Cryptomelane formation from nanocristalline vernadite precursor.

Sylvain Grangeon, Bruno Lanson

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S. Grangeon[1] & B. Lanson[2,3]

[1]*BRGM, 3 avenue Claude Guillemin, 45060 Orléans cedex 2, France*
[2]*Univ. Grenoble Alpes, ISTerre, 38041 Grenoble, France*
[3]*CNRS, ISTerre, 38041 Grenoble, France*
E-mail: s.grangeon@brgm.fr

Vernadite is a nanocristalline and turbostratic phyllomanganate which is ubiquitous in the environment. Its layers, built of MnO_6 octahedra connected through their edges, contain vacancies and (or) isomorphic substitutions, both creating a layer charge deficit that can exceed 1 valence unit per layer octahedron. In addition, vernadite has a high affinity for many trace metals (e.g., Co, Ni and Zn) and frequently contain heterovalent Mn cations which provides this mineral with the capacity to oxidize redox-sensitive trace elements (e.g., As, Se) and organic pollutants. As a result of these exceptional properties, vernadite controls the fate of many trace elements in soils and sediments.

In the environment, vernadite is often found associated with tectomanganates ("tunnel"-like structures) such as cryptomelane, of which it is thought to be the precursor. A sound description of the vernadite-to-cryptomelane transformation, at the atomic scale, is mandatory to be able to understand and thus model the fate of metals initially present in vernadite structure. To contribute to a better understanding of this transformation, we have synthesized vernadite samples having various Mn^{4+}/Mn^{3+} ratios (and thus various layer charge) and we have monitored their transformation, under conditions analogous to those prevailing in soils (dry state and ambient conditions, in the dark) over a time scale of ~10 years [1-2]. Initial samples were characterized using a combination of chemistry, thermogravimetric analyses and powder X-ray diffraction. Samples structural formula ranged between $Na^{+}_{0.06}(H_2O)_{0.30}Mn^{3+}_{0.19}[Mn^{3+}_{0.12}Mn^{4+}_{0.71}Vac_{0.17}O_2]$ (where species under brackets form the layer – "Vac" stands for "layer vacancies", and species on the left are in the interlayer space) and $Na^{+}_{0.27}(H_2O)_{0.30}Mn^{3+}_{0.10}[Mn^{3+}_{0.10}Mn^{4+}_{0.76}Vac_{0.14}O_2]$. Transformation was monitored using high-energy X-ray scattering (with both Bragg-rod and pair distribution function formalisms) and transmission electron microscopy (TEM and STEM). With time, layer Mn^{3+} was found to migrate in the interlayer, probably to reduce strains induced by its Jahn-Teller distorted coordination sphere. When the abundance of interlayer Mn^{3+} reached ~0.3 per layer octahedron, interlayer Mn^{3+} from adjacent layers were found to share their hydration sphere and to form cryptomelane domains (Fig. 1).

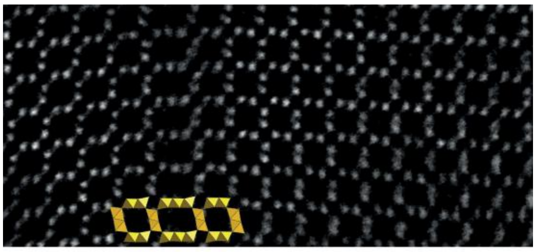

Figure 1. STEM observation of cryptomelane formed from vernadite precursor [2]. Bright spots are individual Mn atoms. Overlaid yellow octahedra at the bottom left of the image materialize MnO_6 octahedra.

This presentation will detail our recent contributions to the understanding of this transformation.

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References:

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[2] Grangeon S., Fernandez-Martinez A., Warmont F., Gloter A., Marty N., Poulain A. & Lanson B (2015) Cryptomelane formation from nanocrystalline vernadite precursor: a high energy X-ray scattering and transmission electron microscopy perspective on reaction mechanisms. *Geochemical Transactions*, **16**, 12.