Late-stage removal of chalcophile elements from the mantle by sulfide liquid extraction to the core

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The U-Pb chronometer reveals a more protracted age of Earth core formation (65-85 Myr; Halliday, 2003) compared to the Hf-W chronometer (30-50 Myr; Kleine *et al*., 2005). These long-lived isotopic systems are ideal for determining the timescale of core formation because the parent-daughter ratios are fractionated by metal-silicate segregation, with moderately siderophile W and slightly siderophile Pb following metallic liquid into the core. The discrepant timescales suggest that a strong U/Pb fractionation took place sometime during the accretionary history of the Earth, that did not affect the Hf-W system (Wood and Halliday, 2005).

Under reducing conditions in the early Earth, liquid Fe metal separated from liquid silicate to form the core. With oxidation of the lower mantle and the continued accretion of volatile-rich material, it is likely that the later stages of Earth differentiation involved the formation of a FeNi-sulfide liquid (O'Neill, 1991). It has been suggested that because Pb displays chalcophile behaviour (Jones *et al*., 1993), contrary to W (Chabot and Jones, 2005; Jana and Walker, 1997), removal of a small portion of this sulfide 'Hadean matte' to the core may have depleted Pb from the mantle, disrupting the U-Pb chronometer (Hart and Gaetani, 2006). The abundance of other chalcophile elements in the mantle would also have been altered by this process, such as Te and Se, useful in evaluating Earth differentiation processes.

Partitioning of Pb, Te, and Se between liquid metal and liquid silicate are presented at 3 GPa and 2233 K, in which both the S content and fO_2 are gradually increased. At IW-2, the partition coefficients (D) for Te and Se show a 3-fold increase with the addition of ~10 wt% S to the metallic liquid, with D_{Te} increasing from 104±18 to 324±68, and D_{Se} from 30±6 to 90±13. A marked increase in D_{Pb} was observed by Ballhaus *et al*. (2006) with the addition of S at low pressure. Similar to Se and Te, higher pressures may increase the magnitude of D_{Pb}, suggesting that segregation of some 'Hadean matte' equilibrated at high P-T conditions in a magma ocean, may have been a significant factor in disrupting the U-Pb age of core formation on the Earth.

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Constraints on atmospheric H_2 from banded iron formations

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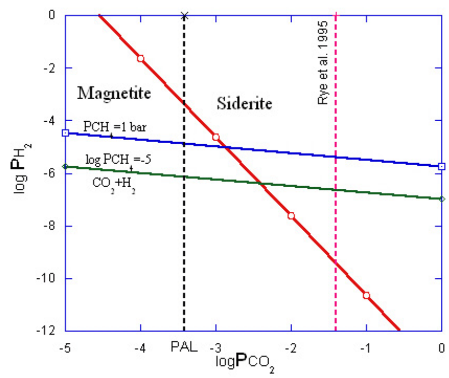
Quartz-magnetite banded iron formations are ubiquitous throughout the Archaean geologic record. Models for the composition of the Archaean atmosphere and ocean must therefore be compatible with the widespread precipitation of magnetite from the ocean. At 25 C magnetite is stable relative to siderite only when the partial pressures of H_2 and CO_2 are so low that their reaction to form methane cannot sustain reproduction by methanogenic organisms (Sleep and Bird, 2007).



If we assume ocean temperatures ~ 25 C and a partial pressure of CO_2 in the atmosphere ~ present value, magnetite stability is only possible at H_2 pressures below ~0.0001 bar. At the maximum CO_2 pressures allowed by Precambrian palaeosols (Rye *et al*., 1995), the hydrogen pressure would be further 5 orders of magnitude lower.

The common presence of magnetite in Archaean sediments is therefore not compatible with models that favour an early Archaean atmosphere characterized by high hydrogen mixing ratios (Tian *et al*., 2005) or with suggestions that H_2 nourished an extensive biosphere prior to the evolution of oxygenic photosynthesis (e.g. Tice and Lowe, 2004).

References

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