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Calorimetric measurements of fusion enthalpies for Ni_2SiO_4 and Co_2SiO_4 olivines and application to olivine-liquid partitioning

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Abstract—Calorimetric measurements of fusion enthalpies for Ni_2SiO_4 and Co_2SiO_4 olivines were carried out using a high-temperature calorimeter, and Ni and Co partitioning between olivine and silicate liquid was analyzed using the measured heats of fusion. The fusion enthalpy of Co_2SiO_4 olivine measured by transposed-temperature drop calorimetry was 103 ± 15 kJ/mol at melting point (1688 K). The fusion enthalpy of Ni_2SiO_4 olivine was calculated based on the enthalpies of liquids in the system $\text{An}_{50}\text{Di}_{50}\text{-Ni}_2\text{SiO}_4$ measured by transposed-temperature drop calorimetry at 1773 K, and was 221 ± 26 kJ/mol at its metastable melting point (1923 K). The fusion enthalpy of Ni_2SiO_4 is the largest among those of olivine group, this is caused by the large crystal field stabilization energy of six-coordinated Ni^{2+} in olivine. The larger fusion enthalpy of Ni_2SiO_4 can account for the large and variable partition coefficient of Ni between olivine and silicate liquid. Based on the comparison between partition coefficients calculated from thermodynamic data and those observed in partition experiments, it is considered that the magnitude of partition coefficients is primarily dependent on the heats of fusion of the components. Furthermore, the activity coefficients for Ni-, Co- and Mn-bearing components in magmatic liquid are nearly of the same magnitude. Copyright © 2003 Elsevier Science Ltd

1. INTRODUCTION

Heats of fusion of minerals are essential quantities required in theoretical analysis and formulations of phase equilibria, element partitioning, heat balance and element diffusion in magmatic system. The fusion enthalpies for common rock-forming minerals in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Na}_2\text{O-K}_2\text{O}$ (forsterite, anorthite, albite, sanidine, diopside, wollastonite, etc.) have been reported by direct calorimetric measurements for the crystalline solids and their glasses or liquids (e.g., Stebbins et al., 1983; Ziegler and Navrotsky, 1986; Richet et al., 1993) and by extrapolation of measured enthalpies of binary and ternary liquids to mineral end members (e.g., Navrotsky et al., 1989; Tarina et al., 1994). On the other hand, calorimetric measurements of enthalpies for silicate liquid and fusion enthalpies of minerals including Fe, Ni, Co and Mn have hardly been reported because of the experimental difficulties in controlling oxygen fugacity and the absorption of transition metals into sample capsules.

Olivine is one of the important minerals in understanding magma generation and evolution, and partition behavior of trace elements (Ni, Co and Mn) between olivine and liquid, as well as, Fe and Mg partitioning has been the subject of various studies (e.g., Colson et al., 1988; Beattie, 1993; Hirschmann and Ghiorso, 1994). However, because their fusion enthalpies have not yet been measured, rigorous thermodynamic analysis for Ni and Co partitioning between olivine and silicate liquid could not be performed.

In the present study, we have carried out calorimetric measurements of fusion enthalpies for Ni_2SiO_4 and Co_2SiO_4 olivines. Several experimental techniques have been tested to obtain reliable data. The fusion enthalpy of Co_2SiO_4 was de-

termined directly by transposed-temperature drop calorimetry between 1373 and 1773 K. The fusion enthalpy of Ni_2SiO_4 was determined by transposed-temperature drop calorimetry for the liquid in the system $\text{An}_{50}\text{Di}_{50}\text{-Ni}_2\text{SiO}_4$ at 1773 K and extrapolation of those results to the composition Ni_2SiO_4 . Based on the fusion enthalpies of M_2SiO_4 (M = Mg, Fe, Ni, Co, Mn) olivines measured in this study and reported in previous works, thermodynamic analysis of element partitioning between olivine and silicate liquid is performed and the factors affecting the variation of partition coefficients are discussed.

2. EXPERIMENTAL PROCEDURE

2.1. Synthesis and Analysis

The powder samples of $\text{CaAl}_2\text{Si}_2\text{O}_8$ anorthite, $\text{CaMgSi}_2\text{O}_6$ diopside and Ni_2SiO_4 and Co_2SiO_4 olivines were prepared from high purity reagents of SiO_2 , Al_2O_3 , MgO , NiO , CoO and CaCO_3 . To make each sample of ~5 g, stoichiometric mixtures of the reagents were ground in an agate mortar with alcohol for 1 h and pressed into pellets.

A pellet of the stoichiometric mixture of anorthite composition was heated slowly to 1773 K in a Pt crucible and kept for 72 h under the atmosphere. Two cycles of heating and grinding were carried out to obtain single-phase anorthite. Forsterite was made using a similar procedure.

The stoichiometric mixture of diopside composition was heated in a Pt crucible from room temperature with rate of 2.2 K/min using a vertical quenching furnace, kept at 1873 K for 1 h, and was dropped into water. The diopside glass obtained by quenching was ground and pressed into pellets. Crystalline diopside was obtained by heating the diopside glass pellets at 1523 K for 72 h in air.

Co_2SiO_4 olivine was synthesized from the stoichiometric oxide mixture by sintering at 1343 K for 68 h in a gas mixing

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furnace, with CO₂:H₂ of 20:1 (volume ratio). To minimize loss of Co from the sample, the pellet of oxide mixture was suspended by Pt87Rh13 wire with a diameter of 0.2 mm.

Ni₂SiO₄ olivine was synthesized from the stoichiometric mixture by sintering in air using a wire loop technique similar to that used in the synthesis of Co₂SiO₄ olivine. Six cycles of heating at 1523–1723 K for 2–3 d and grinding were needed to obtain single-phase crystalline Ni₂SiO₄.

All crystalline materials thus synthesized were checked by X-ray diffraction (XRD) and electron probe microanalyzer (EPMA). X-ray powder diffraction data for these materials agreed with JCPDS files. For the anorthite and diopside samples, no other phases were detected by either XRD and EPMA analyses. A very small amount of cristobalite was observed in synthesized Ni₂SiO₄ and Co₂SiO₄ olivines by XRD and EPMA analyses. The existence of excess silica mineral was probably caused by reaction between the suspending PtRh wire and the sample pellets during long heating duration.

2.2. Calorimetry

Calorimetric measurements were performed using a Setaram MHTC high-temperature calorimeter at Gakushuin University. Its design has been described in Kojitani and Akaogi (1997).

The fusion enthalpy at its melting point ΔH_{T_m} of the Co₂SiO₄ olivine was measured by transposed-temperature drop calorimetry between 1373 and 1773 K under a flowing stream of Ar (1.2 L/h). The experimental technique adopted here is basically the same as that of Kojitani and Akaogi (1995, 1997). The sample capsules were made of 0.03 mm thick Pt foil and the size was 2 mm in diameter and 6 mm in height. The powder sample was packed into the Pt capsules and dropped from outside of the calorimeter (room temperature) into a Pt crucible situated in the calorimeter detector kept at a fixed temperature between 1373–1773 K. In this study, Co-presaturated Pt capsules were used in most of experiments for Co₂SiO₄ to minimize Co loss from the samples. Experiments using Pt capsules without presaturation were also performed at 1473 and 1573 K to check the effectiveness of the presaturation method.

The Co-presaturated Pt capsules were made as follows. The Co₂SiO₄ olivine was placed in Pt capsules and heated for 24 h at the same temperature as used in drop runs under Ar gas. The Pt capsule containing the Co₂SiO₄ olivine was soaked with Pb₂B₂O₅ solvent in Pt crucible at 973 K for more than 8 h. Then the capsule was removed and soaked in nitric acid for ~48 h. After two cycles of ultrasonic wash (with water and acetone) and drying at 450 K, the capsules were observed under a stereoscope to confirm the absence of residues of silicate and borate. The Co contents in the capsules were calculated from differences of weight between before and after the saturation experiments. Co content increased with increasing temperature to a maximum of 6.1 wt% (average) at 1773 K. Compositional homogeneity in Pt were checked by EPMA analyses for some capsules. In the calorimetric runs of Co₂SiO₄ olivine, 40–60 mg of olivine powder was put into the Co-presaturated capsule. The Co contents in Pt capsules used in drop runs at 1773 K were determined to be 4.6–5.7 wt% by EPMA. Those were consistent with the average Co content in the Co-presaturated capsule before experiments (6.1 ± 1.7 wt%), indicating that

there was almost no loss or gain of Co in samples during experiments.

Drops of the sample capsules alternated with drops of standard materials for calibration of enthalpy. Corundum crystals (NBS No. 720, 50–100 mg) were used as the standard material in experiments below the melting point of Co₂SiO₄ (1688 K). Above the melting point, Co₂SiO₄ liquid in some drop runs leaked from the capsule due to its low viscosity and reacted with corundum crystals. Therefore Al₂O₃ powder (15–20 mg) was put in a Pt capsule and used as standard material in the experiments above 1688 K. Heat contents of Al₂O₃ were calculated from Cp of Richet and Fiquet (1991). Those of the PtCo alloy were calculated using Cp of Knacke et al. (1991) and the measured Co content of the Pt capsule, assuming ideal solid solution.

The fusion enthalpy of Ni₂SiO₄ olivine (ΔH_{T_m}) cannot be measured directly because Ni₂SiO₄ decomposes into NiO and cristobalite at 1818 K (Phillips et al., 1963). However, it can be estimated from data of drop experiments for liquids of binary or ternary system of end-member minerals. Navrotsky et al. (1989) performed transposed-temperature drop calorimetry for liquid in An-Fo system at 1773 K. They reported that there is no heat of mixing in that system and calculated ΔH_{T_m} of forsterite by extrapolating enthalpy data for the binary liquid to the Fo end-member. We used a similar method to determine ΔH_{T_m} of Ni₂SiO₄ olivine. Melting relations at 1773 K for systems including An, Di and Ni₂SiO₄ were examined using the vertical quenching furnace to determine compositional range of single-phase liquid suitable to calorimetric measurements. In the An-Ni₂SiO₄ system, liquid and NiAl₂O₄ spinel were observed at 1773 K over the entire range of composition. In the An₅₀Di₅₀-Ni₂SiO₄ system at 1773 K, the compositional range where Ni₂SiO₄ content ($X_{Ni_2SiO_4}$) was less than 50 mol% was above the liquidus surface and liquid + small amounts of NiO were observed at $X_{Ni_2SiO_4} = 60$ mol%. Enthalpies of mixing of the liquids in the An-Fo, An-Di and An-Di-Fo systems can be considered as zero at 1773 K according to the previous studies performed by transposed-temperature drop calorimetry for those liquids (Navrotsky et al., 1989; Kojitani and Akaogi, 1995). This suggests that the enthalpy of mixing of liquid in the An₅₀Di₅₀-Ni₂SiO₄ system is also negligible. Based on the above considerations, transposed-temperature drop calorimetry was carried out for the An₅₀Di₅₀-Ni₂SiO₄ system at 1773 K.

The calorimetric measurements for the An₅₀Di₅₀-Ni₂SiO₄ system including the standard materials and calibration method were performed in the same way as those in the drop runs for the Co₂SiO₄ olivine. Mechanical mixtures of crystalline materials were prepared by grinding together appropriately weighed mixtures (0.6–1.2 g) of An, Di and Ni₂SiO₄ olivine. Grinding for 1 h under alcohol was followed by drying at 480 K to produce the samples for the drop runs. First, the samples of crystalline mixture (22–30 mg), encapsulated in Ni-presaturated Pt capsules prepared by a method similar to Co-presaturated capsules described above, were dropped into the calorimeter at 1773 K under a flowing stream of Ar. However, baselines of heat flow in the calorimeter were always unstable and measured heat contents were not reproducible in repeated experiments. Such instabilities of heat flow had not been observed in the drop runs for Co₂SiO₄. Although the reason is not

Table 1. Results of transposed-temperature drop calorimetry of Co₂SiO₄.

T (K)	Atmosphere	Capsule ^a	State at T	H _T -H ₂₉₈ (kJ/mol) ^b	XCo (wt%) ^c
1373	Ar	PtCo	Solid	194.7 ± 15.5 (5)	0.3
1473	Ar	PtCo	Solid	223.3 ± 8.3 (5)	0.6
1473	Ar	Pt	Solid	236.3 ± 10.9 (5)	
1573	Ar	PtCo	Solid	240.3 ± 6.2 (5)	1.6
1573	Ar	Pt	Solid	251.2 ± 20.4 (5)	
1612	Ar	PtCo	Solid	241.3 ± 18.9 (5)	0.7
1652	Ar	PtCo	Solid	257.7 ± 13.5 (4)	2.4
1673	Ar	PtCo	Solid	278.2 ± 19.0 (5)	2.4
1693	Ar	PtCo	Liquid	340.3 ± 36.0 (5)	2.4
1713	Ar	PtCo	Liquid	363.0 ± 14.6 (5)	3.6
1731	Ar	PtCo	Liquid	373.5 ± 17.2 (5)	5.6
1754	Ar	PtCo	Liquid	388.1 ± 10.6 (6)	4.8
1773	Ar	PtCo	Liquid	393.0 ± 18.7 (13)	6.1

^a Capsule used in experiments. PtCo = capsule presaturated with Co₂SiO₄ before experiments.

^b Error is two standard deviations of the mean, and number in parentheses is number of experiments.

^c Co content (wt%) in Pt capsule used in experiments. Average value calculated from difference of capsule weight between before and after presaturation.

clear, it may be due to Ni diffusion from the Ni-presaturated capsule to the pure Pt crucible situated in the calorimeter. The absorption of Ni into Pt is larger than that of Co and the experimental temperatures for the Ni-bearing system (1773 K) were higher than those of the drop runs for Co₂SiO₄ (1373–1773 K).

Subsequently, drop runs for the An₅₀Di₅₀-Ni₂SiO₄ system were carried out using Pt capsules without presaturation in air (without a stream of gas) to minimize Ni-loss from the samples, then we obtained stable baselines and reliable results. Therefore we report results of the drop experiments using pure Pt capsules in air. Drop runs were also performed for Ni₂SiO₄ olivine and NiO in both air and Ar, and An and Di in an Ar gas stream at 1773 K to examine the effect of technique on the experimental results and to allow comparison of our results against published data.

3. RESULTS

3.1. Drop Calorimetry of Co₂SiO₄

Results of transposed-temperature drop calorimetry for Co₂SiO₄ are shown in Table 1 and Figure 1. The H_T-H₂₉₈ of Co₂SiO₄ olivine measured using Co-presaturated capsules is consistent with that calculated from the heat capacity equation (Robie et al., 1982, 1984) below the melting point (1688 ± 5 K, Masse and Muan, 1965). However, the data derived from Pt capsules without presaturation are slightly larger than the data obtained at the same temperatures using the Co-presaturated capsules (Table 1). This suggests that reliable data can be obtained by using the presaturated capsules and that Co absorption into Pt is an endothermic reaction.

Because the upper limit of experimental temperature of the calorimeter used in the present study is 1773 K, we could not obtain enthalpy data for Co₂SiO₄ liquid over a wide range of temperature. Therefore it is difficult to determine a reliable heat

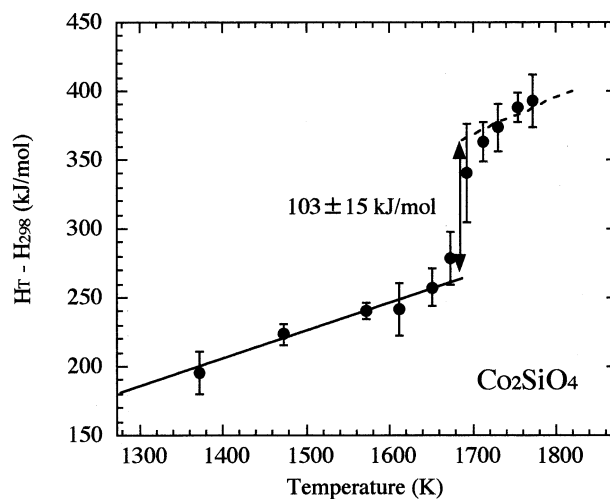


Fig. 1. Enthalpy, H_T^{Ol or Liq} - H₂₉₈^{Ol}, of Co₂SiO₄ olivine determined by transposed-temperature drop calorimetry. Solid line is enthalpy calculated using heat capacity of Co₂SiO₄ olivine (Robie et al., 1982, 1984). Dotted line is enthalpy of Co₂SiO₄ liquid (Eqn. 1) calculated by the least square fitting for the experimental data using heat capacity of Co₂SiO₄ liquid estimated by Hirschmann and Ghiorso (1984).

capacity of the Co₂SiO₄ liquid based on the data shown in Figure 1. The heat capacity of the Co₂SiO₄ liquid had been estimated by Hirschmann and Ghiorso (1994). The heat capacities of divalent metal-oxide liquids are on average 75% of the partial molar heat capacities of the same components in the silicate liquids (Stebbins et al., 1984; Lange and Navrotsky, 1992). Based on this empirical rule, Hirschmann and Ghiorso (1994) estimated the heat capacity of the Co₂SiO₄ liquid using the C_p of CoO liquid (Samsonov, 1982) and the partial molar heat capacity of SiO₂ in the silicate liquid, and assuming no excess heat capacity of mixing. The estimated heat capacity of the Co₂SiO₄ liquid is 250.6 J/K·mol.

When this estimated heat capacity is used, the H_T^{Liquid}-H₂₉₈^{Solid} can be expressed as

$$H_T^{\text{Liquid}} - H_{298}^{\text{Solid}} \text{ (kJ/mol)} = -57.21(\pm 15.3) + 0.2506 T \text{ (K)} \quad (1)$$

by least squares fitting for the data of the present study. The H₁₆₈₈^{Solid}-H₂₉₈^{Solid} calculated using heat capacity of Co₂SiO₄ olivine (Robie et al., 1982, 1984) is 262.7 kJ/mol. Therefore the enthalpy of fusion at the melting point ($\Delta H_{T_m} = H_{1688}^{\text{Liquid}} - H_{1688}^{\text{Solid}}$) is calculated as (H₁₆₈₈^{Liquid} - H₂₉₈^{Solid}) - (H₁₆₈₈^{Solid} - H₂₉₈^{Solid}) = 103 ± 15 kJ/mol.

3.2. Drop Calorimetry of the System An₅₀Di₅₀-Ni₂SiO₄

Results of the transposed-temperature drop calorimetry at 1773 K for the system An-Di-Ni₂SiO₄ and for NiO are listed in Table 2. The H₁₇₃₃^{Liquid}-H₂₉₈^{Solid} for Di (493.3 ± 14.6 kJ/mol) and An₅₀Di₅₀ (540.5 ± 20.4 kJ/mol) and the H₁₇₃₃^{Solid}-H₂₉₈^{Solid} for An (462.9 ± 22.5 kJ/mol) measured in the present study are in agreement with those reported by Navrotsky et al. (1989) (Di, 503.1 ± 14.4 kJ/mol; An₅₀Di₅₀, 548.54 ± 12.4 kJ/mol; An, 465.3 ± 23.1 kJ/mol). Drop runs for Ni₂SiO₄ olivine and NiO using Pt capsules were performed both in air and in Ar. In both

Table 2. Results of transposed-temperature drop calorimetry of Di-An-Ni₂SiO₄ and NiO at 1773 K.

Composition (mol fraction)			Atmosphere	Capsule	State at 1773K	H _T -H ₂₉₈ ^a (kJ/mol) ^a
CaMgSi ₂ O ₆	CaAl ₂ Si ₂ O ₈	Ni ₂ SiO ₄				
0.000	1.000	0.000	Ar	Pt	Solid	462.9 ± 22.5 (8)
1.000	0.000	0.000	Ar	Pt	Liquid	493.3 ± 14.6 (8)
0.000	0.000	1.000	Ar	Pt	Solid	308.8 ± 22.3 (4)
0.000	0.000	1.000	Air	Pt	Solid	271.8 ± 11.3 (9)
0.500	0.500	0.000	Ar	Pt	Liquid	540.5 ± 20.4 (14)
0.467	0.467	0.067	Air	Pt	Liquid	524.2 ± 23.4 (12)
0.429	0.429	0.143	Air	Pt	Liquid	522.8 ± 31.2 (8)
0.385	0.385	0.231	Air	Pt	Liquid	516.8 ± 25.7 (9)
0.333	0.333	0.333	Air	Pt	Liquid	514.1 ± 14.9 (15)
		NiO	Ar	Pt	Solid	100.6 ± 9.0 (5)
		NiO	Air	Pt	Solid	87.9 ± 5.2 (10)

^a Error is two standard deviations of the mean. Number in parentheses is number of experiments.

the Ni₂SiO₄ olivine and NiO, the H₁₇₇₃^{Solid}-H₂₉₈^{Solid} measured under Ar gas were larger than those in air (Table 2). The H₁₇₇₃^{Solid}-H₂₉₈^{Solid} calculated from published heat capacities are 256 kJ/mol for Ni₂SiO₄ olivine (Hirschmann, 1991) and 83.2 kJ/mol for NiO (Barin, 1989). Therefore the measured H₁₇₇₃^{Solid}-H₂₉₈^{Solid} in both the Ni₂SiO₄ olivine and NiO are larger than real values by 6% in drop runs in air and by 17% under Ar gas. Those indicate that endothermic reaction due to Ni absorption into Pt capsules occurred during the drop run, but Ni-loss from samples was smaller in the experiments in air than in Ar.

Figure 2 shows observed enthalpies (H₁₇₇₃^{Liquid}-H₂₉₈^{Solid}) in the system An₅₀Di₅₀-Ni₂SiO₄. The H₁₇₇₃^{Liquid}-H₂₉₈^{Solid} decreases slightly with increasing Ni₂SiO₄ component. When a sample was dropped into the calorimeter, the calorimetric signal returned to the baseline typically in 10–15 min, indicating that

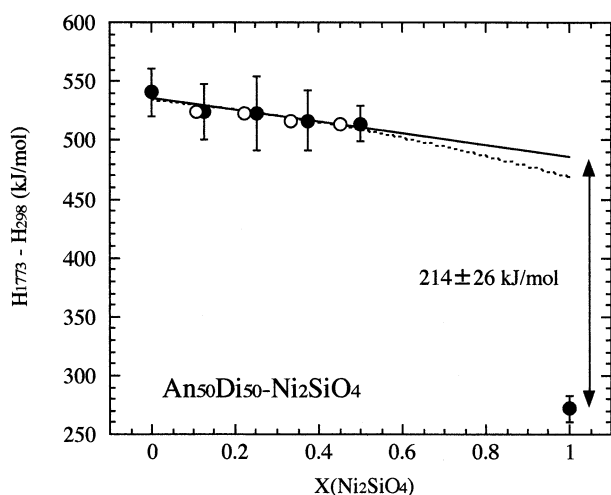


Fig. 2. Enthalpy, H₁₇₇₃^{OL or Liq} - H₂₉₈^{OH}, of liquid in the system An₅₀Di₅₀-Ni₂SiO₄ and Ni₂SiO₄ olivine. Solid circles represent measured enthalpies and liquid compositions of starting materials, and open circles show measured enthalpies and liquid compositions by heating and quenching experiments for 15 min. A straight line indicates enthalpy of An₅₀Di₅₀-Ni₂SiO₄ liquid (Eqn. 2) calculated by the least squares fitting for the experimental data assuming zero heat of mixing. A dotted curve shows enthalpy calculated assuming W_{An₅₀Di₅₀-Ni₂SiO₄}^{Liq} = 30 kJ/mol, H₁₇₇₃^{Liquid}-H₂₉₈^{Solid} = 534.3 - 65.5 X_{Ni₂SiO₄} + 30000 X_{Ni₂SiO₄}(1 - X_{Ni₂SiO₄}).

melting reaction and Ni absorption were completed within 15 min. To examine Ni-losses from samples during the runs, we carried out melting experiments using the same samples and Pt capsules as used in drop runs. Samples were heated for 15 min in air and then quenched in a vertical quenching furnace. Compositions of the liquids and Pt capsules were measured with EPMA (Table 3). The liquid compositions normalized to An₅₀Di₅₀ and Ni₂SiO₄ components are shown in Figure 2. Observed losses of NiO were 11–19 wt% (relative to starting composition). The Ni contents in Pt capsules were 1–3 wt% at the interface and were less than 0.1 wt% at 40 μm apart from the interface.

Assuming zero heat of mixing in the An₅₀Di₅₀-Ni₂SiO₄ liquid, the H₁₇₇₃^{Liquid}-H₂₉₈^{Solid} can be expressed as

$$H_{1773}^{\text{Liquid}} - H_{298}^{\text{Solid}} \text{ (kJ/mol)} = 535.3 - 49.4 X_{\text{Ni}_2\text{SiO}_4} \text{ (mol\%)} \quad (2)$$

based on the weighted linear least squares fitting for the experimental data. The H₁₇₇₃^{Liquid}-H₂₉₈^{Solid} is 485.9 ± 25.7 kJ/mol at X_{Ni₂SiO₄} = 100 and the H₁₇₇₃^{Solid}-H₂₉₈^{Solid} for Ni₂SiO₄ olivine in air is 271.8 ± 11.3 kJ/mol (Table 2). Therefore the enthalpy of fusion of Ni₂SiO₄ olivine at 1773 K (ΔH₁₇₇₃) is calculated as (H₁₇₇₃^{Liquid}-H₂₉₈^{Solid}) - (H₁₇₇₃^{Solid}-H₂₉₈^{Solid}) = 214 ± 26 kJ/mol. No liquid immiscibility was observed in glasses recovered from the quenched experiments at 1773 K. This indicates that if the An₅₀Di₅₀-Ni₂SiO₄ liquid has positive heats of mixing, the interaction energy for a regular solution model, W_{An₅₀Di₅₀-Ni₂SiO₄}^{Liq}, is less than 30 kJ/mol according to W_{An₅₀Di₅₀-Ni₂SiO₄}^{Liq} = RT_c T_c, critical temperature <1773 K). Results of least squares fitting assuming W_{An₅₀Di₅₀-Ni₂SiO₄}^{Liq} = 30 kJ/mol is also plotted on Figure 2 and predicts a value for H₁₇₇₃^{Liquid}-H₂₉₈^{Solid} = 469.0 kJ/mol at X_{Ni₂SiO₄} = 100. This value is within error of that calculated from Eqn. 2 (485.9 ± 25.7 kJ/mol). Therefore, it is considered that no serious difference in the ΔH₁₇₇₃ arises by the different assumptions for the heat of mixing.

Because the endothermic reaction and compositional changes occurred due to Ni absorption in Pt capsules, presumably the enthalpies calculated by Eqn. 2 are larger than the real values by approximately 5–10%. However, this effect is canceled when the fusion enthalpy at 1773 K is calculated, because both of the H₁₇₇₃^{Liquid}-H₂₉₈^{Solid} and H₁₇₇₃^{Solid}-H₂₉₈^{Solid} were measured in experiments in air using Pt capsules without presaturation.

Table 3. Chemical compositions (wt%) of starting materials (mixtures of anorthite, diopside, and Ni₂SiO₄ olivine) used in transposed-temperature-drop calorimetry in the system An₅₀Di₅₀-Ni₂SiO₄ and glass produced by heating of pairs of starting materials and Pt capsules at 1773 K for 15 minutes in vertical quenching furnace. Numbers in parenthesis represent 1 σ .

N ^a	SiO ₂	Al ₂ O ₃	MgO	NiO	CaO	Total
	An(46.67)-Di(46.67)-Ni ₂ SiO ₄ (6.67) ^b , X _{Ni₂SiO₄} ^c = 12.5					
Starting composition	47.44	19.43	7.68	4.07	21.38	100.00
Center ^d 3	47.13 (0.09)	19.18 (0.67)	7.47 (0.22)	3.56 (0.10)	23.81 (0.28)	101.15
Ad. Pt ^e 3	46.86 (0.44)	19.72 (0.11)	7.56 (0.27)	3.24 (0.34)	23.28 (0.64)	100.66
	An(42.86)-Di(42.86)-Ni ₂ SiO ₄ (14.29) ^b , X _{Ni₂SiO₄} ^c = 25.0					
Starting composition	46.12	18.06	7.14	8.82	19.87	100.00
Center ^d 3	45.81 (0.03)	18.06 (0.48)	7.12 (0.18)	7.63 (0.18)	20.93 (0.25)	99.55
Ad. Pt ^e 2	45.65 (0.30)	18.41 (0.17)	7.20 (0.05)	7.69 (0.03)	21.66 (0.52)	100.62
	An(38.46)-Di(38.46)-Ni ₂ SiO ₄ (23.08) ^b , X _{Ni₂SiO₄} ^c = 37.5					
Starting composition	44.55	16.43	6.50	14.45	18.08	100.00
Center ^d 3	44.37 (0.87)	16.50 (0.57)	6.55 (0.06)	12.25 (0.29)	19.29 (0.73)	98.96
Ad. Pt ^e 3	44.40 (0.97)	16.70 (0.10)	6.67 (0.11)	12.33 (0.19)	19.33 (0.48)	99.43
	An(33.33)-Di(33.33)-Ni ₂ SiO ₄ (33.33) ^b , X _{Ni₂SiO₄} ^c = 50.0					
Starting composition	42.66	14.48	5.72	21.21	15.93	100.00
Center ^d 4	43.20 (0.23)	15.03 (0.13)	5.75 (0.25)	18.57 (0.68)	16.77 (0.43)	99.33
Ad. Pt ^e 3	43.22 (0.63)	14.90 (0.42)	6.09 (0.19)	17.65 (1.81)	17.66 (0.73)	99.52

^a Numbers of analyses.

^b Numbers are mol% of anorthite, diopside, and Ni₂SiO₄ olivine in starting materials of experiments.

^c Mole fractions of Ni₂SiO₄ component in the system An₅₀Di₅₀-Ni₂SiO₄.

^d Compositions of center of quench glass.

^e Compositions of glass adjacent to Pt capsules.

The enthalpy of fusion of the Ni₂SiO₄ at its melting point (ΔH_{T_m}) can be calculated from

$$\Delta H_{T_m} = \Delta H_{1773} + \int_{1773}^{T_m} (C_p^{\text{Liquid}} - C_p^{\text{Solid}}) dT. \quad (3)$$

Metastable fusion temperature of Ni₂SiO₄ olivine estimated by Hirschmann and Ghiorso (1994) is 1923 \pm 50 K. Using Eqn. 3 with the ΔH_{1773} obtained in the present study and estimated heat capacity of Ni₂SiO₄ liquid (Hirschmann and Ghiorso, 1994; 238.6 \pm 10 J/K) and of Ni₂SiO₄ olivine (Hirschmann, 1991) and Eqn. 3, the fusion enthalpy for Ni₂SiO₄ at 1923 K is calculated as 221 \pm 26 kJ/mol.

4. HEATS OF FUSION OF M₂SiO₄ OLIVINES (M = Mg, Fe, Mn, Co, Ni)

The fusion enthalpies (ΔH_{T_m}) and entropies ($\Delta S_{T_m} = \Delta H_{T_m}/T_m$) at melting point for the Co₂SiO₄ and Ni₂SiO₄ obtained in this study are compared with other estimates in Table 4, together with those for Mg₂SiO₄, Fe₂SiO₄ and Mn₂SiO₄. The ΔH_{T_m} and ΔS_{T_m} for Ni₂SiO₄ olivine determined by the calorimetric measurements are the largest among those of olivine group. This is qualitatively consistent with the large enthalpy of vitrification of NiCaSi₂O₆ at 975 K ($H_{975}^{\text{Glass}} - H_{975}^{\text{Solid}}$) compared with that for MgCaSi₂O₆ and CoCaSi₂O₆ measured by solution calorimetry (Wright and Navrotsky, 1985).

In thermodynamic analysis of Ni and Co partitioning between olivine and silicate liquid, Hirschmann and Ghiorso (1994) used the ΔS_{T_m} estimated on the basis of statistical mechanical principles for fusion entropies of depolymerized molecular liquids ($\Delta S_{T_m} = R$ per g atom). The ΔS_{T_m} for Co₂SiO₄ olivine measured in the present study agrees with that estimated by Hirschmann and Ghiorso (1994), however, the

measured ΔS_{T_m} of Ni₂SiO₄ olivine is obviously larger than their estimated value.

Figure 3 shows the relationship between the ΔS_{T_m} of olivine group measured by calorimetry and ionic radius of the six-coordinated cations (Shannon and Prewitt, 1969). The ΔS_{T_m} for Fe₂SiO₄ (Stebbins and Carmichael, 1984) and Mn₂SiO₄ (Mah, 1960) by traditional drop calorimetry, and that for Mg₂SiO₄ determined by direct measurement using DSC (Richet et al., 1993) are plotted along with the ΔS_{T_m} for Co₂SiO₄ and Ni₂SiO₄ of the present study. Based on the comparisons among the ΔS_{T_m} of silicate minerals reported previously, Stebbins et al. (1984) found that the entropy of fusion per gram atom for

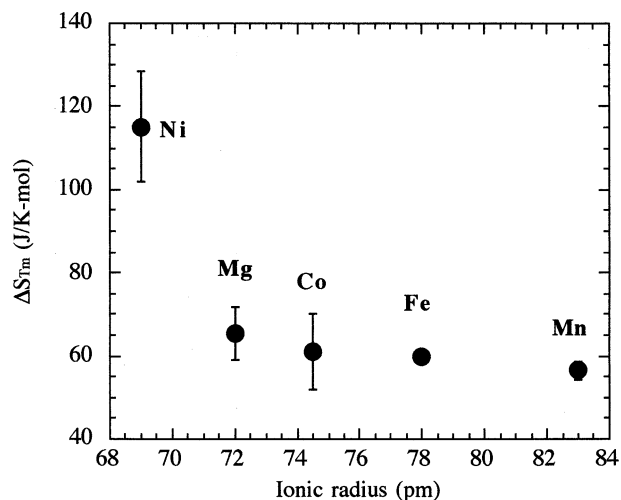


Fig. 3. Entropy of fusion of M₂SiO₄ olivine (M = Mg, Fe, Ni, Co, Mn) at their melting point T_m versus ionic radius of six-coordinated cation (Shannon and Prewitt, 1969).

Table 4. Enthalpies and entropies of fusion of M_2SiO_4 olivines (M = Mg, Fe, Mn, Co, Ni).

Component	T _m (K)	Δ H _{T_m} (kJ/mol)	Δ S _{T_m} (J/K-mol)	Source
Mg ₂ SiO ₄	2174	142 ± 14	65.3 ± 6.4	Richet et al. (1993) ^a
	2163	114 ± 20	52.7 ± 9.2	Navrotsky et al. (1989) ^b
	2163	102.8	47.5	Tangeman et al. (2001) ^c
	2163	130 ± 13	60.1 ± 6.0	Stebbins et al. (1984) ^d
Fe ₂ SiO ₄		113.1 ± 0.5	52.05 ± 0.57	Beattie (1993) ^e
	1490	89.3 ± 1.1	59.9 ± 0.7	Stebbins and Carmichael (1984) ^f
	1490	92.2 ± 0.3	61.9 ± 0.2	Orr (1953) ^f
		109.9 ± 0.6	69.60 ± 0.40	Beattie (1993) ^e
Mn ₂ SiO ₄	1620	89.0 ± 0.5	55.2 ± 0.3	Mah (1960) ^f
		136.0 ± 1.3	91.43 ± 0.89	Beattie (1993) ^e
Co ₂ SiO ₄	1688	103 ± 15	61 ± 9	This study
	1688	97.9	58	Hirschmann and Ghiorso (1994) ^g
Ni ₂ SiO ₄		138.0 ± 4.8	76.25 ± 2.49	Beattie (1993) ^e
	1923	221 ± 26	115 ± 13	This study
	1923	111.5	58	Hirschmann and Ghiorso (1994) ^g
		205.8 ± 5.7	98.44 ± 3.05	Beattie (1993) ^e

^a Direct measurement by differential scanning calorimetry.

^b Value calculated from Δ H_{T_m} at 1773 K by transposed-temperature drop calorimetry and estimated Cp for Mg₂SiO₄ liquid.

^c Value calculated from Δ H_{T_m} at 1773 K by Navrotsky et al. (1989) and Cp of supercooled liquid measured by DSC.

^d Estimated value from systematics in Δ S_{T_m} related to ionic field strength.

^e Estimated value based on thermodynamic analysis assuming empirical solution model for experimental data of element partitioning between olivine and silicate liquid. Values appropriate to centre of the temperature range of the experimental data (about 1500K).

^f Traditional drop calorimetry (hot to cold).

^g Estimated value by statistical mechanical principles for depolymerized molecular liquids (Δ S_{T_m} (J/K-g atom) = R).

silicate minerals increases with decreasing degree of polymerization (the ratio of network forming cations to network modifying cations) and with increasing cation field strength ($z/(r + 1.35)^2$, z = cation charge and r = cation radius) in a group of compounds of the same stoichiometry. However, it is unlikely that the difference of cation field strength is the only cause of the large heats of fusion of Ni₂SiO₄ olivine, because reduction of ionic radius of Ni²⁺ is only 3–16% compared with those of Mg²⁺, Fe²⁺, Mn²⁺ and Co²⁺ but the fusion entropy of Ni₂SiO₄ is about double ΔS_{T_m} of other components (Fig. 3).

Fusion enthalpies of olivine can be related to differences between crystal field stabilization energies (CFSE, Burns and Fyfe, 1964) of transition metals (Fe²⁺, Mn²⁺, Ni²⁺, Co²⁺) in olivines and in orthosilicate liquids. Transition metals in olivine occupy octahedral six-coordinated sites. According to high-temperature spectroscopic studies for the glass and liquid, however, they are dominantly four-coordinated in silicate glass and liquid. Jackson et al. (1993) reported that Fe²⁺ in Fe₂SiO₄ liquid occupies mainly four-coordinated sites based on the X-ray absorption spectroscopy. Farges and Brown (1996) showed by X-ray absorption fine structure spectroscopy that Ni²⁺ in sodium disilicate samples with 2 wt% NiO is five-coordinated in glass, whereas it is dominantly four-coordinated in the liquid. In haplogranitic melt, coordination changes from octahedral to tetrahedral Ni²⁺ with increasing temperature were observed by optical absorption spectra (Keppler and Bagdassarov, 1999). Mn²⁺ in glass of orthosilicate composition (Cooney and Sharma, 1990) and Co²⁺ in silicate and borosilicate glasses (Corrias et al., 1986; Nelson and White, 1986; Keppler, 1992) and haplogranitic melt (Keppler and Bagdassarov, 1999) are also dominantly four-coordinated in those glasses and melt.

Ni²⁺ is well-known as an ion having exceptionally large CFSE in an octahedral field. The CFSE of six-coordinated Ni²⁺

and Fe²⁺ in olivines are 127 and 52 kJ/mol, respectively (Burns, 1970) and CFSE of four-coordinated Ni²⁺ and Fe²⁺ in silicate liquids are 45 kJ/mol (Galoisy and Calas, 1993) and 38 kJ/mol (Brown et al., 1995), respectively. Therefore, differences between CFSE in olivines and in liquids are 82 kJ/mol for Ni²⁺ and 13 kJ/mol for Fe²⁺. Octahedral site preference energies (OSPE, CFSE(octahedral)–CFSE(tetrahedral)) of Ni²⁺, Co²⁺ and Fe²⁺ are, 86.2, 31.0 and 16.7 kJ/mol, respectively (Burns, 1970). The OSPE of Ni²⁺ and Fe²⁺ are nearly consistent with differences between CFSE in olivine and in liquid. Because Mn²⁺ is a transition metal cation without any CFSE, it is expected that the differences between ΔH_{T_m} of MSi_{0.5}O₂ (M = Ni²⁺, Co²⁺, Fe²⁺) and MnSi_{0.5}O₂ olivines are related to the OSPE. The differences of ΔH_{T_m} calculated from the data of the present study, Stebbins and Carmichael (1984) and Mah (1960) are 66 ± 13 kJ/mol for NiSi_{0.5}O₂–MnSi_{0.5}O₂, 7 ± 7 kJ/mol for CoSi_{0.5}O₂–MnSi_{0.5}O₂ and 0.2 ± 1 kJ/mol for FeSi_{0.5}O₂–MnSi_{0.5}O₂. Although the ΔH_{T_m}((Ni, Co or Fe)Si_{0.5}O₂)–ΔH_{T_m}(MnSi_{0.5}O₂) are 15–20 kJ/mol smaller than the OSPE of Ni²⁺, Co²⁺ and Fe²⁺, the differences in values of ΔH_{T_m}((Ni, Co or Fe)Si_{0.5}O₂)–ΔH_{T_m}(MnSi_{0.5}O₂) are comparable to the differences among OSPE of Ni²⁺, Co²⁺ and Fe²⁺. This indicates that the large ΔH_{T_m} of Ni₂SiO₄ is reasonable considering difference between CFSE in olivine and in liquid and that the large ΔH_{T_m} can be attributed to the large CFSE of six-coordinated Ni²⁺ in olivine. The large ΔS_{T_m} (= ΔH_{T_m}/T_m) of Ni₂SiO₄ is likely an exceptional property related to the large ΔH_{T_m}.

5. IMPLICATIONS FOR ELEMENT PARTITIONING BETWEEN OLIVINE AND SILICATE LIQUID

Thermodynamic formulations for temperature and compositional dependence of Ni, Co and Mn partitioning between

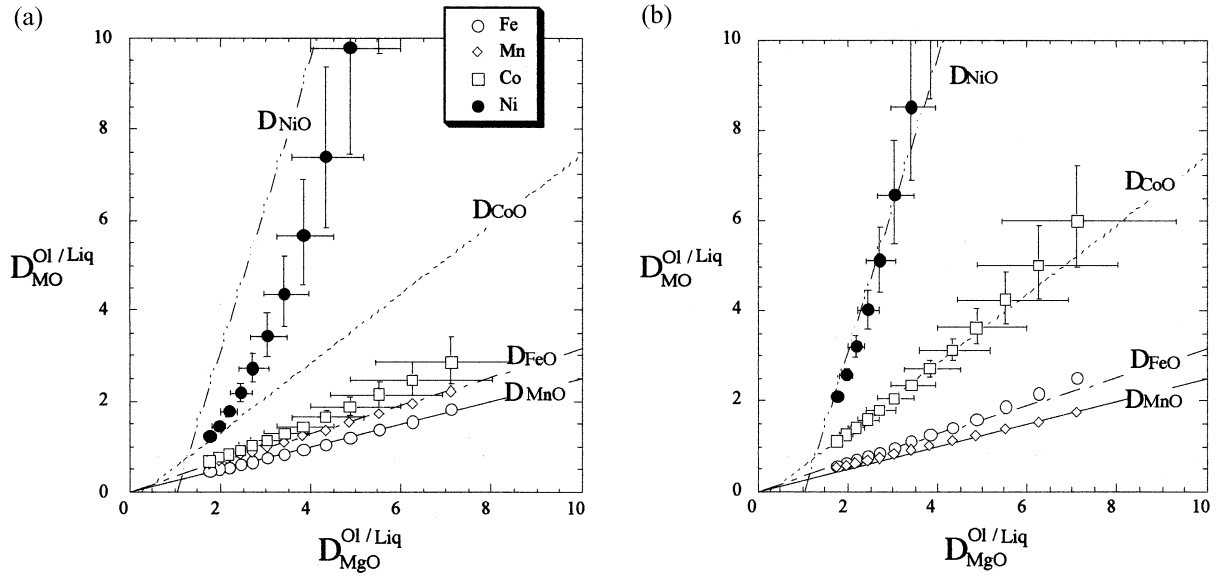


Fig. 4. Relationships between $D_{MO}^{OI/Liq}$ ($M = Fe, Ni, Co, Mn$) and $D_{MgO}^{OI/Liq}$ reported by Beattie et al. (1991) (lines). Symbols represent partition coefficients calculated from Eqn. 13 and A_M and B_M listed in Table 5 assuming (a) $\Delta W_M = 0$ ($M = Mg, Fe, Ni, Co, Mn$) and (b) $\Delta W_{Mg} = 0, \Delta W_{Mn} = -3.6, \Delta W_{Fe} = 2.5, \Delta W_{Co} = 7.8$ and $\Delta W_{Ni} = 8.7$ (kJ/mol). Error bars represent ranges of calculated partition coefficients caused by error of the ΔS_{Tm} for $MgSi_{0.5}O_2, CoSi_{0.5}O_2$ and $NiSi_{0.5}O_2$.

olivine and silicate liquid have been achieved by determination of (1) regular solution parameters for Ni-, Co- and Mn-bearing components in silicate liquid using estimated heats of fusion (ΔH_{Tm} and ΔS_{Tm}) (Hirschmann and Ghiorso, 1994), (2) heats of fusion along the empirical activity model (Beattie, 1993) and (3) both heats of fusion and solution parameters to express heats of mixing in the liquid (Colson et al., 1988; Kinzler et al., 1990; Snyder and Carmichel, 1992) based on the experimental data of those partitioning. In other words, the heats of fusion have been treated as assumed or fitting parameters.

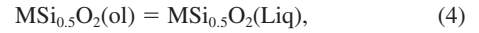
Beattie et al. (1991), based on the 898 published data of the element partitioning and phase equilibrium experiments, found that partition coefficients of divalent oxides between olivine and liquid, $D_{MO}^{OI/Liq}$ ($M = Fe, Mn, Ni, Co, Ca$), can be expressed as linear functions of the $D_{MgO}^{OI/Liq}$. Those relationships are given in Figure 4. We can find the following two interesting points on the Figure 4; (1) The size of $D_{MO}^{OI/Liq}$ at constant $D_{MgO}^{OI/Liq}$ is in the order of $D_{NiO}^{OI/Liq} \gg D_{CoO}^{OI/Liq} > D_{FeO}^{OI/Liq} > D_{MnO}^{OI/Liq}$ and the $D_{NiO}^{OI/Liq}$ varies by more than an order of magnitude. (2) The relationships between $D_{MgO}^{OI/Liq}$ and $D_{MO}^{OI/Liq}$ ($M = Fe, Co, Mn$) are represented as straight lines with near-zero intercepts, however, the line for $D_{MgO}^{OI/Liq}$ and $D_{NiO}^{OI/Liq}$ has a negative intercept. Those indicate that the exchange partition coefficients ($K_{DMO/MgO}^{OI/Liq} = D_{MO}^{OI/Liq}/D_{MgO}^{OI/Liq}$) for Mg-Fe, Mg-Co and Mg-Mn are almost constant throughout magmatic temperatures and compositions but that $K_{DNiO/MgO}^{OI/Liq}$ depends on the $D_{MgO}^{OI/Liq}$. The variation in $K_{DNiO/MgO}^{OI/Liq}$ has been discussed in terms of temperature- and compositional dependence of the $K_{DNiO/MgO}^{OI/Liq}$ (Hart and Devis, 1978; Leeman and Lindstrom, 1978; Takahashi, 1978; Jones, 1984; Seifert et al., 1988).

Beattie et al. (1991) also attempted thermodynamic interpretations of the straight lines among partition coefficients and concluded that those relationships can be explained by assuming that (1) fusion enthalpies of forsterite and other end-mem-

bers are nearly of the same size, (2) differences of heat capacities between solid and liquid are small, and (3) the ratios of activity coefficients ($\gamma_M^{OI} \gamma_{Mg}^{Liq} / \gamma_M^{Liq} \gamma_{Mg}^{OI}$) are the constants.

We discuss here the partition behavior between olivine and silicate liquid based on the heats of fusion obtained by calorimetric measurements, published data of heat capacities and solid solution properties of olivine.

In the following reaction between olivine and liquid for any cation M ($M = Mg, Fe, Ni, Co, Mn$)



the equilibrium condition is

$$RT \ln \left(\frac{X_{MSi_{0.5}O_2}^{OI} \gamma_{MSi_{0.5}O_2}^{OI}}{X_{MSi_{0.5}O_2}^{Liq} \gamma_{MSi_{0.5}O_2}^{Liq}} \right) = (H_T^{Liq, MSi_{0.5}O_2} - H_T^{OI, MSi_{0.5}O_2}) - T(S_T^{Liq, MSi_{0.5}O_2} - S_T^{OI, MSi_{0.5}O_2}), \quad (5)$$

where $H_T^{i, MSi_{0.5}O_2}$ and $S_T^{i, MSi_{0.5}O_2}$ are enthalpy and entropy, respectively, of $MSi_{0.5}O_2$ component in i phase at temperature, T , and $X_{MSi_{0.5}O_2}^i$ and $\gamma_{MSi_{0.5}O_2}^i$ are site-mole fraction and activity coefficient of $MSi_{0.5}O_2$ component in i phase, respectively.

The partition coefficient $D_{MO}^{OI/Liq}$ is a ratio of mole fractions of the MO normalized to simple oxide (SiO_2, Al_2O_3, Na_2O , etc.) in the olivine (X_{MO}^{OI}) and liquid (X_{MO}^{Liq}),

$$D_{MO}^{OI/Liq} = X_{MO}^{OI} / X_{MO}^{Liq}. \quad (6)$$

Then the X_{MO}^{OI} and X_{MO}^{Liq} are related to $X_{MSi_{0.5}O_2}^{Liq}$ as

$$X_{MSi_{0.5}O_2}^{OI} = \frac{3}{2} X_{MO}^{OI} \text{ and } X_{MSi_{0.5}O_2}^{Liq} = \alpha X_{MO}^{Liq} \quad (7)$$

where α is a normalization factor that depends on the concen-

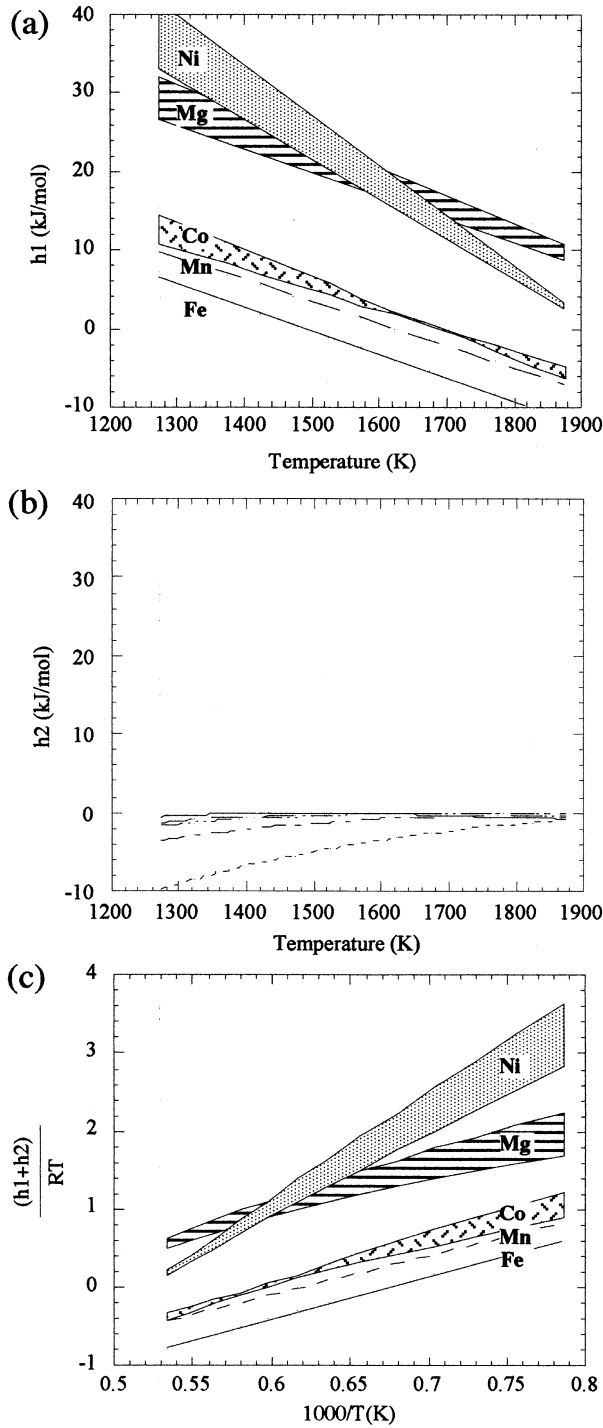


Fig. 5. Temperature dependence of (a) h_1 , (b) h_2 and (c) $(h_1 + h_2)/RT$ in Eqn. 9 calculated from fusion entropies and heat capacities of solid and liquid. Shaded areas in (a) and (c) are ranges of the h_1 and the $(h_1 + h_2)/RT$ caused by error of the ΔS_{Tm} for $MgSi_{0.5}O_2$, $CoSi_{0.5}O_2$ and $NiSi_{0.5}O_2$.

tration of MO in the liquid and on the selection of the liquid end-members. In other words, α depends on how we calculate the configurational entropy for the silicate liquid. When liquid end-members adopted by Hirschmann and Ghiorso (1994)

Table 5. Values of A_M and B_M used to describe temperature dependence of $(h_1 + h_2)/RT$ (see Fig. 5c).

M	A_M	B_M
Mg	-2.307	5505
Fe	-3.693	5477
Mn	-3.230	5221
Co	-3.385	5712
Ni	-6.273	12156

are considered (SiO_2 - TiO_2 - Al_2O_3 - Fe_2O_3 - $MgCr_2O_4$ - Fe_2SiO_4 - $MnSi_{0.5}O_2$ - Mg_2SiO_4 - $NiSi_{0.5}O_2$ - $CoSi_{0.5}O_2$ - $CaSiO_3$ - $NaSiO_3$ - $KAlSi_3O_8$), then the α for the magmatic liquid is generally 1.2–1.6.

Introducing the fusion entropy ($\Delta S_{Tm}^{MSi_{0.5}O_2}$) at the melting point (Tm^M) and the heat capacity difference between olivine and liquid ($\Delta Cp_{MSi_{0.5}O_2}^{Liq-Ol}$) into Eqn. 5 and combining with Eqns. 6 and 7 yields the expression:

$$RT \ln D_{MO}^{Ol/Liq} = \Delta S_{Tm}^{MSi_{0.5}O_2} (Tm^M - T) + \int_{Tm^M}^T \Delta Cp_{MSi_{0.5}O_2}^{Liq-Ol} dT - T \int_{Tm^M}^T \left(\frac{\Delta Cp_{MSi_{0.5}O_2}^{Liq-Ol}}{T} \right) dT + RT \ln \frac{\gamma_{MSi_{0.5}O_2}^{Liq}}{\gamma_{MSi_{0.5}O_2}^{Ol}} + RT \ln \left(\frac{2\alpha}{3} \right) \quad (8)$$

and rearrangement yields

$$\ln D_{MO}^{Ol/Liq} = \left(\frac{h_1 + h_2}{RT} \right) + \frac{RT \ln (\gamma_{MSi_{0.5}O_2}^{Liq} / \gamma_{MSi_{0.5}O_2}^{Ol})}{RT} + \ln \left(\frac{2\alpha}{3} \right), \quad (9)$$

where $h_1 = \Delta S_{Tm}^{MSi_{0.5}O_2} (Tm^M - T)$ and $h_2 = \int_{Tm^M}^T \Delta Cp_{MSi_{0.5}O_2}^{Liq-Ol} dT - T \int_{Tm^M}^T \left(\frac{\Delta Cp_{MSi_{0.5}O_2}^{Liq-Ol}}{T} \right) dT$.

Figures 5a,b show temperature dependence of h_1 and h_2 calculated using the $\Delta S_{Tm}^{MSi_{0.5}O_2}$ ($M = Mn, Co, Ni$) in the present study, $\Delta S_{Tm}^{FeSi_{0.5}O_2}$ by Stebbins and Carmichael (1984), $\Delta S_{Tm}^{MgSi_{0.5}O_2}$ by Richet et al. (1993), and published data of heat capacities. At magmatic temperatures (1300–1800 K), h_1 is always larger than h_2 , suggesting that the size of the $D_{MO}^{Ol/Liq}$ at given temperature is primarily dependent on the size of the $\Delta S_{Tm}^{MSi_{0.5}O_2}$. The $(h_1 + h_2)/RT$ decreases linearly with decrease of $1/T$ (Fig. 5c). This leads to decrease of partition coefficients at higher temperatures, as well known. The relationship is given by

$$\frac{h_1 + h_2}{RT} = A_M + \frac{B_M}{T}. \quad (10)$$

The A_M and B_M determined from the plot of Figure 5c are listed in Table 5. The largest B_M for Ni_2SiO_4 compared with other B_M is caused by the largest fusion entropy of Ni_2SiO_4 . Assuming that there is no excess entropy of mixing in the silicate liquid, the $RT \ln \gamma_{MSi_{0.5}O_2}^{Liq} / \gamma_{MSi_{0.5}O_2}^{Ol}$ can be set as parameters only with compositional dependence, ΔW_M . Then Eqn. 9 is expressed as

$$\ln D_{MO}^{O/Liq} = A_M + \frac{B_M + \Delta W_M/R}{T} + \ln \frac{2\alpha}{3}. \quad (11)$$

For the forsterite ($M = Mg$),

$$\ln D_{MgO}^{O/Liq} = A_{Mg} + \frac{B_{Mg} + \Delta W_{Mg}/R}{T} + \ln \frac{2\alpha}{3}. \quad (12)$$

Eliminating T from Eqns. 11 and 12, rearrangement yields

$$D_{MO}^{O/Liq} = (D_{MgO}^{O/Liq})^\beta \exp(A_M - \beta A_{Mg}) \left(\frac{2\alpha}{3}\right)^{1-\beta} \quad (13)$$

where

$$\beta = \frac{B_M + \Delta W_M/R}{B_{Mg} + \Delta W_{Mg}/R}.$$

Eqn. 13 is temperature-independent thermodynamic formulation for two partition coefficients.

The relationships between $D_{MgO}^{O/Liq}$ and $D_{MO}^{O/Liq}$ ($M = Fe, Ni, Co, Mn$) calculated by Eqn. 13 are shown in Figure 4a, where A_M and B_M in Table 5 are used and $\Delta W_M = 0$ is assumed. The calculated $D_{NiO}^{O/Liq}$, $D_{CoO}^{O/Liq}$ and $D_{FeO}^{O/Liq}$ are somewhat smaller than measured values, and the $D_{MnO}^{O/Liq}$ is larger than the measured one. However, it is interesting to note that Eqn. 13 reproduces the two main features of Ni partitioning: (a) a relatively large $D_{NiO}^{O/Liq}$, and (b) a decreasing $K_{DNiO/MgO}^{O/Liq}$ ($=D_{NiO}^{O/Liq}/D_{MgO}^{O/Liq}$) with decreasing $D_{MgO}^{O/Liq}$ (and increasing temperature as discussed above). This suggests that the partitioning data support the large heat of fusion of Ni₂SiO₄ obtained by calorimetry. Similar Ni-partitioning behavior is also observed in orthopyroxene-liquid partitioning (Beattie et al., 1991). Lindstrom and Weill (1978) carried out experiments of Ni and Co partitioning between diopside and liquid in the system An-Ab-Di. They reported a near constant exchange partition coefficient for Co-Mg between diopside and liquid, while that of Ni-Mg increases with decreasing temperature. Those features are consistent with the variation of the $K_{DCoO/MgO}^{O/Liq}$ and $K_{DNiO/MgO}^{O/Liq}$. Therefore, it is expected that Ni-bearing chain silicate minerals have larger heat of fusion similar to that for the orthosilicate minerals (Ni₂SiO₄).

The differences between the calculated and observed $D_{MO}^{O/Liq}$ in the Figure 4a can be attributed to the assumption of $\Delta W_M = 0$. We optimized the ΔW_M by trial and error analysis so that the values of $D_{MO}^{O/Liq}$ calculated by Eqn. 13 are consistent with the straight lines reported by Beattie et al. (1991). As described above, the size of α is nearly 1.2–1.6 when liquid end-members are assumed to be components of mineral end-members, then the term $(2\alpha/3)^{1-\beta}$ in Eqn. 13 is almost unity. Therefore, we set $\alpha = 1.5$ in the calculation of the ΔW_M . Figure 6 shows best fit values of the ΔW_M ($M = Fe, Mn, Ni, Co$) when ΔW_{Mg} is from -3 to $+3$ kJ/mol. Comparisons of measured and calculated $D_{MO}^{O/Liq}$ are given in Figure 4b.

The fusion entropy of NiSi_{0.5}O₂ estimated by Hirschmann and Ghiorso (1994) (29 J/K-mol) is significantly smaller than the value estimated by calorimetric measurements presented here (57.5 ± 6.5 J/K-mol), suggesting that thermodynamic analysis of Ni partitioning by Hirschmann and Ghiorso (1994) should be reexamined. They determined regular solution parameters for the silicate liquid by least squares fitting of data on

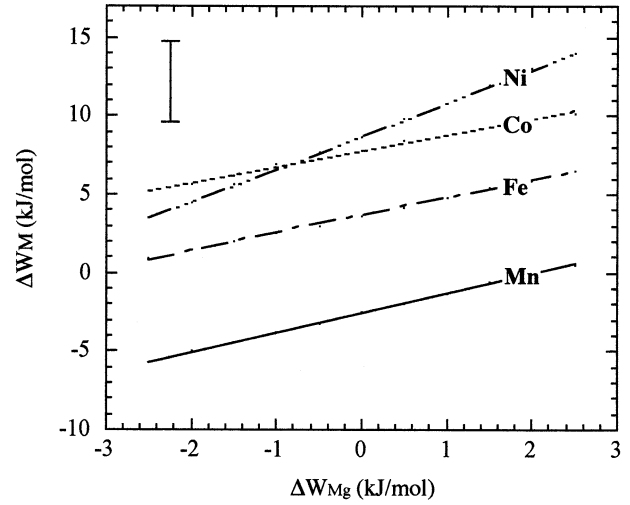


Fig. 6. Variation of the best fit values of ΔW_M ($M = Mg, Fe, Ni, Co, Mn$) to reproduce relationships of two partition coefficients ($D_{MO}^{O/Liq}$ - $D_{MgO}^{O/Liq}$) using Eqn. 13 and A_M and B_M listed in Table 5 ($M = Fe, Ni, Co, Mn$). Error bar shows error of ΔW_{Co} and ΔW_{Ni} estimated from permitted range of the ΔW_M in comparisons of calculated and reported $D_{MO}^{O/Liq}$ shown in Figure 4b.

Ni, Co and Mn partitioning between olivine and liquid. They concluded that the activity coefficient of NiSi_{0.5}O₂ ($\gamma = 3\sim 6$) in the magmatic liquid is always larger than those for MnSi_{0.5}O₂ and CoSi_{0.5}O₂ ($\gamma = 1\sim 3$). For example at 1500 K, assuming that the ΔS_{Tm} of NiSi_{0.5}O₂ is 29 J/K-mol, the $h1 + h2$ in Eqn. 9 is 11 kJ/mol, but it is 25 ± 3 kJ/mol when the ΔS_{Tm} of NiSi_{0.5}O₂ is 57.5 ± 6.5 J/K-mol. This indicates that the term $h1 + h2$ in Eqn. 9 is underestimated and the $RT \ln(\gamma_{NiSi_{0.5}O_2}^{Liq}/\gamma_{NiSi_{0.5}O_2}^{Ol})$ is overestimated by 14 ± 3 ($=25 - 11$) kJ/mol in the analysis of Hirschmann and Ghiorso (1994). If the $\gamma_{NiSi_{0.5}O_2}^{Liq}$ is 3~6 as discussed by them, the $RT \ln \gamma_{NiSi_{0.5}O_2}^{Liq}$ is 14~22 kJ/mol at 1500 K. However, it must be corrected by 14 ± 3 kJ/mol, then the $RT \ln \gamma_{NiSi_{0.5}O_2}^{Liq}$ is $-3\sim 11$ kJ/mol and the $\gamma_{NiSi_{0.5}O_2}^{Liq}$ is 0.8~2.3 at 1500 K. Therefore, it is concluded that non-ideality (size of activity coefficient) of NiSi_{0.5}O₂ in the silicate liquid is nearly the same as those for CoSi_{0.5}O₂ and MnSi_{0.5}O₂ ($\gamma = 1\sim 3$, Hirschmann and Ghiorso, 1994).

Because the $RT \ln \gamma_{NiSi_{0.5}O_2}^{Ol}$ is about -3 kJ/mol at 1500 K when $X_{Fo} > 0.5$ (cf. fig. 1 of Hirschmann and Ghiorso, 1994) and the $RT \ln \gamma_{NiSi_{0.5}O_2}^{Liq} = -3\sim 11$ kJ/mol, the ΔW_{Ni} ($=RT \ln \gamma_{NiSi_{0.5}O_2}^{Liq} - RT \ln \gamma_{NiSi_{0.5}O_2}^{Ol}$) should be 0 to 14 kJ/mol. This is consistent with the range of the calculated ΔW_{Ni} assuming $\Delta W_{Mg} = -3 \sim +3$ kJ/mol (Fig. 6). As indicated by Figure 6, the ΔW_M becomes smaller in the order

$$\Delta W_{Ni} \approx \Delta W_{Co} > \Delta W_{Fe} > \Delta W_{Mn}.$$

Values of $RT \ln \gamma_{NiSi_{0.5}O_2}^{Ol}$ in olivine solid solution can be estimated from interaction energies between M ($M = Fe, Mn, Ni, Co$) and Mg , W_{M-Mg}^{Ol} . The excess energy of Fe-Mg mixing in olivine has been discussed on the basis of phase equilibria (Kawasaki and Matsui, 1983; Sack and Ghiorso, 1989) and calorimetric measurements (Wood and Kleppa, 1981; Kojitani and Akaogi, 1994). The reported W_{Fe-Mg}^{Ol} is $\sim 10\sim 20$ kJ/mol. The W_{Ni-Mg}^{Ol} , W_{Co-Mg}^{Ol} and W_{Mn-Mg}^{Ol} calibrated by the data of

activity measurements, phase equilibria and cation ordering are 4.4 kJ/mol (Hirschmann, 1991), 6.0 kJ/mol and 22.0 kJ/mol (Hirschmann and Ghiorso, 1994), respectively. It is likely that the $RT\ln\gamma_{\text{MSi}_{0.5}\text{O}_2}^{\text{Ol}}$ increases in the order

$$RT\ln\gamma_{\text{NiSi}_{0.5}\text{O}_2}^{\text{Ol}} \approx RT\ln\gamma_{\text{CoSi}_{0.5}\text{O}_2}^{\text{Ol}} < RT\ln\gamma_{\text{FeSi}_{0.5}\text{O}_2}^{\text{Ol}} < RT\ln\gamma_{\text{MnSi}_{0.5}\text{O}_2}^{\text{Ol}},$$

based on the above $W_{\text{M-Mg}}^{\text{Ol}}$. If $\gamma_{\text{NiSi}_{0.5}\text{O}_2}^{\text{Liq}} \approx \gamma_{\text{CoSi}_{0.5}\text{O}_2}^{\text{Liq}} \approx \gamma_{\text{MnSi}_{0.5}\text{O}_2}^{\text{Liq}}$ as described above, differences in the ΔW_{M} shown in Figure 6 can be accounted for by the differences of the $RT\ln\gamma_{\text{MSi}_{0.5}\text{O}_2}^{\text{Ol}}$, since the larger $RT\ln\gamma_{\text{MSi}_{0.5}\text{O}_2}^{\text{Ol}}$ requires smaller values of ΔW_{M} . In summary, it is concluded that the partition behavior of Fe, Mg, Mn, Ni, Co between olivine and silicate liquid is rationalized by the differences of the heats of fusion for end-member components and the excess enthalpies of mixing in olivine solid solution, and that non-idealities of $\text{NiSi}_{0.5}\text{O}_2$, $\text{CoSi}_{0.5}\text{O}_2$ and $\text{MnSi}_{0.5}\text{O}_2$ components in the magmatic liquid are of almost the same magnitude ($\gamma = 1\sim 3$).

6. CONCLUSIONS

The enthalpies of Co_2SiO_4 between 1373 K and 1773 K were measured by transposed-temperature drop calorimetry using Co-presaturated Pt sample capsules in Ar. The enthalpies of Co_2SiO_4 olivine measured below the melting temperature are consistent with those calculated by the reported heat capacity. The fusion enthalpy of Co_2SiO_4 at melting point (1688 K) was 103 ± 15 kJ/mol. The enthalpies of liquid for a portion of $X_{\text{Ni}_2\text{SiO}_4} < 50$ mol% in the system $\text{An}_{50}\text{Di}_{50}\text{-Ni}_2\text{SiO}_4$ at 1773 K and Ni_2SiO_4 olivine were measured by transposed-temperature drop calorimetry using Pt capsules in air. Those results were extrapolated to $\text{Ni}_2\text{SiO}_4 = 1$ and enthalpy of metastable Ni_2SiO_4 liquid at 1773 K was determined. The measured enthalpies were larger than real values by approximately 5–10% since Ni absorption into Pt capsules is endothermic reaction. However, the effect could be canceled in calculation of fusion enthalpy because it was difference between enthalpies of solid and liquid. Determined fusion enthalpies of Ni_2SiO_4 are 214 ± 26 kJ/mol at 1773 K and 221 ± 26 kJ/mol at the melting point, 1923 K. The heat of fusion of Ni_2SiO_4 is significantly larger than those of other end-members of olivine group. The large fusion enthalpy of the Ni_2SiO_4 can be attributed to large CFSE of Ni^{2+} in octahedral sites in olivine. Based on thermodynamic analysis of element partitioning between olivine and silicate liquid, the large heat of fusion of Ni_2SiO_4 can account for large and variable partition coefficient of Ni between olivine and silicate liquid. It is considered that the magnitude of partition coefficients of Ni, Co and Mn are primarily dependent on the heats of fusion of the olivines and excess enthalpies of mixing in olivine solid solution and that activity coefficients for Ni-, Co- and Mn-bearing components in magmatic liquid are nearly of the same magnitude.

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