Experimental report

04/03/2021

Proposal: **5-24-648** **Council:** 10/2019

Title: Verneite (Na2Ca3Al2F14), a pinholefor helium

Research area: Physics

This proposal is a new proposal

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Experimental team: Stefan KLOTZ

Local contacts: Thomas HANSEN

Samples: Na2Ca3Al2F14

Instrument	Requested days	Allocated days	From	To
D20	3	3	19/02/2021	22/02/2021

Abstract:

Verneite (Na2Ca3Al2F14) is a recently discovered aluminofluoride mineral, though the synthetic compound is widely known as "NaCaAlF". We have recently studied its behaviour under pressure and found clear evidence that helium can enter into its structure, but no other gas or molecule. In this proposal we wish to carry out high pressure neutron diffraction measurements to 10 GPa in order to locate helium inside verneite, determine the structural pressure dependence of Na2Ca3Al2F14:He and see if the incorporated helium "freezes" at low temperature. Neutron diffraction is ideal for this purpose and ILL is the only place where such an experiment can be carried out.

Experimental report “Verneite ($Na_2Ca_3A_2lF_{14}$), a pinhole for helium (proposal nr. 5-24-648)

Instrument: D20

Date: 19.-22.2. 2021

Experimental team: Stefan Klotz, Thomas Hansen

Verneite ($Na_2Ca_3Al_2F_{14}$, $I2_13$, Z=4, a=10.26 Å) is a mineral which was recently discovered in the craters of several volcanos [1]. Before its discovery in nature, synthetic Verneite [2] was well known in the diffraction community under the name “NaCaAlF” and is worldwide used as a standard for calibrating diffractometers.

Our recent interest in this compound is related to the possibility to use it as a pressure calibrant for certain inelastic neutron scattering measurements. In-house x-ray data revealed an unexpected and interesting anomaly: Whereas the compression of verneite is entirely regular using the standard methanol-ethanol (ME) mixture as a pressure transmitting fluid, the V(P) dependence shows significant anomalies when the sample is compressed with helium: The unit cell volume is up to ~ 1% larger than expected, the V(P) relation does not follow the same dependence as with methanol-ethanol, and there are kinetic effects, i.e. the unit cell volume increases slowly over time after pressure increase.

The purpose of the D20 experiment was to study the structural pressure dependence of verneite by neutron diffraction, using Helium as pressure transmitting fluid. Neutron diffraction is considerably more sensitive than our x-ray diffraction measurements and will allow precise determination of the internal atomic coordinates, and compare it to our previous data obtained by the same technique using the ME mixture at the Japanese neutron source MLF. It might as well be capable of detecting helium inside the crystal structure, if He atoms are sufficiently ordered.

Verneite was loaded into the PE press together with compressed (2 kbar) helium using the ILL gas loader. Patterns were collected at approximately 5.5, 7, 8 (upstroke), 3.5 and 0.8 (downstroke) GPa. At 5.5 GPa, the sample was cooled to 4.5 K to investigate the temperature dependence and look for possible ordering of He inside verneite (Fig. 1).

Figure 2 shows the refined atomic coordinates and compares it to the data obtained at PLANET (MLF) by neutron diffraction using the ME mixture. At ambient conditions the data sets are remarkably consistent, but under pressure at least two atomic coordinates (F2) show a significantly different behaviour. The compression with ME deforms the AlF_6 octahedra whereas the use of He results in a homothetic compression of these structural units. The pattern at 4.5 K do not reveal any additional reflections from which we conclude that He remains disordered inside verneite. Rietveld simulations with He placed at sites with sufficient space (the 12b site (½½¼)) show that 4 atoms per unit cell and assuming a thermal displacement of 0.5 A has already a barely detectable effect on in the intensities. Note that we can see the helium outside the crystals only once it is solid (crystalline), i.e. not in its fluid state.

To resume, the experiment was a full success and gave considerable evidence for He-insertion into the verneite structure. Also, the experiment demonstrated for the first time the successful use of helium as a pressure transmitting medium, a method which could become standard in the future.

[1] D. Balič-Zunik, A Garavelli, D. Pinto and D. Mitolo, *Minerals* **8**, 553 (2018).
[2] G. Courbion and G. Ferey, J. Solid State Chemistry **76**, 426 (1988).

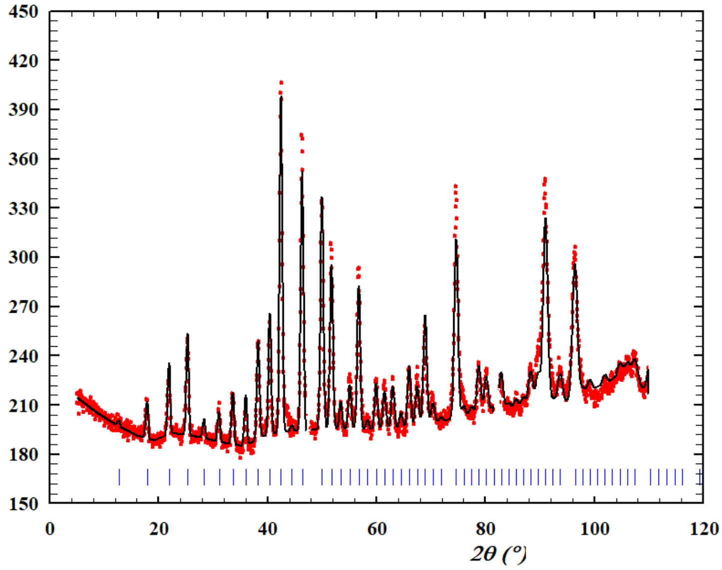

Figure 1. Diffraction pattern collected at 4.5 K and 5 GPa (3 h). Two sharp reflections at 47° and 81° from solid helium were excluded from the refinements.

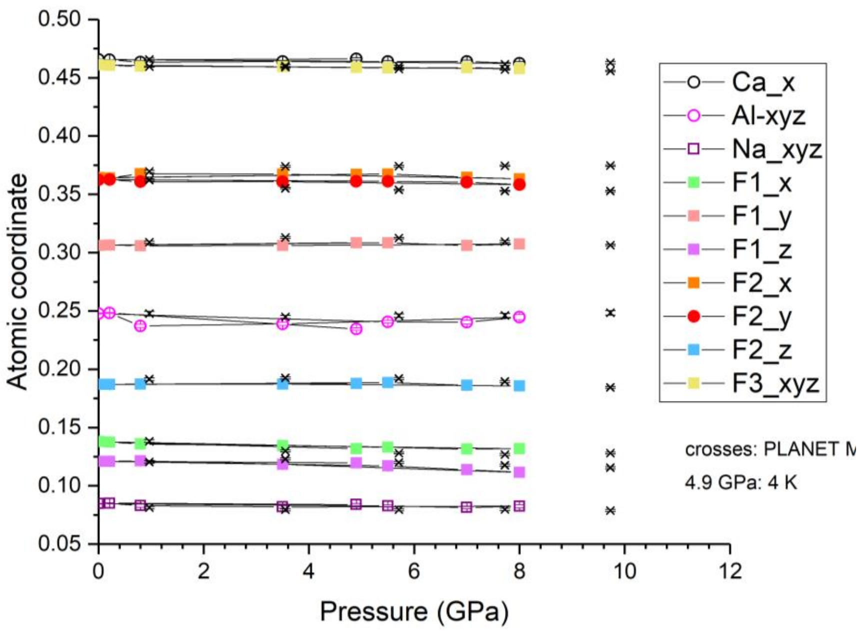

Figure 2. Pressure dependence of atomic coordinates of verneite. Coloured symbols denote D20 data obtained with helium as pressure transmitting medium. The crosses are data obtained at the Japanese neutrons source MLF using methanol-ethanol as PTM. Statistical error bars (esd) are smaller than the symbols. Note the difference in F2_x and F2_y between the data sets.

Edition January 2001