

6-1-2010

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## Publication Information

Klein, F.; Bach, W.; Jons, N.; NcCollom, T.; and Frost, B R. (2010). "Intrinsic Silica Metasomatism During Serpentinization." *Geochimica Et Cosmochimica Acta* 74.12, A522-A522.

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## Intrinsic silica metasomatism during serpentization

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Serpentinization of peridotite is an exceptionally diverse but unsatisfactorily understood process. To gain deeper insights into the reaction pathways of serpentization we link the petrography and mineralogy of serpentized peridotites from ODP Leg 209 with hydrothermal serpentization experiments, phase petrology and geochemical modeling.

In rocks from ODP Hole 1274A hydration of olivine (Ol) generates mesh rims, which reveal a distinct in-to-out zoning from brucite (Brc,  $X_{Mg} \approx 0.8$ ) at the interface with Ol, followed by a zone of serpentine (Srp,  $X_{Mg} \approx 0.95$ ) + Brc ± magnetite (Mgt) and finally Srp and Mgt in the outermost mesh-rims. Completely serpentized peridotites lack Brc. Hydration of orthopyroxene (Opx) produces Fe-rich Srp ( $X_{Mg} \approx 0.89 - 0.92$ ) while talc (Tlc) and Mgt are lacking. Since in a closed system the hydration of Ol and Opx would cause the formation of Srp + Brc and Srp + Tlc, respectively, the absence of Brc and Tlc is indicative of open system conditions and mass transport of  $SiO_2$ , aq from an 'Opx-hydration cell' to an 'Ol-hydration cell'. Phase relations and geochemical reaction path models indicate that mass transport of  $SiO_2$ , aq will be most effective below 400 °C, where the gradient in  $\mu SiO_2$ , aq between both cells is steepest. At T below the quasi-invariant point of Ol, Srp and Brc, the addition of  $SiO_2$ , aq from the Opx cell will destabilize Brc in favor of Srp. Fluid chemistry and petrographic analysis of solid reaction products of hydrothermal serpentization experiments suggest that the hydration of Ol causes the metastable formation of Brc within the stability field of Srp before Srp nucleates, which is in accord with mineral zonings in mesh textures of samples from ODP Hole 1274A. Seeing that reaction pathways during serpentization are strongly dependent on host-rock composition, temperature and fluid flux, further multidisciplinary studies of serpentinites from other abyssal geotectonic environments need to be conducted.

## Earth's accretion and differentiation

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Hf-W and U-Pb isotopic systematics can constrain the timing of Earth's core formation and accretion [e.g. 1], whilst metal-silicate partitioning experiments provide information on the conditions of core formation [e.g. 2]. Assuming complete metal-silicate equilibration during core formation, these geochemical observations are consistent with metal segregation in a deep magma ocean [2] and a rapid early accretion of Earth's main mass in ~10 Myr [3-5], followed by a late Moon-forming giant impact that terminated Earth's accretion, either at ~30 Myr [4] or more likely at ~100 Myr after solar system formation [5, 6]. We developed a geochemical box model for metal-silicate differentiation in the growing Earth and show that the current observations are consistent with a much wider range of possibilities but still provide bounds on Earth's accretion and the conditions of core formation. The Hf-W observations do not provide tight constraints regarding the rate of Earth's accretion but do require that at least 36% of Earth's core formed in equilibrium with Earth's mantle. Siderophile element depletions in Earth's mantle are consistent with as little as 36% equilibration and do not require full metal-silicate equilibration. The U-Pb system is mainly affected by Earth's terminal accretion and, provided Pb was partitioned into Earth's core, dates the last 10% of Earth's accretion to ~4.45 Ga, consistent with the Hf-W age of the Moon-forming impact [6]. This relatively late termination of core formation is difficult to reconcile with the preservation of a <sup>142</sup>Nd signature of a ≤30 Myr differentiation of Earth's mantle because the isolation of the early enriched reservoir [7] would have to have occurred at a time when metal melts were still segregating into Earth's core. This seems implausible, such that the <sup>142</sup>Nd excess of Earth's mantle relative to chondrites [7] is more readily explained if the Earth has non-chondritic relative abundances of refractory elements [5, 8].

[1] Halliday (2004) *Nature* **427**, 505–509. [2] Wade & Wood (2005) *EPSL* **236**, 78–95. [3] Halliday (2008) *PTRSL* **366**, 4163–4181. [4] Jacobsen (2005) *AREPS* **33**, 531–570. [5] Kleine *et al.* (2009) *GCA* **73**, 5150–5188. [6] Touboul *et al.* (2007) *Nature* **450**, 1206–1209. [7] Boyet & Carlson (2005) *Science* **309**, 576–581. [8] Caro *et al.* (2008) *Nature* **452**, 336–339.