Stability of Grandite Garnet in $\text{H}_2\text{O}-\text{CO}_2$ Mixtures at 600°C under 100 MPa

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Abstract

With a fluid pressure of 100 MPa, grandite garnets with various $\text{Fe}/(\text{Fe}+\text{Al})$ ratios have been synthesized hydrothermally from the mixtures of reagent grade of CaO , CaCO_3 , Al_2O_3 , Fe_2O_3 and SiO_2 . Grossular is formed at the CO_2 mole fraction below 0.03, while the assemblage calcite-wollastonite-anorthite becomes stable above the value. An isobaric, isothermal eutectoid point appears in the system $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}-\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}-\text{CO}_2$. The point seems to be located approximately at 90 mole % in the andradite molecule, and 0.8 in the CO_2 mole fraction. This phase relation agrees with the fact that the composition of grandite from skarn-type ore deposits has a tendency towards andradite.

Introduction

Grandite garnet, $\text{Ca}_3(\text{Al,Fe})_2\text{Si}_3\text{O}_{12}$, is one of the most common gangue minerals characterizing the skarn-type ore deposits.

Grossular, $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, decomposes to the assemblage calcite-wollastonite-anorthite with an increase of CO_2 pressure under the condition where temperature is 600°C and fluid pressure is 100 MPa (Gordon and Greenwood, 1971). On the other hand, andradite, $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$, decomposes to the assemblage calcite-magnetite-quartz (Taylor and Liou, 1978). On the basis of these data, Shoji (1977, 1980) has shown schematically the phase relation in the system $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}-\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}-\text{CO}_2$ under the condition where calcite, grandite, prehnite, epidote, magnetite and quartz are stable. A eutectoid point appears in the phase diagram. A similar diagram (Fig. 1) can be drawn at a higher temperature, where calcite, wollastonite, grandite, anorthite, magnetite and quartz are stable.

To reveal the stability of garnet of the grandite series, the mixtures of reagent chemicals of CaO , CaCO_3 , Al_2O_3 , Fe_2O_3 and SiO_2 have been treated hydrothermally at 600°C under 100 MPa.

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FIG. 1. A schematic phase diagram in the system $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ – $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ – CO_2 .

TABLE 1. The list of mineral names with their abbreviations and the chemical formulae.

Abbreviation	Mineral Name	Chemical Formula
ca	calcite	CaCO_3
wo	wollastonite	CaSiO_3
gd	grandite garnet	$\text{Ca}_3(\text{Al,Fe})_2\text{Si}_3\text{O}_{12}$
an	anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$
mt	magnetite	Fe_3O_4
qz	quartz	SiO_2

The phases stated in this paper are listed in Table 1 with their compositions and abbreviations.

Experimentals

Three series were prepared as starting materials. The first series were the mixtures of CaCO_3 , Al_2O_3 , Fe_2O_3 and SiO_2 . CaO was further added to the second and third series. The CaO/ CaCO_3 ratios were 4/6 and 6/4 in the second and third series, re-

spectively. The Fe/(Fe+Al) ratios of starting materials were 0, 20, 40, 50, 60, 80 and 100 atom %, and include 70 atom % in the second and third series. Every oxide was dried at about 1000°C for over 20 minutes, and calcium carbonate was dried at 150°C for a day. These materials were weighted in appropriate proportions in accordance with each starting composition, and mixed for 20 minutes under methylalcohol.

With excess water, a few tens (20–30) milligram of each mixture was sealed in a gold capsule, whose diameter and length were 3 mm, and about 30 mm, respectively. Each starting material was hydrothermally treated at 600°C under 100 MPa for 6 days. After the treatment, each product was observed by the scanning electron microscope, and the phase assemblage was examined by the powder X-ray diffraction method. Calcite, wollastonite, anorthite and magnetite were recognized in addition to grandite garnet in various amounts. Their sizes were very small, and most of them were less than 1 μm . The garnet crystals showed the dodecahedron, and the combination of dodecahedron and trapezohedron. The wollastonite crystals were needle-shaped. The form of other minerals was not clear. The lattice constants of each garnet were determined from the values of d_{642} and d_{420} . The former value was applied in the case of a large amount of garnet, while the latter in a small amount. The measurement condition was as follows: RIGAKU 2013 X-ray Diffractometer, target = Cu, filter = Ni, 30 kV–15 mA, time constant = 1 sec, scanning speed = 1°/min, chart speed = 2 cm/min. Accordingly, the error of determined lattice constants are below 0.001 nm. The fluid composition of each run was determined by the weight method (see Appendix). The measurement was carried out by the Yasumami micro-balance, the detection limit of which was 1 γ . The accuracy is believed to be 1 in CO₂ mole %.

Result and discussion

The results are summarized in Table 1.

In Fig. 2, the observed lattice constant of each garnet is plotted against the composition of the corresponding starting material. The data of the products consisting mostly of garnet (open circles) are scattered near the line joining the grossular and andradite ends. Fig. 3 shows the difference between the observed lattice constant and the value expected from the composition of starting material as a function of CO₂ mole fraction. The grandite synthesized above 600°C contains little amount of water, and the lattice constant increases linearly with an increase of iron content (Shoji, 1975). This implies that the composition of grandite is estimated uniquely from the lattice constant. Consequently, the horizontal axis in Figs. 2 and 3 represents the composition as well as the lattice constant of garnet.

The results are divided into three groups on the basis of the mineral assemblage, and the compositional relation between starting material and synthesized garnet.

FIG. 2. A diagram showing the relation between the compositions of starting materials and the cell constants of synthesized garnets.

The first group is free from garnet. This group appears in the iron-free and CO_2 -rich condition (Table 2). The constituent phases are calcite, anorthite and wollastonite. Grossular is stable at the CO_2 mole fraction below 0.07, while the assemblage calcite-wollastonite-anorthite is stable above the value. The garnet of the second group is inferred to succeed to the $\text{Fe}/(\text{Fe}+\text{Al})$ ratio of the corresponding starting material, because the cell constant is close to the value expected from the composition of starting material. The product of this group consists mostly of grandite garnet, and sometimes a small amount of calcite, except the runs of both ends (Fig. 2). This implies that the garnet was formed in its own field. The garnet of third group has the $\text{Fe}/(\text{Fe}+\text{Al})$ ratio different from the corresponding starting material. The product contains remarkable amounts of calcite, anorthite and wollastonite in addition to garnet. This implies that the run condition was not comfortable for the garnet whose composition is equal to that of the starting material.

FIG. 3. A diagram showing the relation between the compositions of starting materials and the cell constants of synthesized garnets as a function of CO₂ mole fraction.

This experiment examined the formation of grandite garnet, but did not the decomposition of it. For this reason, all of runs may not have been always in thermodynamic equilibrium. If each product was formed under the equilibrium condition, the following discussion is developed.

Fig. 4 shows the relation between the compositions of synthesized garnets and the CO₂ mole fractions. In this diagram, the grandite field is below the curve which passes through the points, (0, 0.03), (20, 0.05), (40, 0.1), (80, 0.6), in the andradite mole % and the CO₂ mole fraction, respectively. Grandite is stable in the region below the line, where carbon dioxide is poor. On the contrary, grandite decomposes to calcite, wollastonite, anorthite and Fe-rich grandite above the line.

The eutectoid point is expected to appear on the extension part of the line. The point seems to be located near 90 mole % in the andradite molecule, and 0.8 in the CO₂ mole fraction.

The composition of grandite occurring in ore deposits of the skarn-type has a tendency towards andradite. For instance, most of garnets from the Kamaishi deposit have the composition ranging from 40 to 100 mole % (Mariko and Nagai, 1980),

TABLE 2. Experimental results.

Composition ¹	Product ²	Lattice Constant of Garnet	CO ₂ Mole Fraction
Mixture of CaCO ₃ , Al ₂ O ₃ , Fe ₂ O ₃ , SiO ₂			
0	ca, an, wo	—	.10
0	ca, an, wo	—	.10
0	gd, ca, an	1.185 nm	.07
20	gd, ca, an	1.189	.06
20	gd, ca, an, wo	1.194	.15
40	gd, ca, an	1.194	.18
50	gd, ca	1.202	.43
60	gd, ca, wo	1.202	.63
80	gd, mt	1.200	.22
100	gd, mt	1.207	.16
Mixture of CaO, CaCO ₃ , Al ₂ O ₃ , Fe ₂ O ₃ , SiO ₂ (CaO:CaCO ₃ = 4:6)			
0	gd, ca, an	1.186 nm	—
20	gd, ca, an	1.190	—
40	gd, ca	1.194	—
50	gd, ca	1.193	.03
60	gd, ca	1.198	.05
70	gd	1.197	—
80	gd	1.202	—
100	gd, mt	1.206	—
Mixture of CaO, CaCO ₃ , Al ₂ O ₃ , Fe ₂ O ₃ , SiO ₂ (CaO:CaCO ₃ = 6:4)			
0	gd, ca, an	1.185 nm	.02
20	gd, ca, an	1.190	.06
40	gd, ca, an	1.191	—
50	gd	1.195	—
60	gd	1.198	—
70	gd	1.200	—
80	gd	1.200	—
100	gd, mt	1.206	—

¹ Fe/(Fe+Al) ratio in atom %.² Abbreviations: an = anorthite, ca = calcite, gd = grandite garnet, mt = magnetite, wo = wollastonite.

FIG. 4. A diagram showing the grandite field as functions of CO₂ mole fraction and composition of garnet.

and those from the Tsumo deposits range from 50 to 100 mole % (Sasaki and Shoji, 1981). The tendency seems to be resulted from not only the supply of iron-rich fluids but also the fact that the eutectoid point is located near the andradite end in the system $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ – $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ – CO_2 .

Conclusion

At 600°C, grossular decomposes to the assemblage calcite-wollastonite-anorthite in a fluid whose pressure is 100 MPa, and whose CO₂ mole fraction is higher than 0.03. The grandite field extends to the isobaric, isothermal eutectoid point with an increase of its iron content. The eutectoid point seems to be located approximately at 90 mole % in the andradite molecule and 0.8 in CO₂ mole fraction. This phase relation explains well the fact that the composition of grandite occurring in skarn tends to the andradite side.

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Appendix

The composition of fluid in a gold capsule is able to be determined by measuring three following weights: the whole weight of capsule (W_1), the weight just after the capsule is holed by a needle (W_2), and the weight after the capsule is dried (W_3). They are written as follows:

$$W_1 = W_{\text{cap}} + W_{\text{sol}} + W_{\text{H}_2\text{O}} + W_{\text{CO}_2} - d_{\text{air}} (W_{\text{cap}}/d_{\text{cap}} + W_{\text{sol}}/d_{\text{sol}} + W_{\text{H}_2\text{O}}/d_{\text{H}_2\text{O}} + W_{\text{CO}_2}/d_{\text{CO}_2}) \quad (1)$$

$$W_2 = W_{\text{cap}} + W_{\text{sol}} + W_{\text{H}_2\text{O}} - d_{\text{air}} (W_{\text{cap}}/d_{\text{cap}} + W_{\text{sol}}/d_{\text{sol}} + W_{\text{H}_2\text{O}}/d_{\text{H}_2\text{O}}) \quad (2)$$

$$W_3 = W_{\text{cap}} + W_{\text{sol}} - d_{\text{air}} (W_{\text{cap}}/d_{\text{cap}} + W_{\text{sol}}/d_{\text{sol}}) \quad (3)$$

where W_{cap} , W_{sol} , $W_{\text{H}_2\text{O}}$ and W_{CO_2} are the weights of container, solid, water and carbon dioxide, and d_{air} , d_{cap} , d_{sol} , $d_{\text{H}_2\text{O}}$, d_{CO_2} are the densities of air, container, solid, water and carbon dioxide, respectively. In each equation, the term involving d_{air} corresponds to the buoyancy caused by air. The weight of carbon dioxide is reduced from equations (1) and (2) as follows:

$$W_{\text{CO}_2} = (W_1 - W_2)/(1 - 1/C_{\text{CO}_2})$$

where $C_{\text{CO}_2} = d_{\text{CO}_2}/d_{\text{air}}$ is the specific gravity of carbon dioxide to air. On the other hand, equations (2) and (3) give the weight of water as follows:

$$W_{\text{H}_2\text{O}} = W_2 - W_3$$

on the assumption that $d_{\text{air}}/d_{\text{H}_2\text{O}}$ is very small.

To estimate the error in this method is difficult. Each weight can be measured accurately by the microbalance. Water runs away in vapor, however, during the measurement of W_2 . For this reason, the weight of CO₂ is overestimated.

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