

Cancrinite-group minerals at non-ambient conditions: a model of the thermo-elastic and structure behavior

Lotti P.*¹, Gatta G.D.^{1,2}, Merlini M.¹, Cámara F.^{3,4}, Rotiroli N.¹, Comboni D.⁵ & Alvaro M.⁶

1. Dipartimento di Scienze della Terra - Università degli Studi di Milano. 2. CNR - Istituto di Cristallografia - Sede di Bari. 3. Dipartimento di Scienze della Terra - Università degli Studi di Torino. 4. CrisDi - Interdepartmental Centre for the Research and Development of Crystallography – Torino. 5. Dipartimento di Scienze della Terra e dell'Ambiente - Università di Pavia. 6. Dipartimento di Geoscienze – Università degli Studi di Padova.

Corresponding email: paolo.lotti@unimi.it

Keywords: cancrinite, high pressure, comparative elastic behavior.

The cancrinite-group of minerals comprises more than ten species sharing the [CAN]-topology of the tetrahedral framework. Their microporous structure has wide 12-ring channels, bound by columns of cages (*can* units). Besides the aluminosilicate composition of the framework (with the only exception of tiptopite, having instead Be and P), the minerals of the cancrinite group show a remarkable chemical variability concerning the extraframework population. Two subgroups can be identified according to the content of the *can* units: the first with Na-H₂O (cancrinite and vishnevite) and the second with Ca-Cl chains (balliranoite and davyne). The channels are stuffed by cations, anions and molecules. In Nature, cancrinite-group minerals occur in the late/hydrothermal stages of alkaline (SiO₂)-undersaturated magmatism and in related effusive or contact rocks. On the technological front, cancrinite-group compounds have been proposed as stable storage form for alkaline waste solutions, of which are common precipitation products.

We aimed to model the thermo-elastic behavior and the mechanisms of (*P,T*)-induced structure evolution of cancrinite-group minerals, focusing to the role played by the extraframework population. The study was restricted to the following (CO₃)-rich and (SO₄)-rich end-members: cancrinite $\{[(\text{Na,Ca})_6(\text{CO}_3)_{1.2-1.7}][\text{Na}_2(\text{H}_2\text{O})_2][\text{Al}_6\text{Si}_6\text{O}_{24}]\}$, vishnevite $\{[(\text{Na,Ca,K})_6(\text{SO}_4)][\text{Na}_2(\text{H}_2\text{O})_2][\text{Al}_6\text{Si}_6\text{O}_{24}]\}$, balliranoite $\{[(\text{Na,Ca})_6(\text{CO}_3)_{1.2-1.7}][\text{Ca}_2\text{Cl}_2][\text{Al}_6\text{Si}_6\text{O}_{24}]\}$ and davyne $\{[(\text{Na,Ca,K})_6((\text{SO}_4),\text{Cl})][\text{Ca}_2\text{Cl}_2][\text{Al}_6\text{Si}_6\text{O}_{24}]\}$. Their high-*P* and low-*T* (*T* < 293 K) behavior was investigated by *in situ* single crystal X-ray diffraction, using diamond-anvil cells and (N₂)-cryo-devices, respectively.

Though sharing a similar volume compressibility [i.e., ~ 0.021 GPa⁻¹, *K*₁₀ ~ 47 GPa] and thermal expansivity [i.e., ~ 4.0-4.5 · 10⁻⁵ K⁻¹], these minerals show a different anisotropic pattern, more pronounced in cancrinite and vishnevite. This behavior is governed by different deformation mechanisms, which reflect the different coordination environments of the cage population between the minerals of the two subgroups. In vishnevite, a *P*-induced re-organization of the channel population took place at *P* >= 3.5 GPa, suggesting that also the channel-constituents (and not only the cage one) can play an active role on the structure response at non-ambient conditions.

In addition, the high-*T* behavior of cancrinite was studied up to 823 K, by *in situ* single-crystal X-ray diffraction. At 748 K, a slow dehydration process takes place towards a (quasi)-anhydrous structure.

These are the first experimental findings aimed to provide a comparative thermo-elastic analysis of the CAN-group compounds, expanding the knowledge about the *P/T*-behavior of isotypic materials with open-framework structures.

PL, GDG and NR acknowledge the Italian Ministry of Education, MIUR-Project: "Futuro in Ricerca 2012 - ImPACT-RBFR12CLQD". MA acknowledges the ERC starting grant N. 307322 to FN.