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Janhaugite, $Na_3Mn_3Ti_2Si_4O_{15}(OH,F,O)_3$, a new mineral from Norway

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Abstract

Janhaugite occurs as reddish brown lamellar aggregates and sprays of crystal prisms in a soda granite (ekerite) at Gjerdingen, Nordmarka, northern Oslo region, Norway. Microprobe analyses give a formula very close to $(Na,Ca)_3(Mn,Fe)_3(Ti,Zr,Nb)_2Si_4O_{15}(OH,F,O)_3$. The mineral is monoclinic $P2_1/n$ with a 10.668(2), b 9.787(4), c 13.931(3)Å, β 107.82(2)°, Z = 4. The strongest reflections [d in Å, (I/I_1), (hkl)] of the powder pattern are: 3.202(60)(310), 2.839(100)($\bar{1}24$), 2.833(90)($\bar{3}22$), 2.782(90)(320,$\bar{1}05$,114,$\bar{2}31$), 1.744(50)(414). Janhaugite crystals have the following properties: elongated along [001], flattened on {010} with prisms {110}, {120}, and {130}; distinct cleavage on {010}; D (meas.) 3.60 g/cm^3, D (calc.) 3.71 g/cm^3 for the empirical formula; Mohs' hardness 5; optically biaxial positive, $2V_Z$ 80°, α 1.770, β 1.828 (both ±0.004) in white light, γ(calc.) 1.910; weak pleochroism, X (nearly colorless) < Y (beige); negative elongation, $c{:}X = +15°$, $b = Z$.

Introduction

Miarolitic cavities are wide-spread in the Permian syenitic and granitic plutonic rocks of the Oslo region, southern Norway. A survey of the mineralogy of these cavities was given by Raade (1972). One of the most interesting rocks in this respect is the so-called ekerite, a sodium-rich alkali feldspar granite carrying aegirine and arfvedsonitic amphibole, which shows a gradation to the corresponding alkali feldspar syenite, called nordmarkite. The petrography and geochemistry of ekerite was described by Dietrich *et al.* (1965).

A mineralogically unique ekerite pluton, measuring about (2 × 4) km^2, is situated ESE of Lake Gjerdingen in Nordmarka, some 30 km N of Oslo. Elpidite, $Na_2ZrSi_6O_{15} \cdot 3H_2O$, and a mineral of the astrophyllite group have been known as rock-forming minerals in this ekerite since 1906 (found by Professor J. Schetelig, but the elpidite was first described in the literature with optical data by Barth (1945)). The mineralogy of the miarolitic cavities of this pluton was briefly treated by Dietrich *et al.* (1965) and Sæbø (1966). A detailed mineralogical investigation of this ekerite is currently being undertaken. An interesting suite of rare fluorides was described by Raade and Haug (1980 and 1981). The latest compilation of the mineralogy is by Raade and Haug (1982). The elpidite-bearing area of the ekerite with miarolitic cavities is confined to the western part of the pluton.

The new mineral janhaugite was encountered during routine X-ray examination of the cavity minerals. It was later found that the new mineral is of wide-spread occurrence in the area and in some parts it must even be considered as a rock-forming constituent. The mineral is named in honor of the person who first observed it, Mr. Jan Haug, an amateur mineralogist who has taken part in the systematic mineralogical investigation of the area. The mineral and name were approved by the Commission on New Minerals and Mineral Names of the I.M.A. in May 1981. Type material is deposited with the Mineralogical-Geological Museum, University of Oslo.

Occurrence, morphology and paragenesis

Janhaugite is found partly as subhedral grains in a more or less dense ekerite and partly in miarolitic cavities as lamellar aggregates and sprays of crystal prisms, mostly up to 4 mm long. Individual crystals are often slightly curved and bent and are vertically striated. Single crystals are rare; they are elongated in the [001] direction and flattened on the clino-pinacoid {010}. Three prisms were identified by goniometric measurements: {110} narrow, {120} prominent, {130} insignificant or lacking. In addition, a rough {001} face and two unidentified {*hkl*} faces were observed. A crystal drawing of janhaugite is shown in Figure 1; a color photograph of the mineral can be found in Raade and Haug (1982). A recent find of the

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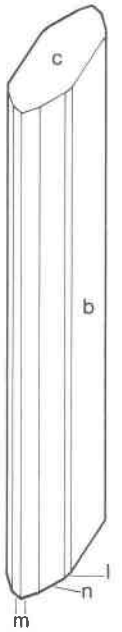

Fig. 1. Clinographic projection of a janhaugite crystal with forms c{001}, b{010}, m{110}, n{120}, and l{130} (drawn with the computer program of Dowty, 1980).

mineral from ekerite adjacent to an aplitic dike, shows large aggregates and sprays up to 1½ cm.

Janhaugite is often found intimately associated with pyrophanite, (Mn,Fe)TiO_3. It may also occur imbedded in a fine-grained light-colored elpidite, which is different from the fibrous orange-colored elpidite found elsewhere in the ekerite. The association of janhaugite with yellow, long prismatic crystals of monazite was also noted. The rare mineral dalyite, $K_2ZrSi_6O_{15}$, has been observed in close contact with janhaugite. It may also be associated with a clay-like mixture of montmorillonite and kaolinite. The mineral found in the Gjerdingen ekerite belonging to the astrophyllite group has been shown by microprobe analyses to be closer to the kupletskite end-member (Mn > Fe) of the astrophyllite–kupletskite series. Kupletskite also occurs in the janhaugite-bearing ekerite, but the amount seems to be less than in the elpidite ekerite from other parts of the pluton.

Physical and optical properties

The color of janhaugite is reddish brown, the streak is light brown, and the luster is vitreous. The mineral is nonfluorescent in UV light. Distinct cleavage was observed on {010}. Twinning was seen under the microscope in a few cases, the twin plane is probably {100}. The Mohs' hardness is about 5 and the mineral is very brittle. The density, measured by suspension in Clerici's solution diluted with water, is 3.60±0.05 g/cm^3.

Janhaugite is biaxial positive, $2V_Z = 80\pm10°$. The indices of refraction, $\alpha = 1.770$ and $\beta = 1.828$ (both ±0.004), were measured by the immersion method in white light. From these data, γ (calc.) = 1.910. The mineral is weakly pleochroic, X (nearly colorless) < Y (beige). It shows negative elongation, $c{:}X = +15\pm3°$, $b = Z$.

X-ray crystallography

X-ray single-crystal study by the Weissenberg and precession methods showed janhaugite to be monoclinic, space group $P2_1/c$, with unit-cell parameters a 10.668, b 9.787, c 14.727Å, β 115.78° (from powder data). We have, however, chosen a reduced cell which corresponds better with the crystal morphology: space group $P2_1/n$, cell parameters a 10.668(2), b 9.787(4), c 13.931(3)Å, β 107.82(2)°, as refined from the indexed X-ray powder pattern (Table 1). The unit-cell volume is V = 1384.7(7) Å^3. The transformation matrix from standard to reduced cell orientation is $[\bar{1}00/0\bar{1}0/101]$.

Ten weak lines in the powder pattern which could not be indexed satisfactorily have been deleted from Table 1. The strongest of these were shown to be caused by paraffin wax in the vaseline used for mounting. Moreover, a close match of these extra reflections with those given for metamict kobeite from Japan on JCPDS card no. 11-259 was noted. A single fragment of unheated kobeite was used for recording this pattern, which was very weak (Hutton, 1957). We suspect the mounting medium to be responsible for at least the strongest lines reported in the powder pattern of unheated kobeite. This is supported by the fact that the two strongest lines (at 4.14–4.16 and 3.74–3.76Å) also appear in the pattern of recrystallized material studied by Hutton, but were not recorded by Masutomi *et al.* (1961).

Chemical composition

Three electron-microprobe analyses on different grains are given in Table 2. These were performed with an ARL instrument equiped with wavelength spectrometers and operated at 15 kV and 0.35 μA. The analytical data were corrected according to the method of Bence and Albee (1968), using α-factors slightly modified from Albee and Ray (1970). The following natural and synthetic standards were used: diopside for Si and Ca, fayalite for Fe, rhodonite for Mn, jadeite for Na, K-feldspar for K, rutile for Ti, apatite for F, and pure oxides for Zr, Nb, and Ta.

The main difference between the three analyses is the antipathetic variation in TiO_2 and ZrO_2 contents. The mean of the three analyses was used for the calculation of the empirical formula (Table 2). Based on a total of 12 cations and assuming (O+OH+F) = 18, the following empirical composition is arrived at: $(Na_{2.75}Ca_{0.20}K_{0.03})_{\Sigma2.98}(Mn_{2.43}Fe_{0.60})_{\Sigma3.03}(Ti_{1.32}Zr_{0.38}Nb_{0.29}Ta_{0.01})_{\Sigma2.00}(Si_{3.84}Ti_{0.15})_{\Sigma3.99}O_{15.00}(OH_{1.40}F_{1.10}O_{0.50})_{\Sigma3.00}$. This requires the addition of 1.63% H_2O to the analysis, which brings the total very close to 100% (Table 2). An ideal formula may be written $Na_3Mn_3Ti_2Si_4O_{15}(OH,F)_3$. Evi-

Table 1. X-ray powder diffraction data for janhaugite

hkl	d_{calc}(Å)	d_{obs}(Å)	I/I_1	*hkl*	d_{calc}(Å)	d_{obs}(Å)	I/I_1
011	7.87	7.89	5	$\bar{4}21$ *	2.329	2.327	20
002	6.63	6.65	30	034 *	2.325		
$\bar{1}12$ *	5.440	5.462	5	115 *	2.325		
200	5.078	5.087	5	$\bar{2}34$	2.310	2.309	5
120	4.408	4.412	<5	$\bar{3}33$	2.285	2.287	<5
$\bar{1}22$	3.919	3.920	40	420	2.254	2.253	20
202	3.542	3.546	20	134 *	2.168	2.165	10
220	3.524	3.529	20	$\bar{3}34$	2.144	2.145	10
122	3.465	3.466	<5	$\bar{1}26$	2.090	2.091	<5
$\bar{1}23$	3.352	3.348	20	510	1.989	1.988	10
212	3.331	3.330	20	$\bar{5}14$ *	1.989		
$\bar{1}14$	3.281	3.280	20	$\bar{4}16$ *	1.957	1.956	20
023	3.280			$\bar{5}22$	1.956		
$\bar{3}12$ *	3.276	3.273	20	$\bar{4}34$ *	1.934	1.933	10
$\bar{2}04$ *	3.272			144	1.870	1.870	<5
$\bar{3}03$ *	3.202	3.202	60	$\bar{6}13$ *	1.744	1.744	50
310	3.199			414	1.743		
031	3.168	3.169	<5	$\bar{2}08$	1.741	1.740	30
130	3.106	3.108	20	117 *	1.739		
123	2.933	2.935	<5	244	1.733	1.732	30
$\bar{1}24$	2.837	2.839	100	226 *	1.716	1.715	30
$\bar{3}22$	2.834	2.833	90	$\bar{3}51$ *	1.714		
$\bar{3}20$ *	2.784	2.782	90	$\bar{2}18$ *	1.714		
$\bar{1}05$ *	2.783			$\bar{4}44$ *	1.714		
114 *	2.781			$\bar{6}14$	1.712	1.712	30
$\bar{2}31$ *	2.781			145 *	1.711		
024	2.745	2.742	40	610	1.668	1.668	20
230	2.745			442 *	1.620	1.619	10
$\bar{2}24$ *	2.720	2.717	40	061 *	1.619		
132 *	2.717			514	1.517	1.516	20
204	2.454	2.454	30	$\bar{5}18$ *	1.516		
041 *	2.406	2.404	30	630	1.503	1.502	10
$\bar{3}31$ *	2.402			128	1.488	1.488	10
$\bar{4}04$	2.402					1.477	<5
$\bar{1}34$ *	2.381	2.379	10			1.466	20
214	2.380					1.418	10
$\bar{3}32$ *	2.379					1.410	<5
140 *	2.379					1.390	<5
$\bar{2}25$	2.375	2.374	20			1.372	10
330	2.349	2.349	5				

Guinier camera, Fe$K\alpha_1$ radiation (λ = 1.93604 Å), quartz monochromator. Internal standard: lead nitrate. Intensities visually estimated. Indexing based on space group $P2_1/n$. Refined cell parameters (from 41 reflections): *a* 10.668(2), *b* 9.787(4), *c* 13.931(3) Å, β 107.82(2)°. * not used for calculation of cell parameters.

Table 2. Electron-microprobe analyses of janhaugite

Oxide	Weight per cent				Elem.	No. of atoms*
	1	2	3	mean		
SiO_2	29.92	29.56	29.89	29.79	Si	3.840
TiO_2	15.87	16.25	13.41	15.18	Ti	1.472
FeO	5.58	4.96	6.03	5.52	Fe	0.595
MnO	22.00	22.87	21.92	22.26	Mn	2.431
CaO	1.51	1.44	1.40	1.45	Ca	0.201
Na_2O	10.67	11.37	11.03	11.02	Na	2.754
K_2O	0.19	0.19	0.19	0.19	K	0.031
ZrO_2	4.51	5.10	8.34	5.98	Zr	0.376
Nb_2O_5	5.10	5.13	4.77	5.00	Nb	0.291
Ta_2O_5	0.26	0.28	0.23	0.26	Ta	0.009
F	2.46	2.80	2.80	2.69	F	1.097
H_2O	n.a.	n.a.	n.a.	1.63**	H	1.402
	98.07	99.95	100.01	100.97	O	16.898
$-O{\equiv}F_2$				1.13		
				99.84		

For analytical details, see text.

n.a. = not analyzed.

* based on Σ cations = 12 (excluding H).

** theoretical value to give (O+OH+F) = 18.

dence for the presence of $(OH)^-$ is provided by the infrared spectrum (Fig. 2). The splitting of the O–H stretching frequency (3550, 3510, and 3460 cm^{-1}) seems to indicate the presence of $(OH)^-$ at three different structural sites. For three different hand-picked batches water determination with the Perkin–Elmer elemental analyser gave (in wt.% H_2O):0.32 (on 3.716 mg; British Museum (Natural History)), 1.6 (mean of duplicates on 2.260 and 2.035 mg; Norsk Hydro A/S, Norway), and 1.3 (do. on 1.926 and 2.964 mg). Whether this result is due to an interlaboratory discrepancy or to a real variation in the (OH):F proportion, cannot be settled at the moment.

From the empirical formula, and with Z = 4, a density of 3.71 g/cm^3 was calculated, in reasonable agreement with the measured density, 3.60 g/cm^3. The mean index of refraction from the Gladstone–Dale relationship is 1.834 using the measured density and 1.860 using the calculated density (*k*-values from Mandarino, 1976). These compare reasonably well with the measured indices given above ($\bar{n}$ = 1.836). The compatibility indices are −0.002 and 0.028 when the measured and calculated densities are used, respectively, and these figures are evaluated as superior and excellent according to Mandarino (1979).

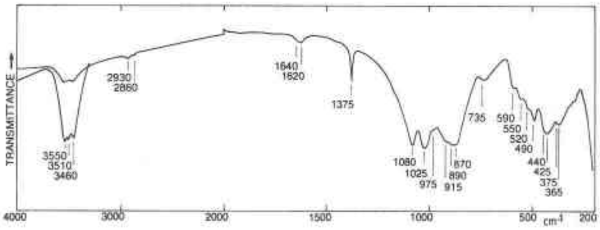

Fig. 2. Infrared spectrum of janhaugite (*ca*. 1 mg in a KJ disc; Beckman spectrophotometer). The high-frequency part was also recorded with a higher sensitivity to show more clearly the relatively sharp O–H stretching frequencies at 3550, 3510, and 3460 cm^{-1}. Small absorptions due to H_2O bending vibrations occur at 1640/1620 cm^{-1}. The SiO_4 tetrahedra give strong absorptions in the region 1080–870 cm^{-1}. Band assignments at lower frequencies are more difficult to make. A spurious band occurs at 1375 cm^{-1}.

An Si:O ratio of 4:15 corresponds to a rather low sharing coefficient (Zoltai, 1960), S = 1.125. The degree of condensation of the SiO_4 tetrahedra in the structure must therefore be small. Until the crystal structure determination has been made, guesses at the possible silicate anions in janhaugite are purely speculative, but configurations like $(Si_2O_7)_2O$ and $(SiO_4)_2(Si_2O_7)$ are compatible with the bulk ratio Si_4O_{15}.

Discussion

The elements F, Mn, Ti, and Zr are especially characteristic for the late-stage fluids of the Gjerdingen ekerite magma. In addition to the Mn-bearing minerals janhaugite, kupletskite, and pyrophanite, rhodochrosite and rhodonite have been found at this locality. Rhodonite was encountered in one sample only, and is associated with two unknown Ca–Mn–Fe-silicates, one of which has the simple formula $Ca(Fe,Mn)_2Si_2O_7$, according to an energy-dispersive electron-microprobe analysis. A similar enrichment of Mn is not known for any other ekerite body in the Oslo region. For instance, in some of the western and southern ekerite plutons, a very iron-rich astrophyllite may occur as an accessory mineral (Dietrich *et al.*, 1965).

Several other silicates containing Na, Mn, Ti, and Zr are known to occur in alkaline syenite pegmatites of the USSR which show certain geochemical and mineralogical similarities to the late-stage ekerite mineralization in the Oslo region. These minerals include kazakovite, $Na_6MnTiSi_6O_{18}$, tisinalite, $Na_3H_3(Mn,Ca,Fe)TiSi_6(O,OH)_{18} \cdot 2H_2O$, and seidozerite, $(Na,Ca)_2Mn(Zr,Ti)Si_2O_7(O,F)_2$, all of which have much higher (Na+Ca):(Mn+Ti+Zr) ratios than janhaugite.

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