

Cryptomelane formation from nanocrystalline vernadite precursor.

Sylvain Grangeon, Bruno Lanson

► **To cite this version:**

Sylvain Grangeon, Bruno Lanson. Cryptomelane formation from nanocrystalline vernadite precursor.. 14ème colloque du Groupe Français des Argiles, May 2016, Poitiers, France. <<http://gfa2016.sciencesconf.org/>>. <hal-01293226>

HAL Id: hal-01293226

<https://hal-brgm.archives-ouvertes.fr/hal-01293226>

Submitted on 24 Mar 2016

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Cryptomelane formation from nanocrystalline vernadite precursor.

S. Grangeon¹ & B. Lanson^{2,3}

¹BRGM, 3 avenue Claude Guillemin, 45060 Orléans cedex 2, France

²Univ. Grenoble Alpes, ISTERre, 38041 Grenoble, France

³CNRS, ISTERre, 38041 Grenoble, France

E-mail: s.grangeon@brgm.fr

Vernadite is a nanocrystalline and turbostratic phyllosilicate which is ubiquitous in the environment. Its layers, built of MnO₆ 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 Mn⁴⁺/Mn³⁺ 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}(H₂O)_{0.30}Mn³⁺_{0.19}[Mn³⁺_{0.12}Mn⁴⁺_{0.71}Vac_{0.17}O₂] (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}(H₂O)_{0.30}Mn³⁺_{0.10}[Mn³⁺_{0.10}Mn⁴⁺_{0.76}Vac_{0.14}O₂]. 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 Mn³⁺ was found to migrate in the interlayer, probably to reduce strains induced by its Jahn-Teller distorted coordination sphere. When the abundance of interlayer Mn³⁺ reached ~0.3 per layer octahedron, interlayer Mn³⁺ 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 MnO₆ octahedra.

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

Acknowledgements: S.G. acknowledges funding from the French National Research Agency (ANR; grant NACRE – ANR-14-CE01-0006).

References:

- [1] Grangeon S., Lanson B. & Lanson M. (2014) Solid-state transformation of nanocrystalline phyllosilicate into tectomanganate: influence of initial layer and interlayer structure. *Acta Crystallographica*, **B70**, 828-838.
- [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.