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THE STABILITY OF THE ASSEMBLAGE ZOISITE + DIOPSIDE

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ABSTRACT

New reversed experimental data on the equilibrium 12 zoisite + diopside = 13 anorthite + 4 grossular + spinel + $6H_2O$ are presented and shown to be consistent with published thermodynamic data. The calculated *T–P* coordinates of the invariant assemblage zoisite–diopside–anorthite–grossular–spinel–clinochlore–water vapor are 610°C, 3.1 kbars. This assemblage is of interest in studies of the high-temperature metamorphism of rodingites because rocks containing stable diopside + zoisite + spinel + H_2O can only have crystallized at pressures more than 3.1 kbars, whereas those containing chlorite + grossular + anorthite + H_2O can only have crystallized below 3.1 kbars. The invariant point thus can serve as a bathogradic reference point in metarodingites.

Keywords: experimental, thermodynamic, equilibrium, diopside, zoisite, anorthite, spinel, chlorite, grossular, metarodingites, bathograde.

SOMMAIRE

Les résultats de nouvelles expériences renversées portant sur l'équilibre 12 zoïsite + diopside = 13 anorthite + 4 grossulaire + spinelle + $6H_2O$ concordent avec les prédictions fondées sur les données thermodynamiques publiées. L'assemblage invariant zoïsite – diopside – anorthite – grossulaire – spinelle – clinochlore – phase aqueuse serait stable à 610°C, 3.1 kbars. Cet assemblage est important pour les études du métamorphisme des rodingites à haute température; l'assemblage diopside + zoïsite + spinelle + H_2O est limité à une pression supérieure à 3.1 kbars, tandis que l'assemblage chlorite + grossulaire + anorthite + H_2O indique une pression inférieure à 3.1 kbars. Le point invariant sert donc de point de référence bathograde pour les métarodingites.

(Traduit par la Rédaction)

Mots-clés: expérimental, thermodynamique, équilibre, diopside, zoïsite, anorthite, spinelle, chlorite, grossulaire, métarodingites, bathograde.

INTRODUCTION

Available evidence suggests that rodingites are metasomatic rocks associated with low-temperature serpentinization of adjacent ultramafic rocks (Coleman 1966, Rice 1983). Deductions on the pressures and temperatures that prevailed during rodingitization and subsequent metamorphism are based on a combination of experimental and theoretical work and field data. This paper reports new reversed experimental data bearing on the reaction: 12 zoisite + diopside = 13 anorthite + 4 grossular + spinel + $6H_2O$.

Rice (1983) has presented a set of computed equilibria that are in agreement with the mineralogy and natural occurrences of metarodingites. Wang (1986) and Wang & Greenwood (1988) have presented direct experimental data on one of these equilibria: grossular + clinochlore = 3 diopside + 2 spinel + 4 H_2O. It was investigated using cold-seal pressure vessels from 550 to 700°C at 0.5 kbars to 4.0 kbars. Analysis of internal consistency by linear programming indicated that the experimental results from that study are consistent with both the data of Berman (1988) and the data base of Helgeson *et al.* (1978).

A combination of the results of Wang (1986) and Wang & Greenwood (1988) with the new data fixes the location of the seven-phase invariant point involving zoisite, diopside, anorthite, grossular, spinel, chlorite and water vapor in the system $CaO–MgO–Al_2O_3–SiO_2–H_2O$.

EXPERIMENTAL PROCEDURE

Apparatus

All experiments were made in René 41 cold-seal pressure vessels, which were placed in horizontal nichrome-wound cylindrical furnaces. Temperatures were maintained by solid-state proportional controllers and measured by sheathed chromel–alumel thermocouples, which were connected to an automatic data-recording system or a calibrated digital thermometer. Pressures were monitored daily on an Ashcroft Maxisafe gauge or a Heise bourdon tube gauge. The reported temperatures and pressures are believed to be accurate to within ± 5°C and ± 20 bars, respectively.

Starting materials

In the system studied, diopside is the only phase that might show solid solution; Wang (1986) and

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TABLE 1. CONDITIONS OF SYNTHESIS OF THE PHASES FROM OXIDE MIXTURES

Phase	Compositions	T°(C)	P (kbar)	t(h)
Zoisite	$Ca_2Al_3Si_3O_{12}(OH)$	550	15	75
Diopside	$CaMgSi_2O_6$	795	2	288
Anorthite	$CaAl_2Si_2O_8$	700	2	240
Grossular	$Ca_3Al_2Si_3O_{12}$	750	2	288
Spinel	$MgAl_2O_4$	795	2	288

TABLE 2. EXPERIMENTAL RESULTS ON THE STABILITY OF ZOISITE + DIOPSIDE

Run No.	T Starting mix	T (°C)	P (Kbar)	t (hrs)	Comments
Wr-6	Oxide mix	725	4	536	An+Grs
WR-7	Oxide mix	550	4	383	An+Grs
WR-8	Oxide mix	550	4	547	An+Grs
WR-5	Oxide mix	600	4	531	An+Grs
WR-15	Zo+Di+An+Grs+Spl	601	4	624	Zo growth, An+Grs present, Di gone
WR-17	Zo+Di+An+Grs+Spl	678	4	516	possible An growth Zo present
WR-18	Zo+Di+An+Grs+Spl	678	4	516	no reaction
WR-19	Zo+Di+An+Grs+Spl	648	4	504	Zo growth, An+Grs present
WR-21	Zo+Di+(An+Grs+Spl)	648	4	504	Zo growth, An+Grs present
WR-13	Oxide mix	650	4	521	An+Grs present, no Zo
WR-22	Zo+Di+An+Grs+Spl	696	4	629	An+Grs growth, Zo present
WR-23	Zo+Di+(An+Grs+Spl)	696	4	629	An+Grs growth, Zo present
WR-25*	Zo+Di+An+Grs+Spl	666	4	718	Zo growth, An+Grs present
WR-26	Zo+Di+An+Grs+Spl	685	4	624	no reaction
WR-28	Zo+Di+An+Grs+Spl	673	4	792	no reaction
WR-30*	Zo+Di+An+Grs+Spl	690	4	792	An+Grs growth, Zo present
WR-40	Zo+Di+An+Grs+Spl	696	4.5	834	possible An growth, almost no reaction
WR-42*	Zo+Di+An+Grs+Spl	683	4.5	834	Zo growth, An present, Grs gone
WR-44*	Zo+Di+An+Grs+Spl	709	4.5	859	An+Grs growth, Zo present
WR-10	Oxide mix	603	4.5	480	An present
WR-11	Oxide mix	650	5	375	An+Grs present
WR-12	An+Grs+Spl	650	5	375	An+Grs present, Spl gone
WR-32	Zo+Di+An+Grs+Spl	650	5	375	Zo present, An+Grs present
WR-13	Oxide mix	725	5	336	An+Grs present, no Zo
WR-33*	Zo+Di+An+Grs+Spl	727	5	336	An+Grs growth, Zo present
WR-34	Zo+Di+An+Grs+Spl	698	5	494	Zo growth, An present Grs gone(?)
WR-36	Zo+Di+An+Grs+Spl	716	5	840	no reaction
WR-38*	Zo+Di+An+Grs+Spl	707	5	840	Zo growth, An present Grs gone

* Key limiting experiments.

Wang & Greenwood (1988) showed that the diopside resulting from the reaction Grs + Clin = 3 Di + 2 Spl + 4 H_2O contains aluminum. [The abbreviations are as recommended by Kretz (1983)]. We deduced that the aluminum content is metastable, and that it has no measurable effect on the position of the equilibrium studied.

The five phases considered in this study were synthesized from oxide mixtures, *i.e.*, periclase, cristobalite, γ-Al_2O_3, lime and distilled water, which were combined according to the desired weight proportion for each phase. To minimize the effect of weighing errors, five-gram batches of oxide mixes were prepared for each phase, and the mixture ground by hand under alcohol for at least 2 hours.

The conditions of synthesis of the phases are given in Table 1. Zoisite was synthesized at 550°C and 15 kbars for 3 days. SEM and XRD examination of the products showed no extraneous phases and no clinozoisite. Attempts to synthesize pure zoisite at 550°C, 4 kbars for one month failed, the products always showing the presence of anorthite with the zoisite. An attempt at 550°C, 10 kbars for 7 days also failed.

All synthetic phases were examined using an optical microscope, X-ray diffraction and a scanning electron microscope. In addition, attempts were made to synthesize from oxide mixtures the stoichiometric phase assemblages on both sides of the reaction, *i.e.*, 12 Zo + Di, and 13 An + 4 Grs + Spl. The assemblage 13 An + 4 Grs + Spl was produced under two different conditions: 4 kbars, 725°C, and 5 kbars, 725°C. Optical examination revealed anorthite and grossular in approximately 4:1 proportions as expected from the stoichiometry of the reaction. No spinel could be seen with the optical microscope, presumably because of its low molar ratio with respect to the other components in the reacting bulk composition.

The assemblage 12 Zo + Di could not be synthesized directly from oxide mixtures at 4 or 5 kbars, although the reaction reversals indicate that synthesis should be possible. The products of these synthesis experiments were always anorthite and grossular, which we believe to be metastable on the basis of our reversal experiments. Several reversal experiments were made using natural zoisite from Buck Creek, North Carolina, which contains 1.5% FeO + Fe_2O_3, 0.03% MnO, and 0.45% MgO. The product of the equivalent (WR-6) containing anorthite + grossular was used as starting material for reversal experiments WR-21 and WR-23. Appropriate amounts of synthetic zoisite and diopside were then added to the anorthite + grossular + spinel mixture for 4:1 and 1:4 ratio of product and reactant.

Reversal experiments

The direction of reaction was determined using the paired capsule technique, in which different starting mixtures were set side-by-side in each pressure vessel. Gold capsules 20 mm long and 3 mm in diameter with 0.2 mm walls with condensed assemblages and approximately 20% water were sealed by welding. The condensed charge for each experiment consisted of powdered mixtures of the reacting assemblages. One capsule held reactants and products in 4:1 ratio, and the other held products and reactants in 4:1 ratio.

Analysis of products

Quenched charges were analyzed with the optical microscope, X-ray diffraction and SEM. XRD scans of products were made with a Norelco diffractome-

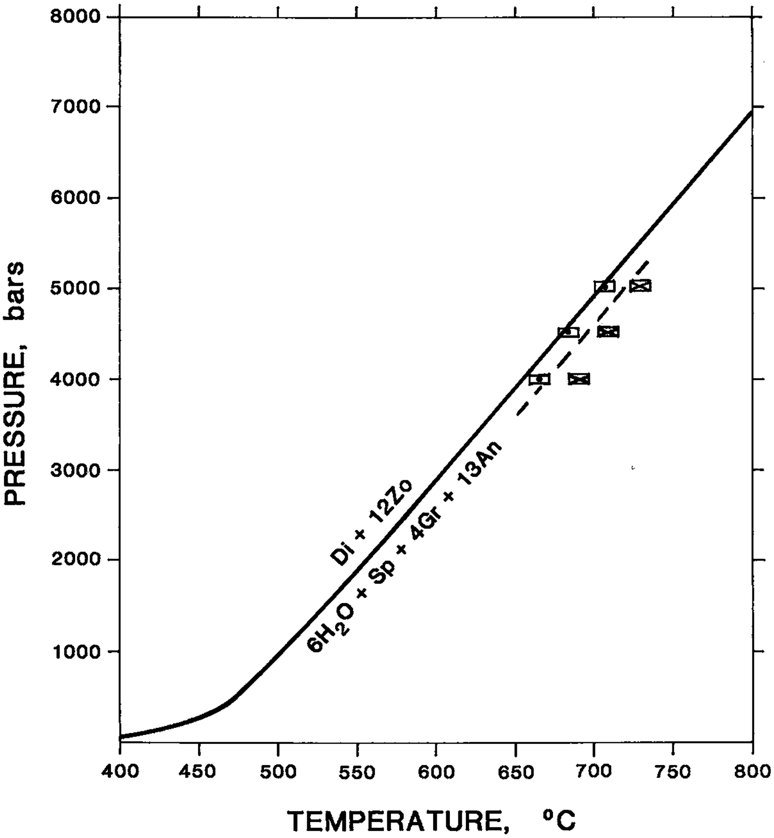

FIG. 1. Calculated equilibrium curves for the reaction 12 Zo + Di = 13 An + 4 Grs + Spl + $6H_2O$. Limiting experimental brackets are from this study. Symbols with central dot represent stable growth of Zo + Di from An + Di + Spl, and those with a cross-mark, the stable growth of An + Di + Spl from Zo + Di. The dots and crosses mark the locations of the nominal P - T conditions of each experiment, and the limits of each box indicate the range of uncertainty in the P–T conditions of each. Only critically limiting experiments are plotted. The solid curve was calculated with data from Table 3, whereas the dashed curve was calculated using a $\Delta H°_f(298,1)$ of 657076 kJ for the reaction. Set text for discussion.

ter using Ni-filtered Cu$K\alpha$ radiation at 2°2θ per minute. Changes in amounts of product and reactant assemblages were detected by changes in intensities of diffraction maxima. Changes in relative peak-height of selected product and reactant phases of more than about 15% were interpreted as evidence of reaction and confirmed by SEM examination.

RESULTS OF EXPERIMENTS

Table 2 summarizes the experimental results of the reversal experiments. Experiments were performed from 550 to 725°C at 4 kbars, from 685 to 709°C at 4.5 kbars and from 650 to 707°C at 5 kbars. Experiments WR-18 and WR-19, using the natural zoisite, gave the same results as experiments WR-17 and WR-21, made using synthetic zoisite under the same conditions. Experiments WR-21 and WR-23, containing the products of experiment WR-6 (synthesized from oxide mixture), gave the same results as experiments WR-19 and WR-22, which started with mixtures of the phases synthesized separately. Key experiments demonstrating reversal are labeled by asterisks. Using the extremes of the uncertainties in pressure and temperature of each experiment, one can define rectangular P–T areas (Fig. 1) within which the univariant reaction must lie. The brackets limiting the equilibrium conditions are: 660 and 690°C at 4 kbars; 683 and 709°C at 4.5 kbars; and 707 and 727°C at 5 kbars.

Figures 1 and 2 show only the critically limiting experiments and various calculated curves separat-

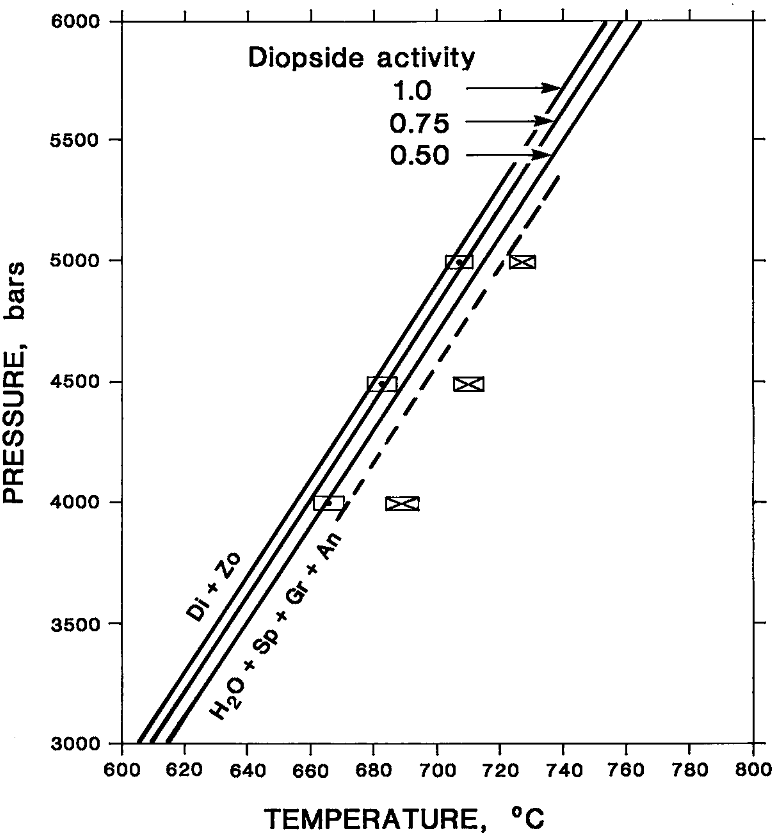

FIG. 2. Equilibrium curves calculated using different values assumed for the activity of Di, and a different $\Delta H^\circ_f(298,1)$. Solid curves show the possible effects of different activities of Di, and the dashed curve shows the effect of a different $\Delta H^\circ_f(298,1)$ of reaction. See text for discussion.

ing stable products from stable reactants. In Figure 1, the solid curve gives the position required by the data of Berman (1988) (see Table 3). Whereas the curve is only just consistent with the experiments, there is no absolute requirement that would force a curve through the midpoints of the brackets. However, a slight change of only 23.08 kJ in the $\Delta H^\circ(298,1)$ of the reactants or products will shift the curve 20°C to the position of the dashed curve. In terms of zoisite, this represents 0.0269% or 1.923 kJ mol^{-1}, or in terms of anorthite it represents 0.042% or 1.775 kJ mol^{-1}. If the difference were distributed between zoisite and anorthite the molar amounts per phase would be approximately halved. Without a full-scale recalculation of the entire database it is not clear how the redistribution should be made, but it is clear that the new experiments are not at odds with the experimental data that underlie the thermodynamic properties presented by Berman (1988).

DISCUSSION AND APPLICATION OF EXPERIMENTAL RESULTS

The equilibrium curve in Figure 1 was calculated with GEOCALC (Perkins *et al.* 1986) using thermodynamic properties for the phases derived from Berman (1988), and listed in Table 3. The curve calculated is consistent with all the reversed experiments, although the low-pressure, low-temperature experiment is close to the combined limits of its uncertainty. As a result, the new experimental data do not provide contradictions nor additional constraints to the data base. Only critical reversal experiments are plotted in Figure 1 because all the others, although consistent, contribute no further constraints to the position of the equilibrium.

The solid calculated curve in Figure 1 was made under the assumption that the activity of each phase is unity. However, Wang (1986) and Wang & Greenwood (1988) demonstrated that diopside from run products may contain aluminum in small amounts, interpreted to involve a metastable substitution of Ca-Tschermak and Mg-Tschermak components. It thus is possible that the activity of diopside in the present study is not unity. As a test of sensitivity to this possibility, the equilibrium curves in Figure 2 also were calculated with different values of diopside activity, *i.e.,* 1.0, 0.75, and 0.50. In addition, we show a curve calculated with unit activity and a larger ΔH, as discussed above.

The computed displacement of equilibrium curves with different activities of diopside is insignificant, but it can be seen that the experimental results are more centrally bisected by curves calculated on the assumption that diopside activity is less than unity. There is, however, no *a priori* reason to favor a central position of the equilibrium curve in relation to bracketting experiments. The critically limiting experiments were analyzed by linear programming (Berman *et al.* 1986) to yield the following thermodynamic values consistent with the new data for the reaction, as balanced for 12 zoisite:

TABLE 3. THERMODYNAMIC PROPERTIES*

Zoisite	$\Delta H^o f$(J)	S^o(J/K)	V(J/bar)	
$Ca_2Al_3Si_3O_{12}(OH)$	-6889488	297.596	13.588	
	K_0	K_1	K_2	K_3
	749.17	-6509.28	-2380525	124858368
Diopside	$\Delta H^o f$(J)	S^o(J/K)	V(J/bar)	
$CaMgSi_2O_6$	-3200583	142.5	6.620	
	K_0	K_1	K_2	K_3
	305.41	-1604.93	-7165973	921837568
Anorthite	$\Delta H^o f$(J)	S^o(J/K)	V(J/bar)	
$CaAl_2Si_2O_8$	-4228730	200.186	10.075	
	K_0	K_1	K_2	K_3
	439.37	-3734.15	0.0	-317023232
Grossular	$\Delta H^o f$(J)	S^o(J/K)	V(J/bar)	
$Ca_3Al_2Si_3O_{12}$	-6632859	255.15	12.538	
	K_0	K_1	K_2	K_3
	573.43	-2039.41	-18887168	2319311872
Spinel	$\Delta H^o f$(J)	S^o(J/K)	V(J/bar)	
$MgAl_2O_4$	-2300312	84.534	3.977	
	K_0	K_1	K_2	K_3
	235.90	-1766.58	-1710415	40616928
Clinochlore	$\Delta H^o f$(J)	S^o(J/K)	V(J/bar)	
$Mg_5Al_2Si_3O_{10}(OH)$	-8909589	435.15	21.147	
	K_0	K_1	K_2	K_3
	1214.28	-11217.13	0.0	-1256253184
Water (V)	$\Delta H^o f$(J)	S^o(J/K)	V(J/bar)	
H_2O	-241816	188.72	2445.03	
	K_0	K_1	K_2	K_3
	135.37	-4816.88	-4076072	0.0

$Cp = K_0 + k_1/T^{0.5} + K_2/T^2 + K_3/T^3$. * (Berman 1988).

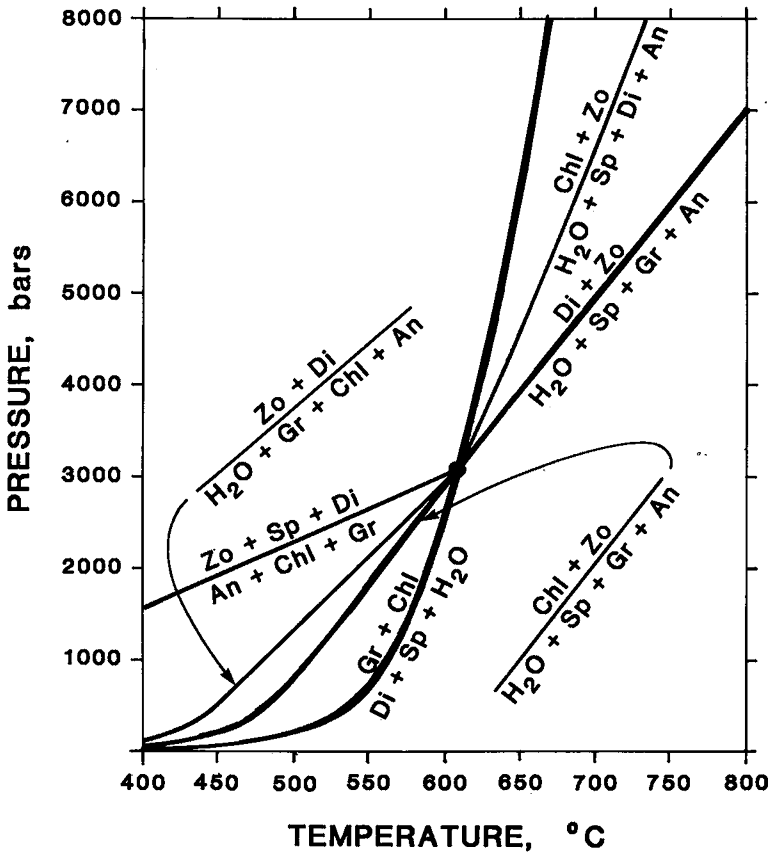

FIG. 3. Calculated position of the univariant equilibria and the related seven-phase invariant point involving An, Chl, Di, Grs, Spl, Zo, and H_2O. The bold curves have been directly measured.

$\Delta S°_r$ (298,1 bar) = 1067.72 to 2367.99 J/Kelvin
$\Delta H°_r$ (298,1 bar) = 561.66 to 1826.22 kJ

for comparison, the same values from Berman (1988) are:

$\Delta S°_r$ (298,1 bar) = 1138.18 J/Kelvin
$\Delta H°_r$ (298,1 bar) = 618.30 kJ

Given the available data, it is not possible to choose between attributing the small difference between our experiments and the Berman (1988) data to solid solution in diopside or to minor modifications of $\Delta H°_f$ (298,1) in anorthite and zoisite. Only a full recalculation of the data base can direct this choice, a labor that is not warranted in the absence of direct inconsistency.

The invariant assemblage zoisite–diopside–anorthite–grossular–spinel–clinochlore – water vapor was investigated by calculation with GE0CALC (Perkins *et al.* 1986) and using the data of Berman (1988). These data are consistent internally and with the data of Wang (1986) and Wang & Greenwood(1988), and with the new data from this study. The results are presented in Figure 3. The calculated invariant point lies at 610°C, 3.1 kbars, close to the simple intersection of the data of Wang & Greenwood (1988), with the new data from this study.

In the application of these results to the metamorphism of rodingites, the invariant point can be used as a pressure reference, or "bathograd" (Carmichael 1978). Specifically, rocks containing stable diopside + zoisite + spinel (+ H_2O) can only have crystallized above 3.1 kbars, and rocks containing stable chlorite + grossular + anorthite (+ H_2O) can only have crystallized at pressures less than 3.1 kbars. Recognition of this fact, and correction for the effects of solid solution, should allow the delineation of bathograds in terranes of metamorphosed ultramafic rocks containing metarodingites.

CONCLUSIONS

New reversed experimental data on the equilibrium 12 zoisite + diopside = 13 anorthite + 4 grossular + spinel + 6H_2O are consistent with the thermodynamic data of Berman (1988) and Helgeson *et al.* (1978). Calculated displacement of equilibrium curves for different (metastable) activities of diopside of appropriate value is insignificant, and no experimental evidence was found for such displacement. Very small changes in the standard enthalpies of formation of zoisite or anorthite (or both) would have the same effect on the position of the equilibrium as a possible solution effect arising from diopside.

A bathogradic point at 3.1 kbars and 610°C based on the invariant assemblage zoisite + diopside + anorthite + grossular + spinel + H_2O will serve in efforts to reconstruct post-metamorphic uplift histories in ultramafic terranes containing metamorphosed rodingites.

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