Uncertainty in pressure difference of empirical geobarometers

Takeshi IKEDA*, Kazuhiro MIYAZAKI** and Hirohisa MATSUURA**

*Department of Earth and Planetary Sciences, Kyushu University, 744 Motoooka, Fukuoka 819-0395, Japan

**Geological Survey of Japan, AIST, Higashi 1-1-1, central 7, Tsukuba 305-8561, Japan

This study evaluates uncertainty in pressure difference of empirical geobarometers derived from thermodynamic properties, which is expressed as:

$$\sigma_{P_2-P_1}^2 = \left(\frac{T_2 - T_1}{\Delta V} \sigma_{\Delta S} \right)^2 + \left(\frac{P_2 - P_1}{\Delta V} \sigma_{\Delta V} \right)^2.$$

The uncertainty is independent of enthalpy and its uncertainty, and increases mainly with increasing temperature difference. Examination of several empirical geobarometers reveals that the uncertainty in pressure difference is smaller than that in pressure estimation by a factor of at least one third within the temperature range of almost every single metamorphic complex.

Keywords: Geobarometers, Pressure difference, Uncertainty

INTRODUCTION

Thermobaric structure of a metamorphic complex provides important information on the location and scale of heat source of metamorphism and crustal deformation during exhumation of the complex. Revealing the thermobaric structure has relied mainly upon geothermobarometry. The uncertainty of geobarometers stems from numerous factors such as thermodynamic properties, activity model, analytical errors of mineral chemistry and ambiguity in interpretation of microstructures (e.g., Kohn and Spear, 1991; Spear, 1993). The first factor leads to the magnitude of uncertainty in pressure (σ_P) generally comparable to 100 MPa (e.g., Hodges and McKenna, 1987; Kohn and Spear, 1991; Eckert et al. 1991). An error of 100 MPa in estimated pressure corresponds to the ambiguity in crustal depth of about 3.6 km. This feature causes difficulty in deciphering precise thermobaric structures in metamorphic complexes, and thus in employing them as constraints to evaluate the validity of any numerical models of crustal evolution. Especially for low-pressure (P) and high-temperature (T) type met-

amorphic complexes, the pressure estimation with σ_P of 100 MPa cannot provide more useful information than presence of sillimanite or andalusite at middle-grade.

On the other hand, pressure difference between the distant samples in a single metamorphic complex is also valuable to estimate an apparent pressure gradient. This feature enables to recognize change in crustal thickness during exhumation. Therefore, the evaluation of the magnitude of uncertainty in estimated pressure difference, $\sigma_{P_2-P_1}$, is also important. It is pointed out that the pressure difference between samples obtained by a single geobarometer involves much smaller uncertainty than the pressure estimation because the uncertainties derived from thermodynamic properties are cancelled out (Kohn and Spear, 1991; Spear, 1993). Ikeda et al. (2017) evaluate $\sigma_{P_2-P_1}$ of two geobarometers of Hoisch (1990) as 10 MPa, much smaller than σ_P for samples with temperature difference of 210 °C, whereby they enable to detect crustal thinning during retrograde stage of the metamorphism. However, it is still not shown in the general form how precise the pressure difference is determined.

This study presents the general expression that describes $\sigma_{P_2-P_1}$, and examines the magnitude of $\sigma_{P_2-P_1}$ of several empirical geobarometers.

doi:10.2465/jmps.170424

T. Ikeda, ikeda@geo.kyushu-u.ac.jp Corresponding author

K. Miyazaki, kazu-miyazaki@aist.go.jp

H. Matsuura, h.matsuura@aist.go.jp

ESTIMATION OF PRESSURE DIFFERENCE

The geobarometry employs fluid-independent reactions that describe stoichiometric relation among phase components expressed as:

$$0 = \sum_i \nu_i \Phi_i \quad (\text{Eq. 1}),$$

where Φ_i and ν_i represent molar chemical formula of phase component i and its stoichiometric coefficient, respectively. The equilibrium condition may be described as a function of P , T , and equilibrium constant (K) in the form:

$$0 = \Delta H - T\Delta S + P\Delta V + RT\ln K \quad (\text{Eq. 2}),$$

where R represents gas constant. Changes of enthalpy, entropy and volume of reaction 1, referred to as ΔH , ΔS , and ΔV , respectively, are usually treated as constant at pressures for crustal depth. Rewriting Eq. 2 shows:

$$P = -\frac{\Delta H}{\Delta V} + \frac{\Delta S - R\ln K}{\Delta V} T \quad (\text{Eq. 3}).$$

This equation represents a line denoted as isopleth for a value of K in P - T space. The reactions with large ΔV , corresponding mostly to net-transfer reactions, are used as geobarometer while exchange reactions with small ΔV are used as geothermometer.

Consider two samples of which temperature is known as T_1 and T_2 , and their equilibrium constant of the reaction used as geobarometer is K_1 and K_2 . Subtraction of Eq. 3 for each sample yields the following equation that describes pressure difference between the samples, $P_2 - P_1$ (Ikeda, 2004):

$$P_2 - P_1 = \frac{\Delta S}{\Delta V}(T_2 - T_1) - \frac{RT_2 \ln K_2 - RT_1 \ln K_1}{\Delta V} \quad (\text{Eq. 4}).$$

It is emphasized that the pressure difference can be described without information of ΔH .

UNCERTAINTY OF PRESSURE AND PRESSURE DIFFERENCE

For the construction of conventional geobarometer, three constants in Eq. 3, ΔH , ΔS , and ΔV , are determined by compiling the thermodynamic properties of minerals or by experiments for the end-member reaction shown as Eq. 1, in which K is unity. The choice of activity model is independent of this procedure, suggesting that σ_P of the

conventional geobarometer stems not only from the thermodynamic properties but also from the activity models and equilibrium constant.

In contrast, empirical geobarometer employs the reactions which contain plural phase components for a single mineral. For instance, the reaction almandine + 2 grossular + muscovite = 3 anorthite + annite contains two components for garnet. It is unable to experimentally determine the P - T position of the end-member reactions directly because a solid solution mineral cannot have pure composition for more than one phase component simultaneously. In the above example, pure almandine never coexists with pure grossular. Alternatively, the thermodynamic properties in Eq. 3 are determined by setting activity models beforehand. A set of chemical composition of the coexisting minerals, of which equilibrium P - T condition is determined experimentally or by conventional geothermobarometry, provides an equilibrium constant K according to the adopted activity models. Substituting these values (P , T , and K) into Eq. 3 yields an equation that contains three variables $\Delta H/\Delta V$, $\Delta S/\Delta V$, and $1/\Delta V$. Multiple regression of plural samples gives a reliable solution as the averages with their standard deviations that are mutually correlated. The uncertainties in pressure and pressure difference of the empirical geobarometers may be, therefore, evaluated based on the assumption that the activity model of minerals is well-established for the relevant geobarometer.

The magnitude of uncertainty in ΔV , i.e., $\sigma_{\Delta V}$ is directly obtained from the standard deviation of $1/\Delta V$. Those in ΔH and ΔS , denoted as $\sigma_{\Delta H}$ and $\sigma_{\Delta S}$, respectively, are obtained by the general expression of error propagation (cf. Spear, 1993):

$$\sigma_Z^2 = \sum_i \sum_j \left(\frac{\partial Z}{\partial x_i} \right) \left(\frac{\partial Z}{\partial x_j} \right) \sigma_i \sigma_j r_{ij} \quad (\text{Eq. 5}),$$

where Z is a parameter as a function of variables x_i and x_j . This corresponds to ΔH and ΔS in this study. The variables x_i and x_j show two of three $\Delta H/\Delta V$, $\Delta S/\Delta V$, and $1/\Delta V$, and r_{ij} refers to the correlation coefficient between the two variables. The obtained $\sigma_{\Delta H}$, $\sigma_{\Delta S}$, and $\sigma_{\Delta V}$ are mutually independent, and are responsible for the uncertainties in pressure and pressure difference. Applying the general expression that represents propagation of uncertainties derived from independent variables (cf. Taylor, 1997) to Eq. 3 yields σ_P as a function of $\sigma_{\Delta H}$, $\sigma_{\Delta S}$, and $\sigma_{\Delta V}$ expressed as:

$$\sigma_P^2 = \left(\frac{1}{\Delta V} \sigma_{\Delta H} \right)^2 + \left(\frac{T}{\Delta V} \sigma_{\Delta S} \right)^2 + \left(\frac{P}{\Delta V} \sigma_{\Delta V} \right)^2 \quad (\text{Eq. 6}).$$

Table 1. List of empirical geobarometers investigated in this study

Geobarometer	Assemblage	Reaction	Reference
H90R1	Grt-Bt-Pl-Qtz	1/3 pyrope + 2/3 grossular + eastonite + 2 quartz = 2 anorthite + phlogopite	1
H90R2	Grt-Bt-Pl-Qtz	1/3 almandine + 2/3 grossular + siderophyllite + 2 quartz = 2 anorthite + phlogopite	1
H90R3	Grt-Ms-Pl-Qtz	1/3 pyrope + 2/3 grossular + muscovite + 2 quartz = 2 anorthite + MgAl celadonite	1
H90R4	Grt-Bt-Ms-Pl-Qtz	1/3 grossular + 1/3 phlogopite + 2/3 muscovite + 2 quartz = anorthite + MgAl celadonite	1
H90R5	Grt-Bt-Ms-Pl	pyrope + grossular + muscovite = 3 anorthite + phlogopite	1
H90R6	Grt-Bt-Ms-Pl	almandine + grossular + muscovite = 3 anorthite + annite	1
GS81R1	Grt-Bt-Ms-Pl	pyrope + grossular + muscovite = 3 anorthite + phlogopite	2
HC85R3	Grt-Bt-Ms-Pl	almandine + grossular + muscovite = 3 anorthite + annite	3
HC85R4	Grt-Bt-Ms-Pl-Qtz	almandine + 2 grossular + 3 muscovite + 6 quartz = 6 anorthite + 3 FeAl celadonite	3
HC85R5	Grt-Bt-Ms-Pl-Qtz	grossular + annite + 2 muscovite + 6 quartz = 3 anorthite + 3 FeAl celadonite	3
HC85R11S	Sil-Grt-Bt-Ms-Pl	annite + 2 muscovite + 15 anorthite = 5 grossular + 3 FeAl celadonite + 12 sillimanite	3
HC85R11K	Ky-Grt-Bt-Ms-Pl	annite + 2 muscovite + 15 anorthite = 5 grossular + 3 FeAl celadonite + 12 kyanite	3
KS90a	Grt-Hbl-Pl-Qtz	6 anorthite + 3 tremolite = 2 grossular + pyrope + 3 tschermakite + 6 quartz	4
KS90b	Grt-Hbl-Pl-Qtz	6 anorthite + 3 Fe-actinolite = 2 grossular + almandine + 3 Fe-tschermakite + 6 quartz	4
GAPES	Grt-Opx-Pl-Qtz	anorthite + enstatite = 2/3 pyrope + 1/3 grossular + quartz	5
GADS	Grt-Cpx-Pl-Qtz	anorthite + diopside = 1/3 pyrope + 2/3 grossular + quartz	5

Abbreviations: Bt, biotite; Grt, garnet; Hbl, hornblende; Ky, kyanite; Ms, muscovite; Pl, plagioclase; Qtz, quartz; Sil, sillimanite.

1, Hoisch (1990); 2, Ghent and Stout (1981); 3, Hodges and Crowley (1985); 4, Kohn and Spear (1990); 5, Newton and Perkins (1982), Eckert et al. (1991).

In contrast, the pressure difference is obtained without information of ΔH (Eq. 4), as described before. Therefore the pressure difference involves ΔS and ΔV as the source of uncertainty. Applying again the general expression of error propagation of independent $\sigma_{\Delta S}$ and $\sigma_{\Delta V}$ provides the uncertainty of pressure difference as:

$$\sigma_{P_2-P_1}^2 = \left(\frac{T_2 - T_1}{\Delta V} \sigma_{\Delta S} \right)^2 + \left(\frac{P_2 - P_1}{\Delta V} \sigma_{\Delta V} \right)^2 \quad (\text{Eq. 7}).$$

Equation 7 represents a general expression that evaluates $\sigma_{P_2-P_1}$ derived from the uncertainties of thermodynamic properties of the reaction. Comparison of Eq. 7 with Eq. 6 emphasizes that not only the term $\sigma_{\Delta H}$ disappears but also the terms $\sigma_{\Delta S}$ and $\sigma_{\Delta V}$ are multiplied by temperature- and pressure-differences, respectively, that are much smaller than absolute temperature and pressure. This suggests that $\sigma_{P_2-P_1}$ is significantly smaller than σ_P .

Use of different geobarometers with similar σ_P pro-

vides the magnitude of $\sigma_{P_2-P_1}$ larger than σ_P by a factor of about $\sqrt{2}$. In contrast, the difference in pressure using the same geobarometer is expressed as Eq. 4. Evaluating $\sigma_{P_2-P_1}$ directly from Eq. 4 leads to the present conclusion. Kohn and Spear (1991) indicate that the uncertainties of thermodynamic properties cancel out in estimating pressure difference based on the same geobarometer. This assertion is appropriate only when temperatures of two samples are identical with assuming $\sigma_{\Delta V} = 0$.

EXAMINATION OF EMPIRICAL GEOBAROMETERS

We estimate σ_P and $\sigma_{P_2-P_1}$ derived from $\sigma_{\Delta H}$, $\sigma_{\Delta S}$, and $\sigma_{\Delta V}$ for the empirical geobarometers listed in Table 1. For this evaluation, we need information of $\sigma_{\Delta H}$, $\sigma_{\Delta S}$, and $\sigma_{\Delta V}$, or alternatively $\sigma_{\Delta H/\Delta V}$, $\sigma_{\Delta S/\Delta V}$, and $\sigma_{1/\Delta V}$ together with the set of r_{ij} that appears in Eq. (5). Kohn and Spear (1990) show the latter information, and the values of $\sigma_{\Delta H}$ and $\sigma_{\Delta S}$ are

Table 2. Thermodynamic properties with their uncertainties and uncertainties in pressure and pressure difference

Geobarometer	ΔH	$\sigma_{\Delta H}$	ΔS	$\sigma_{\Delta S}$	ΔV (10^5)	$\sigma_{\Delta V}$ (10^5)	σ_P^*	$\sigma_{P_2 - P_1}^{**}$ (MPa)		
	(J)	(J)	(J/K)	(J/K)	(J/Pa)	(J/Pa)	(MPa) ΔT ($^{\circ}\text{C}$)	0	200	400
H90R1	31830.6	1284.4	79.0281	1.6027	3.81446	0.05481	55	3	9	17
H90R2	46707.2	1419.2	85.5824	1.5880	3.89856	0.005227	55	0	8	16
H90R3	20681.4	2796.1	69.8341	4.2334	4.17399	0.14807	123	7	22	41
H90R4	21664.0	2027.1	33.7500	3.0804	2.19415	0.10862	171	10	30	57
H90R5	3546.01	4100.13	121.347	5.182	6.37161	0.21862	106	7	18	33
H90R6	55530.4	4094.7	140.635	5.803	6.59940	0.21807	109	7	19	36
GS81R1	-37188.4	2093.0	69.802	4.186	7.27527	0	64	0	12	23
HC85R3	69965	12372	162.992	14.527	7.5400	0	253	0	39	77
HC85R4	189029	31096	352.644	35.719	15.6432	0	303	0	46	91
HC85R5	127813	21401	199.535	24.656	8.1032	0	403	0	61	122
HC85R11S	-124432	38966	-579.128	43.886	-24.6460	0	238	0	36	71
HC85R11K	-214708	39047	-736.280	44.446	-31.6180	0	187	0	28	56
KS90a	79507	12936	-29.14	15.704	-10.9880	0.65198	189	12	31	58
KS90b	35327	15663	-56.09	17.781	-11.9060	0.79382	203	13	33	61
GAPES	8230	2520	-31.048	2.679	-2.373	0	155	0	23	45
GADS	6020	3470	-39.738	2.679	-2.312	0	190	0	23	46

* Calculated based on Eq. 6 at nominal P , T of 600 MPa and 727 $^{\circ}\text{C}$.

** Calculated based on Eq. 7 at nominal pressure difference of 200 MPa.

obtained by Eq. 5. Ghent and Stout (1981), Hodges and Crowley (1985), and Eckert et al. (1991) assume $\sigma_{\Delta V} = 0$. Hodges and Crowley (1985) examine ten fluid-independent net-transfer reactions and conclude that four of them are useful as geobarometers, which are examined in this study. The regression done by Hoisch (1990) also includes the Margules parameters of activity. They are not taken into account in this study, which provides minimum estimate of the uncertainty.

The obtained ΔH , ΔS , and ΔV with their uncertainties are summarized in Table 2. The geobarometers H90R5 and GS81R1 employ the same reaction, as is the case of H90R6 and HC85R3. These two pairs show different thermodynamic properties (Table 2), which is ascribed to the choice of different activity models. The pressure difference is not sensitive to the choice of activity model (cf. Ikeda, 2004). However, use of inadequate activity model may cause large uncertainties in thermodynamic properties. Table 2 also shows σ_P based on Eq. 6 at a nominal P - T of 727 $^{\circ}\text{C}$ (1000 K) and 600 MPa, and $\sigma_{P_2 - P_1}$ based on Eq. 7 at nominal temperature differences of 0, 200, and 400 $^{\circ}\text{C}$ assuming the same pressure difference of 200 MPa.

DISCUSSION AND CONCLUSIONS

The relative uncertainty in ΔV for most geobarometers is as small as less than 5%, except for KS90a and KS90b that

possess 6–7%. The pressure difference has the same relative uncertainty if temperature is the same, as is clear in Eq. 7. This uncertainty is negligibly small less than 13 MPa at pressure difference of 200 MPa (Table 2), and does not exceed 20 MPa at pressure difference of 400 MPa. Thus the main source in $\sigma_{P_2 - P_1}$ originates from ΔS . The magnitude of $\sigma_{P_2 - P_1}$ increases with increasing temperature difference. For temperature difference of 400 $^{\circ}\text{C}$, the magnitude of $\sigma_{P_2 - P_1}$ does not still exceed 60 MPa that is approximately one third of σ_P for most geobarometers. The uncertainties of 60 MPa correspond to the ambiguity in crustal thickness of about 2 km. When we choose a reference condition at middle-grade of a metamorphic complex as P_1 - T_1 , the metamorphic temperatures at any grade of the complex may not exceed ± 400 $^{\circ}\text{C}$ from T_1 . This indicates that we enable to recognize the relative depth of metamorphic rocks with precision of about 2 km.

Low- P and high- T metamorphic complexes show the field P - T curves that intersect the univariant curve of andalusite = sillimanite. This reaction is located between 530 $^{\circ}\text{C}$, 420 MPa of triple point (Bohlen et al. 1991) and about 850 $^{\circ}\text{C}$ at atmospheric pressure. Supposing we examine the pressure difference along the sillimanite isograd of a metamorphic complex, the maximum temperature difference of 320 $^{\circ}\text{C}$ brings the maximum $\sigma_{P_2 - P_1}$ of 50 MPa. This implies that it may be possible to recognize pressure difference along the isograd.

The present evaluation may be applicable to the conventional geobarometers to examine σ_P and $\sigma_{P_2-P_1}$ derived only from ΔH , ΔS , and ΔV of the end-member reactions. The assemblage garnet, plagioclase, kyanite, and quartz (GASP) is extensively used for geobarometry. Newton and Haselton (1981) report $\sigma_{\Delta H}$ and $\sigma_{\Delta S}$ of 1256 J and 4.186 J/K, respectively, for the reaction 3 anorthite = grossular + 2 kyanite + quartz. This provides σ_P of 66 MPa at 727 °C, 600 MPa, while $\sigma_{P_2-P_1}$ of 25 MPa at temperature differences of 400 °C. This uncertainty is smaller than or comparable to the empirical geobarometers.

The arguments lead to the following conclusions. We present Eq. 7 that evaluates the uncertainty in pressure difference of geobarometers derived from thermodynamic properties. The magnitude of $\sigma_{P_2-P_1}$ is less than 60 MPa for most geobarometers examined in this study when temperature difference is less than 400 °C. This suggests that we are able to recognize 2 km difference in crustal thickness of a metamorphic complex.

ACKNOWLEDGMENTS

We are grateful to T. Kawakami, I. Ashchepkov, and C-M Wu for review and T. Tsunogae for editorial handling. This work was financially supported in part by the Japan Society for the Promotion of Science KAKENHI Grant Number JP C25400518.

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Manuscript received April 24, 2017

Manuscript accepted August 2, 2017

Manuscript handled by Toshiaki Tsunogae