## Hercynite as a breakdown product of staurolite from within the aureole of the Ardara Pluton, Co. Donegal, Eire

## BRIAN P. ATKIN

Department of Geology, University of Nottingham, University Park, Nottingham NG7 2RD

SUMMARY. Zincian hercynite is present in pelites within the aureole of the Ardara Pluton. The hercynite is always surrounded by cordierite, garnet, or feldspar and is never in contact with quartz. From textural and chemical evidence it is apparent that the hercynite is produced by the reaction of zincian staurolite  $\rightarrow$  zincian hercynite + cordierite + sillimanite. A temperature of about 725 °C at pressure of about 2.6 kb and an  $f_{O_1}$  below that defined by the Q.F.M. buffer is postulated for this reaction.

HERCYNITE is present in pelites adjacent to the Ardara Pluton and its paragenesis is worthy of special note. The hercynite occurs in a series of small outcrops just west of Narin crossroads, 2 km south-east of Portnoo harbour. It has a very limited occurrence laterally and decreases rapidly in modal amount with distance from the contact.

Petrology. The mineralogy of these pelites is quartz, plagioclase (An 27), biotite, almandine, sillimanite, fibrolite, cordierite, hercynite, staurolite, graphite, ilmenite, and pyrrhotine. Magnetite and muscovite are noticeably absent. The hercynite occurs as clusters of dark-green subhedral grains and is usually associated with cordierite, sillimanite, and staurolite (fig. 1a-d). The three common mineral associations involving hercynite are: Clusters of hercynite enclosed in cordierite; small irregular staurolite grains are occasionally present within the hercynite clusters. Complex intergrowths of hercynite, sillimanite, cordierite, and staurolite; the staurolite always exhibits embayed contacts with the hercynite. And hercynite clusters intergrown with euhedral sillimanite, enclosed in cordierite.

Ilmenite is generally present associated with the hercynite clusters. Almandine is present either as irregular elongate porphyroblasts, which exhibit strongly 'embayed' contacts with the surrounding quartz, or as large subhedral porphyroblasts. Inclusions of biotite, quartz, and staurolite are present in



FIG. 1. (A) Hercynite (H) rimming a corroded staurolite (St) and mantled by cordierite. (B) Cluster of hercynite grains (H) mantled by cordierite (C). (c) and (D) Complex intergrowths of hercynite (H), staurolite (St), and sillimanite (Si) enclosed in cordierite. Note the euhedral sillimanite and the corroded staurolite.

the garnets and the large subhedral garnets often show signs of replacement by biotite (cf. Smellie, 1974). Cordierite is occasionally present in embayments into the garnet porphyroblasts although their mutual boundaries are smooth and show no signs of reaction. Hercynite is present associated with cordierite, staurolite, and sillimanite in embayments or inclusions in the garnet but no evidence is present to suggest that there is any genetic relationship between garnet and hercynite. Hercynite is never seen in contact with quartz.

Discussion. Green spinels are normally indicative of silica-deficient rocks (e.g. Tilley, 1924; Okrusch, 1969; Propac, 1971), and when present in siliceous rocks are generally mantled by cordierite, garnet, etc. (Tilley, 1921; Friedman, 1954).

Turnock and Eugster (1962) determined the stability field of hercynite in silica-deficient assemblages and showed that it is restricted to low  $f_{O_2}$ , Fe-Al rich environments. Richardson (1968) suggested the probability of a hercynite-producing reaction involving the breakdown of staurolite at an  $f_{O_2}$  defined by the Q.F.M. buffer (i.e. staurolite  $\rightarrow$  hercynite+cordierite+sillimanite.

The common association of hercynite, staurolite, cordierite, and sillimanite in these pelites, together with the evidence that where hercynite and staurolite are present the staurolite is always embayed by hercynite, suggests that these minerals are genetically related. The presence of zinc in both the staurolite and hercynite (Table I), together with the textural evidence suggests that the following reaction was involved in the production of hercynite:

zincian staurolite  $\rightarrow$  zincian hercynite +

The presence of graphite in these rocks will buffer the  $f_{O}$ , of the vapour phase in equilibrium with the rock to below that of the Q.F.M. buffer at temperatures in excess of 600 °C (French and Eugster, 1968). It is, therefore, apparent that the reaction involved in the production of hercynite in these rocks is directly analogous to the reaction involving the breakdown of staurolite postulated by Richardson (1968). However, before attempting to relate the P-T conditions quoted by Richardson (1968) for this reaction to the Ardara rocks, we have to consider that the presence of MgO in the staurolite, cordierite, and hercynite (Table I) in these rocks implies that the univariant boundaries and invariant points of Richardson's (1968) fig. 6 constructed for a Mg-free system become divariant areas when MgO is added to the system.

The presence of almandine in the Ardara rocks, although not directly involved in this reaction, indicates that the P-T conditions for the hercyniteproducing reaction in the Ardara aureole must be equivalent to 'invariant point 2' of Richardson's (1968) fig. 6. This implies that these hercynitebearing rocks crystallized at about 2.6 kb and 725 °C. In the absence of any experimental work on the effect of ZnO on the stability of hercynite and staurolite we must accept the possibility that the presence of ZnO in these phases may also affect the P-T conditions for this reaction.

The absence of magnetite and the presence of ZnO and MgO in the hercynite prevent estimates

6 No. of ions on the basis I 2 3 4 5 of 32(O) for hercynite SiO<sub>2</sub> 0.084 72.07 0.20 28.86 36.38 49.64 Si 37.37 TiO<sub>2</sub> 0.03 14.809 0.65 0.16 0.88 3.72 0.06 Al 16.03 Fe<sup>3+</sup> Al<sub>2</sub>O<sub>3</sub> 54.46 1.115 13.84 54.76 20.83 32.36 21.03 Fe<sub>2</sub>O<sub>3</sub> 0.92 6.22§ 2.14 Ti 0.022 1.04‡ Mg Fe<sup>2+</sup> FeO 6.24 30·45§ 11.38\* 18.70‡ 9.61\* 32.56‡ 0.877 MnO 5.898 0.06 0.02 0.05 0.04 2.14 7.99 MgO 2.67 Zn 1.196 2.41 0.76 7.04 6.43 3.93 CaO Mn 0.020 0.48 1.86 Na<sub>2</sub>O 0.83 0.30 \_ K<sub>2</sub>O 1.13 1. Whole rock 9.36 ZnO 141 ppm 7.02 2.31 < 0.05 < 0.05 <0.05 2. Hercynite 3. Staurolite Total 100.064 4. Biotite 101.64 98.67 97.31 98.07 101.09 5. Corderite 6. Garnet

TABLE I. Chemical analyses of whole rock and selected mineral constituents

cordierite + sillimanite.

\* Total iron expressed as FeO.

† Total includes 0.97 %  $H_2O$ , 0.05 %  $P_2O_5$ , 0.37 % S and 0.23 % C.

‡ Wet chemical analysis.

 $\ensuremath{\S}$  FeO and Fe2O3 in hercynite calculated assuming perfect stoichiometry.

based on the comparison of coexisting hercynite and magnetite (Turnock and Eugster, 1962).

The restriction of hercynite to this one small series of outcrops is due to the absence elsewhere in the Ardara aureole of staurolite in rocks of this grade. The presence of the staurolite in these rocks could be due to their high ZnO content, which may increase its stability field (Hollister, 1969; Guidotti, 1970; Ashworth, 1975). This however, cannot be verified as there is no experimental evidence to suggest that zincian staurolite is stable at higher temperatures than pure ferroan staurolite. Also the presence of ZnO in other staurolites from within the Ardara aureole has not as yet been investigated.

The presence of this breakdown reaction in the Ardara aureole is important in that kyanite is present both in rocks adjacent to the Ardara pluton and in the outer part of the inner aureole (Atherton *et al.*, 1975) and therefore if the estimate of 2.6 kb for the pressure at which this breakdown reaction occurred is correct it implies that the kyanite also crystallized at about this pressure. This is clearly not in agreement with Holdaway (1971), who considered that pressures of at least 6 kb are necessary for the production of kyanite in thermal aureoles.

Acknowledgements. I wish to thank Dr. M. P. Atherton for advice and guidance given throughout this work, undertaken at the University of Liverpool during the tenure of a N.E.R.C. studentship.

## REFERENCES

- Ashworth (J. R.), (1975). Contrib. Mineral. Petrol. 53, 281-91.
- Atherton (M. P.), Naggar (M. H.), and Pitcher (W. S.), 1975. Am. J. Sci. 275, 432-43.
- French (B. M.) and Eugster (H. P.), 1968. J. Geophys. Res. 70, 1529-39.
- Friedman (G. M.), 1954. J. Geol. 62, 336-74.
- Guidotti (C. V.), 1970. J. Petrol. 11, 277-336.
- Holdaway (M. J.), 1971. Am. J. Sci. 271, 97-131.
- Hollister (L. S.), 1969. Ibid. 267, 352-70.
- Okrusch (M.), 1969. Contrib. Mineral. Petrol. 22, 32-72.
- Propac (G.), 1971. Neues Jahrb. Mineral. Abhdl. 115, 120-2.
- Richardson (S. W.), 1968. J. Petrol. 9, 467-88.
- Smellie (J. A. T.), 1974. Mineral Mag. 39, 878-88.
- Tilley (C. E.), 1921. Geol. Mag. 8, 305-12.
- —— 1924. Q. J. Geol. Soc. 80, 22-71.
- Turnock (A. C.) and Eugster (H. P.), 1962. J. Petrol. 3, 533-65.
- [Manuscript received 28 October 1977;
- revised 13 December 1977]