Are the thermodynamic properties of natural and synthetic Mg$_2$SiO$_4$-Fe$_2$SiO$_4$ olivines the same? ☙

Charles A. Geiger[1],*, Noreen M. Vielreicher[1], and Edgar Dachs[1]

[1]Department of Chemistry and Physics of Materials, Section Materials Science and Mineralogy, Salzburg University, Jakob Haringer Strasse 2a, A-5020 Salzburg, Austria

Abstract

It is not known if the thermodynamic behavior of some minerals and their synthetic analogues are quantitatively the same. Olivine is an important rock-forming substitutional solid solution consisting of the two end-members forsterite, Mg$_2$SiO$_4$, and fayalite, Fe$_2$SiO$_4$. We undertook the first heat capacity, C_P, measurements on two natural olivines between 2 and 300 K; nearly end-member fayalite and a forsterite-rich crystal Fo$_{0.904}$Fa$_{0.096}$. Their $C_P(T)$ behavior is compared to that of synthetic crystals of similar composition, as found in the literature. The two natural olivines are characterized by X-ray powder diffraction and ^{57}Fe Mössbauer spectroscopy. The X-ray results show that the crystals are well crystalline. The Mössbauer hyperfine parameters, obtained from a fit with two Fe^{2+} quadrupole split doublets, are similar to published values measured on synthetic olivines. There are slight differences in the absorption line widths (i.e., FWHM) between the natural and synthetic crystals. C_P (2 to 300 K) is measured by relaxation calorimetry. The C_P results of the natural nearly end-member fayalite and published values for two different synthetic Fa$_{100}$ samples are in excellent agreement. Even C_P resulting from a Schottky anomaly and a paramagnetic-antiferromagnetic phase transition with both arising from Fe^{2+} are similar. There are slight differences in the Néel temperature between the natural 63 K and synthetic ~65 K fayalites. This is probably related to the presence of certain minor elements (e.g., Mn^{2+}) in the natural crystal. The third-law entropy, $S°$, value is 151.6 ± 1.1 J/(mol·K). C_P behavior of the natural forsterite, Fo$_{0.904}$Fa$_{0.096}$, and a synthetic olivine, Fo$_{90}$Fa$_{10}$, are in excellent agreement between about 7 and 300 K. The only difference lies at $T < 7$ K, as the former does not show Debye T^3 behavior, but, instead, a plateauing of C_P values. The $S°$ value for the natural forsterite is 99.1 ± 0.7 J/(mol·K).

Keywords: Thermodynamics, calorimetry, heat capacity, entropy, olivine, ^{57}Fe Mössbauer spectroscopy

Introduction

The database of thermodynamic properties of rock-forming minerals is large. However, in spite of the great amount of research that has been done, there are still various outstanding issues. One important issue concerns the thermodynamic behavior of minerals and their synthetic analogues. This is critical because there is an underlying assumption in the community that there are no or negligible energetic differences between synthetic and natural crystals. The compilation of calorimetrically determined properties of Robie and Hemingway (1995) contains, for example, results obtained on both natural and synthetic phases. Internally consistent thermodynamic databases use phase-equilibrium and calorimetric results, obtained on the two types of crystals as well, to derive "best-fit" values of different thermodynamic functions. There could be, though, quantitative differences in the thermodynamic properties for some minerals.

Helgeson et al. (1978) wrote in their "Summary and Critique of the Thermodynamic Properties of Rock-Forming Minerals" that the two types of phases could behave differently. However, since then, little research has addressed this issue. Geiger and Dachs (2018) did analyze the standard third-law entropy, $S°$, value of various "end-member" silicate garnets both synthetic and natural. In two cases (i.e., almandine and andradite), there was no marked difference between synthetic and natural crystals in terms of calorimetric heat-capacity measurements, $C_P(0–300 K)$, which were used to obtain $S°$. They noted, though, that older calorimetric $C_P(0–300 K)$ measurements may not have been fully quantitative in some cases because of different technical issues. On the other hand, in the case of grossular, Ca$_3$Al$_2$Si$_3$O$_{12}$, where multiple calorimetric studies on various natural and synthetic crystals have been made and in several independent laboratories, there are small but measurable variations in $C_P(T)$ behavior and $S°$ values (Dachs et al. 2012; Geiger and Dachs 2018).

Constant pressure heat capacity, $C_P(T)$, is an essential thermodynamic function of any crystalline substance, especially at low temperatures (Westrum 1962)[1]. It can be measured directly via calorimetry. It is defined as

$$C_P = \left(\frac{dH}{dT}\right)_P \tag{1}$$

where H is the enthalpy. From it, $S°$ can be calculated via:

$$S° - S^{T=0K} = \int_0^{298.15} \frac{C_P}{T} dT \tag{2}$$

assuming $S^{T=0K} = 0$. $S°$ can also be considered the calorimetric entropy.

Olivine is an important substitutional solid-solution silicate consisting of the two end-members forsterite, Mg_2SiO_4, and fayalite, Fe_2SiO_4. It occurs in meteorites, asteroids, and in solid planets and their moons, and it is the most abundant phase in Earth's upper mantle. A precise knowledge of olivine's thermodynamic properties is crucial for undertaking various mineralogical, petrological, geochemical, and geophysical investigations. One area of current geochemical and metamorphic research is focusing on mineral carbonation and serpentinization of peridotite (Keleman et al. 2011). Here, relatively low-temperature olivine-bearing reactions are of importance. Olivine's thermodynamic behavior is complex and involves the atomic mixing of Fe^{2+} and Mg over two crystallographically independent octahedrally coordinated sites M1 and M2. Their mixing is temperature and composition dependent. Moreover, intermediate Fe^{2+}-bearing olivines show a low-temperature magnetic phase transition and a Schottky anomaly. Robie et al. (1982a, 1982b) measured the low-temperature C_P (5–300 K) of synthetic end-member forsterite and fayalite, respectively, using adiabatic calorimetry. Dachs et al. (2007) also measured both end-members and, in addition, a number of synthetic intermediate-composition, $(Mg_{1-x},Fe_x^{2+})_2SiO_4$, crystals using relaxation calorimetry. As best we know, no $C_P(0–300 K)$ measurements have been made on natural olivine.

In light of this, this study presents first low-temperature C_P measurements of two different composition natural olivines. The results are compared to those obtained on synthetic crystals, and an analysis of the thermodynamic behavior is made and conclusions drawn.

METHODS

Samples

Two natural olivine samples with different compositions, including a nearly end-member fayalite and a forsterite ($Fo_{0.904}Fa_{0.096}$), were selected for study. They are described in Table 1. Their compositions are given in Table 2. A fayalite-rich rock chip (Rockport, Massachusetts) roughly two centimeters in size was crushed to a sand size and clear olivine grains were carefully hand-picked under a binocular to obtain a clean separate. The forsterite-rich olivine (Pyaung-gaung Mine, Myanmar) was prepared as a doubly polished platelet, about $3.3 \times 4.3 \times 1.0$ mm, as taken from a larger single crystal.

X-ray powder diffraction, ^{57}Fe Mössbauer spectroscopy, and low-temperature C_P measurements

Sample purity was checked via X-ray powder diffraction (XRPD) using a Bruker D8 Advance with DaVinci-Design diffractometer (Bruker AXS, Karlsruhe, Germany). Splits from both samples were ground, mounted on a single-crystal silicon holder and measured using $CuK\alpha$ radiation (40 kV, 40 mA) in continuous mode between $5° \leq 2\theta \leq 95°$ with a step size of 0.015° and 0.15 s/step. The diffractometer has a Bragg-Brentano beam geometry with a fixed 0.3° divergence slit, primary and secondary side 2.5° Soller slits, a 4.0° antiscatter slit, and an energy-dispersive Lynxeye detector (opening angle 2.934°). Silicon powder NBS SRM 640b was used as an external calibration standard. Data were plotted using DIFFRAC.EVA (ver. 5.0.0.22, 2019, Bruker AXS Inc., Wisconsin, U.S.A.).

The experimental ^{57}Fe Mössbauer spectroscopic setup has been described before (Palke et al. 2015). In brief, ^{57}Fe Mössbauer transmission spectra were recorded in a horizontal arrangement using a $^{57}Co/Rh$ single-line source with constant acceleration and a symmetric sawtooth velocity shape. The absorption data

TABLE 2. Published microprobe results for the two studied olivine samples in oxide wt% and the calculated crystal-chemical formulas based on four O atoms

Sample	NMNH R3517[a]	NFo90/C1[b]
SiO_2	29.78	40.9
FeO	66.48	9.4
MgO	0.05	49.4
MnO	2.14	–
ZnO	0.54	–
NiO/Ni_2O_3	0.04	0.3
CaO	0.05	–
TiO_2	Trace	–
CoO	0.10	–
Total	99.18	100.0
Si	1.01	1.00
Fe^{2+}	1.89	0.19
Mg	–	1.80
Mn^{2+}	0.06	–
Zn^{2+}	0.01	–
Ni	–	0.01
Total	2.97	3.00

[a] Cloutis (2015), [b] Belley et al. (2009).

were collected in a multi-channel analyzer having 1024 channels and the velocity calibration was made using a 30 μm thick α-Fe foil. The FWHM associated with the ^{57}Co source is 0.243 ± 0.015. A powdered sample was contained in a plastic disk held a Cu-ring of 10 mm inner diameter, covered with high-purity Al-foil on the backside. The folded spectrum was evaluated by using Lorentzian-shaped doublets using the program RECOIL.

$C_P(T)$ was measured three times at 60 different temperature increments from 300 down to 2 K. The mass of the polycrystalline fayalite sample was 15.47 mg. The mass of the forsterite crystal platelet was 30.57 mg. The Quantum Design relaxation calorimeter and the experimental setup used to measure C_P have been described before (Dachs and Bertoldi 2005; Geiger and Dachs 2018) and are not repeated here. Measurements on standard Al_2O_3 and/or MgO single crystals (Geiger and Dachs 2018) are made on a regular basis to check the experimental accuracy.

RESULTS

The X-ray results show that both samples are primarily olivine with only minor amounts of other phases (Online Material[2] Figs. OM1a and OM1b). The ^{57}Fe Mössbauer spectra are shown in Figures 1a and 1b and they can be fitted well with two Fe^{2+} doublets. The fit parameters are given in Table 3. The amount of Fe^{3+} in both samples is very minor, based on the minimal to nil absorption between 0.0 and 1.0 mm/s. No attempt was made to account for possible differences in the recoil-free fraction for Fe^{2+} at M1 and M2.

The $C_P(T)$ data from the relaxation-calorimetry measurements of the two natural olivines are compared with the C_P behavior of synthetic olivines of similar compositions in Figures 2a and 2b. The data for the former samples are average values obtained from three separate $C_P(2–300 K)$ measurements (cf. raw data in Online Material[1] Tables OM1a and OM1b and 1σ errors). The data for the two different synthetic fayalite samples are the smoothed values given in Robie et al. (1982b) and Dachs et al. (2007). A pronounced paramagnetic-antiferromagnetic magnetic transition and a Schottky anomaly, both related to Fe^{2+}, are apparent in the data of the fayalites. The Néel temperature, T_N, of the magnetic

TABLE 1. Olivines used for investigation

Label	Locality (source)	Sample description and references
NFo90/C1	Pyaung-gaung Mine, Mogok, Katha District, Myanmar (E. Ferré)	~5 mm size gemmy-like crystals within metamorphosed dolomitic limestone[a,b]
NMNH R 351700	Rockport, Massachusetts, U.S.A. (Smithsonian Institute)	Isolated fayalite-rich rock masses in pegmatite and granite; xenolithic[c,d,e,f]

[a] Belley et al. (2009), [b] Harlow and Thu (2014), [c] Palache (1950), [d] Dyar et al. (1998), [e] Rose et al. (2009), [f] Cloutis (2015).
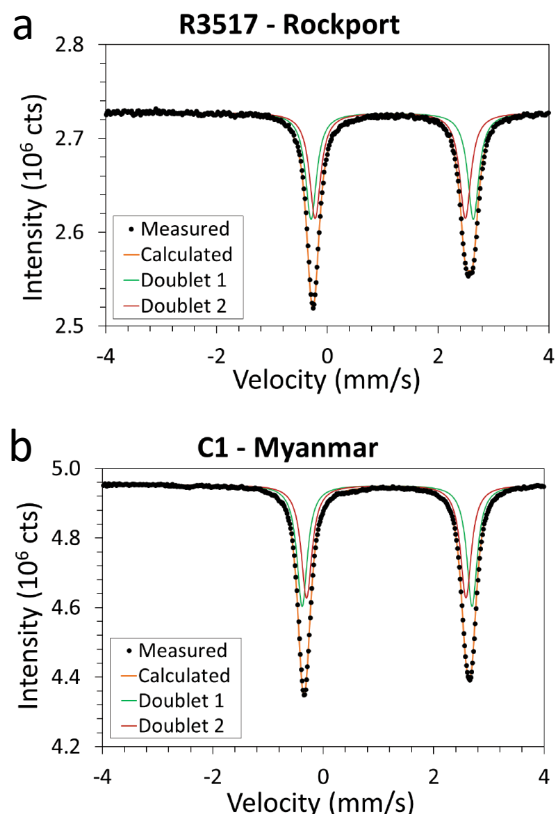
Figure 1. ^{57}Fe Mössbauer spectra of natural olivine samples. (**a**) NMNH R3517 fayalite from Rockport, Massachusetts, U.S.A. and (**b**) C1/NFo90 forsterite from Mogok, Myanmar. The spectra are fitted with two different symmetric quadrupole split doublets. The green doublet with the larger quadrupole split value corresponds to Fe^{2+} at the octahedrally coordinated M2 site and the red doublet with the smaller value to Fe^{2+} at M1 (see Table 3). (Color online.)
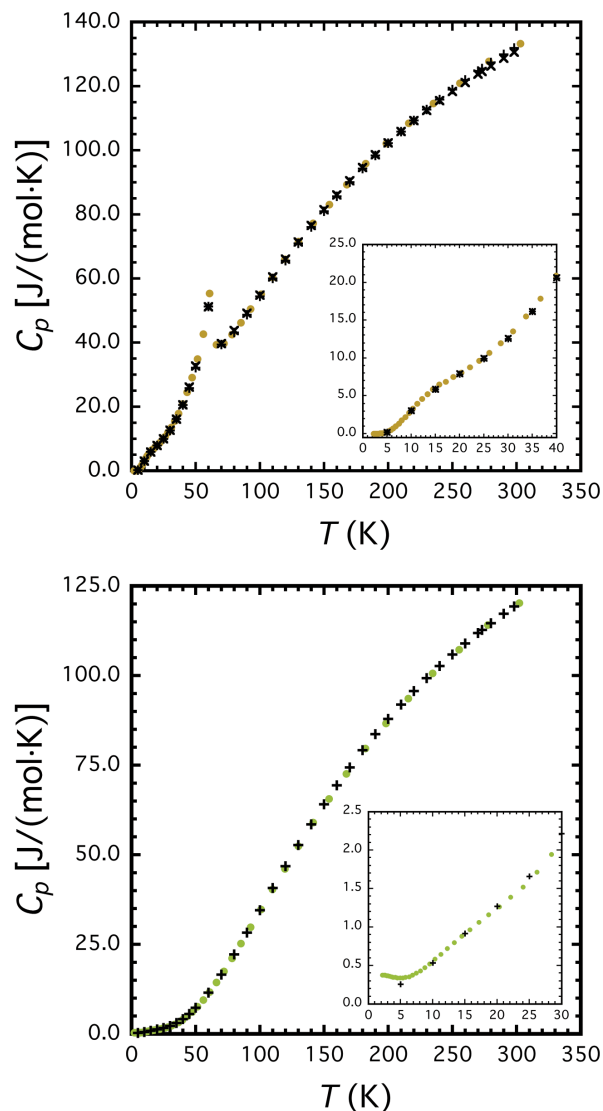
Figure 2. C_P data from 2 to 300 K. (**top**) The brown circles are data for nearly end-member fayalite NMNH R3517 from Rockport, Massachusetts, U.S.A., the "x" symbols (Dachs et al. 2007) and the "+" symbols (Robie et al. 1982b) for synthetic fayalite. The inset shows the lowest temperature region and note the Schottky anomaly. (**bottom**) The green circles are data for the natural forsterite, Fo$_{0.904}$Fa$_{0.096}$, from the Pyaung-gaung Mine, Mogok, Katha District, Myanmar, and the "+" symbols for synthetic Fo$_{90}$Fa$_{10}$ (Dachs et al. 2007). The inset shows the lowest temperature region and note the plateauing of C_P values for the natural crystal below about 7 K. (Color online.)

transition is 64.9 K (Robie et al. 1982b) or 64.5 K (Dachs et al. 2007) for synthetic fayalite and 63.1 K for the natural Rockport sample. A weak and broad Schottky anomaly, arising from the spin-orbit interaction for Fe^{2+}, is centered at about 15 K for both types of crystals (Fig. 2a). The $S°$ value calculated (Eq. 2) for the Rockport sample is 151.6 ± 1.1 J/(mol·K) [$S°$ is taken to be equal to $S^{\text{calorimetric}}$ at 298.15 K and the entropy contribution for the temperature region between 0 and 2 K is negligible being about 0.003 J/(mol·K)]. Uncertainties in $S°$ associated with relaxation calorimetry are discussed in Geiger and Dachs (2018, Table 1). The $S°$ value for Rockport olivine is indistinguishable from the values obtained for synthetic fayalite of 151.0 ± 0.2 J/(mol·K) (Robie et al. 1982b) and 151.4 ± 0.1 J/(mol·K) (Dachs et al. 2007).

Figure 2b shows the C_P(2–300 K) results for the natural forsterite of composition Fo$_{0.904}$Fa$_{0.096}$ and a synthetic olivine of comparable composition of Fo$_{0.90}$Fa$_{0.10}$ (Dachs et al. 2007). The intensity of the magnetic phase transition (i.e., magnon contribution to C_P) and T_N decrease with decreasing Fe^{2+} in olivine (Dachs

TABLE 3. Fit parameters for the ^{57}Fe Mössbauer spectra (two Fe^{2+} quadrupole split doublets were fit to the spectra of both olivine samples)

Sample	Doublet 1: Fe^{2+} at M2				Doublet 2: Fe^{2+} at M1				χ^2
	Δ mm/s	Δ mm/s	Γ mm/s	Area %	Δ mm/s	δ mm/s	Γ mm/s	Area %	
Fayalite NMNH R3517	2.93	1.17	0.24	50.0	2.71	1.13	0.24	50.0	1.17
Forsterite NFo90/C1	3.08	1.15	0.24	50.9	2.89	1.14	0.24	49.1	1.94

Note: The parameters for Δ (quadrupole splitting), δ (isomer shift relative to α-Fe foil), and Γ (FWHM) are given to the second decimal and one decimal for the areas. Errors in the former are less than ±0.02 mm/s, whereas for the areas they are less than about ±5%.

et al. 2007; Geiger et al. 2019). For this forsterite-rich olivine, the C_P data show a very weak and broad feature that is centered roughly at 20 K, and that probably is magnetic in nature. A very weak possible Schottky anomaly is centered at about 13 K. Both can only be resolved and separated from the vibrational (phonon) C_P, by model calculations (Dachs et al. 2007). $S°$ for the synthetic $Fo_{0.90}Fa_{0.10}$ sample is 99.5 J/(mol·K) (Dachs et al. 2007) and for the natural crystal we calculate 99.1 ± 0.7 J/(mol·K) (this includes 0.03 J/(mol·K) for the temperature region between 0 and 2 K).

DISCUSSION

Natural vs. synthetic crystals

Olivine can be synthesized in the laboratory without the use of a flux and from high-purity component oxides. The experiment involves relatively short sintering times at high temperature (e.g., $T > 1000$ °C). For Fe^{2+}-bearing crystals the f_{O_2} conditions must be controlled. The resulting crystals are typically fine grained, roughly 1 to 100 μm in size. In nature, on the other hand, crystals can grow at lower temperatures (e.g., metamorphic regimes), and they do so over geologic time periods. They can be coarse grained ranging up to centimeters in size (of course, natural crystals can have varying modes of origin). Consequently, differences in the structural state, that is Fe^{2+}-Mg order-disorder over the M1 and M2 sites, between synthetic and natural olivines can occur because of the different crystallization processes. Natural crystals from metamorphic or plutonic settings can, in general, be more ordered in terms of atomic structure compared to their synthetic analogues. Ordered crystals typically have stronger chemical bonding than disordered ones of the same composition. It follows that $C_P(T)$ and $S°$ values for the former should be smaller than the latter. Heat capacity and entropy effects related to long-range cation order-disorder in Fe^{2+}-Mg olivine solid solutions have not been investigated in a quantitative manner.

Natural olivine is expected to generally contain higher concentrations of minor or trace elements compared to synthetic crystals prepared from high purity reactants. Finally, there is also the issue of defect chemistry and point defects to consider and, here, there could also possibly be differences between synthetic and natural crystals. Some natural olivines may contain a little Fe^{3+} (Ejima et al. 2012), and minor structural OH^- can be present as well (Miller et al. 1987). What do the results of our X-ray, ^{57}Fe Mössbauer and C_P measurements show?

X-ray diffraction and ^{57}Fe Mössbauer spectroscopic interpretation

The X-ray results indicate that both olivine samples are nearly pure. Only small amounts (about <1%) of other phases could be identified. The olivine powder diffraction peaks are intense and narrow in width indicating good crystallinity (Online Material[1] Fig. OM1). The ^{57}Fe Mössbauer spectra can be fit well with two Fe^{2+} quadrupole-split doublets (Bancroft et al. 1967; Dyar et al. 2009). The amount of Fe^{3+} in both samples is very minor based on the minimal to nil absorption between about 0.0 and 1.0 mm/s (Fig. 1).

In terms of high-spin Fe^{2+} in olivine and for a first-order analysis, the magnitude of the quadrupole splitting gives a measure of the asymmetry of the charge distribution around the Fe nucleus

(i.e., octahedral M-site distortion). It consists of valence and lattice terms, whereby the latter decreases with increasing distortion. The isomer shift measures the s electron contact density at the Fe nucleus (i.e., is a function of the ligand coordination). Single-crystal diffraction results on olivine indicate that M1 is smaller in volume and more distorted than M2 at room temperature (Princivalle 1990). The assignments of the two Fe^{2+} doublets in Table 3 follow this reasoning. The areas of the two doublets for both samples are similar. For the fayalite, the areas should be similar (assuming that the small amount of Mn^{2+} in the olivine is not located largely at either M1 or M2). The spectrum of the forsterite sample may show a slight tendency for Fe^{2+} to favor M2, but the difference in doublet areas is within experimental error. The hyperfine parameters of both natural olivines (Table 3) are in good agreement with those obtained on synthetic samples of similar composition (Dyar et al. 2007), except possibly for the quadrupole split value for doublet 2 for our fayalite (i.e., 2.71 mm/s) vs. that of an end-member composition synthetic fayalite (i.e., 2.76 mm/s).

A possible systematic difference between the spectra of natural and synthetic olivines may lie in the values of the absorption line widths (i.e., FWHM). For the two natural crystals they are the same with values of 0.24 mm/s, whereas synthetics give values of about 0.29 mm/s for Fa_{100} and 0.27 mm/s for $Fo_{90}Fa_{10}$ (Dyar et al. 2009) A precise crystal-chemical interpretation of the line widths is difficult to make, but larger widths may reflect more nearest or next-nearest neighbor atomic disorder (i.e., structural heterogeneity).

$C_P(T)$ and $S°$ behavior

The C_P(2–300 K) behavior of natural fayalite and synthetic Fa_{100} is in excellent agreement. Even C_P arising from magnon contributions and the Schottky anomaly is the same for the two crystal types. This agreement is a notable result, we think, considering the very different origins of the two olivine samples. There is a slight difference of about 2 K between the T_N values (~65 K for synthetic samples vs. 63 K for the natural crystal). In the case of "end-member composition" silicate garnets, small variations in T_N can arise from minor concentrations of "impurity" cations occurring in solid solution (Geiger et al. 2019). This is possibly the case here as well because the natural fayalite contains some Mn^{2+} substituting for Fe^{2+}. Because Mn^{2+} and Fe^{2+} have similar masses (54.94 and 55.85 amu, respectively) and ionic radii in sixfold coordination (83 pm vs. 78 pm), their vibrational (phonon) behavior in olivine should be similar. There is excellent agreement among the $S°$ values for synthetic fayalite of 151.0 ± 0.2 J/(mol·K) (Robie et al. 1982b) and 151.4 ± 0.1 J/(mol·K) (Dachs et al. 2007) and for the natural fayalite [151.6 ± 1.1 J/(mol·K)].

The $C_P(T)$ behavior of the natural forsterite $Fo_{0.894}Fa_{0.106}$ and the synthetic $Fo_{90}Fa_{10}$ sample (Dachs et al. 2007) are in excellent agreement between about 7 and 300 K. It would appear that any phonon difference arising from possible variations in Fe^{2+}-Mg order-disorder are minimal to nil. The only observable differences in C_P behavior lies at $T < 7$ K. The natural crystal does not show Debye T^3 behavior but instead a quasi-plateauing of C_P values between about 2 and 7 K (Fig. 2b).

A physical interpretation for this result is difficult to make.

There is very little research, of any type, on silicates at such low temperatures. Many older adiabatic calorimetry investigations were only made down to roughly 8 K. However, one could speculate that the plateauing is due to an "impurity" atom such as Fe^{3+}. Gmelin (1969) undertook very low C_P measurements down to 0.5 K on MgO and proposed that 340 ppm Fe^{3+} gives rise to an anomaly centered at roughly 1–2 K. Such concentrations of Fe^{3+} in natural olivine are possible, but more work is required to fully explain the nature of this C_P anomaly. This very low-temperature behavior is not of great significance for chemical thermodynamic calculations but rather for its thermal physical nature. The $S°$ of the crystal is 99.1 ± 0.7 J/(mol·K) and, thus, the same as that measured for synthetic $Fo_{0.90}Fa_{0.10}$ having a value of 99.5 ± 0.1 J/(mol·K) (Dachs et al. 2007).

IMPLICATIONS

This work shows that there are no significant $C_P(T)$ differences in a chemical thermodynamic sense between two selected natural olivine samples and their synthetic equivalents, despite their contrasting crystallization histories and small differences in chemistry. Further $C_P(T)$ measurements on additional intermediate olivine compositions are required to get a more complete handle on any possible thermodynamic differences between both types of phases. In addition, calorimetric measurements to determine enthalpies of formation and mixing could be useful as well. $\Delta C_P(298\ K)$ mixing behavior for olivines across the forsterite-fayalite join, calculated from IR spectra, may be nonideal according to Hofmeister and Pitman (2007).

For silicates, most low-temperature calorimetric studies have concentrated on end-member compositions in the case of substitutional-solid-solution systems. Moreover, older calorimetric work was sometimes done on minerals that were not always well-characterized structurally (e.g., structural state) and sometimes even compositionally. For these reasons, $C_P(T)$ and $S°$ behavior for various silicate solid solutions and phases showing atomic order-disorder are, in general, still not fully understood.

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Endnote:

[1]"The solid state researcher so often has occasion to acknowledge the extraordinary wealth of information that can be obtained about substances from low-temperature heat capacity determinations that one is tempted to attribute to such measurements a more fundamental significance than to any other unique method of investigation."
[2]Deposit item AM-21-27764, Online Materials. Deposit items are free to all readers and found on the MSA website, via the specific issue's Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2021/Feb2021_data/Feb2021_data.html).