Mg-rich staurolite from the Iratsu epidote amphibolite body, central Shikoku

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Mg-rich staurolites are found in corundum-bearing rocks from the Iratsu epidote amphibolite body in the highest grade metamorphic area of the Sanbagawa metamorphic belt. The staurolites have high Mg/(Mg+Fe) ratios up to 0.6, and are mostly represented by a chemical formula, (Mg+Fe)_{3-1.5}Al_{18-X}Si_{8}O_{46}, calculated as Li_{2}O- and H_{2}O-free. It was formed with garnet, zoisite and amphibole at the highest metamorphic conditions of the Sanbagawa metamorphism, and subsequently replaced by an aggregate consisting of chlorite, paragonite and margarite during a retrograde metamorphism represented by a pressure decrease. Although Fe-rich staurolite has been treated as a typical mineral in the intermediate-pressure metamorphic belt, Mg-rich staurolite is present in the high-pressure metamorphic belt.

Introduction

Staurolite occurs commonly in medium-grade metamorphic pelites and is used as a key mineral in metamorphic zonation. It is treated as a Fe-rich mineral as well as garnet, and its Mg/(Mg+Fe) ratio is up to 0.35. Such Fe-rich staurolite was a typical mineral in the intermediate pressure-type metamorphism. Ward (1984) and Schreyer et al. (1984) found Mg-rich staurolite in a metatroctolite from Fiordland, New Zealand, and in a sapphire-garnet rock from Limpopo belt, Southern Africa, respectively. Ward (1984) used the term "Magnesium staurolite" to denote the staurolite with magnesium cations in excess of all others except aluminum and silicon. However, terminology and endmember of staurolite have not been established yet because of its complex crystal chemistry (Holdaway et al., 1986a).

This paper reports an occurrence of Mg-rich staurolite from the Iratsu epidote amphibolite body in the Sanbagawa metamorphic belt which is one of atypical high-pressure metamorphic belts (Miyashiro, 1973).

Petrography and mineral composition

Staurolite was found in corundum-bearing rocks from the Iratsu epidote amphibolite body in the Sanbagawa metamorphic belt (Fig. 1). Corundum is also a rare mineral in the belt and has been found only from the body to date. The staurolite occurs mainly around corundum in spinel granulite and corundum-bearing epidote amphibolite. As the samples were already described by Yokoyama (1980) and Minakawa and Momoi (1982), petrographical features around the staurolite are described
In addition to the samples mentioned above, staurolite is found as an inclusion of garnet in corundum-free epidote amphibolite from the Iratsu body.

The spinel granulite was composed of aluminous pyroxenes, plagioclase and spinel, prior to the Sanbagawa metamorphism. Most of the plagioclases were decomposed into zoisite, quartz and kyanite. Garnet and amphibole occur commonly along the grain boundaries among the mafic minerals. Corundum occurs around spinel. The staurolite is colorless and is up to 0.2 mm in width, mostly associated with corundum (Fig. 2A). It is sometimes included by garnet and amphibole. Staurolite-corundum aggregate is rarely surrounded by kyanite (Fig. 2B). The staurolite is partly replaced by a fine-grained aggregate consisting mainly of chlorite. Yokoyama and Mori (1975) and Yokoyama (1980) concluded that garnet, amphibole, corundum and zoisite were formed at the highest metamorphic grade of the Sanbagawa metamorphism. Hence it is interpreted that the staurolite was also formed at the same conditions as the major minerals in the Iratsu epidote amphibolite.

Corundum-bearing epidote amphibolite, described by Minakawa and Momoi (1982), is a boulder in the Hodono valley (Fig. 1). It is composed of zoisite-rich and amphibole-rich layers, characteristic in the Iratsu epidote amphibolite. Outcrop of the corundum-bearing epidote amphibolite has not been confirmed yet. It is probable that the rock occurred as an inclusion of the Higashi-akaishi peridotite body. As epidote amphibolites with a banded
structure in the peridotite body are consanguineous with those in the Iratsu body (Banno and Yokoyama, 1977), it is tentatively inferred that it was derived from the Iratsu epidote amphibolite body. The specimen has a similar mineral assemblage to the secondary one of the spinel granulite mentioned above and is composed mainly of coarse-grained garnet, amphibole, zoisite and corundum. The latter two minerals sometimes exceed 5 cm in diameter (Minakawa and Momoi, 1982). The staurolite is mostly associated with corundum (Fig. 2C). It occurs rarely within a corundum-free and zoisite-rich layer (Fig. 2D). The crystal of staurolite is colorless in thin section with a width up to 0.3 mm, apparently in equilibrium with the other major minerals. The staurolite and corundum are partly replaced by fine-grained aggregates of chlorite, margarite and paragonite, whereas garnet and hornblende are rarely replaced by chlorite-zoisite and chlorite-albite, respectively.

Chemical compositions of minerals

All the constituent minerals have been analysed by energy dispersive spectrometer (EDS) in National Science Museum. Accelerating voltage and Faraday cup current are 15kV and $1.4 \times 10^{-9}$ A, respectively. Natural and synthetic materials are used as standards. Corrections were made by ZAF method of Statham (1979). Precision and detection limits of the analyses with the EDS and the ZAF method are similar to those obtained by Dunham and Wilkinson (1978, 1980). Analyses of major elements are checked by the other EDS in Kyoto University and trace elements by the wavelength dispersive spectrometer (WDS) in Waseda University.

As chemical compositions of the constituent minerals can be referred to the original paper describing the samples, only analyses of representative staurolites and their surrounding minerals are listed in Table 1. H$_2$O and Li$_2$O are important constituents of the staurolite (Holdaway et al., 1986b). Although no attempt was made to analyse the elements because of the paucity of material. H$_2$O contents of the staurolites will be less than 1.8 wt% as it co-exists with garnet (Holdaway et al., 1986b). Li$_2$O will be less than 0.2 wt% as do most of the staurolites. ZnO content is mostly within the detection limit (0.2 wt%) of the EDS. High ZnO content (1.7 wt%) is found in a Fe-rich staurolite highly replaced by chlorite, margarite and paragonite (Table 1b, st-4).

Staurolites in the spinel granulite have narrow range of Mg/(Mg+Fe) ratio ($X_{Mg}$), whereas those in the epidote amphibolite have variable $X_{Mg}$ ratio. Staurolite with low $X_{Mg}$ is found in contact with or within an aggregate of chlorite-paragonite-margarite. Coarse-grained staurolites and inclusions in corundum have quite high $X_{Mg}$ (more than 0.45), compared with those reported from the pelites from the intermediate pressure-type metamorphic rocks. The $X_{Mg}$ values (Fig. 3) are up to 0.60, slightly higher than magnesium staurolite so far reported (Ward, 1984). The staurolites in the spinel granulite are different in Si, Al and (Mg+Fe) contents from those in the epidote amphibolite. The former is rich in Si and Al and the latter in (Mg+Fe).

Because of complexity of structural formula and nonstoichiometric nature, staurolites without analyses of H$_2$O and Li$_2$O are plotted in a diagram (Fig. 4) showing correlation between Fe+Mg+Zn and Si+Ti+Al−8 (Al', octahedral Al) on the basis of O=46 (Griffin et al., 1982; Ward, 1984). In spite of variable range of Si, Al and (Mg+Fe), all the data are plotted almost linearly in Fig. 4A. As suggested for the magnesium staurolite in New Zealand by Ward (1984), it seems likely that slope of the line shows a substitution of 3 (Fe+Mg+Zn) = 2(Al').
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Table la. Chemical compositions of representative minerals

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<th>sample</th>
<th>spinel granulite</th>
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<tr>
<td>CaO</td>
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<td>7.910</td>
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O= 46 46 12 46 12 25 46 12

Si 7.852 7.958 2.994 7.910 3.016 6.043 7.927 2.999
Ti 0.028
Al 17.271 17.069 2.026 17.108 1.960 5.859 17.177 1.984
Cr 0.381 0.013
Fe 1.870 0.956
Mn 0.043 0.019 0.024 0.024
Mg 2.927 2.394 0.903 2.331 1.157 1.733 1.313
Ca 0.640 0.542 3.976 0.714
Total 29.512 29.507 7.993 29.537 8.005 15.977 29.264 8.003

X*= 0.52 0.53 0.39 0.52 0.47 0.48 0.58

Mineral abbrev. st; staurolite, gt; garnet, zoi; zoisite, co; corundum am; amphibole
*Fe as FeO, **Fe as Fe2O3, #; ZnO=0.74 Zn=0.148

Table lb. Chemical compositions of representative minerals

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<td>Total</td>
<td>98.14</td>
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O= 46 46 12 46 12 46 25 3 23

Ti 0.023 0.028 0.022 0.042 0.019
Al 17.620 17.787 1.985 17.650 1.994 17.862 5.669 1.996 2.920
Cr 0.012 0.063
Fe 1.365 1.526 0.965 1.734 0.957 2.026 0.247 0.004 0.557
Mn 0.021 0.018 0.057
Mg 2.131 1.695 1.514 1.622 1.308 0.562 3.282
Ca 0.603 0.756 4.055 1.798
Total 29.157 29.057 8.048 29.101 8.017 23.976 16.004 2.000 15.892##

X*= 0.61 0.53 0.61 0.48 0.58 0.22 0.85

* Fe as FeO, **Fe as Fe2O3, #; ZnO=1.74 Zn=0.349, ##; Na2O=3.68 Na=1.004, K2O=0.67 K=0.120
Fig. 3. Histogram of $100 \times \text{Mg}/(\text{Mg}+\text{Fe})$ ratio in staurolite. Vertical axis is a number of analysis.

Fig. 4. $(\text{Mg}+\text{Fe}+\text{Mn}+\text{Zn})$ atoms versus $(\text{Si}+\text{Al}+\text{Ti}-8)$ atoms for staurolite. (A), staurolites from the Iratsu epidote amphibolite body; (B), staurolites from the other localities. All the data are calculated as $O=46$ and $H_2O$-and Li$_2$O-free. Line (a), $(\text{Mg}+\text{Fe})_{2+1.5}\text{Al}_{18-x}\text{Si}_8\text{O}_{48}$; Line (b), $(\text{Mg}+\text{Fe})_{x+1.8}\text{Al}_{16-x}\text{Si}_8\text{O}_{48}$. Slopes of the lines show a substitution of $2\text{Al}=3(\text{Mg}+\text{Fe})$. Line (a) to (b) is of $\text{Si}(\text{Mg}+\text{Fe})=2\text{Al}$. 

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Garnet has a wide compositional range especially in CaO content in the spinel granulite (Yokoyama and Mori, 1975). However, garnets in the epidote amphibolite and around staurolite in the spinel granulite have a small range in CaO content; 7.5-9.0 wt% in the former and 6-8 wt% in the latter. In spite of the similarity of X_{Mg} of staurolite in two samples, X_{Mg} values in garnets are different. As shown in Fig. 5 presenting a relation of Mg/(Mg+Fe) ratio between garnet and staurolite directly surrounding it, garnet in the spinel granulite is more Fe-rich than coexisting staurolite, whereas vice versa in the epidote amphibolite. Epidote group minerals are usually zoisite with pistacite molecule less than 4% in both the samples. Amphibole is pargasite. Mica group minerals and chlorite, replacing aluminous minerals such as corundum, staurolite and garnet, are not properly analysed due to their fine-grained or aggregate nature. Albite, replacing amphibole, is usually pure albite with anorthite content less than 1%. It does not occur around corundum and staurolite.

**Discussion**

Although metamorphic minerals in the Sanbagawa belt have been studied in detail, staurolite has not been found in the belt (Banno, 1964; Higashino, 1975 and others). In both the corundum-bearing rocks described above, staurolites were equilibrated with zoisite, garnet and amphibole which were formed at the highest metamorphic conditions of the Sanbagawa metamorphism. The local occurrence mostly around corundum suggests that the lack of natural staurolite was due to the absence of very aluminous bulk compositions in the Sanbagawa metamorphic belt, as suggested for the other Mg-rich staurolites by Schreyer et al. (1984) and Ward (1984).

Stability field of staurolite and its-bearing assemblages have been studied by many workers. Most of them are determined at the
conditions of presence or absence of quartz, biotite and muscovite. They are not applicable to the staurolite-bearing rocks in the Iratsu epidote amphibolite body. Fe-staurolite, in Fe-Si-Al-O-H system, has a wide stability field even down to 1 kb (Richardson, 1968), whereas Mg-staurolite itself is stable more than approx. 10 kb at 700°C (Schreyer and Seifelt, 1969). Mg-rich staurolite similar in composition to those reported here can be formed at about 25 kb and 700°C from quartz tholeiite compositions as a starting material (Hellman and Green, 1979). Metamorphic conditions of Mg-rich staurolites from New Zealand and South Africa are 7 kb at 800°C and 12 kb at 700°C, respectively (Ward, 1984; Schreyer et al., 1984). The experiments and estimated conditions suggest that magnesium staurolite prefers high pressure conditions.

No experimental data is constrained for the staurolite-bearing assemblage in the Iratsu epidote amphibolite body. As the staurolites were formed under the same conditions as the surrounding rocks in the body, the metamorphic conditions for the magnesium staurolites are 500–600°C and 10–15 kb, estimated from the other metamorphic assemblages in the body (Yokoyama, 1980). Aggregate of chlorite, paragonite and margarite, replacing staurolite and corundum, may be formed during the retrograde stage of the Sanbagawa metamorphism. The retrograde stage will be due to uplift of the body (Brothers and Yokoyama, 1982; Kunugiza et al., 1986). Hence it will be reasonable that the Fe-rich staurolite (Table 1b, st-4) in the aggregate was formed or re-equilibrated at the lower pressure conditions than those mentioned above.

Fe-staurolite has been treated as a typical mineral in the intermediate-type metamorphism and has not been reported from the high-pressure metamorphic belt. Although occurrences of all the Mg-rich staurolites reported are restricted in silica-depleted and aluminous rocks, staurolite is present even in the high-pressure metamorphic belt.

Chemical formula for staurolite has been proposed by many authors (Naray-Szabo and Sasvari, 1958; Smith, 1968; Griffin et al., 1982), but it is still quite enigmatic and their end-members and site preferences have not been confirmed yet, even in staurolite with precise analyses of Li₂O and H₂O (Holdaway et al., 1986a). Proposed chemical formulas for staurolite are written as follows; H₂Fe₄Al₄Si₈O₄₈ (Naray-Szabo and Sasvari, 1958), (Fe, Mg, Zn)₂₅.₅₋₁₂.₂₅xAl₁₋₅₂Si₁₈₂₋ₐ₋₅₂O₄₆H₄ (Griffin et al., 1982) where x is the number of octahedral Al atoms. H₂₅Fe₆(Al₁₇.₄₆Fe₀.₂₅)Fe₀.₂₅(Si₇.₆₅Al₀.₃₅)O₄₆, for Fe-dominant staurolite (Holdaway et al., 1986a) and H₄₆Fe₃(Al₁₇.₄₆Fe₀.₂₅)Fe₀.₂₅(Si₇.₆₅Al₀.₃₅)O₄₈ for H-dominant staurolite (Holdaway et al., 1986a).

Staurolites in corundum-bearing epidote amphibolite (Fig. 4A) give rather a simple formula, (Mg, Fe)₃₊₁.₅ₓAl₁₋ₓSi₈O₄₆ on the basis of O=46 and H₂O-free, different in chemical formula from the proposed ones. In spite of their data plotted along a line (a) in Fig. 4A, the formulas for natural staurolites are not summarised simply so far.

Griffin et al. (1982) found correlation between (Mg+Fe) and octahedral Al. Ward (1984) suggested that the substitution of 2Al (octahedral site) by 3(Mg+Fe) occurs in the magnesium staurolite. Fairly linear relation shown in Fig. 4A and B supports an adequate correlation between octahedral Al and (Mg+Fe). However, such a plotting can not be simply treated. When oxygen number is fixed as 46 and tetrahedral sites for Si are partly filled by Al, their data can not be always plotted linearly but depending on an amount of tetrahedral Al as well as other elements such as Ti and Zn. Ward (1984) suggested the substitution from a line with high regression (r=0.99).
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It is simply due to that his data used have only faint variation of tetrahedral Al from 0.46-0.47, compared with 0.0 to 1.0 for natural staurolites. Shift of the line by tetrahedral Al is explained by a substitution of Si(Mg+Fe)=2Al (Fig. 4) and is shown graphically in Fig. 4B.

In the staurolites except those in the spinel granulite, tetrahedral Al is negligible, resulting that the line for those staurolites (Fig. 4A) is represented by a tentative formula; \( (\text{Mg} + \text{Fe})_{2+3.75} \text{Al}_{1.8-x} \text{Si}_x \text{O}_{4.5} \). On the other hand staurolites in the spinel granulite are plotted slightly away from the line, due to presence of tetrahedral Al around 0.1. Although it will be reasonable that the 2Al=3(Mg+Fe) is the most prominent substitution in the staurolite and Si(Mg+Fe)=2Al is the subordinate one, overall structural formula for the staurolite, where Li$_2$O and H$_2$O are essential and important, can not be confirmed.

Fig. 5 shows data on the elemental partitioning of Mg and Fe between Mg-rich staurolite and garnet. Perchuk (1969) proposed a thermometer for the pairs from metamorphic pelites. Such partitioning can not be used as a thermometer, because site occupancies of Mg and Fe are quite uncertain in the staurolite. Futhermore, Smith (1968) and Holdaway et al. (1986a) suggested that there are many sites for Mg and Fe and each of them prefers different sites. Staurolites in two samples from the Iratsu body have similar Mg/(Mg+Fe) ratios around 0.5 but are different in amounts of octahedral and tetrahedral Al. Preference of Fe between staurolite and garnet is clearly different in two samples (Fig. 5). If Mg substitutes octahedral Al site as suggested by Smith (1968), discrepancy of the partitioning is enlarged in two samples. Ferric ion will be a possible candidate to explain the discrepancy, but an amount of ferric ion will be negligible because coexisting phase is zoisite and presence of ferric ion disturbs the correlation in Fig. 4.

As partitioning of Mg and Fe at one site should be the same or similar in two samples, staurolite may have sites for Fe, more preferable than those for Mg.

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四国，五良津緑簾石角閃岩体中の十字石
横山 一己・後藤 隆
マグネシウムに富んだ十字石が三波川帯の最高温度で変成された五良津緑簾石角閃岩体中から発見された。この十字石は今までに報告された十字石よりマグネシウムに富み、Mg/(Mg+Fe) 比が 0.6 に達し、Li2O と H2O が少ないとして計算すればほとんどが (Mg+Fe)3+x Al2-x Si5O16 の構造式で表わされる。十字石は緑簾石や角閃石と同じ条件で形成され、圧力低下時に緑泥石等により一部置換された。十字石は中圧型変成帯中に典型的な鉱物であるが、三波川帯のような高圧型変成帯からははじめてである。
Iratsu, 五良津; Hodono, 保土野; Higashi-akaishi, 東赤石。