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# Cancrinite-group minerals behavior at non-ambient conditions

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Cancrinite-group minerals occur in the late stages of alkaline ($SiO_2$)-undersaturated magmatism and in related effusive or contact rocks. So far only few studies have been devoted to the description of the thermo-elastic behavior, phase-stability and $P/T$-structure evolution (at the atomic scale) of this mineral group.

Cancrinite-group minerals have an open-framework structure characterized by the [CAN]-topology. The [CAN]-framework shows large 12-ring channels, parallel to the $c$ crystallographic axis, bound by columns of cages, the so-called *can* units. While very limited chemical variation is observed in the framework composition (the composition is almost always $[Si_6Al_6O_{24}]$) a remarkable chemical variability is reported for the extraframework components in the cancrinite-group minerals. Two subgroups can be identified according to the extraframework content of the *can* units: the cancrinite- and the davyne-subgroups, showing Na-$H_2O$ and Ca-Cl chains, respectively. The channels are stuffed by cations, anions and molecules.

We aimed to model the thermo-elastic behavior and the mechanisms of the ($P$,$T$)-induced structure evolution of cancrinite-group minerals, with special interest on the role played by the extraframework population. The study was restricted to the following ($CO_3$)-rich and ($SO_4$)-rich end-members: cancrinite *sensu stricto* $\{[(Na,Ca)_6(CO_3)_{1.2-1.7}][Na_2(H_2O)_2][Al_6Si_6O_{24}]\}$, vishnevite $\{[(Na,Ca,K)_6(SO_4)][Na_2(H_2O)_2][Al_6Si_6O_{24}]\}$, balliranoite $\{[(Na,Ca)_6(CO_3)_{1.2-1.7}][Ca_2Cl_2][Al_6Si_6O_{24}]\}$ and davyne $\{[(Na,Ca,K)_6((SO_4),Cl)][Ca_2Cl_2][Al_6Si_6O_{24}]\}$. Their high-$P$ and low-$T$ ($T < 293$ K) behavior was investigated by means of *in-situ* single-crystal X-ray diffraction, using diamond-anvil cells and ($N_2$)-cryosystems, respectively. The high-$T$ behavior of cancrinite has also been studied by means of *in-situ* single-crystal X-ray diffraction with a resistive heater.

Cancrinite minerals share a similar volume compressibility and thermal expansivity at ambient conditions (cancrinite has $K_{V0}$ = 45(2) GPa and $\alpha_{V,293K}$ = 4.88(8)$\cdot 10^{-5}$ $K^{-1}$; vishnevite has $K_{V0}$ = 49(2) GPa; balliranoite has $K_{V0}$ = 48(3) GPa and $\alpha_{V,293K}$ = 4.6(4)$\cdot 10^{-5}$ $K^{-1}$; davyne has $K_{V0}$ = 46.5(11) GPa and $\alpha_{V,293K}$ = 4.2(4)$\cdot 10^{-5}$ $K^{-1}$). However, these minerals show different thermo-elastic anisotropy schemes, more pronounced in the cancrinite-subgroup minerals. This behavior is governed by different deformation mechanisms of the crystal structure, which likely reflect the different coordination environments of the cage-cations between the minerals of the cancrinite- and davyne-subgroups ($i.e.$ $Na^+$ and $Ca^{2+}$, respectively). In addition, a $P$-induced re-organization of the extraframework population is observed, in vishnevite, at $P \geq 3.5$ GPa, suggesting that the channel-constituents can also affect the elastic and structural behavior and the phase stability of these minerals at non-ambient conditions.

Besides common features likely ascribable to the [CAN]-topology, the nature of the extraframework population appears to control significantly the ($P$,$T$)-induced structure evolution and thermo-elastic behavior of the cancrinite-group compounds.

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