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Kaatialaite, a new ferric arsenate mineral from Finland

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Abstract

Kaatialaite occurs admixed with arsenolite and other minor phases as a pale gray to yellow powdery weathering product on löllingite from the granite pegmatite at Kaatiala, Kuortane, W. Finland. Microchemical analysis yields a formula close to $FeAs_3O_9 \cdot 6H_2O$ (or $Fe(H_2AsO_4)_3 \cdot 3H_2O$) for the natural material. The X-ray powder pattern is identical with that of synthetic $FeAs_3O_9 \cdot 8H_2O$ (or $Fe(H_2AsO_4)_3 \cdot 5H_2O$), showing that the water content may be variable. Physical properties and X-ray data were determined by examination of synthetic material. The substance is monoclinic $P2_1$ or $P2_1/m$; the cell parameters refined from powder data are $a = 15.363(5)$, $b = 19.844(5)$, $c = 4.736(2)$Å, $\beta = 91.77(3)°$; Z = 4. The strongest lines in the X-ray powder pattern are [d in Å, (I/I_1), (hkl)]: 9.94(50)(020), 8.33(100)(120), 7.68(70)(200), 6.08(40)(130,220), 3.410(40)(231), 3.153(45) $(2\bar{4}1)$. For the natural mineral the corresponding d-values and intensities are: 9.91 (s), 8.35 (vs), 7.72 (s), 6.09 (m), 3.408 (m), 3.159 (m). The synthetic material is optically biaxial positive, $2V_Z = 15 \pm 2°$; the refractive indices are $\alpha = 1.581 \approx \beta$ (calc. 1.582), $\gamma = 1.625$ (both ± 0.002); extinction angle $Z{:}c \approx 3°$. The measured and calculated densities are 2.64 ± 0.02 and 2.62 g/cm^3 respectively. The crystal-chemical formula $Fe(H_2AsO_4)_3 \cdot 3\text{–}5H_2O$ is favored by the infrared study, whereas the formula $FeAs_3O_9 \cdot 6\text{–}8H_2O$ seems to be more compatible with the detailed thermal investigations (DTA, TGA, and stepwise heating).

Introduction

The new species kaatialaite occurs as a secondary mineral on löllingite from the Kaatiala granite pegmatite, located in the parish of Kuortane, W. Finland. The geochemistry of this pegmatite was described by Nieminen (1978), in which references to the older literature can be found. A description of the löllingite was given by Pehrman (1950).

The mineral was collected on the mine dumps by the first author in 1971. The type material comprises one holotype and three cotype specimens and the total amount of kaatialaite may be estimated at a few hundred mg at most. The mineral is named from the locality, and the description and name were approved by the Commission on New Minerals and Mineral Names of the I.M.A. in May 1982. One cotype specimen will be deposited with the British Museum (Natural History), and the rest is kept at the Mineralogical-Geological Museum, University of Oslo.

Natural and synthetic material

Gray to yellow powdery coatings on löllingite from Kaatiala were X-rayed and found to consist of arsenolite plus an additional, unknown mineral. This was subse-

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quently shown to be identical with the synthetic compound with the formula $Fe_2O_3 \cdot 3As_2O_5 \cdot 16H_2O$ or $Fe(H_2AsO_4)_3 \cdot 5H_2O$ described by Ronis *et al.* (1967), also given as $FeAs_3O_9 \cdot 8H_2O$ on JCPDS card 22-625. Scanning electron micrographs revealed blocky aggregates with no discernible crystal forms, except for small octahedra of arsenolite.

A similar but blue coating consists of arsenolite with another mineral which has not been identified. Scorodite and parasymplesite were identified on weathered samples of löllingite from Kaatiala by S. Lahti (pers. comm., 1981).

Owing to its fine-grained and impure nature, only X-ray powder data and a chemical analysis of the natural material could be obtained. In order to characterize fully the new mineral, more data were obtained from synthetic material. The synthesis of the compound is described by Ronis *et al.* (1972) and summarized as follows: To 1000 ml of a 1.2M solution of arsenic acid (As_2O_5 dissolved in water) add 0.3 moles $Fe(NO_3)_3 \cdot 9H_2O$ and 50 ml 11N HNO_3. Evaporate to dryness at 500°C to obtain a solid of composition $Fe_2O_3 \cdot 4As_2O_5$. Add 50 ml water to 100 g of this product and keep the mixture in a closed vessel in a water bath for 3–4 days (4 hr were found to be sufficient). Filter off the solid and wash it quickly with water followed by ether then allow it to dry in air. The final product has the composition $Fe_2O_3 \cdot 3As_2O_5 \cdot 16H_2O$.

Physical properties

The synthetic material forms aggregates of very rough, tabular, transparent six-sided crystals a few tenths of a millimeter across. The crystals are greenish blue with vitreous luster when freshly prepared, but fade to pale green and lose their transparency within a couple of months, recrystallizing to feathery aggregates of thin laths elongated parallel to the **c** axis, with oblique terminations, though the X-ray powder pattern is unchanged. The substance is colorless in thin section, optically biaxial positive with $2V_Z = 15 \pm 2°$. The refractive indices α 1.581 and γ 1.626 (both ±0.002) were measured in white light using the immersion method. The value of β is very close to α (calculated to be 1.582). The elongation of the laths is positive with extinction angle $Z{:}c \approx 3°$. The hardness could not be measured with any reliability and the measured density is 2.64±0.02 g/cm³ (pycnometer method).

X-ray crystallography

X-ray single-crystal studies using the Weissenberg and precession methods showed the substance to be monoclinic with space group $P2_1$ or $P2_1/m$, the former being the more probable according to a Laue diagram. The indexed X-ray powder data for both synthetic and natural material are given in Table 1. The former pattern is very close to that published in Ronis *et al.* (1967). The refined cell parameters for the synthetic material are a 15.363(5), b 19.844(5), c 4.736(2)Å, β 91.77(3)°; V = 1443.2(9)Å³.

Table 1. X-ray powder diffraction data for kaatialaite

Synthetic[1]				Natural[2]	
hkl	d_{calc}(Å)	d_{obs}(Å)	I/I_1	d_{obs}(Å)	I_{est}
110	12.144	12.15	5		
020	9.922	9.94	50	9.91	s
120	8.334	8.33	100	8.35	vs
200	7.678	7.68	70	7.72	s
210	7.161	7.16	10		
130 *	6.075	6.08	40	6.09	m
220 *	6.072				
230	5.011	5.02	5		
040 *	4.961	4.96	10		
310 *	4.956				
140	4.721	4.71	5		
011	4.605	4.616	5		
$10\bar{1}$	4.564	4.576	5		
101	4.485	4.478	30	4.46	w
111	4.375	4.379	5		
021	4.273	4.281	5		
240	4.167	4.170	<5		
121	4.087	4.093	<5		
$20\bar{1}$ *	4.086				
330	4.048	4.046	5		
150 *	3.843				
400	3.839	3.839	20	3.82	m-w
410	3.769	3.768	30	3.76	m
221	3.690	3.688	5		
340	3.562	3.559	15		
$30\bar{1}$ *	3.530				
250	3.526	3.525	20	3.53	m
$23\bar{1}$ *	3.476				
$31\bar{1}$	3.476	3.481	15		
231	3.407	3.410	40	3.408	m
311	3.373	3.374	10		
430	3.320	3.316	10		
321 *	3.236				
160	3.233	3.231	10		
$24\bar{1}$	3.154	3.153	45	3.159	m
051 *	3.041				
331 *	3.040				
260	3.038	3.036	30	3.039	m
440 *	3.036				
510 *	3.035				
$15\bar{1}$	2.995	2.998	10		
$41\bar{1}$ *	2.993				
151	2.972	2.972	10		
411 *	2.906	2.901	10		
$42\bar{1}$ *	2.896				
$34\bar{1}$	2.876	2.879	5		
251	2.809	2.810	25	2.799	m
$43\bar{1}$	2.753	2.754	15		
061	2.711	2.711	5		
$16\bar{1}$	2.678	2.674	5		
161 *	2.662				
270	2.659	2.659	5	2.667	w
$50\bar{1}$	2.614	2.616	<5		
441	2.528	2.528	10		
$52\bar{1}$	2.527				
451	2.361	2.359	10	2.354	w
280 *	2.360				

1. Diffractometer, $CuK\alpha_1$ radiation (λ = 1.54050 Å), graphite monochromator. Internal standard: lead nitrate. Intensities equal peak heights. Indexing based on space group $P2_1$ or $P2_1/m$. Refined cell parameters (from 39 reflections, given different weights according to their intensities): a 15.363(5), b 19.844(5), c 4.736(2) Å, β 91.77(3)°. * not used for calculation of cell parameters.
2. Kaatiala, Kuortane, Finland. 9 cm Debye-Scherrer camera, Fe radiation, Mn filter. Arsenolite lines are omitted.

Chemical composition

Table 2 gives the chemical analysis of impure, natural kaatialaite which was hand-picked under a binocular microscope. Water and CO_2 were determined using a Perkin-Elmer 240 elemental analyser and the remainder by atomic absorption spectrophotometry. Total arsenic was determined directly, pentavalent arsenic was determined after volatilization of trivalent arsenic (present in the form of arsenolite, As_2O_3) as AsF_3, and trivalent arsenic was calculated by difference. Small amounts of S

Table 2. Chemical analysis of kaatialaite

Oxide	Wt.%	Elem.	No. of atoms*
CaO	3.00		
MgO	0.24		
Al_2O_3	0.58	Al	0.076
Fe_2O_3	11.2	Fe^{3+}	0.930
As_2O_3	14.2		
As_2O_5	51.9	As^{5+}	2.996
CO_2	1.73		
H_2O	16.2	(H_2O	5.965)
Total	99.05		

Analyst: V.K. Din. BM(NH) Lab. No. 7825.

Analytical methods, see text.

SO_3 was detected using an electron microprobe.

* based on 9 oxygen atoms (water-free), after deducting CaO, MgO, As_2O_3, and CO_2 (impurities of arsenolite, calcite, gypsum, etc.).

probably due to admixed gypsum, were detected with an electron microprobe, but SO_3 was not determined. After deducting CaO, MgO, As_2O_3, and CO_2 as impurities (arsenolite, calcite, gypsum, *etc.*), the remainder gives the empirical formula (based on O = 9, water-free): $(Fe^{3+}_{0.93}Al_{0.08})_{\Sigma 1.01}As^{5+}_{3.00}O_{9.00} \cdot 5.97H_2O$, or ideally $FeAs_3O_9 \cdot 6H_2O$ (the number of water molecules is slightly less than 5.97 if the water content of the minor gypsum contamination is taken into consideration). The natural material contains less water than the synthetic, but as is shown later, the water of crystallization is loosely bonded and may be quite variable in kaatialaite.

With a Z value of 4, the calculated density of the synthetic product is 2.62 g/cm³, in good agreement with the measured density. The Gladstone–Dale relationship gives a compatibility index $1-(K_p/K_c) = 0.0048$, based on the theoretical composition and calculated density, which is in the superior category as defined by Mandarino (1981).

Thermal behavior

The crystal-chemical formula of the synthetic material has been expressed as $Fe(H_2AsO_4)_3 \cdot 5H_2O$ (Ronis *et al.*, 1967 and 1974), but with very little supporting evidence. A detailed thermal study, therefore, was performed.

The DTA curve (Fig. 1) shows two strong and sharp endothermic peaks at 80 and 150°C, corresponding to the loss of water in two steps. These are followed by some minor endothermic deflections (*e.g.*, at 350°C). At 640°C there is apparently a small exothermic effect followed by further distinct endothermic peaks, at 690 (shoulder), 780, 920, 1075, and 1140°C, corresponding to the loss of As_2O_5 (or $As_2O_3 + O_2$) in varying amounts. X-ray examination of the product formed at 1200°C showed a mixture of $\alpha-Fe_2O_3$ and an unknown compound.

The weight-loss steps on a separately recorded TGA curve correlate fairly well with the endothermic changes shown on the DTA diagram. Distinct steps occur at 110°C (14.6% weight loss), 200 (8.9%), 670 (6.6%), 820 (29.6%), and 890 (8.9%), the total weight loss being 68.6%. In a TGA run to 930°C (68.3% weight loss) the end product was the high-temperature form of $FeAsO_4$ (d'Yvoire and Ronis, 1968), but in a second run to 1000°C, for which data are reported above, small amounts of $Fe_2O_3 \cdot 2FeAsO_4$ (Korinth and Royen, 1965) were found in addition to $FeAsO_4$.

The results of stepwise heating experiments in an open furnace (Thermolyne 10500) using 0.12–0.26 g of material are given in Table 3. The choice of temperatures was guided by the results of the DTA and TGA studies already described. The discrepancies are due to disequilibrium conditions during the short DTA and TGA runs. Several intermediate heating products were identified and the end product was in this case $\alpha-Fe_2O_3$, which corresponds to a total weight loss of 86.0%. The most significant results are that $FeAs_3O_9 \cdot 4H_2O$ (or $Fe(H_2AsO_4)_3 \cdot H_2O$) is formed below 110°C, and that eight water molecules are lost below *ca.* 300°C. It was found that the corresponding anhydrous compound $FeAs_3O_9$ is capable of very rapid absorption of large amounts of water from the atmosphere, rehydrating to the "tetrahydrate" or even to the "octahydrate", depending on the ambient humidity.

A thermogravimetric study of synthetic kaatialaite in the temperature range 550–1040°C was reported by d'Yvoire *et al.* (1974). Their results are in general agreement with ours, except that our stepwise heating experiments yielded $Fe_2As_4O_{12}$ and $FeAsO_4$ at lower temperatures (100 and 150° lower respectively). D'Yvoire *et al.* formulate the intermediate product $Fe_2As_4O_{12}$ as $Fe^{3+}_2As^{3+}(As^{5+}O_4)_3$, which means that a partial reduction of arsenic must have taken place.

Korinth and Royen (1965) observed the formation of a product of composition $Fe_2O_3 \cdot 2FeAsO_4$ after heating $FeAsO_4$ at *ca.* 800–900°C. Our data (Table 3) show that this compound is identical with the mineral angelellite, Fe

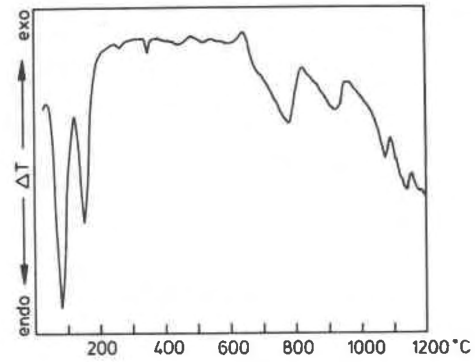

Fig. 1. DTA curve of synthetic kaatialaite (sample weight 54 mg; rate of heating 10°C/min in air at 1 atm; reference material Al_2O_3).

Table 3. Heating experiments on synthetic kaatialaite

T(°C)	1	2	3	4
110	18½	13.3	$FeAs_3O_9 \cdot 4H_2O$ [22-341]	12.7(-$4H_2O$)
220	25	21.1	$FeAs_3O_9 \cdot 4H_2O$*	
400/I	25½	25.9	$FeAs_3O_9 \cdot 4H_2O$*	25.3(-$8H_2O$)
400/II	24	25.5	$FeAs_3O_9 \cdot 8H_2O$** [22-625]	25.3
640	24	31.5	unknown	
690	22	53.3	$Fe_2As_4O_{12}$ [27-1166]	45.5
760	22½	67.3	$FeAsO_4$(high-T) [21-910]	65.7
820	24	74.2	$Fe_2O_3 \cdot 2FeAsO_4$† [19-616] + $FeAsO_4$(high-T)	75.9
960	20	89.3	α-Fe_2O_3 (hematite)	86.0
1090	12	85.7	α-Fe_2O_3 (hematite)	86.0

1. Duration (hours).
2. Weight loss (per cent).
3. Phases identified by X-ray diffraction [ref. to JCPDS].
4. Theoretical weight loss (per cent).

* partial rehydration ** complete rehydration

† identical with angelellite $Fe(AsO_4)_2O_3$ [13-121].

$(AsO_4)_2O_3$, which occurs as a fumarolic exhalation product in Argentina.

Infrared spectrum

The presence of water molecules in synthetic kaatialaite is shown by the broad band of H_2O stretching vibrations in the frequency range 3000–3400 cm^{-1}, and by the H_2O deformation bands at 1620 and 1670 cm^{-1} (Fig. 2). Two distinct bands at 2380 and 1225 cm^{-1} are characteristic of strong hydrogen bonds, and indicate the presence of As–OH groups. The 2380 cm^{-1} band can be ascribed to a ν(O–H) stretching vibration and that at 1225 cm^{-1} to an O–H in-plane bending vibration. The small absorptions at 770 and 755 cm^{-1} (which are more pronounced in Nujol mull spectra) may possibly be due to O–H out-of-plane bending vibrations. The presence of dihydrogen arsenate groups [$(H_2AsO_4)^-$ or $(AsO_2(OH)_2)^-$] in kaatialiate is thus substantiated by the infra-red spectrum. The stretching vibrations of the As–O bond produce bands at 865 and 845 cm^{-1}, and the O–As–O bending vibration absorbs at 465 cm^{-1}. Very small absorptions at 1390, 1125, and 635 cm^{-1}, as well as the numerous low-frequency bands, are left unassigned. It should be noted that the infrared spectrum of the lower hydrate formed at 110°C is virtually identical with that of the higher hydrate.

Discussion

There are two possible crystal-chemical formulas for kaatialaite: $FeAs_3O_9 \cdot 8H_2O$ and $Fe(H_2AsO_4)_3 \cdot 5H_2O$. The former is apparently supported by the dehydration experiments referred to above. If it is assumed that As^{5+} is present in its normal four-fold coordination, a condensation of the AsO_4–tetrahedra is implied, either to rings or infinite chains. However, such condensation is improbable in the case of kaatialaite, a low-temperature arsenate formed by weathering.

The latter formula is supported by the infra-red study. Thus the lower hydrate formed at 110°C may be $Fe(H_2AsO_4)_3 \cdot H_2O$, which transforms easily to $FeAs_3O_9$ at 200–300°C. $FeAs_3O_9$ may be a real polyarsenate (d'Yvoire *et al.*, 1974), it is very unstable, reversibly absorbing water from the air to form one of the two hydrated compounds (Table 3). However, it is strange that the loss of the single water molecule from $Fe(H_2AsO_4)_3 \cdot H_2O$ is not detectable by DTA or TGA. One possibility is that the loss is masked by the simultaneous transformation of the dihydrogen arsenate to a polyarsenate with a concomitant loss of water. Determination of the crystal structure of kaatialaite should help to resolve this ambiguity.

The analysis of the natural substance indicates that the water content may be variable, and the formula of kaatialaite is best written as $FeAs_3O_9 \cdot 6\text{–}8H_2O$ or $Fe(H_2AsO_4)_3 \cdot 3\text{–}5H_2O$. Recrystallization of synthetic crystals under normal atmospheric conditions shows that water is variably lost and taken up, depending on the humidity.

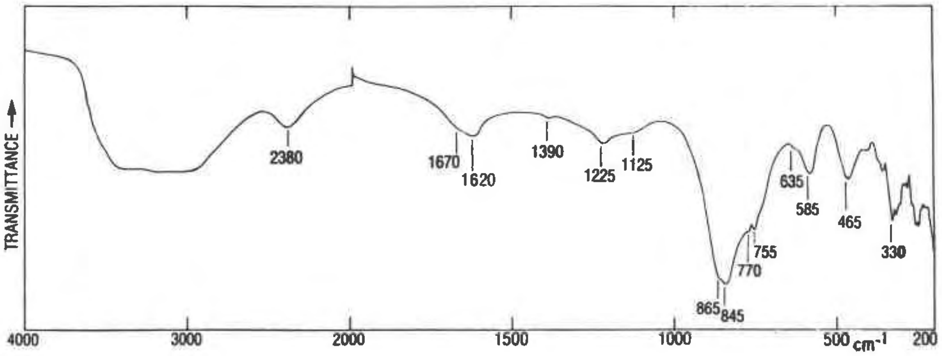

Fig. 2. Infrared spectrum of synthetic kaatialaite in KI.

Like kaatialaite, five other minerals contain Fe^{3+} and As^{5+} and form at low temperatures though they are otherwise unrelated in crystal-chemical and structural respects. The minerals are scorodite, $FeAsO_4 \cdot 2H_2O$; kankite, $FeAsO_4 \cdot 3.5H_2O$; pitticite, $FeAsO_4 \cdot 4.5\text{–}5H_2O$ (X-ray amorphous); ferrisymplesite, $Fe_3(AsO_4)(OH)_3 \cdot 5H_2O$ (a poorly characterized mineral); and angelellite, $Fe_4(AsO_4)_2O_3$.

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