The formation of a diffusion reaction skarn by pure thermal metamorphism.

(With Plates I and II.)

By W. Q. KENNEDY, D.Sc., F.R.S.

Dept. of Geology, University of Leeds.

[Taken as read 6 November 1958.]

Summary. Veins and nodules of cornstone, enclosed in sandstone, have reacted to the thermal influence of a Tertiary dolerite dyke by the development of a wollastonite reaction skarn. This can be shown to have formed as a result of pseudomorphous replacement of the quartz grains by wollastonite, due to outward diffusion of calcium. The process is believed to have taken place at the inversion temperature of quartz (573° C.).

ALTHOUGH metamorphic diffusion is frequently invoked to explain various phenomena of metamorphic rocks, it is normally a matter of considerable difficulty to obtain convincing petrological proof of its action as distinct from that of high-temperature regional or contact metasomatism. The best evidence is perhaps provided by the so-called 'reaction-skarns' (Magnusson, 1936, p. 343) that sometimes develop, under the influence of regional or regional-thermal metamorphism, at the contacts between pre-existing carbonate and silicate rocks by interchange of constituents across the mutual boundaries. Such reaction-skarns have, so far, been described mainly from the Archaean rocks of Fenno-Scandia, where, however, the problem of their origin is rendered somewhat more complex in detail by the possible presence of regionally or locally derived (magmatic) emanations, and by the poly-metamorphic nature of the rocks concerned. It is consequently a matter of interest to record a particularly simple example, from a Scottish locality, in which a diffusion-reaction skarn has formed at a sedimentary contact, under the influence of pure thermal metamorphism induced by the intrusion of a dolerite dyke.

The locality in question is situated on the southern shore of the Firth of Clyde, close to the Renfrewshire–Ayrshire boundary, and immediately to the south of the village of Inverkip (Geological Survey, Scotland, one-inch-to-the-mile map, sheet 29). At this point the rocks exposed on the shore consist of typical red fluviatile sandstones and subordinate greenish marls of Upper Old Red Sandstone age, which enclose a massive, pale-coloured, concretionary limestone or *cornstone*. The cornstone is nodular in character, with irregular upper and lower surfaces, and shows a tendency to vein and replace the enclosing rocks. It appears to be a relatively pure calcite rock, with scattered quartz grains and a little argillaceous or feldspathic material as the only impurities, and is comparable in nature, structure, and presumably origin, with the surface limestones or calcretes of South Africa.

Immediately to the south of Inverkip village these sediments are intersected by a broad (50-foot), NNW.-trending olivine dolerite dyke (Tertiary), which has converted the siliceous portions of the cornstone into a mass of fine-grained wollastonite for a distance of a foot or more outwards from its contact. The associated sandstones are less strongly affected and although darkened and obviously metamorphosed, have not suffered complete recrystallization, and still retain the original clastic forms of the sand grains.

The most interesting effects, and those to which attention is here particularly directed, concern the metamorphism of individual veins and nodules of cornstone. These have reacted to thermal metamorphism in a characteristic manner and now consist of a central core of relatively pure, recrystallized, bluish calcite-marble separated from the enclosing sandstone by a narrow, sharply defined zone of dense wollastonite from a few millimetres up to a centimetre or so in width (pl. I, figs. 1 and 2). For a further distance of several millimetres beyond the outer margin of the wollastonite zone the sandstone may be darkened owing to the development of tiny granules of grossular and a little wollastonite in the brownish, siliceous cement.

The central core of calcite-marble usually contains some small scattered patches of wollastonite and isolated tiny crystals of grossular, representing original quartz grains and aluminous (feldspathic) impurities, but appears to have suffered no material change in composition apart from the loss of carbon-dioxide due to the formation of the silicate minerals. The wollastonite zone, on the other hand, has no sedimentary chemical counterpart, and represents a true reaction-skarn developed at the expense of the enclosing sandstone by outward diffusion of lime from the adjacent cornstone under the influence of pure thermal metamorphism. This is very clearly indicated in thin section by the essentially monomineralic character of the wollastonite zone, which normally contains, in addition to the main mineral, only a very small amount of grossular, but neither residual quartz nor calcite, and by the fact that the forms of the original quartz grains, now replaced by aggregates of wollastonite, are still clearly to be discerned (pl. II, figs. 1 and 2). The pseudomorphous replacement of quartz by wollastonite, in this manner, illustrates the operation of Lindgren's 'law of equal volumes' (Lindgren, 1933, p. 93) and could have been effected only by diffusion of lime into the reacting zone and concomitant removal of silica.[1] It can be demonstrated, moreover, that the wollastonite zone has developed *entirely* at the expense of the enclosing sandstone, as the relict quartz grain structure is sometimes seen to extend from the inner to the outer margin.[2] The inner margin consequently marks the original (sedimentary) phase boundary, and the reaction must, therefore, have involved *one-way* (outward) migration of calcium, presumably in the form of the oxide.

This is consistent with the experimental results obtained by Jagitsch, Bengtson, and Perlstroem (Niggli, 1948, p. 391) who showed that when tablets of PbO and $PbSiO_3$ were heated in contact at temperatures between 600° C. and 700° C. the formation of an intermediate reaction zone of Pb_2SiO_4 could best be explained by assuming that PbO (in the form of the oxide) had diffused across the original phase boundary and reacted with the material of the adjacent tablet. The possibilities of diffusion have also been discussed by Adams in connexion with an investigation of two refractory bricks, of different composition, burned in contact at high temperature in a laboratory kiln (Adams, 1930). Subsequent examination showed that calcium had diffused from one brick into and through the substance of the other, where it accumulated with a well-defined 'front' beyond which the proportion of the element dropped abruptly to that characteristic for the second brick. At the same time, silica was displaced from the highly transfused area and accumulated partly in advance of the calcium front. The parallelism with the Renfrewshire occurrence is here very evident despite the fact that the experimental temperatures (*c.* 1400° C.) were far in excess of those ever encountered in rock metamorphism.

---

[1] The conversion of each cubic centimetre of quartz into an equal *volume* of wollastonite would necessitate the addition of 1·4 g. of CaO, and the simultaneous removal of 1·15 g. of SiO_2. The excess silica appears to have diffused *outwards* into the adjacent sandstone as it has obviously not reacted with calcite to form additional wollastonite at the inner margin of the zone.

[2] Normally, however, the inner part of the zone, adjacent to the calcite-marble core, is more coarsely crystalline than the outer, and the relict structures are there partially or wholly obliterated, possibly owing to an effect of 'Sammelkristallization'.

The nature of the diffusion mechanism was not discussed in these experimental cases, but some evidence is available with regard to the manner of operation of the process in the formation of the Renfrewshire reaction skarn. Two types of diffusion mechanism, involving inter-granular diffusion on the one hand, and solid state or intra-granular diffusion on the other, can be distinguished on the basis of the microscopical evidence as follows:

Inter-granular diffusion is clearly indicated in those instances where, towards the outer margin of the wollastonite zone, isolated cores of unreplaced quartz still persist locally in the centres of the original grains. The replacement has here extended inwards from the margins of the grains towards their centres, and must, therefore, be attributed to the presence of an inter-granular medium.

Elsewhere, however, the diffusion front is very sharply defined and can be seen to cut abruptly across adjacent quartz grains without respect to their boundaries (pl. II, figs. 1 and 2). In such instances the process obviously did not depend primarily or necessarily on the presence of an inter-granular medium, but must have operated, in part at least, as solid state or *intra-granular diffusion* in the form of an evenly advancing front.

Irrespective of the actual nature of the diffusion process, however, it is very evident that the development of the wollastonite reaction skarn represents a sufficiently unusual phenomenon to require some special explanation. Under apparently similar conditions, in other instances, no such reaction has taken place, and the operation of some exceptional factor must, therefore, be postulated to explain the enhanced reactivity. This can scarcely depend on any chemical peculiarity of the materials concerned and must be attributed to a physical cause, such as a unique temperature control. It is suggested, therefore, that the reaction took place under the accelerating influence of crystallographic inversion at the transition point of quartz (573° C.). This view is supported by the following considerations:

It is known from experimental work (Hedvall, quoted by Turner and Verhoogen, 1951, p. 405) that crystallographic inversion has an accelerating influence on the reactivity of quartz, as ferric oxide 'is capable of diffusion into the quartz lattice only when the lattice itself is in process of inversion, namely, in the vicinity of 573° C., and again above 900° C.'. And in the present example temperatures falling within the range of the required order of magnitude are suggested by the presence of wollastonite, by the failure of quartz to recrystallize completely, and by the stable co-existence of wollastonite and calcite at the inner margin of the wollastonite zone. These features show that while the temperature was sufficiently high to produce wollastonite by the reaction

$$CaCO_3+SiO_2 = CaSiO_3+CO_2 \qquad (I)$$

it was insufficient to cause the formation of spurrite by the reaction of wollastonite and calcite as follows:

$$3CaCO_3+2CaSiO_3 = 2Ca_2SiO_4.CaCO_3+CO_2. \qquad (II)$$

The most recent information (Harker and Tuttle, 1956, p. 252; Tuttle and Harker, 1957, p. 228) indicates that, at atmospheric pressure, reaction I takes place at, or slightly below, 400° C., and reaction II below 700° C. The reaction temperature increases with pressure, but in rock metamorphism, for various reasons, this factor probably has no great influence (Barth, 1952, p. 288). Nevertheless, it is desirable to examine the possible pressure conditions that may have prevailed at the time of the reaction. A very rough estimate can be based on the field evidence, which shows that whereas the wollastonite skarn and the associated dyke are exposed at sea-level, dykes belonging to the same Tertiary (Mull) Swarm are exposed on the high ground to the south-west at altitudes of up to 1600 or 1700 feet. The skarn could therefore have formed below a cover of this order of magnitude, equivalent to a rock pressure of approximately 2000 lb. per square inch. At this pressure, according to the data of Harker and Tuttle (op. cit., 1956 and 1957), reaction I would take place at a temperature of 550° C., and reaction II at a temperature of approximately 870° C. It can be assumed, therefore, that the temperature of formation of the wollastonite reaction skarn lay within the range of 400°–650° C. at atmospheric pressure, or 550°–850° C. at a maximum rock pressure of 2000 lb. per square inch. These ranges both include the significant crystallographic inversion point of quartz (573° C.) at which greatly enhanced reactivity might be expected.

The formation of the reaction skarn is therefore attributed to a fortuitous and exceptional physical control, whereby the rocks attained the inversion temperature of quartz for a sufficient period of time to allow the reaction to take place.

In conclusion, the writer would again emphasize that this represents an exceptional occurrence and mainly serves to demonstrate a principle, the importance of which as a factor in metamorphism still remains to be established.

References.

ADAMS (F. D.), 1930. Canad. Journ. Research, vol. 2, p. 153.

BARTH (Tom. F. W.), 1952. Theoretical petrology, a textbook on the evolution of rocks. New York (John Wiley and Sons) [M.A. **11**–514].

HARKER (R. I.) and TUTTLE (O. F.), 1956. Amer. Journ. Sci., vol. 254, p. 239 [M.A. **13**–176].

MAGNUSSON (N. H.), 1936. Quart. Journ. Geol. Soc., vol. 92, p. 332.

NIGGLI (P.), 1948. Gesteine und Minerallagerstätten, Bd. 1. Basel (Birkhäuser) [M.A. **10**–349].

TURNER (F. J.) and VERHOOGEN (J.), 1951. Igneous and metamorphic petrology. New York (McGraw-Hill).

TUTTLE (O. F.) and HARKER (R. I.), 1957. Amer. Journ. Sci., vol. 255, p. 226.

EXPLANATION OF PLATES I AND II

PLATE I. Thermally metamorphosed 'cornstones' from Renfrewshire. Approximately natural size.

FIG. 1. Vein type.

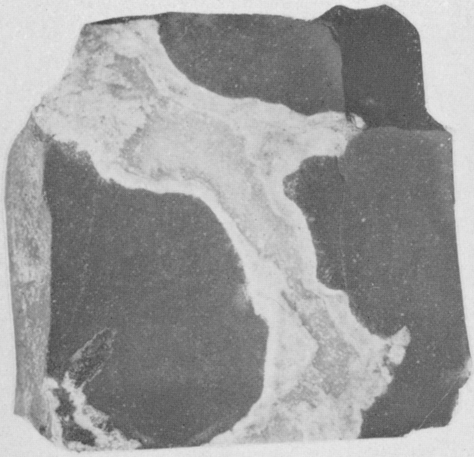
FIG. 2. Nodular type.

Dark areas = enclosing sandstone, white = wollastonite, grey = calcite marble.

PLATE II. Photomicrographs of outer margin of wollastonite reaction skarn against enclosing sandstone. × 60 diameters.

FIG. 1. Ordinary light.

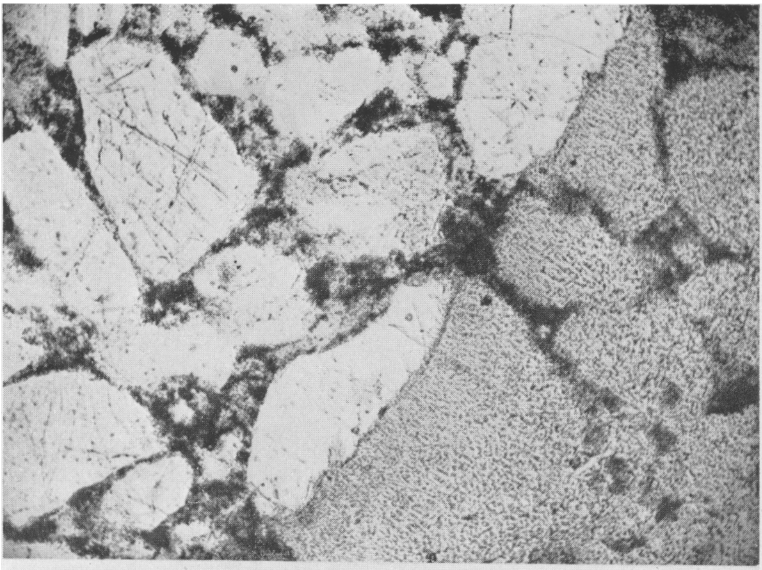
FIG. 2. Crossed nicols.



1

2

W. Q. Kennedy: A diffusion reaction skarn



1

2

W. Q. Kennedy: A diffusion reaction skarn