Highlights & Breakthroughs contribution for American Mineralogist on "The effect of disequilibrium crystallization on Nb-Ta fractionation in pegmatites: constraints from crystallization experiments of tantalite-tapiolite" by Marieke Van Lichtervelde, Francois Holtz and Frank Melcher

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The metal tantalum (Ta) is becoming increasingly valued due to its use in modern technology such as mobile phones and tablets. The major application of this metal is in tantalum capacitors, which are have unrivaled performance-for-size and high reliability. Ta is typically hosted in columbite-group minerals (CGMs) which are also known colloquially as 'coltan' (columbite-tantalite) in Central Africa. Economic deposits of Ta are rare and commercial production of the metal comes from a limited number of countries, hence leading to classification of Ta as a "strategic resource" (Linnen et al. 2012). Significant production of Ta originates from war-torn regions of Central Africa, leading some countries - including the USA - to introduce legal requirements on tracing the origin of Ta-concentrates. These requirements have led to projects attempting to mineralogically and geochemically fingerprint CGMs from various deposits (Melcher et al. 2015).

The common feature of CGMs is compositional zonation expressed as Ta/(Ta+Nb) and Mn/(Mn+Fe) ratios. The origin of this zonation in CGM's is enigmatic as it records intense fractionation of chemically-similar elements on a very fine scale, and is one of the key characteristics which can be used for identification of the petrogenetic sources of the minerals. Mechanisms proposed to explain this phenomenon require the involvement of melts and fluids of contrasting compositions, both internally and externally-derived (e.g. Neiva et al. 2015).

The CGMs are usually found in pegmatites: granitic rocks containing very large crystals (London 2008). While the origin of pegmatites has been debated over the years, currently-accepted theory states that pegmatites crystallize from super-cooled granitic melts (London 2008). Instead of compositional characteristics, such as high volatile contents, the theory emphasizes the role of the thermal history of the intrusions. Pegmatites can be formed from a melt of ordinary granitic compositions without anything more than moderate water content. This theory explains giant crystal size, graphic-intergrowth of K-feldspar and quartz and mineralogical zonation of associated, evolved-intrusions. However the relationship between the crystallization of super-cooled melts and the textures of CGMs so far remains elusive.

Lichtervelde et al. (2018) demonstrate that complex zonation of natural CGMs could be reproduced by experiments at supersaturated conditions. They found that within a single experiment, composition of CGMs crystals could very widely, and to an amazing extent, they were able to reproduce the range of compositions observed in natural CGMs worldwide. The zonation of crystals is explained by super-saturation in the melt, coupled

with slow lattice diffusion post-crystallization. Highly-zoned crystals form in a closed system without evidence of liquation or fluid separation, thus suggesting that it could be an entirely magmatic phenomenon. While some of the compositions used in the experiments contain fluxing elements (i.e. F and P) it seems that these components were not essential for the development of zonation. In parallel with the model of London (2008) the emphasis has shifted to thermal history, rather than compositional characteristics of the melts. Another intriguing finding of the study is the observation in experimental CGMs of ordering-disordering phenomena: occurrence of Ta and Nb in Fe and Mn sites and vice versa. These compositional features might prove instrumental in constraining the conditions of formation of pegmatite minerals.

Equilibrium and disequilibrium could be closely related phenomena. Lichtervelde et al. (2018) found that while grains of CGMs could be intensively zoned, the compositional ranges are not random. Coexisting crystals of columbite-tantalite and tapiolite form tight clusters with end-member compositions which systematical shifts in experimental data and natural samples. This suggests that equilibrium was established between some zones of two minerals while other zones grew with metastable compositions.

While it is clear that new data present a significant advancement in understanding the crystallization of pegmatitic systems in the context of CGM, many related questions require further research. What is the role of ordering-disordering phenomena in compositional zonation and stability of CGM? How often do CGMs reach saturation in granites beyond their occurrence in rare metal-enriched pegmatites? What is the significance of these minerals for crustal scale Nb-Ta fractionation? Further studies are necessary and new experimental approaches and ideas may well pave the way for explaining well-known features of these important and enigmatic minerals.

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Lichtervelde, M.V., Holtz, F., and Melcher, F. (2018) The effect of disequilibrium crystallization on Nb-Ta fractionation in pegmatites: constraints from crystallization experiments of tantalite-tapiolite. American Mineralogist.

Linnen, R.L., Lichtervelde, M.V., and Černý, P. (2012) Granitic pegmatites as sources of strategic metals. Elements, 8, 275–280.

London, D. (2008) Pegmatites, 347 p. The Mineralogical Association of Canada.

Melcher, F., Graupner, T., Gäbler, H.-E., Sitnikova, M., Henjes-Kunst, F., Oberthür, T., Gerdes, A., and Dewaele, S. (2015) Tantalum–(niobium–tin) mineralisation in African pegmatites and rare metal granites: Constraints from Ta–Nb oxide mineralogy, geochemistry and U–Pb geochronology. Ore Geology Reviews, 64, 667–719.

88 Neiva, A.M.R., Gomes, C.L., and Silva, P.B. (2015) Two generations of zoned crystals of
89 columbite-group minerals from granitic aplite–pegmatite in the Gouveia area,
90 central Portugal. European Journal of Mineralogy, 27, 771–782.

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