EXPERIMENTAL EVIDENCE FOR HIGH-PRESSURE TRANSFORMATION OF MERRILLITE AND Na-BEARING PHOSPHATES.

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Introduction: Merrillite and apatite are most important phosphate minerals in meteorites [1]. In the shock-melt veins of the heavily shocked chondrite and martian meteorites, apatite is often transformed to high-pressure polymorph tuite [2, 3], stable in static high-pressure experiments at pressures above 12 GPa [4]. Surprizingly, merrillite is also transformed to tuite-structured phase according to Raman spectroscopy and synchrotron X-ray diffraction [5, 6]. However, compositions of merrillite and apatite are different and no synthetic high-pressure phase of merrillite composition was obtained. In this work, we provide data on the synthesis of merrillite and some other Na-bearing phosphates at 15-20 GPa and show their relevance to high-pressure phosphates in meteorites.

Methods: Starting merrillite Ca₉NaMg(PO₄)₇ was synthesized from a mixture of phosphates in the experiment at 1 atm and 1450 °C for 3 hours. This merrillite, as well as a mixture of phosphates with the addition of Na-carbonate flux, was studied at pressures of 6, 15 and 20 GPa and 1400-1600 °C using multianvil technique at GRC, Ehime University.

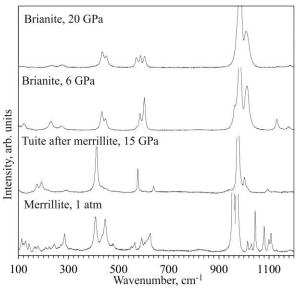


Fig.1. Raman spectra of synthesized merrillite and brianite at high-pressures.

Results and discussion: Examination of the obtained samples using Raman spectroscopy show that, at 15 and 20 GPa, merrillite has a spectrum similar to tuite (Fig.1), which is consistent with observations in chondrite and iron meteorites [5, 6]. Most likely, these phases are isostructural, and Mg and Na play the role of impurities in the Ca₃(PO₄)₂ tuite. Unfortunately, in these experiments, it was not possible to obtain large crystals of the high-pressure phase of merrillite. An additional phase in the experiments was phosphate with the composition of buchwaldite Na(Ca_{0.75}Mg_{0.25})PO₄. The Raman spectrum of this phosphate differs from the spectrum of buchwaldite at 1 atm and has poor quality. In runs with a mixture of phosphates and carbonate flux at 15 and 20 GPa, merrillite did not crystallize. The products of the experiments were tuite and Na-phosphate composition corresponding to brianite Na₂MgCa(PO₄)₂ (Fig.1). The Raman spectrum of this phase at 15 and 20 GPa correspond to brianite at 1 atm and 6 GPa, which indicates its strong stability at high pressures at least up to 20 GPa.

The solvent in the form of alkaline carbonatite melt was not formed since all Na was bound to phosphates.

The carbonate phase was represented by magnesite. As a result of the experiments, it was found that the Na-carbonate melt is not a reasonable flux for the crystallization of high-pressure phosphates. Perhaps an appropriate solvent is potassium carbonate, which is planned to be used in subsequent experiments.

Acknowledgments: This work was supported by Russian Foundation for Basic Research (No 17-05-00851).

References: [1] Rubin A. E. and Ma C. (2017) *Chemie der Erde Geochem.* 77: 325-385. [2] Xie X. et al. (2003) *Eur. J. Mineral.* 15: 1001-1005. [3] Tomioka N. and Miyahara, M. (2017) *Met. Planet. Sci.* 52: 2017-2039. [4] Murayama J. K. et al. (1986) *Phys. Earth Planet. Inter.* 44: 293-303. [5] Xie X. et al. (2013) *Met. Planet. Sci.* 48: 1515-1523. [6] Litasov K. D. and Podgornykh N. M. (2017) *J. Raman Spectr.* 48: 1518-1527.