Iraqite, a new rare-earth mineral of the ekanite group

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SUMMARY. Iraqite, a new mineral of the ekanite group from northern Iraq, has the composition $(Ln_{1.33} Th_{0.66} x_{0.15}) (K_{1.07} y_{0.93}) (Ca_{3.49} Ln_{0.35} Na_{0.16}) (Si_{15.69} Al_{0.27}) (O_{39.93} F_{0.07})$ where x = U, Pb, Zr, Fe, Mg, and Cu, and y is presumed to be vacant sites. It occurs in granite in contact with dolomitic marble. The colour is pale greenish yellow; H $4\frac{1}{2}$; D_{calc} 3·28 and D_{meas} 3·27 (Berman balance), both corrected for minor impurity and non-structural water. Optically it is uniaxially negative with ω 1·590 and ϵ 1·585 though some sections show anomalous extinction up to 7°. Space group is $P4/mcc$ with a 7·61±0·01 Å and c 14·72±0·02 Å. Strongest lines of the indexed powder pattern are 5·28(100), 3·31(100), 2·64(100), 7·36(80), 3·38(80), 3·40(60), 2·17(40), 7·62(30). Thermal data are given.

TYPE ekanite is a metamict thorium calcium silicate found in the gemstone placers of Sri Lanka. It was first described by Anderson *et al.* (1961) and called after the discoverer and gemmologist F. L. D. Ekanayake. Alkali analogues of ekanite were later described from central Asia (Ginzburg *et al.*, 1965), the name kanaekanite having since been used to describe this species (Povarennykh and Dusmatov, 1970). An 'ekanite' similar in chemical composition to those of central Asia has also been recorded from St. Hilaire, Quebec (Perrault and Richard, 1973) and the name kanaekanite would appear to be appropriate for this mineral. Iraqite was found at Shakhi-Rash mountain, Hero, Qala-Diza in northern Iraq, where it occurs in coarsely crystalline granite in contact with dolomitic marble containing olivine and diopside. It differs from other minerals of the ekanite group in having a significant content of rare earths and although radioactive it is not metamict, type ekanite from Sri Lanka being the only known member to occur in the metamict state.

Physical properties. The mineral is pale greenish yellow in colour with a dull lustre and possessing a whitish streak; under the binocular microscope a pearly lustre is discernible. Although crystal faces are not developed, three orthogonal cleavages are present, two good cleavages being seen in basal section while the third is poor.

Fracture is uneven with a hardness on Mohs' scale of $4\frac{1}{2}$. Vickers hardness numbers show a range of values from 245 to 314. Specific gravity determinations on five separate fragments show measured values of 2·94 to 2·98 by Berman balance, a mean value of 3·27 being obtained when corrected for minor impurity and non-structural water. Under the microscope iraqite was observed to be porous. The mineral is insoluble in both cold and hot hydrochloric, sulphuric, and nitric acids. No pyro-electric effects were observed.

Optical properties. In transmitted light iraqite is colourless, and is generally uni-axially negative with straight extinction. Some sections, however, show extinctions ranging up to 7° with biaxial characteristics. The refractive indices were determined as ω 1·590 and ϵ 1·585 with B 0·005. The mineral does not fluoresce under short or long wave ultraviolet light.

X-ray data. Powder data (Table I) were obtained from photographs taken with Cu-$K\alpha$ radiation in a 114·6 mm diameter Debye-Scherrer camera. Intensities were visually estimated by comparison with an intensity scale; no allowance was made for any preferred orientation effects that might have been introduced during the preparation of the sample mount. Examination of the reflections show the space group to be consistent with either $P4/mcc$ or $P4cc$. The powder data for iraqite are closely similar to those recorded for 'ekanite' (= kanaekanite) from St. Hilaire, Quebec (Perrault and Richard, 1973). Structural work by Richard and Perrault (1972) and by Mokeeva and Golovastikov (1966) has shown the ekanite group to be centrosymmetric with space group $P4/mcc$. Cell parameters for iraqite were determined by the method of least squares, utilizing ThO_2 as an internal standard: a 7·61±0·01 Å, c 14·72±0·02 Å; $a:c = 1:1·934$; V 852·5±3·5 Å³. Assuming one formula unit in the unit cell and the atomic ratios derived in Table II the calculated density is 3·28 g/cm³.

Heated powder samples of iraqite and of type metamict ekanite from Sri Lanka (BM 1961, 472) show somewhat different behavioural patterns. Ekanite heated to 800 °C remained amorphous but on heating to 1000 °C for three hours produced an apatite-type pattern. Similar treatment with iraqite produced no change in its crystalline state, but the apatite-type pattern appeared on heating to 1250 °C in air for one hour. This was accompanied by a minor cristobalite phase. In both cases the presence of a minor closely similar body-centred tetragonal phase was also noted, which became the main phase produced on heating ekanite to 1250 °C and which is similar to the high-temperature phase previously recorded by Anderson *et al.* (1961). Temperatures at which the various phases derived from ekanite appear differ somewhat from those given by the above authors and are more in keeping with those found by the Institute of Crystallography and Petrology, ETH, Zürich, quoted by Gübelin (1961, 1962).

Chemical and thermal analysis. Chemical data are given in Table II; in addition to the full wet-chemical analysis the rare-earth constituents were individually determined by X-ray fluorescence spectrometry. Electron-probe microanalysis indicated the rare earths were evenly distributed throughout the mineral. Allowance for contamination by very minor calcite (presence shown in X-ray powder photograph) and by sulphur, assumed present in the form of pyrite, was made in the calculation of the formula. On the basis of 40 (oxygen+fluorine) ions in the unit cell the derived formula is

TABLE I. *X-ray powder data for iraqite*

hkl	d_{calc}	d_{obs}	I	hkl	d_{calc}	d_{obs}	I
100	7·61 Å	7·62 Å	30	400	1·903 Å	1·900 Å	15
002	7·36	7·36	80	315	1·863	1·862	2
110	5·38	5·36	15	410	1·846	—	—
102	5·29	5·28	100	402	1·842 ⎫	1·837	12
112	4·34	4·34	2	008	1·840 ⎭		
200	3·81	3·81	1	411	1·832 ⎫	1·830	12
004	3·68	3·68	5	324	1·831 ⎭		
210	3·40	3·40	60	226	1·813	1·811	12
202	3·38	3·38	80	330	1·794 ⎫		
211	3·32 ⎫	3·31	100	412	1·790 ⎪	1·790	6
104	3·31 ⎭			217	1·789 ⎪		
212	3·09	3·08	12	108	1·788 ⎭		
114	3·04	3·03	5	306	1·764	1·762	6
213	2·80	2·79	3	332	1·743 ⎫	1·739	2
220	2·69	2·69	15	118	1·741 ⎭		
204	2·65	2·64	100	413	1·728	—	—
300	2·54 ⎫	2·53	20	316	1·718	—	—
222	2·53 ⎭			325	1·715	—	—
214	2·50	2·50	8	420	1·702	1·702	10
006	2·45	2·45	1	421	1·691 ⎫	1·689	2
310	2·41 ⎫	2·40	3	404	1·690 ⎭		
302	2·40 ⎭			422	1·658 ⎫	1·658	8
311	2·38	—	—	208	1·657 ⎭		
106	2·34	2·33	3	414	1·650	1·650	8
312	2·29	2·28	1	218	1·619 ⎫	1·618	12
116	2·23	—	—	334	1·613 ⎭		
215	2·23	—	—	423	1·608	—	—
224	2·17	2·17	40	326	1·600	—	—
313	2·16	2·16	5	317	1·584	1·583	1
320	2·11	2·11	3	415	1·564	—	—
321	2·09 ⎫	2·09	6	424	1·545	1·543	4
304	2·09 ⎭			500	1·522 ⎫		
206	2·06	2·06	15	430	1·522 ⎪	1·517	6
322	2·03	2·03	15	228	1·519 ⎪		
314	2·01	2·01	4	431	1·514 ⎭		
216	1·990	1·989	15	406	1·503	1·503	2
323	1·939	1·936	1				

The measurements were made on photographs taken in a 114·6 mm diameter camera with Cu-$K\alpha$ radiation ($\lambda = 1·5418$ Å).

$(Ln_{1·33} \, Th_{0·66} \, x_{0·15}) \, (K_{1·07} \, y_{0·93}) \, (Ca_{3·49} \, Ln_{0·35} \, Na_{0·16}) \, (Si_{15·69} \, Al_{0·27}) \, (O_{39·93} \, F_{0·07})$ where $x = $ U, Pb, Zr, Fe, Mg and Cu, and y is presumed to be vacant sites. No hydroxyl from the H_2O^+ was found to be necessary to balance the total (silicon +aluminium) ions present, and the calculations have been made on a water-free basis. The non-structural nature of the H_2O^+ would be in keeping with the equivalence of the unheated and heated (1000 °C, air) powder patterns of iraqite and also with information from differential thermal analysis. This showed a virtually featureless thermogram with an ill-defined endotherm corresponding to moisture loss, followed by a shallow endothermic

TABLE II. *Chemical data*

I		2				3	
K_2O	2·76			K	1·068 1·07	La	45·0
CaO	10·73*			Ca	3·488 ⎫	Ce	42·4
Na_2O	0·27			Na	0·159 ⎬ 4·00	Pr	2·9
La_2O_3	6·78	La	0·759	Ln	0·353 ⎭	Nd	5·6
Ce_2O_3	6·44	Ce	0·715			Sm	1·1
Pr_2O_3	0·44	Pr	0·049			Gd	0·6
Nd_2O_3	0·88	Nd	0·095			Yt	2·4
Sm_2O_3	0·17	Sm	0·018				
Gd_2O_3	0·10	Gd	0·010				
Yt_2O_3	0·25	Yt	0·040				
ThO_2	9·54			Ln	1·333 ⎫		
ZrO_2	0·17			Th	0·659 ⎪		
UO_2	0·65†			Zr	0·025 ⎪		
PbO	0·35			U	0·044 ⎪		
Fe_2O_3	0·10‡			Pb	0·029 ⎬ 2·14		
MgO	0·02			Fe	0·023 ⎪		
CuO	0·07			Mg	0·009 ⎪		
SiO_2	51·7			Cu	0·016 ⎭		
Al_2O_3	0·77			Si	15·686 ⎫		
P_2O_5	0·01			Al	0·275 ⎬ 15·96		
F	0·07			P	0·003 ⎭		
Sum, less O ≡ F	92·24			F	0·067 ⎫ 40·00		
H_2O^+	3·51			O	39·933 ⎭		
H_2O^-	0·90						
CO_2	1·00 ⎱ 2·27%						
CaO	1·27 ⎰ calcite						
S	0·14 ⎱ 0·26%						
Fe	0·12 ⎰ pyrite						
	99·18						

* 12·0—1·27% for calcite
† Recorded as U_3O_8 = 0·68%
‡ 0·27—0·17% for pyrite

1. Wet chemical analysis except Zr, rare earths, and Th by X-ray fluorescence analysis and U by delayed neutron activation.
2. Atomic ratios to 40(oxygen+fluorine).
3. Composition of rare-earth elements, atoms %.

depression between 200 °C and 900 °C representing gradual elimination of the remaining H_2O. A simultaneous thermogravimetric analysis showed a total weight loss of 5·2 %. Although higher thermal energy was required to remove the balance of non-hygroscopic water, this does not appear to be sufficiently well defined to suggest the presence of structurally orientated hydroxyl ions in the lattice. No further clarification was provided by infrared analysis, which showed only a broad-banded spectrum similar to that described for kanaekanite (Richard and Perrault, 1972).

All members of the ekanite group so far analysed show incomplete filling of the potassium sites, and in the case of the type ekanite from Sri Lanka apparently all such sites are vacant (Mokeeva and Golovastikov, 1966; Richard and Perrault, 1972). No other ekanite-group mineral analysed to date has a rare-earth content comparable to

that of iraqite, the previous highest value recorded being that for a kanaekanite from central Asia with a value of 2·39 % (Ginzburg *et al.*, 1965). The rare-earth content of iraqite is such that not only do these elements fill more than half the sites occupied by thorium in the type Sri Lanka ekanite, but also some of the calcium positions as well. Iraqite can thus be described as the rare-earth member of the ekanite group; it is chemically closer to kanaekanite than it is to ekanite in that, like the former mineral, more than half the potassium sites are filled.

Iraqite is named after the country of origin. The Commission on New Minerals and Mineral Names has accepted it as a new mineral and approved the name.

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