In the course of a larger study on the origin of possible protoliths for the manganiferous iron ores of the Early Proterozoic Cuyuna iron range in east-central Minnesota, we have characterized a number of mineral associations found within the manganese-rich parts of the Trommald Formation. One association is characterized by the presence of aegirine. Aegirine in the Trommald Formation was first described by Grout (1946) from core drilled on the property of Merritt Number Two mine near Ironton, Minnesota (Grout & Wolff 1955). Grout (1946) recognized two varieties of aegirine, a green variety occurring in cross-cutting veins, and a brown variety occurring as disseminated groundmass material, as intraclasts, and as “oolites” consisting of rounded grains rimmed by what he believed to be hematite and chert.

Although unusual, aegirine is not an uncommon mineral in many iron–manganese and manganese ore deposits. Aegirine or aegirine-augite occurs in contact or regionally metamorphosed bedded manganese or iron–manganese ore deposits of Jurassic age in Japan (Kato et al. 1982, Hiroi et al. 1987). In the Proterozoic iron formation of the southern part of the Labrador Trough (Klein 1966), the aegirine occurs in a manganiferous zone in mineral assemblages containing rhodonite, rhodochrosite, and calderite, the Mn,Fe-garnet. In the southeastern Bababudan Hills of Karnataka, India, aegirine occurs in banded iron-formation intercalated within the Dharwar Supergroup, a low-metamorphic-grade volcanosedimentary sequence of Archean age (Mukhopadhyay et al. 1980, Chadwick et al. 1986). In each example, important questions remain concerning the source of the sodium, as well as to the timing of its introduction relative to

**Abstract**

Aegirine occurs in manganese-rich parts of the Trommald Formation on the Cuyuna iron range of east-central Minnesota. Textural attributes imply that the aegirine is pre-, syn-, and post-depositional in age. Thus its paragenesis spans the depositional and possibly the deformational history of the host rock. The aegirine ranges from 84 to 95% NaFeSi2O6; no relationship was found between textural attributes and composition. The presence of aegirine and its textures require that Na-rich fluids were an integral part of the formation of the manganese-rich parts of the iron formation throughout their development. These features set the Trommald Formation apart from other Early Proterozoic iron formations of Lake Superior type in the region.

**Keywords:** aegirine, Na-pyroxene, iron formation, sedimentary micronodules, electron-microprobe analyses, Cuyuna iron range, Minnesota.

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**Mots-clés:** aegyrine, pyroxène sodique, formation de fer, micronodules sédimentaires, données à la microsonde électronique, gisements de fer, chaîne de Cuyuna, Minnesota.
the depositional – diagenetic – metamorphic history of the host rock. In the Cuyuna range, well-preserved primary textures provide an opportunity to evaluate the early paragenetic history of the aegirine-bearing mineral assemblages.

**GEOLOGICAL SETTING**

The Cuyuna iron range of east-central Minnesota (Fig. 1) was discovered in 1904 and became a major mining district of Fe and Fe–Mn ore. The range is divided into three structural entities: Emily district, North range, and South range (Fig. 2), each with its own characteristic stratigraphic and structural attributes (Southwick et al. 1988, Morey & Southwick 1993). The rocks of the North and South ranges are separated by a major structural discontinuity inferred to be a north-verging thrust fault, and both are overlain unconformably by strata of the Emily district. The rocks of the South range have been assigned to the Mille Lacs Group, those of the North range, to the North Range Group, and those of the Emily district, to the Animikie Group (Morey & Southwick 1993). This stratigraphic arrangement is considerably different from that in the older literature (e.g., Morey & Van Schmus 1988), which assumed that the various parts of the Cuyuna range could be correlated via a single interval of deposition of iron-rich sediments.

The North Range Group has been divided into three formations (Schmidt 1963), the Mahnomen, Trommald, and Rabbit Lake (Fig. 3). The lowermost Mahnomen Formation can be divided into a lower member, which lacks ferruginous components (Southwick et al. 1988), and an upper member dominated by beds of ferruginous argillite and lean iron-formation interlayered with nonferruginous argillite, siltstone, and quartzose sandstone. The Trommald Formation, the main iron-formation of the North range, is a chemically precipitated unit that includes units of oxide, carbonate, and silicate iron-formation (Schmidt 1963). The uppermost Rabbit Lake Formation can be divided into a lower member of black mudstone intercalated with beds of iron formation and units of volcanogenic origin, and an upper member of slate, carbonaceous mudstone, graywacke, and thin units of iron-rich strata.

The North range of the Cuyuna range was regionally metamorphosed to the upper greenschist facies during the Penokean orogeny, which peaked between 1870 and 1850 Ma (Southwick et al. 1988). We estimated an equilibrium metamorphic temperature from coexisting carbonates within the upper part of the
Fig. 2. Generalized geological map of the Cuyuna range (after Southwick et al. 1988).

Fig. 3. Stratigraphy of the main units of the Cuyuna North range. Geology is from a hole drilled on the Merritt mine property.
Trommald Formation. Most of the carbonates fall compositionally along or very close to the calcite–rhodochrosite binary join, which was experimentally investigated by Goldsmith & Graf (1957). On the basis of their determination of the position of a solvus between kutnahorite and rhodochrosite, the equilibrium metamorphic temperature for the Trommald Formation near the Merritt mine was estimated at between 480° and 490°C. A temperature of 450°C was estimated for the cross-cutting carbonate veins. A regional metamorphic pressure has not yet been determined for the Penokean orogeny in this area. Seventy-five km to the east, the pressure of the Penokean metamorphism was estimated to range between 4.5 and 8 kbars (Holm & Selverstone 1990).

STRATIGRAPHY OF THE TROMMALD FORMATION

As part of this study, we have divided the formation into three members, an upper member consisting mainly of red, thick-bedded, manganese-rich, oxide iron-formation, a middle member consisting of black, laminated, carbonate–silicate iron-formation, and a lower member consisting of a gray, thin-bedded, carbonate–silicate iron-formation (Fig. 3). The upper member is equivalent to the thick-bedded facies of Schmidt (1963), whereas the middle and lower members combined correspond to his thin-bedded facies.
The upper member typically consists of thick beds of so-called "granular" or "cherty" iron formation intercalated with thinner beds of iron and manganese oxides (Grout & Wolff 1955). The term "cherty", however, is a misnomer in that "cherty" units in the vicinity of the Merritt mine actually contain very little free silica, as either chert or quartz. Much of the red groundmass described as jasper or as admixed chert and hematite by Grout & Wolff (1955) is either aegirine or rhodonite admixed with various amounts of hematite, magnetite, hyalophane, rhodochrosite, and calcite, as well as minor amounts of stilpnomelane and magnesiorebeckite.

A common characteristic of the upper member of the Trommald Formation is the occurrence of spheroidal structures typically consisting of rounded grains of one or more minerals coated by other minerals (Figs. 4A, C). These features have been described as oolites (Grout 1946, Grout & Wolff 1955), but have physical attributes more akin to those typical of oncolites. However, unlike typical oolites or oncolites, the mineralogy of these micronodules is highly variable. In one striking example, the core consists of rhodonite mantled successively by hematite, hyalophane, and rhodochrosite. Spheroidal structures such as this clearly did not form in a simple sedimentary environment, but rather in a rapidly changing, dynamic chemical system in which the cation ratios changed significantly over time. For this reason, instead of the terms "oolite" or "oncolite", the purely descriptive term "micronodule" will be used for these structures in order to avoid any genetic connotation.

The middle and lower members of the Trommald Formation differ mainly in bedding attributes and in the gradual increase in the ratio of carbonate to silicate minerals with higher stratigraphic position. However, both members are typical carbonate–silicate iron-formation consisting predominantly of manganese siderite, ferroan khatnaborite or managanan ankerite, stilpnomelane, minnesotaite, hematite, magnetite, quartz, and chamosite.

Textural Attributes of the Aegirine

Aegirine has been found only in the upper member of the Trommald Formation. It is most abundant in a zone some 7.5 m thick in the lower part of the unit. This particular layer forms a marker bed that was mapped in the Merritt Number Two and Ferro mines (Grout 1946, Schmidt 1963) and thus appears to be continuous along strike for at least 600 m.

The aegirine in these rocks has textural attributes that imply a complex paragenesis. It occurs as rounded clasts (Fig. 4A), as rims around these and other grains (Figs. 4A–C, 5A, B), within cross-cutting veins (Fig. 5D), and most commonly as a fine-grained to cryptocrystalline, tan to light-brown groundmass (Fig. 5C), which locally includes blade-like crystals up to 0.25 mm in length (Fig. 4D). Aegirine with a fine-grained to cryptocrystalline habit occurs locally within layers or lenses oriented parallel to bedding, but more commonly occurs in zones that cut the original layering. Locally, the cross-cutting zones seem to be related to alteration fronts, which penetrated the host rock along zones of weakness (Fig. 5C).

Rounded clasts of aegirine occur in a number of different forms. In some clasts, the aegirine occurs as a single crystal (Fig. 4A); in others, it has a fine-grained habit similar to that in groundmass material. Still other clasts have aegirine intergrown with rhodonite. Typically, these clasts form the core of the previously described micronodules (Figs. 4A, C). Surrounding the aegirine core are thinly laminated, red-colored bands composed of microcrystalline aegirine and hematite. In much of the earlier literature, this surrounding material was identified as jasper or as admixtures of hematite and chert. In many cases, the rim is opaque in transmitted light, but the detailed layering is revealed by a combination of reflected and transmitted light.

Some of the aegirine cores in the micronodules have angular appendages of similar compositions protruding from the edges of the rounded clasts (Fig. 4C). The exact significance of the angular appendages is not well understood, but in some cases they seem to occur along microcracks. We suggest that the angular appendages are recrystallized rim material crystallographically joined to the core grain.

Aegirine also occurs as a zoned rim around other types of grains, including those consisting of manganese oxides, quartz, rhodonite, and rhodochrosite (Figs. 5A, B). In these cases, the aegirine is brownish yellow and very fine grained, but not cryptocrystalline. As such, it resembles the groundmass material except for its internal laminated structure. The rim of these micronodules typically is concentric around the core, and the structure resembles an oolite.

Aegirine also occurs in both monomineralic and polymineralic veins. In the polymineralic veins, the aegirine occurs with quartz, Mn-oxides and managanan calcite. These veins cut across original layering and are clearly secondary in nature. The origin of vug-like aegirine-cored grains such as the one illustrated in Figure 4B is less obvious. Most likely, these are examples of dissolution of the original grain; the resulting void was then filled with small euhedral crystals of aegirine and, later, quartz. It is clear from the observations summarized above that the different textural varieties of aegirine could not have formed concurrently. The rounded nature of some of the aegirine clasts implies that both crystalline and cryptocrystalline aegirine was formed and rounded prior to deposition at its final resting site. In contrast, the aegirine rim on the micronodules and the stratiform aegirine layers suggest a syndepositional origin,
whereas cross-cutting aegirine zones and veins are clearly postdepositional features, though not necessarily formed at the same time.

CHEMICAL ATTRIBUTES OF THE AEGIRINE

Electron-microprobe analyses show that the aegirine in the Trommald Formation ranges in composition from approximately 84 to 95 mole % NaFeSi₂O₆. In general, most compositions are fairly close to the end-member (Table 1), as had been reported by Grout (1946). There is slightly more compositional variability in aegirine of very fine grained to cryptocrystalline habit (groundmass material) (analysis #7, Table 1) than in the coarser grained, euhedral varieties. However, the observed difference could simply result from the presence of other mineral phases finely intergrown with the aegirine. In general, there are only minor compositional differences among grains judged from textural criteria to be of pre-, syn-, or postdepositional origin. In the micronodules in which the core consists of either a manganese carbonate or manganese oxide, the associated rim is a tan to brown aegirine with a composition consistent with the aegirine stoichiometry (Table 1). Where the core is itself aegirine, the associated rim of aegirine is red, and has an iron content (Table 2) much higher than is consistent with the aegirine stoichiometry. However, the Na₂O+CaO to SiO₂ ratios of these varieties are nearly identical to those for typical aegirine. Therefore, it is likely that the high iron values result from the presence of intergrown hematite. Given that
the diameter of the electron-microprobe beam was approximately 5 μm, the hematite must be intergrown on a scale of a few micrometers or less.

**DISCUSSION**

Aegirine and aegirine-augite form in a number of different geological environments. Sodic pyroxenes comprise an important mineral series in sodium-rich igneous rocks (Bailey & Schairer 1966), and have been reported to occur as alteration products in oceanic basalts (Laverne 1987). They have been described from carbonatite intrusive complexes and the associated fennites (Sutherland 1969). In this setting, the almost pure aegirine tends to be associated with late-stage, low-temperature alkali metasomatism (Andersen 1989). Aegirine and aegirine-augite also occur in metamorphic rocks of appropriate composition over a wide range of pressure-temperature conditions, ranging from very low grade within the lawsonite zone to blueschist-facies rocks (Deer et al. 1978). Aegirine also apparently forms under authigenic conditions, as in the Green River Formation in the western United States (Milton & Eugster 1959), at Caithness, Scotland (Fortey & Michie 1978), and in the Kumolinsk syncline, Kazakhstan (Deet et al. 1978). This probably reflects the lower solubility of other cations in the sodic pyroxene structure at low

| TABLE 1. RESULTS OF ELECTRON-MICROPROBE ANALYSES*1 OF AEGIRINE |
|---|---|---|---|---|---|
| SiO₂ | 52.83 | 52.21 | 52.63 | 52.55 | 53.09 |
| Al₂O₃ | 0.77 | 0.71 | 0.68 | 0.34 | 0.59 |
| TiO₂ | 0.00 | 0.00 | 0.04 | 0.01 | 0.01 |
| Fe₂O₃ | 31.46 | 30.10 | 31.34 | 29.93 | 31.38 |
| FeO* | 1.83 | 2.51 | 1.68 | 3.36 | 2.73 |
| MgO | 0.00 | 0.00 | 0.01 | 0.01 | 0.08 |
| MnO | 0.44 | 0.68 | 0.59 | 1.01 | 0.15 |
| CaO | 0.20 | 1.04 | 0.51 | 1.58 | 0.21 |
| Na₂O | 12.68 | 12.10 | 12.57 | 11.81 | 12.53 |
| K₂O | 0.00 | 0.02 | 0.01 | 0.02 | 0.01 |
| Total | 100.21 | 99.37 | 100.06 | 100.62 | 100.77 |

**Number of ions on the basis of 6 atoms of oxygen**

| Si | 2.020 | 2.019 | 2.017 | 2.017 | 2.022 |
| A1 | 0.035 | 0.032 | 0.031 | 0.015 | 0.026 |
| Ti | 0.000 | 0.000 | 0.001 | 0.000 | 0.000 |
| Fe³⁺ | 0.965 | 0.876 | 0.904 | 0.864 | 0.899 |
| Fe²⁺ | 0.038 | 0.081 | 0.054 | 0.108 | 0.087 |
| Mg | 0.000 | 0.000 | 0.001 | 0.000 | 0.000 |
| Mn | 0.014 | 0.022 | 0.019 | 0.033 | 0.005 |
| Ca | 0.008 | 0.043 | 0.021 | 0.065 | 0.009 |
| Na | 0.940 | 0.907 | 0.934 | 0.879 | 0.925 |
| K | 0.000 | 0.001 | 0.001 | 0.000 | 0.000 |
| mole % | 93 | 90 | 89 | 89 | 92 |

*1 Analyzed material was taken from the Merritt drill hole. Depths are as follows: 1) 79.98 m, 2) 79.98 m, 3) 79.98 m, 4) 79.98 m, 5) 79.98 m, 6) 80.04 m, 7) 84.43 m, 8) 87.78 m, 9) 80.59 m, 10) 80.59 m, 11) 84.76 m, 12) 84.76 m, 13) 80.59 m.

Data reduction was done using a PAP correction routine (Pouchou & Pichoir 1984).

**#** FeO/Fe₂O₃ ratios were estimated assuming stoichiometry.  
**#** Calculated using the method of Morimoto (1989).
This reaction is particularly sensitive to the concentration of NaCl in the reacting solution. If one extrapolates the data shown in Figure 6 to lower temperatures, the data suggest that aegirine possibly could form from hematite and chert in the presence of a solution with a NaCl concentration equivalent to that of seawater (~0.5 molar NaCl) at temperatures of around 200°C and 1 kbar of pressure. However, authigenic aegirine in the Green River Formation apparently formed at or near room temperature (Milton & Eugster 1959). To form at these lower temperatures, aegirine probably requires hypersaline fluids to be present in the system. The stability of aegirine also is influenced by the oxygen fugacity of the system. In more reducing environments, Na-amphibole, such as riebeckite, becomes the stable Na-phase (Ernst 1968).

The experimental data outlined above were anticipated by Grout (1946), who speculated that the aegirine in Trommald Formation formed by the reaction of chert and hematite in the presence of a sodium-rich hypogene hydrothermal solution. Unfortunately, today as in 1946, there is no definitive evidence as to the source of the sodium-bearing solutions. Gair (1973, 1975) argued that thin layers of riebeckite and aegirine-augite in the Negaunee Iron Formation of the Marquette district in northern Michigan formed syn-genetically with the iron formation, and suggested that these sodium-rich layers formed in shallow water under evaporative conditions. However, textural relationships in the Trommald Formation are considerably more complex. Cores of the micronodules could represent eroded detritus from older igneous rocks, but no other detrital material has been found in these rocks, and one would expect the composition of the pyroxene to differ from that formed later. Therefore, it is likely that the rounded grains formed on or just beneath the seawater-sediment interface, where chert and hematite were being precipitated and where they could react with a sodium-rich solution. However, that this solution was not a simple evaporative concentration is indicated by the presence of other constituents, such as manganese silicate and carbonate and, especially, barium silicate in the micronodules (McSwiggen et al. 1992). We suggest that a submarine hydrothermal system vented complex brine solutions that flowed onto the sediment-water interface and penetrated through the sediment, beneath the sediment-water interface. Evidence for a penetrative sodium-rich solution includes the cross-cutting aegirine-rich zones, which appear to be related to alteration fronts that penetrated the host rocks along zones of weakness.

A reasonable model for this kind of mineralization is the present-day Red Sea. It is a rift basin, the lower part of which is filled by hot saline brines derived from a hydrothermal vented system channeled by faults along the margins of the basin (El Shazly 1990). Sediments beneath the brine pools contain magnetite-hematite and pyroxene. The latter is con-

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### TABLE 2. COMPOSITION OF RIMS OF INTERGROWN AEGIRINE AND HEMATITE

<table>
<thead>
<tr>
<th>(wt.%)</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>Ideal</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>41.24</td>
<td>40.59</td>
<td>42.03</td>
<td>37.41</td>
<td>52.02</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.35</td>
<td>0.40</td>
<td>0.61</td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.04</td>
<td>0.04</td>
<td>0.10</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃*</td>
<td>46.59</td>
<td>47.87</td>
<td>46.71</td>
<td>32.08</td>
<td>34.56</td>
</tr>
<tr>
<td>MgO</td>
<td>0.05</td>
<td>0.01</td>
<td>0.04</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>0.71</td>
<td>0.59</td>
<td>0.59</td>
<td>0.54</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>0.54</td>
<td>1.02</td>
<td>0.50</td>
<td>0.58</td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td>10.31</td>
<td>9.22</td>
<td>9.71</td>
<td>8.79</td>
<td>13.42</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.00</td>
<td>0.01</td>
<td>0.02</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.55</td>
<td>100.31</td>
<td>99.92</td>
<td>100.00</td>
</tr>
<tr>
<td>(Na₂O+CaO)/SiO₂</td>
<td>0.26</td>
<td>0.25</td>
<td>0.24</td>
<td>0.25</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Analyses are from the Merritt drill hole. Depths are as follows: 14) 80.04 m, 15) 79.98 m, 16) 79.98 m, 17) 79.98 m.

* Total iron calculated as Fe₂O₃.

Electron-microprobe procedures, see Table 1.

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The wide range of conditions under which aegirine can form implies that its stability is less dependent on temperature and pressure, and more dependent on compositional controls, in particular the molar proportions of Na. The upper stability-limits in terms of temperature and pressure have been investigated by Bailey (1969) and Gilbert (1969), and the low-temperature stability limits by Likhoydov (1981) using the reaction:

\[ 0.5 \text{Fe}_2\text{O}_3 + 2 \text{SiO}_2 + \text{NaCl} + 0.5 \text{H}_2\text{O} = \text{NaFeSi}_2\text{O}_5 + \text{HCl} \]

over a temperature range of 350°C to 500°C (Fig. 6).

---

**Fig. 6.** Stability of aegirine relative to hematite and quartz (after Likhoydov 1981).
considered to have formed from the interaction of a high-
temperature, Na-rich fumarolic fluid with the iron
oxide and chert sediments (El Shazly 1990). Although
the Red Sea deposits and the Trommald Formation
are similar in many respects, the textural attributes
reported from the Trommald Formation have not been
described from the Red Sea or, for that matter, from
any other locality known to us.

ACKNOWLEDGEMENTS

This project was partially supported by the U.S.
Bureau of Mines – Selective Mining in Minnesota. It
also benefitted from the earlier work of Roberta
Lamons. We thank T. Frisch, E. Grew, and D. Hogarth
for their very helpful comments and suggestions for
improving this manuscript, and Ian Steele for assis-
tance with the electron-microprobe analyses.

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Received July 14, 1993, revised manuscript accepted October 28, 1993.