N92-10888

WATER/ROCK INTERACTIONS IN EXPERIMENTALLY SIMULATED "DIRTY SNOWBALL" AND "DIRTY ICEBALL" COMETARY NUCLEI

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Introduction. In the "dirty snowball" model for cometary nuclei [1], comet-nucleus materials are regarded as mixtures of volatile ices and relatively non-volatile minerals or chemical compounds. Although results from the *Giotto* and *Vega* spacecraft flybys of comet P/Halley indicate a complex chemistry for both the ices and dust in the nucleus [2], carbonaceous chondrite meteorites are still regarded as useful analogs for the rocky component [3]. Previous considerations of the behavior of water in cometary nuclei have focussed on theoretical evaluations of the effects of phase transitions on heat balance [4] or the kinetics of ice retention [5]. Apparently, less attention has been paid to water/mineral interactions despite the wealth of information about the mineralogical dependence of water behavior in frozen soils [6]. To help elucidate the possible physical geochemistry of cometary nuclei, we report preliminary results of calorimetric experiments with two-component systems involving carbonaceous chondrites and water ice.

Based on collective knowledge of the physics of water ice [7,8], three general types of interactions can be expected between water and minerals at sub-freezing temperatures: (a) heterogeneous nucleation of ice by insoluble minerals; (b) adsorption of water vapor by hygroscopic phases; (c) freezing- and melting-point depression of liquid water sustained by soluble minerals. The relative and absolute magnitudes of all three effects are expected to vary with mineral composition.

Samples and Methods. Two series of experiments were performed in a differential scanning calorimeter (DSC) with homogenized powders (silt-sized and finer grains) of whole-rock meteorites and comparison samples [9]. In Series 1, approximately equal masses of mineral/rock powder and deionized water were blended into mud at room temperature (295-298 K) and crimp-sealed in an aluminum container; a physically separate droplet of deionized water, overhanging the mud, served as internal standard. Series 2 used the same procedure except that a dry mineral/rock sample was exposed only to water vapor from the overhanging droplet. Each sample container was placed in a Perkin-Elmer DSC-2C instrument and cooled at 10 K/min to $\leq$ 200 K, followed by re-heating at 10 K/min, under a continuous gas purge of 20 cm^3 Ar/min. (Experiments down to 100 K verified absence of significant transitions below 200 K). DSC heat-flow data were acquired during multiple freeze/thaw cycles. Certified mercury (ΔH(melt) = 11.469 J/g at 234.3 K; National Institute of Standards and Technology SRM-2225) was used for DSC primary calibration. Separate experiments were performed on the Allende (CV3), Murchison (CM2), Orgueil (CI), Holbrook (L6), and Pasamonte (eucrite) meteorites as well as on peridotite PCC-1 (U. S. Geological Survey), saponite (Clay Minerals Society SapCa-1), montmorillonite (CMS STx-1), and serpentine (Franciscan Formation, California).

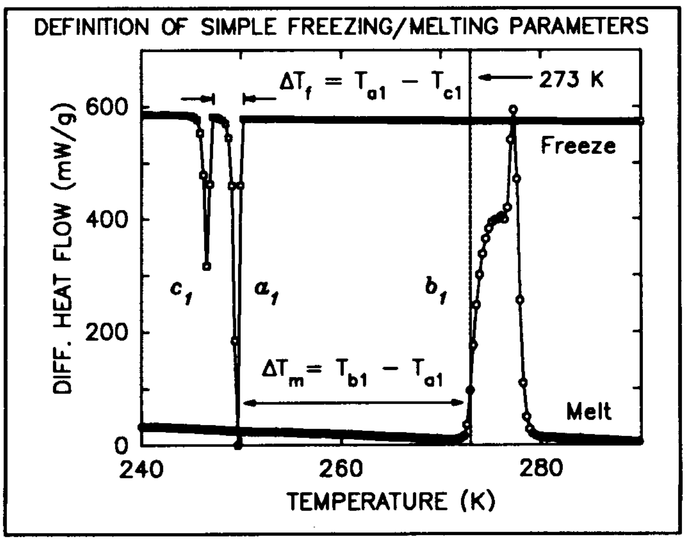

Figure 1. Simple parameters measured from DSC extrapolated-onset temperatures of freezing and melting peaks for water in sample (peaks a, b) and internal standard (peak c). The 273 K reference marker is not part of the parameterization.

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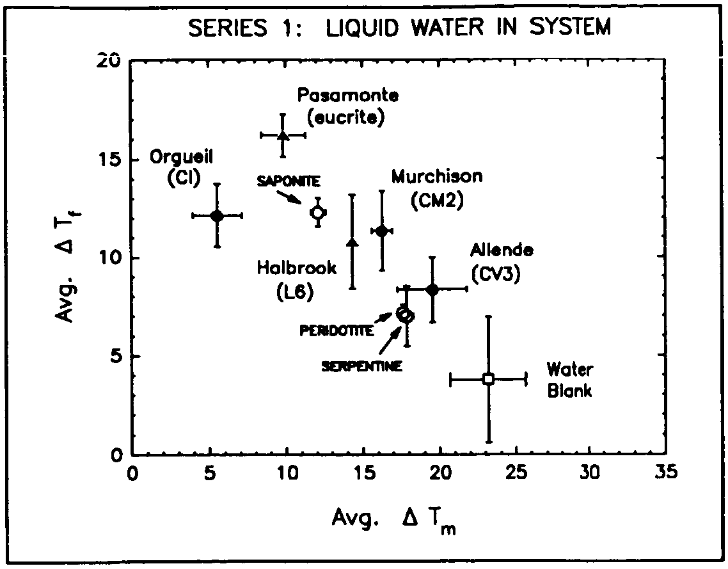

Figure 2. Summary of freezing/melting parameters measured for Series 1 ("dirty iceball") experiments. Points with error bars represent mean (± one standard deviation of the mean) results from replicate (3-4) analyses of individual samples. The overall negative trend of data points indicates control by heterogeneous nucleation of ice. Deviation of the Orgueil point from the trend reflects additional freezing- and melting-point depression by water-soluble salts.

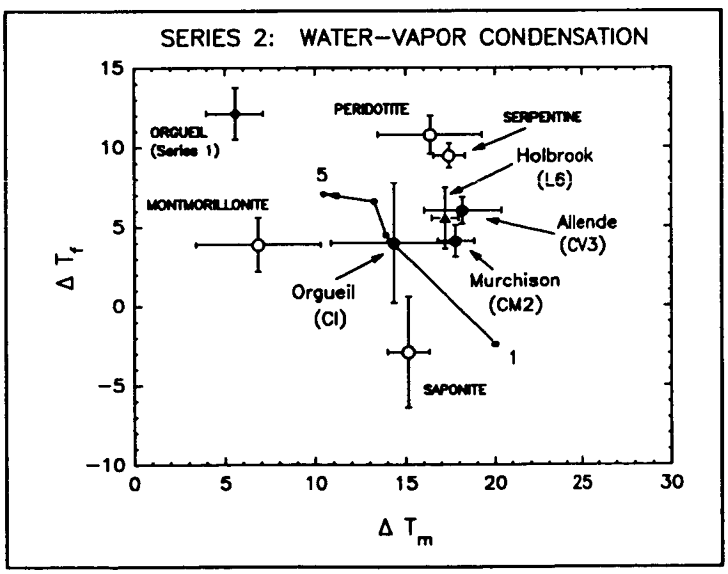

Figure 3. Summary of freezing/melting parameters measured for Series 2 ("dirty snowball") experiments. Points with error bars represent mean (± one standard deviation of the mean) results from replicate (3-4) analyses of individual samples. Numbered points (1-5) denote individual cycles for Orgueil. Absence of coherent trends (cf., Fig. 2) indicates different control of water/rock interaction relative to those involving liquid water. Here samples are distinguished mostly by their relative sorption of water vapor. Orgueil exhibits transition from "snowball" to "iceball" with repeated thermal cycling.

Although the DSC data contain substantial "fingerprint" (analog pattern) information for each sample [9], we wish to convey the systematics of water/rock interactions by reducing the measurements to simple parameters that describe the freezing and melting behavior of water. Accordingly, the parameters ΔT_m and ΔT_f are defined (Fig. 1) to quantitatively describe how mineralogy affects freezing and melting relative to a pure water internal standard. We emphasize that much additional diagnostic information could be derived by analyses of DSC peak shapes and enthalpic ratios; our use of ΔT_m and ΔT_f here serves only to conveniently summarize variations in water/rock systems under freezing conditions.

Results. *SERIES 1.* These experiments can be considered "dirty iceball" simulations in which water is uniformly distributed in a relatively dense mixture. Because freezing of water depends heavily on heterogeneous nucleation [7,8], and the aluminum container is a relatively poor nucleator, liquid water undercools substantially before freezing in the absence of minerals. The mineral/rock substrates were distinguished by their relative abilities to nucleate ice from undercooled water [9]. If heterogeneous nucleation was the only (or dominant) control of freezing, and melting-point depression by dissolved material was not important, a plot of ΔT_f vs. ΔT_m should comprise a negatively sloping data trend (i.e., ΔT_f and ΔT_m should be inversely correlated as defined in Fig. 1). Indeed, experimental results are consistent with dominance of heterogeneous nucleation (Fig. 2).

The trend among mineral and rock samples can be understood in terms of the major minerals in each material. As reviewed previously in another context [10], the relative ice-nucleation abilities of igneous silicates are expected to be olivine ~ plagioclase << pyroxene. Phyllosilicates are expected to exhibit a wide range of nucleation abilities; non-expandable clays (e.g., chlorites) are generally expected to be better nucleators than expandable clays (e.g., montmorillonite, saponite) [10]. The ice-nucleation effectiveness of montmorillonite-type clays, however, is expected to vary with degree of interlayer expansion which, in turn, will depend on degree of hydration and identities of interlayer cations [10]. As a kaolinite-type clay, serpentine is expected to be no more than a moderately good nucleator. Among our test samples, the poorest ice nucleators contain high abundances of olivine (e.g., peridotite, Allende) whereas the best ice nucleators are composed mostly of pyroxene (e.g., Pasamonte). The phyllosilicate-rich meteorites, Murchison and Orgueil, show intermediate ice-nucleation abilities that probably reflect a complex interplay of water with igneous silicates, clay minerals, and possibly organic matter. A second minor "melting" peak in frozen Orgueil, and a systematic decrease in the onset of melting in both Orgueil and Murchison [9], further suggest interactions of water with hygroscopic minerals. In fact, the deviation of Orgueil from the overall inverse trend in Fig. 2 can be understood as effects of freezing- and melting-point depressions created by dissolved salt minerals (e.g., epsomite).

SERIES 2. These experiments can be considered "dirty snowball" simulations in which water is progressively condensed within a porous substrate; in contrast with the "iceball" simulation, liquid water is less important and uniformity may be established only after significant elapsed time. Whereas freeze/thaw cycling of Series 1 samples revealed little, if any, systematic change with time, data for Series 2 samples showed pronounced changes with successive thermal cycles. Freezing and melting peaks controlled by the mineral/rock samples grow during successive freeze/thaw cycles, presumably as water vapor is progressively adsorbed and condensed on the initially dry samples. Characteristic signatures are well established after 3-5 cycles. Effects are seen in all three of the carbonaceous chondrites but are most pronounced for Orgueil, probably as a consequence of its abundant hygroscopic phyllosilicates and sulfates. For the complete suite of samples, absence of a coherent trend among the parameterized data (Fig. 3) indicates that, in contrast with Series 1, heterogeneous nucleation was not the dominant effect. The apparent formlessness of the simple $\Delta T_f/\Delta T_m$ parameterization belies the fact that better inter-sample discrimination is achieved by comparison of the full DSC curves [9]. For Orgueil, in particular, average values of the ΔT parameters fail to convey time-dependent changes. Successive "snowball" cycles for Orgueil gave parameterized results that showed a systematic trend toward "iceball" behavior (points 1-5 moving toward Series 1 point in Fig. 3).

Implications for In-Situ Cometary Analyzers. Besides identification of volatile ices (not addressed in this paper), DSC-type experiments could help diagnose the rocky component of a comet nucleus. In addition to conventional high-temperature DSC, in which minerals are identified by phase-transition or decrepitation reactions, low-temperature DSC could sense the freezing interactions of minerals with water. Based on our freezing/melting data, we would expect (at the minimum) that eucrites could be distinguished from ordinary and carbonaceous chondrites and that Orgueil-type chondrites could be distinguished from other chondrites. Additional experimental work would be necessary, however, to establish the possible effects of other volatile ices, minerals, and organic matter.

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