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The influence of sulfur on partitioning of siderophile elements

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Abstract—Sulfur is a potential light element in the liquid outer core of the Earth. Its presence in segregating metal may have had an influence in distribution of metal-loving (siderophile) elements during early accretion and core formation events in the Earth. The observed “excess” abundance of siderophile elements in the terrestrial mantle, relative to an abundance expected from simple core-mantle equilibrium at low temperature and pressure, may indicate a reduction in the iron-loving tendency of siderophile elements in the presence of sulfur in the metallic phase. The present experimental partitioning study between iron-carbon-sulfur-siderophile element bearing liquid metal and liquid silicate shows that for some siderophile elements this sulfur effect may be significant enough to even change their character to lithophile. Large and intricate variations in metal-silicate partition coefficients ($D^{\text{met/sil}}$) have been observed for many elements, e.g., Ni, Co, Ge, W, P, Au, and Re as a function of sulfur content. Moderately siderophile elements Ge, P, and W show the most significant response (sulfur-avoidance) by an enhanced segregation into the associated sulfur-deficient phases. Highly siderophile elements Ir, Pt, and Re show a different style of sulfur-avoidance (alloy-preference) by segregating as sulfur-poor, siderophile element-rich alloys. Both groups are chalcophobic. $D^{\text{met/sil}}$ for Ni, Co, and Au moderately decreases with increasing sulfur-content in the liquid metal. $D^{\text{met/sil}}$ for chalcophile element, Cr, in contrast, increases with sulfur. Irrespective of the sulfur-content, in the presence of a carbon-saturated liquid metal, P is always lithophile. The general nonmetal-avoidance tendency of siderophile elements (and acceptance of chalcophile elements) in the liquid metal, postulated by Jones and Malvin (1990) in the Fe-Ni-S(sulfur)-M(siderophile) system is found to be present in the metal-silicate system as well. A sulfur-bearing liquid metal segregation can potentially reduce the metal-loving nature of many elements to explain the excess paradox. Sulfur-bearing core segregation, however, might require an efficient draining of exsolved immiscible sulfide liquids from the molten silicate, or an increasing siderophilicity of sulfur at high pressure to reduce the mantle sulfur content to the observed (<300 ppm) value. Moreover, the chondritic relative abundance pattern of many moderately or highly siderophile elements in the upper mantle is not explained by the presence of sulfur in the segregating metals. Core formation is more complex and intricate than equilibrium segregation. Copyright © 1997 Elsevier Science Ltd

1. INTRODUCTION

Formation of a metallic core is perhaps the single most profound early differentiation event a homogeneously accreted terrestrial planet can experience. Simple processes of metallic core segregation should have depleted many core-loving (siderophile) elements in the Earth's mantle by factors varying from 10 to 1000 more than what is actually observed in the mantle derived rocks. This “excess” abundance of siderophile elements is either an artifact of our expectations from evidences provided by meteorites, or a by-product of considering a simple core-mantle equilibrium, based on metal-silicate partition coefficients ($D^{\text{met/sil}}$) determined between solid Fe-Ni metal and liquid silicates at low temperature, atmospheric pressure conditions. A plethora of hypotheses over more than three decades have been proposed to explain this excess paradox. Examples include: (a) heterogeneous accretion, perhaps with an addition of a late-stage

oxidized chondritic veneer after an early equilibrium core segregation in the highly reduced state (Wanke et al., 1984; Schmidt et al., 1989); (b) segregation of Fe-S-O liquid which is less receptive to siderophile elements than solid Fe-Ni metal (Brett, 1976, 1984), (c) partial retention of accreting sulfide and sulfur-loving moderately siderophile elements in the mantle (Arculus and Delano, 1981); (d) homogeneous accretion and equilibrium metal-silicate interaction at ultrahigh pressure at the core-mantle boundary (Ringwood, 1984); (e) inefficient core separation with a small fraction of metal (subsequently oxidized) being trapped in the residual mantle to buffer the siderophile element inventory (Jones and Drake, 1986), (f) core segregation at ultrahigh temperature (3000–3500 K) in a magma ocean scenario (Murthy, 1991); (g) core segregation at highly reduced condition with enhanced solubilities of neutral siderophile element species in the mantle (Colson, 1992); (h) pressure-induced coordination change of transition metal ions in silicate melts and corresponding solubility increase of siderophile elements in silicate liquid (Kepler and Rubie, 1993), (i) homogeneous accretion with continuous core formation (Azbel et al., 1993), (j) two-step core-

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