Experimental studies of CaEsk component in pyroxene at high PT

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It was discovered in the 1960-70s that many eclogitic pyroxenes show nonstoichiometry, ('excess SiO_2 ') caused by the reaction:

 $CaAl(AlSi)O_6 + 3SiO_2 \leftrightarrow Ca\Box Al_2Si_4O_{12}.$

The reaction runs to the right by substitution of Si for Al in tetrahedral sites, displacing Al to M1 octahedral sites, where it is electrically balanced by a vacancy. The right side of the reaction has a smaller volume than the left, hence increasing pressure drives the reaction to the right. Day & Mulcahy [1] showed three possible ways of SiO₂-exsolution: (1) vacancy consumption in non-stoichiometric pyroxene; (2) dissolution of Ti-phases in pyroxene or garnet; (3) reactions between accessory phases and either pyroxene or garnet. We have conducted a series of 'dry' experiments in a Walker-style multianvil apparatus at P = 6, 8, 10, 12 GPa, and T = 900, 1000, 1100 and 1200°C using powdered glass of the composition (wt%): $SiO_2 = 58.29$, $Al_2O3 = 24.12$, MgO = 5.44, CaO = 11.37, Na₂O = 0.78. Our experiments demonstrate that at given bulk chemistry the Px with the largest CaEsk value is crystallized at P=6 to 8GPa at all temperature ranges; with increasing P up to 12GPa and T up to 1200°C the CaEsk component tends to decrease. Our data are in a good agreement with experiments by [2] because CaEsk component exhibits similar tendency, though the values of the CaEsk components are significantly different due to differences in the bulk chemistry chosen as starting materials. For example, Px synthesized from the starting material A toleiite at 10GPa, 1200°C contains CaEsk = 0.10 [2], whereas at similar conditions we have synthesized Px with CaEsk = 0.19. Our experiments showed that the nonstoichiometry of omphacite reaches a maximum between 5 and 8 GPa, followed by rapid decrease in CaEsk component when stishovite becomes stable in the assemblage and the pyroxene progressively dissolves into garnet, culminating in a garnetite at ca. 15 GPa. We conclude, CaEsk component can be responsible for SiO₂ lamellae exsolution formation in pyroxenes uplifted from depth not more than 180 km, and therefore decompressed from P = 6 - 8GPa to ambient pressures.

[1] Day & Mulcahy (2007) *JMG* **25**, 35–70. [2] Irifune *et al.* (1986) *EPSL* **77**, 245–256.

The role of Ca pools in the calcification process of foraminifera

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Proxy relationships, e.g. the oxygen isotope fractionation of foraminiferal calcite *vs*. temperature, are important tools in paleo climate reconstruction. However, it has been realized that the reliability of proxies depends on our understanding of the biomineralization process, and on the quantification of species-specific variability of proxy relationships.

For foraminifera a number of conceptual models on the transport of ions from seawater to the site of calcification have been published. Most of these models are based on the assumption that seawater, including the constituent ions Ca and CO₃, is taken up in vacuoles (a process termed endocytosis) and transported to the site of calcification [1]. However, calculations of the Ca fluxes necessary for endocytosis-based calcification [2] and measurements of the free Ca concentration within these vacuoles show that the presence of Ca pools would be required. An observational evidence for the presence of Ca pools does not exist to date. We present data obtained for the benthic foraminifera *Amonia tepida*, which raises the question, if trans-membrane transport of Ca from seawater directly to the site of calcification is a plausible mechanism to explain foraminiferal calcification.

Bentov & Erez (2006) Geochem. Geophys. Geosys. 7(1).
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