ABSTRACT

In three veins from the lower part of Deep Sea Drilling Project Hole 504B, 298 meters below the top of basement, primary augite is replaced by aegirine-augite. This transformation occurs only in subophitic basalts, at the contact with veins which always include a dark-olive, Mg-rich clay mineral.

Talc occurs in one of these veins; it can be regarded either as a vein constituent or as a product of augite alteration. Melanite (Ca,Fe,Ti-rich garnet) appears in only one of these three veins, where a Ca-carbonate is associated with a Mg-rich clay mineral. The occurrence of melanite in Hole 504B could be due to the conjunction of particular conditions: (1) basalt with a subophitic texture, (2) presence of hydrothermal fluids carrying Ca, Fe, Si, Ti, Al, Mg, and Na, (3) rather high temperatures. Possibly the melanite and aegirine-augite formed by deuteric alteration.

INTRODUCTION

The aim of this paper is to describe very unusual secondary parageneses in basalts from the lower part of Hole 504B, drilled on 5.9-m.y.-old crust on the south flank of the Costa Rica Rift. Melanite (Ti-rich andradite) and secondary aegirine-augite were found in veins 298 meters below the top of basement, and deeper, where temperatures rather higher than those which cause classical low-temperature alteration were probably reached (Honnorez et al., this volume).

ANALYTICAL METHODS

In altered basalts, secondary minerals—particularly clay minerals—are sometimes plucked out during thin-section preparation, preventing complete observation with an optical microscope.

Electron-microprobe analyses were carried out at the Centre Oceanologique de Bretagne (Brest, France). During the analyses, the accelerating voltage was kept at 15.0 kV. The electron-beam incidence has a take-off angle of about 42 °, and the limit of detection is about 500 ppm. The precision of the method used is about 1% of the absolute value of the measured concentration.

SAMPLE DESCRIPTION

In oceanic basalts, titanomagnetite is the first magmatic mineral to be altered. Then, olivine and possibly plagioclase are replaced by secondary products, but pyroxene is the magmatic mineral regarded as more resistant to alteration. Usually, pyroxene is completely fresh in basalts altered at low temperatures.

From the lower part of Hole 504B, three samples contain partly altered pyroxene crystals. These rocks are subophitic basalts, and the altered pyroxene crystals are always in direct contact with a secondary-mineral vein.

Each of these samples deserves description, because the vein mineral paragenesis of each is particular.

Sample 504B-40-1, 37–39 cm (depth below sediment/basement interface 298 m)

A 0.2- to 0.5-mm thick vein crosses the basalt. It is mainly composed of a calcium carbonate mineral (Table 1) occurring as anhedral or euhedral crystals, and a dark-olive-green clay mineral without obvious crystal boundaries. I could not determine whether this carbonate is calcite or aragonite or a mixture of both. The clay mineral (Table 2) is MgO-rich (=24%), richer in Al₂O₃ (=9%) and poorer in SiO₂ (=41%) than most of the analyzed smectites from Hole 504B (Honnorez et al., this volume). Because of its particular chemistry, this clay mineral may not be pure smectite, but a regular mixed-layer clay mineral instead. This point will be addressed in a future study.

Almost all of the pyroxene crystals are partly altered all along the vein. Those portions of the pyroxene crystals adjacent to the vein wall are replaced by a bright-

Table 1. Microprobe analyses of Ca-carbonate in the vein of Sample 504B-40-1, 37–39 cm.

<table>
<thead>
<tr>
<th>Component</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
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</tr>
<tr>
<td>Al₂O₃</td>
<td>—</td>
</tr>
<tr>
<td>FeO*</td>
<td>—</td>
</tr>
<tr>
<td>MnO</td>
<td>—</td>
</tr>
<tr>
<td>MgO</td>
<td>—</td>
</tr>
<tr>
<td>CaO</td>
<td>63.80</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.06</td>
</tr>
<tr>
<td>K₂O</td>
<td>—</td>
</tr>
<tr>
<td>TiO₂</td>
<td>64.00</td>
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<tr>
<td>Na₂O</td>
<td>0.06</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.01</td>
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<tr>
<td>TiO₂</td>
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<tr>
<td>Na₂O</td>
<td>0.10</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.79</td>
</tr>
<tr>
<td>Total</td>
<td>64.74</td>
</tr>
</tbody>
</table>

*Total iron as FeO.
green material with weak birefringence (0.009–0.010) and a somewhat granular or fibrous appearance. This green zone generally is thin (<0.005 mm). Numerous tiny, colorless or pale-green needles (maximum length 0.4 mm; maximum width 0.005 mm) have crystallized perpendicularly to the green zone, or all around the pyroxene crystals (Fig. 1).

In order to determine and visualize the chemical differences between fresh and altered pyroxene, both electron-microprobe analyses and X-ray scanning microphotographs were used (Table 3, Fig. 2). Compared to the fresh pyroxene, the green altered zone is richer in Na, Ti, and Fe, and poorer in Al and Mg. (Fig. 3). Ca, Si, and H2O contents have been affected only slightly by Si, and H2O contents have been affected only slightly by this transformation; thus, the green material has the composition of a Ti-rich aegirine-augite.

It was difficult to determine the chemical composition of the colorless needles because of their very small size. Nevertheless, it does not seem to be drastically different from the aegirine-augite replacing magmatic augite in this sample. Because of the relationship between augite, aegirine-augite, and the colorless needles, one can assume that they are also a replacement product of augite.

A confused area occurs in some parts of the vein zone, where one observes small green crystals isolated in a dark-olive clay-mineral matrix. Some of the green crystals are fragments of aegirine-augite, whereas some others, much rarer, are euhedral crystals of unidentified minerals.

The most striking feature of this vein-paragenesis is the presence of a Ti,Ca,Fe-rich garnet, which occurs only in this sample. Four crystals were found in three thin-sections. The garnet crystals often are adjacent to the vein walls; one of them grew partly around a feldspar microphenocryst, the second one is in contact with pyroxene crystals, and the fourth one appears not to be adjacent to the vein wall.

The garnet crystals have hexagonal cross-sections (Figs. 1, 4, and 5) and are 0.2 mm in diameter; they display a dark-brownish-green color without crossed polars, with a very slight apparent zoning. A very particular twin is observed (Fig. 6), which is similar to what Lacroix (1892) called the “pyreneitic” twin type.

Chemical analyses (Table 4) indicate that the garnet belongs to the andradite group. Its high TiO2 content (0.71–6.42%) is characteristic of melanite (1–5% TiO2) or shorlomite (TiO2 > 5%) (Deer et al., 1963). The TiO2 content varies within the same crystal; this important point appears clearly on X-ray pictures showing zoning of Ti and Al. In Figures 5 and 7, one can observe in a melanite crystal the concentric disposition of thin Ti-rich and Al-poor layers, parallel to the crystal edges; Mg, Si, Ca, and Fe do not contribute to the zoning. Thus, the variations of the chemical composition of the solution during the crystallization of melanite are probably responsible for this zoning. In any case, Ti and Al seem to have been “mobile” during garnet formation. It is clear in Ti and Al distribution pictures that the growth of this crystal was disturbed by a Mg-rich and Al-poor mineral, which could not be identified (Fig. 5).

Sample 504B-52-3, 103–107 cm (depth 395 m)

The studied vein (width <1 mm) is made up of a dark-olive-green clay mineral, and much more rarely by a slightly flexible, colorless, highly birefringent mineral. The clay mineral could not be analyzed because it was poorly polished. The colorless mineral is talc (Table 2), which either contains small amounts of iron or is mixed with a Fe-rich smectite. No carbonate was observed.
Rare colorless needles occur, the chemistry of which is similar to that of talc (Table 2). As in Sample 504B-40-1, 37-39 cm, the edges of the pyroxene crystals which are in contact with the vein are altered to aegirine-augite (Table 3), which is more Na- and Fe-rich than fresh magmatic augite. There appears to be no significant variation of Ti content in these minerals, unlike the Core 40 sample previously described. All along this vein, a very particular sequence is observed (Fig. 8): from a fresh pyroxene to the center of the vein, one can successively observe (1) a somewhat fibrous aegirine-augite and tiny patches of a granular, orange, probably Fe-rich material; (2) talc, as a thin (0.02 mm) layer; (3) a dark-olive clay mineral. Moreover, some of the aegirine-augites have
a granular appearance; an analyzed granular aegirine-augite is even more Fe-rich (up to 20.7%) and MgO-poor (6.1%) than fibrous aegirine-augite (Table 3, analysis 13).

The element distribution is shown by X-ray scanning in microphotographs (Fig. 9). Notice that the dark-olive clay mineral is Mg-rich, whereas the Mg- rich smectite that we usually found in Hole 504B (Honnorez et al., this volume) is colorless or very pale green. This suggests that the dark-olive clay mineral is not pure smectite, but possibly a mixed-layer clay mineral or a mixture of clay minerals.

Talc occurs only in this sample. Because of its location in the vein salband, it can be regarded either as a vein constituent or as a product of augite alteration. Fibrous talc associated with the dark-olive clay mineral clearly is a vein component. The role of the thin talc layer located close to aegirine-augite is more uncertain; in Figure 10, the average chemical compositions of unaltered aegirine-augite, secondary aegirine-augite, and talc from this sample are compared. Unaltered aegirine has a composition intermediate with respect to NaO, FeO*, and MgO. Thus, it seems that, when aegirine is altered, Fe, and Na are concentrated in aegirine-augite, and Mg in talc. A hypothetical reaction is suggested:

\[\text{augite} + \text{SiO}_2 + H_2O (+ N\text{a}_2O) \rightarrow \text{aegirine-augite} + \text{talc} + \text{CaO} (+ \text{Al}_2O_3)\]

One may assume that, during this reaction, part of the Mg necessary to form talc comes from the alteration of augite, but that another part may come from another source, which is also responsible for talc and the Mg-rich, dark-olive clay mineral of the vein.

### Sample 504B-58-1, 9–13 cm (depth 445 m)

The vein crossing this sample is composed of a dark-olive-green clay mineral (white to orange between crossed polars), and pyrite. The clay mineral is MgO-rich (20%) and Al\(_2\)O\(_3\)-rich (6.5%) (Table 2). It probably is not pure smectite, but a mixed-layer clay mineral or a mixture of clay minerals. This important point will be determined by X-ray diffraction in a future study.

Most of the pyroxene crystals are fresh, even near the vein. Only a few crystals show an aegirine-augite layer (Table 3), similar to those described above.

Table 5 summarizes the modes of occurrence of aegirine-augite in Hole 504B.

### DISCUSSION ON THE OCCURRENCE OF AEGIRINE-AUGITE, MELANITE, AND TALC

#### Aegirine-Augite

Fortey et al. (1978) mentioned the occurrence of aegirine-augite of possible authigenic origin in Devonian sediments of Scotland. The aegirine-augite composition is remarkably pure and very close to that of a unique occurrence of authigenic aegirine in the lacustrine Green River Formation of Wyoming, U.S.A. (Milton et al., 1960; Hay, 1966); these authors suggest that the aegirine-augite "formed in hypersaline conditions in which sodium may have been derived from contemporaneous alkaline volcanism within the Orcadian basin". However, the compositions of both this authigenic aegirine-augite and that of igneous or metamorphic origin are different (Table 6). On the other hand, the Hole 504B aegirine-augite composition is very similar to that of some of the igneous and metamorphic aegirine-augite.
The formation of aegirine-augite from augite adjacent to natrolite veins in analcite-olivine dolerite has been described by Suzuki (1938).

I suggest that several conditions favored formation of secondary aegirine-augite from magmatic augite of Hole 504B basalts:

1) The veins are found in subophitic basalts. This texture may allow a stability of chemical conditions in the veins for a long time, hence the transformation of augite.
2) The presence of a dark-olive, Mg-rich clay mineral in the veins suggests very local chemical and thermical conditions.
Figure 3. $\text{Na}_2\text{O}-\text{MgO}-\text{FeO}^*$ diagram showing chemical variations resulting from alteration of primary augite to secondary aegirine-augite in Hole 504B. The lines link unaltered and altered augite of the same pyroxene phenocryst.

![Figure 3](image.jpg)

3) Higher temperatures occurred than those prevailing during low-temperature alteration, because aegirine-augite was observed only in the lowest part of the Hole 504B (and below 298 m), where measured temperatures range from 59 to 125°C (Becker et al., this volume).

The small number of samples from Hole 504B where aegirine-augite occurs does not allow me to conclude much more about the conditions of formation of this mineral.

**Melanite**

According to Deer et al. (1963), melanite and shorlomite occur either in alkaline igneous rocks such as nepheline syenite, ijolite, phonolite, and nephelinite, or in skarns.

A chemical analogy exists between the mineral parageneses associated with melanite in Hole 504B and in skarns. Various elements were necessary to form melanite in the vein of Sample 504B-40-1, 37-39 cm:

1) Ca, Fe, and Si are also responsible for Ca-carbonate and dark-olive-clay-mineral formation in the vein. Recall that primary minerals in the host basalt are less altered than those of adjacent samples from similar depths; plagioclase is fresh and olivine is only partly replaced by smectite and carbonates (Honnorez et al., this volume). Thus, I think that these elements mainly come from circulating hydrothermal fluids, not from the alteration of the nearby magmatic minerals.

2) Ti also may come from hydrothermal fluids, because aegirine-augite is richer in Ti than unaltered augite, and because the Ti content of the other primary transparent minerals (olivine, plagioclase) is not affected by alteration.

Thus, it seems that the metasomatic hydrothermal addition of Ca, Si, Fe, and Ti allowed the formation of melanite.

Hydrogarnets thought to be hydrothermal in origin have been found in sediments at DSDP Site 251 (Kempe et al., 1974; Cook et al., 1974), but no garnet has been found in the basaltic basement cores until now.

In their extensive review of low temperature metasomatic garnets in marine sediments, Easton et al. (1977)
Figure 5. Scanning electron photomicrograph of a melanite crystal in Sample 504B-40-1, 37-39 cm. Same crystal as in Figure 4. The Al, Si-rich area is a plagioclase lath. In melanite, Si, Mg, Ca, and Fe contents are constant, whereas Al and Ti contents vary in compositional zones. Si- and Mg-rich, colorless needles can be seen in melanite. Two edges of the crystal occur in the upper left and right corners.

ruled out the possibility that hydrogrossular found in chalk overlying the basement at DSDP Site 251 had an "origin by baking or low-grade contact metamorphism", because (1) "the basalt is basement and not an intrusive sill"; (2) "if the growth of such garnets was caused by thermal metamorphism, their occurrence would be widespread". They propose an origin by primary precipitation from circulating sea water hydrothermal solutions, at about 170°C.

However, the garnets from Site 251 are very different from those from Hole 504B; they are hydrogarnets without Ti.
The emplacement of the subophitic basalt, circulating fluids carry large amounts of Si, Ca, Fe, Mg, Ti, Al, and Na along cracks. Because of the relative “impermeability” of the basalt texture, these hot fluids do not diffuse very much in the basalt, but move along the crack, where they cool probably slowly, allowing the formation of:

1) Large euhedral and anhedral Ca-carbonate crystals (Ca);
2) dark-olive, Mg-rich clay minerals (Mg, Si, Al);
3) aegirine-augite (Fe, Na, (Ti)); and
4) melanite crystals (Fe, Ca, Si, Ti, Al).

Deer et al. (1963) mention the possibility that andradite forms from aegirine according to the reaction:

$$2\text{NaFeSi}_2\text{O}_6 + 3\text{CaO} \rightarrow \text{aegirine}$$

$$\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12} + \text{Na}_2\text{O} + \text{SiO}_2$$

andradite

Although two crystals of melanite from Hole 504B grew against aegirine-augite, I cannot affirm that melanite crystallized from aegirine-augite.

As described earlier, the garnet is zoned: Ti and Al are in concentric layers parallel to the crystal edges. This means that Ti and Al were “mobile” during the formation of melanite, but Ti has been considered immobile in alteration (Cann, 1970; Pearce and Cann, 1973; Pearce et al., 1975). This could mean that melanite did not form under alteration conditions, but possibly at higher temperatures, in contrast to hydrogarnets from Site 251.

It should be noted that such occurrences of andradite-type garnets have been described in ophiolitic pillow lavas. Juteau (1970) mentioned the presence of andradite in spilitic breccias from the submarine volcanic complex of Sayrun (Turkey). In this case, two conditions were necessary for andradite to form: a volcanic rock rich in calcite and iron oxides, and an important thermal metamorphism. The following reaction was proposed:

$$3\text{CaCO}_3 + 2\text{Fe}_2\text{O}_3 + 3\text{SiO}_2 \rightarrow \text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12} + 3\text{CO}_2$$

calcite

andradite

The circulation of hot fluids explains the formation of andradite (gain of SiO₂, and probably H₂O, O₂, etc., and loss of CO₂; Even et al., 1973).

Blanco-Sanchez (1978) thinks that this andradite, which is associated with analcile or hematite and calcite, could have formed in the zeolite facies or prehnite–pumpellyte facies; it occurs in veins and amygdales. The temperature of its formation probably did not exceed 400°C.

Thus, the mode of occurrence of andradite and melanite in Hole 504B seems not to differ very much from those described in ophiolitic pillow lavas.

According to Coombs et al. (1977), the temperature of formation of andradite found in metasediments (zeolite facies) from New Zealand is at least 300 to 400°C.

Experimental studies (Huckenholz and Hölz, 1977; Taylor and Liou, 1976) on the stability of andradite...
have shown the importance of oxygen fugacity to its formation.
Thus, one can ascribe the very unusual occurrence of melanite in Hole 504B to the conjunction of the following particular conditions:
1) Subophitic texture, allowing a long interaction between hydrothermal fluids and basalts;
2) The presence of hydrothermal fluids very rich in Ca, Fe, Si, Ti, Al, Mg, and Na;
3) Rather high temperatures.

Talc
Because of the distribution of talc in Hole 504B, and its very unusual location, one may assume that particu-
lar chemical and thermodynamic conditions were necessary for talc to crystallize (an environment very rich in Mg and Si, and probably temperatures higher than in the upper part of Hole 504B; Honnorez et al., this volume).

Although melanite and aegirine-augite from Hole 504B seem to have an hydrothermal origin, one must not rule out the possibility that these minerals formed by deuteric alteration. At the end of the crystallization of the basalt, late-stage magmatic solutions and volatile fluids are able to move along cracks and to alter magmatic minerals. The location of the aegirine-augite and melanite at the vein salband supports this hypothesis.

SUMMARY AND CONCLUSIONS

In three veins from the lower part of Hole 504B, below 298 meters sub-basement depth, primary augite is replaced by aegirine-augite with an increase of Na and Fe. This transformation occurs only at the contact with a vein, which is always composed of a dark-olive Mg-rich clay mineral.

Melanite (Ca,Fe,Ti-rich garnet) appears in a single sample where Ca-carbonate is associated with a Mg-rich clay mineral in the vein. Melanite formation seems to be due to hydrothermal fluids bringing Ca, Fe, Ti, Si, Mg, Al, and Na.

A future systematic study of the materials composing all the veins of the lower part of Hole 504B should allow determination of the frequency, distribution, and formation conditions of these unusual secondary minerals.

ACKNOWLEDGMENTS

I would like to thank M. Bohn for his help during the electron microprobe analyses; T. Juteau and C. Mevel for reviewing the manuscript; and J. Honnorez for offering critical comments.

NOTE ADDED IN PROOF

Since I submitted this paper (May 1981) I have found two more veins that contain aegirine-augite in subophitic basalts. Fassaita occurs in one of them. These occurrences and X-ray data for the veins will be discussed and published at a later date.

REFERENCES


Figure 9. Scanning electron photomicrograph of the wall of a vein of Mg-rich clay mineral, with primary augite replaced by aegirine-augite and talc.
Table 5. Mode of occurrence of aegirine-augite in veins in Hole 504B altered basalts.

<table>
<thead>
<tr>
<th>Sample (interval in cm)</th>
<th>Depth within Basement (m)</th>
<th>Mineral Paragenesis in the Veins</th>
</tr>
</thead>
<tbody>
<tr>
<td>504B-40-1, 37-39</td>
<td>298</td>
<td>Ca-carbonate, dark-olive Mg-rich clay mineral, melanite, colorless needles with composition close to aegirine-augite</td>
</tr>
<tr>
<td>504B-52-3, 103-107</td>
<td>395</td>
<td>Talc, dark-olive Mg-rich clay mineral, colorless needles with composition close to talc</td>
</tr>
<tr>
<td>504B-58-1, 9-13</td>
<td>445</td>
<td>Dark-olive Mg-rich clay mineral, pyrite</td>
</tr>
</tbody>
</table>

Table 6. Comparison of microprobe analyses of aegirine-augite.

<table>
<thead>
<tr>
<th>Component</th>
<th>Analyses</th>
</tr>
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<tbody>
<tr>
<td>SiO₂</td>
<td>52.31</td>
</tr>
<tr>
<td>TiO₂</td>
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</tr>
<tr>
<td>Al₂O₃</td>
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<tr>
<td>Fe₂O₃</td>
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<td>MnO</td>
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</tr>
<tr>
<td>F</td>
<td>n.d.</td>
</tr>
<tr>
<td>Total</td>
<td>100.69</td>
</tr>
</tbody>
</table>

Notes: Aegirine and aegirine-augite from (1) Devonian lacustrine beds of Caithness (Fortey et al., 1978); (2) the Assynt Complex (Sabine, 1950); (3) the Ben Loyal Complex (King, 1942); (4) Clen Lui (Mac-Lachlan, 1951); (5) Narsaassuk (Boggild, 1953); (6) Hole 504B; tr. = trace; n.d. = not determined.