

ELECTRON MICROPROBE ANALYSIS OF MELILITE AND GARNET FROM THE OKA COMPLEX, QUEBEC

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ABSTRACT

Melilites from the jacupirangite-okaite-carbonatite series of the Oka complex are essentially unzoned, show very slight Na/Mg increases in the series and project very closely to the $\text{Ca}_2\text{MgSi}_2\text{O}_7 - \text{CaNaAlSi}_2\text{O}_7$ composition join similar to melilites from other alkalic rock intrusions. Andradite garnets rimming melilite and from melilite-free carbonatite have less than 3 percent TiO_2 . The rimmed melilite is depleted in Na compared with unrimmed melilite in carbonatite. Melilite has precipitated through a wide temperature range, and has undergone magmatic reaction at low temperature enriching the residual magma in Na. Fractionation of melilite may be effective in producing residual magma with high K/Na.

INTRODUCTION

The alkalic rock-carbonatite complex at Oka, Quebec has a wide variety of mineral assemblages (Gold 1963) including melilitic rocks, the okaite series (Stansfield 1923; Davidson 1963). These rocks consist of jacupirangite (titanaugite-, magnetite-, melilite-rich rocks), okaite (melilite-, hauyne-, nepheline-rich rocks), and carbonatite. Watkinson (1970) concluded that the okaite series is a product of fractional crystallization of a carbonated nephelinitic parent, in light of experiments in the join $\text{NaAlSiO}_4 - \text{CaCO}_3 - \text{H}_2\text{O}$ (Watkinson & Wyllie 1971). Because of the wide range of chemical compositions of melilite (Christie 1964; Edgar 1965) it was thought that melilite from Oka might show chemical variation reflecting strong fractional crystallization. Gold (1966) has published analyses of Oka melilites, but the CO_2 and P_2O_5 values suggest that the specimens possibly contain inclusions. Petrographic examination of the Oka rocks confirmed that inclusions are common in melilite and showed that melilite has undergone varying degrees of alteration. It was anticipated that electron microprobe analysis might avoid these problems and also allow analysis of melilite that has undergone partial magmatic reaction (Watkinson 1970).

TABLE 1. ELECTRON MICROPROBE ANALYSES OF MELLILITES.

All Fe is calculated as FeO. Melilite 1 is from jacupirangite; 2 and 3 from okaite; 4 and 5 from carbonatite. Mineral assemblages and locations are given in Appendix I.

| | 1 | 2 | 3 | 4 | 5 |
|--------------------------------|-------|-------|-------|-------|-------|
| SiO ₂ | 42.3 | 41.5 | 41.1 | 41.8 | 43.7 |
| Al ₂ O ₃ | 8.21 | 8.86 | 9.08 | 8.91 | 6.25 |
| FeO | 2.72 | 2.49 | 2.81 | 1.93 | 2.27 |
| MnO | 0.25 | 0.17 | 0.23 | 0.42 | 0.82 |
| MgO | 7.07 | 6.84 | 6.38 | 6.61 | 7.66 |
| CaO | 33.5 | 33.6 | 33.1 | 32.1 | 32.5 |
| SrO | 1.03 | 1.04 | 1.00 | 1.11 | 1.30 |
| Na ₂ O | 3.95 | 3.88 | 4.08 | 4.81 | 4.18 |
| K ₂ O | 0.19 | 0.22 | 0.26 | 0.13 | — |
| Total | 99.27 | 98.56 | 98.07 | 97.89 | 98.68 |

TABLE 2. COMPARISON OF ELECTRON MICROPROBE (A) AND WET CHEMICAL ANALYSES (B) OF W1 DIABASE.

All Fe calculated as FeO. Analysis b is the "preferred" values of Ingamells & Suhr (1963).

| | a | b |
|--------------------------------|------|------|
| SiO ₂ | 51.9 | 52.9 |
| Al ₂ O ₃ | 15.5 | 15.0 |
| TiO ₂ | 1.11 | 1.09 |
| FeO | 9.41 | 9.95 |
| MnO | 0.19 | 0.17 |
| MgO | 6.46 | 6.52 |
| CaO | 10.8 | 10.9 |
| K ₂ O | 0.69 | 0.63 |
| Na ₂ O | 2.28 | 2.15 |

TABLE 3. MICROPROBE ANALYSES OF CORE AND RIM OF ONE GRAIN OF MELLILITE 4.

| | Core | Rim |
|--------------------------------|------|------|
| SiO ₂ | 42.1 | 41.7 |
| Al ₂ O ₃ | 8.65 | 8.65 |
| FeO | 1.88 | 2.09 |
| MnO | 0.40 | 0.40 |
| MgO | 6.71 | 6.77 |
| CaO | 32.2 | 32.3 |
| SrO | 1.07 | 0.95 |
| Na ₂ O | 4.59 | 4.78 |
| K ₂ O | 0.12 | 0.12 |

ELECTRON MICROPROBE ANALYSIS

Analytical determinations were carried out on an ARL-EMX microprobe at the University of Toronto under the guidance of J. C. Rucklidge. Operating conditions were 15 kv accelerating voltage and 0.5 μ a sample current measured on diopside, and a focused electron beam (approximately 2 μ m diameter). Each polished thin section was translated a few microns between ten-second counts to avoid the possibility of volatilization from the specimen and the results of at least six sets of counts were averaged for each grain of melilite. Four to seven grain averages are made for each section. The standards used were synthetic oxide and silicate compounds. The data were processed using the program written by Rucklidge (1967) and the results are given in Tables 1 and 4.

An estimate of the accuracy of the probe analysis may be made from a comparison of the author's analysis of a glass made from the standard diabase W-1 and wet chemical analysis (Table 2); details of the procedure are described by Rucklidge *et al.* (1970).

Melilite. Representative specimens from the okaite series were selected with the help of A. Davidson, and microprobe analyses were made on melilites in pyroxene-, melilite-, and carbonate-rich rocks. The location and petrography of each specimen are described in Appendix I. Nine-element analyses were made, and other elements were sought but not detected in a wave-length scan of specimen 4. Rare earths were specifically sought but not detected in spite of their presence in associated calcic minerals in this specimen.

Gold (1963) noted that melilites from Oka are commonly unzoned unlike melilites from many other occurrences. Very slight zoning is evident microscopically in melilites from some Oka carbonatites, but the extent of chemical variation is negligible as in illustrated by analyses of the core and rim of an optically zoned melilite (Table 3). There is a suggestion of very slight Na and Fe enrichment in the rim. Perhaps the optical zoning may be related to variation of the ferrous/ferric ratio within a grain.

Garnet. Garnets occur in carbonatite at Oka as discrete euhedral to anhedral grains and as anhedral grains rimming melilite (Watkinson 1970). Analyses of garnets from three occurrences are presented in Table 4. Na and K were not detected. Zoning of garnets from Oka carbonatites is apparent optically, and chemical variations were shown by microprobe to occur from grain to grain especially in TiO₂ content. These variations were not extensive in the specimens examined, compared to the results of Gomes (1969) on garnets from nepheline syenites. The Oka garnets have

low Ti and Mg, and high Si and Ca compared with garnets from other carbonatites (Howie & Wooley 1968).

DISCUSSION

Melilite. Melilites 1, 2, 3 and 4 (Table 1) are from jacupirangite, fine- and coarse-grained okaite and melilite carbonatite respectively. This succession of rock types at Oka has been suggested by Davidson (1963) to be the order of crystallization of the rocks on fractionation of magma. Watkinson (1970) has shown that the succession of rocks of the okaite series is strikingly similar to phase assemblages encountered at decreasing temperatures in the composition join $\text{NaAlSiO}_4 - \text{CaCO}_3 - \text{H}_2\text{O}$ and that the succession at Oka may be related by fractional crystallization of a carbonated nephelinitic parent magma by analogy with the experimental study (Watkinson & Wyllie 1971). Appreciable temperature variation during crystallization of the okaite series is further attested to by the crystallization temperatures of okaite (855 and 765°C) and carbonatite (730 and 720°C) determined by Conway & Taylor (1969) based on oxygen isotopic fractionation between coexisting calcite and magnetite.

The occurrence of melilite in this variety of mineral assemblages generated by fractional crystallization through a broad temperature interval would suggest that the melilite might show extensive chemical variation. However, the analyzed melilites show very little variation (Table 2); there is a slight tendency for Na enrichment and Ca and Mg depletion through the succession.

TABLE 4. ELECTRON MICROPROBE ANALYSES OF GARNETS.

All Fe is calculated as Fe_2O_3 . Garnet 1 rimming melilite 5 in carbonatite; 2 and 3 are euhedral garnets from carbonatite. Mineral assemblages and their locations are given in Appendix I.

| | 1 | 2 | 3 |
|-------------------------|------|-------|------|
| SiO_2 | 35.9 | 36.3 | 34.7 |
| TiO_2 | 1.38 | 1.92 | 1.89 |
| Al_2O_3 | 2.17 | 2.78 | 2.04 |
| Fe_2O_3 | 26.6 | 27.0 | 25.6 |
| MnO | 0.37 | 0.49 | 0.57 |
| MgO | 0.17 | 0.17 | 0.15 |
| CaO | 32.5 | 32.6 | 32.9 |
| TOTAL | 99.1 | 101.3 | 97.9 |

The chemical variation is emphasized when the data are projected onto the join $\text{Ca}_2\text{MgSi}_2\text{O}_7$ (akermanite) — $\text{Ca}_2\text{Al}_2\text{SiO}_7$ (gehlenite) — $\text{Na}_2\text{Si}_3\text{O}_7$ (Figure 1); $\text{Na}_2\text{Si}_3\text{O}_7$ is the hypothetical end member of Na + Si for Ca + Al substitution in gehlenite. The analyses of melilite from intrusive alkalic-rock complexes including those from Oka (Gold 1966), Turja (Ramsay 1921) and Iron Hill (Larsen & Hunter 1914) plot very close to the $\text{Ca}_2\text{MgSi}_2\text{O}_7$ — $\text{NaCaAlSi}_2\text{O}_7$ join (Figure 1). The electron probe analyses 1-4 exhibit a minor trend towards the sodic melilite, consistent with preliminary phase relations in the join $\text{Ca}_2\text{MgSi}_2\text{O}_7$ — $\text{CaNaAlSi}_2\text{O}_7$ — $\text{Ca}_2\text{Al}_2\text{SiO}_7$ (Schairer, Yoder & Tilley 1967). They showed that melilite crystalline solutions are very Na poor at high temperatures and contain a maximum of about 50 weight percent $\text{NaCaAlSi}_2\text{O}_7$ at the lowest stability temperatures at 1 bar pressure. Edgar (1965) showed that the maximum $\text{NaCaAlSi}_2\text{O}_7$ content of melilite at 1 kbar $P_{\text{H}_2\text{O}}$ is about 60 weight per- and from Christie's (1962) data the value is about 40% at 6 kbar $P_{\text{H}_2\text{O}}$. These values are in general range of analysis 4 (Figure 1). Kushiro (1964) showed, however, that the range of crystalline solution of $\text{NaCaAlSi}_2\text{O}_7$ in $\text{Ca}_2\text{MgSi}_2\text{O}_7$ increases under dry conditions to high pressures.

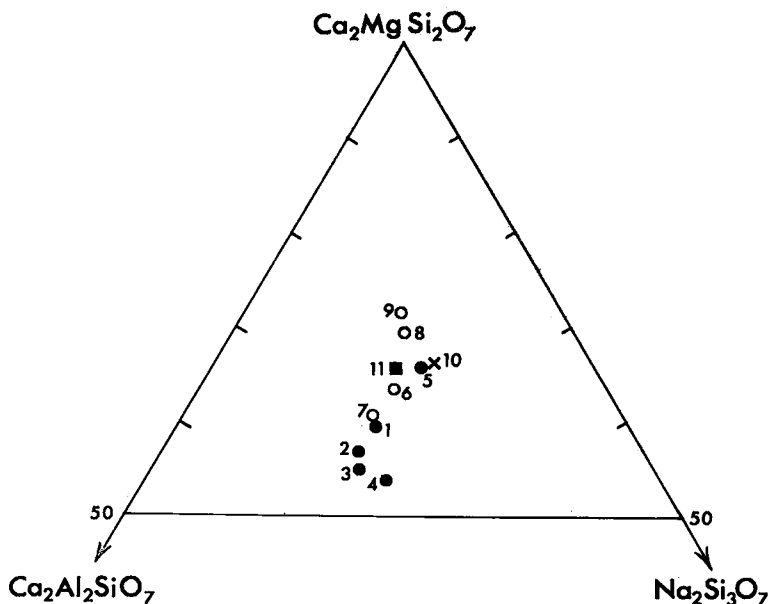


FIG. 1. Compositions of melilites projected onto the join $\text{Ca}_2\text{MgSi}_2\text{O}_7$ — $\text{Ca}_2\text{Al}_2\text{SiO}_7$ — $\text{Na}_2\text{Si}_3\text{O}_7$ (atomic percent). Microprobe analyses, 1-5 this paper; 6-9 from Gold (1969); 10 from Larsen & Hunter (1914).

The analysis of melilite 5 is slightly lower in Na and Al compared to the other carbonatitic melilite and there is a further slight depletion in the rim relative to the core. This melilite has partial to complete rims of garnet plus minor amphibole and mica, which has been interpreted by Watkinson (1970) to be the result of a peritectic reaction of melilite in carbonatite magma analogous to reactions of melilite during cooling in synthetic carbonate-rich liquid. Melilite resorption would enrich the low-temperature magma in Na because garnet and the other crystalline products contain little Na. This may allow crystallization to proceed to lower temperatures and may be important to the process of fenitization if the Na is partitioned strongly into a free vapor phase.

Garnet 1 (Table 4) occurring in the rim around melilite 5 is very similar in composition to euhedral garnet 2 and 3 from carbonatite which is consistent with the hypothesis that garnet 1 formed in a peritectic reaction with magma that later precipitated garnet, rather than formed by hydrothermal alteration of some melilites as suggested by Davidson (1963).

Crystallization of silica-deficient, alkalic magma may produce melilite rocks and if melilite, which has a high Na/K ratio, is fractioned very potassic magmas may be derived. However, melilite readily undergoes peritectic reaction to produce Na-poor minerals and the Na may be returned to the residual magma or associated vapor phase.

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APPENDIX I

Locations of analyzed minerals from the Oka complex and mineral assemblages in approximate order of decreasing abundance.

Melilite 1. Husereau Hill. Jacupirangite containing titanaugite, melilite, hauyne, biotite, perovskite, magnetite, apatite and trace interstitial calcite.

2. Husereau Hill. Fine-grained okaite containing melilite, hauyne, biotite, perovskite, magnetite, apatite.

3. Husereau Hill. Coarse-grained okaite, containing melilite, biotite, hauyne, perovskite, magnetite, apatite and interstitial calcite.

4. Bond Zone. Melilite carbonatite containing calcite, melilite, biotite, perovskite, magnetite, apatite and trace garnet.

5. Bond Zone. Melilite carbonatite containing calcite, melilite, garnet, niocalite, apatite, magnetite, amphibole, trace perovskite and monticellite.

Garnet 1. From specimen with melilite 5.

2. Bond Zone. Garnet carbonatite containing calcite, magnetite, garnet, melilite (and alteration products), biotite, apatite, niocalite, monticellite, perovskite.

3. Bond Zone. Garnet carbonatite containing calcite, garnet, magnetite, biotite, apatite, niocalite, perovskite.

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