

Murataite-pyrochlore complex oxide series for actinide immobilization: Nanoscale structure and complexity

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Synthetic murataite, an analogue of a rare titanate mineral, was identified in Synroc ceramic designed for immobilization of high-level nuclear waste [1, 2]. Five volume percent of this phase accumulated about 40% of the total uranium present in the sample. Laverov *et al.* [3] discovered different murataite varieties, *Mu-3*, 5, 7, and 8, where numbers correspond to the multiplicity of murataite *a* cubic unit cell parameter with respect to the same parameter of the fluorite unit cell. Experimental studies demonstrated that the crystallization sequence of phases in the U (Pu)-Zr-Mn-Fe-Ti-Al-O complex system can be expressed as: Pyrochlore - *Mu-7* - *Mu-5* - *Mu-8* - *Mu-3*. In murataite ceramic, typical grains contain pyrochlore and *Mu-5* at the core surrounded by *Mu-8* and *Mu-3* phases. Since the most actinide-bearing phases are encapsulated by low-actinide varieties, this creates an additional barrier for actinide leaching and increases chemical durability of murataite ceramics. Recently, we have been able to structurally characterize *Mu-3*, 5 and 8 varieties of synthetic murataite and to demonstrate their polysomatic nature, in agreement with the earlier proposal by Urusov *et al.* [4]. It turns out that members of the murataite-pyrochlore series are the result of nanoscale mixing of murataite and pyrochlore structures. For instance, the structure of *Mu-5* [5] is a complex framework consisting of pyrochlore unit cells uniformly distributed in murataite-type recombined structure. The structure of *Mu-8* contains alternating murataite and pyrochlore unit cell modules separated by transitional structure.

[1] Morgan & Ryerson (1982) *J. Mater. Sci. Lett.* **1**, 351–352.

[2] Laverov *et al.* (1998) *Dokl. Earth Sci.* **363**, 1104–1106.

[3] Laverov *et al.* (1998) *Dokl. Earth Sci.* **363**, 1272–1274.

[4] Urusov *et al.* (2005) *Dokl. Earth Sci.* **401**, 319–325.

[5] Krivovichev *et al.* (2010) *Angew Chem. Int. Ed.* **49**, 9982–9984.

The lamprophyre problem: Return to the roots

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The term ‘lamprophyre’ has been introduced in 1874 by Gümbel for Variscan mafic post-collisional dykes from the Bohemian Massif characterized by phenocrysts of mafic mica embedded in a feldspar groundmass (minette and kersantite type). In analogy to these, Rosenbusch in 1887 added the amphibole-bearing types such as vogesite and camptonite, from which spessartite was subsequently distinguished. Unfortunately, during the 20th century, petrologists enlarged this ill-understood group by incorporating different rocks containing mafic phenocrysts, such as kimberlites, lamproites, nepheline-, leucite- and melilite-bearing rocks. This resulted in a single large supergroup of polygenetic rocks termed the ‘lamprophyre clan’. In contrast, recent understanding of lamprophyres provides a sound basis for rejecting such a variable group of polygenetic origin [1, 2]. As true lamprophyres, we can now recognize five original types (end-members) among which there are continuous transitions: minette, kersantite, vogesite, spessartite and partly camptonite (in the original sense). It is important to note, that not every rock labelled as a true lamprophyre falls into this group. For example a ‘peralkaline minette’ is not a lamprophyre but very probably corresponds to a lamproite [c. f. 3, 4].

Since the term camptonite is usually used for an alkaline ‘lamprophyre’ variety (in fact volatile-rich basalt), I recommend not to use it in context with the true lamprophyres. Lamprophyre varieties containing kaersutitic amphibole can be easily described as titanospessartite or titanovogesite, respectively (Table 1). Moreover, the last proposed variety fills the gap in the current nomenclature.

predominant mafic mineral with "OH" group			
predom. felsic mineral	Al-undepleted phlogopite/ biotite	Mg-hastingsite + others Ca amphiboles	kaersutite
Kfs	minette	vogesite	titanovogesite
Pl	kersantite	spessartite	titanospessartite

Table 1: Proposed principal subdivision for the true lamprophyres. (Kfs = K-feldspar, Pl = plagioclase)

[1] Le Bas (2007) *Geology Today* **23**, 167–168. [2] Krmíček (2010) *Acta Mus. Moraviae, Sci. geol.* **2**, 5–63. [3] Hall (1982) *Mineral. Mag.* **45**, 257–66. [4] Krmíček *et al.* (2011) *Lithos* **121**, 74–86.