

## Secondary ilvaite in a dolerite dyke from Rogaland, SW Norway

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**ABSTRACT.** Ilvaite is an alteration product of carbonate, which itself replaced clinopyroxene, in a Precambrian tholeiitic dyke. Additional secondary minerals are ferroactinolite, cummingtonite, chlorite, biotite, prehnite, and epidote. Microprobe analyses demonstrate that the ilvaite is close to the ideal end-member composition  $[\text{CaFe}_2^{2+}\text{Fe}^{3+}\text{Si}_2\text{O}_8(\text{OH})]$  and that only cummingtonites,  $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$  0.77-0.39, and carbonates (solid solutions between calcite and dolomite, dolomite and ankerite, magnesite and siderite) show significant compositional variations. It is estimated that ilvaite formed at temperatures  $< 470^\circ\text{C}$  and at pressures  $< 2$  kbar, probably during a low-grade metamorphic event (or events) associated with the Caledonian orogeny. The fluids involved in the alteration process contained both  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , initial fluids probably being richer in  $\text{CO}_2$  than later ones. Ilvaite may be more common in hydrothermally altered igneous rocks than previously supposed.

**ILVAITE,**  $\text{CaFe}_2^{2+}\text{Fe}^{3+}\text{Si}_2\text{O}_8(\text{OH})$ , is a relatively rare mineral which typically occurs in Ca-Fe-Si skarn deposits (Fonteilles, 1962; Bartholomé and Dimanche, 1967; Burt, 1971a; Verkaeren, 1974; Plimer and Ashley, 1978). It is also found in contact metamorphosed iron formations (Ramdohr, 1927; Dietrich, 1972) and as a late-stage alteration product in some igneous rocks, perhaps the best-known examples of which are the Upper Border Group of the Skaergaard intrusion (Wager *et al.*, 1957; Naslund *et al.*, 1983), and the Basistoppin sill (Douglas, 1964) which intrudes the upper part of the Skaergaard intrusion.

The mineral occurs as an alteration product in a dolerite dyke from Rogaland, SW Norway, and has not been previously reported from Rogaland despite the occurrence in this region of iron-rich metamorphic assemblages containing andradite and hedenbergite (minerals which are frequently associated with ilvaite in skarn deposits). Moreover, its mode of occurrence is quite unlike that in most other igneous rocks in that other extremely Fe-rich silicates are absent. In this paper we discuss the paragenesis and mineral chemistry of the assemblage in the dykes.

*Geological setting.* The high-grade metamorphic and intrusive complex of Rogaland (Hermans *et al.*, 1975) is cut by the Egersund dyke swarm which trends N  $70^\circ$  W (Antun, 1956). The precise age of intrusion is unknown, but the dykes cut all other formations in the area which have ages  $> 850$  Ma (Pasteels and Michot, 1975; Priem, 1980; Wielens *et al.*, 1981). A single K-Ar age of 663 Ma has been reported for one of the dykes (Verstevee, 1975) and palaeomagnetic data (Storetvedt and Gidskehaug, 1968; Poorter, 1972) support a late Precambrian age.

The Egersund dykes are olivine tholeiites and tholeiites. Often they are remarkably fresh with glass preserved in the chilled margins but alteration is always apparent in the centres of the dykes and in a few cases has completely obliterated the magmatic textures. The main alteration minerals are carbonates, calcic amphiboles, Mg-Fe amphiboles, serpentine, chlorite, sericite, and brown and green mica. Rare prehnite, epidote, and ilvaite also occur. Sulphides are ubiquitous and are mostly secondary. Stilpnomelane has been tentatively identified in one sample.

*Occurrence of ilvaite.* Abundant ilvaite occurs in a narrow ( $< 1$  m wide) dyke which is exposed 1.25 km to the east of Åna Sira and intrudes the Åna Sira anorthosite massif (NGU grid coordinates 3506-64640). A chemical analysis of this dyke together with the CIPW norm is given in Table I, from which the tholeiitic character is evident. The analysis shows 0.25%  $\text{CO}_2$  and 1.34% additional LOI which is assumed to represent  $\text{H}_2\text{O}$ . The moderate  $\text{Mg}/(\text{Mg} + \Sigma\text{Fe}^{2+})$  ratio (0.47) of this sample is noteworthy.

The dyke contains rare phenocrysts of olivine, now mostly pseudomorphed, set in a sub-ophitic intergrowth of augite and plagioclase with ilmenite, titaniferous magnetite, and minor apatite. All these minerals are locally altered, the plagioclase to sericite, the ilmenite to leucoxene, and titaniferous magnetite and augite to fine-grained,

TABLE I. *Chemistry and norm of ilvaite-bearing dyke*

Chemical analysis		CIPW norm	
SiO <sub>2</sub>	48.4	or	3.5
TiO <sub>2</sub>	2.42	ab	24.5
Al <sub>2</sub> O <sub>3</sub>	15.6	an	28.5
Fe <sub>2</sub> O <sub>3</sub>	2.02	di-wo	7.4
FeO	10.3	di-en	3.8
MnO	0.12	di-fs	3.4
MgO	6.09	hy-en	8.6
CaO	9.67	hy-fs	7.7
Na <sub>2</sub> O	2.85	ol-fo	2.1
K <sub>2</sub> O	0.58	ol-fa	2.1
P <sub>2</sub> O <sub>5</sub>	0.39	mt	3.0
CO <sub>2</sub>	0.25	il	4.7
LOI*	1.34	ap	0.9
Total	100.03		100.2†
Mg			
(Mg + ΣFe <sup>2+</sup> )		0.47	

\* Adjusted for amount of CO<sub>2</sub> determined by analysis.

† CIPW norm calculated on a volatile-free basis.

opaque, indeterminable material. It should be stressed that this type of alteration is common in many samples from the Egersund dyke system and is not necessarily related to the occurrence of the major secondary or alteration minerals described below.

Ilvaite occurs in fine-grained aggregates (< 1 mm in diameter) and is mostly opaque in thin section although locally a characteristic pleochroism ( $\alpha$  red brown,  $\gamma$  opaque to dark-red brown) is evident. These aggregates are quite irregular in shape and do not appear to be pseudomorphs after any of the primary magmatic minerals. They frequently include, or partially rim, grains of carbonate (fig. 1a). The only other mineral which is intimately associated with ilvaite is blade-like chlorite, which is included in the ilvaite aggregates (fig. 1b). The augite and plagioclase crystals in contact with the aggregates of ilvaite inevitably appear to be corroded.

Calcic amphibole mostly occurs as spherical aggregates (< 1 mm diameter) of thin green fibrous crystals. The aggregates are partially rimmed by tangentially arranged laths of plagioclase feldspar. Occasionally, bundles of fibres of calcic amphibole penetrate into, and apparently replace, crystals of primary augite.

Cumingtonite occurs as fine-grained masses of fibrous crystals pseudomorphing olivine. Cumingtonite, serpentine, chlorite, carbonate, and

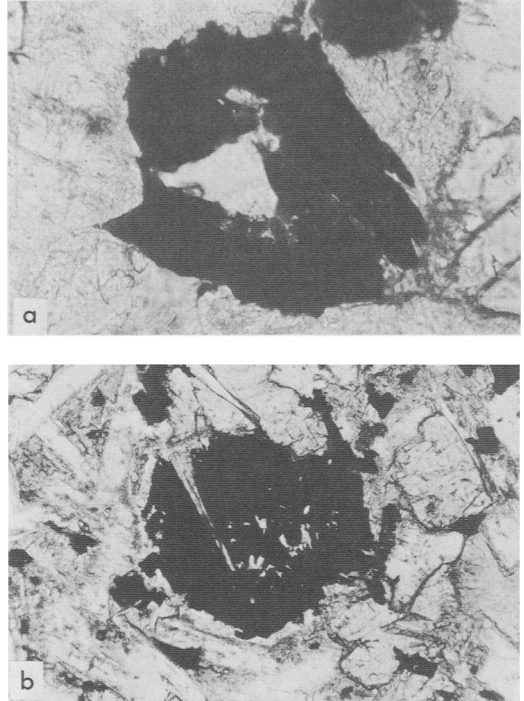


FIG. 1. (a) Fine-grained aggregate of ilvaite enclosing grain of carbonate. Width of field 0.18 mm. (b) Rounded aggregate of ilvaite with inclusions of carbonate (light coloured) and needle-like crystal of chlorite (grey). Width of field 0.84 mm.

iddingsite are the main minerals which replace olivine in the Egersund dykes. Cumingtonite also occurs in bundles that are not pseudomorphs.

Chlorite and biotite are not abundant, while prehnite occurs mostly in veins associated with carbonate and rarely in altered plagioclase phenocrysts. The veins are not common but transect the margin of the dyke and the country rock. Epidote is very rare and so is carbonate in the ilvaite-bearing dyke, but it is abundant in some dykes of the Egersund system. The carbonate occurs mainly with quartz in sub-spherical aggregates (up to 1 mm in diameter) partially surrounded by tangentially arranged laths of primary plagioclase (comparable to the calcic amphibole described above). It also occurs in irregularly shaped patches between the augite and the plagioclase and in the prehnite-bearing veins.

*Mineral chemistry.* Representative microprobe analyses (fully corrected) are reported in Tables II and III.

The compositions of the primary magmatic minerals will be reported in detail elsewhere. In

brief, the olivines ( $\text{Fo}_{75-66}$ ) and augites [ $\text{Mg}/(\text{Mg} + \Sigma\text{Fe}^{2+}) 0.72-0.51$ ] are not particularly Fe-rich and the compositions of the primary magmatic minerals are unchanged where they are in contact with ilvaite and other secondary minerals or alteration products (for example, carbonates, calcic amphibole). Thus, augites in contact with ilvaite plot within the compositional field of fresh pyroxenes from the dyke (fig. 2).

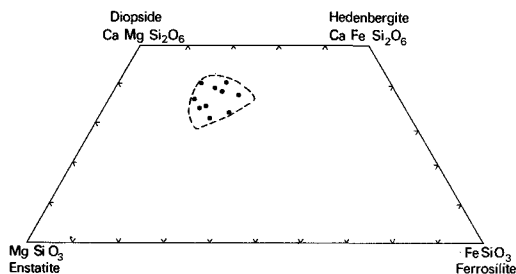


FIG. 2. Compositions of clinopyroxenes in contact with ilvaite plotted in the conventional Ca-Mg-(Fe+Mn) diagram (all iron calculated as  $\text{Fe}^{2+}$ ). The dotted line encloses the compositional field of fresh clinopyroxenes in the same dyke (including those in the chilled margin).

Multiple analyses of ilvaite reveal little chemical variation and the average composition, together with a range, is given in Table II. Prior to analysis, the sample current was adjusted to give 100% totals on plagioclase and augite so that the reported total should be accurate. The amount of  $\text{Fe}_2\text{O}_3$  was calculated by assuming that the cation sum is 6 on the basis of 8.5 oxygens. The average composition is close to that of ideal ilvaite; only small amounts of Al (presumably replacing  $\text{Fe}^{3+}$  and, or, Si), Mg, and Mn (which presumably replace  $\text{Fe}^{2+}$  and Ca) occur. The analysis of ilvaite in the Skaergaard intrusion recently reported by Naslund *et al.* (1983) is likewise close to the ideal composition. In contrast, ilvaites from some skarn deposits contain up to 14 wt. % MnO (Leonard *et al.*, 1962; Plimer and Ashley, 1978).

According to the classification scheme described by Leake (1978), the calcic amphiboles are ferro-actinolites whereas the monoclinic Mg-Fe amphiboles are cummingtonites and magnesio-cummingtonites (Table III). The ferro-actinolites show a relatively restricted range of composition [ $\text{Mg}/(\text{Mg} + \Sigma\text{Fe}) 0.46-0.36$ ;  $\text{Al}_2\text{O}_3$  1.3-2.4 wt. %] and contain only minor amounts of  $\text{TiO}_2$ , MnO, and  $\text{Na}_2\text{O}$ . However, the low Ca-amphiboles show quite a wide range of composition in terms of  $\text{Mg}/(\text{Mg} + \Sigma\text{Fe})$  which ranges from 0.77-0.39.  $\text{Al}_2\text{O}_3$  (1.8-4.4 wt. %) is mostly quite high whereas

TABLE II. Average composition of ilvaite in Egersund dyke

	1	2
$\text{SiO}_2$	29.5	28.9 -30.4
$\text{TiO}_2$	0.04	0- 0.30
$\text{Al}_2\text{O}_3$	0.78	0.23- 1.41
$\text{Fe}_2\text{O}_3^*$	18.7	18.5 -19.5
$\text{FeO}^*$	33.6	32.7 -34.0
MnO	1.02	0.66- 2.0
MgO	0.38	0- 0.75
CaO	13.8	13.4 -14.3
Total	97.8	
Number of cations on the basis of 8.5 O		
Si	1.991	
Ti	0.002	
Al	0.062	
$\text{Fe}^{3+}$	0.953	
$\text{Fe}^{2+}$	1.900	
Mn	0.059	
Mg	0.039	
Ca	0.995	
Sum	6.001	

\* Values calculated assuming  $\Sigma$  cations = 6 on the basis of 8.5 oxygen atoms.

1. Average composition of ilvaite (18 analyses).
2. Range of values shown by analyses used to obtain column 1.

both CaO and  $\text{Na}_2\text{O}$  are relatively low. Calculations made on the assumption that  $\Sigma$  cations  $-(\text{Ca} + \text{Na} + \text{K}) = 13$  or  $\Sigma$  cations  $-(\text{Na} + \text{K}) = 15$  on the basis of 23 oxygens indicate that the ferro-actinolites contain 1-3 wt. %  $\text{Fe}_2\text{O}_3$  and that the cummingtonites and magnesio-cummingtonites contain negligible  $\text{Fe}_2\text{O}_3$ .

The compositions of the amphiboles are plotted on a Ca-Mg-( $\text{Fe}^{2+} + \text{Mn}$ ) diagram in fig. 3. The compositions of two adjacent grains of ferro-actinolite and cummingtonite are shown in fig. 3b, on which previously reported compositions of coexisting amphibole pairs which contain < 2.5 wt. %  $\text{Al}_2\text{O}_3$  (Klein, 1968; Cameron, 1975) have also been plotted. It is evident that the  $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$  ratios of the ferro-actinolites are too low for them to have formed in equilibrium with the cummingtonites. Correction of the ferro-actinolite analyses for the presence of  $\text{Fe}^{3+}$  does not alter this conclusion (fig. 3b).

The chlorites and the biotites proved difficult to analyse because they mostly occur in fine-grained intergrowths with each other or, in the case of chlorite, with ilvaite. The chlorites are diabantites

TABLE III. *Electron-microprobe analyses of amphiboles, chlorite, biotite, epidote, prehnite and carbonates in the Egersund dyke*

	Actinolite	Cumingtonite	Chlorite	Biotite	Epidote	Prehnite	Carbonate			
SiO <sub>2</sub>	50.4	56.6	49.9	29.7	36.5	38.3	44.1	—	—	0.2
TiO <sub>2</sub>	—	0.11	0.23	1.45	3.52	—	—	—	—	—
Al <sub>2</sub> O <sub>3</sub>	2.30	3.33	4.48	12.9	11.5	22.6	23.8	—	—	—
FeO*	24.8	12.4	29.0	32.2	27.7	13.0	0.64	0.3	7.0	51.2
MnO	0.44	—	0.39	0.30	—	—	—	0.3	0.4	0.4
MgO	7.87	23.8	13.0	11.6	9.29	0.28	—	0.1	17.3	9.0
CaO	11.5	0.44	0.73	1.02	0.57	22.4	27.4	56.3	30.1	0.2
Na <sub>2</sub> O	0.48	0.26	—	—	—	—	—	—	—	—
K <sub>2</sub> O	—	0.48	0.12	—	6.85	—	—	—	0.1	—
Total	97.8	97.4	97.9	89.2	95.9	96.6	95.9	57.0	54.9	61.0
Number of cations on the basis of										
	O = 23	O = 23	O = 23	O = 28	O = 22	O = 25	O = 22	O = 6	O = 6	O = 6
Si	7.701	7.837	7.503	6.399	5.710	6.306	6.056	—	—	0.02
Ti	—	0.012	0.028	0.235	0.414	—	—	—	—	—
Al	0.416	0.544	0.794	3.276	2.121	4.386	3.851	—	—	—
Fe <sup>2+</sup> *	3.171	1.437	3.646	5.802	3.624	1.790	0.074	0.01	0.14	1.12
Mn	0.058	—	0.050	0.054	—	—	—	0.01	0.01	0.01
Mg	1.794	4.904	2.921	3.726	2.167	0.068	—	0.005	0.60	0.35
Ca	1.878	0.066	0.119	0.236	0.096	3.951	4.037	1.98	0.75	0.005
Na	0.143	0.073	—	—	—	—	—	—	—	—
K	—	0.086	0.024	—	1.367	—	—	—	—	—

\* All iron as FeO or Fe<sup>2+</sup>.

(Deer *et al.*, 1962) and contain relatively high TiO<sub>2</sub>. This is not likely to be due to contamination during analysis as many of the analysed chlorites were included in ilvaite. The biotites, like the chlorites, are relatively Fe-rich and they contain 3–5 wt. % TiO<sub>2</sub>. The low K<sub>2</sub>O contents (< 6.9 wt. %) suggest that some chlorite was included in the analysis. Prehnite and epidote are close to the ideal end-member compositions of these minerals (Table III).

The carbonates in the Egersund dykes have a wide range of composition. The ilvaite-bearing dyke has nearly pure calcite, but the carbonates in other dykes show a wide range of solid solution between calcite and dolomite, dolomite and ankerite, and magnesite and siderite (Table III). Members of all three solid-solution series can occur in a single thin section and even within one sub-spherical aggregate of carbonate grains. In the latter case, there is no evidence for a zonal arrangement of the different types of carbonate. Individual grains are also unzoned.

*Discussion.* Most previously reported occurrences of ilvaite are in iron-rich rocks. This is self-evident in the case of Ca-Fe-Si skarns (Fontailles, 1962; Bartholomé and Dimanche, 1967;

Burt, 1971a, Verkaeren, 1974; Plimer and Ashley, 1978), but is also true in the case of the granophyric Basistoppin sill (Wager *et al.*, 1957; Douglas, 1964), the Upper Border Group of the Skaergaard intrusion (Wager *et al.*, 1957; Naslund *et al.*, 1983), the Triassic granophyre from the Dillsburg area, SE Pennsylvania (Hotz, 1953), the micropegmatitic diorite from south-eastern Papua (Baker, 1953), and the hydrothermally altered andesites and rhyolites from the Noranda region, Quebec (Machairas and Blais, 1966). In addition to ilvaite, most of these examples also contain Fe (and sometimes Mn)-rich silicates such as fayalite, hedenbergite, almandine, and andradite. The occurrence of ilvaite in the Egersund dolerites is thus unusual in that neither the host rock nor the associated silicates are particularly iron-rich. The only comparable occurrence of ilvaite appears to be in the Precambrian gabbros of Missouri, described by Desborough and Amos (1961), although these authors do not give a chemical analysis of the rock.

The ilvaite in the Egersund dykes is associated with ferro-actinolite and minerals believed to be of low-temperature origin (e.g. prehnite, epidote, sericite, chlorite, carbonates) which leads us to con-

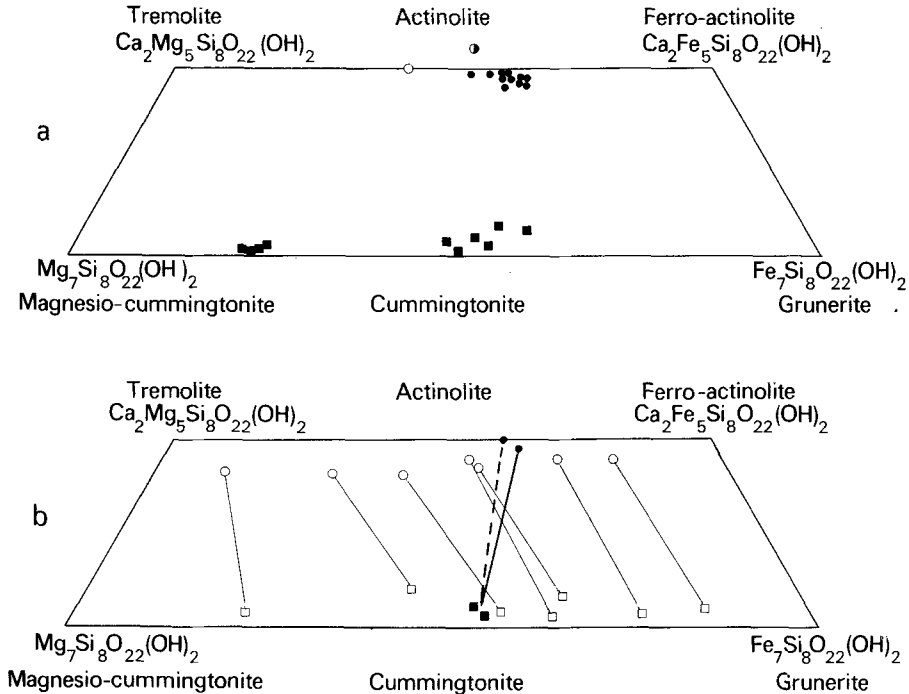


FIG. 3. (a) Compositions of amphiboles in ilvaite-bearing dyke. Filled circles, actinolites in spherical aggregates; half-filled circles, actinolite pseudomorph after clinopyroxene; open circle, actinolite in prehnite-bearing vein; squares, cummingtonite and magnesio-cummingtonite. (b) Compositions of coexisting amphibole pairs which contain less than 2.5 wt. %  $\text{Al}_2\text{O}_3$  reported by Klein (1968) and Cameron (1975). The heavy tie-line connects adjacent grains of cummingtonite and actinolite in the ilvaite-bearing dyke and the dotted tie-line shows the effect of correcting the actinolite analysis for the presence of ferric iron.

clude that it is of low-temperature, secondary origin and is not a late-crystallizing magmatic mineral as proposed by Desborough and Amos (1961). This conclusion is supported by stable isotope studies of carbonates in the dyke system which seem to predate the formation of ilvaite. The isotopic composition of carbon ( $\delta^{13}\text{C}$  from  $-4$  to  $-5.4$ ‰) and oxygen ( $\delta^{18}\text{O}$  from  $+9$  to  $+12$ ‰) is similar to that of carbonates in veins and secondary carbonates in Rogaland (unpublished data; see also Sauter, 1983), whose formation is thought to be related to Caledonian metamorphism.

It is not possible to place precise constraints upon the  $P$ - $T$  conditions under which the ilvaite formed; the wide compositional range shown by the carbonates prohibits application of the calcite-dolomite geothermometer, and the ferro-actinolite-cummingtonite geothermometer of Cameron (1975) cannot be used because of the non-equilibrium relationships shown by the amphiboles in the Egersund dykes. However, theoretical (Burt, 1971b; Saleminck, pers. comm., 1983) and experimental

(Gustafson, 1974) studies indicate that ilvaite is stable only at temperatures  $< 470^\circ\text{C}$ . Available evidence (Barton *et al.*, work in progress) suggests that these dykes, and hence probably the ilvaite also, crystallized at pressures below about 2 kbar. Swanenberg (1980) found that the conditions of entrapment of  $\text{H}_2\text{O}$ - $\text{CO}_2$  fluid inclusions in samples from Rogaland were c.  $300^\circ\text{C}$  and 1-2 kbar and, furthermore, suggested that low-density, monophasic carbonic fluid inclusions in rocks adjacent to one of the Egersund dolerites formed at temperatures  $< 500^\circ\text{C}$  and at low pressures (probably  $< 2$  kbar). During the formation of ilvaite,  $f_{\text{O}_2}$  was probably fairly low (Burt, 1971b), close to that defined by the QFM buffer (Saleminck, pers. comm., 1983; see also Naslund *et al.*, 1983).

Several reactions have been described for the formation of ilvaite from calcic pyroxenes in skarn deposits (Machairas and Blais, 1966; Bartholomé and Dimanche, 1967), and these could be applicable to the formation of ilvaite in the Egersund dolerites because the pyroxenes in contact with the ilvaite are



are found as alteration products in the Egersund dykes and also the  $P$ - $T$  conditions estimated for the formation of retrograde (i.e. Caledonian) minerals in the basement of Rogaland (Swanenberg, 1980; Sauter *et al.*, 1983) agree well with the estimated conditions for the formation of ilvaite. The occurrence of both carbonates and hydrous minerals as alteration products and in veins cutting the dyke system indicate that  $\text{CO}_2$  and  $\text{H}_2\text{O}$  were important components of the fluid phase and the occurrence of sulphides suggests that S may have also been present. The tendency for ilvaite, and probably ferro-actinolite, to replace carbonates in some dykes, together with the fact that carbonates tend to be abundant in the more southerly dykes whereas hydrous phases are abundant in the dykes to the north-west (i.e. towards the Caledonian front), suggests that the fluids were initially  $\text{CO}_2$ -rich and later became  $\text{H}_2\text{O}$ -rich. This proposal finds support in the results of the fluid inclusion study of Swanenberg (1980), who concluded that the interaction between the two types of fluid probably occurred in the unmixing region in a salt-bearing  $\text{H}_2\text{O}$ - $\text{CO}_2$  system. Swanenberg also noted that the Egersund dyke system and the fractures parallel to them may have acted as channelways through which the hydrothermal fluids passed. This suggestion is supported by our own field and petrographic observations on the dyke system.

The occurrence of ilvaite in the Egersund dykes is important because the host rock is not particularly Fe-rich, the ilvaite is not associated with particularly Fe-rich minerals, alteration is localized and has not affected the texture or mineralogy (or, probably, the chemistry) of the rock to a great degree, and the fluids responsible for the alteration were rich in  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , initial fluids probably being richer in  $\text{CO}_2$  than later ones. Since  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are likely to have been important components of the fluid phase responsible for the alteration of many magmatic rocks, we conclude that ilvaite may be more common in altered igneous rocks than has hitherto been realized. This may well be true also of babingtonite,  $\text{Ca}_2\text{Fe}^{2+}\text{Fe}^{3+}\text{Si}_5\text{O}_{14}(\text{OH})$ , a mineral chemically similar to ilvaite, which has recently been described from an Archaean metabasalt from the Pilbara Block, Western Australia (Barley, 1982), but which apparently does not occur in association with particularly Fe-rich minerals.

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