Apophyllite and other zeolite-type minerals from the Whin Sill of the northern Pennines

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Abstract

Apophyllite, analcite, chabazite, prehnite and stilbite are described from pectolite-, chlorite-, calcite- and quartz-bearing veins and joint coatings in the late Carboniferous quartz dolerite of the Whin Sill of the northern Pennines. These veins represent the final hydrothermal stages in the sill's emplacement and are not related to the widespread lead–zinc–barium–fluorite mineralization of the northern Pennine orefield. Thermogravimetric studies of apophyllites from the two Whin Sill occurrences reveal that at one locality the minreal is fluorapophyllite, at the other hydroxyapophyllite.

KEYWORDS: analcite, apophyllite, chabazite, northern Pennines, pectolite, prehnite, thermogravimetric analysis, Whin Sill.

Geology of the Whin Sill

THE Whin Sill comprises a series of quartz-dolerite sills and associated dykes intruded into the Lower Carboniferous sediments of the northern Pennines and a large area of south and east Northumberland. Numerous descriptions of the petrography have been published, prominent amongst which are those by Teall (1884*a*,*b*), Holmes and Harwood (1928), Tomkeieff (1929), Smythe (1930), Dunham (1948), Harrison (1968), and Randall (1980). In addition accounts of hydrothermal alteration of Whin Sill rocks have been given by Wager (1929*a*,*b*), Dunham (*op. cit.*), Dunham *et al.* (1968), and Ineson (1968).

The age of the intrusion has long attracted attention. Arguing from purely geological and stratigraphical evidence various authors have deduced a late Carboniferous (Stephanian) age (e.g. Holmes and Harwood, 1928; Dunham, 1932). K–Ar determinations by Fitch and Miller (1967) suggest a date of 295 ± 6 Ma.

Mineralisation of the Whin Sill

In the extensive literature on the Whin Sill numerous authors have made reference to the widespread occurrence of a suite of minerals developed in joints in the sill and attributed these to a late hydrothermal phase in the cooling of the intrusion. To date minerals recorded from this suite include chlorite, bowlingite, calcite, quartz, sericite, albite, anatase and titanite (e.g. Wager, 1929*b*; Fitch and Miller, 1967). Wager (*op. cit.* p. 234) commented that zeolites were found rarely with calcite and quartz in early joints though the zeolite species were not named. However the widespread occurrence of pectolite has long been known in this paragenesis (e.g. Holmes and Harwood, 1928; Tomkeieff, 1929; Smythe, 1930). Early alteration of some of the pectolite to stevensite has been noted by Randall (1959) and Young and Schofield (1990). Other zeolite-type minerals have been reported from only a handful of localities. Wager (*op. cit.* p. 232)

Mineralogical Magazine, June 1991, Vol. 55, pp. 203–207

noted the presence of prehnite at Cowshill, Weardale, where in addition Randall (*op. cit.* p. 223) made brief reference to the occurrence of apophyllite. Datolite has been found at Barrasford Quarry, Northumberland (Randall, *op. cit.*).

Recent collecting in Weardale and Teesdale has revealed new occurrences of prehnite and apophyllite and in addition has provided specimens of analcite, chabazite and stilbite, three species not previously recorded from the Whin Sill.

Apophyllite. Passing reference was made by Randall (1959, p. 223) to the presence of apophyllite at Copt Hill Quarry, Cowshill, Weardale [NY 8515 4080], though no description or analytical details of the mineral were given. Examination of several collections of north of England minerals has revealed examples of well-crystallised apophyllite from this locality, mostly collected early this century, no doubt when the quarry was working. Notable specimens are in the Russell Collection at the British Museum (Natural History). In the examples seen by the writers the apophyllite forms lustrous colourless crystals composed of a combination of prism (100) and pyramid (111) terminated by (001) faces. Vertical striations are conspicuous on (100). Crystals are generally up to 5 mm long and commonly encrust white to pale buff fibrous pectolite.

Although the Whin Sin is still well exposed at Copt Hill the faces are inaccessible and no mineralisation is now visible in this disused and flooded quarry.

More recently apophyllite has been found in some abundance in the underground workings of Cambokeels fluorspar mine (otherwise known as Cammock Eals Mine), Eastgate, Weardale [NY 935 383]. The sill, here at the horizon of the Jew Limestone, is approximately 70 m thick and hosts important vein oreshoots of fluorspar in the Slitt Vein. The entire thickness of the sill is penetrated by the main inclined adit and haulage way. The winch chamber at the foot of the main incline exposes a roughly horizontal belt, up to 3 m thick, of very closely jointed dolerite approximately 45 m below the top of the sill. The numerous vertical and sub-horizontal joint surfaces here are commonly open and up to 3 mm wide. Well-crystallised apophyllite commonly encrusting analcite is locally abundant in these fissures. The mineral typically forms stout, colourless clear or slightly turbid white prisms in which the most prominent faces are (100) and (001), the latter commonly exhibiting a rather uneven or rough surface. Pyramid (111) faces, though invariably present, are generally small. Most of the apophyllite crystals are up to 4 mm long though a few crystals up to 7 mm long have been collected. In places apophyllite is coated by crusts, up to 1 mm thick, of pure white silky, fibrous pectolite.

A second roughly horizontal belt of closely-spaced jointing carrying the same mineralisation is exposed in the sides of the haulage incline approximately 10 m vertically beneath the winch chamber. Exposures here are much less clear but this belt appears to be around 2 m thick. No other exposures of analcite or apophyllite-bearing dolerite have been observed in the mine.

Thin sections of the dolerite immediately adjacent to the apophyllite and analcite crusts show no evidence of alteration other than a very thin film of very dark green chlorite locally beneath some of the analcite crystals.

The apophyllites from both Copt Hill and Cambokeels have been studied by differential thermal analysis, the results of which are described below.

Analcite. Although no record of this mineral from the Whin Sill has so far been published, specimens of analcite from Copt Hill Quarry, Weardale, consisting of crusts of colourless trapezohedral crystals on dolerite are in the Russell Collection of British minerals in the British Museum (Natural History).

At Cambokeels Mine [NY 935 383] analcite, commonly accompanied by apophyllite, is very abundant encrusting the numerous joint surfaces exposed in the winch chamber and in the small exposures of mineralised dolerite in the haulage incline. Analcite occurs as crusts up to 30 cm across, composed of clear colourless trapezohedra. Individual crystals are typically small (up to 2 mm) but in a very few more widely spaced joints, rare isolated crystals up to 6 mm across have been collected. Incompletely developed trapezohedra which 'bridge' the joint walls are common. The analcite is commonly accompanied by, and locally overgrown by, small colourless apophyllite crystals up to 2 mm in length. A few colourless rhombohedral 'nail-head' calcite crystals up to 2 mm across are associated with these minerals in some specimens.

At High Force Quarry, Upper Teesdale [NY 878 290], analcite occurs as clear colourless trapezohedral crystals up to 1 mm across which in places form continuous crusts up to 12 cm across on joint surfaces of dolerite pegmatite. A few twinned crystals of chabazite locally encrust the analcite. The best examples of analcite collected here were obtained from fallen blocks at the foot of the main northern face of the quarry. In these specimens, as in those from Cambokeels Mine, the dolerite immediately beneath the analcite

crusts shows no sign of alteration. A little colourless analcite was observed *in situ* in narrow stilbite-bearing fissures in slightly chloritised dolerite pegmatite at one point near the foot of the northern face.

Chabazite. This mineral is also recorded here for the first time from the Whin Sill from three localities.

At Cambokeels Mine chabazite is a rare associate of apophyllite in the joints exposed in the winch chamber. A few specimens have been obtained of white interpenetrant twinned rhombohedra up to 3 mm across encursting apophyllite. A little white fibrous pectolite encrusts these crystals locally. Specimens collected from the mine dumps show thin (<1 mm) crusts of colourless crystalline chabazite, unaccompanied by any other mineral on unaltered dolerite. The provenance of these specimens in the mine is unknown.

Chabazite has been collected from loose blocks at Force Garth Quarry, Teesdale [NY 873 282], where it occurs as colourless ill-formed rhombohedra up to 0.5 mm across forming crusts on joint surfaces of unaltered dolerite.

A few specimens of chabazite have also been obtained from the main face of the nearby High Force Quarry [NY 878 290]. Here the mineral occurs as colourless rhombohedra up to 0.75 mm across which commonly exhibit penetration twinning, forming patchy crusts locally associated with stilbite on dolerite pegmatite.

Prehnite. Wager (1929, p. 323) noted prehnite, accompanied by calcite and quartz, filling a joint in the dolerite of Copt Hill Quarry, though no description of the mineral was given. The only other record of prehnite in association with the Whin Sill is as a constituent of contact altered impure limestones and calcareous shales in Teesdale (Robinson, 1973).

Prehnite has recently been found partly filling joints in dolerite at Force Garth Quarry. Some specimens collected here show pale green coarsely crystalline prehnite forming lenses up to 5 mm wide and over 5 cm long in the centre of a vein of pale pinkish-buff radiating pectolite. The prehnite encrusts pectolite which forms the walls of the vein. A little similar coloured pectolite occurs filling a very narrow (<0.5 mm wide) central vug in the prehnite lens. Other specimens show prehnite on dolerite with a later crust of fibrous pectolite encrusting the prehnite.

Stilbite. This mineral, recorded here for the first time from the Whin Sill, has been found *in situ* in the main northern face of High Force Quarry [NY 878 290]. It occurs as colourless, lustrous, tabular prisms up to 1.5 mm long lining numerous closely spaced open fissures up to 3 mm wide in slightly chloritised dolerite pegmatite. The stilbite is locally accompanied by small crystals of analcite and chabazite though the relationship of these three minerals with one another is not clear.

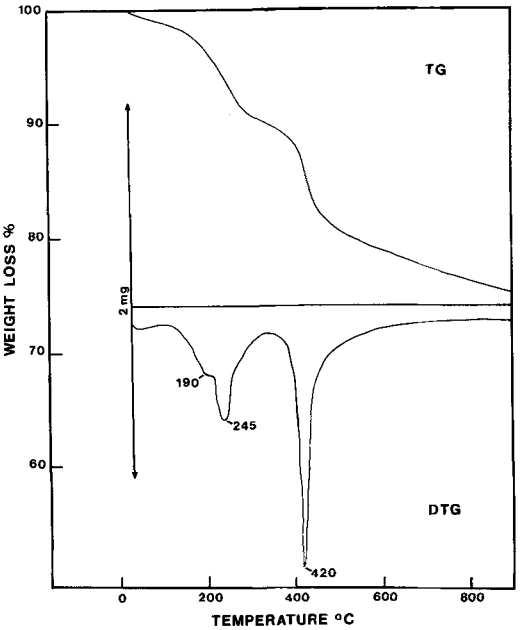

FIG. 1. Thermogravimetric (TG) traces and their differentials (DTG) for Copt Hill apophyllite.

Thermal studies of apophyllite

Many minerals containing interstitial water and/or hydroxyl groups are amenable to qualitative or quantitative estimation by differential thermal methods of analysis (DTA). One case where this method is of special value is in distinguishing quickly and easily between hydroxyapophyllite and fluorapophyllite.

The earliest record found of the thermoanalytic characterisation of an apophyllite is that of Koza and Masuda (1926–9) on a sample from Maze, Echigo Province, Japan. Their sample dehydrated stepwise as shown by two endothermic events with peak maxima at 400 and 500 °C respectively. This work, the first ever differential thermal analysis (DTA) of zeolitic minerals, was carried out on primitive apparatus. Koizumi (1953) reported work on a sample from the Kamioka Mine, Gifu Pref., Japan, in which the same events were recorded at 334 and 440 °C respectively. Ivanova (1961) presented data on a

specimen of unstated origin suggesting that the appropriate peak maxima should be 350 and 400 but she used a heating rate in excess (60 K min^{-1}) of that normally regarded as appropriate to the accurate determination of thermal analysis events (i.e. 12–20 K min^{-1}).

The most recent report is that of Bartl and Pfeifer (1976). Their work recorded a more complex DTA thermal profile with events at 320, 350 and 450 °C. Unfortunately they did not record their heating rate or the instrument used. Furthermore their upper limit of temperature was 600 °C and the origin of the sample examined was not stated. Bartl and Pfeifer, however, are the only authors who have reported thermal methods to ascribe a fluoride content to apophyllite, illustrating by neutron diffraction evidence, that F^- was diadochically replaced by OH^- in the sample studied.

In this study, two samples, one from Copt Hill Quarry and the second from Cambokeels Mine, were examined by thermogravimetric analysis (TG). The instrument used was a Mettler TA 3000 system with a microprocessor control and data analysis facility. The heating rates were 20 K min^{-1}. The thermoanalytic profiles recorded are shown in Figs 1 and 2. Very clear differences can be seen especially on the differential trace (DTG). The Copt Hill samples (Fig. 1) shows major events with T_m = 245 and 420 °C, with a shoulder occurring at about 190 °C on the first peak. The total weight loss (to 900 °C) observed was 22.99% with 9.02% lost in the first stage followed by 13.11% in the second major stage. The balance was a small loss of 0.86% at about 806 °C.

For the Cambokeels sample (Fig. 2) the first event again has a shoulder associated with it but now the main feature is at 276 °C with the shoulder at 350 °C. Other differences are that the second major event now is at T_m = 445 °C and a new feature appears at T_m = 732 °C. The associated weight losses are 8.56, 7.28 and 4.04% respectively totalling 19.88%.

When considering these total weight losses, both are in excess of that expected (17.81%) from the normally accepted empirical formula of $KCa_4Si_8O_{20}(OH).8H_2O$, but this is common (Marriner *et al.*, 1990). The principal differences between the two samples can be taken as illustrating the absence of OH^- in the Cambokeels sample, i.e. it is a fluorapophyllite, and the Copt Hill sample is a hydroxyapophyllite. The exact interpretation of the synergism between H_2O/OH^- and H_2O/F^- prompted weight losses, together with their link to cation composition, requires further work. The link between F^- content and the occurrence of a high temperature thermal event has been noted frequently in fluorapophyllites (Marriner *et al.*, *op. cit.*).

The relative lack of direct agreement between the T_m values recorded here and those in previous literature are due to uncertainties of the earlier equipment and conditions, particularly as their sample sizes would be much larger than those used in this work (6–16 mg).

Discussion

The minerals described here clearly belong to the suite of late-stage joint fillings which are restricted to the sill itself. Their composition is consistent with redistribution of elements derived by hydrothermal alteration of the primary constituents of the sill during its final cooling stages (e.g. Wager, 1929*b*). No sulphides other than minor amounts of pyrite, pyrrhotite and rare traces of chalcopyrite or any of the gangue minerals which characterise the main northern Pennine mineralisation, e.g. fluorite, ankerite, baryte, have been found in any of these occurrences. Similarly none of the zeolite-type minerals discussed above, has been found in any of the northern Pennine deposits. The occurrence of the barium-zeolite harmotome within otherwise typical northern Pennine vein assemblages at one

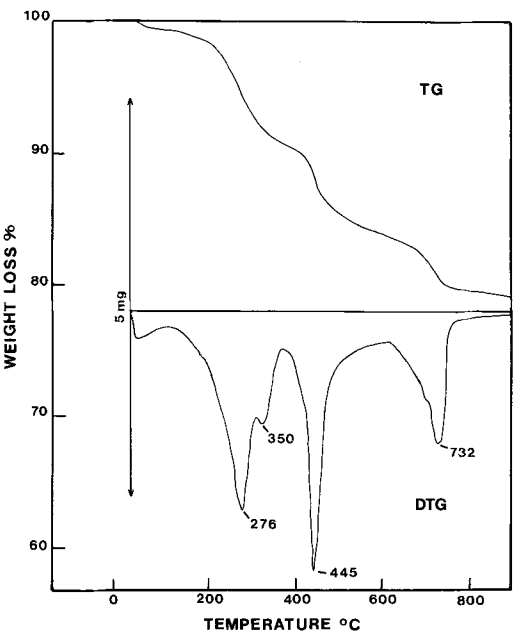

FIG. 2. Thermogravimetric (TG) traces and their differentials (DTG) for Cambokeels apophyllite.

or two localities has been attributed to reactions between mineralising fluids and Whin Sill wall-rock during a phase of barium mineralisation (Young and Bridges, 1984).

Recent estimates of 284 ± 40 Ma for the onset of northern Pennine mineralisation (Dunham *et al.*, 1968) overlap the date of 295 ± 6 Ma for the emplacement of the Whin Sill. Clearly the two events could well have been very close in time. More recently Young *et al.* (1985) have suggested a reaction between early mineralising fluids and still hot Whin dolerite to account for the remarkable deposit of magnetite-rich ore in Teesdale. However the striking mineralogical differences between the joint fillings in the Whin Sill and the northern Pennine deposits reflect two separate mineralising processes.

Acknowledgements

X-ray diffraction determinations by B. Beddoe-Stephens and K. Siddiqui (BGS) are gratefully acknowledged. The help and advice of G. F. Marriner is gratefully acknowledged. H. Enamy is thanked for carrying out the thermal analyses. Thanks are also due to the late J. P. Fuller of the Department of Mineralogy, British Museum (Natural History) for arranging access to the Russell Collection of British minerals. The management of Hargreaves Quarries, Teesdale, and Weardale Minerals are thanked for allowing access to their workings. D. Strutt of Weardale Minerals is thanked for helpful discussion on the geology of Cambokeels Mine. Mrs. J. Dunkley and Mrs. P. Campbell are thanked for preparing the typescript. This paper is published by permission of the Director, British Geological Survey (NERC).

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[*Manuscript received 26 January 1990; revised 12 September 1990*]