MINERALOGICAL MAGAZINE, SEPTEMBER 1979, VOL. 43, PP. 371-5

High-temperature pyroxenes from an ironstone at Scourie, Sutherland

A. C. BARNICOAT AND M. J. O'HARA[1]

Grant Institute of Geology, University of Edinburgh

SUMMARY. The coexistence of clinopyroxene (Wo18 En32 Fs44 Rh06) and pigeonite (Wo8 En35 Fs50 Rh07) in a meta-ironstone from Scourie is described. By comparison with experimental data, the temperature at which they were in equilibrium is estimated as at least 1000 °C. The exsolution history of the two pyroxenes is documented. As the rock is an unambiguous metasediment, its presence among granulite facies rocks containing evidence of metamorphism at pressures greater than 10 kbar constrains at least part of the Scourie complex to a supracrustal origin and indicates that tectonic processes of burial were operative in the late Archaean.

UNTIL recently, little work has been done upon the quantitative estimation of the metamorphic conditions of the Scourian complex of north-west Scotland. Muecke (1969) suggested that conditions of 700-800 °C and 7-9 kbar were attained. O'Hara (1977) and O'Hara and Yarwood (1978) postulated that the highest grade conditions were 1150 ± 100 °C and 15 ± 3 kbar. Evidence is presented in this paper that the temperature must have been at least 1000 °C: pressures cannot be readily constrained by the assemblages described here. The assemblage quartz-magnetite-iron-bearing-pyroxene buffers oxygen fugacity, but owing to uncertainties in the pressure at all stages in the evolution of this rock, no further discussion of this is presented, other than to point out that the oxygen fugacity will have been slightly higher than that buffered by the assemblage quartz-fayalite-magnetite.

General description

The rock is composed of quartz (*c.* 30% by volume), magnetite, (*c.* 20%) and clino- and orthopyroxenes (*c.* 50% total pyroxene). Minor quantities of garnet are present. The rock is therefore similar in composition to those described by Floran and Papike (1978) and is thus derived from a sedimentary ironstone containing quartz, hematite, and probably ankerite and greenalite.

The ironstone is found as a prominent rib of rock set in basic gneisses in the first inlet west of the pier on the northern coast of Scourie Bay. It is traceable only for a short distance. The 30-cm-thick layer has reacted with the surrounding basic gneiss, giving rise to a set of zones at the margins of the ironstone. The outermost parts of the layer consist of red garnet and quartz forming a band 1 cm thick. The abundant anhedral garnet contains both euhedral and vermicular inclusions of quartz. This is followed by a 0.5 cm band of magnetite crystals. Inside this, the ironstone is quartz-rich, but rapidly becomes richer in pyroxenes and magnetite. The remainder of the layer is composed almost solely of these three minerals, which are heterogeneously distributed on a small scale. Magnetite crystals, which are rimmed by a thin layer of garnet when at the edge of the layer, are clustered in small lenses parallel to the regional foliation, which is also defined by pods rich in quartz. The pyroxenes are variable in appearance: some are highly exsolved, others consist of separate grains intergrown to suggest an origin by exsolution and later coarsening, while others occur as separate grains. In places, fibrous amphibole is present either as an overgrowth on, or replacing, the pyroxenes.

Analytical techniques

All probe analyses were performed using a Link System EDS unit attached to a Cambridge Microscan 5. An accelerating voltage of 20 kV, a beam current of 6 nA, and a live counting time of 100 s were used. The beam was used both focused to a 1 μm spot and defocused to about 50 μm in diameter to give average analyses of areas containing fine exsolution lamellae. The correction procedure is that of Statham (1976).

Mineralogy

Minor minerals. Quartz grains in the ironstone have an average size of 0.5-1.0 mm; some are strained and show subgrain structures. Magnetite is present as grains and aggregates of variable size,

---

[1] Now at University College, Aberystwyth.

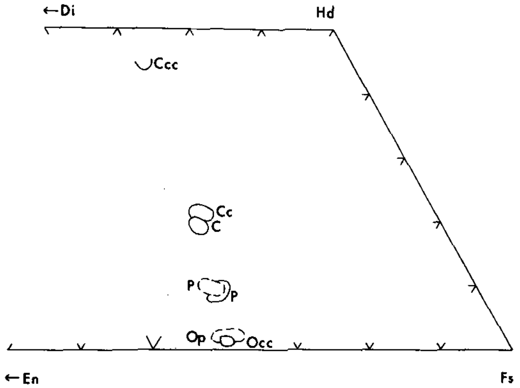

FIG. 1. Composition of probed pyroxenes, neglecting MnO and Al_2O_3. For abbreviations see fig. 2.

up to about 10 × 1 mm. Very narrow lamellae of an aluminous material may be altered exsolution bodies of hercynitic spinel. The only readily detectable minor components of this magnetite are aluminium and manganese, present at about 0.5 wt. % Al_2O_3 and 0.2 % MnO. Pyrrhotine is present in concentrations up to 1 % in some sections. It is frequently partially replaced by marcasite. Pyrite and chalcopyrite also occur in trace amounts.

Garnet. Garnets of two different compositions are present in the rock: a lower-manganese garnet within the outermost zone of the layer, and a high-manganese garnet within the layer, as a rim to magnetite grains (see Table I). In each analysis aluminium is insufficient to fill the R^{3+} site, and up to 9 mol % of the site must be filled with Fe^{3+} (in the case of the high-manganese garnet). Much of the garnet around the magnetite-rich layer contains many vermicular inclusions of quartz, giving rise to spongy garnets with up to 30 % quartz inclusions.

Pyroxenes. The earliest pyroxenes detectable in the rock, which are present in the centre of the layer, have a grain size of 0.5–1 mm. Two types of early pyroxene may be distinguished, one is now pleochroic from pale red to pale green and contains fine lamellae, the other is pale green and complexly exsolved—three sets of lamellae being visible optically. Defocused beam probe analyses, compounded as necessary, show that the first of these pyroxenes had a pigeonitic bulk composition, the second was a low-calcium ferroaugite (see Table I and fig. 1). The exsolution history of these pyroxenes is chronicled in fig. 2. Exsolution lamellae of clinopyroxene (Cp) parallel to (100) occur within the pigeonite. Exsolution within the low-calcium ferroaugite occurred in two crystallographic directions: the early pigeonitic lamellae (Pc) are usually parallel to (001) but occasionally occur parallel to (100). The clinopyroxene lamellae within them (Cpc) are also parallel to (001); the obtuse angle between (001) and (100) is greater in the latter case (see fig. 3). Subsequently, the clinopyroxene host exsolved orthopyroxene parallel to (100) (Occ) and the pigeonite lamellae inverted to orthopyroxene (Oppc) with the exsolution of clinopyroxene parallel to (100) (Cppc) (see figs. 1, 2). The lamellae (Cp) within the pigeonite are 1–2 μm thick. The early lamellae of pigeonite within the clinopyroxene (Pc) are about 150 μm across; the later lamellae (Cpc,

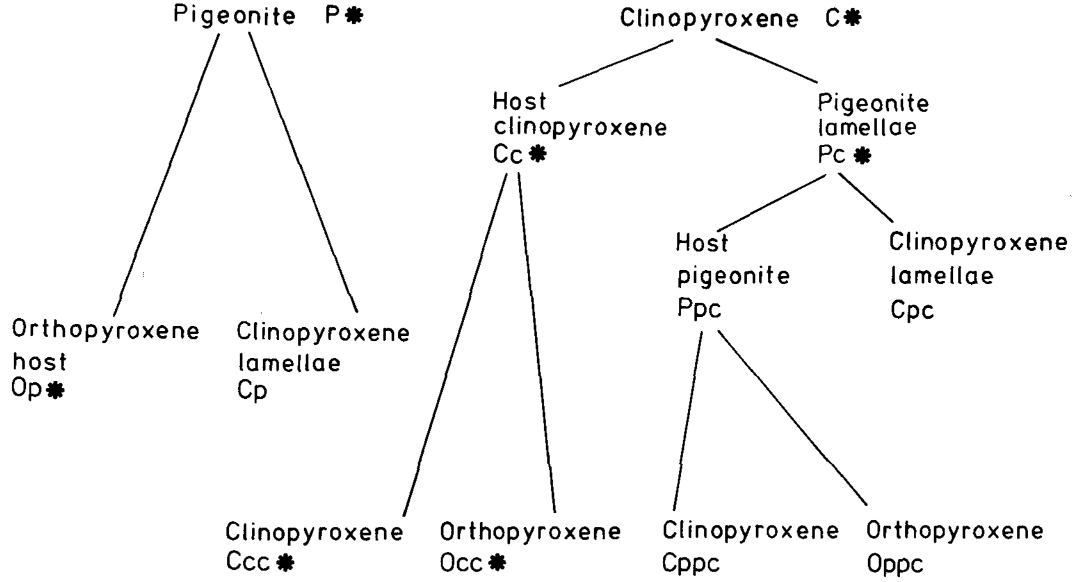

FIG. 2. Flow chart of exsolution within the pyroxenes. Pc indicates pigeonite from clinopyroxene. Cpc clinopyroxene from pigeonite, and that pigeonite from clinopyroxene, etc. Asterisk indicates probed phase.

TABLE I. *Analyses of garnets and pyroxenes*

	GT1	GT2	P1(d)	P2(d)
SiO_2	37.94	37.10	50.52	50.20
Al_2O_3	20.57	18.89	0.67	0.32
FeO	29.44	21.71	28.26	30.49
Fe_2O_3	1.22	2.91	—	—
MnO	3.36	9.88	3.95	4.32
MgO	2.17	1.68	11.92	11.60
CaO	6.76	7.53	5.10	3.88
Na_2O	—	—	—	—
Total	101.46	99.70	100.42	100.81

	OP	C1(s)	C1(a)	C2(a)
SiO_2	50.28	51.72	50.96	49.68
Al_2O_3	0.56	0.58	0.65	0.71
FeO	31.33	25.46	26.81	25.97
Fe_2O_3	—	—	—	—
MnO	4.82	3.10	3.04	3.33
MgO	12.70	9.66	10.60	10.82
CaO	0.77	9.30	7.40	8.69
Na_2O	—	0.63	—	—
Total	100.46	100.45	99.46	99.26

	Cc(d)	Pc(d)	Ccc	Occ
SiO_2	49.63	49.94	51.87	49.45
Al_2O_3	0.74	0.55	0.81	0.50
FeO	25.26	29.59	15.93	32.84
Fe_2O_3	—	—	—	—
MnO	3.14	4.27	1.95	4.65
MgO	10.61	11.96	9.56	11.84
CaO	9.68	3.65	20.45	0.77
Na_2O	—	—	—	—
Total	99.06	99.96	100.57	100.05

(d) signifies a defocused beam analysis; (a) an average analysis, compiled by area weighting of defocused beam analyses; (s) a mechanical scan analysis.

Fe_2O_3 in garnet calculated by assuming a formula of the form R_8O_{12}.

For abbreviations see text and fig. 2.

Cppc, Oppc) are generally *c.* 2 μm wide but occasionally more. Fig. 3 shows the three sets of lamellae present in the clinopyroxene. Those phases coarse enough to be probed are indicated on fig. 2, and the compositions given in Table I and fig. 1. The pyroxenes contain small oriented bodies of magnetite, especially near grain boundaries. Pyroxene-pyroxene grain boundaries are marked by small grains of magnetite and quartz. Evidently there has been oxidation during cooling and exsolution. This manifests itself on fig. 1 as a shift in the tie lines towards the Ca-Mg join with decreasing temperature.

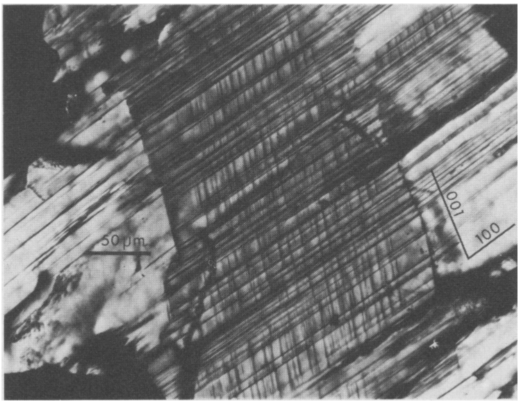

FIG. 3. Photomicrograph of an exsolved clinopyroxene grain. An (001) lamella of pigeonite (Pc) is seen, containing fine (001) lamellae of clinopyroxene (Cpc). Orthopyroxene and clinopyroxene lamellae parallel to (100) cut diagonally across everything. Crossed polars.

Discussion

Pyroxene paragenesis. The recent publication by Lindsley *et al.* (1974*a*) and Mori (1978) of data on subsolidus pyroxene assemblages in the system $CaO\text{-}MgO\text{-}FeO\text{-}SiO_2$ greatly aids the interpretation of the data presented above. The Scourie pyroxenes are very poor in Al and Ti, but contain substantial quantities of Mn, so a close comparison with the experimentally determined phase relations is possible if Mn is treated correctly. If manganese is ignored (solid symbols, fig. 4) a minimum

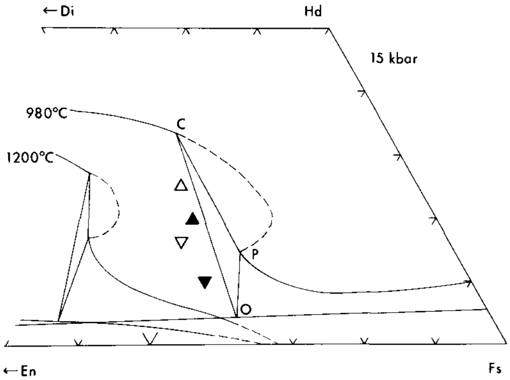

FIG. 4. Comparison of the composition of early clinopyroxene and pigeonite with the experimental data of Lindsley *et al.* (1974*a*) and Mori (1978), showing the composition limits of clinopyroxene (C), pigeonite (P), and orthopyroxene (O). Closed symbols represent the Scourie pyroxenes calculated manganese-free, open symbols are the data recalculated into the system $(Ca+Mn)_2Si_2O_6\text{-}Mg_2Si_2O_6\text{-}Fe_2Si_2O_6$.

temperature of 1050 °C for the stable coexistence of the Scourie pyroxenes is obtained by linear interpolation of the experimental data. The wollastonite contents of the Scourie pyroxenes are lower than those determined experimentally for the three phase assemblage. Data at lower pressure (up to 5 kb, Ross and Huebner, 1975) shows that the wollastonite content of pigeonite decreases with decreasing pressure. However, other rocks in the Scourie district indicate that pressure at the peak of metamorphism must have exceeded 10 kb (O'Hara and Yarwood, 1978). High temperature spinel lherzolites are present, and the reaction boundary

$$\text{garnet} \rightarrow \text{plagioclase} + \text{spinel} + \text{pyroxene(s)}$$

has been crossed. The analogous reaction in CMAS is virtually isobaric at 14 kbar (Herzberg, 1975). It therefore appears that ignoring the manganese content of pyroxenes leads to incorrect results.

However, both Lindh (1974) and Bostwick (1976) conclude from data upon natural pyroxenes that manganese competes with calcium for the M2 site. If the Scourie pyroxenes are recalculated on this basis (i.e. in terms of $(Ca+Mn)_2Si_2O_6$–$Fe_2Si_2O_6$–$Mg_2Si_2O_6$) and compared with the experimental data (open symbols, fig. 4), the natural pyroxenes plot much closer to the experimental compositions. Experimental data on the effect of manganese upon pyroxene stability is sparse (Lindsley *et al.*, 1974*b*; Bostwick, 1976), but indicates that for $Fe/(Fe+Mg)$ values of 0.75, the addition of 5 mol% rhodonite to the system depresses the lower stability limit of pigeonite by 50 °C. In the light of this, it may be concluded that the Scourie pyroxenes equilibrated at a temperature in excess of 1000 °C.

The compositions of the lower-temperature pyroxenes now present (e.g. Ccc and Occ) suggest a very low equilibration temperature of *c.* 600°: the effect of manganese (8 mol% rhodonite in orthopyroxene, 3 mol% in clinopyroxene) here is completely unknown. The bulk composition of these pyroxenes, as noted above, is more magnesian than the earlier pyroxenes, due to the oxidation of iron during the cooling of the rock.

Metasedimentary origin. The Scourie ironstone is remarkably close in composition to Precambrian ironstones described in Minnesota by various workers (e.g. Floran and Papike, 1978), and there is therefore little doubt about its sedimentary origin. Metasediments have been reported from the Scourie complex in the past by several workers (Bowdidge, 1969; Barooah, 1970) but the sedimentary origin of these rocks has been questioned on the basis of their chemistries by Holland and Lambert (1975). Whilst the role played by the extraction of partial melts, and by reaction with adjoining layers, must not be overlooked, it is possible to explain the derivation of putative meta-arkoses, quartzites, and calcium-rich compositions from igneous parent rocks. It is not possible to derive a manganiferous ironstone from any igneous rock, so the Scourian complex must contain some sedimentary material, and it is possible that large parts of the complex may be of supracrustal origin. The suggestion of Holland and Lambert (1975) that the Scourie complex is directly derived from the mantle therefore becomes untenable; further evidence of a supracrustal origin for at least part of the Scourie complex comes from a garnet-biotite-titanomagnetite layer from Scourie More, described by Bowdidge (1969).

The close association of a sedimentary ironstone with high-pressure assemblages, found in adjacent outcrops, demonstrates that some process, presumably tectonic, capable of burying rocks to depths of 40 km or more was operative in the late Archaean. The Scourie complex was subsequently exposed as a pre-Torridonian land surface by *c.* 1000 Ma.

Acknowledgement. A. C. B. acknowledges receipt of a NERC studentship.

REFERENCES

Barooah (B. C.), 1970. Significance of calc-silicate rocks and meta-arkose in the Lewisian complex south-east of Scourie. *Scot. J. Geol.* **6**, 221–5.

Bostwick (T. R.), 1976. The effect of Mn in the stability and phase relations of iron-rich pyroxenes. Unpubl. MS thesis, State University of New York at Stony Brook.

Bowdidge (C. R.), 1969. Petrological studies of Lewisian basic and ultrabasic rocks near Scourie, Sutherland. Unpubl. Ph.D. thesis, University of Edinburgh.

Floran (R. J.) and Papike (J. J.), 1978. Mineralogy and petrology of the Gunflint iron formation, Minnesota–Ontario: correlation of compositional and assemblage variations at low to moderate grades. *J. Petrol.* **19**, 215–88.

Herzberg (C. J.), 1975. The stability of pyrope-rich garnet within the spinel-lherzolite facies. Progress in Experimental Petrology, third report. NERC publications, Series D, No. 6, 1976.

Holland (G. J.) and Lambert (R. St. J.), 1975. The chemistry and origin of the Lewisian gneisses of the Scottish mainland: the Scourie and lower assemblages and sub-crustal accretion. *Precambrian Res.* **2**, 161–88.

Lindh (A.), 1974. Manganese distribution between coexisting pyroxenes. *Neues Jahrb. Mineral., Monatsh.* 335–45.

Lindsley (D. H.), King (H. E.), Turnock (A. C.), and Groves (J. E.), 1974*a*. Phase relations in the pyroxene quadrilateral at 980 °C and 15 kbar. *Geol. Soc. Am. Abstracts with Programs*, **6**, 846.

—— Tso (J.), and Heyse (J. V.), 1974*b*. Effect of Mn on the stability of pigeonite. Ibid. **6**, 846–7.

Mori (T.), 1978. Experimental study of pyroxene equilibria in the FeO system CaO–MgO-FeO-SiO$_2$. *J. Petrol.* **19,** 45–65.

Muecke (G. K.), 1969. Petrogenesis of granulite facies rocks from the Lewisian of North-west Scotland. Unpubl. D.Phil. thesis, University of Oxford.

O'Hara (M. J.), 1977. Thermal history of excavation of Archaean gneisses from the base of the continental crust. *J. Geol. Soc. Lond.* **134,** 185-200.

—— and Yarwood (G.), 1978. High pressure–temperature point on an Archean geotherm, implied magma genesis by crustal anatexis, and consequences for garnet-pyroxene thermometry and barometry. *Phil. Trans. R. Soc. Lond.* A **288,** 441–56.

Ross (M.) and Huebner (J. S.), 1975. A pyroxene geothermometer based on composition–temperature relationships of naturally occurring orthopyroxene, pigeonite and augite. Extended abstracts, International conference on geothermometry and geobarometry, Pennsylvania State University.

Statham (P. J.), 1976. A comparative study of techniques for quantitative analysis of X-ray spectron obtained with a Si(Li) detector. *X-ray Spectrom.* **5,** 16–28.

[*Manuscript received 2 January 1979;*
revised 21 March 1979]