Application of micro X-ray diffraction on lamellar, black shale related Mn ore, Urkut, Hungary

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Urkut (Hungary) hosts the largest Toarcian Mn ore deposit in Europe. It consists of both carbonate and oxide ore sequences. We studied a complete carbonate profile, consisting of a black shale sequence with two Mn-bearing horizons. This is the first time that this very fine-grained (µm- and nm-sized), lamellar sedimentary sequence was traced by systematic, real micrometer scale studies, including structural (micro X-ray diffraction), textural, and chemical (SEM+EDS, cathodoluminoscope) observations. These data contribute substantially to the earlier genetic models.

The lamellar ore structure is a result of parallel or exclusive existence of phases recording redox conditions (and their changes). Mn occurs both in carbonate and (recently subordinatate) oxide phases in the carbonate ore. Ore-forming *carbonate minerals* display a complex texture. Three different types of Mn-Ca carbonates were identified: 1) the main carbonate is a fine grained, sometimes nodular (pseudomorph after nodular manganite) Ca-rhodochrosite [d_{104}=2.865(1) Å], 2) Ca-rhodochrosite pseudomorph after Radiolarians, and 3) in smaller amounts in the ore, a post-diagenetic Ca [d_{104}=2.876(2) Å] Mn calcite [d_{104}=2.99 Å], showing red cathodoluminescense. The *Mn-oxide phase* of the carbonate sequence is manganite. No Mn^{4+}-oxide phase was found. *Fe* occurs both in reduced (euhedral and framboidal pyrite) and oxidized form (goethite and sheet silicates).

Manganite can be regarded as the primary ore accumulation form of Mn. It may be the result of oscillating suboxic/oxic conditions near the seabottom. In restored suboxic conditions microorganisms could utilize first Mn^{3+}, then Fe^{3+} when oxidizing organic material. With increasing concentration of Mn^{2+}_{aq} and $HCO_3^-{}_{aq}$ (org), fine grained Ca-rhodochrosite (d_{104}=2.865(1) Å) precipitated, and allotigenic calcite, such as Radiolarian pseudomorphs, was also metasomatised by Mn^{2+}. This two-way Ca-rhodochrosite formation model explains the typical $\delta^{13}C$ values (~12–15) and the poor correlation between Mn and $\delta^{13}C$ values published earlier [1].

[1] Polgari *et al.* (1991) *J. Sediment. Petrol.* **31** (3), 348–393.

Siderophile elements and the single-stage core formation hypothesis

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The abundances of siderophile elements in the bulk silicate Earth (BSE) indicate that its iron-rich core most probably form at high pressure and high temperature in a magma ocean (e.g. Walker *et al*. 1993; Hillgren *et al*. 1994; Thibault & Walter 1995; Li & Agee, 1996). This is consistent with physical models of planetary accretion (Davies 1985; Benz & Cameron 1990; Tonks & Melosh 1993). Recent experimental works have proposed that the BSE concentrations of several siderophile elements are consistent with a scenario of single-stage equilibration at the base of a magma ocean ~700 km deep (Li & Agee 1996; Righter *et al.* 1997; Chabot & Agee 2003). More recent models using temperature sensitive partitioning data for V and Nb have casted doubt on this interpretation since the required basal temperature should greatly exceed that of the mantle liquidus (Wade & Wood 2005; Corgne *et al*. 2008; Wood *et al*. 2008). This temperature mismatch is meaningless in the framework of the magma ocean theory because the temperature at the base of the magma ocean should approximate that of the mantle liquidus. To resolve this anomaly, it has been suggested that the building materials of the Earth were initially reduced materials and then became progressively oxidized with time (Wade & Wood 2005; Corgne *et al*. 2008; Wood *et al*. 2008). Thus, rather than resulting from a single-stage event at relatively fixed conditions of high pressure and high temperature, the Earth's core may in fact have formed in a more complex event, imprinted by heterogeneous accretion and the progressive growth of the planet and its magma ocean.

Here, we present an alternative to the dynamic model by showing that a single-stage core formation event could explain the mantle contents of the best-constrained siderophile elements (Ni, Co, V, Mn, Cr, Nb) provided that the core contains a few weight percents of oxygen. Our calculations based on partitioning and metallurgy data reveal that V and Nb become less siderophile with increasing the O content of core-forming materials, while the behaviour of Ni, Co, Cr and Mn is little affected. Since other light element candidates C, Si and S do not influence significantly the siderophile behaviour as does O, we conclude that a single-stage core formation scenario is a viable hypothesis only if O is a non-negligible contributor to the density deficit of the Earth's core relative to pure Fe or Fe-Ni alloy.