

Low-temperature specific heat capacity measurements and application to Mars thermal modeling

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ABSTRACT

Data returned from Martian missions have revealed a wide diversity of surface mineralogies, including in geological structures interpreted to be sedimentary or altered by liquid water. These terrains are of great interest because of their potential to document the environment at a time when life may have appeared. Intriguingly, Martian sedimentary rocks show distinctly low thermal inertia values (i.e. $300 - 700 \text{ J m}^{-2} \text{ K}^{-1} \text{ s}^{-1/2}$, indicative of a combination of low thermal conductivity, specific heat capacity, and density). These low values are difficult to reconcile with their competent bedrock morphologies, whereas hundreds of bedrock occurrences, interpreted as volcanic in origin, have been mapped globally and display thermal inertia values $> 1200 \text{ J m}^{-2} \text{ K}^{-1} \text{ s}^{-1/2}$. Bedrock thermal inertia values are generally assumed to be driven by their bulk thermal conductivity, which in turn is controlled by their micro- and macro-physical properties (i.e., degree and style of cementation in the case of detritic rocks, horizontal fractures and layering, etc.), and not by their density (well-known from terrestrial analog measurements, and with modest variability) or specific heat capacity (generally uncharacterized for non-basaltic materials below room temperature). In this paper, we demonstrate that specific heat capacity cannot be a potential cause for the differential thermophysical behavior between magmatic and sedimentary rocks through a series of experimental $C_p(T)$ measurements at 100–350 K using differential scanning calorimetry. The results on 20 Martian-relevant minerals investigated in this work indicate that these materials exhibit very similar specific heats, ranging from $0.3\text{--}0.7 \text{ J g}^{-1} \text{ K}^{-1}$ at 100 K to $0.6\text{--}1.7 \text{ J g}^{-1} \text{ K}^{-1}$ at 350 K. When used in a Martian thermal model, this range of C_p values translate to very small surface temperature differences, indicating that uncertainty in composition (and its effect on the specific heat) is not a noticeable source of thermal inertia variability for indurated units on Mars. We therefore conclude that the low thermal inertia value of sedimentary rocks compared to magmatic/volcanic rocks is likely due to their low apparent bulk conductivity, which bears information on their internal physical structure. Future work combining the analysis of thermal observations acquired at various local times and seasons will help further characterize this heterogeneity.

1. Introduction

1.1. Thermal inertia of sedimentary rock units

Rocks associated with aqueous environments have been identified on Mars based on their morphologies (i.e. channels, beds, delta, lakes etc. (McCauley et al., 1972; Milton, 1973; Carr and Clow, 1981; Christensen, 2003; Hynek et al., 2010), composition (resulting from precipitation or alteration (Ehlmann and Edwards, 2014 and references therein)), and also from their micro-scale properties observed by rovers (Squyres et al., 2004; Squyres and Knoll, 2005; Squyres et al., 2006; Lewis et al., 2008; Squyres et al., 2009; Squyres et al., 2012). These environments are of significant interest to the planetary community because they record a diversity of near-surface conditions throughout Mars' history. In addition, several of these environments may have preserved a record of past biological activities as well as prebiotic compounds,

making them prime target locations for future sample return missions. As of today, five groups of deposits have been identified:

i Phyllosilicate-bearing units have been discovered in the Noachian terrains, as part of layered units (i.e., Nilli Fossae, Mawrth Vallis, Gale Crater, etc.), excavated by impacts from deep rock formation, and in alluvial fans (i.e. Holden, Eberswalde, Terby, Jezero) (Loizeau et al., 2007; Ehlmann et al., 2009; Wray et al., 2009; Michalski et al., 2010). Depending on the location and geological context, a number of environments and processes have been proposed for their formation, including alteration of volcanic ash, sub-aerial weathering of basaltic regolith during wet periods, shallow marine sedimentation of sorted transported clays, impact-generated or geo/hydro-thermal alteration of the crust, or other aqueous diagenetic processes. These units are the most widely distributed record of a possible near-surface Noachian wet environment, with mineral

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types capable of preserving evidence of early life. High-resolution imagery demonstrates the indurated nature of these units (sometimes associated with polygonal fracturing). Phyllosilicates can make up a significant fraction (up to 70%) of rock units (Michalski et al., 2010; Poulet et al., 2014).

- ii Chloride-bearing units have been identified in Noachian terrains and proposed to originate from playas or saline lakes. These multi-meters thick units are of great interest for their potential to preserve a record of biological activities. Like phyllosilicates, these light-toned and polygonally fractured layers present vast exposures of indurated materials. Chloride-bearing minerals could account for ~25% of these rock units (Osterloo et al., 2008, 2010), though more recent work has refined these abundances via detailed spectroscopy modeling (Glotch et al., 2016).
- iii Hematite-bearing units are found in the late Noachian terrains, in Terra Meridiani, and seem to be frequently associated with sulfates (Glotch and Christensen, 2005; Glotch and Rogers, 2007). These terrains may have resulted from deposition in shallow acidic saline surface waters, or from diagenetic processes associated with rising groundwater. Hematite-bearing units are exposed as layered indurated units and comprise up to ~50% of these rock units (Christensen et al., 2000a; Squyres et al., 2004; Glotch and Rogers, 2007).
- iv Sulfate-bearing units are observed in various layered units, most noticeably in Hesperian formations. They may be associated with airfall sedimentation of pyroclastic materials into standing water, precipitates, groundwater alteration, or surficial chemical erosion (Gendrin et al., 2005; Wray et al., 2010). Sulfates present the unique property of being embedded in segregated sedimentary layers, and associated with distinct rock competences. These units may represent the best-preserved and accessible formations associated with Hesperian liquid water. Sulfate minerals make up to ~40% of these rock units in Meridian Planum.
- v Carbonate-bearing units are not ubiquitously found on Mars, but are thought to be associated with the alteration of common crustal minerals by liquid water from Noachian to Hesperian ages (Glotch, 2010; Harvey, 2010; Michalski and Niles, 2010; Morris et al., 2010; Glotch and Rogers, 2013). Carbonates (other than those found in the dust (Bandfield et al., 2003) are often found in association with phyllosilicates (Ehlmann and Edwards, 2014) and can comprise up to 25% of these rock units (Edwards and Ehlmann, 2015).

Intriguingly, published thermal inertia values for the sedimentary/ altered materials listed above ($300\text{--}700 \text{ J m}^{-2} \text{ K}^{-1} \text{ s}^{-1/2}$, see Table 1), are systematically and significantly lower than those expected for in-place consolidated materials, especially when compared to their volcanic/magmatic counterparts ($1200\text{--}2200 \text{ J m}^{-2} \text{ K}^{-1} \text{ s}^{-1/2}$) that are routinely observed on the planet from orbit (Edwards et al., 2009) (Fig. 1), and on the ground (Ferguson et al., 2006). Thermal inertia I is defined as a product of the bulk thermal conductivity k , bulk density ρ ,

and the specific heat capacity C_p of the surface such that:

$$I = \sqrt{k\rho C_p} \quad (1)$$

where each of these parameters is a function of temperature. I represents the subsurface's ability to store heat during the day and release it at night, and is thus a critical property in understanding diurnal and seasonal variations of the surface temperature on Mars (Putzig et al., 2005). In Eq. (1), the thermal conductivity k is a fundamental parameter controlling planetary surface temperatures, because it varies by ~4 orders of magnitude as a function of the physical nature of the regolith (Wechsler and Glaser, 1965; Neugebauer et al., 1971; Kieffer et al., 1976). This large range of possible values is due to the complex nature of heat transfer from grains to grains, which is strongly controlled by the configuration of the inter-grain regions (see a review in Presley and Christensen (1997)). In contrast, the density only varies by a factor ~2 as a function of a function of porosity, and the square root nature of Eq. (1) yields a marginal influence of the density or porosity on the bulk thermal inertia. Additional discussions regarding the relative contributions and potential variability of k , ρ , and C_p for geological materials can be found in Jakosky (1986) and Piqueux and Christensen (2009).

On Mars, the stark difference between the thermal inertia of sedimentary vs. magmatic unit does not appear to originate from subpixel mixing with fines, dust mantling, or low intrinsic density, for the following reasons:

- High-resolution surface imagery (when available) does not display a systematic mixing of materials correlated specifically with one unit type. More importantly, hundreds of magmatic bedrock occurrences have been identified with high thermal inertias ($> 1200 \text{ J m}^{-2} \text{ K}^{-1} \text{ s}^{-1/2}$ (Edwards et al., 2009)), demonstrating that subpixel mixing is far from systematic on indurated units. For completeness, we recognize that other magmatic units that are not associated with intact bedrock likely exist (Edwards et al., 2014) and have not been identified as such possibly due to subpixel mixing with Aeolian materials. Similarly, sedimentary units may have been misidentified as magmatic units based on their compositions and relatively high thermal inertia (Rogers et al., 2018).
- Systematic mantling of sedimentary rocks on Mars by dust is unlikely because sedimentary/altered units are primarily identified by their unique spectral properties. Therefore, dust mantling has to remain optically thin (i.e. not exceeding a few microns in thickness), which is also thermally thin (Kieffer et al., 2006). In other words, global and extensive dust mantling cannot explain the systematically low inertia values of sedimentary/altered rock units, or they would not be detectable.
- Extremely high-porosity (i.e., low density) indurated materials might exist as part of the sedimentary record, but the thermal inertia may only decrease by a modest factor compared to a porosity-free material (i.e. $\phi = 0.3$ or less) due to the square root relation

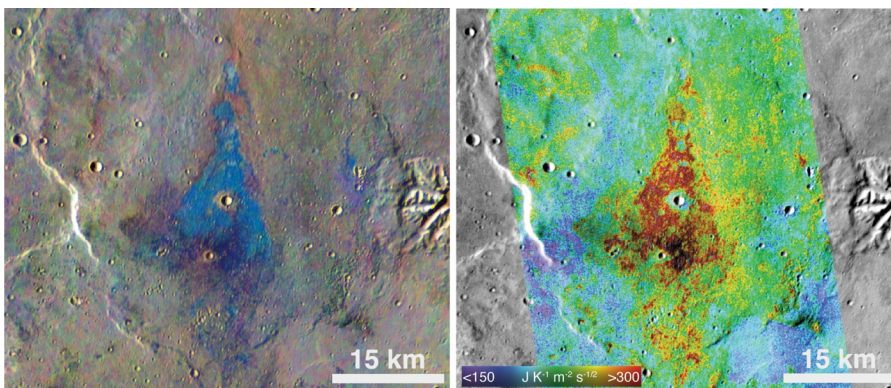


Fig. 1. (Left) Thermal Emission Imaging System (THEMIS) decorrelation stretch image (Edwards et al., 2011) of a chloride-sedimentary unit from Osterloo et al. (2008) (~346.6°E, 25.3°S), where blue hues are indicative of chloride-bearing materials. (Right) THEMIS-derived thermal inertia map of the same chloride-bearing unit, which clearly illustrates that these sedimentary rocks are of low-moderate thermal inertia.

Table 1

List of common mineralogical species on Mars and associated outcrop thermal inertia values. The specific heat capacity of all species listed in the “Mineral” column have been determined in this work, where different mineral groups are separated by colors. See the Results, Appendix sections and Table 2 for details (See References: Chojnacki and Hynek, 2008; Bandfield et al., 2000; Ehlmann et al., 2008; Bandfield, 2002; Golombek et al., 2014; Hamilton et al., 2001; Hamilton and Christensen, 2005; Hutchison et al., 2005; Jensen and Glotch, 2011; Loizeau et al., 2012; Mangold et al., 2008; Milam et al., 2007; Benisek and Dachs, 2013; Mustard et al., 2005; Poulet et al., 2005; Rogers and Christensen, 2007; Smith and Bandfield, 2012; Wyatt and McSween, 2002).

#	Mineral	Group	Key References	Outcrops Thermal Inertias	
1	Halite	Chloride	<i>Osterloo et al.</i> , 2008, 2010 <i>Glotch et al.</i> , 2010 <i>Jensen and Glotch</i> , 2011	Typical values: 329 - 446 Jm ⁻² K ⁻¹ s ^{-1/2} (from <i>Osterloo et al.</i> , 2010)	Secondary
2	Sylvite				
3	Epsomite	Sulfate	<i>Gendrin et al.</i> , 2005 <i>Hutchison et al.</i> , 2005 <i>Mangold et al.</i> , 2008	Typical values: 300 - 700 Jm ⁻² K ⁻¹ s ^{-1/2} (from <i>Chojnacki and Hynek</i> , 2008)	
4	Gypsum (alabaster)				
5	Gypsum (selenite)				
6	Magnesite	Carbonate	<i>Ehlmann et al.</i> , 2008 <i>Glotch and Rogers</i> , 2013 <i>Edwards and Ehlmann</i> , 2015	Typical values: 400 - 500 Jm ⁻² K ⁻¹ s ^{-1/2} (from <i>Edwards and Ehlmann</i> 2015)	
7	Siderite				
8	Nontronite	Phyllosilicate	<i>Poulet et al.</i> , 2005 <i>Loizeau et al.</i> , 2007 <i>Wray et al.</i> , 2009 <i>Loizeau et al.</i> , 2012	Typical values: < 550 Jm ⁻² K ⁻¹ s ^{-1/2} (from <i>Loizeau et al.</i> , 2007; <i>Smith and Bandfield</i> , 2012)	
9	Montmorillonite				
10	Kaolinite				
11	Hematite	Oxide	<i>Christensen et al.</i> , 2000a <i>Glotch et al.</i> , 2005 <i>Glotch and Rogers</i> , 2007	Maximum values: < 450 Jm ⁻² K ⁻¹ s ^{-1/2} (from <i>Golombek et al.</i> , 2014)	Primary
12	Olivine	Olivine	<i>Mustard et al.</i> , 2005 <i>Edwards et al.</i> , 2008 <i>Koeppen and Hamilton</i> , 2008 <i>Edwards and Ehlmann</i> , 2015	Primary phases always account for a significant fraction of the sediments studied in this work (at least 10s of %)	
13	Forsterite				
14	Enstatite	Pyroxene	<i>Bandfield et al.</i> , 2002 <i>Mustard et al.</i> , 2005 <i>Rogers and Christensen</i> , 2007		
15	Hypersthene				
16	Anorthite	Plagioclase Feldspar	<i>Bandfield et al.</i> , 2000 <i>Hamilton et al.</i> , 2001 <i>Wyatt and McSween</i> , 2002 <i>Rogers and Christensen</i> , 2007 <i>Milam et al.</i> , 2010		
17	Albite				
18	Andesine				
19	Orthoclase	Alkali Feldspar	<i>Bandfield et al.</i> , 2004 <i>Christensen et al.</i> , 2005 <i>Hamilton and Christensen</i> , 2005		
20	Microcline				

between I and ρ in Eq. (1). The values for I reported in the literature (Table 1) thus indicate that high porosity/low density is not the main factor in explaining the low sedimentary rock thermal inertias. We note that the intrinsic density of most geological materials is well-known (Waples and Waples, 2004).

From this analysis, we conclude that the low apparent thermal

inertia of Martian sedimentary rocks is not due to observational artifacts, and is instead linked to the specific heat capacity and/or thermal conductivity of the rock units.

Vasavada et al. (2017) and Edwards et al. (2018) have established *in situ* that the macro-scale properties of sedimentary rocks have the potential to explain part of their low apparent thermal inertia values. In particular, horizontal heterogeneity whose typical scale is smaller than

the length scale of a diurnally-forced solar insolation heat pulse of period P , i.e., smaller than a diurnal skin depth δ defined as:

$$\delta \equiv \sqrt{\frac{kP}{\rho C_p \pi}} = \frac{I}{\rho C_p} \sqrt{\frac{P}{\pi}} \quad (2)$$

disrupts the flow of heat in the subsurface and may result in lower apparent thermal inertia values. This effect was observed with the Ground Temperature Sensor onboard Curiosity (Vasavada et al., 2017; Edwards et al., 2008) and yielded deformed diurnal curves in addition to lower apparent thermal inertias. These authors demonstrated that an analysis of thermal data acquired over the course of a full diurnal cycle may provide new and unique information on the internal structure of bedrock units such as internal layering, inter-bed joint conductivity, horizontal fracturing, etc. that may in turn help constrain the history of these deposits. However, with the specific heat as a free parameter whose value may vary significantly as a function of temperature and material composition (Robertson, 1988), thermal conductivity cannot be uniquely constrained, and the macroscale properties of sedimentary rocks may not be adequately derived.

We note a limit to this statement regarding the potential variability of C_p : the specific heat capacity of a geological assemblage of multiphase materials is controlled by the mineralogical composition, simply because the bulk specific heat is a linear combination of the specific heat of the individual constituent materials. Thus, while a wide range of mineralogical species have identified remotely and in Martian meteorites (Papike et al., 2009 and references therein), few actually make up a large fraction of rock units at the scale of spacecraft measurements. For this reason, in this paper we focus the discussion and experimental work on mineralogical species that are abundant enough in bedrock units (see Section 1.1) to control the bulk specific heat, and we ignore mineralogical species of low modal abundance.

1.2. Specific heat capacity of Martian materials under relevant conditions

Knowledge of the specific heat capacity (the adjective “specific” means “per unit of mass”) and its temperature dependence in the 130–320 K range relevant for Mars are relatively limited for many geological materials (Touloukian et al., 1970; Gottschalk, 1997; Waples and Waples, 2004). With the exception of basalt and a few minerals noted below, most published specific heat measurements of volcanic and igneous rocks were performed at or above room temperature (Buettner, 1963; Winter and Saari, 1969; Waples and Waples, 2004), despite the diversity of materials identified on planetary bodies (e.g. quartz-bearing granitoids (Bandfield et al., 2004), dacite (Christensen et al., 2005; Koeppen and Hamilton, 2008), amorphous silica (Squyres et al., 2008), as well as many phases related to aqueous environments, various glasses (Morris et al., 2006), and other primitive materials identified on asteroids (Larson et al., 1983; Licandro et al., 2007). Extrapolation of these specific heat capacity measurements to lower temperatures is not a satisfactory option because the Debye temperature of most materials is usually unknown. Practically, the Debye temperature indicates the approximate limit below which quantum effects may be observed, leading to an inflexion of the specific heat trend where extrapolation of existing data is highly speculative (Horai and Simmons, 1970). Most common materials are known to have specific heat values significantly lower than that of silica glass (Robertson, 1988), with $C_p(T)$ varying by large factors above room temperature. For example, the specific heat for clay-like minerals is significantly lower than that of basalt (i.e. up to a factor of 2 at room temperature). More importantly, the trend above room temperature suggests much larger differences below room temperature (Robertson, 1988).

Our survey of the literature on low-temperature $C_p(T)$ measurements on the minerals investigated in this work has returned a relatively small set of relevant measurements. Robie et al. (1982) examined

the specific heat of synthetic forsterite (Mg_2SiO_4) between 5 and 380 K and found a normal sigmoidal trend at low temperatures (data reproduced in Fig. 2). A similar study with synthetic enstatite (MgSiO_3) had also been carried out (Krupka et al., 1985), and showed the same behavior in the 5–385 K range. Both of these samples, however, were essentially pure single crystals grown in the laboratory using high-temperature furnaces, and only contain magnesium end-members. Natural olivine and pyroxenes, on the other hand, comprise of significant fractions of iron, whose effect on the specific heat remains to be investigated. A number of alkali feldspars ($\text{NaAlSi}_3\text{O}_8$ and KAlSi_3O_8) had been explored by Openshaw et al. (1976), with their specific heats also exhibiting smooth sigmoidal curves between 15 and 375 K. However, the albite data published in that work were uncorrected for the presence of KAlSi_3O_8 and $\text{CaAl}_2\text{Si}_2\text{O}_8$ in solid solution. The specific heat of $\text{CaAl}_2\text{Si}_2\text{O}_8$ itself (anorthite) had been measured earlier both as a glass and in the crystalline form (Robie et al., 1978), where the latter is found to display a consistently larger $C_p(T)$ between 6 and 385 K. As for the phyllosilicates, a sigmoidal $C_p(T)$ curve has also been reported for kaolinite from 7 to 380 K (Robie and Hemingway, 1991), albeit with ~ 1.5 wt% TiO_2 impurity in their samples. More recently, Prieto-Ballesteros and Kargel (2005) conducted a study on the thermal properties of potential non-ice components on Europa (e.g. natron, mirabilite, epsomite), but those specific heat data were restricted to only above 173 K. A compilation of $C_p(T)$ data from these previous publications is presented in Fig. 2. Note that this figure is not meant to be an exhaustive list of all available low-temperature $C_p(T)$ for geologic materials, but only on those pertinent to this study (readers are referred to the cited works, as well as Robie et al. (1989), for data on other materials). Where appropriate, our measured $C_p(T)$ values will be cross-checked with published data, both to validate our experimental protocol (Section 2.3), as well as to determine the extent to which the physical nature of the sample (synthetic single crystals vs natural particulate minerals) affects the specific heat behavior. It is also noted that most of the earlier works shown in Fig. 2 were discreet measurements where C_p data were obtained at specific temperature points. As such, these datasets often have relatively low temperature resolution (on the order of a few degrees). In contrast, our $C_p(T)$ measurements are carried out under continuous scan mode, with data obtained every 50 mK (detail in Section 2.2).

2. Specific heat capacity measurements

2.1. Sample selection and preparation

Table 1 lists all the samples that are characterized in this work. Our selection contains mineralogical species identified on Mars that comprise a significant fraction of sedimentary rocks whose thermal inertia is puzzlingly low (samples 1–11). In addition, we have included nine igneous composites (samples 12–20) that are frequently found in these sedimentary units, but for which $C_p(T)$ below room temperature are typically not well-characterized.

Seventeen out of the 20 samples used in this work originate from Arizona State University's collection (Fig. 3), which has been established over the last few decades for the construction of a spectral library of geological materials. These samples were often used as reference standards for the interpretation of thermal infrared data acquired on Earth, Mars, and elsewhere (Christensen et al., 2000b). They were used “as received” for the heat capacity measurements (i.e. not washed or treated with chemicals) to avoid altering their geochemical natures. The samples are typically particulated with grain size ranges between 700–1000 μm , and are available from Arizona State University upon request. The remaining three samples used in this work (NaCl , KCl , and epsomite $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) are obtained commercially (J. T. Baker, ACS grade). The temperature range over which heat capacities data are obtained for each sample are listed in Table 2.

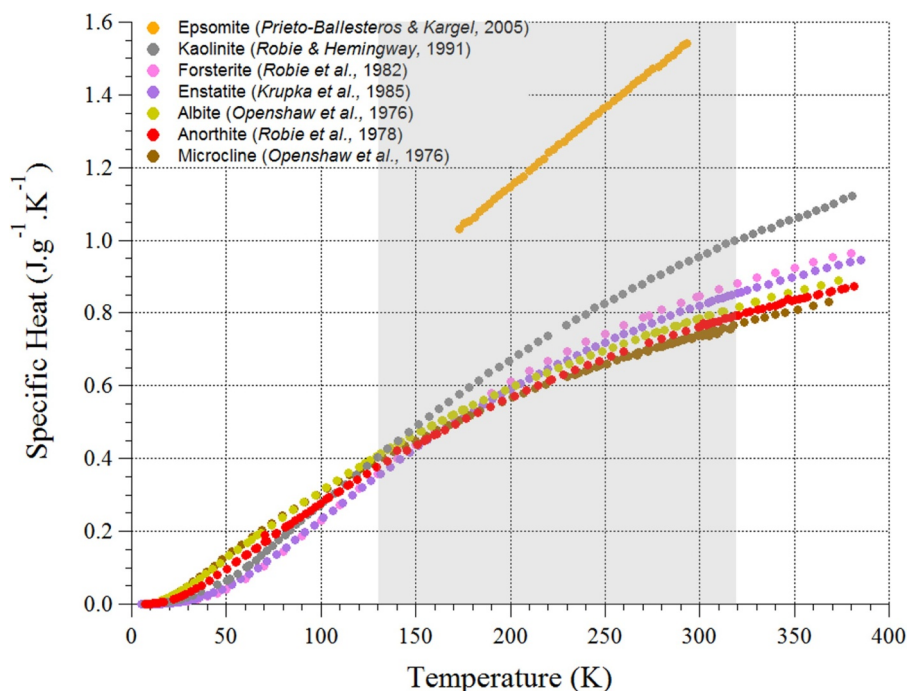


Fig. 2. Compilation of published specific heat data for some geologic minerals examined in this work. The shaded portion highlights the 130–320 K range relevant for Mars.

2.2. Measurement technique

Specific heat capacity measurements were performed at ambient pressure using a standard commercial Setaram BT2.15 cryogenic differential scanning calorimeter, partially described elsewhere (Sieglar et al., 2012; Muñoz-Iglesias et al., 2018). The calorimeter is cooled via liquid nitrogen and is equipped with a furnace, enabling operation in the temperature range 80–473 K. It contains two identical stainless steel cells (one for the sample, and one used as a reference, each with a volume capacity of 8.5 cm³) which are housed inside the calorimetric block. During each measurement, the reference cell is kept empty, while the sample cell is loaded with ~2–8 g of the sample to be investigated. Calvet elements (consisting of three-dimensional arrays of 64 thermocouples) are used to measure the temperature differential between the two cells as a function of time, which is then used to derive the heat flow to the sample. Cooling and heating ramps are pre-programmed using Setaram's Calisto software. A typical temperature profile consists of cooling the calorimeter to 80 K, followed by a heating ramp to 400 K (or 350 K for hydrated samples such as epsomite) at a constant rate of 0.25 K/min, then final cooling to room temperature. Since there is always a lag between the temperature of the furnace and the temperature of the sample, a few hours are added at the end of each ramp to allow for equilibration, yielding a total of ~52 h for a full scan.

The same pre-programmed temperature evolution used for the sample is then applied on a blank run, which is used to subtract the contribution of non-perfectly identical response of the two thermopiles from the sample's heat flow values. This very slight difference between the two thermopiles tends to introduce additional noise that is most prominent around room temperature, which may sometimes result in residual blank subtraction and a small “kink” in the experimental $C_p(T)$ data around 295 K.

The obtained datasets consist of a series of time-tagged temperatures (for both the sample and the furnace) and heat flow values (evenly spaced in increment of 12.6 s). The sample heat flow (dq/dt) at time t is obtained by subtracting the heat flow of the blank run from the sample run at the same point in time. The specific heat capacity C_p , defined as the ratio of the heat flow to the sample and the resulting change in temperature dT/dt divided by its mass m , can be expressed as:

$$C_p(T) = \frac{dq/dt}{m \times dT/dt} \quad (3)$$

where the C_p notation is used generically for the specific heat obtained at constant pressure. Note that the distinction between C_p and another common form of specific heat capacity, C_v for constant volume, is only meaningful in the gas phase which can undergo large changes in pressure and volume. For condensed phases, C_p and C_v are practically



Fig. 3. Example of particulate samples used for $C_p(T)$ measurements, available from the Arizona State University spectral library collection (Christensen et al., 2000b).

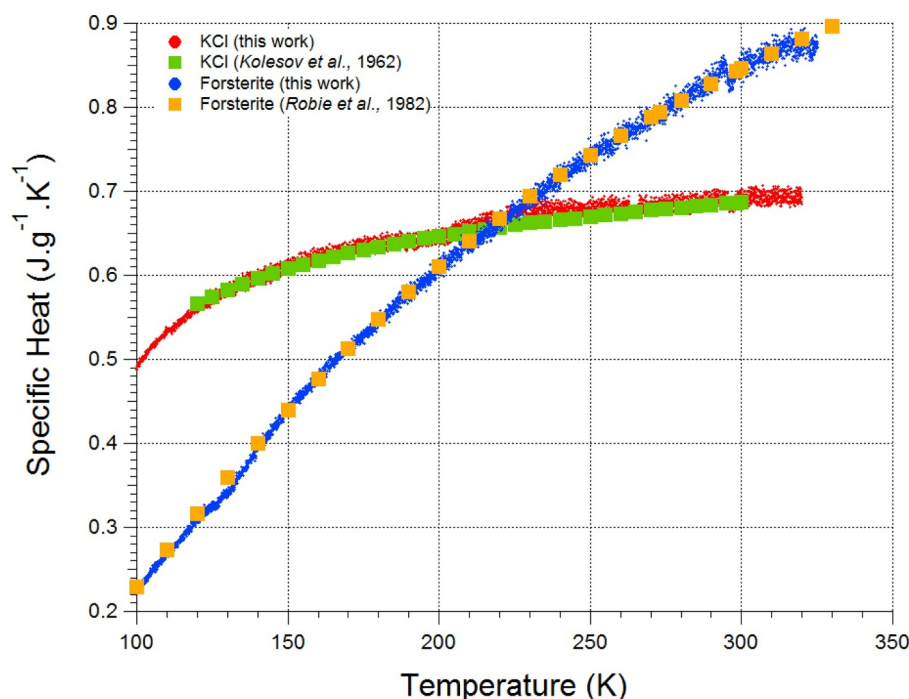


Fig. 4. Comparison of specific heat data obtained from this work with those in the literature for KCl (Kolesov et al., 1962) and synthetic forsterite (Robie et al., 1982).

identical.

In the literature, the $C_p(T)$ curve is most commonly reported in the form of a Shomate formulation:

$$C_p(T) = a + bT + cT^2 + dT^3 + \frac{e}{T^2} \quad (4)$$

where the coefficients a , b , c , d , and e are obtained by a least-squares fit of the experimental $C_p(T)$ data. For each sample measured in this work, we also provide a simple third-order polynomial fit of the form

$$C_p(T) = f + gT + hT^2 + iT^3 \quad (5)$$

which is sometimes preferred by numerical modelers for being less resource intensive and faster to compute (Kieffer, 2013). This simple power series fit is usually associated with larger residuals.

2.3. Validation of measurement technique, error and accuracy

To assess the accuracy of our experimental technique, we compare the specific heat data obtained from our laboratory runs with two

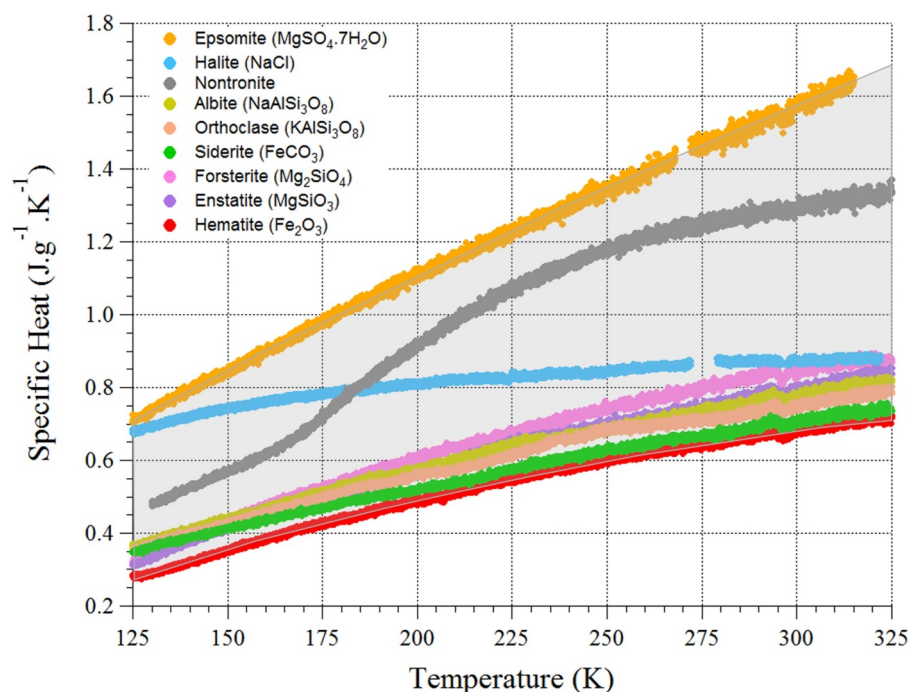


Fig. 5. Summary of experimental specific heat capacities of representative species in each mineral group. Shaded area denotes the range of $C_p(T)$ for Martian-relevant minerals, from highest (Epsomite) to lowest (Hematite).

Table 2

Empirical fit parameters of the specific heat (in $\text{Jg}^{-1}\text{K}^{-1}$) of the minerals investigated in this work, with colors separating mineral groups. Temperature column indicates the range over which experimental data are acquired.

#	Mineral	T (K)	Empirical Shomate Coefficients (Eqn. 4)					Empirical 3 rd -Order Polynomial Coefficients (Eqn. 5)				
			a (Jg ⁻¹ K ⁻¹)	b (Jg ⁻¹ K ⁻²)	c (Jg ⁻¹ K ⁻³)	d (Jg ⁻¹ K ⁻⁴)	e (Jg ⁻¹ K)	f (Jg ⁻¹ K ⁻¹)	g (Jg ⁻¹ K ⁻²)	h (Jg ⁻¹ K ⁻³)	i (Jg ⁻¹ K ⁻⁴)	
1	Halite	100-320	0.61	2.32×10 ⁻³	-6.96×10 ⁻⁶	8.05×10 ⁻⁹	-1952.9	0.0546	7.71×10 ⁻³	-2.55×10 ⁻⁵	2.97×10 ⁻⁸	
2	Sylvite	100-320	1.05	-4.03×10 ⁻³	1.67×10 ⁻⁵	-2.28×10 ⁻⁸	-2924.2	0.2325	3.71×10 ⁻³	-9.29×10 ⁻⁶	6.56×10 ⁻⁹	
3	Epsomite	120-315	-0.544	1.2×10 ⁻²	-2.55×10 ⁻⁵	2.95×10 ⁻⁸	1475	-0.12	7.67×10 ⁻³	-9.6×10 ⁻⁶	9.6×10 ⁻⁹	
4	Gypsum (alabaster)	100-330	-0.342	9.11×10 ⁻³	-2.03×10 ⁻⁵	2.07×10 ⁻⁸	675	-0.12	6.72×10 ⁻³	-1.13×10 ⁻⁵	9.13×10 ⁻⁹	
5	Gypsum (selenite)	110-330	-0.169	7.16×10 ⁻³	-1.27×10 ⁻⁵	1.00×10 ⁻⁸	130	-0.13	6.79×10 ⁻³	-1.14×10 ⁻⁵	8.42×10 ⁻⁹	
6	Magnesite	120-350	0.681	-3.12×10 ⁻³	2.34×10 ⁻⁵	-3.16×10 ⁻⁸	-3402	-0.14	4.47×10 ⁻³	-1.75×10 ⁻⁶	-3.06×10 ⁻⁹	
7	Siderite	105-325	0.781	-4.70×10 ⁻³	2.60×10 ⁻⁵	-3.59×10 ⁻⁸	-2854	-0.09	4.3×10 ⁻³	-7.04×10 ⁻⁶	5.7×10 ⁻⁹	
8	Nontronite	130-330	-9.98	9.26×10 ⁻²	-2.72×10 ⁻⁴	2.79×10 ⁻⁷	41151	-0.168	1.24×10 ⁻³	3.74×10 ⁻⁵	-8.36×10 ⁻⁸	
9	Montmorillonite	130-320	-9.04	8.58×10 ⁻²	-2.58×10 ⁻⁴	2.7×10 ⁻⁷	35926	-0.22	2.2×10 ⁻³	3.1×10 ⁻⁵	7.37×10 ⁻⁸	
10	Kaolinite	100-330	-1.28	1.56×10 ⁻²	-3.96×10 ⁻⁵	4.04×10 ⁻⁸	3340	-0.23	4.7×10 ⁻³	9.66×10 ⁻⁷	-1.08×10 ⁻⁸	
11	Hematite	100-325	-0.276	5.26×10 ⁻³	-7.85×10 ⁻⁶	3.35×10 ⁻⁹	145	-0.2295	4.79×10 ⁻³	-6.06×10 ⁻⁶	1.088×10 ⁻⁹	
12	Olivine	125-365	-0.720	1.22×10 ⁻²	-3.67×10 ⁻⁵	4.48×10 ⁻⁸	-216	-0.38	6.8×10 ⁻³	-1.18×10 ⁻⁵	7.388×10 ⁻⁸	
13	Forsterite	100-325	-0.535	8.55×10 ⁻³	-1.73×10 ⁻⁵	1.35×10 ⁻⁸	623	-0.3356	6.46×10 ⁻³	-9.47×10 ⁻⁶	3.51×10 ⁻⁹	
14	Enstatite	110-330	-1.11	1.42×10 ⁻²	-4.13×10 ⁻⁵	4.79×10 ⁻⁸	2828	-0.306	6.18×10 ⁻³	-1.26×10 ⁻⁵	1.26×10 ⁻⁸	
15	Hypersthene	110-350	-0.158	4.82×10 ⁻³	-7.02×10 ⁻⁶	4.57×10 ⁻⁹	-642	-0.332	6.5×10 ⁻³	-1.28×10 ⁻⁵	1.14×10 ⁻⁸	
16	Anorthite	125-350	1.61	-1.11×10 ⁻²	4.46×10 ⁻⁵	-5.24×10 ⁻⁸	-7707.4	-0.206	5.4×10 ⁻³	-1.02×10 ⁻⁵	9.87×10 ⁻⁹	
17	Albite	120-350	-0.372	7.19×10 ⁻³	-1.55×10 ⁻⁵	1.41×10 ⁻⁸	808	-0.176	5.4×10 ⁻³	-9.45×10 ⁻⁶	7.17×10 ⁻⁹	
18	Andesine	125-360	-0.0165	3.73×10 ⁻³	-3.98×10 ⁻⁶	1.32×10 ⁻⁹	-653	-0.1661	5.08×10 ⁻³	-8.35×10 ⁻⁶	6.19×10 ⁻⁹	
19	Orthoclase	120-350	-0.644	9.45×10 ⁻³	-2.27×10 ⁻⁵	2.2×10 ⁻⁸	2032	-0.144	4.8×10 ⁻³	-7.14×10 ⁻⁶	3.74×10 ⁻⁹	
20	Microcline	120-320	-0.896	1.25×10 ⁻²	-3.52×10 ⁻⁵	3.9×10 ⁻⁸	2805	-0.147	5.1×10 ⁻³	8.8×10 ⁻⁶	6.3×10 ⁻⁹	

representative minerals whose specific heats are extremely well-known down to very low temperatures: sylvite (KCl) and forsterite. The results in Fig. 4 indicate that our specific heat data for KCl are very consistent ($< 5\%$ variation) with the literature (Kolesov et al., 1962) throughout the temperature range 100–320 K. Our values for forsterite also show excellent agreement with the previous results by Robie et al., (1982) between 100 and 325 K, with a maximum error of $< 4\%$ at 130 K. It is noteworthy that the Robie et al., (1982) measurement was conducted on single crystal forsterite grown in the laboratory at 2200 K whereas our sample is natural and consists of a multitude of small grains (Fig. 3). This suggests that synthetic single crystals are fairly good representative of natural samples in terms of $C_p(T)$ behavior. Both of these test runs with KCl and forsterite have shown that our experimental protocol is valid and performs very well on at least two different classes of minerals. In addition, our measurement technique provides $C_p(T)$ values at a much finer temperature resolution than what have been published thus far (typically a few degrees compared to 50 mK in this case).

The typical sensitivity of our calorimeter is ± 0.1 mK for the temperature, and ± 0.1 μ W for the heat flow. With a mass accuracy of ± 0.1 mg, a standard propagation of error calculation yields an uncertainty of $< 0.002\%$ for the specific heat (which is better than ± 14 μ JK $^{-1}$ g $^{-1}$ at 100 K and ± 34 μ JK $^{-1}$ g $^{-1}$ at room temperature for all samples examined in this work).

3. Results and discussion

3.1. Overview of specific heat capacity measurement results

As the primary goal of this work is to assess whether heat capacity can be a potential cause for the low apparent thermal inertia of Martian sedimentary rocks rather than the $C_p(T)$ values themselves, we present in this section an abridged summary of the experimental results in order to give an overall perspective of minerals' thermal behavior. Detailed data and sample-by-sample analyses for all 20 minerals are available in the Appendix. Since most minerals in the same group tend to have very similar C_p values and $C_p(T)$ dependence, we have selected one representative member from each group, and plot the groups together in Fig. 5 for legibility.

A few general observations can be made from the synthesis of the experimental data:

- The $C_p(T)$ curves display a continuous behavior between 130–320 K with little indication of anomaly or phase transition. All minerals exhibit higher specific heat capacities as the temperature increases, as expected for solids.
- Of the 20 minerals considered in this work, epsomite has the highest specific heat while hematite possesses the lowest. This is consistent with the high water content in epsomite, whose hydrogen bonding capability results in strong lattice binding energies.
- The phyllosilicate group displays a distinctive sigmoidal $C_p(T)$ curves, indicating a noticeably higher temperature dependence than the rest in the 175–225 K range. This sigmoidal behavior is known for other minerals, as shown in Fig. 2. In contrast, the chloride salts (halite and sylvite) yield relatively flat temperature dependence.
- Aside from the three groups already mentioned (sulfates, phyllosilicates, and chlorides), all the other groups are fairly similar in terms of specific heat values and temperature dependence, as indicated by the lower six traces in Fig. 5.
- For all minerals, a third-order polynomial fit of the experimental $C_p(T)$ data (Eq. 5) tends to agree reasonably well with a more rigorous fit using the Shomate expression (Eq. 4). Even for the phyllosilicate group where the worst mismatch occurs, the largest deviation for the third-order polynomial fit is only $\sim 8\%$. Thus, the simpler computational approach preferred by numerical modelers appears to be valid for a vast number of cases.

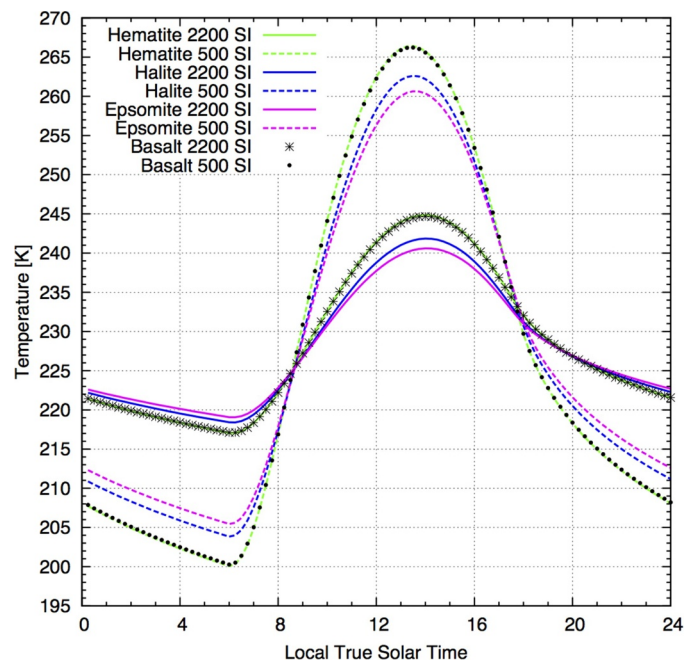


Fig. 6. Modeled surface temperatures for three compositional end-members listed in Table 2 displaying extreme C_p values (e.g., hematite, halite, and epsomite). A lunar basalt is added for completeness (Fuji and Osako, 1973) with and without temperature dependence. Two families of curves are included: bedrock material taken at 2200 Jm $^{-2}$ K $^{-1}$ s $^{-1/2}$ and intermediate (500 Jm $^{-2}$ K $^{-1}$ s $^{-1/2}$). 0°N, albedo = 0.19, Ls = 0. The standard modeling assumption of basaltic composition results in a modest underestimation of the temperature at night (~ 5 K for bedrock, ~ 2 K for intermediate inertia material), and a modest underestimation during the day, always yielding an overestimation of the apparent thermal inertia (see Fig. 7).

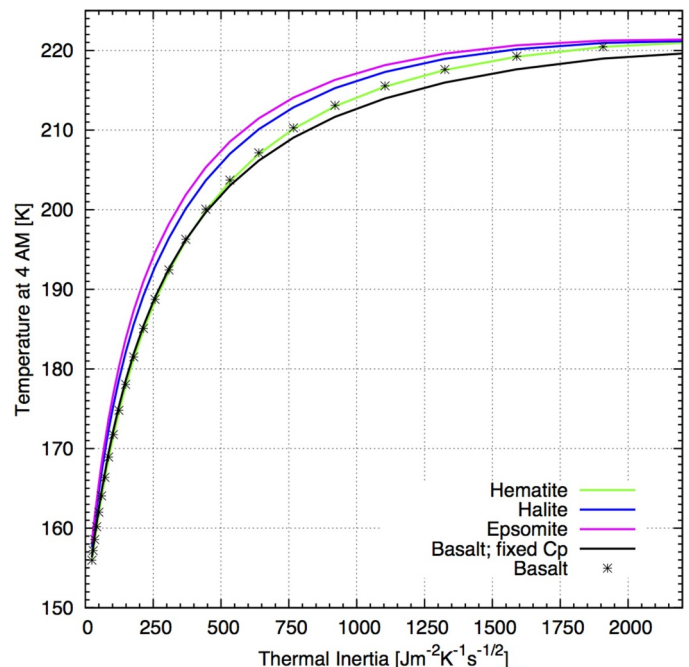


Fig. 7. Graphical example of a lookup table linking nighttime temperature and surface layer thermal inertia, using KRC (Kieffer, 2013) with three compositional end-members listed in Table 2 displaying extreme C_p values (e.g., hematite, halite, and epsomite). A lunar basalt (Fuji and Osako, 1973) is added for completeness (with and without temperature dependence). 0°N, albedo = 0.19, Ls = 0.

- Section 2.3 demonstrates that $C_p(T)$ measurements done on a single crystal does not result in the kind of variability that one would have potentially expected when compared to a natural, more homogeneous sample. This implies that future work using structurally simpler samples (especially for rare/precious materials) would be entirely adequate.
- The specific heat capacities of the minerals examined in this work have a lower bound of $0.3\text{--}0.7\text{ Jg}^{-1}\text{K}^{-1}$ at 125 K and an upper bound of $0.6\text{--}1.7\text{ Jg}^{-1}\text{K}^{-1}$ at 325 K (shaded area in Fig. 5). From the perspective of specific heat, such values and temperature variations suggest that composition is unlikely to be a source of thermal inertia variability for bedrock units on Mars. This is further elaborated in the subsequent section.

3.2. Application to Mars and discussion

Thermal inertia values for Mars are generally derived from individual nighttime observations (Ferguson et al., 2006a and references therein), although other *ad hoc* approaches have been proposed (Ferguson et al., 2006b; Audouard et al., 2014; Vasavada et al., 2017). The quantitative derivation of thermal inertia relies on the modeling of diurnal temperatures under standard conditions and their inversion in order to link observed surface temperatures (most often at night) with regolith thermophysical properties. Most often, this process assumes basaltic specific heat capacity values and ignores temperature or composition dependence (Neugebauer et al., 1971). While the temperature dependence of regolith properties is indeed a modest factor for Mars (Piqueux and Christensen, 2011), our laboratory work (Fig. 5) demonstrates that composition can impact specific heat capacity values by a factor of ~ 2 .

When applying these new $C_p(T)$ trends (Table 2) into a numerical model calculating the surface temperatures on Mars (Kieffer, 2013) assuming bedrock thermophysical properties and standard Mars conditions (i.e., high bulk conductivity and no porosity, see Fig. 6 caption for details), the impact on modeled surface temperatures is modest, i.e., up to ~ 5 K at night as a function of composition, and up to 6 K near noon under standard representative conditions, even with these idealized cases. For comparison, we have also provided a set of cases with intermediate thermal inertia values (i.e., $500\text{ Jm}^{-2}\text{K}^{-1}\text{s}^{-1/2}$), showing (as expected) an even less pronounced impact of composition and temperature, i.e. up to ~ 2 K at night, and up to ~ 5 K near noon.

Fig. 7 provides a graphical example of a set of lookup tables used to derive apparent thermal inertia from night-time surface temperatures. Standard modeling assumption of basaltic composition always results in a modest overestimation of the apparent thermal inertia, simply because basalt is associated with the lower specific heat capacity values compared to other material investigated in this study. As a result, sedimentary rock units whose thermophysical behavior is driven by non-basaltic material are always somewhat overestimated by a basaltic assumption, and the thermal inertia values derived in the literature, if anything, are overestimated. Generally, a large volume fraction of the sedimentary units described in the literature bearing the mineralogical species studied in this paper is composed of basaltic materials (see references in Table 1), whose specific heat is presumably adequately parameterized (Fujii and Osako, 1973) and accounted for in models. In other words, the specific heat capacity of the alteration mineralogies (e.g. salts, clays, Fe-oxides) unique to Martian sedimentary materials only accounts for a relatively small fraction of the bulk specific heat of these units in the first place (with the majority fraction being basaltic) (e.g., Ehlmann and Edwards, 2014). As such, it would require extreme deviations in amount of alteration phases (commonly only 20%) from basaltic compositions to have a significant effect on the bulk thermal inertia, and this effect would only yield a reduction of the apparent thermal inertia.

We therefore conclude that the low apparent thermal inertia of sedimentary outcrops on Mars is not due to a compositional effect on

specific heat capacity values. Other potential sources of this anomaly could be associated with systematic high rock porosities and/or low apparent thermal conductivities. Indeed, extensive in situ observations by the Curiosity rover in Gale crater suggest that the macro-scale properties of sedimentary rocks could be the source of this behavior: simple fit to the Ground Temperature Sensor temperature data (Vasavada et al., 2017) yields unrealistically low thermal inertia values for bedrock units (their Fig. 2 and Table 3), an issue found to be ubiquitous to Mars sedimentary units (Table 1). However, these authors also demonstrate that full diurnal temperature curves (as opposed to a few limited local times available from orbit) of multiple sedimentary outcrops are consistent with a layered subsurface, composed of bedrock-like materials laminated with thin internal insulators preventing the effective flow of heat to depths exceeding a few centimeters. They proposed that this internal structure could reflect the effect of laminations, cracks, or joints, all ubiquitous on visible images. While this interpretation of the temperature trends remains speculative, it highlights the fact that macro-scale properties can be theoretically linked to thermal behavior, and that it matches high resolution in situ visible and thermal infrared observations.

Our work further adds to the understanding of sedimentary rocks thermal behavior on Mars by demonstrating that their unique low thermal inertia values do not stem from their specific heat capacity. Small porosity variations for competent rocks are also unlikely to affect thermal inertia, as mentioned in Section 1.1. Therefore, the bulk thermal conductivity is likely the driver for the low inertia values. Recent work (Vasavada et al., 2017) suggests that near-surface internal bedrock structures might be constrained from orbit, with the potential prospect of linking their formation mechanism with the thermophysical properties.

4. Conclusions

We have conducted laboratory measurements on the specific heat capacities for a suite of 20 Mars-relevant mineralogical samples from 100 to 350 K at a resolution of 50 mK. Literature data for sylvite and forsterite were used for validation of our experimental technique, which is shown to be consistent with published data to within 5% over the entire temperature range of interest. The major conclusions of this study are that:

- All $C_p(T)$ curves exhibits a continuous trend of increasing specific heat capacities with temperature, with little indication of anomaly or phase transition.
- Epsomite exhibits the highest heat capacities of all the minerals examined. This is consistent with its high water content which results in a strongly hydrogen-bonded lattice.
- In a vast number of cases, a third-order polynomial fit of the $C_p(T)$ data agrees very well with a more rigorous, commonly used Shomate fit that includes an additional $1/T^2$ term. Thus, the simpler computational approach preferred by modelers seems entirely adequate.
- In addition, the exact crystal structure of a mineral does not have an apparent effect to its heat capacity, i.e. single crystal samples grown in the laboratory are fairly good representatives of natural ones for conducting $C_p(T)$ measurements.
- The specific heat values for all the minerals investigated in this work varies from $0.3\text{--}0.7\text{ Jg}^{-1}\text{K}^{-1}$ at 100 K to $0.6\text{--}1.7\text{ Jg}^{-1}\text{K}^{-1}$ at 350 K. This range is rather small and cannot explain the distinctively low thermal inertia of sedimentary units compared to magmatic units.
- Since neither material densities nor specific heat capacity by themselves seem to explain the low thermal inertia of sedimentary units, thermal conductivity of sedimentary rocks and effects of porosity is likely the dominant factor (as suggested in other published works).

5. Appendix

This section provides detailed experimental $C_p(T)$ data and analyses for all 20 mineralogical samples, organized by their mineral groups. The chloride minerals (halite and sylvite) are presented in Section 5.1, the sulfate minerals (epsomite and gypsum) are in Section 5.2, the carbonates (magnesite and siderite) in Section 5.3, the phyllosilicates

(nontronite, montmorillonite, kaolinite) in Section 5.4, hematite in Section 5.5, forsterite and olivine in Section 5.6, pyroxenes (enstatite and hypersthene) in Section 5.7, plagioclase feldspars (albite, anorthite, andesine) in Section 5.8, and alkali feldspars (microcline and orthoclase) in Section 5.9. Each of the measured $C_p(T)$ curve is fitted using both a Shomate equation as well as a third-order polynomial, as detailed in Section 2.2. All empirical fitting coefficients are listed in Table 2.

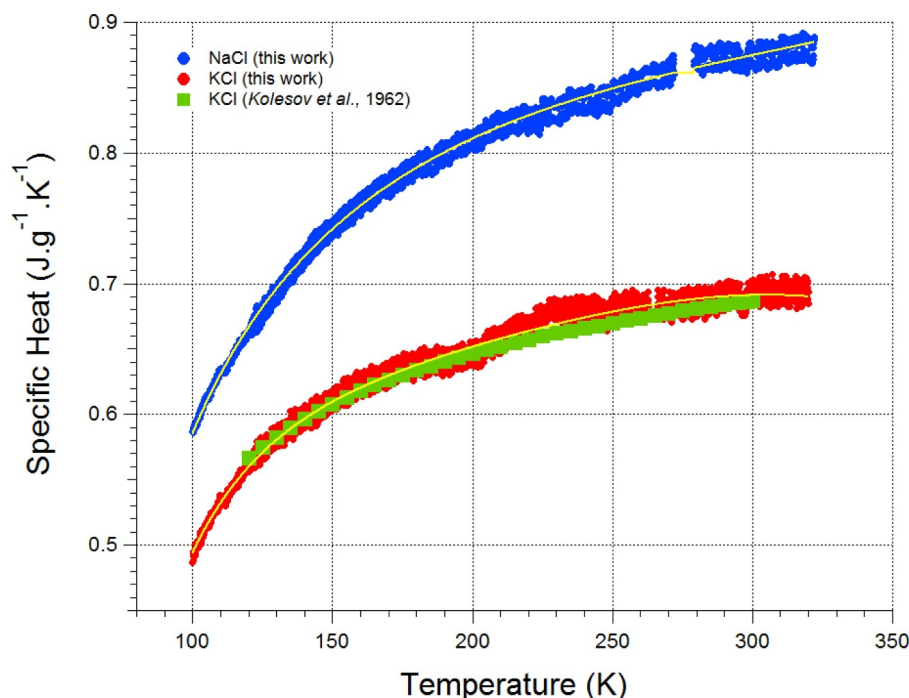


Fig. 8. Specific heat capacities of halite (NaCl) and sylvite (KCl) as measured from our experiments, in comparison to literature data for KCl (shown in squares). Solid lines represent the Shomate fits of the experimental data.

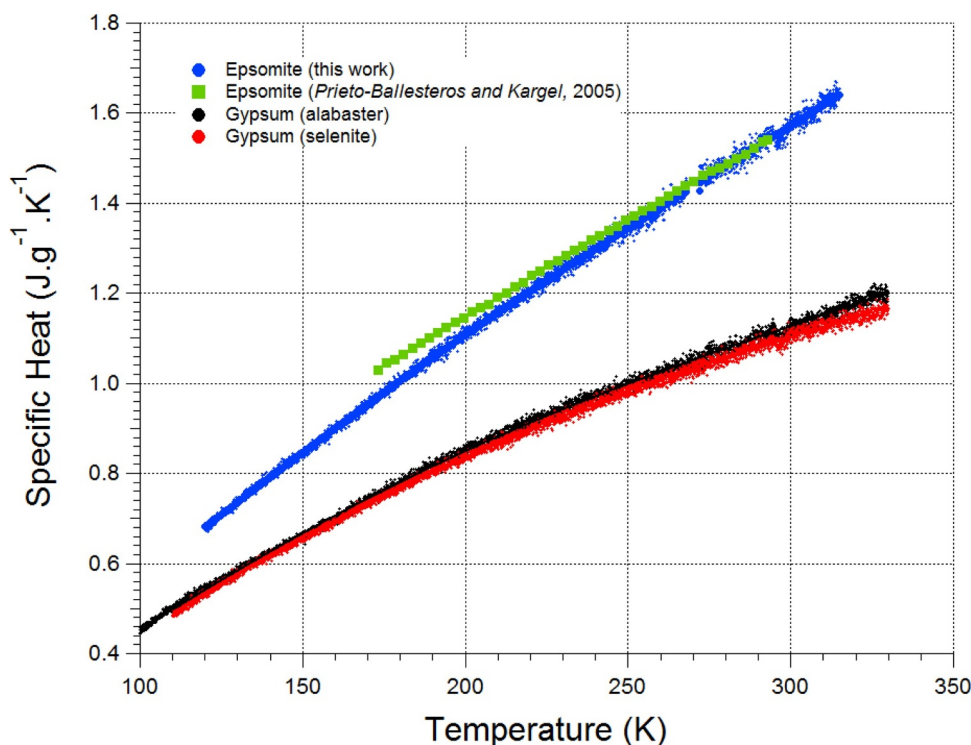


Fig. 9. Experimental specific heats of the sulfate minerals examined in this work: epsomite, alabaster gypsum, and selenite gypsum from 100–330 K. Data for epsomite from Prieto-Ballesteros and Kargel (2005), available between 173–293 K, are included for comparison.

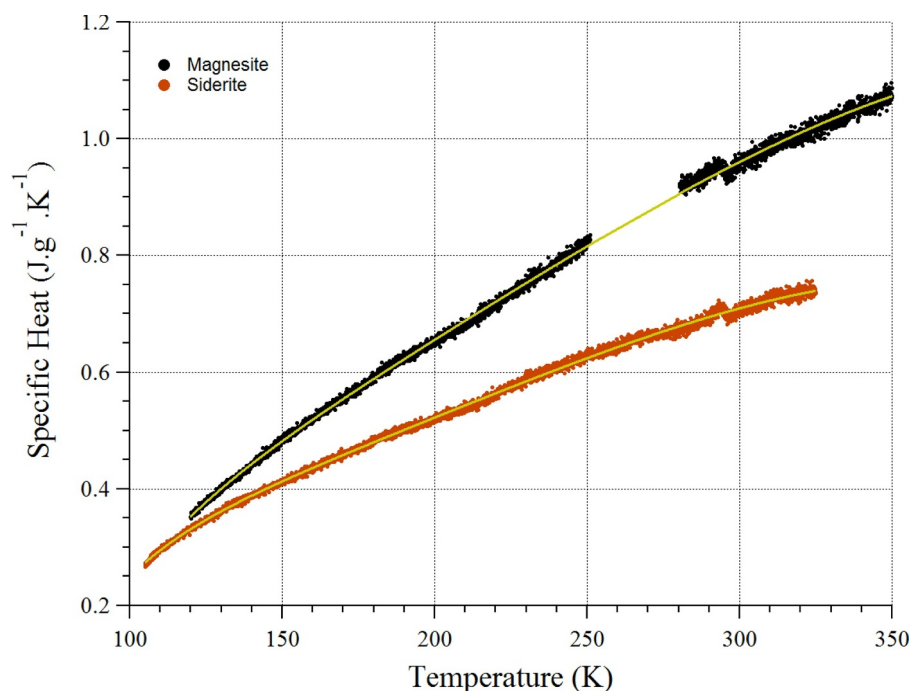


Fig. 10. Experimental specific heat capacities of magnesite and siderite. Solid lines show the Shomate fits of the experimental data.

5.1. Chlorides

As noted in the Introduction, numerous chloride-bearing deposits have been identified in vast beds of sedimentary evaporites across the southern highlands of Mars. The specific heats of two representative anhydrous chloride minerals, halite (NaCl) and sylvite (KCl), are examined in this study over the temperature range 100–320 K. In contrast to the extremely well-known specific heat of KCl at low temperatures (which was used as a validation of our experimental technique in Section 2.3), the $C_p(T)$ of NaCl (to the best of our knowledge) remains largely uncharacterized below room temperature, though the heat

capacities of various NaCl-KCl crystalline solutions have been measured (Benisek and Dachs, 2012). Fig. 8 shows the experimental specific heat of NaCl, obtained under identical conditions as those for the KCl data presented in Fig. 4. Compared to KCl, NaCl exhibits a very similar temperature dependence, but with a slightly steeper curvature. Its C_p value is $\sim 20\%$ higher than that of KCl at the lower temperatures, which increases to $\sim 28\%$ near room temperature. The larger specific heat of NaCl compared to KCl is expected due to its tighter and more compact crystal lattice. The data gap around 270 K for NaCl is due to the presence of a small amount of hydrohalite ($\text{NaCl}\cdot 2\text{H}_2\text{O}$) in the sample, which has been removed from the specific heat plot to enable a more accurate Shomate

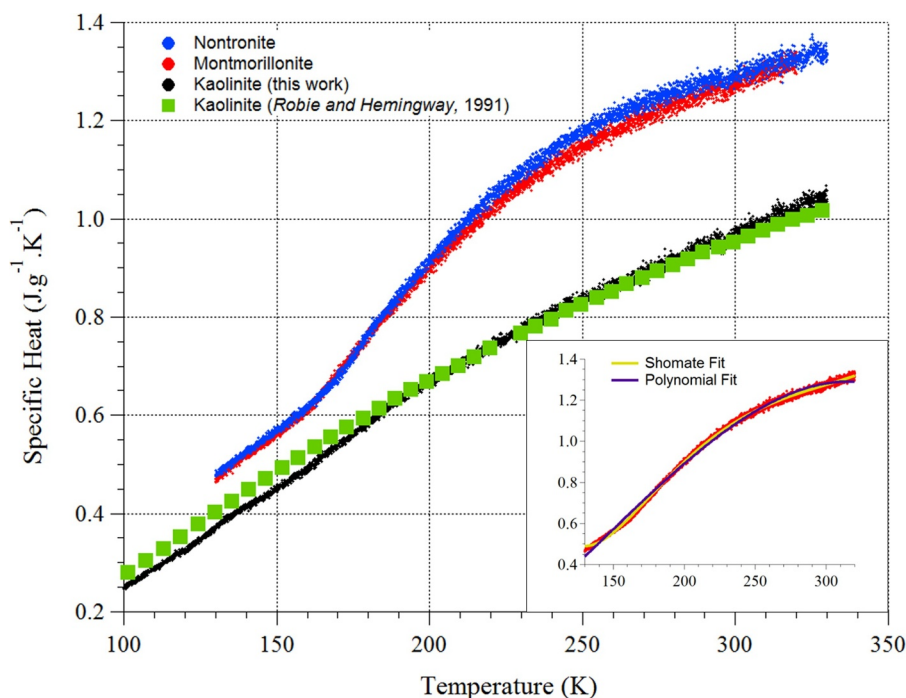


Fig. 11. Experimental specific heat capacities for the phyllosilicate minerals. Literature data for kaolinite (Robie and Hemingway, 1991) are shown for comparison (squares). Inset juxtaposes the Shomate and the third-order polynomial fits for montmorillonite, demonstrating the slightly better performance of the former in fitting the $C_p(T)$ data.

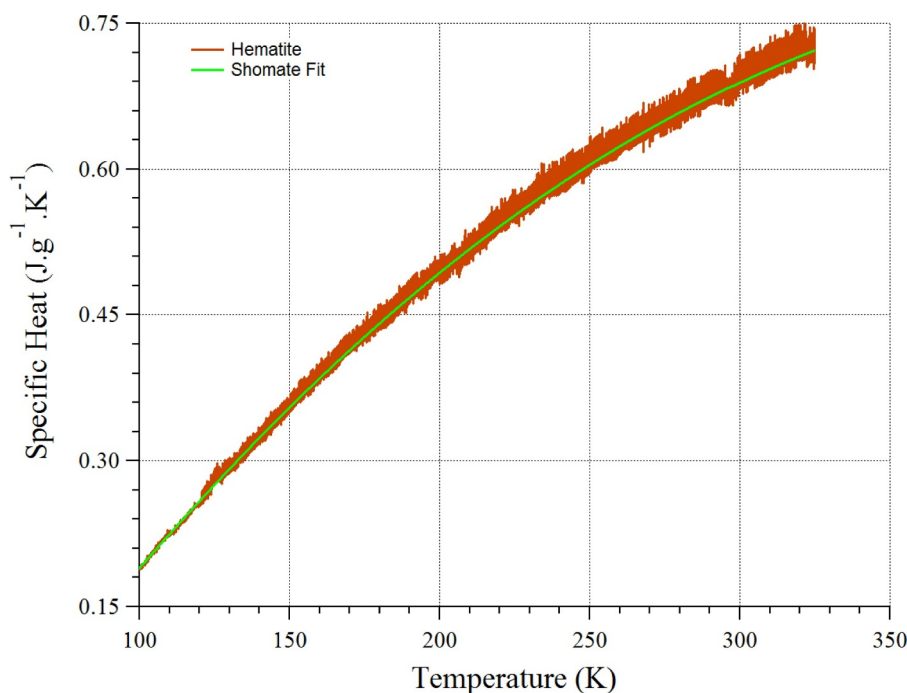


Fig. 12. Experimental specific heat capacity of hematite. Shomate and third-order polynomial fits appear identical.

fit (yellow line). The third-order polynomial fit virtually overlaps with the Shomate fit for both of these samples (omitted from Fig. 8 for clarity).

5.2. Sulfates

For the sulfate minerals, we examined epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and two varieties of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$): alabaster and selenite. Gypsum had been detected on Mars by orbital observations, and was suggested to be present in a bright mineral vein by the Opportunity rover (Squyres et al., 2012). The experimental results shown in Fig. 9 indicates that both varieties of gypsum have very similar specific heats and temperature dependence (alabaster is $\sim 5\%$ higher than selenite at 110 K and $\sim 3\%$ higher at 330 K). Meanwhile, epsomite exhibits a much larger specific heat and more pronounced temperature dependence (almost 50% higher at 315 K) than both gypsum varieties. This is consistent with the higher water content in epsomite, as the presence of water molecules in the crystal lattice increases its binding energy substantially over the less hydrated ones. Previous data for epsomite (Prieto-Ballesteros and Kargel, 2005), displayed as green squares in Fig. 9, also show very good agreement with our data at temperatures above 250 K. There is a slight deviation (up to $\sim 6\%$) at the lower temperatures, which is attributable to the much faster heating rate used in their study (60 K/min) compared to ours (0.25 K/min). Despite this discrepancy, the two datasets remain overall consistent and exhibit essentially the same trend. The fits of our data with both the Shomate equation and a third-order polynomial are virtually identical for all the sulfate minerals (not shown for clarity).

5.3. Carbonates

Results for the carbonate minerals are presented in Fig. 10. Two types of carbonates are examined: magnesite (MgCO_3) and siderite (FeCO_3). The former is found to have a significantly higher specific heat than its iron counterpart near room temperature, though their values are fairly comparable below 120 K. The $C_p(T)$ curve of magnesite thus exhibits a markedly steeper slope, with the specific heat value increasing by about a factor of 3 between 120 and 325 K compared to only about two-fold for siderite over the same range. The gap in the

magnesite data between 260 and 280 K is due to the melting of a small amount of lansfordite ($\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$) in the sample, which has been removed from the $C_p(T)$ curve to ensure a proper Shomate fit over the entire temperature range (yellow line). Similar to the chloride and sulfate minerals examined previously, there is no discernable difference between a Shomate and a third-order polynomial fit for both of these carbonate minerals (not shown in Fig. 10 for clarity). The empirical parameters for both fits can be found in Table 2 (lines 6–7).

5.4. Phyllosilicates

The experimental heat capacities for the phyllosilicate minerals are shown in Fig. 11. We examined three varieties: nontronite, montmorillonite, and kaolinite, with the latter being commonly formed as a product of weathering or hydrothermal alteration of feldspar-rich rocks. Compared to the other solids examined in this work, the $C_p(T)$ curves for phyllosilicates show a distinctly sigmoidal shape, especially for nontronite and montmorillonite. While the C_p of these two minerals are fairly similar over the temperature range examined, they are both significantly higher than that of kaolinite by $\sim 30\%$. Previous data on the specific heat capacity of kaolinite have been included as green squares (Robie and Hemingway, 1991) and show very good agreement with our data (discrepancies range from $\sim 9\%$ smaller at 100 K to $\sim 2\%$ greater at 330 K). These minor differences at the two end temperatures could be attributed to the presence of various impurities (e.g. $\sim 1.5 \text{ wt\% TiO}_2$ in their kaolinite sample).

The inset of Fig. 11 juxtaposes a Shomate (yellow) and a third-order polynomial fit (purple) of our montmorillonite data. Due to the distinctly sigmoidal nature of the specific heat capacity curve, the latter performs relatively poorer than the Shomate formulation in terms of fitting the data, especially in the low temperature regime. Nonetheless, even in the worst-case scenario, the largest error for the third-order polynomial fit is still only $\sim 8\%$. The same phenomenon is also observed for nontronite and kaolinite (not shown for clarity). Therefore, the simpler computational approach preferred by numerical modelers appear to be fairly adequate for analyzing specific heat data. The empirical parameters for both fits can be found in Table 2 (lines 8–10).

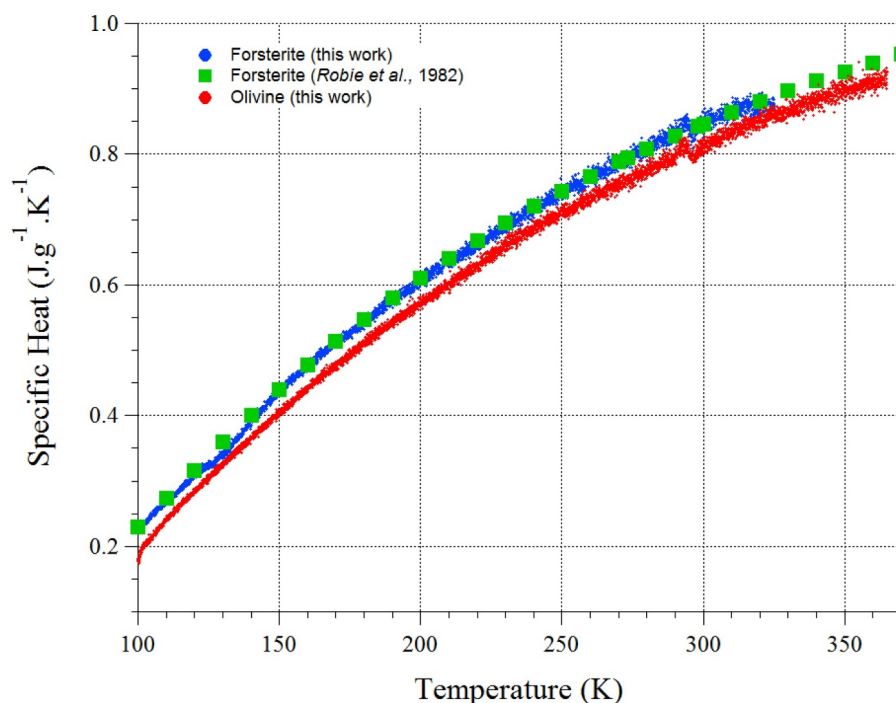


Fig. 13. Measured specific heat capacities of forsterite and olivine. Previous data on single crystal forsterite (Robie et al., 1982) are included for comparison.

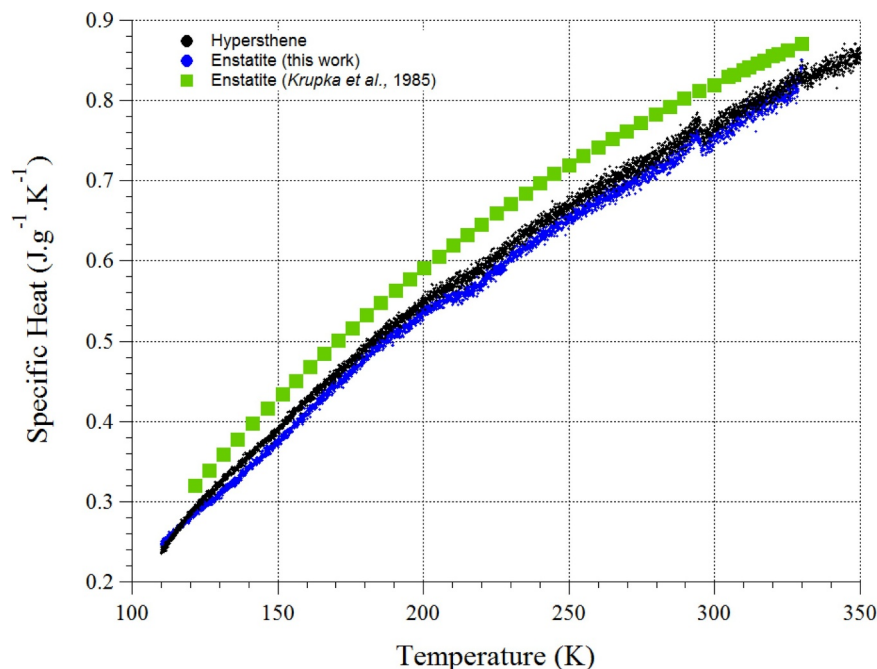


Fig. 14. Specific heat capacities of hypersthene and enstatite. Data for synthetic enstatite from Krupka et al. (1985) are included for comparison.

5.5. Hematite

The $C_p(T)$ curve of hematite is displayed in Fig. 12, together with a Shomate fit of the experimental data. The C_p value ranges from $0.288 \text{ J g}^{-1} \text{ K}^{-1}$ at 130 K to a maximum value of $0.75 \text{ J g}^{-1} \text{ K}^{-1}$ at 322 K, an increase of almost a factor of 3 over the Martian-relevant temperature range. At room temperature, the known specific heat capacity of hematite is $0.649 \text{ J g}^{-1} \text{ K}^{-1}$ (Chase, 1998), which is within 5% of our experimental measurement. In this instance, the third-order polynomial fit of the data yields an identical curve to the Shomate fit (omitted from Fig. 12 for clarity).

5.6. Olivine

The olivine group minerals are one of the most important constituents of igneous rocks. They have the general formula M_2SiO_4 , where M represents divalent Mg, Fe, Mn, Ni, Ca, or Co ions. Natural olivine is a solid-state solution (formula $(\text{Fe}_x\text{Mg}_{1-x})_2\text{SiO}_4$), with the two relevant end-member being forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4). We examined in this work the specific heats of forsterite from 100 K to 325 K, and up to 365 K for a natural olivine sample. The results are presented in Fig. 13, showing the expected similarity in shape between the two $C_p(T)$ curves. As magnesium-based minerals typically have

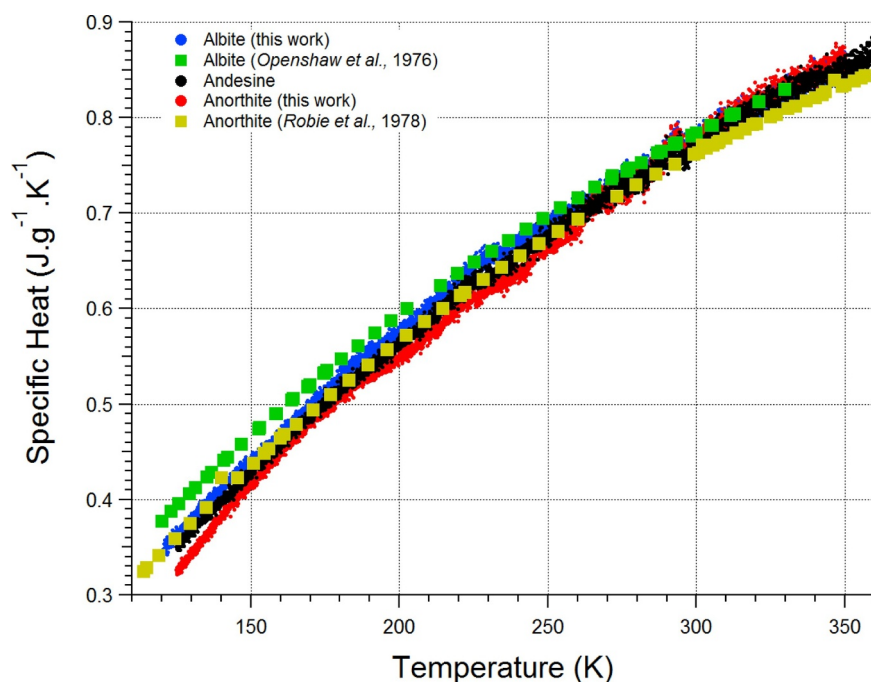


Fig. 15. Experimental specific heat capacities of albite, andesine, and anorthite. Data for low albite from [Openshaw et al. \(1976\)](#) and synthetic crystalline anorthite from [Robie et al. \(1978\)](#) are included for comparison.

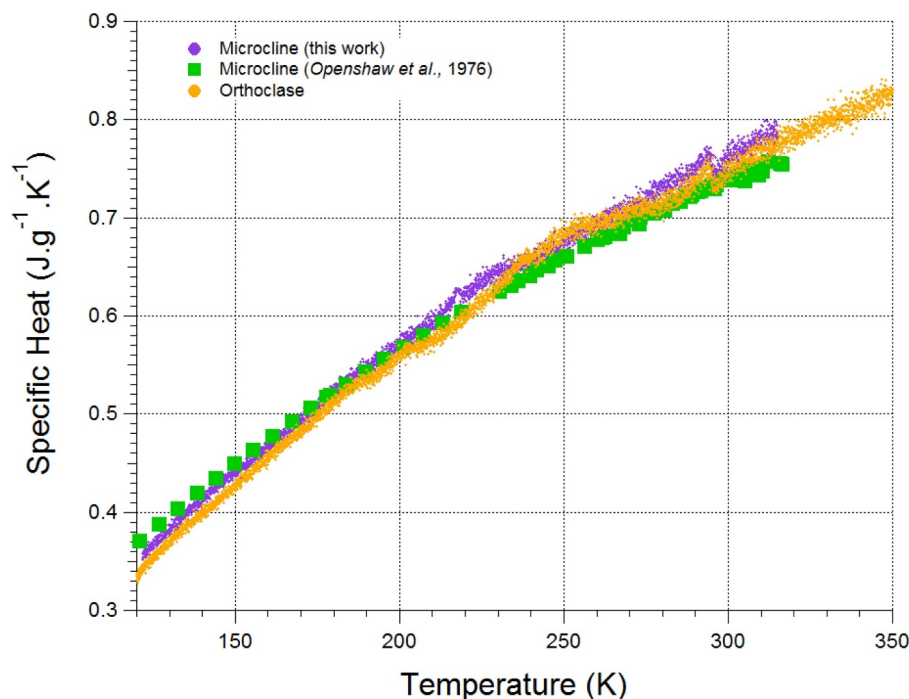


Fig. 16. Specific heat capacities of the KAlSi_3O_8 feldspar minerals. Results for microcline from [Openshaw et al. \(1976\)](#) are included for comparison.

higher C_p than iron-containing ones (as seen for the case of magnesite versus siderite in Fig. 10), natural olivine is expected to have a lower C_p than forsterite. Fig. 13 demonstrates that the specific heat of olivine is consistently below that of forsterite by about 13%–20% over the entire temperature range. Assuming linear mixing, it can be approximated that our olivine sample contains ~80–87% forsterite, which is in line with the typical ~90% forsterite composition of terrestrial olivine. Previous data obtained on single crystal forsterite ([Robie et al., 1982](#)) show excellent agreement with our experimental results, as validated in Section 2.3. Both the Shomate and third-order polynomial fits (not

shown) are consistent and perform very well for these datasets.

5.7. Pyroxenes

For the pyroxene group, the heat capacities of hypersthene and an enstatite sample from Bamble, Norway were measured. The data are shown in Fig. 14 together with those obtained on a synthetic enstatite sample that is “essentially pure, stoichiometric MgSiO_3 ” ([Krupka et al., 1985](#)). The specific heat of the natural enstatite is found to be lower than that of the synthetic sample by ~8%; however, the shape of the

two $C_p(T)$ curves remain overall consistent. This indicates that while the absolute C_p value may vary somewhat based on the amount of impurities, its temperature dependence does not appear to be very sensitive to composition. The C_p of hypersthene (black trace) is found to be very close to that of the natural enstatite, only ~3% higher over the entire temperature range. Both the Shomate and the third-order polynomial equations provide very good fits on the pyroxene samples (not shown for clarity).

5.8. Plagioclase feldspars

The experimental specific heat capacities of the plagioclase feldspar minerals (albite, andesine, and anorthite) between 120–360 K are shown in Fig. 15. All three of the plagioclase minerals show very similar C_p values, ranging from 0.32 to 0.35 Jg⁻¹K⁻¹ at 130 K to ~0.8 Jg⁻¹K⁻¹ at 320 K. Previous results on a low albite sample (Openshaw et al., 1976) show very good agreement with our data above 250 K. Below this temperature, our albite sample exhibits noticeably lower specific heat capacity, with the largest deviation of about 8% at 120 K. This discrepancy could be due to the fact that their low albite data were uncorrected for the presence of KAlSi₃O₈ and CaAl₂Si₂O₈ in solid solution. Prior results for synthetic crystalline anorthite (Robie et al., 1978) also show good agreement with our data, which the largest deviation of ~7% at the low temperature regime. Our natural anorthite sample also displays a slightly steeper slope than the synthetic one (signifying a somewhat higher dependence on temperature).

5.9. Alkali feldspars

Finally, the heat capacities of the alkali feldspars are shown in Fig. 16. Two polymorphs of KAlSi₃O₈ (microcline and orthoclase) were examined, with both exhibiting very similar, smooth $C_p(T)$ curves between 120 and 320 K. The specific heat of microcline is slightly higher than that of orthoclase, but by only ~1–2% over the entire temperature range. Both $C_p(T)$ curves fit very well to the Shomate equation, with almost identical coefficients (Table 2, lines 19–20). The third-order polynomial fits virtually overlap with the Shomate fits, and are omitted from the plot for clarity. Previous measurements of the heat capacities of microcline over the range 15–371 K (Openshaw et al., 1976) show good agreement with our results below 220 K. Above this temperature, our microcline sample exhibits slightly higher values, but the deviation is only ~2.5%. Thus, the two polymorphs of KAlSi₃O₈ feldspars have practically the same heat capacities.

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