

Extremely Phosphorous Olivines in a Prehistoric Burning site slag

Schneider, Philipp¹ Tropper, Peter¹ Konzett, Jürgen¹ Kaindl, Reinhard¹

¹University of Innsbruck, Institute of Mineralogy and Petrography, Innrain 52 A-6020 Innsbruck, Austria

In this study, in the course of the special research project HiMAT (history of mining activities in the Tyrol and adjacent areas) at the University of Innsbruck, we report extremely P-rich olivines from partially molten quartzphyllites from the presumably La-Tène (450-15 B.C.) age sacrificial place at the Goldbichl, near Innsbruck, Northern Tyrol, Austria. During partial melting, foamy patches of dark glassy material formed at the surface of the rocks and also as layers within the rocks. Overall, the pyrometamorphic rocks contain the mineral assemblage olivine + orthopyroxene + plagioclase + spinel + glass. During the investigation of slag samples from this prehistoric sacrificial burning site, extremely P-rich microdomains were found, where P-rich olivine was found. The textures within these domains indicate strongly disequilibrium conditions. The phosphorus-rich olivine formed along reactions involving apatite, and coexists with graffonite (Fe, Ca, Mg, Mn)₃(PO₄)₂. In terms of its chemical composition, it shows a wide range in composition with P ranging from 0.3 to 0.55 apfu, which corresponds to up to 23 wt.% P₂O₅! This are the highest P-contents in olivine reported from rocks on the Earth surface so far! Boesenberg et al. (2004) conducted experiments concerning the P-incorporation in olivine. They were able to synthesize P-rich rims around San Carlos olivine and predicted that olivine is capable to incorporate a maximum of 27 wt.% P₂O₅. This amounts to a substitution of 70% of the tetrahedral Si by P on the T-site in olivine. Besides high temperatures in excess of 1000 – 1100°C and strong disequilibrium conditions, an extreme low oxygen fugacity is necessary to form P-rich olivines (Tropper et al., 2004). Bearing these constraints in mind, we tried to synthesize phosphoran olivine in a high-T furnace from the oxides MgO, SiO₂ and Ca₃PO₄ at temperatures of 1200°C for several hours. After the experiment, the charge was air-quenched to obtain disequilibrium growth of olivine. So far, we obtained single crystals of olivine with up to 1 wt.% P₂O₅. Micro-Raman spectroscopy measurements on the P-olivines indicate that P-bearing olivines can easily be identified with this method due to the strong signals of the SiO₄- and PO₄-vibration. The external vibrations at low wavenumbers are very distinctly developed. This might be due to the effect of P⁽⁵⁺⁾ on the M₁⁽²⁺⁾ and M₂⁽²⁺⁾ positions. The substitution mechanism is 2P + M_{1,2} = 2Si + (Mg,Fe)M_{1,2} so phosphorous can only incorporated in combination with a vacancy on the M_{1,2} position therefore it is expected that the substitution of P causes a decrease in symmetry.

References

- Boesenberg, J.S. et al. (2004): An experimental study of phosphoran olivine and its significance in main group pallasites. *Lun. Planet. Sci.* XXXV
- Tropper, P. et al. (2004): Experimental investigations on the pyrometamorphic formation of phosphorous-bearing olivines in partially molten metapelitic gneisses. *Eur.J.Mineral.* 16: 631-640

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