

Fe³⁺ partitioning systematics between orthopyroxene and garnet in well-equilibrated mantle xenoliths

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Ferric iron to total iron ratios in coexisting orthopyroxene and garnet from eighteen mantle xenoliths from Siberia (Udachnaya, Obnazhennaya) and Mongolia (Dariganga) were measured by ⁵⁷Fe Mössbauer spectroscopy at room temperature. The xenoliths include both coarse and sheared types and were checked for equilibrium based on textural and compositional criteria. A further check was made through cross-evaluation of thermometric estimates using internally consistent thermometers (cf. [1]). Thermobarometric estimates encompass a large P–T field (1.9–6.4 GPa; 740–1295 °C) relevant to Earth's upper mantle in both on-craton and off-craton settings. The Mössbauer data show that the partitioning of Fe³⁺ between orthopyroxene and garnet is essentially independent of the temperature of equilibration, but varies significantly with pressure. The $(\text{Fe}^{3+}/\text{Fe}_{\text{tot}})_{\text{Grt}}/(\text{Fe}^{3+}/\text{Fe}_{\text{tot}})_{\text{Opx}}$ ratio increases with pressure and is lower than unity at P < ca. 3.5 GPa and higher than unity at higher pressure. These partitioning systematics imply that thermometers based on Fe–Mg exchange equilibrium between orthopyroxene and garnet will fail at very low and very high pressure if redox conditions in the natural rocks are different from those in the experiments that were used to calibrate the thermometer. In particular, increased bulk Fe³⁺ contents due to more oxidized conditions will lead to over-estimated Opx–Grt temperatures at low P and under-estimated temperatures at high P. Conversely, decreased bulk Fe³⁺ contents due to more reduced conditions will lead to under-estimated Opx–Grt temperatures at low P and over-estimated temperatures at high P. The observed Fe³⁺ systematics may in part explain recognized inconsistencies between two-pyroxene and Opx–Grt thermometry of mantle xenoliths (cf. [1]).

[1] Nimis & Grütter (2010), *Contrib. Mineral. Petrol.* **159**, 411–427.

Dynamical and isotopic perspectives on accretion and core formation

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Numerical modelling of accretion suggests the following characteristics: Mars-sized bodies can form fast (~1 Myr) but completing an Earth takes longer (10–100 Myr); late-stage impacts can remove (or add) material in a stochastic fashion; the “feeding zone” of a growing planet expands with time. All these characteristics can potentially be quantified using cosmochemical measurements.

Isotopic systems such as Hf–W [1], Pd–Ag [2] and Fe–Ni [3] provide constraints on the timing of core formation. The biggest challenge is to better understand the degree of mantle re-equilibration during large impacts [4]. Re-equilibration occurs at cm-scales during impacts involving Mm-scale objects; it is thus hard to model numerically, but can perhaps be better quantified via laboratory experiments [5]. The effective conditions under which core formation occurred can also be probed with stable Fe or Si isotopes, though the presence of S complicates matters [6].

The bulk compositions of planets may have been affected by late-stage removal of material [7], and spall fragments such as the Moon produced [8]. Models show that smaller surviving bodies show more variability in bulk chemistry and isotopic signatures [9]; larger bodies experience more averaging and are harder to fragment. Stochastic late impacts may be responsible for the variable amount of “late veneer” apparently added to the terrestrial planets [10].

Feeding zone expansion and the Pd–Ag [2] and I–Xe systems [11] both suggest late impactors are more volatile-rich. Later impactors may also have been more oxidized [12], but recent high-P partitioning experiments suggest this is not required [13].

Late-stage impacts probably caused several episodes of regional if not global melting. For both Earth and Mars, mantle convection subsequent to these magma ocean episodes has not been able to erase initial heterogeneities [11,14].

[1] Kleine *et al.* *GCA* 73, 2009 [2] Schonbachler *et al.*, *Science* 328, 2010 [3] Dauphas *et al.*, *LPSC* 44, 2013 [4] Daphuas & Pourmand, *Nature* 473, 2011. [5] Deguen *et al.* *EPSL* 310, 2011 [6] Shahar *et al.*, *LPSC* 44, 2013 [7] O'Neill & Palme, *PTRSL-A* 366, 2008. [8] Cuk & Stewart, *Science* 338, 2012 [9] Dwyer *et al.*, this meeting [10] Bottke *et al.*, *Science* 330, 2010 [11] Mukhopadhyay, *Nature* 486, 2012 [12] Rubie *et al.* *EPSL* 301, 2011 [13] Siebert *et al.* *Science* 339, 2013. [14] Halliday *et al.* *Space Sci. Rev.* 96, 2001.