

## Experimental Formation of Ferrisicklerite, $\text{Li}_{1-x}(\text{Fe}^{3+}, \text{Mn}^{2+})\text{PO}_4$ from Natural Triphylite, $\text{Li}(\text{Fe}, \text{Mn})\text{PO}_4$ Single Crystals.

Schmid-Beurmann, Peter<sup>1</sup> Geisler, Thorsten<sup>1</sup>

<sup>1</sup>Universität Münster, Institut für Mineralogie, Corrensstr. 24, 48149 Münster

Solid solutions between triphylite ( $\text{LiFePO}_4$ ) and lithiophilite ( $\text{LiMnPO}_4$ ) are known as primary phosphate minerals in granitic pegmatites. They crystallize at temperatures below 500°C. With decreasing temperature they undergo a topotactic redox reaction with the surrounding fluid. Such reaction leads to a loss of lithium and the oxidation of the iron and manganese, resulting in the phases of the Mason-Quensel-sequence: ferrisicklerite – sicklerite ( $\text{Li}_{1-x}(\text{Fe}^{3+}, \text{Mn}^{2+})\text{PO}_4$ ) and heterosite – purpurite sicklerite ( $\text{Fe}^{3+}, \text{Mn}^{3+})\text{PO}_4$  [Quensel (1937), Mason (1941), Fransolet et al., (1985)]. The aim of our study is to clarify the temperature conditions and oxygen fugacities under which such reactions occur, and to elucidate the underlying reaction mechanism. Hydrothermal experiments show that heterosite ( $\text{FePO}_4$ ) can be synthesized directly from synthetic triphylite ( $\text{LiFePO}_4$ ) powders at 120°C.  $\text{KMnO}_4$  in 0.1N HCl was used as oxidizing agent. In order to investigate the progress of the reaction, cuboids with edge length of ~ 2.5 mm were cut from a natural triphylite single crystal ( $\text{Li}(\text{Fe}^{3+}_{0.74}\text{Mn}^{2+}_{0.21}\text{Mg}_{0.05})\text{PO}_4$ , from Palermo Mine, N.H./USA). The samples were treated under the same conditions as mentioned above. After run durations of 7 to 28 days examination of thin sections made from the treated cuboids revealed the formation of a redish brown, up to 100  $\mu\text{m}$  thick reaction rim around unreacted triphylite in the center of the cuboids. The reaction product was identified as ferrisicklerite ( $\text{Li}_{1-x}(\text{Fe}^{3+}, \text{Mn}^{2+})\text{PO}_4$ ) by X-ray powder diffraction and Mössbauer spectroscopy. Microprobe analysis including Fe, Mn, P, Mg, Na, K and Ca revealed no significant change in the concentrations of these elements across the reaction boundary, except for K. The K concentration was below the detection limit in the triphylite core but showed a continuous increase in the ferrisicklerite rim towards the fluid solid interface. Raman spectra of ferrisicklerite formed in an aqueous solution enriched in  $^{18}\text{O}$  showed significant shifts of their Raman bands towards lower frequencies relative to spectra of samples formed in water of “normal” isotopic composition, indicating the incorporation of  $^{18}\text{O}$  in the ferrisicklerite lattice. Our results support the hypothesis that an interface-coupled dissolution-reprecipitation operating at an inward moving reaction front is the responsible mechanism of reaction.

### References

- Fransolet, A.M., Keller, P., Fontan, F. (1985): The phosphate mineral associations the Tsaobismund pegmatite. *Contrib. Min Petrol*, 92, 502 – 517.
- Mason, B. (1941) Minerals of the Varuträsk pegmatite. XXVIII. *Geologiska Föreningens i Stockholm Förhandlingar*, 63, 117-175.
- Quensel, P. (1937): Minerals of the Varuträsk pegmatite. I. The lithium-manganese phosphate –minerals. *Geologiska Föreningens i Stockholm Förhandlingar*, 59, 77-6.

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submitted by: **Schmid-Beurmann,**  
**Peter**  
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