

## The heat of fusion of fayalite

J. F. STEBBINS

Earth Sciences Division, Lawrence Berkeley Laboratory  
Berkeley, California 94720

AND I.S.E. CARMICHAEL

Department of Geology and Geophysics  
University of California, Berkeley, California 94720

### Abstract

The relative enthalpies ( $H_T - H_{300K}$ ) of crystalline fayalite ( $\text{Fe}_2\text{SiO}_4$ ) and of the liquids resulting from the melting of fayalite in platinum and iron-plated capsules have been measured from 985 to 1705 K by drop calorimetry. Analyses of the samples quenched from the liquid show that because of incongruent melting and disproportionation of FeO during cooling, a mixture of phases was produced, possibly including the mineral laihunite ( $\approx \text{Fe}_3(\text{SiO}_4)_2$ ). Measured enthalpies have been corrected for these effects, resulting in an enthalpy of equilibrium, incongruent melting at 1490 K of  $88.4 \pm 1.1 \text{ kJ mol}^{-1}$  and an enthalpy of hypothetical congruent melting of  $89.3 \pm 1.1 \text{ kJ mol}^{-1}$ .

### Introduction

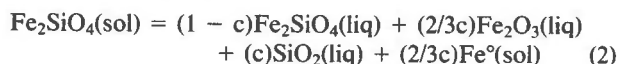
Measurements of the enthalpy of liquid silicates in this laboratory have recently been used to evaluate of the heats of fusion ( $\Delta H_f$ ) of anorthite (Weill et al., 1980), albite, sanidine, diopside, and nepheline (Stebbins et al., 1983). Because these liquids are glass formers, it was necessary to include solution calorimetric measurements of enthalpy differences between solids and glasses in the calculation of  $\Delta H_f$ . However, liquids near  $\text{Fe}_2\text{SiO}_4$  in composition crystallize during quench by normal methods, and, in principle,  $\Delta H_f$  for fayalite can be determined by drop calorimetry alone. Measurement of the relative enthalpy of the liquid above the melting point ( $T_f$ ), and of the relative enthalpy of the solid below  $T_f$ , are required. These results can then be extrapolated to  $T_f$  and subtracted:

$$\Delta H_{f,T_f} = (H_{T_f}^{\text{liq}} - H_{T_f}^{\text{sol}}) - (H_{T_f}^{\text{sol}} - H_{T_f}^{\text{sol}}) \quad (1)$$

“Liq” symbolizes liquid and “sol” the crystalline solid, while  $T_f$  is the quench reference temperature at which the calorimetric measurement is made, or 300 K for the results given here.

Orr (1953) conducted drop calorimetry experiments on crystalline fayalite and on the liquid produced by its melting in a sealed, platinum–10% rhodium capsule. He assumed that the liquid composition could be treated as exactly  $\text{Fe}_2\text{SiO}_4$ , and used equation 1 to interpret his results. Two effects must certainly have complicated Orr’s experiments. One is iron loss from the liquid to the

platinum, and the other is the incongruent melting behavior of fayalite (Bowen and Schairer, 1932), for which:



The constant  $c$  is fixed at equilibrium, but must be derived from experiment. Thus, equation 1 is not applicable, as a change in the liquid composition away from  $\text{Fe}_2\text{SiO}_4$  results in the formation of phases other than pure fayalite on cooling in the calorimeter.

The purpose of this study is to combine new results with those of Orr (1953) to estimate the enthalpy change of reaction 2 (essentially  $\Delta H_f$  for incongruent melting) and then to estimate how closely it approximates the value for the special, hypothetical case of  $c = 0$ , or congruent melting. We have analyzed the products of two sets of experiments, in order to determine liquid compositions and the phases present on quench. The first was designed to duplicate the runs of Orr (1953), and the second to approach more closely the equilibrium, incongruent melting of fayalite in a closed system.

### Experimental techniques

#### Starting materials

The starting material for sample C-2 was fayalite synthesized from Fe metal,  $\text{Fe}_2\text{O}_3$ , and  $\text{SiO}_2$  by sintering in an iron crucible in an inert atmosphere at  $1050^\circ\text{C}$ . The fayalite for C-1 was produced by S. Bohlen at UCLA in a gas mixing furnace, with  $f_{\text{O}_2} \approx 10^{-13}$  at  $1100^\circ\text{C}$ . Both samples were composed of fine, light brownish

green, transparent grains, and contained no magnetic impurities. Phases other than fayalite were not detected by powder X-ray diffraction. Wet chemical and microprobe analyses (Table 2) indicate that both were stoichiometric fayalite. The small quantity of  $\text{Fe}_2\text{O}_3$  reported in the starting material for C-1 is inconsequential in the interpretation of the results.

### Calorimetry

Enthalpy data were collected with a diphenyl ether drop calorimeter with a reference temperature ( $T_r$ ) of 300 K, coupled to a Pt-40%Rh wire wound furnace. Apparatus and techniques were described by Weill et al. (1980) and Stebbins et al. (1983). Sample size was about 2 g. Results were calibrated by running NBS720 sapphire standard reference material once for every one or two sample drops. Capsules were made from 0.25 mm thick Pt-10%RH sheet and tubing, were argon filled and sealed by arc welding. The interior of the capsule used for sample C-2 was plated with a layer of iron about 0.03 mm thick to limit reaction with the platinum. The number of runs on C-2 was minimized, also to reduce the chance of interaction. Neither capsule showed weight changes greater than a few tenths of a milligram during the experiments, indicating that no significant oxygen gain or loss occurred.

### Analysis of samples after experiments

Samples were examined after calorimetry by microscope in transmitted and reflected light, by X-ray diffraction, and by electron microprobe and wet chemical analysis. Total iron was determined by ammoniacal thioglycolic acid, and is reported in Table 2 as  $\text{FeO}_{\text{tot}}$ . Two techniques were used to measure ferrous iron content. The colorimetric method described by Wilson (1960) includes metallic iron as FeO, whereas the titrimetric method of Wilson (1955) responds differently. The sensitivity of both techniques to  $\text{Fe}^0$  was calibrated by analyzing samples containing known amounts of the metal. Combination of the three analyses yields true values for ferrous, ferric, and metallic iron content. The precision of the total iron analysis is estimated from replicates to be about  $\pm 0.5\%$  of the amount present. The errors in  $\text{Fe}_2\text{O}_3$  ( $\pm 20\%$ ) and in  $\text{Fe}^0$  ( $\pm 50\%$ ) are much larger, as the values are calculated from small differences between large numbers.

## Experimental results

### Calorimetry

Measurements of  $H_T - H_{300}$  for liquid and solid are reported in Table 1 and are plotted in Figure 1. Run numbers included in the table indicate the order in which experiments were conducted. Data on the solid at 1350 K agree well with those of Orr (1953), while our results at 985 K are significantly higher for unknown reasons. As the composition of the liquid produced by melting fayalite is not exactly  $\text{Fe}_2\text{SiO}_4$ , the solid assemblage formed during quench includes phases other than fayalite. The heat capacity of this mixture will be slightly different from that of the pure mineral. For this reason, data from runs on the solid at 1350 K repeated after experiments in the liquid region are 0.8% higher than results collected before the sample was melted and recrystallized. The enthalpy measured for a sample equilibrated at 1441 K falls between the curves for solid and liquid (Table 1 and Fig. 1), indicating that (as in Orr's work) partial melting took place. This is also expected if a mixture of phases was present:

Table 1. Drop calorimetric data on crystalline and melted fayalite.  $T$  in K,  $\Delta H = H_T - H_{300}$  K, in  $\text{J g}^{-1}$ . Run numbers indicate order in which measurements were made.

Sample C-2: Fe plated capsule <sup>1</sup>					
run	T	$\Delta H$			
238	1520	1516.2			
241	1520	1523.6			
242	1524	1532.5			
Sample C-1: Platinum-Rhodium capsule					
below peritectic T			above peritectic T <sup>1</sup>		
run	T	H	run	T	H
198	1352	923.8	210	1521	1564.4
199	1351	923.5	211	1521	1554.4
202	1351	925.5	213	1521	1559.2
294	985	578.9	215	1617	1686.7
205	985	588.5	218	1615	1692.3
208	985	573.8			
			219	1705	1775.2
223 <sup>2</sup>	1350	934.5	221	1704	1778.9
226 <sup>2</sup>	1350	928.1			
229 <sup>3</sup>	1441	1446.2	230	1615	1671.9
runs 210-220: $\Delta H = 1.1960 T - 255.86 \text{ J g}^{-1}$					
$\sigma_H = 9.2 \text{ J g}^{-1}$			$\sigma_{C_p} = 0.045 \text{ J g}^{-1} \text{ K}^{-1}$		

1. Completely molten except for minor Fe metal precipitated during incongruent melting.
2. Repeated after runs in liquid region.
3. Partly molten (see text)

the tridymite-fayalite-magnetite eutectic, for example, occurs at 1413 K (Muan, 1955). Our data for the liquid region for sample C-1 (no iron plating) agree with those of Orr, suggesting that the same degree of iron loss and oxidation of the liquid took place in both. These results, however, are for a liquid which did not have the composition of the equilibrium peritectic point. In sample C-2, iron plating eliminated interaction between the sample and the platinum capsule (see below), thus allowing equilibrium to be obtained.

### Characterization of run products

Knowledge of the composition of the liquids present at high temperature in the calorimetry samples, and of the phases present on quench, is essential to the interpretation of the enthalpy measurements. Sample C-1 was analyzed after it was heated for a total of about 10 hr at various temperatures in the liquid region and then quenched from 1615 K. C-2 was opened after being run for a total of less than two hours at 1520 K. Iron loss from the liquid is the only likely cause for composition change in these experiments, and can occur by solution in the platinum capsule or by precipitation during incongruent melting of the starting material. Microprobe analyses of the capsule wall of C-1 (which had no original plating) showed an iron content of at least 15% at the contact with the silicates, dropping to near zero by 0.1 mm into the platinum. Summing over the area of the capsule in contact with the melt, an iron loss of 1-2% as FeO from the sample is required. The iron plating of C-2 remained intact, with a layer of pure iron adjacent to the sample. Iron that precipitated on capsule walls during melting could not be distinguished from the original plating in C-2, but several small masses of the metal were observed among the silicate grains at the

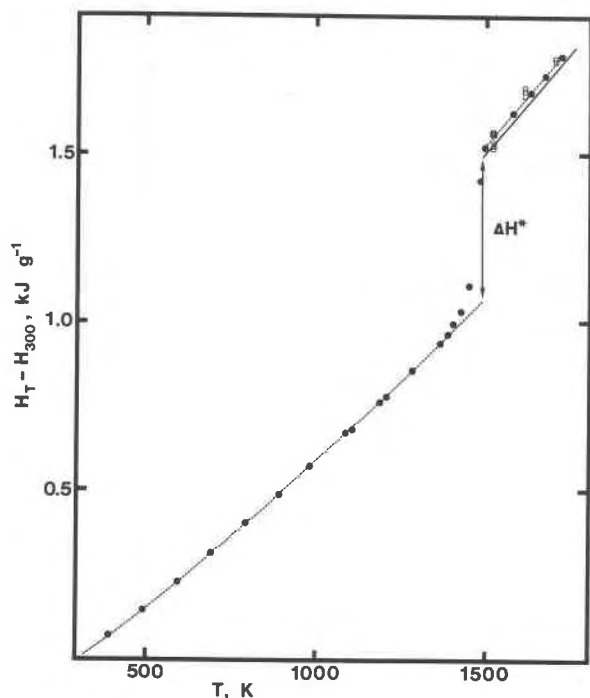
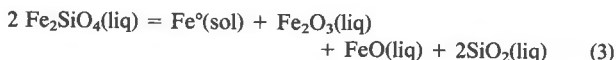


Fig. 1. The relative enthalpies of crystalline and of molten fayalite. Solid dots are for samples contained in platinum-10% rhodium capsules, as reported by Orr (1953), squares are runs in Pt-10%Rh made in the present study, and open circles are runs in an iron-plated capsule. The broken lines are the fits of Orr (1953), while the solid heavy line is that chosen here to represent the liquid in equilibrium with iron metal.  $\Delta H^*$  is not the heat of incongruent melting, but must be corrected for the presence of phases other than fayalite in the quench products from the liquid.

bottom of the capsule, showing that some iron did settle out of the liquid.

Bulk chemical analyses of C-2 and C-1 are given in Table 2. The material analyzed did not include metal precipitated onto or dissolved in the capsule walls. Comparison with starting material compositions confirms the greater iron loss and correspondingly more oxidized state of C-1. The analyses of C-2 indicate that about  $0.5 \pm 0.5\%$  iron as FeO was lost from this sample, presumably as metal that precipitated during melting. The  $\text{Fe}_2\text{O}_3$  content of the equilibrium peritectic liquid produced by this reaction (equation 2) and deduced from iron loss data alone, would thus be between 0 and 2 wt.%. C-2 also contained about 1.5%  $\text{Fe}^\circ$  in the bulk analysis. The metal was apparently dispersed as extremely fine opaque grains, too small to be detected by microprobe. We assume that this material is unrelated to the coarse iron particles that accumulated at the capsule bottom, and that it formed during quench, precipitating metastably before fayalite could nucleate and begin to crystallize. Iron metal formation during quench resulted in an increase in the ferric iron content of the run products (beyond that produced by incongruent melting) through the reaction:



The products marked "liq" are components of a single liquid phase. Each mole of metal formed during quench generated one mole of ferric iron, and the amount of  $\text{Fe}_2\text{O}_3$  in the original liquid can thus be calculated by subtracting the mole fraction of  $\text{Fe}^\circ$  from the mole fraction of  $\text{Fe}_2\text{O}_3$  in the quenched sample. The value obtained is about 2 wt.%, within the range estimated from the loss in total iron, and surprisingly close to the analysis given by Bowen and Schairer for a sample run in an iron crucible (2.3%). The liquid in their experiments apparently did not disproportionate during quench (and therefore did not increase in ferric iron content), probably because some fayalite remained unmelted and served to nucleate the mineral during cooling. This possibility is suggested by the fact that the temperature of their experiment at the "peritectic" was 12 K lower than that at which Orr (1953) reported complete melting. This minor discrepancy in temperature was, in turn, probably due to difficulty of distinguishing a small amount of unmelted starting material from the mixture of crystals formed on quench.

Microscopic examination showed that both of our calorimetry samples were made up mostly of long, "feathery" quench crystals of fayalite ranging from light to medium brown in thin section. Tiny rosettes of a colorless mineral, probably a silica polymorph, were occasionally associated with thin layers of opaque material visible along fayalite grain boundaries. Within and among the fayalite grains were clusters of dendritic magnetite crystals up to  $100 \mu\text{m}$  long but too thin ( $< 1 \mu\text{m}$ ) to analyze by electron microprobe. This phase was more abundant and coarser grained in C-1. Dendrites in both samples were coated with a dark brown to opaque material, which in reflected light was seen to be mostly an extremely fine grained intergrowth of at least two phases. This material also filled interstices between fayalite grains. The total modal abundance of non-fayalite material was about 10-20%, consistent with the bulk chemical analysis.

Interpretation of the calorimetric data depends on the charac-

Table 2. Chemical analyses of "fayalite" liquid drop calorimetry samples. All results in weight per cent.

	sample C-1		sample C-2		theoretical fayalite
	starting material	after calorimetry	starting material	after calorimetry	
$\text{SiO}_2$	n.d.	n.d.	29.4 <sup>1</sup>	29.8	29.5
$\text{FeO}_{\text{tot}}^2$	70.3	68.9	70.7 <sup>1</sup>	70.1	
$\text{Fe}^{\circ 3}$	0	n.d.	0	1.5	
$\text{FeO}^4$	69.7	61.5	70.7 <sup>1</sup>	62.3	70.5
$\text{Fe}_2\text{O}_3^5$	0.7 <sup>6</sup>	8.7	0 <sup>1</sup>	6.5	
$\text{Fe}_2\text{O}_3(\text{liq})^7$				2.1	

n.d. indicates not determined.

- Analyses by electron microprobe. FeO and  $\text{Fe}_2\text{O}_3$  calculated by comparison with 100% total.
- Total iron as FeO.
- Calculated from  $\text{FeO}_{\text{tot}}$  and two different types of analyses for FeO (see text). Determined to be 0 in starting materials by absence of magnetic material.
- Actual composition for starting materials and for run products of C-2. May contain a small amount of metallic iron in C-1 run products.
- Calculated from FeO and  $\text{FeO}_{\text{tot}}$  analyses.
- No ferric iron was detected by Mössbauer spectroscopy on this sample. (S.R. Bohlen, personal communication)
- Calculated composition of the liquid in equilibrium with metallic iron at 1520 K, assuming that the Fe metal was produced during quench.

terization of the phases present in the interstitial material. This could not be done with certainty, but enough information was obtained to allow useful approximations to be made. No glass was observed after careful microscopic search of thin sections and grain mounts, and therefore glass probably makes up less than 2% of the sample. Microprobe analyses of the interstitial residuum (with ferric iron computed by difference from 100% total) scattered widely about the composition  $\text{Fe}_3\text{O}_4 \cdot 2\text{SiO}_2$  (Fig. 2), as would be expected if the material was the result of iron removal from the  $\text{Fe}_2\text{SiO}_4$  composition (equation 3). The  $\text{Fe}_3\text{O}_4 \cdot 2\text{SiO}_2$  component could be a mixture of magnetite and a silica polymorph, and these were seen in the sample. This is also, however, the reported stoichiometry of the mineral laihunite (Fleischer et al., 1978). Single crystal X-ray diffraction studies by Professor Adolf Pabst of the University of California at Berkeley (written comm., 1981) did in fact reveal one grain (of six silicate grains analyzed from the C-1 run products) that had the shortened *c* unit cell dimension characteristic of laihunite ( $a = 4.83$ ,  $b = 10.29$ ,  $c = 5.83\text{\AA}$ ).

### Heat of fusion calculations

Our results and those of Bowen and Schairer (1932) are consistent if we assume that the fayalite peritectic liquid contains about 2 wt.%  $\text{Fe}_2\text{O}_3$ . Equation 2 for equilibrium melting can then be rewritten:

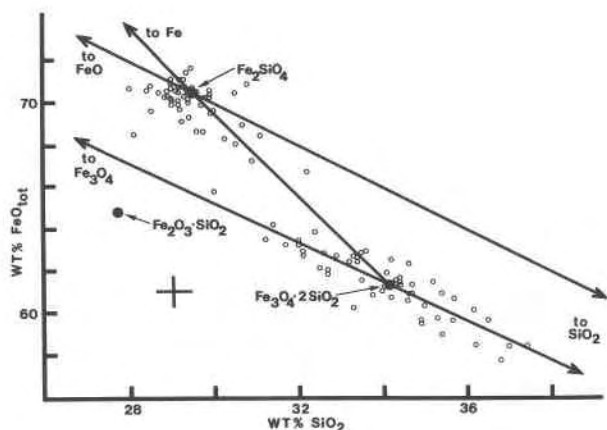
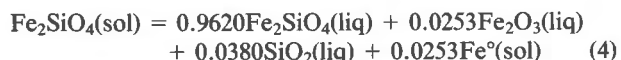


Fig. 2. Microprobe analyses of sample C-1 after quenching from 1615 K, in wt.%  $\text{SiO}_2$  and total iron as FeO. Analyses falling on the line between FeO and  $\text{SiO}_2$  total to 100%, while those below this line contain  $\text{Fe}_2\text{O}_3$  and have low totals. Points near  $\text{Fe}_2\text{SiO}_4$  are from transparent silicate grains, while those along the  $\text{Fe}_3\text{O}_4$ - $\text{SiO}_2$  join are from dark brown to opaque interstitial material. The means of the two clusters of points are within a few tenths of one percent of these stoichiometric compositions. The cross shows the size of typical standard deviations in the analyses of homogeneous fayalite grains and can be taken as instrumental precision. The two lines extending off the plot to the right are not parallel, but converge to pure  $\text{SiO}_2$ . Note that the non-fayalite points cannot be obtained by simple addition of oxygen to fayalite (resulting in  $\text{Fe}_2\text{O}_3$ - $\text{SiO}_2$ ), but must be related by removal of metallic iron. Data for sample C-2 show a similar distribution.

Drop calorimetry on melted fayalite actually measures the enthalpy difference between the liquid plus metal as shown on the right hand side of equation 4, and a mixture of fayalite and other phases (symbolized by "mix" below) whose bulk composition is that of fayalite and which could form this mineral. With  $\Delta H_T^{\text{liq}}$  indicating this directly measured enthalpy,

$$\Delta H_T^{\text{liq}} = H_T^{\text{liq}+\text{Fe}} - H_{300}^{\text{mix}} \quad (5)$$

To fix  $\Delta H_T^{\text{liq}}$  at a temperature near to the peritectic, the data from sample C-2 are clearly more appropriate than the results either from our sample C-1 or from Orr (1953), as equilibrium could be reached between liquid and metallic iron in C-2 only. To calculate the heat of fusion as a function of temperature, however, we must rely on a value for the liquid heat capacity derived from data collected for samples run in platinum capsules, as these cover a range of temperature. We have chosen the  $C_p$  result for sample C-1, which is well within error of that of Orr (1953). The iron loss measured in C-1 (Table 2) indicates that the liquid contained about  $3.7 \pm 1$  wt.%  $\text{Fe}_2\text{O}_3$  just before quench. To correct the measured  $C_p$  for this composition to that of the equilibrium peritectic liquid, we have taken data on the heat capacity of the precipitated iron metal from Robie et al. (1979), and assumed that (as in many alloy systems without phase transitions) the excess  $C_p$  of mixing of Pt in Fe is negligible (Hultgren et al., 1973). Using the partial molar heat capacities of the liquid components FeO and  $\text{Fe}_2\text{O}_3$  derived by linear regression of data on a wide range of silicate liquid compositions (Carmichael and Stebbins, 1982), the necessary adjustment in  $C_p$  is only 0.18%. The correction of the measured  $C_p$  to pure  $\text{Fe}_2\text{SiO}_4$  liquid is still only 0.34%. Both factors are much less than experimental error in  $C_p$  (about 3.5%), and have been ignored in the following calculations. Similarly, small changes in the liquid composition with temperature should not affect the heat capacity significantly.

With the relative enthalpy constrained to equal that of C-2 at 1520 K, and the  $C_p$  from the data on C-1,

$$\Delta H_T^{\text{liq}} = -295.23 + 1.1960T \text{ J per g sample} \quad (6)$$

With "fay" symbolizing pure, crystalline fayalite, the enthalpy of the equilibrium incongruent melting reaction ( $\Delta H_{\text{inc}}$ ) at the peritectic temperature ( $T_{\text{inc}}$ ) can now be calculated from:

$$\Delta H_{\text{inc}} = \Delta H_{T_{\text{inc}}}^{\text{liq}} - (H_{T_{\text{inc}}}^{\text{fay}} - H_{300}^{\text{fay}}) - (H_{300}^{\text{fay}} - H_{300}^{\text{mix}}) \quad (7)$$

To calculate the high temperature enthalpy of crystalline fayalite ( $H_{T_{\text{inc}}}^{\text{fay}} - H_{300}^{\text{fay}}$ ), we have chosen the equation of Robie et al. (1982), which is based on the drop calorimetry of Orr (1953) and is constrained by heat capacities measured by adiabatic calorimetry between 5 and 383 K. Enthalpies calculated from this equation can be refitted by a simplified expression, which yields points that are

the same within 200 J mol<sup>-1</sup> between 900 and 1900 K:

$$H_T - H_{300} = 123.80T + 3.1167 \times 10^{-2}T^2 - 36771 \text{ J mol}^{-1} \quad (8)$$

The last term on the right hand side of (7) is the enthalpy change of the reaction of the mixture of phases to form fayalite at 300 K. If the non-fayalite mixture of phases were made up primarily of glass, the computed heat of fusion could be too low by 10–15%. Little or no glass was observed, however, and any correction to the enthalpy of fusion should be small. If the mixture included a high proportion of laihunite, a precise correction could not be made, as no thermochemical data are available for this mineral. The error probably would not be large: as a first approximation, heats of fusion of structurally similar minerals are comparable. Iron metal, magnetite, and a silica polymorph (assumed here to be tridymite) probably made up much of the non-fayalite part of the quench products. The heat of the reaction of these materials to form fayalite can be calculated, with:



Using data from Robie et al. (1979),  $\Delta H$  for reaction 9 is  $-121.0$  J per g of magnetite. Because additional, disequilibrium disproportionation occurred during quench of the drop calorimetry samples, more of the non-fayalite mixture of phases was formed than is represented by equation 4. The analysis of C-2 in Table 2 indicates that 0.0946 g of Fe<sub>3</sub>O<sub>4</sub> per g of sample must be combined with iron and SiO<sub>2</sub> to produce fayalite. If it is assumed that all of the interstitial residuum is a mixture of magnetite and tridymite, then  $H_{300}^{\text{fay}} - H_{300}^{\text{mix}}$  is  $-11.45$  J per g of sample, or about 2.5% of  $\Delta H_{\text{inc}}$ .

The enthalpy of incongruent melting (reaction 4) can thus be expressed as a function of temperature:

$$\Delta H_{\text{inc}} = 67.689T + 4.404 \times 10^{-3} T^2 - 3.889 \times 10^6 T^{-1} - 8.237 \times 10^{-6} T^3 + 7770 \text{ J mol}^{-1} \quad (10)$$

With the simplified equation for the solid (equation 8), from 900 to 1900 K:

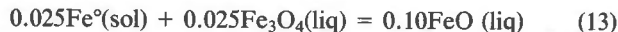
$$\Delta H_{\text{inc}} = 119.91 T - 3.1167 \times 10^{-2} T^2 - 21057 \text{ J mol}^{-1} \quad (11)$$

The heat of incongruent melting at the 1 bar peritectic temperature of 1490 K is therefore  $88.4 \pm 1.1$  kJ mol<sup>-1</sup>. The error bracket was chosen as twice the standard error calculated from the uncertainty in the calorimetric data and an assumption of an uncertainty of 50% in the ferric iron content of the peritectic liquid. Errors due to uncertainty in the relative proportions of the quench phases in our experiments are probably considerably smaller.

Finally, we can approximate the enthalpy of the hypothetical congruent melting reaction:



The enthalpy of reaction 4 can be corrected to that of reaction 12 by adding the enthalpy change of the reaction:



The heat of reaction 12 can in turn be approximated as  $0.025 \times 35$  kJ mol<sup>-1</sup> from estimates of the heat of fusion of Fe<sub>3</sub>O<sub>4</sub> and FeO, and of the reaction between iron and the crystalline oxides (Robie et al., 1979). Adding the resulting 900 J mol<sup>-1</sup> to  $\Delta H_{\text{inc}}$ , we calculate  $\Delta H_{\text{f, congruent}}$  to be  $89.3 \pm 1.1$  kJ mol<sup>-1</sup>. Surprisingly enough, the value calculated by Orr (1953) is only 3.3% greater than this result.

The calorimetric results presented here can be independently checked by calculation of the initial slope of the fayalite melting curve. Using the approximation of congruent melting, the results of Mo et al. (1982) for the liquid volume, and those of Smyth (1975) and Suzuki et al. (1981) for the solid volume, the Clapeyron slope ( $\Delta H_f/T_f \Delta V_f$ ) is 121 bar K<sup>-1</sup>. This value compares well with high pressure experiments of Lindsley (1967), which show an average slope of  $150 \pm 20$  bar K<sup>-1</sup> from 0 to 10 kbar.

### Acknowledgments

We would like to thank S. R. Bohlen and M. L. Rivers for synthesizing fayalite starting materials, and A. Pabst for providing the results of single crystal X-ray diffraction studies of the quench products. S. R. Bohlen and A. Navrotsky provided careful and constructive reviews. The work was supported in part by NSF grant EAR-78-03642 to Carmichael, and in part was prepared for the director, Office of Basic Energy Sciences, Division of Engineering, Mathematics, and Geosciences, of the U.S. Department of Energy, under contract W-7405-ENG-48.

### References

- Bowen, N. L. and Schairer, J. F. (1932) The system, FeO–SiO<sub>2</sub>. American Journal of Science, series, 5, 24, 177–213.
- Carmichael, I. S. E. and Stebbins, J. F. (1982) Silicate liquid heat capacities: new data on partial molar heat capacities and  $C_p$  at the glass transition. Transactions of the American Geophysical Union, 63, 1137.
- Fleischer, M., Cabri, L. J., Chao, G. Y., and Pabst, A. (1978) Ferrifayalite (new mineral names). American Mineralogist, 63, 424.
- Hultgren, R., Desai, P. D., Hawkins, D. T., Gleiser, M., and Kelley, K. K. (1973) Selected Values of the Thermodynamic Properties of Binary Alloys. American Society for Metals, Metals Park, Ohio.
- Lindsley, D. H. (1967) Pressure–temperature relations in the system FeO–SiO<sub>2</sub>. Carnegie Institute of Washington Year Book, 65, 226–230.
- Muan, A. (1955) Phase equilibria in the system FeO–Fe<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>. Transactions of the American Institute of Mining and Metallurgical Engineers, 203, 965–976.
- Orr, R. L. (1953) High temperature heat contents of magnesium orthosilicate and ferrous orthosilicate. Journal of the American Chemical Society, 75, 528–529.
- Robie, R. A., Hemingway, B. S., and Fisher, J. R. (1979) Thermodynamic properties of minerals and related substances

- at 298.15 K and 1 bar ( $10^5$  Pascals) pressure and at higher temperature. United States Geological Survey, Bulletin 1452, revised edition.
- Robie, R. A., Finch, C. B., and Hemingway, B. S. (1982) Heat capacity and entropy of fayalite ( $\text{Fe}_2\text{SiO}_4$ ) between 5.1 and 383 K: comparison of calorimetric and equilibrium values for the QFM buffer reaction. *American Mineralogist*, 67, 463–469.
- Smyth, J. R. (1975) High temperature crystal chemistry of fayalite. *American Mineralogist*, 60, 1092–1097.
- Stebbins, J. F., Carmichael, J. S. E., and Weill, D. F. (1983) The high temperature liquid and glass heat contents and the heats of fusion of diopside, albite, sanidine, and nepheline. *American Mineralogist*, 717–730.
- Suzuki, I., Seya, K., Takei, H., and Sumino, Y. (1981) Thermal expansion of fayalite,  $\text{Fe}_2\text{SiO}_4$ . *Physics and Chemistry of Minerals*, 7, 60–63.
- Weill, D. F., Stebbins, J. F., and Carmichael, I. S. E. (1980) The heat of fusion of anorthite. *Contributions to Mineralogy and Petrology*, 74, 95–102.
- Wilson, A. D. (1960) The micro-determination of ferrous iron in silicate minerals by a volumetric and a colorimetric method. *Analyst*, 85, 823–827.
- Wilson, A. D. (1955) A new method for the determination of ferrous iron in rocks and minerals. *Bulletin of the Geological Society of Great Britain*, no. 9, 56–58.

*Manuscript received, January 27, 1983;  
accepted for publication, August 30, 1983.*