Ilvaite, an alteration product replacing olivine in the Skaergaard intrusion

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Abstract

Ilvaite, $CaFe_2^{2+}Fe^{3+}(OH)Si_2O_8$, is an abundant mineral in the upper part of the Skaergaard intrusion of East Greenland. It occurs in these rocks as an alteration product replacing fayalitic olivine. Analyses of unaltered olivine and ilvaite demonstrate that the replacement process requires the removal of FeO and MgO from the olivine and the addition of CaO, H_2O, and O_2. Single crystal X-ray diffraction studies indicate that the Skaergaard ilvaite is the orthorhombic polymorph. It is suggested that the ilvaite crystallized under conditions of high fH_2O, low fCO_2, low fO_2, and moderate T during the subsolidus cooling of the intrusion.

Introduction

Numerous detailed studies have been made of olivine alteration products (Wilshire, 1958; Gay and LeMaitre, 1961; Haggerty and Baker, 1967; Baker and Haggerty, 1967; Champness, 1970; Ganyuchenkov and Barabanov, 1972; Kohlstedt and Vander Sande, 1975; Delvigne et al., 1979; and Moseley, 1981). Although these studies have described several phases which occur as deuteric alteration products of olivine, none of them has reported ilvaite. The only reported occurrences of ilvaite in altered olivine are in the Skaergaard intrusion, in olivine diabase from Elfdalen, Sweden, and in the Basistoppen sill which has intruded the upper part of the Skaergaard intrusion (Ramdohr, 1969; Douglas, 1964). Ilvaite, a relatively rare mineral, typically occurs as a late forming mineral in Ca–Fe–Si skarn deposits (Burt, 1971). The ilvaite in the Skaergaard intrusion is believed to have formed from the interaction of olivine and a fluid phase and is probably the result of an unusual set of conditions which operated during the cooling of the pluton.

Occurrence

Ilvaite is a common alteration product of olivine in the Upper Border Group γ (UBGγ) unit of the Skaergaard intrusion. This unit has been described as a mixture of "ferrodiorite" and "melanogranophyre" (Wager and Brown, 1967), but most samples would be classified as quartz diorite or tonalite using the system of Streckeisen (1976). UBGγ rocks are medium to coarse-grained with rare finer-grained layers and are composed primarily of plagioclase (andesine to oligoclase), clinopyroxene (ferroaugite to ferrohedenbergite), fayalitic olivine, quartz,

magnetite–ulvöspinel, ilmenite–hematite, apatite, and micropegmatite (Naslund, 1980). Zircon and titanite are accessory minerals; ilvaite, chlorite, serpentine, sericite, epidote, titanite, rutile, hornblende, and calcite are present as alteration minerals.

The Skaergaard ilvaite is opaque in thin section and occurs as anhedral patches around the margins and along fractures in olivine crystals (Fig. 1). The ilvaite forms patches up to 1.5 mm across and in some samples replaces up to 75% of individual olivine crystals. Serpentine is commonly associated with ilvaite in Skaergaard olivines, but the proportions of ilvaite and serpentine vary from sample to sample. Hematite was detected in the X-ray diffraction mount of one sample, but it is not an abundant phase in these rocks. Olivine grains adjacent to plagioclase, apatite, pyroxene, and/or quartz may contain ilvaite. No correlation was observed between the adjacent mineral type and the amount of ilvaite present in the olivine. In some samples, olivine grains adjacent to plagioclase were surrounded by a rim of ferroaugite 0.1 to 0.5 mm in thickness. In these samples, contacts between olivine and plagioclase have developed the sequence plagioclase, ferroaugite, ilvaite, olivine or plagioclase, ferroaugite, serpentine, ilvaite, olivine (Fig. 2).

X-ray crystallography

The ilvaite from the Skaergaard intrusion was first identified by comparison of its diffraction pattern with that of JCPDS #25-149. The diffraction pattern was obtained from a polycrystalline grain mount in a 114.6 mm Gandolfi camera, using Cr$K\alpha$ in a helium atmosphere.

In a detailed crystallographic study of the compound, Dietrich (1972) noted that there are two polymorphs of ilvaite. The orthorhombic polymorph occurs in a columnar and more coarsely-crystalline form. The monoclinic

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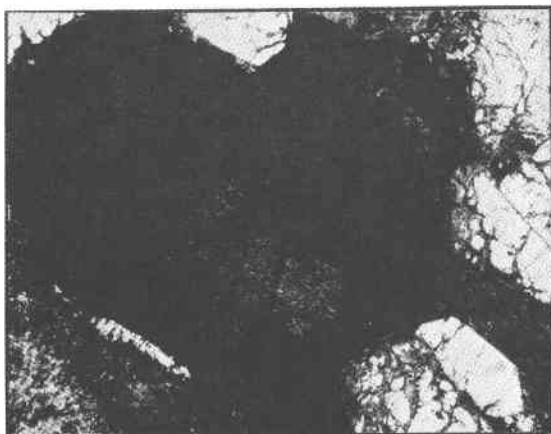[1] Present address: Department of Geology, Miami University, Oxford, Ohio 45056.

Fig. 1. Olivine grain in sample KG-247 75% replaced by ilvaite. Photo includes: grains of olivine (ol), ilvaite (il), plagioclase (pl), and apatite (ap); and patches of serpentine (se) and myrmekite (my).
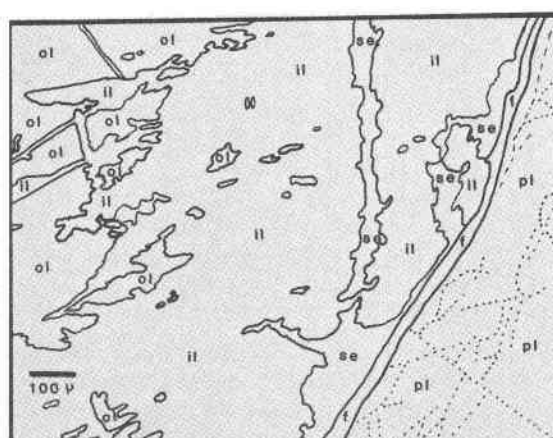

Fig. 2. Margin of olivine grain in sample KG-131 with the contact sequence plagioclase (pl)–ferroaugite (f)–serpentine (se)–ilvaite (il)–olivine (ol).

form (Dietrich, 1972) crystallizes in a fine felt-like aggregate. Dietrich noted that both polymorphs occur together in the contact metamorphic ore deposits at Gruba, Oberhalbstein, Switzerland; and he distinguished the monoclinic form by its β angle of 90.22° and the concomitant separation of hkl and $hk\bar{l}$ diffraction peaks.

Three lines of evidence suggest that the Skaergaard ilvaite is the orthorhombic polymorph. First, precise lattice constants were determined by a least-squares refinement of 12 reflections obtained from the Gandolfi pattern. The refinement used monoclinic cell constraints. The β angle was refined to 90.10 (17)° which deviates by less than 0.6σ from 90°. Second, no diffraction lines on the Gandolfi pattern showed hkl–$hk\bar{l}$ splitting. Third, the coarsely crystalline equant habit of the grains is consistent with Dietrich's orthorhombic polymorph.

The space group of orthorhombic ilvaite is $Pbnm$ (#62) (Dietrich, 1972)[2]. The space group of the monoclinic polymorph has not been reported. Single crystal precession photographs of the Skaergaard ilvaite were taken

using $MoK\alpha$ radiation. The precession suite showed diffraction symmetry consistent with space group $Pbnm$ (#62) or $P2_1nb$ (#33). The centrosymmetric space group $Pbnm$ was chosen because it was used in the structure determinations of Takeuchi (1948) and Belov and Mokejeva (1951), and we had no evidence to indicate that the crystal is not centrosymmetric.

Chemical composition

Major element analyses of coexisting ilvaite and olivine in three Skaergaard samples were performed using a MAC electron microprobe with Krisel automation and

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[2] Dietrich actually assigned space group. $Pbmn$ (#53) to Strunz's (1937) cell parameters, but this space group is not equivalent to $Pcmn$ (#62) reported by Strunz (1944) by any axis transformation of Strunz's original parameters. We presume this is an oversight caused by transposing the glide and mirror plane symbols. The same error is present in Takeuchi's (1948) study where the correct Schoenflies notation is given for space group $Pbnm$ (#62), but the space group symbol is given as $Pbmn$ (#53).

Table 1. Electron microprobe chemical analyses of Skaergaard ilvaite

	71-07	131-14	247-05	Average	Theoretical
†Oxide Weight Percent					
SiO_2	28.48	28.91	28.13	28.51	29.40
TiO_2	0.05	0.12	0.06	0.08	——
Al_2O_3	0.06	0.06	0.63	0.25	——
*Fe_2O_3	19.37	19.04	19.38	19.26	19.53
*FeO	34.87	34.30	34.87	34.68	35.15
MnO	1.08	0.59	0.93	0.87	——
MgO	0.20	0.38	0.32	0.30	——
CaO	12.54	12.96	13.35	12.95	13.72
**H_2O	2.18	2.22	2.19	2.20	2.20
Total	98.83	98.58	99.86	99.10	100.00
Cations per 9 Oxygens					
Si	1.97	1.99	1.93	1.96	2.00
Ti	0.00	0.00	0.00	0.00	——
Al	0.00	0.00	0.05	0.02	——
Fe^{3+}	1.01	0.99	1.00	1.00	1.00
Fe^{2+}	2.02	1.97	2.00	2.00	2.00
Mn	0.06	0.02	0.06	0.05	——
Mg	0.02	0.02	0.02	0.02	——
Ca	0.93	0.96	0.98	0.96	1.00
H	1.00	1.00	1.00	1.00	1.00

†Cr_2O_3, V_2O_3, P_2O_5, Na_2O, and K_2O <.05% each

*Fe^{2+}/Fe^{3+} assumed to be 2/1

**H_2O calculated based on 1 H^+ per 9 oxygen

Bence–Albee on-line data reduction (Finger, 1974; Bence and Albee, 1968). The accelerating voltage was 15 kV, the sample current was 500 mA, and the counting limits were set at 30 seconds or 30,000 counts. The analyses are

Table 2. Electron microprobe chemical analyses of Skaergaard olivines

	KG-71	KG-131	KG-247
†Oxide Weight Percent			
SiO_2	30.05	31.89	29.58
TiO_2	0.09	0.06	0.10
Al_2O_3	0.02	0.01	0.01
FeO	65.98	57.90	62.97
MnO	1.24	0.93	1.45
MgO	2.65	9.68	3.07
CaO	0.36	0.25	0.49
Total	100.39	100.72	97.67
Cations per 4 Oxygen			
Si	0.994	0.997	0.999
Ti	0.002	0.001	0.003
Fe^{2+}	1.825	1.514	1.779
Mn	0.035	0.025	0.041
Mg	0.131	0.451	0.155
Ca	0.013	0.008	0.018
End member calculations			
FO%	6.56	22.67	7.83
FA%	93.44	77.33	92.17

†Na_2O, K_2O, and P_2O_5 <.05% each

presented in Tables 1 and 2. The proportions of FeO and Fe_2O_3 in ilvaite were calculated from ΣFeO assuming Fe^{2+}/Fe^{3+} = 2.0. The proportion of H_2O in ilvaite was calculated assuming one hydrogen per nine oxygen in the unit cell.

Discussion

Studies by Burt (1971) on the stability of ilvaite in Ca–Fe–Si skarns indicate that ilvaite is stable under conditions of relatively high fH_2O, low fCO_2, moderate to low temperature, and low fO_2. Available data suggest that these conditions occurred during the subsolidus cooling of the Skaergaard intrusion. Cooling models based on oxygen isotope data (Taylor and Forrester, 1979; Norton and Taylor, 1979) indicate that the Skaergaard intrusion was in contact with circulating groundwater during its post-magmatic cooling. These models suggest that the solidified Skaergaard intrusion cooled from 1000°C to 600°C during a period of approximately 70,000 years, cooled to 310°C after an additional 100,000 years, and cooled to near ambient temperature (230°C) during the next 200,000 years. Oxygen fugacity during the cooling of the Skaergaard rocks was probably buffered by reactions between quartz, olivine, magnetite, and ilmenite. Calculations based on analyzed UBG oxide minerals (Naslund, 1980) and experimental data (Buddington and Lindsley, 1964) suggest that the UBG rocks cooled under relatively reducing conditions near the quartz–fayalite–magnetite temperature-fO_2 curve (Fig. 3). Calcite is not common in UBGγ samples suggesting that fCO_2 was low during the hydrothermal alteration of these rocks. Estimates of total

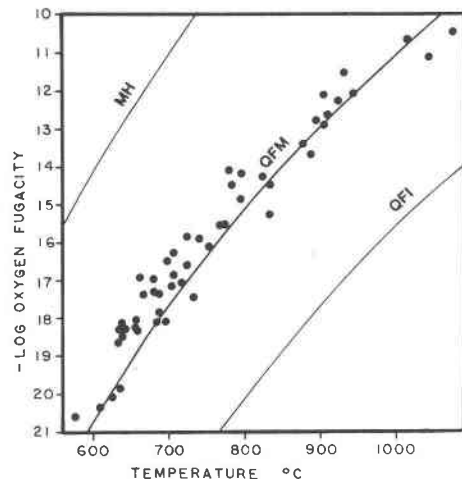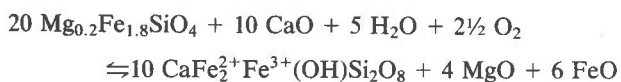
Fig. 3. Calculated temperatures and oxygen fugacites from exsolved magnetite–ulvöspinel and ilmenite–hematite in UBG samples (Naslund, 1980). Calculations are based on the experimental data of Buddington and Lindsley (1964). The buffer curves for magnetite–hematite (MH), quartz–fayalite–magnetite (QFM), and quartz–fayalite–iron (QFI) are from Eugster and Wones (1962). UBG oxide minerals are presumed to have reequilibrated during subsolidus cooling.
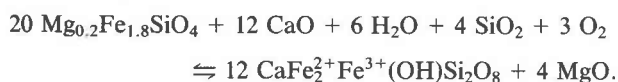
pressure at the UBGγ horizon during crystallization range from 500 bars to 1000 bars (Lindsley, *et al.*, 1969; Williams, 1971).

The UBGγ unit of the Skaergaard intrusion has been intruded by the post Skaergaard Basistoppen intrusion, a strongly differentiated, gabbroic sill approximately 500 m thick. Several lines of evidence indicate that the Basistoppen magma was emplaced before the Skaergaard intrusion had completely cooled (Douglas, 1964; Taylor and Forrester, 1979; Schwarz *et al.*, 1979). Heat from the cooling Basistoppen magma may have contributed to the hydrothermal alteration of the Skaergaard olivines. Olivine from the Basistoppen intrusion also contains ilvaite as an alteration mineral (Douglas, 1964).
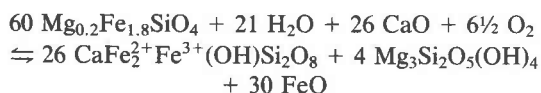
The composition of ilvaite and unaltered olivine indicate that the alteration process requires the addition of CaO, H_2O, and O_2 and the removal of MgO and FeO as follows:
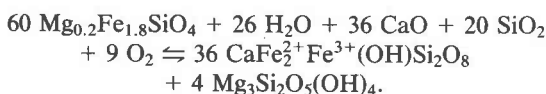
$$20\ Mg_{0.2}Fe_{1.8}SiO_4 + 10\ CaO + 5\ H_2O + 2\tfrac{1}{2}\ O_2$$
$$\leftrightarrows 10\ CaFe_2^{2+}Fe^{3+}(OH)Si_2O_8 + 4\ MgO + 6\ FeO$$

The reaction could also be written as:

$$20\ Mg_{0.2}Fe_{1.8}SiO_4 + 12\ CaO + 6\ H_2O + 4\ SiO_2 + 3\ O_2$$
$$\leftrightarrows 12\ CaFe_2^{2+}Fe^{3+}(OH)Si_2O_8 + 4\ MgO.$$

If serpentine is involved, the reaction could proceed as follows:

$$60\ Mg_{0.2}Fe_{1.8}SiO_4 + 21\ H_2O + 26\ CaO + 6\tfrac{1}{2}\ O_2$$
$$\leftrightarrows 26\ CaFe_2^{2+}Fe^{3+}(OH)Si_2O_8 + 4\ Mg_3Si_2O_5(OH)_4 + 30\ FeO$$

or:

$$60\ Mg_{0.2}Fe_{1.8}SiO_4 + 26\ H_2O + 36\ CaO + 20\ SiO_2 + 9\ O_2 \leftrightarrows 36\ CaFe_2^{2+}Fe^{3+}(OH)Si_2O_8 + 4\ Mg_3Si_2O_5(OH)_4.$$

Free oxygen in these reactions could also be expressed by the addition of H_2O and the removal of H_2, and variations in the Fe–Mg ratios of the olivine and serpentine will affect the quantities of the reactants and products. In any case, however, CaO, H_2O, and O_2 must have been added to the olivine during the alteration process. The distribution of ilvaite around the margins of olivine grains suggest that the ilvaite grew from the margins inward. There is no evidence, however, to suggest that CaO was derived from any immediately adjacent CaO-bearing mineral phases. Chemical components were probably transported to and away from the site of alteration in a fluid phase traveling along grain boundaries.

Ilvaite is not a common mineral phase, and its occurrence as an alteration product of olivine is particularly rare. The conditions which led to the formation of ilvaite in the Skaergaard intrusion probably included: 1) emplacement of the magma at a depth sufficient to allow relatively slow subsolidus cooling, but shallow enough to allow the circulation of ground water; 2) emplacement into permeable country rock; and 3) the development of extreme iron-enrichment and the crystallization of iron-rich olivine (fayalite 80–100%). It is believed that the transfer of material into and away from the site of alteration was facilitated by the circulation of hydrothermal fluids. Parts of the Skaergaard intrusion which contain fayalitic olivine, but which are adjacent to relatively impermeable gneissic country rock, do not contain ilvaite. Likewise, parts of the Skaergaard intrusion which are adjacent to relatively permeable basaltic country rock, but which contain more magnesium-rich olivine, contain serpentine but do not contain ilvaite.

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