

RARE-ELEMENT PEGMATITES - FROM NATURAL SYSTEMS TO THE EXPERIMENTAL LAB

by

Marieke Van Lichtervelde

Institute for Research and Development
Laboratoire Géosciences Environnement Toulouse, France

Rare-element pegmatites are sources of strategic metals used in the high-tech industry (tantalum in micro-capacitors, lithium in ion batteries, rare-earth elements in green technologies such as photovoltaic panels or wind turbines; see Linnen et al. 2012 for a review). Two main types of pegmatites can be distinguished: the Lithium-Cesium-Tantalum-bearing (LCT) pegmatites, which are peraluminous in composition and are generally emplaced in late to post-orogenic settings, and the Niobium-Yttrium-Fluorine (NYF) pegmatites, which are peralkaline and generally emplaced in anorogenic settings. The ASI (aluminosilicate index = Al/alkali ratio) and the flux content (Li-F-B-P) are therefore important compositional parameters influencing rare-metal enrichment in pegmatitic melts. In particular, fluxes considerably lower melt viscosity and solidus temperature, allowing pegmatitic melts to travel kilometres away from their source before crystallisation starts.

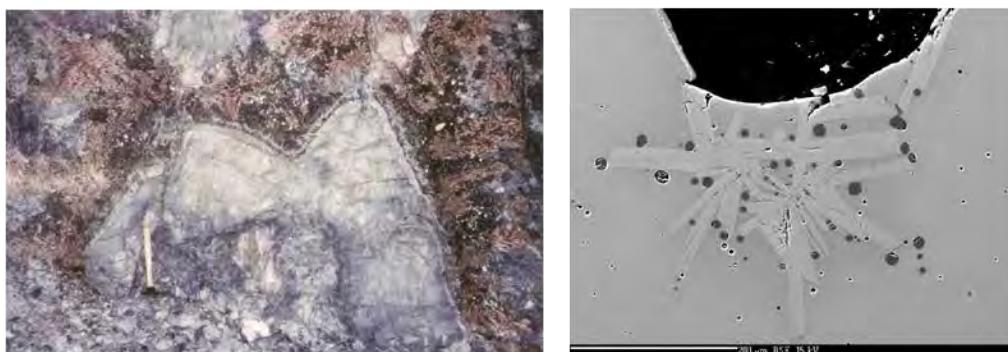


Fig. 1

left: giant K-Feldspar surrounded by red dendritic amblygonite in the Tanco pegmatite; right: Albite laths surrounded by bubbles of immiscible melt (dark grey) in an experiment at 600°C-200MPa. Both pictures illustrate boundary layer processes with incompatible components being concentrated at the crystallization front of rapidly growing crystals.

The most fractionated pegmatites are characterised by large (kilometre scale) dykes, complex internal structures, giant crystal size, and complex mineralogical textures and assemblages. These characteristics are the result of rapid, disequilibrium crystallisation from undercooled, flux-rich melts. Fluxes decrease the nucleation rates by preventing the formation of crystal nuclei, and increase the growing rates by promoting high element diffusivities. Therefore, flux-rich pegmatitic melts may keep low viscosity down to low temperatures (300-400°C), and aqueous fluids may not be the principal controller of pegmatite evolution like stated in old models (Jahns and Burnham 1969). In newly-invoked models of pegmatite formation (London 2009 and references therein), elevated flux concentrations enable extremely high water solubilities in the melts, therefore promoting low melt viscosity, high element mobility and low solidus temperatures. By inhibiting nucleation, they enable the melt to be cooled down to temperatures well below its solidus, a process known as supercooling or undercooling. Such melts can form at the crystallisation front of the consolidating pegmatite through the exclusion of incompatible elements, a process known as boundary layer process. Boundary layers may also concentrate rare metals as their solubilities considerably increase with flux contents and alkali/alumina ratios.

In complement to investigating individual pegmatites and their petrography/mineralogy, experimentation may bring relevant information to pegmatite formation processes, such as viscosity and solubility measurements, crystallisation kinetics or interactions between metals. Our experimental studies in Hanover (Bartels et al. 2010, Fiege et al. 2011, Van Lichtervelde et al. 2010) using flux-rich water-saturated pegmatitic melts at 200 MPa and temperatures ranging between 700 and 1200°C, demonstrate that the ASI (Al/alkali) ratio is more important than any other parameter (flux content, temperature, fO_2) in influencing rare metal solubilities. An interesting observation comes from the comparison of the zircon and manganotantalite solubility products where zircon and manganotantalite are dissolved alone or in association in a pegmatitic melt. Solubility products are systematically lower where both minerals are dissolved together compared to where they are dissolved alone. This solubility difference is more strongly marked in peralkaline melts than in peraluminous melts. This not only shows that Zr and Ta metals compete for the same structural sites in the melt, but also that this competition is in favor of Ta over Zr in peraluminous conditions and in favor of Zr over Ta in peralkaline conditions (Van Lichtervelde et al. 2011). These results may explain why Zr mineralisations are generally associated with peralkaline systems whereas Ta mineralisations are associated with peraluminous pegmatites, and show the importance of investigating metal interactions in order to understand rare-metal enrichment processes in granitic melts.

In flux-rich pegmatitic melts, crystallization experiments successfully result in the formation of rare metal-bearing minerals such as Nb-Ta oxides, zircon or rutile (Van Lichtervelde et al. 2011). With various degrees of supercooling imposed to the experiment, one can reproduce the different textures observed in pegmatites: small undercooling rates (< 50°C) result in medium-grained equant crystals representative of granitic textures, whereas large undercooling rates (> 200°C) result in coarse-grained dendritic crystals typical of some pegmatitic textures (Fig. 2). Immiscibility processes were also observed by Bartels (2012) in dehydrated conditions (Fig. 1, right), at the crystallization front of albite crystals. This is evidence that many complex interrelated processes are involved in pegmatite formation, which still deserve further investigation, using both natural systems and experimentation.

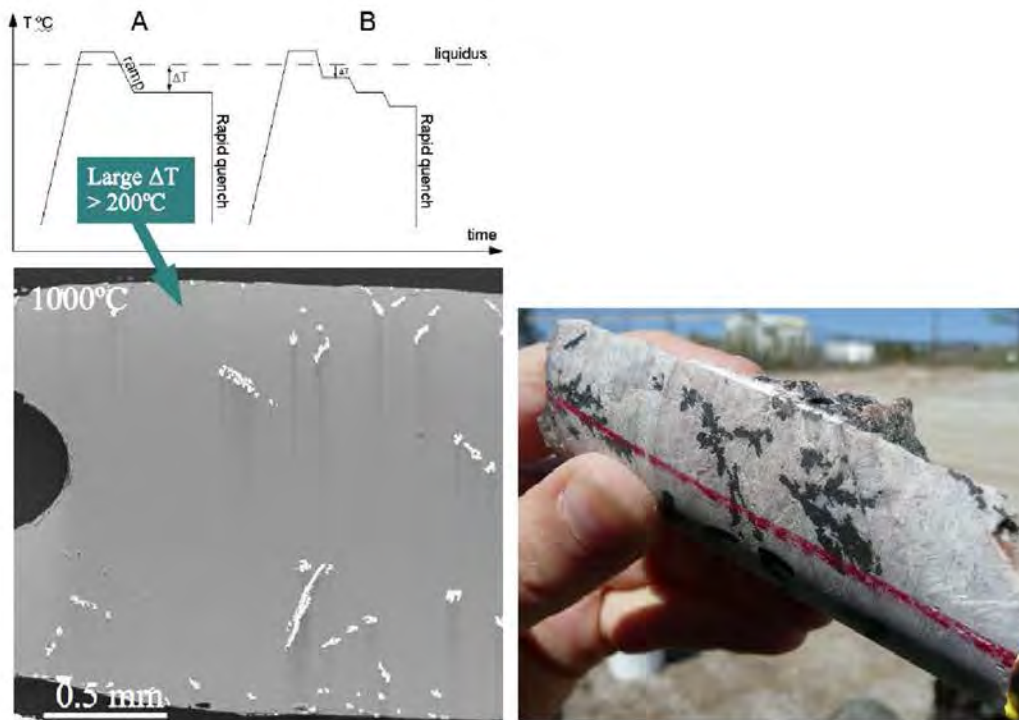


Fig. 2

Crystallisation experiment reproducing dendritic textures for manganotantalite using large supercooling. Such textures are comparable to dendritic Nb-Ta oxides observed in the Tanco pegmatite (right).

References

- BARTELS, A. (2012): The influence of fluorine, boron, phosphorus and lithium on the viscosity of hydrous pegmatitic melts, PhD thesis, Hannover.
- BARTELS, A., HOLTZ, F. & LINNEN, R. L. (2010): Solubility of manganotantalite and manganocolumbite in - pegmatitic melts. *Am. Mineral.* 95, 537-544.
- FIEGE, A., KIRCHNER, C., HOLTZ, F., LINNEN, R.L. & DZIONY, W. (2011): Influence of fluorine on the solubility of manganotantalite ($MnTa_2O_6$) and manganocolumbite ($MnNb_2O_6$) in granitic melts - An experimental study. *Lithos*, 122, 165-174.
- JAHNS, R.H. & BURNHAM, C.W. (1969): Experimental studies of pegmatite genesis. I. A model for the derivation and crystallization of granitic pegmatites. *Economic Geology*, 64, 843-864.
- LINNEN, R.L., VAN LICHTERVELDE, M. & ČERNÝ, P. (2012): Granitic pegmatites as sources of strategic metals. *Elements*, 8, 275-280.
- LONDON, D. (2009): The origin of primary textures in granitic pegmatites. *Can. Mineral.*, 47, 697-724.
- VAN LICHTERVELDE, M., HOLTZ, F., DZIONY, W., LUDWIG, T. & MEYER, H.-P. (2011): Incorporation mechanisms of Ta and Nb in zircon and implications for pegmatitic systems. *American Mineralogist*, 96, 1079-1089.
- VAN LICHTERVELDE, M., HOLTZ, F. & HANCHAR, J.M. (2010): Solubility of manganotantalite, zircon and hafnon in highly-fluxed peralkaline to peraluminous pegmatitic melts. *Contrib. Mineral. Petrol.*, 160, 17-32.