Ilvaite, an alteration product replacing olivine in the Skaergaard intrusion

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Abstract

Ilvaite, CaFe\(^{3+}\)Fe\(^{3+}\)(OH)Si\(_2\)O\(_8\), 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\(_2\)O, 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 H\(_2\)O, low CO\(_2\), low C\(_2\), 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; Delville 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). 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 \(\gamma\) (UBG\(\gamma\)) 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). UBG\(\gamma\) 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 CrKa 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
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).

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, Oberhalbein, Switzerland; and he distinguished the monoclinic form by its $\beta$ angle of $90.22^\circ$ and the concomitant separation of $hk\bar{l}$ and $h\bar{k}l$ 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 $\beta$ angle was refined to 90.10 (17)$^\circ$ which deviates by less than 0.6$^\circ$ from 90$^\circ$. Second, no diffraction lines on the Gandolfi pattern showed $hk\bar{l}$-$h\bar{k}l$ splitting. Third, the coarsely crystalline equant habit of the grains is consistent with Dietrich's orthorhombic polymorph.

The space group of orthorhombic ilvaite is $Pbnn$ (#62) (Dietrich, 1972). The space group of the monoclinic polymorph has not been reported. Single crystal precession photographs of the Skaergaard ilvaite were taken using Mo$K\alpha$ radiation. The precession suite showed diffraction symmetry consistent with space group $Pbnn$ (#62) or $P2_1nb$ (#33). The centrosymmetric space group $Pbnn$ 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 2 Dietrich actually assigned space group $Pbnn$ (#53) to Strunz's (1937) cell parameters, but this space group is not equivalent to $Pcnn$ (#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 $Pbnn$ (#62), but the space group symbol is given as $Pbnn$ (#53).
Table 1. Electron microprobe chemical analyses of Skaergaard ilvaite

<table>
<thead>
<tr>
<th></th>
<th>71-07</th>
<th>131-14</th>
<th>249-05</th>
<th>Average</th>
<th>Theoretical</th>
</tr>
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<tbody>
<tr>
<td><strong>Oxide Weight Percent</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>SiO₂</td>
<td>28.48</td>
<td>28.91</td>
<td>28.13</td>
<td>28.51</td>
<td>29.40</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.05</td>
<td>0.12</td>
<td>0.06</td>
<td>0.08</td>
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</tr>
<tr>
<td>Al₂O₃</td>
<td>0.06</td>
<td>0.06</td>
<td>0.63</td>
<td>0.25</td>
<td>—</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>19.37</td>
<td>19.04</td>
<td>19.38</td>
<td>19.26</td>
<td>19.53</td>
</tr>
<tr>
<td>FeO</td>
<td>34.87</td>
<td>34.30</td>
<td>34.87</td>
<td>34.68</td>
<td>35.15</td>
</tr>
<tr>
<td>MnO</td>
<td>1.08</td>
<td>0.59</td>
<td>0.93</td>
<td>0.87</td>
<td>—</td>
</tr>
<tr>
<td>MgO</td>
<td>0.20</td>
<td>0.38</td>
<td>0.32</td>
<td>0.30</td>
<td>—</td>
</tr>
<tr>
<td>CaO</td>
<td>12.54</td>
<td>12.96</td>
<td>13.35</td>
<td>12.95</td>
<td>13.72</td>
</tr>
<tr>
<td><strong>H₂O</strong></td>
<td>2.18</td>
<td>2.22</td>
<td>2.19</td>
<td>2.20</td>
<td>2.20</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>98.83</td>
<td>98.58</td>
<td>99.86</td>
<td>99.10</td>
<td>100.00</td>
</tr>
</tbody>
</table>

| 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 | 1.00 | 0.00 | 0.00 | 0.00 | — |
| Fe³⁺ | 0.00 | 0.00 | 0.05 | 0.02 | — |
| Fe²⁺ | 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 |

| **Cr₂O₃, V₂O₅, P₂O₅, Na₂O, and K₂O < 0.05% each** |
| **Fe²⁺/Fe³⁺** assumed to be 2/1 |
| **H₂O** 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 presented in Tables 1 and 2. The proportions of FeO and Fe₂O₃ in ilvaite were calculated from ΣFeO assuming Fe²⁺/Fe³⁺ = 2.0. The proportion of H₂O 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 fH₂O, low fCO₂, moderate to low temperature, and low fO₂. 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-fO₂ curve (Fig. 3). Calcite is not common in UBGγ samples suggesting that fCO₂ was low during the hydrothermal alteration of these rocks. Estimates of total

![Fig. 3](image-url)
pressure at the UBGy horizon during crystallization range from 500 bars to 1000 bars (Lindsley, et al., 1969; Williams, 1971).

The UBGy unit of the Skaergaard intrusion has been intruded by the post Skaergaard Basistoppen intrusion, a strongly differentiated, gabbroic sill approximately 300 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, H2O, and O2 and the removal of MgO and FeO as follows:

\[
20 \text{Mg}_2\text{Fe}_{1.8}\text{SiO}_4 + 10 \text{CaO} + 5 \text{H}_2\text{O} + 2\frac{1}{2}\text{O}_2 \\
\Rightarrow 10 \text{CaFe}^{2+}\text{Fe}^{3+}(\text{OH})\text{Si}_2\text{O}_8 + 4 \text{MgO} + 6 \text{FeO}
\]

The reaction could also be written as:

\[
20 \text{Mg}_2\text{Fe}_{1.8}\text{SiO}_4 + 12 \text{CaO} + 6 \text{H}_2\text{O} + 4 \text{SiO}_2 + 3 \text{O}_2 \\
\Rightarrow 12 \text{CaFe}^{2+}\text{Fe}^{3+}(\text{OH})\text{Si}_2\text{O}_8 + 4 \text{MgO}
\]

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

\[
60 \text{Mg}_2\text{Fe}_{1.8}\text{SiO}_4 + 21 \text{H}_2\text{O} + 26 \text{CaO} + 6\frac{1}{2}\text{O}_2 \\
\Rightarrow 26 \text{CaFe}^{2+}\text{Fe}^{3+}(\text{OH})\text{Si}_2\text{O}_8 + 4 \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 \\
+ 30 \text{FeO}
\]

or:

\[
60 \text{Mg}_2\text{Fe}_{1.8}\text{SiO}_4 + 26 \text{H}_2\text{O} + 36 \text{CaO} + 20 \text{SiO}_2 \\
+ 9 \text{O}_2 \\
\Rightarrow 36 \text{CaFe}^{2+}\text{Fe}^{3+}(\text{OH})\text{Si}_2\text{O}_8 \\
+ 4 \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4
\]

Free oxygen in these reactions could also be expressed by the addition of H2O and the removal of H2, 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, H2O, and O2 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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