Goldschmidt 2022 Abstract
https://doi.org/10.46427/gold2022.12231

Ca-phosphates in the deep Earth: Phase stability and volatile incorporation of tuite, γ-$Ca_3(PO_4)_2$

TRISTAN PAUSCH[1], JASEEM VAZHAKUTTIYAKAM[1], ANTHONY C. WITHERS[2], THOMAS LUDWIG[3], BASTIAN JOACHIM-MROSKO[1] AND JÜRGEN KONZETT[1]

[1]University of Innsbruck
[2]University of Bayreuth
[3]Universität Heidelberg

Presenting Author: Tristan.Pausch@uibk.ac.at

Phosphorus and volatiles bound in Ca-phosphates affect processes in the Earth's interior including partial melting and melt migration, element partitioning and redistribution. The anhydrous Ca-phosphate tuite, which is the high-P breakdown product of apatite, has the potential to host incompatible trace elements [1]. Its suitability as a volatile carrier and its stability field in the major lithologies of the subducting lithosphere, however, remain to be explored.

Multianvil experiments were conducted at 15 to 25 GPa and 1600 to 2000 °C, using a spinel lherzolite doped with β-$Ca_3(PO_4)_2$ and a trace element mix as starting material. The coexisting phases that were stable within this P-T range include tuite, majoritic garnet, ringwoodite, forsterite, clinoenstatite, bridgmanite, Ca-perovskite, ferropericlase, and melt.

At 25 GPa/1600°C, after the breakdown of majorite which was found to contatin up to 2 wt% P_2O_5, tuite is the main phosphorus-carrying mineral. At 1800°C tuite is not stable anymore, which indicates that the upper T-stability of tuite is close to the average current mantle adiabat. Therefore, tuite is eminently suitable as an incompatible trace-element carrier in both subduction zones and convecting mantle P-T regimes.

Secondary-ion mass spectrometry analyses show that tuite and Ca-Pv can incorporate significant amounts of REE. At 20 GPa/1600°C, $REE_{tuite}/REE_{Ca\text{-}Pv}$ concentration ratios are 0.17 for Ce, 0.28 for Gd and 0.09 for Lu. At 25 GPa/1600°C these ratios are 0.09, 0.09 and 0.04, respectively. This indicates an increasing ability of Ca-Pv to fractionate REE compared to tuite. As can be expected both tuite and Ca-Pv strongly fractionate LREE with Ce_N/Lu_N = 21.4 and 11 for tuite and Ca-Pv at 20 GPa/1600°C (normalized to CI chondrite [2]). Thus Ca-Pv is likely to be the major host of REE in primitive mantle whereas tuite is an additional important REE and the most important P-carrier in metasomatically altered mantle.

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