Phase Stability of Triphylite, LiFePO4, and the Phases of the Mason-Quensel-Sequence

Schmid-Beurmann, Peter¹; Moavenian, Mohsen¹; Hatert, Frédéric²

¹Univ. Kiel, Institut für Geowissenschaften, Olshausenstr.40, D-24098 Kiel ²Laboratory of Mineralogy, B.18, University of Liège, B-4000 Liège, Belgium

The minerals of the system triphylite-lithiophilite, Li(Fe,Mn)PO₄, belong to the sequence of primary phosphate minerals which crystallised during the late stage of pegmatite formation.

The examination of thin sections [1,2] reveals that a redox occurs, which leds to loss of lithium and oxidation of the di-valent manganese and iron according to:

 O_2 + LiFePO₄ => FePO₄ + $\frac{1}{2}$ (Li₂O)_{aq} and

 $\begin{array}{l} \frac{1}{4} O_2 + LiMnPO_1 => MnPO_1 + \frac{1}{2} (Li_2O)_{nq} \\ \text{The educt triphylite and the Li-depleted products,} \\ Li_{(1-x)}Fe^{2+} {}_{(1-x)}Fe^{3+} {}_{x}PO_4 \text{ (Ferrisicklerite) and FePO_4} \end{array}$ (Heterosite) of such a topotactic reaction are members of the so-called Mason-Quensel-sequence [3].

The aim of the study is to investigate the temperature conditions and oxygen fugacities under which such reactions

In a first step the phase agglomeration in the section LiFePO₄ - FePO₄ was investigated in synthesis runs.

Hydrothermal experiments were carried out in the section LiFePO₄ -FePO₄ at temperatures between 400 - 650°C and in the pressure range between 0.1 and 0.3 GPa. Starting mixtures consisting of Li₃PO₄, FePO₄ (Berlinite-Type) and Fe in compositional steps of $x_{LiFePO4} = 0.25$ were reacted in the presence of H₂O for 3 - 7 days. No external buffer was applied in order to avoid oxidation or reduction of the bulk.

Under the applied conditions triphylite, Fe₇(PO₄)₆ and Fe₄(PO₄)₃(OH)₃, a compound of lazulite-type, were identified as run products.

No oxidation or reduction of ferrous (LiFePO₄)and ferric (FePO₄)end-member compositions were observed indicating that the mean valence state of the samples was preserved.

Inspection of triphylite lattice parameters revealed no detectable formation of a solid solution with a FePO₄ component under such conditions.

Further experiments include oxidation reaction with LiFePO4 as starting material under the control of oxidising buffers like Hematite/Magnetite or cuprite/tenorite.

[1] Quensel, P. (1937): Minerals of the Varuträsk pegmatite. 1. The lithium-manganese phosphates. Geologiska Föreningens i Stockholm Förhandlingar, 59, 77-6.

[2] Mason, B. (1941): Minerals of the Varuträsk pegmatite. XXIII. Some iron-manganese phosphate> minerals and their alteration p special reference to material > from Varuträsk. Geologiska Föreningens i Stockholm Förhandlingar, 63, 117–75. [3] Fransolet, A.M., Keller, P., Fontan, F. (1985): The phosphate mineral associations the Techniques of

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Geochemistry and geochronology of Archean Hutti-Maski greenstone belt, Eastern Dharwar Craton, South India

Schmidt, Alexander¹; Balakrishnan, Srinivasan²; Anand, Rajagopal²; Mezger, Klaus³

¹Institut für Mineralogie, Abteilung Petrologie und Geochemie, Johann Wolfgang Goethe-Universität Frankfurt am Main ²Department of Earth Sciences, University of Pondicherry, India ³Zentrallabor für Geochronologie, Institut für Mineralogie, Westfälische Wilhelms-Universität

The gold-bearing, hook-shaped Archean Hutti-Maski greenstone belt is located at the western margin of the Eastern Dharwar Craton in South India. The rocks within the belt consist predominantly of mafic to felsic volcanic suites and minor sediments including banded iron formation and greywacke. The belt is surrounded by distinct granitic and granodioritic intrusions to the north and east, and the Peninsular Gneiss Complex (PGC) to the west. It has undergone at least three deformation phases [1]. Metamorphism reached at least middle amphibolite facies conditions, but the rocks were almost completely overprinted by a later greenschist facies metamorphism. In the Hutti-Maski schist belt gold-mineralisation is associated with quartz veins and occurs along N-S trending

Rb-Sr ages of 2.3 Ga from two biotites separated from metabasalt samples in contact with quartz veins inside the Hutti Goldmine date the end of the greenschist facies metamorphism. Formation of the quartz veins is a consequence of massive fluid flow during metamorphism which overprinted the schist belt. Biotite samples from granodiorites surrounding the schist belt yield similar Rb-Sr ages of 2.3 Ga which are interpreted as cooling ages. Zircon and sphene from granitic samples give U-Pb ages ranging from 2.47 to 2.57 Ga and date the crystallization of the intrusions. Nd model-ages range from 2.60 to 2.76

Initial Nd and Sr isotope ratios show that the rocks of the schist belt were derived from a mantle source and have undergone small amounts of contamination with continental crust. Analysis of common Pb on feldspars from the granitic bodies show a mixing curve and favour the conclusion that the intrusions were part of an island arc setting with contamination by fluids derived from dehydrating subducting slabs and associated sediments. Occurrence of pillowed basalts associated with shallow water sediments supports the theory of an island arc setting which led to the formation of the Hutti-Maski schist belt. Trace element patterns for the granitic samples show TTG-signatures with positive Sr-anomalies indicating a slab component/melt, therefore supporting the theory of an island are setting with slab dehydration/melting at medium depth.

[1] Roy, A., (1979): Polyphase Folding Deformation in the Hutti-Maski Schist belt, Karnataka: Journal of the Geological Society of India, v. 20, p. 598-607.

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