

## Evidence of Bacterial Molybdenum Isotope Fractionation

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Although the trace metal molybdenum (Mo) is not very abundant, its occurrence is manifold. Molybdenum cofactors play key roles for many enzymes [1, 2, 3] during nitrogen fixation [4], nitrogen reduction, and other processes [5]. Enzymes use trace metals to catalyze chemical reactions by taking advantage of different oxidation states. Molybdenum is available to organisms as molybdate ( $\text{MoO}_4^{2-}$ ) and varies in oxidation states between +IV, +V and +VI, hence mobilizing two electrons [1]. We have investigated Mo concentrations and the Mo isotopic composition ( $\delta^{98/95}\text{Mo}$ ) of cell fractions of the bacterial strain *Escherichia coli* MC4100. Differential centrifugation was used to separate cytosol, cell membrane and LSP ("low speed pellet"). The cytosol, the intracellular fluid, had the lowest Mo concentrations, and the cell membrane itself the highest Mo concentration. First Mo isotope abundance results suggest that the incorporation of Mo into the cell is associated with isotopic fractionation during production of membrane-anchored Mo-containing proteins and the water-soluble Mo-containing proteins found in the periplasm.

[1] Schwarz et al. (2009) *Nature* **Volume 460**, 839-847. [2] Schneider et al. (1991) *Analytical Biochemistry* **Volume 193**, 292-298. [3] Blaschke et al. (1991) *Archives of Microbiology* **Volume 155**, 164-169. [4] Zerkle et al. (2011) *Geobiology* **Volume 9**, 94-106. [5] Magalon et al. (2011) *Coordination Chemistry Reviews* **Volume 255**, 1159-1178.

## High pressure experimental constraints on majorite transformation of chromium-rich garnets

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### Garnet-Majorite transformation

Garnet is an important constituent of the upper mantle, as is evidenced by its frequent occurrence in mantle xenoliths and as inclusions in diamonds. With increasing pressure silica is incorporated into the octahedral site of garnet resulting in a majorite component [1]. The transformation of garnet to majorite is reported to depend on a number of factors besides pressure, such as bulk compositions and presence of other Al bearing phases (such as cpx) or melt [2]. Furthermore, the presence of the minor element chromium has been suggested to decrease the majorite stability with increasing pressure [3].

If true, the effect of chromium on majorite transformation has implications for the interpretation of the formation depth of diamond inclusions as the Cr/(Cr+Al) ratio is much higher in depleted lithospheric mantle compared to fertile mantle [4].

### Experimental methods

To investigate this further, we performed sub-solidus high-pressure high-temperature experiments in a Walker-type multi anvil press (Bristol design) at pressures of 6, 9 and 12 GPa, and a range of temperatures. The starting materials consist of silicate glasses in the system  $\text{Cr}_2\text{O}_3\text{-CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ , with varying  $\text{Cr}_2\text{O}_3/(\text{Al}_2\text{O}_3+\text{Cr}_2\text{O}_3)$ . Electron microprobe is used to determine the concentration of major and minor elements in the different phases.

### Results

All experiments yielded garnet, opx, olivine and (minor) cpx as stable phases. Preliminary results indicate that for constant pressures and temperatures, the majorite component in garnet decreases with increasing Cr/(Cr+Al) of the bulk composition. There also appears to be a small temperature effect on the stability of the majorite component in garnet but more experiments are needed to confirm this.

[1] Akaogi and Akimoto (1977) *Physics of the Earth and Planetary Interiors* **15**, 90-106. [2] Draper et al (2003) *Physics of the Earth and Planetary Interiors* **139**, 149-169. [3] Klemme (2004) *Lithos* **77** 639-646. [4] Stachel (2001) *European Journal of Mineralogy* **13**, 883-892.