Experimental report

05/03/2024

Proposal: **5-11-450**

Council: 4/2023

Title: On the labyrinthine structure of the zeolite paulingite, $(Ca,K,Na,Ba)10(Si,Al)42O84\cdot34H2O$

Research area: Other...

This proposal is a new proposal

Main proposer: **Giacomo Diego GATTA**

Experimental team:

Local contacts: Oscar Ramon FABELO ROSA
Laura CANADILLAS DELGADO

Samples: Paulingite (mineral) / $(Ca,K,Na,Ba)10(Si,Al)42O84\cdot34H2O$

Instrument	Requested days	Allocated days	From	To
D19	7	6	25/08/2023	01/09/2023
D9	12	5	17/11/2023	24/11/2023
ORIENTEXPRESS	1	1		

Abstract:

Paulingite, $(K,Na,Ca0.5,Ba0.5)10(Al10Si32O84)\cdot nH2O$ (with n = 27¿44, Z = 16), is a chemically complex zeolite mineral. Despite the geochemical and industrial interest on this mineral (or its synthetic counterpart), only a few studies were devoted to it. Its structure was solved by single-crystal X-ray diffraction (s.g. Im-3m, a=34.8 Å), and is considered the most complex one among the zeolitic frameworks. The main limit of the previous X-ray studies is that the H sites in paulingite structure were never located; therefore, its H-bonding network is completely unknown. The aim of the present study is a reinvestigation of the crystal structure/chemistry of paulingite by single-crystal neutron diffraction (20 K) and other techniques, in order to provide: a) an unambiguous location of all the proton sites and the description of the complex H-bonding network; b) the anisotropic displacement parameters of all the atomic sites, including the H-sites; c) a description of the crystal chemistry of this zeolite based on modern analytical protocols; d) its thermal behaviour along with the mechanisms, at the atomic scale, which govern any potential structure transformations.

Experimental Report - Proposal 5-11-450
On the labyrinthine structure of the zeolite paulingite, $(Ca,K,Na,Ba)_{10}(Si,Al)_{42}O_{84}\cdot 34H_2O$

Paulingite is a zeolite found in vesicles in basalt flows, with ideal chemical formula: $(K,Na,Ca_{0.5},Ba_{0.5})_{10}(Al_{10}Si_{32}O_{84})\cdot nH_2O$ (with n = 27–44, Z = 16). In nature, K- and Ca-rich paulingite samples have been found. The crystal structure of paulingite was solved and refined by Gordon et al. (1966) in the space group *Im*-3*m*, and its tetrahedral framework was designated with the IZA-code ‘‘PAU’’. A structural re-investigation was carried out later by Lengauer et al. (1997). The tetrahedral framework topology of paulingite is considered the most complex one among the zeolitic framework types. The PAU framework type (topological symmetry: *Im*-3*m*, with idealized a = 34.838 Å) is composed by the secondary building units 4 and 8, forming a connecting double 8-ring (D8R), which links alternatively the α-cage (truncated cuboctahedron) and the γ-cage (gmelinite-type cage). The principal channel systems in PAU framework are represented by two parallel (and independent) sets of a three-dimensional channel systems (8-membered ring channels) oriented along the principal axes and shifted ½, ½, ½ against each other. Along [111], a further channel system exists. A view of the complex tetrahedral framework of paulingite is shown in Fig. 1. Having available single-crystals of various mm-size (already checked by single-crystal X-ray diffraction in our home lab), we ask for D19 (or D9) instrument to collect a complete data set at low-*T* (20 K) to reduce the ADP’s and better locate light atoms. We expect to provide:

a) an unambiguous location of all the proton sites and the description of the complex H-bonding network expected in paulingite structure, alongside its low-*T* induced rearrangement;

b) the anisotropic displacement parameters of all the atomic sites, including the H-sites;

c) a description of the crystal chemistry of this natural zeolite based on modern analytical protocols, with a particular attention to the potential framework and extraframework substituents;

The single-crystal neutron data collection was performed at 20 K on D19 diffractometer. The unit-cell parameters proved a metrically cubic lattice (with a= 35.108(1)Å), with reflection conditions compatible to the *Im*-3*m* space group. A total number of 56618 reflections were collected ($-36 \leq h \leq 35$, $-35 \leq k \leq 38$, $-28 \leq l \leq 41$, Max. 2-theta = 120.97°, lambda 1.459 Å), out of which 3639 were unique with R(int) = 0.124 and R(sigma) = 0.0458. The structure refinement is in progress.

References

Gatta G.D., Scheidl K.S., Pippinger T., Skála R., Lee Y., Miletich R. (2015) *Micropor. Mesopor. Mater.*, 206, 34–41.

Gordon K.E., Samson S., Kamb W.B. (1966) *Science*, 154, 1004–1007.

Lengauer C.L., Giester G., Tillmanns E. (1997) *Mineral. Mag.*, 61, 591–606.

Figure 1. Skeletal (*left side*) and polyhedral (*right side*) representation of the PAU framework type, and (*bottom*) 8-membered ring channel parallel to <100> viewed perpendicular to the channel axis (after Gatta *et al.* 2015).