Progressive metasomatism in the flint nodules of the Scawt Hill contact-zone.

(With Plate XXI.)

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IN describing the chief assemblages of the Scawt Hill contact-zone in Co. Antrim brief reference was made to the occurrence of wollastonite and xonotlite associated with the flint nodules of the contact-altered chalk.[1] A more detailed examination of these nodules has now been made and the study of a large number of examples has revealed an interesting group of mineral assemblages which have developed by a progressive metasomatism of these siliceous bodies.

The nodules, despite the fundamental mineral changes which have affected them, can be readily recognized in the contact-zone retaining as they do the characteristic form of the original nodule and being sharply demarcated from the larnite-spurrite-rocks by which they are encased. Where the metasomatism is more intense as the junction is approached, the larnite-rock in the vicinity of the nodules tends to become in some examples—not in all—darker, due to an increase in the spinel or magnetite content. A Liesegang effect is sometimes produced by the development of a series of roughly concentric rings in which is found an increase in dark mineral content (spinel and magnetite). Three types of altered nodules may be distinguished, but all three are connected by gradational varieties.

Type *a*.—Where little metasomatism is involved the principal metamorphic effects are seen in a recrystallization of the chalcedony to granular quartz, while the immediate boundary against the larnite-rock is a narrow sheath of fine-grained wollastonite. At this stage migration of lime has usually begun and the nodule is veined by narrow stringers consisting of wollastonite crystals. Smaller crystals are also found enclosed in and interstitially among the quartz grains.

[1] C. E. Tilley, Min. Mag., 1931, vol. 22, pp. 443–444.

This is a case of pure lime metasomatism demanding nothing more than migration from solutions inherent in the limestone originally encasing the nodules.

Type *b*.—A more fundamental change is revealed in other types of nodules which, when broken open, reveal a peripheral greenish ring gradually encroaching towards the white centre of the nodule. In the large nodules various stages of partial to complete replacement can be studied. Examination of the greenish zone shows it to be composite and made up largely of a fine-grained sheaf of fibres in which are set clear pearly laths of wollastonite ranging in size up to 15×1 mm.

Where the metasomatism is incomplete the core of the nodule is built up of quartz grains enclosing and interstitially surrounded by the same fibrous material which forms the bulk of the green periphery. This passes out—usually rapidly—into the green zone in which practically all quartz has disappeared. Ultimately in the case of the smaller nodules the whole is converted into a green coloured assemblage in which porphyroblasts of wollastonite can be readily recognized by the unaided eye.

Under the microscope the green zones are seen to be built up of divergent sheaves of xonotlite surrounding porphyroblasts of wollastonite. These xonotlite sheaves vary in colour from point to point. Some are practically colourless, whilst others are of a distinct green tint and are pleochroic. The colourless xonotlite has already been noticed forming fibres elongated along γ with straight extinction. In cross-section the bundles give 2V very small, sensibly uniaxial, and positive; refractive indices somewhat variable but average α 1·578, γ 1·590. Between the colourless fibres and others distinctly green and pleochroic there are all gradations. The markedly green variety has γ green, α lighter green to light brown-green. The similarity in orientation and the gradation the fibres exhibit in refraction, double refraction, and colour indicate that the colour is due essentially to replacement by ferrous iron.

The wollastonite laths have the usual habit elongated along the *b*-axis with prominent (100) faces, and twinning on (100). Outgrowths of xonotlite from the wollastonite laths are frequently developed.

At this stage there is an incipient development of a greenish monoclinic pyroxene found amongst the felt of xonotlite fibres and exceptionally appearing even in small porphyroblasts as green hedenbergitic diopside. In some examples aegirine occurs as fine fibres in the same fashion.

These constituents make up the greater part of the green zones, but sporadically developed are found small areas or nests filled with colourless fibrous okenite, often associated with recrystallized quartz. The okenite has the optical properties of that described by Bøggild.[1] The extinction of the fibres while frequently parallel shows in different fibres values up to 30°, confirming the low symmetry which Bøggild has already indicated. Elongation positive, 2V large, and the sign is negative though this is not readily determined. The refraction is less than that of quartz γ 1·540 and the double refraction like that of the associated quartz 0·009. These properties identify the mineral with okenite. Nevertheless in some sections the refraction of otherwise similar material is somewhat greater, reaching a figure of γ 1·553. Material corresponding to this value is recorded for okenite by Lacroix.[2] Whether this variation is due to variable water content is not known, but it is clear that a systematic examination of okenite, in view of the discrepancies in the data that appear in the literature, is required.

An analysis of a nodule of type *b* is given on p. 517. It reveals a surprising content of soda, which from the microscopic features is unexpected. The wollastonite fibres were separated from the rock, and the fibrous material which is almost wholly xonotlite, but still containing a small percentage of pyroxene fibres and a little okenite and quartz which it was impossible to separate from the felt, gave on partial analysis SiO_2 50·45, $(Al,Fe)_2O_3$ (all Fe determined as Fe_2O_3) 5·66, CaO 27·94, Na_2O 4·41, K_2O 0·82, MgO n.d., H_2O 7·41 %. It is clear that the bulk of this soda must be present in the xonotlite which has also a high water content comparable with the figure given by Shannon for the Leesburg xonotlite.[3] Part of it is no doubt water adsorbed on the surface of the fine fibres.

In its soda content the xonotlite is most comparable to the natroxonotlite described by Williams from the Potash Sulphur Springs region, Arkansas,[4] which has CaO 36·72, Na_2O 4·41 %. The greenish

[1] O. B. Bøggild, Kgl. Danske Vidensk. Selsk. Mat.-fys. Meddel., 1922, vol. 4, no. 8, pp. 15–16. [Min. Abstr., 2–59.]

[2] A. Lacroix, Bull. Soc. Min. France, 1885, vol. 8, p. 341; 1887, vol. 10, p. 316.

[3] E. V. Shannon, Proc. United States National Museum, 1925, vol. 66, art. 28, p. 12. [Min. Abstr., 3–204.]

[4] J. F. Williams, Annual Report Geol. Survey Arkansas, 1891, vol 2 (for 1890), p. 356.

colour of much of the xonotlite of Scawt Hill must be ascribed to ferrous iron which with sodium is replacing the calcium of the pure lime-xonotlite.

Type *c*.—A still more fundamental metasomatism is revealed in certain other nodules which are less abundantly developed. Here again the form of the characteristic flint nodule is preserved. These nodules are distinguished by their coarse grain size and abundant wollastonite. As compared with the nodules already described the areas intervening between the wollastonite nodules are much darker in colour and built up of coarser grained material. The clear pearly wollastonites reach up to 25×10 mm. in size and are frequently sheathed by a fibrous alteration product.

Under the microscope the dark areas between the wollastonite blades are seen to be composed of a strongly zoned pyroxene as relatively large crystals up to 3 mm., and less abundant melilite. The sheath around the wollastonite blades is seen to consist of pectolite partly in parallel growth and extending along the cleavages, but passing out into divergent fibres of the same mineral.

The pectolite is characterized by its high double refraction, α 1·597, γ 1·633, uniform positive elongation and sign. The parallel growth of the pectolite around the wollastonite is revealed not only in the longitudinal but also in the cross-sections, the (100) and (001) cleavages of the wollastonite passing into the narrow mantle of pectolite which in this orientation has the acute bisectrix (γ) emerging from the section. The pectolite is clearly developing from the wollastonite and in some cases the wollastonite forms a mere residual in an aggregate of pectolite fibres.

The pyroxenes of the nodule are characteristically strongly zoned and in various nodules range from green augite through aegirine-augite to aegirine, the last of which may form separate crystals or as a peripheral zone to the green augite or aegirine-augite. The pleochroic scheme of the aegirine is γ brown, β brown-green, α grass-green. The aegirine-augite is pleochroic in the same tints, but less strongly marked. The aegirine itself appears to pass out in places to an acmite of brown tint with but feeble pleochroism.

The melilite has the features characteristic of this mineral in the hybrid zone,[1] but it is now in various stages of replacement, principally by magnetite, which develops thickly along the cleavages and fractures. Among the birefringent felt of fibres simultaneously

[1] C. E. Tilley, loc. cit., p. 455.

developed with the magnetite is cebollite, with other fibres of indeterminate character owing to the fine confused texture, which does not permit unravelling of their optical properties. In addition to occurring as a replacement of melilite, magnetite also occurs interstitially among the pyroxenes, while there is usually a small amount of pyrrhotine associated with it. Small nests of okenite like those already described are also found, but xonotlite is typically absent.

The profound metasomatism which the flint nodules have experienced render chemical analyses of these assemblages instructive. Two such analyses executed on material of type *b* and type *c* are set down below, together with a previously recorded analysis of a metasomatized chalk rock.

	I.	II.	III.
SiO_2	51·57	42·58	22·52
TiO_2	0·14	0·61	0·57
Al_2O_3	1·10	2·73	10·11
Fe_2O_3	1·85	4·29	4·58
FeO	2·17	4·77	2·90
MnO	0·42	0·68	—
MgO	0·94	2·27	4·93
CaO	30·25	32·93	46·36
BaO	0·15	0·22	—
Na_2O	3·59	2·67	1·06
K_2O	0·52	0·20	0·05
H_2O+	5·66	5·03	0·78
H_2O-	1·10	0·19	0·08
P_2O_5	n.d.	0·05	0·19
CO_2	0·56	0·55	5·08
Cr_2O_3	nil	nil	—
S	0·14	0·49	0·49 (SO_3)
			0·18 (FeS)
	100·16	100·26	99·88
Fe/Mg	5·3	4·9	1·8
Sp. gr.	2·69	2·92	—

I. Xonotlite-wollastonite-rock (type *b*).
II. Wollastonite-pyroxene-melilite-rock (type *c*).
III. Metasomatized chalk (spurrite-merwinite-gehlenite-spinel-(calcite)-rock). Min. Mag., 1931, vol. 22, p. 445.

The first two analyses show that from the incoming solutions the chief constituents replacing the silica of the flint nodule are CaO—for which the source is largely the encasing limestone,—Na_2O, and iron oxides. These have been selectively absorbed and partook of reaction with SiO_2 to form the constituent minerals. Alumina, which in the metasomatized chalk is often abundantly precipitated in the form of spinel and gehlenite, plays here a subordinate role and is only significantly represented in type *c* where it appears in the form of melilite.

The preservation of the characteristic shape and form of the flint nodules—sharply marked off from the surrounding limestone—renders these metasomatic assemblages particularly convincing examples of a replacement process unaccompanied by volume change. It is indeed a striking case of the rule of equality of volume, a thesis which Lindgren [1] has repeatedly urged for metasomatism. The incoming of CaO, Na_2O, iron oxides, and water has been accompanied by an outward migration of silica. Comparing the specific gravities of the original flint nodule (2·65) and a rock of type *c* (2·92) it is readily seen that for every 100 c.c. of flint nodule involved there has been an effective outward migration of 140 grams of silica, which has no doubt played its part in the silication of the carbonate casing.

EXPLANATION OF PLATE XXI.

FIG. 1. Flint nodule (partly metasomatized) in larnite-spurrite-spinel-rock. Scawt Hill, Larne, Co. Antrim. $\times \frac{1}{2}$.

FIG. 2. Section through metasomatized flint nodule. Scawt Hill. The interior of the flint nodule has at this stage suffered little change and consists of a fine-grained quartz aggregate. The interior zone passes rapidly into a coarser zone built of quartz with interstitial soda-xonotlite, and this zone again into the peripheral zone consisting essentially of wollastonite (clear areas) and fibrous radiating nests of brown to greenish soda-xonotlite. $\times 16$.

[1] W. Lindgren, Bull. Geol. Soc. America, 1925, vol. 36, p. 247.

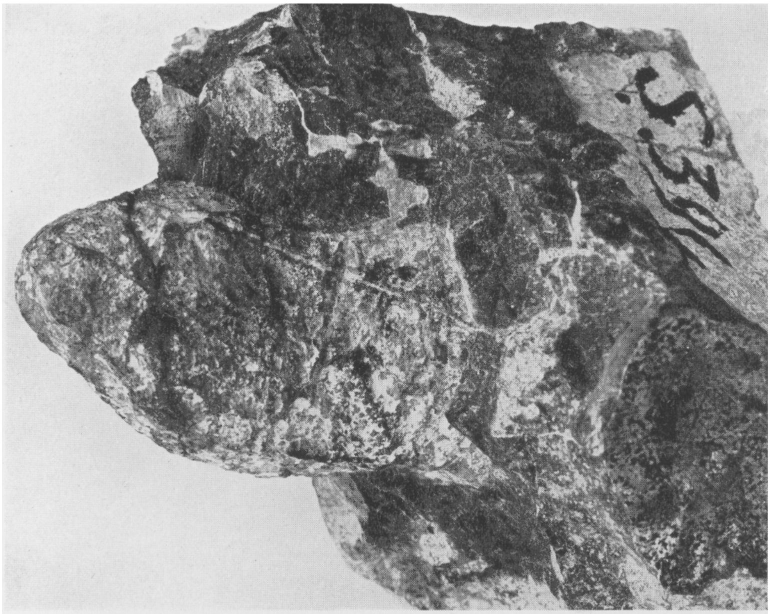

FIG. 1.

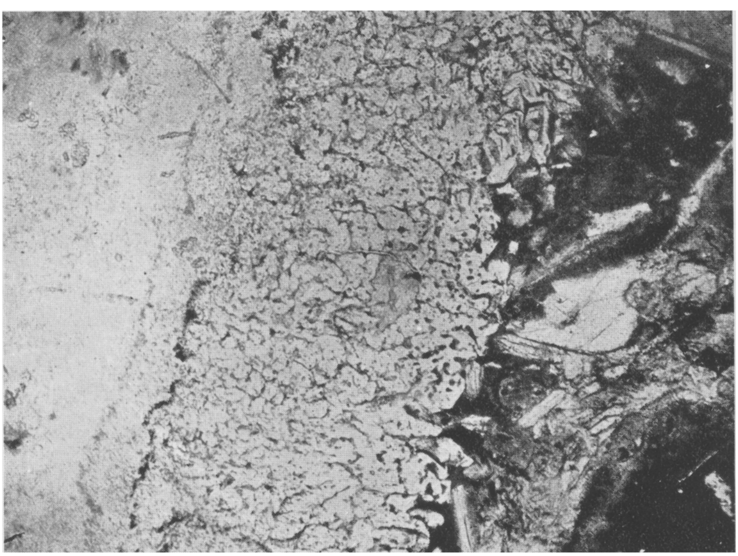

FIG. 2.

C. E. TILLEY AND A. R. ALDERMAN: METASOMATISM OF FLINT NODULE.