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Original Article

Relationship Between Solidification Depth of Granitic Rocks and Formation of Hydrothermal Ore Deposits

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Abstract

Chemical analysis of biotite in representative granitic rocks in Japan shows that the total Al (^{T}Al) content changes with the metal type of the accompanying hydrothermal ore deposits and increases in the following order: Pb-Zn and Mo deposits < Cu-Fe and Sn deposits < W deposits < non-mineralized granitic rocks. The ^{T}Al content of biotite in granitic rocks may be a useful indicator for distinguishing between mineralized and non-mineralized granitic rocks. A good positive correlation is seen between the ^{T}Al content of biotite and the solidification pressure of the granitic rocks estimated by sphalerite and hornblende geobarometers and the mineral assemblages of the surrounding rocks. These facts suggest that the ^{T}Al content of biotite can be used to estimate the solidification pressure (P) of the granitic rocks. The following empirical equation was obtained:

$$P\ (kb) = 3.03 \times {}^{T}Al - 6.53\ (\pm 0.33)$$

where ^{T}Al designates the total Al content in biotite on the basis O = 22. According to the obtained biotite geobarometer, it is estimated that Pb-Zn and Mo deposits were formed at pressures below 1 kb, Cu-Fe and Sn deposits at 1–2 kb, W deposits at 2–3 kb and non-mineralized granitic rocks were solidified at pressures above 3 kb.

Keywords: biotite, solidification depth, geobarometer, granitic rock, hydrothermal ore deposit.

1. Introduction

Many hydrothermal ore deposits have been formed in relation to granitic rocks. Among hydrothermal ore deposits, skarn-type ore deposits have a clear genetic relationship to granitic rocks. In Japan, the skarn-type ore deposits have been classified into Kamioka-Nakatatsu (Pb-Zn), Chichibu (Cu-Fe-Pb-Zn) and Kamaishi (Cu-Fe) types (Miyazawa 1977). Based on the textures of the related granitic rocks, it was considered that the formation depth of Pb-Zn deposits is relatively shallow, whereas that of Cu-Fe deposits is relatively deep (Shimazaki, 1975). Using a sphalerite geobarometer, Shimizu and Shimazaki (1981) showed that Pb-Zn deposits were formed in shallow environments below 1 kb, whereas Cu-Fe deposits were formed in deep environments of 1–2 kb.

Previous experimental results also support the importance of pressure in the formation of hydrothermal ore deposits. Experiments on the pressure dependence of the element partitioning between magma and hydrothermal solutions (Urabe, 1987) showed that despite dependence on the chemical composition of magma, transition elements can be partitioned preferentially into hydrothermal solutions with decreasing pressure. This may be attributable to the formation of higher-order chloro complexes of metals (tri-chloro complex and tetra-chloro complex) in the hydrothermal solutions (Fahlquist & Popp, 1989; Uchida *et al.*, 1995, 1998). According to the experiments, the formation

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constants of higher-order chloride complexes of divalent metals increase with decreasing pressure and increasing temperature. Because the solidus temperature is relatively high at lower pressures under water-saturated conditions, it is expected that hydrothermal solutions with a high potential of mineralization will be discharged from granitic magmas under low pressure conditions, combined with the temperature effect on the partitioning of metals between rocks and hydrothermal solutions (Uchida *et al.*, 2003). In other words, metals such as Pb, Zn, Cu and Fe, which generally dissolve in hydrothermal solutions in the form of chloride complexes, are preferentially partitioned into hydrothermal solutions, and hydrothermal solutions rich in these metals (ore-forming hydrothermal solutions) are released from the granitic rocks in shallow environments. This means that hydrothermal ore deposits will be formed when granitic magmas are solidification in shallow environments.

In addition, the partitioning of chlorine between magma and hydrothermal solutions depends significantly on the pressure. Chlorine tends to remain in magma at pressures lower than 1–1.5 kb (Nakano & Urabe, 1989; Shinohara, 2003), and highly saline hydrothermal solutions with a high mineralization potential are finally discharged from magma.

In this way, the solidification depth of magma, namely the solidification pressure, seems to significantly affect the formation of hydrothermal ore deposits. Therefore, in order to clarify the relationship between the solidification depth of granitic rocks and the formation of hydrothermal ore deposits, the granitic rocks in the 15 districts (Fig. 1) of Japan with or without hydrothermal mineralization were investigated and compared to each other. This study was focused especially on the total Al (^{T}Al) content of biotite in granitic rocks as a possible pressure indicator.

2. Hornblende geobarometer

As mentioned in the previous section, the solidification depth (pressure) of magma is one of the important factors controlling the formation of hydrothermal ore deposits. Thus a study on the relationship between the solidification pressure of granitic rocks and the existence of hydrothermal ore deposits or metal types may provide important information for ore exploration.

A hornblende geobarometer is a useful tool for estimating the solidification pressure of granitic rocks. This geobarometer is based on the ^{T}Al content of hornblende in granitic rocks, which increases with the solidification pressure. This geobarometer is applicable to granitic rocks with a mineral assemblage of Hb + Bi + Pl + Q + Kf. The following reaction occurs among these minerals (Hollister *et al.*, 1987).

$$\text{Phlogopite} + 2\ \text{Quartz} + 2\ \text{Anorthite} = \text{Tschermakite} + \text{Orthoclase}. \quad (1)$$

Because the total volume of the right side is smaller than that of the left side, the reaction proceeds to the right at higher pressures based on Le Chatelier's principle. Therefore, the ^{T}Al content of hornblende increases with increasing pressure.

The calibration of a hornblende geobarometer was carried out by Hammarstrom and Zen (1986), Hollister *et al.* (1987), Johnson and Rutherford (1989), Thomas and Ernst (1990) and Schmidt (1992), based on field data or experimental data. The experimental calibration was performed over a pressure range of 2.5–13 kb. Because a mineral assemblage of Bi + Kf is unstable at pressures higher than 13 kb, this pressure is the upper limit of application for a hornblende geobarometer. Agreement among the calibration curves is not necessarily good, and a difference of 1 kb is observed among the calibrations. However, the pressure dependences are similar.

At pressures below 2 kb, the straightness of the calibration curve is not assured because the solidus temperature of granitic rocks increases rapidly with decreasing pressure, but it is supposed that the ^{T}Al content of hornblende is proportional to pressure. We tried to calibrate a hornblende geobarometer below 2 kb using a sphalerite geobarometer. The formation pressures for the following mines have been estimated by Shimizu and Shimazaki (1981) and Shimizu (1986): Yaguki mine (Cu–Fe), 1.5 kb; Ohkawame mine (Mo), 1.3 kb; Kamaishi mine (Cu-Fe), 1.2 kb; Chichibu mine (Cu-Fe-Pb-Zn), 0.6 kb; and Suzuyama mine (Sn), 1–1.2 kb. The chemical analysis of hornblende in the related granitic rocks was carried out using an energy dispersive X-ray microanalyzer (a scanning electron microscope JSM-5400, JEOL; equipped with an energy dispersive X-ray spectrometer QX-200JI, LINK). The calibration curve below 2 kb (Fig. 2) was obtained using the aforementioned data for the formation pressures obtained by a sphalerite geobarometer and the ^{T}Al values of hornblende in the related granitic rocks obtained in the present study (Table 1). The obtained calibration curve is compared in Fig. 3 with the calibration curves previously obtained above 2 kb. The calibration curve below 2 kb obtained in the present study seems to be

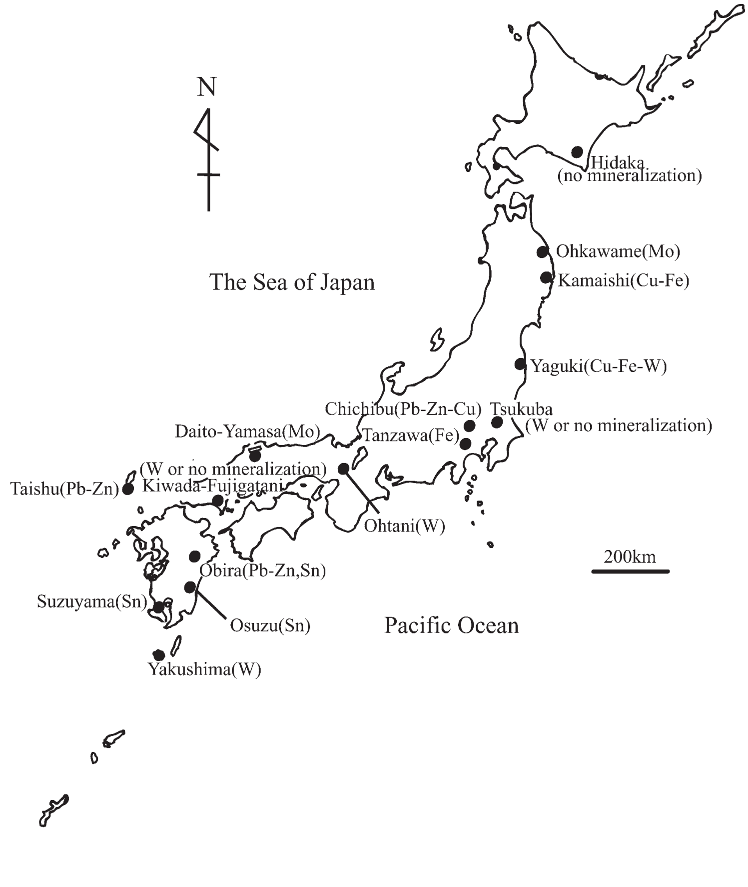

Fig. 1 Map of the investigated districts and metal types.

the most concordant with that of Thomas and Ernst (1990) among the calibration curves above 2 kb.

3. Application of a hornblende geobarometer to granitic rocks

A hornblende geobarometer was applied to granitic rocks mainly related to skarn-type deposits. The chemical compositions of hornblende in the following hornblende-bearing granitic rocks, which are obviously related to hydrothermal ore deposits, were analyzed in the present study: quartz diorite of the Chichibu mine (Cu-Fe-Pb-Zn), granodiorite of the Yaguki mine (Cu-Fe-W), the Ganidake complex of the Kamaishi mine (Cu-Fe), granitic rocks around the Ohkawame mine (Mo), the Suzuyama granite of the Suzuyama mine, the Yushin and Azegamaru quartz diorites (Fe) in the Tanzawa district, granite porphyry of the Obira mine (Pb-Zn) and the Inada coarse granite (W) in the Tsukuba district. The energy dispersive X-ray microanalyzer was used for the chemical analysis of hornblende. The rim of hornblende was analyzed with the microanalyzer.

Figure 4 shows the relationship between the Mg/(Mg + Fe) molar ratio and the ^{T}Al content of hornblende in the aforementioned granitic rocks. The data for hornblende of the Uchiyama granite around the Taishu mine (Pb-Zn) in Fig. 4 were taken from Ikemi *et al.* (2001). Among the granitic rocks genetically related to the Chichibu, Kamaishi and Yaguki mines, the ^{T}Al content increases in the order of Chichibu mine < Kamaishi mine < Yaguki mine, and this indicates that the formation pressure increases in this order. In other words, this result shows that Cu-Fe deposits were formed at relatively higher pressures than Pb-Zn deposits. This is concordant with the conclusion of Shimazaki (1975). Moreover, Fig. 4 shows that Mo deposits (Ohkawame mine) and Sn deposits (Suzuyama mine) were formed at nearly the same pressure as Cu-Fe deposits. In contrast, W deposits (Inada coarse granite in the Tsukuba district and the western granodiorite of the Yaguki mine) have high formation pressures.

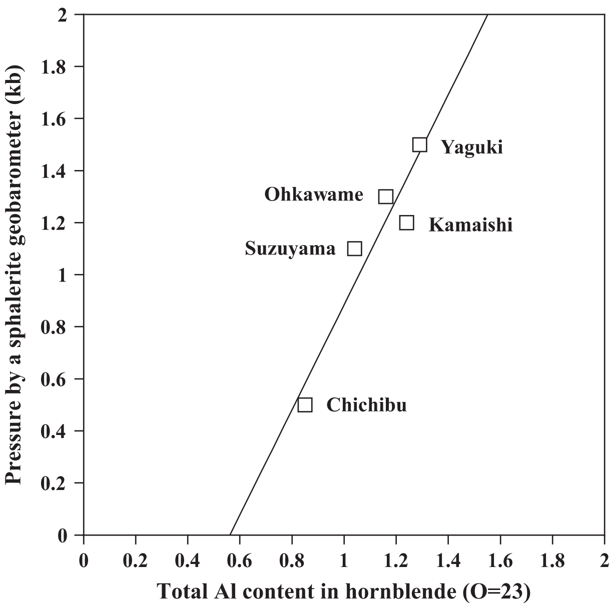

Fig. 2 Relationship between the total Al content of hornblende (O = 23) in the granitic rocks related to hydrothermal mineralization and the formation pressure estimated by a sphalerite geobarometer.

4. Relationship between ^{T}Al contents of hornblende and biotite

Under relatively high pressures, the reaction (1) proceeds to the right, and the ^{T}Al content of hornblende increases with increasing pressure. Because a phlogopite component in biotite is consumed during progress of reaction (1), the ^{T}Al content of biotite increases at the same time. In this context, chemical analysis of the biotite included in the aforementioned granitic rocks was carried out, and the correlation between the ^{T}Al contents of hornblende and biotite was examined. The energy dispersive X-ray microanalyzer was used for the chemical analysis of biotite. The analysis results are shown in Fig. 5. The correlation is not necessarily good, but the ^{T}Al content of biotite tends to increase with an increase in the ^{T}Al content of hornblende.

5. Relationship between ^{T}Al content of biotite in granitic rocks and metal type

In order to confirm a difference in the ^{T}Al content of biotite by metal type, chemical analysis of biotite in the granitic rocks was performed (Table 1). In the present study, the analysis was carried out on granitic rocks in the 15 districts including granitic rocks related to Pb-Zn, Mo, Cu-Fe, Sn or W deposits, and also granitic rocks without mineralization (Fig. 1). Characteristics of these granitic rocks are summarized in Table 1.

The relationship between the ^{T}Al content and the Mg/(Mg+Fe) molar ratio of biotite in the investigated granitic rocks is shown in Fig. 6 by metal type. Obviously the mean ^{T}Al content of biotite is low for the granitic rocks related to Pb-Zn and Mo deposits, and increases in the order of granitic rocks related to Pb-Zn and Mo deposits < granitic rocks related to Cu-Fe and Sn deposits < granitic rocks related to W deposits < non-mineralized granitic rocks. Judging from the previous studies concerning skarn type deposits, this order seems to correspond to an increase in the solidification depth of the related granitic rocks. As is obvious in Fig. 6, the ^{T}Al content is higher in the granitic rocks related to W deposits and those without mineralization than those related to Pb-Zn, Cu-Fe, Sn and Mo deposits. Judging from the intimate relationship to plutonic rocks, it is considered that W deposits were formed in a deep environment (Nakano, 2003). This is concordant with the relatively high ^{T}Al content of biotite. In the case of Mo deposits in Japan, they occur as veins and are considered to have been formed in shallow environments (Nakano, 2003). This is also concordant with the low ^{T}Al content of biotite in the related granitic rocks. In this way, the ^{T}Al content of biotite in granitic rocks seems to increase with the solidification pressure and seems to be a useful indicator for estimating their solidification pressure. Based on sphalerite and hornblende geobarometers, the Ohkawame Mo deposit was estimated to have been formed at relatively high pressures similar to those for the Cu-Fe deposits. However, the ^{T}Al contents of biotite in the granitic rocks related to other Mo deposits are as low as those in the granitic rocks related to Pb-Zn deposits, which are considered to have been formed under relatively low pressure conditions.

There is a possibility that the ^{T}Al content of biotite is proportional to the Al_2O_3 content of granitic rocks. Hence, the relationship between ^{T}Al content of biotite and alumina saturation index, $Al_2O_3/(CaO+Na_2O+K_2O)$ molar ratio, of the granitic rocks was examined. An X-ray fluorescence spectrometer NP-2100 (X 'Unique II, Philips) was used for the bulk chemical analysis of the granitic rocks. The relationship between the alumina saturation index and the ^{T}Al content of biotite is shown in Fig. 7. A slightly positive correlation is observed, but it is not necessarily clear. Rather, granitic rocks with all types of metal deposits, such as Pb-Zn, Mo, Cu-Fe, Sn and W deposits and also granitic rocks without mineralization, are observed at

Table 1 Characteristics of the granite rocks investigated in the present study

Mine or district	Granitic rock	Metal type	Mgt/Ilm series	I/S type	SiO_2 content wt%	Mineral assemblage	$Al_2O_3/(CaO+Na_2O+K_2O)$	^{T}Al of biotite O = 22
Hidaka	Cordierite tonalite	No mineralization	Ilm	S-I	63–68	Q-Pl-Bi-Mus	1.15	3.440
	Hornblende tonalite	No mineralization	Ilm	I	65–70	Q-Pl-Bi	0.98	2.853
Ohkawame mine	Granitic rock in the mining district	Mo	Mgt	I	71–76	Q-Pl-Kf-Bi-(Hb)	0.95	2.559
	Granitic rocks in the zones I and II	Mo	Mgt	I	59–66	Q-Pl-Kf-Bi-Hb	0.83	2.396
Kamaishi mine	Ganidake granodiorite	Cu-Fe	Mgt	I	65–67	Q-Pl-Kf-Bi-Hb	0.89	2.646
	Ganidake diorite/diorite porphyry	Cu-Fe	Mgt	I	52–57	Q-Pl-Kf-Bi-Hb	0.79	2.703
Yaguki mine	Eastern granodiorite	Cu-Fe	Mgt	I	68–70	Q-Pl-Kf-Bi-Hb	0.88	2.485
	Central granodiorite	Cu-Fe	Mgt	I	65–68	Q-Pl-Kf-Bi-Hb	0.88	2.557
	Western granodiorite	Cu-Fe-W?	Mgt	I	69–72	Q-Pl-Kf-Bi-Hb	0.94	2.735
Tsukuba	Tsukuba two mica granite	No mineralization	Ilm	I	70–72	Q-Pl-Kf-Bi-Mus	0.95	3.497
	Inada coarse-grained granite	W	Ilm	I	72–73	Q-Pl-Kf-Bi-(Mus)	0.92	2.695
	Kamishiro fine-grained granodiorite	No mineralization	Ilm	I	69–71	Q-Pl-Kf-Bi-(Mus)	0.94	3.367
	Inada medium-grained granodiorite	No mineralization	Ilm	I	70–71	Q-Pl-Kf-Bi-(Mus)	0.94	3.233
	Inada fine-grained granite	No mineralization	Ilm	I	70–72	Q-Pl-Kf-Bi-(Mus)	0.98	3.356
	Tsukuba porphyritic granodiorite	No mineralization	Ilm	I	70–73	Q-Pl-Kf-Bi-(Mus)	0.97	3.305
Chichibu mine	Quartz diorite	Cu-Fe-Pb-Zn	Mgt	I	59–65	Q-Pl-(Kf)-Bi-Hb	0.87	2.397
Tanzawa	Yushin tonalite	Fe	Mgt	I	65–71	Q-Pl-Bi-Hb	0.89	2.749
	Azegamaru tonalite	Fe	Mgt	I	51–55	Q-Pl-Hb	0.80	2.537

continued

Table 1 Continued

Mine or district	Granitic rock	Metal type	Mgt/Ilm series	I/S type	SiO_2 content wt%	Mineral assemblage	$Al_2O_3/(CaO+Na_2O+K_2O)$	^{T}Al of biotite O = 22
Ohtani mine	Gyojayama granite	W	Ilm	I	67–70	Q-Pl-Kf-Bi	1.06	3.045
Daito-Yamasa mine	Yamasa leucocratic granite	Mo	Mgt	I	72–76	Q-Pl-Kf-Bi	0.99	2.422
	Leucocratic granite complex	Mo	Mgt	I	73	Q-Pl-Kf-Bi	1.01	2.403
	Kawai Hb-Bi hybrid rock	Mo	Mgt	I	68–70	Q-Pl-Kf-Bi-(Hb)	1.01	2.426
Fugigatani-Kiwada mine	Nakayamagawa complex	No mineralization	Ilm	I	73–76	Q-Pl-Kf-Bi	1.07	3.202
	Habu granodiorite	W	Ilm	I	70–72	Q-Pl-Kf-Bi	1.01	2.932
	Shimokuhara granite	No mineralization	Ilm	I	71–75	Q-Pl-Kf-Bi	0.97	3.357
	Osogoe complex	W	Ilm	I	74–75	Q-Pl-Kf-Bi	0.96	2.984
Taishu mine	Uchiyama granitic rock and others	Pb-Zn	Mgt-Ilm	I	69–76	Q-Pl-Kf-Bi	1.00	2.409
Obira mine	Granite porphyry	Pb-Zn	Ilm	I	59–65	Q-Pl-Kf-Bi-Hb	0.88	2.506
	Biotite granite	Sn	Ilm	S-I	75–77	Q-Pl-Kf-Bi	1.06	2.824
	Porphyrytic granite	Sn	Ilm	S	76	Q-Pl-Kf-Bi-Hb	1.09	2.898
Osuzu mine	Osuzu granodiorite/granite porphyry	Sn	Ilm	I-S	66–73	Q-Pl-Kf-Bi-Mus	1.12	2.880
Suzuyama mine	Suzuyama granite porphyry	Sn	Ilm	I	66–68	Q-Pl-Kf-Bi	0.93	2.534
Yakushima	Yakushima granite	W	Ilm	I	67–70	Q-Pl-Kf-Bi	0.94	3.182

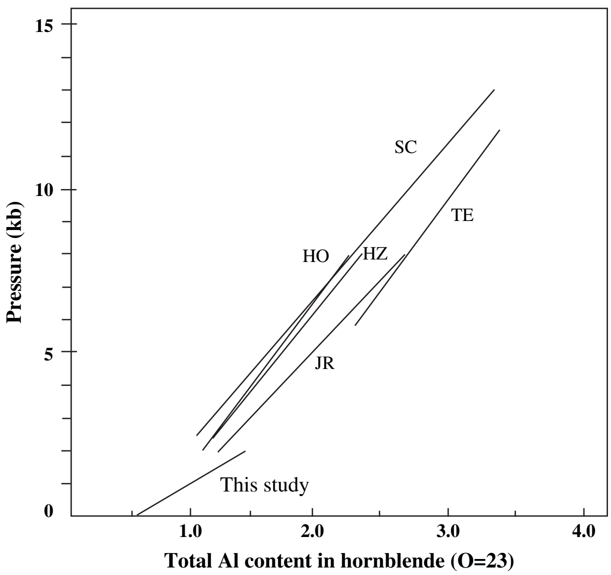

Fig. 3 Comparison of hornblende geobarometers. Present study: calibration curve of a hornblende geobarometer obtained by a sphalerite geobarometer. HZ, Hammarstrom and Zen (1987); Ho, Hollister *et al.* (1988); JH, Johnson and Rutherford; TE, Thomas and Ernst (1990); SC: Schmidt (1992).

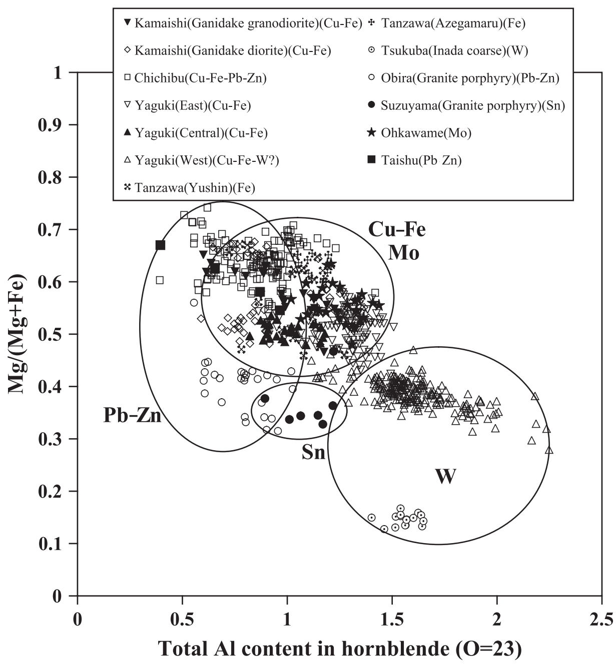

Fig. 4 Relationship between Mg/(Mg + Fe) molar ratio and total Al content in hornblende (O = 23) by metal type.

$Al_2O_3/(CaO + Na_2O + K_2O)$ molar ratios ranging from 0.9 to 1.0. A hornblende geobarometer suggests that the ^{T}Al content of hornblende depends on only pressure but not the alumina saturation index of the coexisting magma. This is also applicable to biotite coexisting with hornblende (Fig. 5). The ^{T}Al content of biotite not coexisting with hornblende increases the same as that of biotite coexisting with hornblende in the order of granitic rocks related to Pb-Zn and Mo deposits < granitic rocks related to Cu-Fe and Sn deposits < granitic rocks related to W deposits < non-mineralized granitic rocks. This suggests that the ^{T}Al content of biotite in granitic rocks increases with the solidification pressure.

6. Possibility of a biotite geobarometer

As mentioned here, it seems that the ^{T}Al content of biotite in granitic rocks depends on the solidification pressure. In order to confirm this hypothesis, data for the solidification pressures of granitic rocks were collected, and the relationship between the solidification pressure of granitic rocks and the ^{T}Al content of biotite in the granitic rocks was examined.

The formation pressure of the Yaguki mine (Cu–Fe), the Ohkawame mine (Mo), the Kamaishi mine (Cu-Fe), the Chichibu mine (Cu-Fe-Pb-Zn) and the Suzuyama mine (Sn) has been estimated to be 1.5, 1.3, 1.2, 0.6, and 1–1.2 kb, respectively, by a sphalerite geobarometer (Shimizu & Shimazaki, 1981; Shimizu, 1986). The

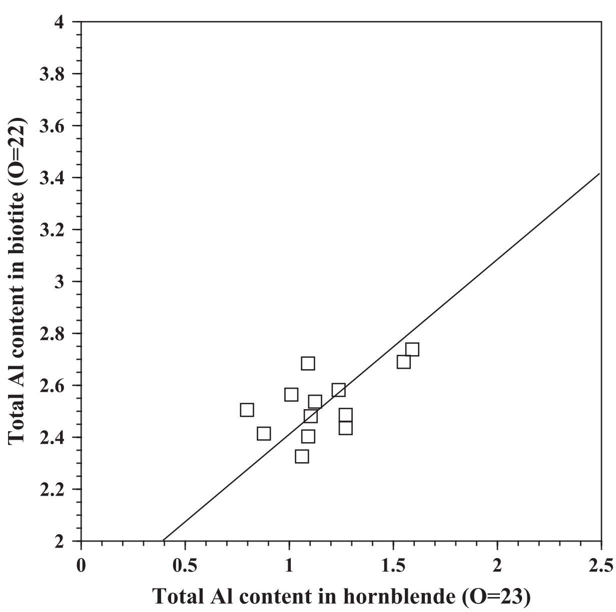

Fig. 5 Relationship between total Al contents of hornblende (O = 23) and biotite (O = 22) in the granitic rocks.

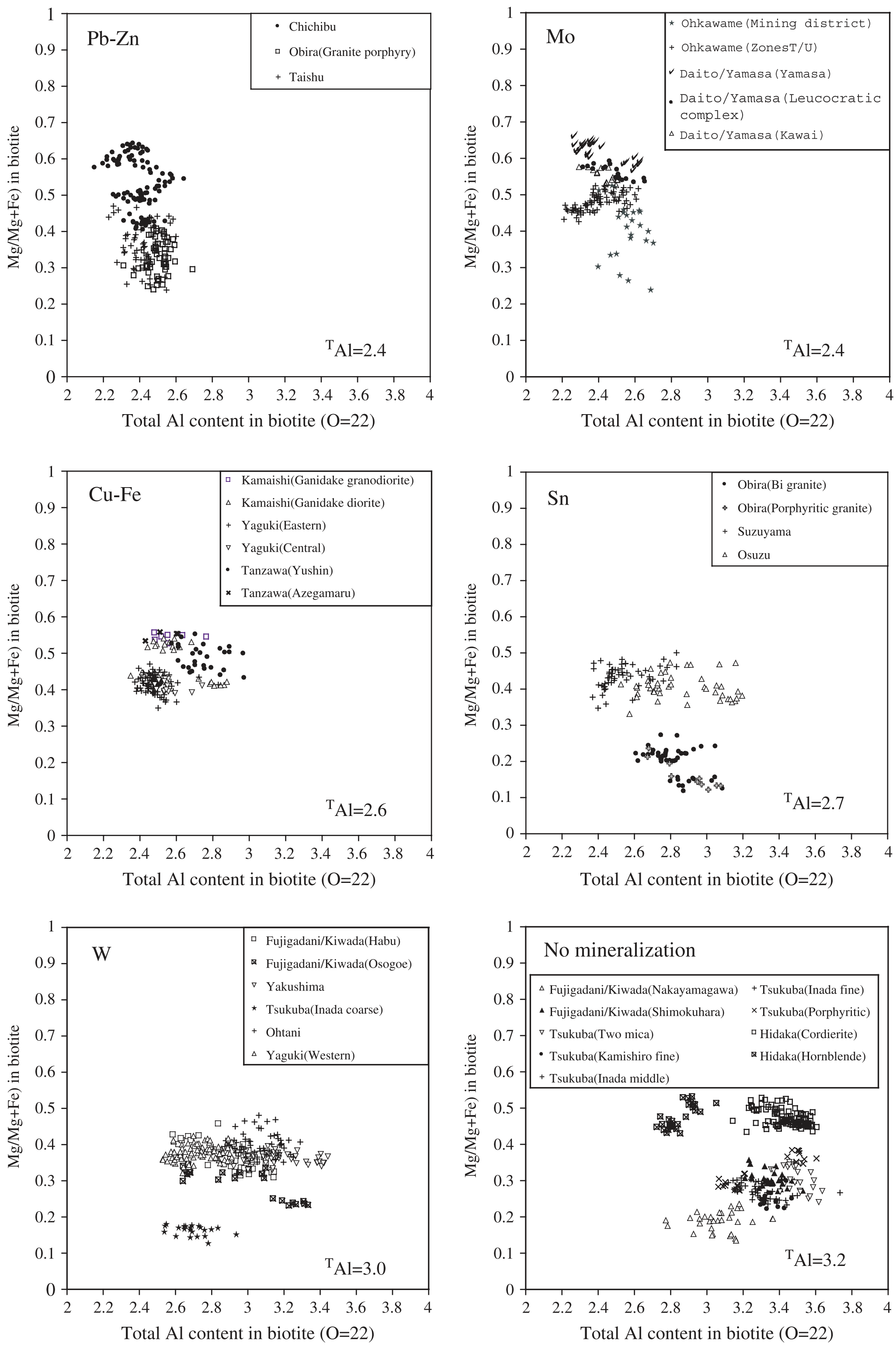

Fig. 6 Chemical composition Mg/(Mg + Fe) versus total Al content (^{T}Al) of biotite (O = 22) in the granitic rocks by metal type.

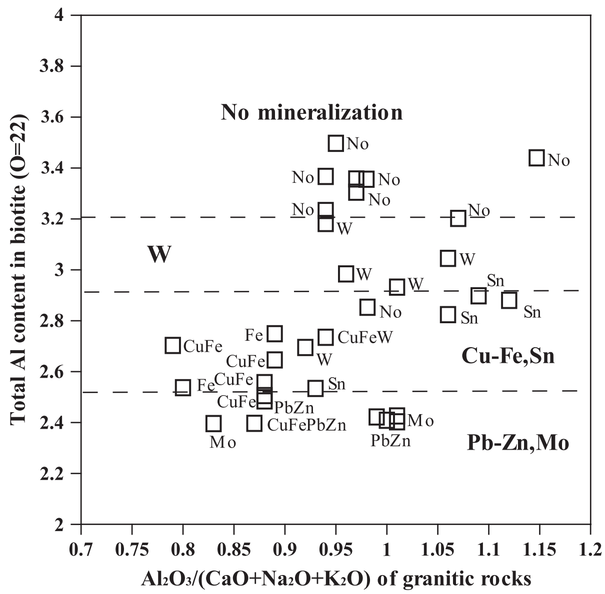

Fig. 7 Relationship between the $Al_2O_3/(CaO + Na_2O + K_2O)$ molar ratio of granitic rocks and total Al content of biotite (O = 22) by metal type.

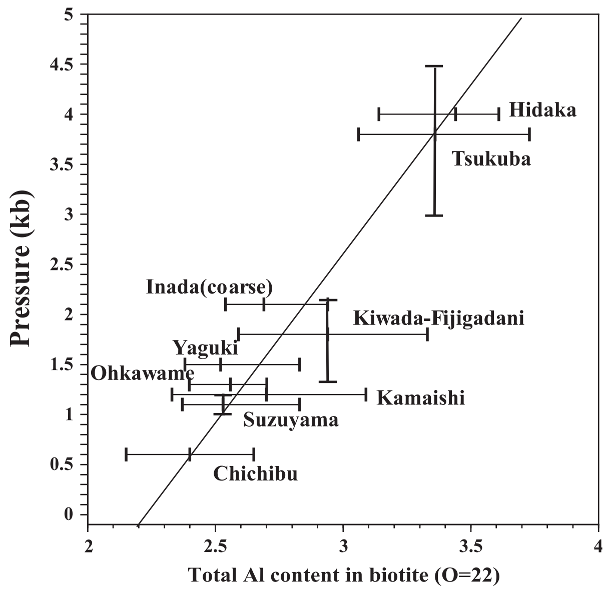

Fig. 8 Calibration of a biotite geobarometer for granitic rocks.

formation pressure estimated by a sphalerite geobarometer was assumed to be equal to the solidification pressure of the genetically related granitic rocks.

By using the hornblende geobarometer of Thomas and Ernst (1990), which is most consistent with the hornblende geobarometer calibrated below 2 kb by the sphalerite geobarometer (Fig. 3), the solidification pressures of the Inada coarse granite and the granitic rocks genetically related to the Kiwada and Fijigadani mining districts are estimated as 2.1 and 1.4–2.2 kb, respectively (data from Takahashi, 1993). In addition, the solidification pressure of the granitic rocks in the Tsukuba area except for the Inada coarse granite is estimated as 3–4.5 kb based on the mineral assemblages of the surrounding metamorphic rocks (Shiba, 1982) and that of the middle tonalite in the main zone of the Hidaka metamorphic belt is estimated to be 4 kb (Shimura *et al.*, 1992). Fig. 8 shows the relationship between the estimated solidification pressure of these granitic rocks and the ^{T}Al content of biotite. A positive correlation between these is clearly seen, and the ^{T}Al content of biotite increases with increasing solidification pressure. This indicates that the ^{T}Al content of biotite in granitic rocks can be used as a geobarometer. The following empirical equation was obtained:

$$P\ (kb) = 3.03 \times {}^{T}Al - 6.53(\pm 0.33) \quad (2)$$

where ^{T}Al is the total Al in biotite on the basis of O = 22. The pressure dependence of the ^{T}Al content of biotite in granitic rocks may be ascribed to a volume reduction due to a tschermakite substitution between biotite and coexisting magma.

Because biotite is commonly found in granitic rocks, a biotite geobarometer is applicable to almost all granitic rocks.

7. Summary

Chemical analysis of biotite in granitic rocks indicates that the ^{T}Al content of biotite differs with metal type, that is, ^{T}Al content increases in the following order: Pb-Zn and Mo deposits < Cu-Fe and Sn deposits < W deposits < non-mineralized granitic rocks. Because this order is concordant with the formation pressure estimated by a hornblende geobarometer, it is supposed that the ^{T}Al content of biotite reflects the formation pressure.

A good correlation was observed between the solidification pressure estimated by sphalerite and hornblende geobarometers and also by mineral assemblages of the surrounding rocks and the ^{T}Al content of biotite. Based on this biotite geobarometer, it is estimated that Pb-Zn and Mo deposits formed at pressures below 1 kb, Cu-Fe and Sn deposits at 1–2 kb, W deposits at 2–3 kb and non-mineralized granitic rocks were solidified at pressures above 3 kb.

In this way, the ^{T}Al content of biotite of granitic rocks may be a useful indicator in the exploration of hydrothermal ore deposits related to granitic rocks.

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