Local replacement of calcite by Fe–Mg carbonates in the albite–biotite zone in Sanbagawa basic schists

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During retrograde metamorphism of carbonate-rich basic schists from the Asemi-gawa area, a part of host calcite formed near the peak of metamorphism has been locally replaced by Fe–Mg containing two different types of carbonate inclusions. One type is Fe-dolomite ($\text{FeCO}_3=8.8$ mol.%) accompanied by $\text{Ca}_2(\text{FeCO}_3=1.5\%$, $\text{MgCO}_3=2.7\%$) in the inner part of the replacement. The other one, Mg-ankerite ($\text{FeCO}_3=16.6\%$) is accompanied by $\text{Ca}_3(\text{FeCO}_3=3.2\%$, $\text{MgCO}_3=7\%$) and $\text{Ca}_4(\text{FeCO}_3=3.2\%$, $\text{MgCO}_3=0.6\%$) in the outer part such of the replacement. An origin of carbonates can be explained by the reactions between a fluid phase containing Mg^{2+} and Fe^{2+} and a host calcite₁ during retrograde metamorphism.

Keywords: Calcite, Replacement, Ankerite, Retrograde, Metamorphism, Fluid phase

I. Introduction

Enami and Higashino (1988) have described dolomite from Sanbagawa schists in pelitic and basic schists of the albite–biotite and oligoclase–biotite zones. It occurs in two modes: (1) as independent and coarse crystals (0.1–0.2 mm); and (2) as rounded and small crystals (0.01–0.1 mm) dispersed among the coarse calcite crystals. The independent crystals of dolomite are always replaced by secondary calcite and are included in garnet porphyroblasts. Hence they are prograde minerals. According to these authors, the coexisting independent crystals of dolomite and calcite show temperatures of about 540°–570°C and 580°–620°C in the albite–biotite and oligoclase–biotite zone, respectively.

During petrological work on basic schists of the Asemi-gawa area, it was found that a part of the host coarse-grained calcite has been

locally replaced by Fe–Mg calcite with two different types of inclusions in it. One is Fe-dolomite and the other, Mg-ankerite (Figs. 1a, 1b, 3, 4). In the following, we will describe their modes of occurrence and discuss their genesis.

Fig. 1a. The host calcite (Cal_1) replaced by younger carbonates (mixtures of calcite_{2,3,4} with a Fe-dolomite and Mg-ankerite). Sample RB-3, plane-polarised light.

Fig. 1b. The replaced part by younger carbonates. The inner part is formed by Cal_2 with Fe-dolomite inclusions and is older than the outer part, which is formed by Cal_3 and Cal_4 with Mg-ankerite inclusions.

II. Sample, locality, petrography and mineral chemistry

The Sanbagawa metamorphic belt of central Shikoku, has been divided into four zones, namely chlorite, garnet, albite-biotite and oligoclase-biotite zone (Enami, 1983; Higashino, 1990). In the Asemi-gawa area, 120-m north from the Kuwano-kawa bridge on the right bank of the Asemi-gawa river, two basic schists RB-3a and RB-3b were collected from the albite-biotite zone. A Hitachi microprobe equipped with a Kevex analytical system, Kevex using 8,000+Quantum detector was used throughout, following the method described by Mori and Kanehira (1984), and Hirajima and Banno (1991). To the analysis of carbonate data acquisition was performed for 40–100 seconds.

The major constituents of these basic schist are albite porphyroblast ($X_{\text{an}}=0.01$, epidote and barrosite as inclusions), barrosite (Brs), epidote (Ep), chlorite (Chl), phengite (Phg), ilmenite (hematite lamella in ilmenite), actinolite (Act), sphene (Spn) and calcite (Cal). These samples contain coarse, brownish and hypidiomorphic carbonate grains, up to 1 cm coarse. Four types of calcite (Cal_1 , Cal_2 , Cal_3 ,

Cal_4 ; Table 1) can be distinguished in it. The large and single calcite is accompanied by an aggregate of calcite and quartz (Qtz), where calcite also includes small and rounded barrosite, epidote, albite and quartz as inclusions. In the matrix a typical mineral assemblage for the basic schist in the albite-biotite zone is present, i.e. $\text{Ab}+\text{Qtz}+\text{Brs}+\text{Chl}+\text{Ep}$ (Higashino *et al.*, 1982, Radvanec *et al.*, 1994).

In these samples the prograde minerals are as following:

$\text{Ab}+\text{Ep}+\text{Brs}+\text{Phg}_1(\text{Al}_2\text{O}_3=28.75 \text{ wt}\%, \text{Fe}/(\text{Fe}+\text{Mg})=0.47)$ in the matrix or $\text{Phg}_1(\text{Al}_2\text{O}_3=26.49 \text{ wt}\%, \text{Fe}/(\text{Fe}+\text{Mg})=0.52$; an rounded inclusion in carbonate) + $\text{Chl}_1(\text{Al}_2\text{O}_3=19.93 \text{ wt}\%, \text{Fe}/(\text{Fe}+\text{Mg})=0.32$; occurring parallel to schistosity) + $\text{Ilm}+\text{Qtz}+\text{Cal}_1$. Calcite₁ is often present as a mixture of two parts with slightly different compositions, one is $\text{Cal}_{1-L}(\text{FeCO}_3=1.1 \text{ mol}\%, \text{MgCO}_3=1.9\%, \text{MnCO}_3=1\%)$ and is lighter in a backscattered electron images (BEI) than earlier formed $\text{Cal}_{1-D}(\text{FeCO}_3=0.3 \text{ mol}\%, \text{MgCO}_3=0.3\%, \text{MnCO}_3=0.1\%)$, the darker part (Table 1, Fig. 2).

The retrograde mineral assemblage that occurs at the contact with the host calcite₁ (Fig. 1) is:

$\text{Spn}+\text{Act}+\text{Chl}_2(\text{Al}_2\text{O}_3=18.67\%, \text{Fe}/(\text{Fe}+$

Table 1. Representative analytical data of Carbonates

Mineral	Cal ₁ -L	Cal ₁ -D	Cal ₂	Fe-Dol	Cal ₃	Mg-Ank	Cal ₄
BEI	light	dark		in Cal ₂		in Cal ₃	
FeO	0.77	0.19	1.09	6.69	2.30	10.71	2.25
MnO	0.70	0.06	0.70	1.24	0.72	1.32	0.91
MgO	0.78	0.14	1.11	15.72	2.87	13.16	0.25
CaO	53.77	55.97	53.99	31.03	50.66	29.84	52.30
CO ₂ *	43.97	43.96	43.99	45.44	43.74	44.93	44.48
Total	99.99	100.32	100.88	100.12	100.29	99.96	100.29
Fe	0.011	0.003	0.015	0.177	0.031	0.291	0.032
Mn	0.010	0.001	0.010	0.033	0.010	0.036	0.013
Mg	0.019	0.003	0.027	0.740	0.071	0.636	0.006
Ca	0.960	0.993	0.948	1.050	0.888	1.037	0.949
Sd	1.1	0.3	1.5	8.8	3.2	14.6	3.2
Rds	1.0	0.1	1.0	1.7	1.0	1.8	1.3
Mgs	1.9	0.3	2.7	37.0	7.0	31.8	0.6
Cc	96.0	99.3	94.8	52.5	88.8	51.8	94.9

Fe-Dol: Fe-dolomite, Mg-Ank: Mg-ankerite

* CO₂ is calculated on stoichiometry

Mg)=0.43)+Phn₂(Al₂O₃=25.47 wt%, Fe/Fe+Mg=0.49)+hematite(Hem; inclusions in Cal₂)+Qtz. In this assemblage, Cal₂(FeCO₃=1.5 mol.%, MgCO₃=2.7%) contains Fe-dolomite (Fe-Dol, FeCO₃=8.8 mol%) and Cal₃ (FeCO₃=3.2%, MgCO₃=7.0%) contains Mg-ankerite (Mg-Ank, FeCO₃=14.6%) respectively. Calcite₄(FeCO₃=3.2%, MgCO₃=0.6%) with goethite (Gt) crystallised in earlier formed carbonate (Cal₃). Goethite a weathering mineral always develops along the cleavage of the host Cal₁. Calcite₂, calcite₃ with inclusions of Mg-Fe carbonates and calcite₄ are present only as the replacement of the host calcite₁, near the retrograde matrix mineral assemblage (Figs. 1a, 1b, 3, 4). Representative analyses of carbonates are shown in Table 1.

The Fe richest group of carbonates, that occur as irregular and tabular inclusions in calcite₃, is termed ankerite herein (Reeder, 1990), following Deer *et al.* (1962, 1992) who extended, the term ankerite to include dolomitic carbonate with Ca<0.5 and Mg/

Fig. 2. Calcite₁ as a mixture of the Cal₁-D (Fe, Mg, Mn poor calcite) and the Cal₁-L (younger calcite with a low content of Fe, Mg, Mn). For the chemical composition see Table 1. Back-scattered electron images (BEI).

(Mg+Fe+Mn)<1/4 (Fig. 5a).

III. Relationship between host calcite and Fe-Mg carbonates

Most carbonates in here studied basic schists are calcite₁ (Fig. 2, Table 1). They had to be formed just after the peak of the metamorphism, because rounded Brs, Ep, Ab, Spn inclusions occur in it. At the boundary with the retrograded matrix (Act+Chl₂+Png₂+Qtz+Spn), a part of the Cal₁ has been replaced by a mixture of Cal₂+Cal₃+Cal₄ 1-8 mm width (Figs. 1a, 1b). These Cal₂ and Cal₃ contain rounded Fe-dolomite and an irregular or tabular Mg-ankerite inclusions, respectively. The replacement of Cal₁ by Cal₂+Cal₃+Cal₄ is always discerned by the interference colour under the crossed polars and confirmed by BEI

Fig. 3. The small rounded inclusions of Fe-dolomite (Fe-Dol) distributed in Cal_2 . An irregular to tabular forms of Mg-ankerite (Mg-Ank) inclusions is present only in calcite₃ (Cal_3). Hem: hematite. Back-scattered electron images (BEI).

Fig. 4. The relationship between Cal_2 and $\text{Cal}_3 + \text{Cal}_4$ having the irregular to tabular grain inclusions of the Mg-ankerite. The calcite₄ occurs the youngest in calcite₃. Back-scattered electron images (BEI). The chemical compositions of carbonates see Table 1.

and micro-probe analysis. Very often the replacement develops along the cleavage of Cal_1 (Figs. 1a, 1b). As shown in Fig. 1, the replaced carbonate is composed of inner and outer parts as shown in Fig. 1b. The inner part is Cal_2 with Fe-dolomite inclusions and appears predated the outer part (shaded in Fig. 1b), which is Cal_3 with Mg-ankerite inclusions accompanied by the youngest Cal_4 . However an opposite interpretation that the outer part is earlier than the inner part, is not impossible (Figs. 1a, 1b, 4). The Cal_3 with inclusions of Mg-ankerite was also formed, at the boundary with rim of host Cal_1 (Figs. 1a, 1b). There mainly is presented a mixture of Cal_3 with an irregular and tabular type of Mg-ankerite inclusions, but Cal_2 is rarely present, too. This different textural relationships between ($\text{Cal}_2 + \text{Fe-Dol}$) and ($\text{Cal}_3 + \text{Mg-Ank} + \text{Cal}_4$) are

seen on figures 3 and 4 and the chemically, in the Table 1. The youngest calcite₄ occurs in calcite₃ (Fig. 4).

The chemical relationship between relics of the host calcite₁ and other carbonates of different stages Cal_{2-4} are shown in CaCO_3 – $\text{CaMg}(\text{CO}_3)_2$ – $\text{CaFeMn}(\text{CO}_3)_2$ diagram (Fig. 5). The Fe-dolomite and Mg-ankerite are plotted in two separate groups, because Fe-dolomite occurs only in Cal_2 and Mg-ankerite accompanied by Cal_4 only in Cal_3 respectively.

IV. Discussion

Enami and Higashino (1988) interpreted coarse dolomite crystals in primary calcite as an exsolution product, formed by re-equilibrium of Mg-rich primary calcite. New data in this work suggest a more complex process of

Fig. 5. a: The nomenclature of carbonates and solid solutions in system CaCO_3 - MgCO_3 - FeCO_3 at 450°C . C, calcite solid solution; S, siderite-magnesite solid solution; D, dolomite solid solution from Rosenberg in Reeder (1990).

b: The schematic relationships between the host calcite₁, calcite₂, calcite₃ and calcite₄.

c: Calcite-Dolomite-Ankerite diagram of carbonates studied in this paper. The ankerite line was drawn according to the ratio $\text{Fe} : \text{Mg} = 1 : 4$ in dolomite-ankerite formula (Deer *et al.*, 1992).

the replacement in the host calcite_{1-D}, which has at least three successive stages. The first stage forms calcite_{1-L}, probably near the estimated temperature of the peak of metamorphism ($T = 450^\circ\text{--}550^\circ\text{C}$; Table 1, Figs. 2, 5). The second stage of the replacement is recognised by exsolution texture of Fe-Dol inclusions in calcite₂, which is similar to that observed by Emami and Higashino (1988, Fig. 2). The third stage forms the irregular or tabular Mg-ankerite in calcite₃ and calcite₄ under lower temperature (probably lower than 300°C) than the second stage which was $450^\circ\text{--}400^\circ\text{C}$ (Fig. 6). Comparing all the stages of replacement of calcite₁, the cations exchanged between carbonates and fluid are calculated as follows assuming equal volume of the replacement. The temperatures of the reactions were calculated using the carbonate geothermometry of Powell *et al.* (1994) be estimated as follows:

Stage 1.

Stage 2.

Fig. 6. A plot of $X_{\text{Fe-dol}}$ against $X_{\text{Mg-Cal}}$, comparing $\text{Cal}_2\text{-FeDol}$ with $\text{Cal}_4\text{-MgAnk}$ fields using the carbonate geothermometry of Powell *et al.* (1984). Solid circles are from Enami and Higashino (1988).

($T=450^\circ\text{--}400^\circ\text{C}$ estimated between $\text{Cal}_2\text{-FeDol}$, using the carbonate geothermometry, Powell *et al.*, 1984, Fig. 6)

Stage 3.

($T=300^\circ\text{C}$ estimated between $\text{Cal}_4\text{-Mg-Ank}$, using the carbonate geothermometry, Powell *et al.*, 1984, fig. 6)

The materials exchanged between carbon-

ate and fluid differs at different stages, and such change can not be explained by the change of the pressure and temperature. It follows that the metamorphic rocks are open system for fluid and fluid migrated in certain volume of rocks. As far as the carbonate developed from Cal_1 , the volume of carbonate phase must have slightly expanded.

The fluid phase containing Mg^{2+} and Fe^{2+} can be derived from the following reaction proposed by Banno *et al.* (1984) for albite-biotite zone:

This reaction produced an enough amount of H_2O for local replacement. In the fluid phase the source or an amount of CO_2 has not yet been sought. One possibility is the combustion of graphitic materials of pelitic schists during metamorphism of Sanbagawa belts.

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