Planetary and Space Science 87 (2013) 146–156

Contents lists available at ScienceDirect

Planetary and Space Science

journal homepage: www.elsevier.com/locate/pss

The measurement of meteorite heat capacity at low temperatures using liquid nitrogen vaporization

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ARTICLE INFO

Article history:
Received 29 March 2013
Received in revised form
8 July 2013
Accepted 16 July 2013
Available online 27 July 2013

Keywords:
Heat Capacity
Meteorites
Asteroids
Physical properties
Laboratory

ABSTRACT

Meteorite heat capacity (specific heat) is an essential parameter in modeling many aspects of the orbital and internal evolution of small solar system bodies, and can be a tool for characterization of the material in a meteorite itself. We have devised a novel method for the measurement of this quantity in whole-rock samples of meteorites, at low temperatures typical of asteroids. We insert the sample in liquid nitrogen, measure the mass of nitrogen boiled off due to the heat within the sample, and calibrating against measurements of pure quartz with a temperature-averaged heat capacity of 494 J/kg K we calculate the temperature-average heat capacity of the sample. We show that this method is accurate, rapid, inexpensive, and non-destructive. Preliminary results for chondrites and metal rich meteorites are in excellent agreement with the literature data for meteorites, and hold the promise that such measurements may not only produce values useful to modelers but they also may provide an efficient way to classify whole meteorite samples and characterize subtle differences between meteorites of different compositional classes.

1. Introduction

The heat capacity of a substance is the energy involved in changing the temperature of that material. It is usually reported as a specific heat (per unit mass) with the SI units of Joules per Kelvin, per kilogram. By analogy to the well-understood “heat capacity at constant pressure” of an ideal gas, the symbol usually used to indicate heat capacity is C_p.

Heat capacity is an essential parameter in understanding many aspects of the physical nature of asteroids. Understanding the thermal evolution of small solar system bodies requires knowing how much energy is required for every degree of temperature change. Some of the most important non-gravitational forces that change the way small bodies alter their spin or change their orbits around the Sun, the Yarkovsky and YORP effects, depend on how their surfaces collect, hold, and re-emit the heat of incident sunlight. In addition, models for the brightness of meteors, and models for the response of planetary surfaces to impact cratering, depend (along with other factors) on the heat capacity of the material involved. The best method to determine the heat capacity of asteroidal material is the direct measurement of analogous meteorites.

Beyond these uses, however, heat capacity is itself an independent measure of a meteorite's composition, as it depends on the materials present in the sample. Thus measuring heat capacity could provide a non-destructive way of indicating the bulk composition of a whole meteorite.

Only a handful of meteorite heat capacities have been published, virtually all of them measured at temperatures at or above 300 K; and some of these have been problematical. For example, Matsui and Osako (1979) measured values for a handful of meteorites from room temperature to 450 K but in a later paper (Yomogida and Matsui, 1983) they rejected these data, citing the small sizes of the samples measured and the possibility that metallic iron may have been overrepresented in them. Instead, in their later work, they preferred to use values calculated from meteorite modal compositions.

Beech et al. (2009) report the heat capacity of two chondrites and an iron meteorite; one chondrite sample was measured at room temperature and the others at 350 K. A plot in Szurgot (2011)

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http://dx.doi.org/10.1016/j.pss.2013.07.009

shows room-temperature values of heat capacity for a dozen ordinary chondrites, but only in Szurgot et al. (2012) do they report a specific value given for a specific meteorite, with a description of the procedure used. These are to date the only hand samples of meteorites for which reliable specific heats have been published, all of them measured at temperatures at or above room temperature.

While most heat capacities are measured at room temperature or higher, there is a commercial measurement system designed for the semiconductor industry, the Quantum Design Physical Properties Measurement (QDPPM) System, which covers the cold temperatures found in the asteroid belt. Unfortunately it only measures small samples (less than 1 g), and measurements with it are expensive both in terms of sample consumption and time. One such measurement of a sub-gram piece of a meteorite, the shergottite Los Angeles, was published in Opeil et al. (2012).

Both theory and the Los Angeles measurement indicate that heat capacity is a strong function of temperature, especially at the lower temperatures found in the asteroid belt. Typically one expects that, in the absence of phase changes, the dependence at low temperature will follow a characteristic curve similar to that derived by Debye (1912). To determine meteorite heat capacities in this temperature range for larger samples, we have developed a new, non-destructive procedure that provides an average value for this quantity over the temperature range of 77 K to 300 K. Given the simplicity and non-destructive nature of this method, it could be well adapted for occasional use in a small laboratory or as part of an undergraduate research project.

2. Technique

A Dewar containing liquid nitrogen is placed on a balance and its mass is measured over time as the nitrogen evaporates (see Fig. 1). The sample is dropped into the Dewar and the amount of nitrogen boiled off due the heat from the sample is determined. By measuring how many grams of nitrogen are needed to cool the sample from room temperature (about 300 K; the actual ambient temperature is recorded for each run) down to liquid nitrogen temperature (77 K), and knowing the latent heat of liquid nitrogen, one can derive the total heat content of the sample. Dividing this by the sample mass and the change in temperature, one arrives at the average heat capacity of the sample over this range of temperature. Assuming a typical Debye temperature dependence for heat capacity over this range, this average value is a good representation of the heat capacity of materials at temperatures typical of the asteroid belt, around 200 K (cf. Lim et al., 2005, noting that the subsolar temperatures reported there are $\sqrt{2}$ times larger than the equilibrium temperature).

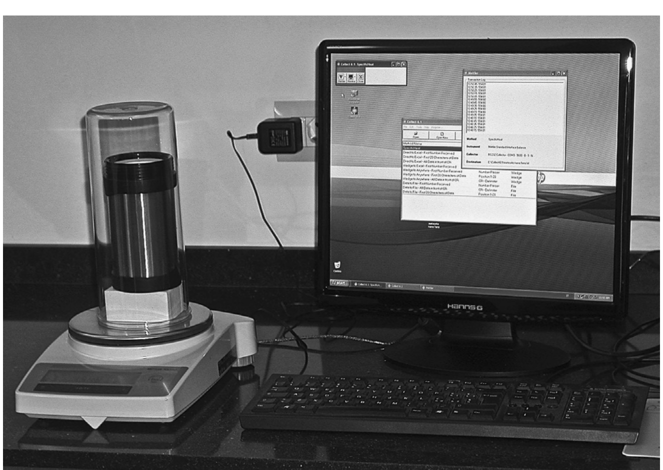

Fig. 1. The experimental setup. The weight of a Dewar filled with liquid nitrogen is recorded automatically at ten-second intervals, before and after the insertion of a meteorite sample. The Dewar (left) sits on small box to prevent temperature changes within the electronic scale. Nitrogen evaporating from the Dewar fills the clear cover, preventing the buildup of frost.

A data run starts with the Dewar being filled and placed onto the scale. To prevent condensation of water frost on the Dewar, we place a transparent cylindrical container over the Dewar; the evaporating nitrogen purges water vapor out of this container and prevents the formation of significant condensation on the Dewar. For many runs, a piece of quartz was introduced at this time as a “boiling chip” to produce extra nitrogen gas, in order to insure that excess water vapor is quickly driven out of the system. After at least thirty minutes, we begin the data collection to determine the rate of evaporation before the first sample is inserted. After at least twenty minutes of these data, the first sample is then dropped into the liquid nitrogen. Samples follow in twenty minute intervals; usually five samples can be accommodated during one data run (or six if they are small). Once the remaining liquid nitrogen has been evaporated, the samples are removed from the Dewar and the entire system is allowed to come back to room temperature, waiting a day before the next run is attempted. (Each sample can be identified by its unique mass among the samples collected out of the Dewar; care in identification must be taken if two samples have identical masses!)

A critical question is the time needed for the meteorite to reach thermal equilibrium with the liquid nitrogen. Numerical integration of the thermal diffusion equation for the case of a spherical meteorite shows that the center will come within 2 K of equilibrium in a time $t=0.55\ [(C_p\ \rho\ R^2)/k]$, where ρ is the density, the meteorite radius is R, and the thermal conductivity is k. Over the temperature range of interest, the values of k and especially C_p are functions of temperature (cf. Opeil et al., 2010, 2012), but one can estimate an upper limit to the cooling time simply by using room temperature values. (The strongest temperature variation is with C_p, which we expect may drop by a factor of two during the cooling, and the cooling time varies linearly with C_p).

For an iron meteorite, typical numbers might be $C_p=450$ J/kg K, $k=25$ J/s K m, and $\rho=7500$ kg/m^3, so a 1 cm radius iron should equilibrate in under ten seconds. For a rocky meteorite, with typical values of $C_p=800$ J/kg K, $k=1$ J/s K m, and $\rho=3500$ kg/m^3, a 1 cm radius sample (roughly 15 g) should equilibrate in under two minutes. In practice, we find that even for the largest samples – to date, the masses of the samples measured have ranged from 5 g to 50 g – the vigorous boiling of the liquid nitrogen has ceased (indicating that the system is close to equilibrium) in much less than five minutes after the sample is inserted. By using a twenty minute interval between sample insertions, we insure that the system has returned to thermal equilibrium long before the time the next sample is introduced.

The Dewar system weight is measured with a Mettler Toledo PB4002-S/FACT with automatic internal calibration, which can record masses up to 4100 g at a precision of 0.01 g. The scale itself can become cold if the Dewar comes to low temperature, which we have observed will slightly change its response (in the second decimal place); to prevent this, the Dewar is normally set on a small cardboard box placed between it and the scale pan. Typically, the total mass of the system (including the weight of the Dewar and cover) is in the neighborhood of 1000 g and the steady-state evaporation rate is on the order of 0.01 g/s. Data is read out through an RS232 port to a desktop computer where it is recorded using the PerkinElmer Collect software package. For the experiments reported here, we collected and recorded the system weight every ten seconds.