



Kruijenite, $\text{Ca}_4\text{Al}_4(\text{SO}_4)\text{F}_2(\text{OH})_{16}\cdot 2\text{H}_2\text{O}$, a new mineral with microporous structure from the Eifel paleovolcanic region, Germany

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Abstract

The new mineral kruijenite, ideally $\text{Ca}_4\text{Al}_4(\text{SO}_4)\text{F}_2(\text{OH})_{16}\cdot 2\text{H}_2\text{O}$, was found in a calcic xenolith from tephra of the Feuerberg paleovolcano situated near Daun, Eifel paleovolcanic region, Rhineland-Palatinate, Germany. It is associated with fluorite, calcite, aragonite, cuspidine, magnesioferrite, hematite, sharyginite, harmunite, and an insufficiently investigated hydrous Ca-Mg-Al silicate. Kruijenite occurs as pale greenish-yellow to colourless long prismatic tetragonal crystals up to 0.1 mm × 1 mm in cavities typically combined in radiating or random aggregates. The mineral is brittle, with Mohs' hardness of 3; D_{calc} is 2.573 g/cm³. The IR spectrum is given. Kruijenite is optically uniaxial (–), $\omega = 1.576(3)$, $\epsilon = 1.561(3)$. The chemical composition (wavelength dispersive spectrometer Oxford INCA Wave 700 EPMA analyser, H_2O calculated from structural data) is: CaO 32.38 wt%, Al_2O_3 27.75 wt%, Cr_2O_3 1.45 wt%, SO_3 8.09 wt%, F 5.84 wt%, H_2O 25.64 wt%, $-\text{O}=\text{F}$ –2.46 wt%, total 98.69 wt%. The empirical formula is $\text{Ca}_{4.00}(\text{Al}_{3.77}\text{Cr}_{0.13})_{\Sigma 3.90}(\text{SO}_4)_{0.70}\text{F}_{2.13}(\text{OH})_{16.17}\cdot 1.79\text{H}_2\text{O}$ ($Z=2$). Kruijenite is tetragonal, space group $P4/ncc$, $a = 12.9299(4)$ Å, $c = 5.2791(3)$ Å, $V = 882.57(6)$ Å³, $Z = 2$. The crystal structure was solved and refined to $R = 0.121$. Kruijenite represents a novel structure type. Its structure is based on the microporous pseudo-framework built by $\text{Al}(\text{OH})_6$ octahedra and $\text{CaF}_2(\text{OH})_6$ polyhedra. The strongest reflections of the powder X-ray diffraction pattern [d (Å) (hkl)] are: 9.12 Å (77%) (110), 4.565 Å (100%) (220), 4.084 Å (50%) (310), 2.964 Å (74%) (321), 2.694 Å (27%) (411), 2.321 Å (24%) (431), 2.284 Å (29%) (511), 2.217 Å (22%) (321, 530), 1.971 Å (40%) (611). The mineral is named in honor of the Dutch collector of Eifel minerals Fred Kruijen (born in 1956).

Keywords Kruijenite · New mineral · Hydrous calcium aluminium fluorosulfate · Microporous crystal structure · Calcic xenolith · Feuerberg quarry · Eifel

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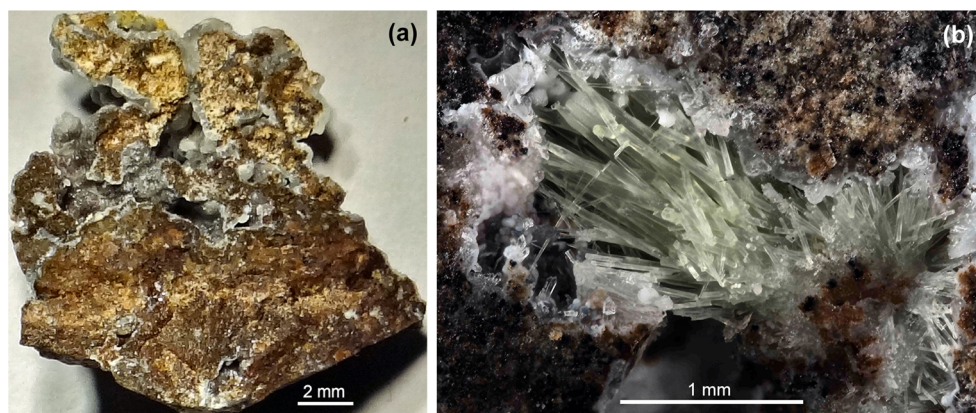
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Introduction

Metasomatic assemblages formed as a result of the interaction of alkaline magma with xenoliths of different rocks are very diverse in their mineral composition. This feature is due to significant variations in local conditions of mineral formation including spatial and temporal variations of temperature and different patterns of transport of volatile components. One of the most interesting objects in this respect is the Eifel paleovolcanic region in Germany. Alkaline basalts and pyroclastic rocks with inclusions of sedimentary, as well as metamorphic silicate and carbonate rocks are uncovered there by numerous quarries (Hentschel 1987, Baumgärtl and Cruse 2007, Meyer 2013). Most studies of the mineralogy of xenoliths from alkaline effusive rocks of Eifel were carried out on material from the Bellerberg volcano situated near Ettringen, Rhineland-Palatinate, Germany.

Fig. 1 White-light images of samples. **a** Fragment of the xenolith in which kruijenite was discovered. Image courtesy Cor Kokke. **b** Aggregate of prismatic crystals of kruijenite. Image courtesy Fred Kruijen



Our studies of a number of metasomatically altered xenoliths from the Feuerberg paleovolcano situated in the Hinterweiler municipality, 7 km north of Daun town in West Eifel show that their chemical composition differs significantly from that of most xenoliths from other places of the Eifel region. The quarry uncovers basaltic lapilli tuffs and dykes composed of olivine-melilite nephelinite with xenoliths of Devonian limestones. The main specific feature of the investigated xenoliths from Feuerberg is high F content fluorite and cuspidine which are the main fluorine-concentrating minerals.

This paper describes the new fluorine-bearing mineral from Feuerberg, **kruijenite** (the name is pronounced like “kru:yenait”), which was named in honor of the Dutch amateur collector of Eifel minerals Fred Kruijen (b. 1956), an author of numerous articles in popular scientific periodicals. In addition, Fred Kruijen is an outstanding micro-mineral photographer who made a lot of high-quality photos of Eifel minerals.

The mineral and its name have been approved by the IMA CNMNC (IMA 2018–057). The type specimen is deposited in the collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia, with the registration number 5233/1.

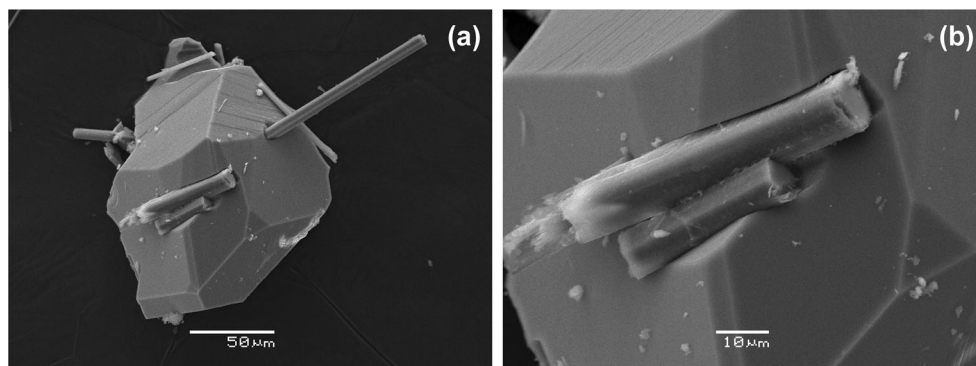
Samples and experimental

The material containing kruijenite (fragments of an altered calcic xenolith from tephra whose initial size was about 20 cm across, see Fig. 1a) was collected in 2016 by the Dutch collector Cor Kokke. The xenolith contains cavities incrustated by calcite.

The minerals composing the xenolith are fluorite, calcite, aragonite, cuspidine, magnesioferrite, hematite, sharyginite, harmunite, and an insufficiently investigated hydrous Ca-Mg-Al silicate (Figs. 1b, 2, 3). These minerals have metasomatic origin and are products of pyro-metamorphic and further hydrothermal alteration of a calcic xenolith under exposure of volatile components of magma. Kruijenite is one of the latest minerals in this association. Based on morphological features, including idiomorphic and xenomorphic forms of adjacent individuals, the following sequence of mineral formation was determined: sharyginite + harmunite → magnesioferrite → fluorite → cuspidine → calcite + kruijenite + hydrous Ca-Mg-Al silicate.

In order to obtain infrared (IR) absorption spectrum (Fig. 4), powdered sample of kruijenite was mixed with dried KBr, pelletized, and analyzed using an ALPHA FTIR spectrometer (Bruker Optics) with a resolution of

Fig. 2 Secondary electron images. **a** Prismatic kruijenite crystals atop a calcite crystal. **b** Same sample, detail enlargement



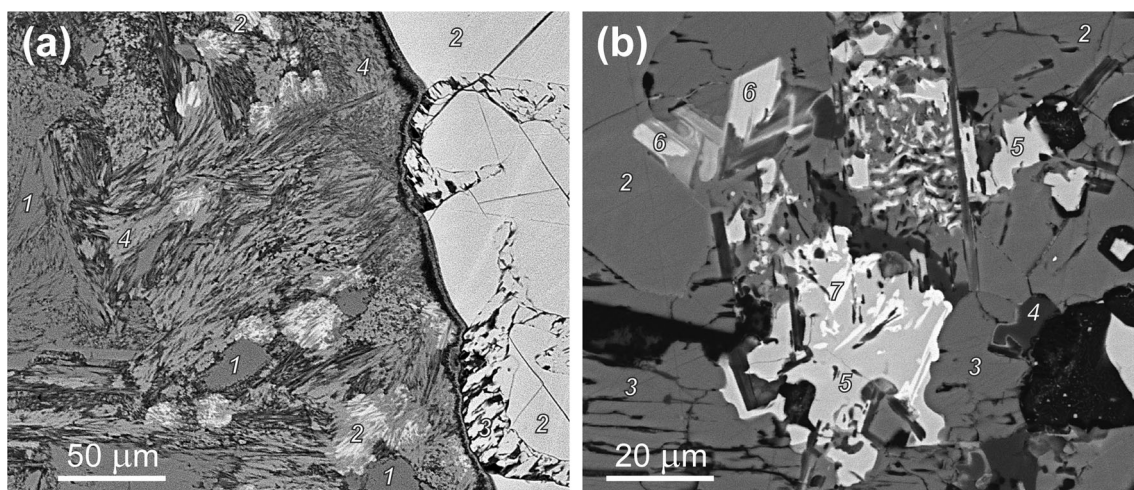


Fig. 3 Backscattered electron (BSE) images. Note that the two images were obtained with different contrast and brightness settings; therefore BSE intensities cannot be directly compared. **a** Mineral assemblage

containing kruijenite. **b** Minerals associated with kruijenite. Symbols used: 1 – kruijenite, 2 – fluorite, 3 – cuspidine, 4 – calcite, 5 – magnesioferrite, 6 – sharyginite, 7 – harmunite

4 cm^{-1} and 16 scans. The IR spectrum of a pellet of pure KBr was used as a reference.

Eighteen spot analyses were carried out using a digital scanning electron microscope Tescan VEGA-II XMU equipped with a wavelength dispersive Oxford INCA Wave 700 spectrometer with the accelerating voltage of 20 kV, electron beam current of 20 nA, and beam diameter of 3 μm . The reference and calibrating materials and lines analyzed are: albite ($\text{K}\alpha$) for Al, Cr metal ($\text{K}\alpha$) for Cr, BaSO_4 ($\text{K}\alpha$) for S and CaF_2 ($\text{K}\alpha$) for F. Counting time was 40 s for each component. Data processing has been carried out using ZAF correction procedure and least-squares method. CO_2 was not determined because bands of CO_3^{2-} groups are absent in the IR spectrum. H_2O was calculated from structural data.

Powder X-ray diffraction data were collected using a Rigaku R-Axis Rapid II diffractometer (curved image plate detector, Debye-Scherrer geometry, $d = 127.4\text{ mm}$, $\text{CoK}\alpha$ radiation, 40 kV, 15 mA). Single-crystal X-ray diffraction study of kruijenite was carried out using a four-circle Xcalibur S diffractometer equipped with a CCD detector at room temperature. Crystal data, data collection information and structure refinement details are given in Table 1. Full sphere of three-dimensional data was collected. The data were corrected for Lorentz and polarization effects. Crystal structure model was obtained by direct methods and refined based on 498 unique reflections with $I > 2\sigma(I)$ with the use of SHELX software package (Sheldrick 2008).

Fig. 4 Infrared absorption spectrum of kruijenite

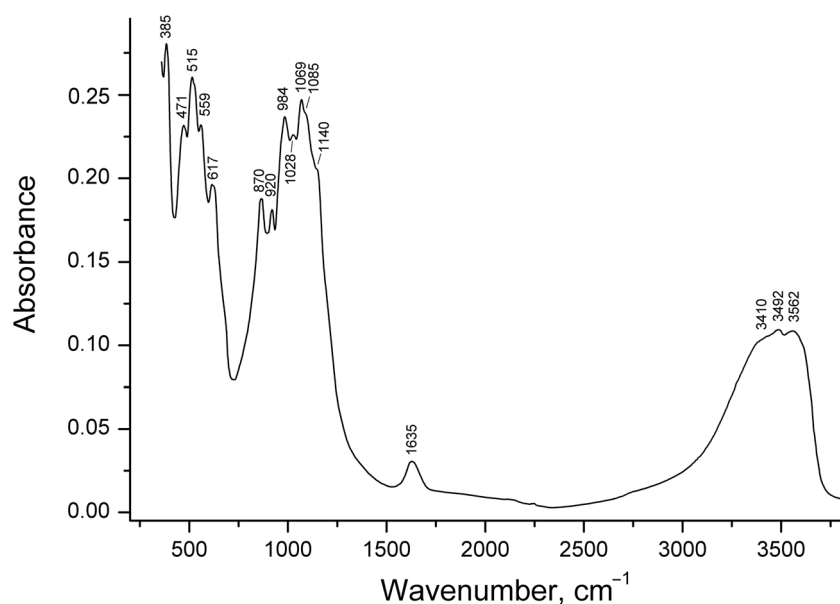


Table 1 Crystal data, data collection information and structure refinement details for kruijenite

Formula	Ca ₄ Al ₄ (SO ₄) _{0.72} F ₂ (OH _{15.44} O _{0.56})·2H ₂ O
Formula weight	1366.00
Temperature (K)	293(2)
Radiation and wavelength (Å)	MoK α ; 0.71073
Crystal system, space group, <i>Z</i>	Tetragonal, <i>P4/ncc</i> , 2
Unit cell dimensions (Å)	<i>a</i> = 12.9299(4), <i>c</i> = 5.2791(3)
<i>V</i> (Å ³)	882.57(6)
Absorption coefficient μ (mm ⁻¹)	1.64
<i>F</i> ₀₀₀	696
Crystal size (mm)	0.02 × 0.04 × 0.22
Diffractometer	Xcalibur S CCD
θ range for data collection (°) / Collection mode	3.15–28.27 / full sphere
Index ranges	–17 ≤ <i>h</i> ≤ 17, –17 ≤ <i>k</i> ≤ 17, –7 ≤ <i>l</i> ≤ 7
Reflections collected	12,634
Independent reflections	552 (<i>R</i> _{int} = 0.1707)
Independent reflections with <i>I</i> > 2 σ (<i>I</i>)	498
Data reduction	CrysAlisPro, Agilent Technologies, v. 1.171.37.35 (Agilent Technologies, 2014)
Absorption correction	multi-scan Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
Structure solution	direct methods
Refinement method	full-matrix least-squares on <i>F</i> ²
Number of refined parameters	51
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.1206, <i>wR</i> 2 = 0.2283
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1321, <i>wR</i> 2 = 0.2342
Goodness of fit	1.399
Largest diff. Peak and hole (e/Å ³)	0.77 and –0.60

Results and discussion

Physical properties

Kruijenite forms pale greenish-yellow to colourless long prismatic tetragonal crystals up to 0.1 mm × 1 mm. They occur in cavities and typically combined in radiating or random clusters up to 2 mm in size, as well as dense aggregates intergrown with calcite.

The new mineral is brittle, with Mohs' hardness of 3. Cleavage is not observed. Density could not be measured because of small sizes of crystals and monomineral

Table 3 Powder X-ray diffraction data for kruijenite

<i>I</i> _{obs}	<i>d</i> _{obs} (Å)	<i>I</i> _{calc} [*]	<i>d</i> _{calc} ^{**} (Å)	<i>h k l</i>
77	9.12	100	9.143	110
9	6.45	10	6.465	200
100	4.565	76	4.571	220
50	4.084	35	4.089	310
1	3.898	1	3.899	211
1	3.232	0.5	3.232	311
1	3.045	0.5	3.048	330
74	2.964	77	2.966	321
27	2.694	28	2.696	411
3	2.637	9	2.640	002
3	2.584	8	2.586	102
20	2.534	7, 16	2.536, 2.536	112, 421
7	2.400	16	2.401	212
24	2.321	22	2.322	431
29	2.284	28	2.286	511
22	2.217	21, 8	2.218, 2.217	312, 530
3	2.154	2	2.155	600
3	2.124	5	2.126	322
9	2.044	8, 5	2.045, 2.044	402, 531
1	2.019	1	2.019	412
40	1.971	47	1.972	611
8	1.949	13	1.949	422
3	1.906	3	1.906	621
2	1.846	3	1.847	432
19	1.828	13, 13	1.829, 1.829	512, 550
2	1.810	1	1.811	631
12	1.793	12	1.793	640
1	1.776	1	1.776	522
7	1.727	7, 4	1.728, 1.728	442, 711
8	1.697	4, 6	1.698, 1.698	532, 641
19	1.683	0.5, 22	1.683, 1.683	213, 721
4	1.669	7	1.669	602
1	1.616	2, 0.5	1.616, 1.616	313, 622
8	1.580	26, 1	1.580, 1.580	323, 651
5	1.568	5	1.568	820
7	1.534	15, 4	1.535, 1.535	413, 741
9	1.503	1, 15, 1	1.503, 1.503, 1.503	423, 712, 821
1	1.483	0.5	1.483	642
12	1.455	2, 16	1.455, 1.455	433, 831
2	1.428	2, 1	1.428, 1.428	732, 910
2	1.356	3, 0.5	1.355, 1.255	613, 761
2	1.320	1, 2, 1	1.320, 1.320, 1.320	004, 662, 931
4	1.306	2, 3, 4	1.306, 1.306, 1.306	114, 752, 770
4	1.293	7	1.293	860
2	1.274	3	1.274	941

*For the calculated pattern, only reflections with intensities ≥ 0.5 are given; **for the unit-cell parameters calculated from single-crystal data

Table 2 Analytical data for kruijenite (mean of 18 spot analyses)

Constituent	Mean (wt%)	Range (wt%)	Standard deviation (wt%)
CaO	32.38	31.36–33.23	0.43
Al ₂ O ₃	27.75	27.06–28.86	0.43
Cr ₂ O ₃	1.45	0.67–2.06	0.285
SO ₃	8.09	7.54–8.58	0.28
F	5.84	4.63–7.29	0.85
H ₂ O*	25.64		
–O=F	–2.46		
Total	98.69		

*Calculated from structural data

aggregates. Density using the empirical formula and single-crystal X-ray diffraction data is 2.573 g/cm³. Kruijenite is non-fluorescent under the UV radiation.

Under plain polarized light ($\lambda = 589$ nm) kruijenite is uniaxial (–), $\omega = 1.576(3)$, $\epsilon = 1.561(3)$. Under the microscope kruijenite is colourless, non-pleochroic.

Infrared spectroscopy

The absorption bands in the IR spectrum of kruijenite (cm⁻¹; s – strong band, sh – shoulder) and their

Table 4 Coordinates, equivalent displacement parameters (U_{eq} , in \AA^2) of atoms, site occupancy factors (s.o.f.) and site multiplicities (Q) for kruijenite

Site	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}	s.o.f.	Q and Wyckoff symbol
Ca	0.85108(9)	0.35108(9)	0.75	0.0181(4)	1	8 <i>f</i>
Al	0.04210(13)	−0.04210(13)	0.25	0.0140(5)	1	8 <i>f</i>
O(1)	0.6778(3)	0.4470(3)	0.6334(8)	0.0137(10)	1	16 <i>g</i>
H(1)	0.704(2)	0.5147(10)	0.663(11)	0.03(2)*	1	16 <i>g</i>
O(2)	0.0168(3)	0.0869(3)	0.4272(8)	0.0130(9)	1	16 <i>g</i>
H(2)	0.0688(11)	0.1367(14)	0.393(11)	0.04(3)*	1	16 <i>g</i>
F	0.25	0.75	0.5	0.0168(14)	1	4 <i>b</i>
S(1)	0.25	0.25	−0.291(14)	0.093(9)**	0.18	4 <i>c</i>
S(2)	0.25	0.25	−0.335(15)	0.093(9)**	0.18	4 <i>c</i>
OS	0.1577(18)	0.245(2)	−0.065(5)	0.087(8)*	0.36	16 <i>g</i>
Ow	0.159(3)	0.252(4)	−0.305(8)	0.098(12)*	0.25	16 <i>g</i>

* U_{iso} ; **anisotropic displacement parameters of the split sites S(1) and S(2) were restrained to be equal. The positions of H atoms were found from difference Fourier synthesis and O–H distances were softly restrained at 0.95(1) \AA

assignments are: 3562, 3492, 3410sh (O–H stretching vibrations of H_2O molecules and OH groups), 1635 (bending vibrations of H_2O molecules), 1140sh, 1085sh, 1069s [$\nu_3(F_2)$ – asymmetric stretching vibrations of SO_4^{2-} anions], 1028, 984 s [$\nu_1(A_1)$ – symmetric stretching vibrations of SO_4^{2-} anions], 920, 870 (Al···O–H and Ca···O–H bending vibrations), 617 [$\nu_4(F_2)$ – bending vibrations of SO_4^{2-} anions], 559, 515 s (Al–O stretching vibrations), 471 [$\nu_2(E)$ – bending mode of SO_4^{2-} anions], 385 s (Ca–O stretching vibrations). Very weak bands in the range from 2000 to 2400 cm^{-1} correspond to overtones and combination modes.

The presence in the IR spectrum of a single band of nondegenerate H–O–H bending vibrations (at 1635 cm^{-1}) indicates the presence of only one kind of water molecules. High intensities of the bands of nondegenerate symmetric stretching vibrations of SO_4^{2-} anions (at 984 and 1028 cm^{-1}) indicate the presence of two kinds of strongly distorted SO_4 tetrahedra, in accordance with the structural data (see below).

Characteristic bands of BO_3^{3-} , CO_3^{2-} , and NO_3^- are absent in the IR spectrum of kruijenite. The spectrum is unique and can be used for the reliable identification of this mineral.

Table 5 Selected interatomic distances (\AA) in the structure of kruijenite*

Ca – F	$2.2711(14) \times 2$	Al – O(1)	$1.865(4) \times 2$
– O(1)	$2.403(4) \times 2$	– O(2)	$1.940(4) \times 2$
– O(2)	$2.472(4) \times 2$	– O(2)	$1.954(4) \times 2$
– O(1)	$2.634(4) \times 2$		
S(1) – OS	$1.69(6) \times 2$	S(2) – OS	$1.70(6) \times 2$
– OS	$1.88(6) \times 2$	– OS	$1.86(7) \times 2$

* The distances for SO_4 tetrahedra are given for the averaged S and O sites. We assume that the S(1), S(2) and OS sites are split further along the *c* axis thus giving more reliable S–OS distances

Chemical data

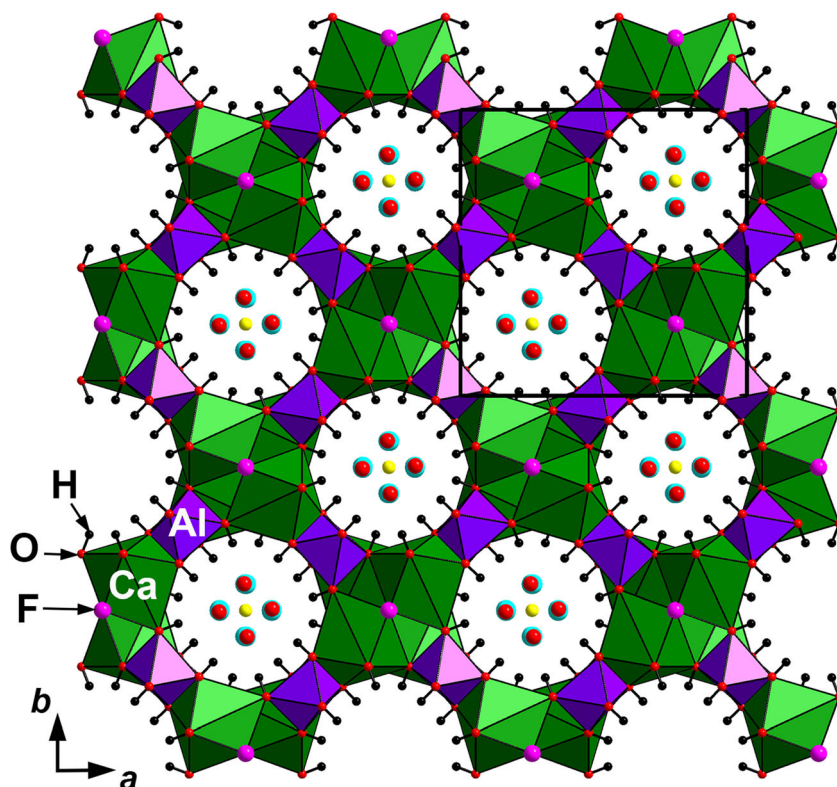
Chemical composition of kruijenite is given in Table 2. Contents of other elements with atomic numbers above 8 are below detection limits. The empirical formula (based on, $Z = 2$) is $\text{Ca}_{4.00}(\text{Al}_{3.77}\text{Cr}_{0.13})_{\Sigma 3.90}(\text{SO}_4)_{0.70}\text{F}_{2.13}(\text{OH})_{16.17} \cdot 1.79\text{H}_2\text{O}$. This formula was calculated on the basis of 22.89 O + F atoms *pfu*, in accordance with refined site occupancies.

The simplified formula is $\text{Ca}_4\text{Al}_4(\text{SO}_4)\text{F}_2(\text{OH})_{16} \cdot 2\text{H}_2\text{O}$. This formula can be rewritten by separating the structural unit (pseudo-framework) from the interstitial complex (channel constituents) as follows: $[\text{Ca}_4\text{Al}_4(\text{OH})_{16}\text{F}_2][(\text{SO}_4) \cdot 2\text{H}_2\text{O}]$. The Gladstone–Dale compatibility index (Mandarino 1981) is good: $1 - (K_p/K_c) = 0.043$.

X-ray diffraction data and crystal structure

The tetragonal unit cell dimensions refined from the powder data (Table 3) using a WinX^{pow} Software (2002) are: $a = 12.930(2)$, $c = 5.278(1)$ \AA , $V = 882.4(5)$ \AA^3 . Unfortunately, even the best of many tested crystals of kruijenite showed not very high quality. As a result, a rather high final *R* value of 12.1% was obtained. Thus, we consider our results for kruijenite only as the structure model. All attempts to refine the structure with lower symmetry involving twinning did not improve the model significantly: In all cases *R* values were higher than 10% and the channel content was strongly disordered. For this reason, we report the structure model of kruijenite in the space group $P4/ncc$, but we do not exclude that actually the averaged structure model has been obtained due to the poor quality of the crystal. However the reasonable values of thermal displacement parameters (Table 4) and interatomic distances (Table 5) for fully occupied sites, as well as good agreement between the measured and calculated powder X-ray diffraction patterns (Table 3) show that the model is correct.

Fig. 5 Crystal structure of kruijenite. Sulphur atoms are shown as yellow circles and positions of O sites of water molecules as blue circles. The unit cell is outlined



The structure of kruijenite (Fig. 5) is unique: the mineral represents a novel structure type. The structure is based on the microporous pseudo-framework built by $\text{Al}(\text{OH})_6$ octahedra and $\text{CaF}_2(\text{OH})_6$ eight-fold polyhedra. Al-centred octahedra share edges to form zig-zag chains running along the c axis (Fig. 6a). Ca-centred polyhedra share the F–F edge to form dimers; adjacent dimers are also connected via common F–O(1) edges thus building columns along [001] (Fig. 6b). Each

column is connected with four octahedral chains sharing common O–O edges with Al-centred octahedra (Fig. 6c).

There are two crystallographically non-equivalent O sites and one F site which participate in the formation of the pseudo-framework. Both O atoms belong to OH-groups. The positions of H atoms were detected from difference Fourier synthesis and O–H distances were softly restrained at 0.95(1) Å. Bond-valence calculations

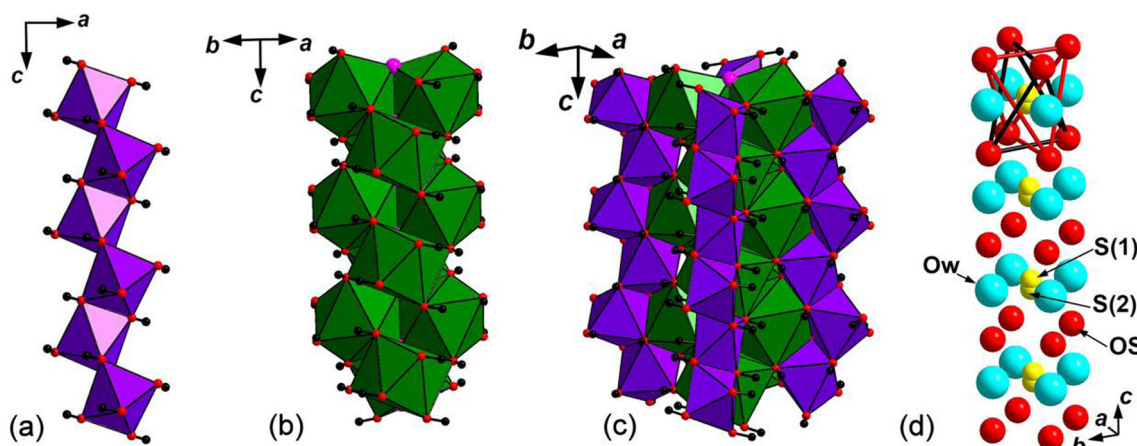


Fig. 6 Structural peculiarities of kruijenite. **a** Chain of Al-centred octahedrons. **b** Column of Ca-centred polyhedrons. **c** Column consisting of connected chains of Al- and Ca-centred octahedrons. **d** Visualisation of the channel content. Two possible SO_4 tetrahedrons are shown (one with

black edges and another with red edges). The split S sites (yellow spheres), O atoms bonded to S atoms (red) and O atoms of water molecules (blue) are marked with arrows

Table 6 Bond valence calculations for kruijenite (only for the fully occupied sites)

	Ca	Al	Σ
O(1) = OH	0.30 ^{x2↓} 0.17 ^{x2↓}	0.55 ^{x2↓}	1.02
O(2) = OH	0.25 ^{x2↓}	0.46 ^{x2↓} 0.45 ^{x2↓}	1.16
F	0.31 ^{x2↓x4→}		1.24
Σ	2.06	2.92	

Bond-valence parameters are taken from Gagné and Hawthorne (2015) for Ca–O and Al–O and from Brese and O’Keeffe (1991) for Ca–F

(Table 6) show that F site is slightly overbonded (1.24 v.u.) that may be caused by minor O^{2-} admixture. Minor F^- admixture as well as minor O^{2-} admixture could also occur in the O sites of OH groups. This is in a good agreement with chemical data indicating 4.26 F atoms per 8 Ca (some excess of F is assumed to occupy O sites of OH groups), as well as parameters of hydrogen bonds estimated from the IR spectrum (see below). In addition, there is only one band of Ca–O-stretching vibrations in the IR spectrum (at 385 cm^{-1}), which indicates ordering

of F and OH groups (different local situations around Ca would result in the splitting of this band).

All H sites of OH groups are located inside the wide channels (with approximate diameter of 7.4 \AA) running along the *c* axis. These channels contain water molecules and significantly distorted SO_4 tetrahedra. The S site is split along [001]: we fixed two sub-sites S(1) and S(2) and, moreover, assume additional splitting which is confirmed by the very high value of U_{33} for S(1) and S(2) sites. The same assumption refers to the OS (O atom bonded to S) site. We believe that taking into account additional splitting of S and OS positions could result in more reliable S–OS distances in tetrahedra. Due to the strongly disordered nature of these sites and possible further splitting, the s.o.f. values for S(1), S(2), OS and Ow (O atom of water molecule; see also Table 4) were fixed in accordance with chemical data.

Kruijenite represents a new structure type and is chemically related to kuzelite $\text{Ca}_4\text{Al}_2(\text{SO}_4)(\text{OH})_{12}\cdot 6\text{H}_2\text{O}$. Both minerals are known only in calcic xenoliths hosted by basic igneous rocks (Blass and Graf 2001). Comparative data for kruijenite and kuzelite are given in Table 7.

Table 7 Comparative data for kruijenite and kuzelite

Mineral	Kruijenite	Kuzelite
Formula	$\text{Ca}_4\text{Al}_4(\text{SO}_4)\text{F}_2(\text{OH})_{16}\cdot 2\text{H}_2\text{O}$	$\text{Ca}_4\text{Al}_2(\text{SO}_4)(\text{OH})_{12}\cdot 6\text{H}_2\text{O}$
Crystal system	Tetragonal	Trigonal
Space group	<i>P4/ncc</i>	<i>R-3</i> or <i>R3</i>
<i>Unit cell data:</i>		
<i>a</i> (Å)	12.9299	5.76
<i>c</i> (Å)	5.2791	53.66
<i>V</i> (Å ³)	882.57	1542
<i>Z</i>	2	3
Strongest reflections of the powder	9.12 (77)	8.972 (100)
X-ray diffraction pattern: <i>d</i> , $\square(I, \%)$	4.565 (100) 4.084 (50) 2.964 (74) 2.694 (74) 2.321 (24) 2.284 (29) 2.217 (22) 1.971 (40)	4.476 (70) 4.004 (30) 2.882 (30) 2.362 (40) 2.190 (40) 2.071 (35)
Density (g cm ⁻³)	2.573 (calc.)	1.99 (meas.) 2.014 (calc.)
<i>Optical data:</i>		
ω	1.576	1.504
ϵ	1.561	1.485
Optical sign	(–)	(–)
Wavenumbers of IR absorption bands (cm ⁻¹)	3562, 3492, 3410, 1635 1140, 1085, 1069, 1028, 984, 920, 870, 617, 559, 515, 471, 385	3650, 3600, 3100, 1650, 1150, 1105, 1095, 975, 780, 530, 415, 290
Source	This work	Pöllmann et al. 1997

In the structure of kruijenite, SO_4 tetrahedra and water molecules located in the channels are connected with the pseudo-framework *via* the system of H-bonds [O(1)–H(1)⋯OS with the H(1)⋯OS distance of 1.995 Å, O(1)–H(1)⋯Ow with H(1)⋯Ow distance of 2.107 Å, O(2)–H(2)⋯OS with the H(2)⋯OS distance of 1.922 Å, and O(2)–H(2)⋯Ow with the H(2)⋯Ow distance of 2.127 Å. The content of the channels is shown on Fig. 6d. According to the correlation $\nu \text{ (cm}^{-1}\text{)} = 3632 - 1.79 \cdot 10^6 \cdot \exp.[-d(\text{H} \cdots \text{O})/0.2146]$ found by Libowitzky (1999), corresponding calculated wavenumbers of O–H stretching IR absorption bands are 3469, 3535, 3401, and 3543 cm^{-1} which is in a good agreement with the observed values (Fig. 4).

The most interesting structural feature of kruijenite is a positively charged microporous pseudo-framework hosting sulfate anions and water molecules, which is an indication of possible anion-exchange properties (in particular, the ability to accumulate sulfate anions) of compounds belonging to this structure type. It could be a natural “forefather” of a novel structural family of ion-exchangers potentially interesting for use in chemical technologies.

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