

## REVIEW

of the PhD thesis “**Crystal Chemistry of Natural Layered Double Hydroxides**”

by Elena S. Zhitova

The PhD thesis by Elena Zhitova contains a lot of new data on crystal chemistry and mineralogy of quintinite,  $[\text{Mg}_4\text{Al}_2(\text{OH})_{12}][(\text{CO}_3)(\text{H}_2\text{O})_3]$ , represented in nature by several polytype modifications, three of which (*-2H-3c*, *-1M* and *-2H*) have been first discovered in this work. The crystallographic and crystal chemical data of all known natural layered double hydroxides (LDH) are summarized in one of the included publications. The major part of the thesis is devoted to X-ray crystallography (based mainly on single-crystal XRD data) and crystal chemistry of quintinites from Kovdor alkaline-ultrabasic complex, Kola peninsula, and Bazhenovskoe chrysotile asbestos deposit, Urals. The work on this complicated material is detailed and very accurate, even it can be considered as elegant. The author, based on the analysis of reciprocal diffraction patterns containing both sharp and diffuse reflections, has obtained well-substantiated results on site occupancies, cation ordering, stacking of layers and other structural features of quintinites. As a result, the polytype diversity of this mineral is described and the precise crystal chemical characterization of each polytype modification is given.

My critical comments are not numerous and not “hard”. (1) The thesis title has been formulated too widely whereas new, original data were obtained only for the quintinite series, a part of large LDH family. It would be better to use the title like “Crystal Chemistry and Polytypism of Quintinite(s)”. The object itself is very interesting and complicated and it seems sufficient for the successful presentation of thesis for a PhD degree in mineralogy and crystallography. (2) Unfortunately the comparative table of chemical data (even if EMPA, without  $\text{H}_2\text{O}$  and  $\text{CO}_2$  determination) of studied samples is absent in the thesis. These data are scattered in publications but not combined that hampers the comparison of samples in both the Mg:Al ratio and character and amounts of admixture cations (maybe these characteristics influence to polytypism?). The  $M^{2+}:M^{3+}$  ratio determines the mineral species: one of the most interesting mineralogical results obtained by Elena Zhitova is re-determination of well-known (and well-represented in worldwide mineral collections) specimens of “hydrotalcite” and “manasseite” ( $M^{2+}:M^{3+} = 3:1$ ) from Kovdor and Bazhenovskoe as different polytypes of quintinite ( $M^{2+}:M^{3+} = 2:1$ ). It was found from the EMPA and confirmed by the data on cation site occupancies. (3) For the mineralogical purposes it would be useful to summarize and discuss the X-ray powder data of different polytypes of quintinite as well as the differences between quintinites and members of the hydrotalcite-manasseite series in this aspect.

I have some statistics of observations seems representative (several dozens cases) and showing that, unlike quintinites typically forming relatively perfect, weakly divergent crystals, hydrotalcite-manasseite series minerals occur mainly as imperfect, significantly curved and/or split flakes and strongly corrugated mica-like aggregates. Probably the main cause of this difference is in the Mg:Al ratio in cationic layers (specific defects in the case of Mg:Al = 3:1?). Maybe now or in future Elena can explain this feature of the Mg-Al LDH minerals.

The thesis of Elena Zhitova is interesting, informative and well-organized. The obtained results are essentially novel and can be considered as significant contribution to mineralogy and crystal chemistry of LDH, large family of compounds important in both Earth sciences and modern chemical technologies. Elena Zhitova showed high qualification as crystallographer and crystal chemist successfully solving objectively complicated problems. Undoubtedly she deserves the PhD degree of Saint-Petersburg State University.

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