

HIGH PRESSURE, NEAR-LIQUIDUS PHASE RELATIONS IN Fe-C-S SYSTEMS AND IMPLICATIONS FOR COMPOSITION, STRUCTURE, AND PROCESS OF FORMATION OF METALLIC CORES IN PLANETARY BODIES. R. Dasgupta^{1,2}, A. Buono², G. Whelan², and D. Walker², ¹Department of Earth Science, Rice University, 6100 Main Street, MS-126, Houston, TX 77005; ²Lamont-Doherty Earth Observatory, Columbia University, 61 Route 9W, Palisades, NY 10964 (E-mail: Rajdeep.Dasgupta@rice.edu).

Introduction: The Earth's outer core is known to be ~10% less dense than pure metallic Fe-Ni liquid [1, 2] and thus is thought to contain ~10% light elements [e.g., 1] with proposed candidates including sulfur (S), carbon (C), oxygen (O), hydrogen (H), and silicon (Si). The presence of minor, lighter alloying elements is also argued for metallic cores of other planetary bodies including inner terrestrials planets such as Mars and Mercury [e.g., 3,4] and for bodies beyond the asteroid belt including Jupiter's moons Io, Ganymede, and Europa [5,6]. While the light element composition in cores of various planetary bodies remains unknown, it is likely that more than one light alloying element is present [7,8]. But, experimental data on the effect of light elements on melting relations of iron in multi-component systems and the mutual solubility of various light elements in molten Fe has been limited. Previous experiments in multi-component systems have explored the phase relations in Fe-S-Si, Fe(\pm Ni)-S-O, and Fe(\pm Ni)-C-S. To add to the discussion on the mutual compatibility of carbon and sulfur in the metallic core of planetary bodies and to investigate the crystallization behavior of inner core in a multi component system we have performed new high pressure experiments in the Fe-C-S systems.

Experiments and Analysis: We investigated the near-liquidus phase relations in Fe-C-S ternary at 2-6 GPa and 1050-2000 °C. Experiments were performed in a piston cylinder and a multi-anvil device using MgO (Fe-5wt.%C-5wt.%S and Fe-5wt.%C-15wt.%S) and graphite (Fe-13wt.%S, Fe-5wt.%S, Fe-wt.1.4%S) capsules. Run products were imaged and analyzed for Fe, S, C, and O using an electron probe micro analyzer on Al-coated samples.

Results: The phase assemblage for Fe-5wt.%C-5wt.%S evolve from a completely molten system at high temperatures to Fe-metal+Fe-carbide+melt at low temperatures (Fig. 1) via Fe-carbide+melt at intermediate temperatures. The liquidus increases from 1100-1150 °C at 2 GPa to 1375-1450 °C at 6 GPa, as the sole liquidus carbide phase changes from Fe₃C to Fe₇C₃. With cooling, Fe-metal appears between 1100 and 1050 °C at 2 GPa and between 1200 and 1100 °C at 6 GPa. At 6 GPa, between 1200 and 1300 °C, Fe₃C breaks down to produce a more carbon-rich carbide, Fe₇C₃ and melt. Over the pressure range of investigation, the liquidus temperature for the bulk composition

Fe-5wt.%C-15wt.%S is *ca.* 50-100 °C lower than that of the bulk composition with 5 wt.% sulfur; it is 1100 \pm 50 °C at 2 GPa and between 1250 and 1350 °C at 6 GPa. At 2-5 GPa, above the liquidus, for this composition, we observe the presence of two quenched melt phases (Fig. 1A), one carbide-rich and sulfur-poor and the other sulfide-rich and carbon-poor. Texturally the melt phases appear to be immiscible, with blobs of carbide-rich quenched melt in a mat of sulfide-rich melt (Fig. 1B). No immiscibility texture is observed for superliquidus conditions at 6 GPa, and a single, sulfur and carbon bearing quenched melt is observed.

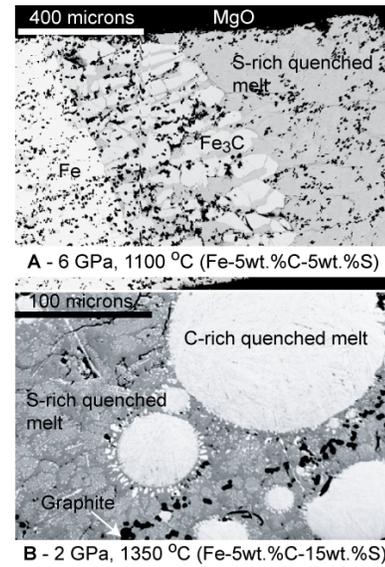


Fig. 1. BSE images of experiments showing (A) a coexistence of metallic Fe, Fe₃C, and S-rich quenched metallic melt in the crystallization interval of Fe-5wt.%C-5wt.%S, and (B) blobs of C-rich quenched metallic melt in a mat of S-rich melt in a superliquidus condition at 2 GPa for Fe-5wt.%C-15wt.%S.

Fe-5wt.%C-5wt.%S. At both 2 and 6 GPa, the melt in equilibrium with metallic-Fe and/ or Fe₃C is S-rich and C-poor and the melt becomes progressively S-rich and C-poor with decreasing temperature and melt fraction.

Fe-5wt.%C-15wt.%S. Immiscible liquids at the superliquidus conditions show systematic compositional changes as a function of pressure and temperature (Fig. 2). Both carbon and sulfur-rich alloys show stronger compositional evolution with pressure than

with temperature, suggesting that pressure has a much greater role in causing the miscibility gap in Fe-C-S system (Fig. 2).

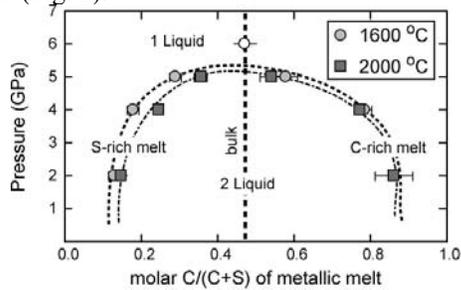


Fig. 2. P - X diagram showing the miscibility gap between carbon-rich and sulfur-rich conjugate metallic liquids with respect to molar $C/(C+S)$. Closure of the miscibility gap is consistent with textural evidence for the existence of two liquids at 5 GPa and one liquid at 6 GPa.

Discussion: The near-liquidus melting phase relations determined in this study shed light on to the evolution and formation of metallic cores in planetary bodies in the presence of both carbon and sulfur. Our experiments demonstrate that modest amount of carbon has a non-negligible effect on the liquidus of Fe-S system. At 6 GPa the Fe-5wt.%C-5wt.%S liquidus is 150-200 °C lower than the liquidus of Fe-5 wt.%S whereas the Fe-5wt.%C-15wt.%S liquidus is ~50 °C higher than the Fe-15wt.%S. With carbon content of 5 wt.% or more, the first crystallizing phase is Fe-carbide and then metallic Fe. Thus for a carbon-rich metallic core the inner core could be a mixture of iron carbide and metallic iron while a sulfur-rich metallic liquid would likely segregate as an outer core. This is consistent with the recent observation of Fei et al. [9], where similar crystallization sequence in a Fe-C-S system has been observed to 20 GPa. Our study also shows that at pressures beyond 6-7 GPa the crystalline carbide phase of interest is Fe_7C_3 and not Fe_3C and planetary metallic cores with modest C and S content is likely to crystallize a carbon-rich (and sulfur-poor), denser inner core and a sulfur-rich, lighter outer core. Our results of liquid immiscibility in the Fe-C-S ternary is broadly in agreement with the one-atmosphere data [10] and the recent high pressure data of Corgne et al. [11]. They suggest that at a given P - T the solubility of carbon diminishes with increasing sulfur content of Fe-metallic liquid. The miscibility gap is observed to close sharply as a function of pressure as the mutual solubility of carbon and sulfur in molten Fe is enhanced with pressure (Fig. 3).

Thus, for planetary cores that are entirely molten or at least have a molten outer core and are also rich in sulfur and carbon, liquid immiscibility induced stratifi-

cation is expected where the core pressure is less than 6 GPa.

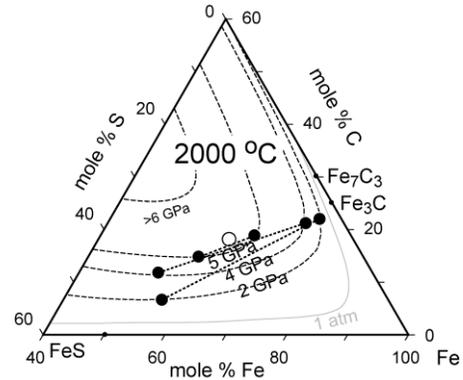


Fig. 3. Fe-rich portion of Fe-C-S ternary showing mutual solubility of C and S as a function of pressure at a constant temperature of 2000 °C. Also shown for reference is the location of the 1 atmosphere solvus [10].

But we expect no such immiscibility in a molten metallic outer core for the terrestrial planets such as Earth, Venus, and Mars, where relevant core pressures are in the order ≥ 136 GPa, ≥ 100 GPa, and ≥ 23 GPa. In terms of the core pressures among terrestrial planets, only Mercury and Io, with the CMB pressures of 7-8 GPa and 7 GPa respectively, present the closest cases where outer core immiscibility could have taken place in the early stage of their growth but on the other hand, the core compositions for terrestrial planets might be too depleted in carbon [e.g., 12] for them to have core stratification owing to interaction between carbon and sulfur in metallic melt. Although their compositions are poorly constrained, volatile-rich interior compositions could be better argued for large icy satellites and solid icy planets. Jovian satellite Europa, for example, likely has a CMB pressure as low as 5 GPa and hence its core may have experienced an immiscibility induced stratification, if sufficiently enriched in carbon and sulfur.

- References:** [1] Birch F. (1952) *JGR*, 57, 227-286. [2] Shanker J. et al. (2004) *PEPI*, 147, 333-341. [3] Lodders K. (1997) *Icarus* 126, 373-394. [4] Morgan J. W. and Anders E. (1980) *PNAS* 77, 6973-6977. [5] Anderson J.D. et al. (1997) *Science* 276, 1236-1239. [6] Anderson J.D. et al. (2001) *JGR* 106, 32963-32969. [7] McDonough W.F. (2003) *Treat Geochem* 2, 547-568. [8] Badro J. et al. (2006) *EPSL*, 254, 233-238. [9] Fei Y. et al. (2008) *LPS XXXIX*, Abstract# 1687. [10] Raghavan V. (1988) *JAPD* 4, 133-142. [11] Corgne et al. (2008) *GCA* 72, 2409-2416. [12] Dasgupta R. and Walker D. (2008) *GCA* 72, 4627-4641.