo less siderophile than they are in the absence of volatile elements will also make Fe, Co, W, and P too lithophile to be consistent with their observed abundances in the mantle. The observed Fe abundances in the mantle put limits on redox ability to explain the *excesses* of other siderophile elements. Furthermore it is unlikely that redox effects can be fine tuned to give chondritic relative abundance values in the mantle as needed. Nevertheless, the possible effects of redox equilibria have long been known to be commensurate in importance with pressure and temperature effects upon siderophile element distribution and should continue to be considered in any analysis of core formation. Copyright © 1999 Elsevier Science Ltd

1. INTRODUCTION

The role, if any, of volatile elements in the early evolution of the Earth is controversial. Many recent theories of formation of the earth suggest the presence of various volatile species during or after the major events of core segregation. For example, the theory of inhomogeneous accretion of the earth suggests progressive change in the condition of the early earth from volatile-free (metal-rich) reducing to volatile-rich (silicate- and oxide-rich) oxidizing. Core segregation may have occurred during the reducing stage, whereas accretion of the oxidized (metal-free) planetesimals followed by volatile-rich late chondritic veneer may post-date the core formation (Wanke et al., 1984). Other theories suggest the presence of a primitive H₂–He rich or impact-generated H₂O–CO₂ rich atmosphere during the early stages of accretion. Substantial heating, melting of the accreting materials, and generation of a magma ocean at the surface of the growing planet have been proposed as a consequence of the trapping of accretionary heat by the massive volatile-rich atmosphere (Sasaki 1990; Ahrens 1990; Abe 1993). On the other hand, Ringwood's (1990) scenario of a homogeneously accreting early earth did not consider any role for volatile effects during core formation, and Richter et al. (1997a) suggested that dissolved H₂O, at <2 wt% in the molten silicate has no noticeable effect on element distribution.

Siderophile element abundances in the mantle are sensitive to the core formation process in the earth and might be expected to contribute to a resolution of these issues. The stepped abundance pattern of moderately and highly siderophile elements, the near-chondritic ratios of many moderately (e.g., Ni/Co) and highly (e.g., Ir/Os) siderophile elements, and the excess abundances of many siderophile elements relative to the abundance expected from core segregation at low temperature and pressure characterize the terrestrial mantle. Inhomogeneous accretion scenarios consider the addition of late chondritic veneer to be responsible for the observed chondritic and excess abundances of siderophile elements. However, recent theories of ultrahigh temperature (>2000°C), high pressure (>20 GPa) core segregation attempt to make metal–silicate equilibrium at the base of a magma ocean responsible for these unique features of mantle geochemistry (Murthy 1991, Li and Agee 1996, Righter et al., 1997b). Righter et al. (1997b) consider metal–silicate equilibrium at the upper mantle/lower mantle boundary in a hydrous magma ocean to be a viable scenario. They postulate that the presence of water would extend the thickness of a magma ocean, but would not affect the distribution of siderophile elements among liquid metal and liquid silicate phases.

Any role for water or other volatile species like CO₂, CH₄, or H₂ in the core formation process can be evaluated with reference to mantle siderophile element geochemistry and also with respect to physical plausibility.

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