Killalaite, a new mineral from Co. Sligo, Ireland

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SUMMARY. Killalaite occurs in a thermally metamorphosed limestone at Killala Bay, near Inishcrone, Co. Sligo. It is a secondary mineral and occurs in cavities and veins with calcite or afwillite in spurrite–wollastonite rocks. It is found in well-formed colourless crystals, up to 2 mm long, with a characteristic penetrative twinning observed under crossed nicols as a cross 'bow-tie', cleavage (100) perfect, (010) good, (001) poor. The crystals are monoclinic, biaxial, $2V_\alpha 26°$, refractive index $\alpha\ 1\cdot635$ and $\gamma\ 1\cdot642$, optic axial plane (010), $\beta = [010]$ (elongation), $\gamma: [001] \approx 16°$, density calculated from RI $\sim 2\cdot88$, provisional approximate cell dimensions a 9·3, b 9·9, c 7·7 ($\pm$0·1 Å), $\beta \sim 105°$ and $Z = 2$. Electron microprobe analysis gave CaO 57·0, SiO_2 39·8; H_2O (by difference) 3·2; MgO, Al_2O_3, and Fe_2O_3 together $< 0·3$ weight %, composition $2Ca_3Si_2O_7 . H_2O$. The stronger lines of the X-ray powder pattern are: 3·03, 2·824, 2·724, 2·275, 2·224, 1·688, 1·673, and 1·413 Å. It probably formed in a CO_2-deficient hydrothermal environment in the PT range of 350° to 550 °C and 500 to 3500 bars. The mineral is named after the name of the locality, Killala Bay, and should be pronounced as killalahite. Type material is preserved at the Ulster Museum and at the British Museum (Natural History).

KILLALAITE is a new hydrous calcium silicate mineral from a thermally metamorphosed limestone near Inishcrone, along the eastern shore of Killala Bay, Co. Sligo. The limestone is traversed by numerous parallel basalt–dolerite dykes running east–west across the shore line. Two of these dykes have caused extensive thermal metamorphism and the mineral assemblages are reminiscent of the dolerite–chalk contact of Scawt Hill, Co. Antrim. A general account of the geology of the Inishcrone area is given in the Geological Survey of Ireland Memoirs (Symes and Baily, 1879) and in recent publications a brief description of the mineralogy of these contacts is given (Emeleus and Preston, 1969; Nawaz, 1972). A detailed mineralogical study of the contact rocks is in progress. The common primary mineral assemblages in the order of increasing distance from the contact are: gehlenite–larnite (bredigite)±spurrite; larnite (bredigite)–spurrite±gehlenite; spurrite–wollastonite–rankinite (kilchoanite)–tilleyite±cuspidine; spurrite–calcite±cuspidine; calcite–wollastonite; calcite–grossular; and calcite–quartz.

The primary mineral assemblages have been altered by hydrothermal activity and the alteration can be traced from partial to complete so that in any one thin section the primary and secondary mineral assemblages can be seen next to one another. Killalaite is developed in spurrite-rich rocks now altered to assemblages containing calcite, scawtite, cuspidine, afwillite, xonotlite, and other hydrated calcium silicates. It occurs in veins and cavities in the altered rocks and is associated with either calcite or afwillite. In one thin section it is seen to replace tilleyite.

Physical and optical properties. Killalaite can be easily distinguished from the related minerals by its characteristic rhombic cross-sections showing cross 'bow-tie' twins (fig. 1c) and its optical properties. It occurs as well-formed crystals (fig. 1a) up to 2 mm in length; longitudinal sections of the crystals show one perfect and one good cleavage at 90° to each other (fig. 1b) and cross-sections show one perfect and one poor cleavage, parallel to the rhombic outline, at 75° to each other. Extinction is parallel in longitudinal sections but inclined in cross-sections and assuming the perfect cleavage to be (100) and the other two cleavages as (010) and (001) the mineral is monoclinic, elongation [010] and $\beta \approx 105°$. Refractive index (in sodium light) is α 1·635, γ 1·642 ($\pm$002), $2V_\alpha$ 26 ($\pm 2°$) measured on universal stage, density calculated from refractive index is 2·88 g/cm³, optical orientation is $\beta =$ [010], $\gamma : c$[001] $\approx$ 16° (in obtuse β), optic axial plane (010). Killalaite shows a complicated penetrative twinning; the nature of twinning remains unresolved except that the composition plane includes the *b*-axis.
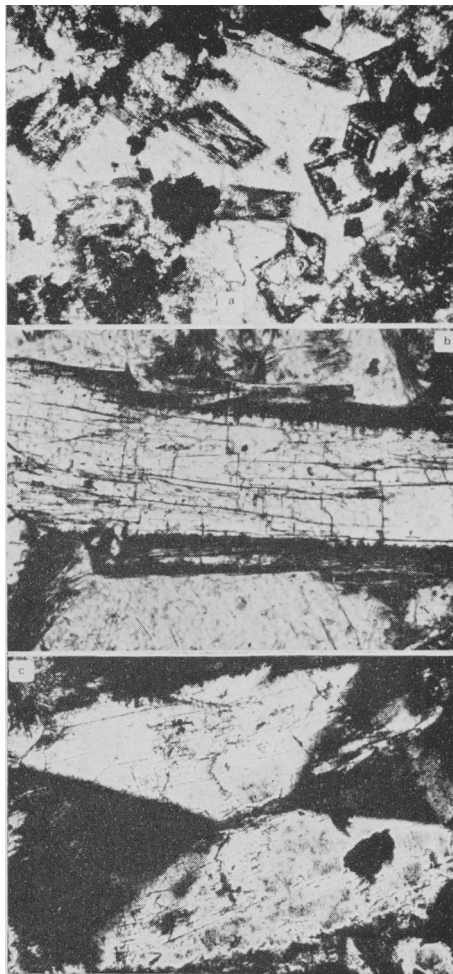

FIG. 1. a: Killalaite crystals in a vein of calcite. The squarish crystal (right middle) is $\frac{1}{2}$ mm. across. b: A longitudinal section of killalaite showing two cleavages, the length is close to 2 mm. c: A section nearly parallel to (010) showing the (100) cleavage trace and the penetration twinning, crystal size as in a. All three photomicrographs taken under partially crossed nicols.

Chemical composition. The chemical composition of killalaite was determined by electron microprobe analysis using a synthetic standard of an augite composition. The standard was tested for homogeneity as well as composition against afwillite, merwinite, monticellite, and spinel and found satisfactory. Killalaite crystals were found to be free of compositional zoning and only areas free of inclusions and alteration products were probed at an operating voltage of 20 kV. In addition to the main constituents listed below, MgO, Fe_2O_3, and Al_2O_3 were each found to be < 0·1 wt. %. Water was calculated by difference. Microchemical tests for CO_2 and F were negative.

Killalaite: CaO 57·0$\pm$1 %, SiO_2 39·8$\pm$1 %, H_2O 3·2 (by difference);
$2Ca_3Si_2O_7.H_2O$:   56·57 %,   40·40 %,   3·03 %.

The analysis compares rather well with the theoretical composition $2\ Ca_3Si_2O_7 . H_2O$. Rankinite and kilchoanite would give a similar analysis but their properties are quite distinct and the manner of its occurrence suggests that water is an integral part of the killalaite structure.

X-ray powder data. The X-ray powder pattern of killalaite was obtained with a 114·85 mm. dia. camera using nickel-filtered copper radiation. Crystals were extracted from the calcite matrix, which acted as internal standard. The X-ray pattern (Table I) is unique. Using the estimated values of density and the β angle and assuming $Z = 2$,

TABLE I. *X-ray powder diffraction data for killalaite**

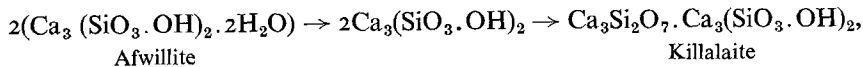| d	I	d	I	d	I	d	I
7·40	3	3·03†	80	2·055	10	1·566	3
6·75	10	2·97	2	1·975	15	1·550	3
5·45	1	2·85	2	1·920†	30	1·520†	30
5·10	25	2·824	100	1·876†	30	1·493	1
4·97	3	2·724	60	1·849	2	1·469†	8
4·50	5	2·650	5	1·815	10	1·413†	40
4·35	5	2·560	30	1·766	5	1·357†	5
3·86†	30	2·540	30	1·748	15	1·285	5
3·38	30	2·275†	45	1·720	5	1·233†	5
3·30	10	2·250	10	1·688	35	1·108	10
3·19	25	2·224	45	1·673	35	1·044†	20
3·09	25	2·150	3	1·620†	30		

* Camera dia. 114·85 mm, Ni filtered Cu radiation, line intensities visually estimated.
† Peak intensities modified by calcite impurity acting as internal standard.

approximate unit cell dimensions were calculated to be a 9·3, b 9·9, and c 7·7 ($\pm$0·1 Å) and the first seven lines were indexed as (001), (110), (101), (111), (020), (200), and (120). Complete indexing was not attempted because of uncertainty in the choice of the unit cell and the assumptions employed. The b, c, and β values of the deduced cell bear resemblance with the corresponding values of tilleyite and the a value is close to $a/2$ of tilleyite, which suggests that the two structures are related.

Discussion. Scawtite and cuspidine are the main alteration products of the spurrite-bearing rocks and killalaite either occurs with coarsely crystallized calcite and afwillite in veins and cavities in the altered rocks or as replacements of tilleyite, indicating that both afwillite and killalaite were formed later than scawtite, cuspidine, and tilleyite. Both killalaite and afwillite are altered to xonotlite and must have formed before xonotlite. Cuspidine is by no means restricted to the late-stage secondary assemblages where it occurs as lanceolate porphyroblasts. In the primary assemblages it is associated with spurrite and calcite or spurrite, wollastonite, rankinite (kilchoanite), and tilleyite as subhedral to rounded twinned grains and must have a wider stability field than that proposed by Van Valkenburg and Rynders (1958). Spurrite, wollastonite, and rankinite were formed at high temperature and very low pressure. Tuttle and Harker's (1957) experimental data on the reaction (calcite+wollastonite = spurrite+ CO_2) indicates CO_2 pressures below 500 bars in the temperature range of 700° to

1000 °C. The presence of rankinite suggests temperatures nearer the upper limit of the above range and with temperature dropping to the lower limit the stability field of tilleyite (Harker, 1959) and kilchoanite (Roy et al., 1960) was probably reached. The vapour phase contained some F as well since cuspidine is a constituent. With the temperatures below 700 °C and the pressures much higher and the vapour phase containing more H_2O than CO_2 spurrite and kilchoanite became unstable. Tilleyite, however, is stable at H_2O pressure of 3500 bars (McConnell, 1958) down to a temperature of 550 °C below which it breaks down to afwillite and calcite. The experimental data on scawtite (Harker, 1965) are at variance with the present paragenesis and Harker's temperature range of 140 to 300 °C is too low, probably owing to a very low partial pressure of CO_2 being realized in his study. Xonotlite is probably stable below about 400 °C under similar conditions (Roy, 1958), which leads to the conclusion that the stability field of afwillite and killalaite lies between about 350° and 550 °C at pressures ranging between about 500 to 3500 bars. Dehydration of afwillite occurs in stages as shown by its d.t.a. curve (McLaughlin, 1952), which contains a broad endothermic peak between 250° and 450 °C with several steps, of which the largest at 370 °C was suspected to correspond with the formation of killalaite according to the scheme:

$$2(Ca_3 (SiO_3.OH)_2.2H_2O) \rightarrow 2Ca_3(SiO_3.OH)_2 \rightarrow Ca_3Si_2O_7.Ca_3(SiO_3.OH)_2,$$
$$\text{Afwillite} \qquad\qquad\qquad\qquad\qquad\qquad \text{Killalaite}$$

but a thermal study of the Inishcrone afwillite at atmospheric pressure by X-ray powder diffraction showed that afwillite is stable up to 370 °C, the only change being broadening of powder lines. Between 380 and 410 °C killalaite was not detected and instead kilchoanite was formed, which on standing for a few days changed to calcite. These results contradict those of Moody (1952), Heller (1952), and Taylor (1955) who found γ-Ca_2SiO_4 as the thermal product of afwillite. At higher temperatures dellaite and wollastonite were formed in accordance with Roy et al. (1960). This failure to obtain killalaite perhaps reflects the importance of CO_2 in the vapour phase and its influence upon pressure-dependent equilibria involving a vapour phase. Killalaite as an equivalent of phase Z (Roy, 1958; Roy et al., 1960), kilchoanite (Agrell and Gay, 1961), or rustumite (Agrell, 1965) is discounted on the grounds of its unique optical and physical properties and the X-ray powder pattern.

Conclusions. Killalaite is a new hydrous calcium silicate mineral and its association with afwillite suggests that it probably formed hydrothermally in the temperature range of 350 to 550 °C in a CO_2-deficient environment. The pressure conditions are difficult to estimate owing to the fact that either appropriate equilibria are independent of pressure or experimental data involving a binary or possibly a ternary vapour phase (CO_2–H_2O–F) are lacking. Available experimental data on the systems involved suggests that during the formation of killalaite in the late stages fluid pressures probably ranged between 500 and 3500 bars.

REFERENCES

AGRELL (S. O.), 1965. *Min. Mag.* **34** (Tilley Vol.), 1–15.
—— and GAY (P.), 1961. *Nature*, **189**, 743.
EMELEUS (C. H.) and PRESTON (J.), 1969. *Field excursion guide to the Tertiary volcanic rocks of Ireland.* Belfast (Dorman & Sons).
HARKER (R. I.), 1959. *Amer. Journ. Sci.* **257**, 656–67.
—— 1965. *Min. Mag.* **34** (Tilley Vol.), 232–6.
HELLER (L.), 1952. [*Proc. Third Internat. Symp. Chem. Cement*, 237], quoted in HELLER and TAYLOR, *Crystallographic Data for the calcium silicates*, London (HMSO), 1956.
MCCONNELL (J. D. C.), 1958. *Min. Soc. Bull.*, No. 6.
MCLAUGHLIN (R. J.), 1952. In MOODY, 1952.
MOODY (K. M.), 1952. *Min. Mag.* **29**, 838.
NAWAZ (R.), 1972. *Sci. Proc. Royal Dublin Soc.*, Series A, **4**, 371–2.
ROY (D. M.), 1958. *Amer. Min.* **43**, 1009–28.
—— GARD (J. A.), NICOL (A. W.), and TAYLOR (H. F. W.), 1960. *Nature*, **188**, 1187–8.
SYMES (R. G.) and BAILY (W. H.), 1879. *Geol. Surv. Ireland, Memoir* 53.
TAYLOR (H. F. W.), 1955. *Acta Cryst.* **8**, 440.
TUTTLE (O. F.) and HARKER (R. I.), 1957. *Amer. Journ. Sci.* **255**, 226–34.
VAN VALKENBURG (A.) and RYNDERS (G. F.), 1958. *Amer. Min.* **43**, 1195–1202.

[*Manuscript received 7 May 1973*]

Note added in proof: A qualitative proof of the hydrous nature of killalaite is provided by its decomposition under the electron beam and by the evolution of water when it is heated in a test tube.