Reports

Chemistry of Lunar Basalts with Very High Alumina Contents

Abstract. *A chemically distinct group of lunar rocks with the trace element characteristics of basaltic lunar rocks is apparently ubiquitous on the lunar surface. Such rocks have been found at the Apollo 15, Apollo 16, and Luna 20 landing sites. They may be derived from the plains-forming material that has been designated Cayley Formation.*

Prior to the return of the Apollo 16 and Luna 20 samples, selenomorphological studies suggested that in many highland areas an older crust was overlain by younger extrusive volcanic rocks (*1*). The absence of unambiguous volcanic textures and structures at the Apollo 16 site, along with ubiquitous breccias, has cast some doubt on this interpretation of morphological characteristics (*2, 3*). However, detailed chemical and isotopic studies of samples from this site have produced evidence that basaltic rock with a very high concentration of Al_2O_3 may be quite common in this area. Rocks with similar chemical compositions occur at the Apollo 15 and Luna 20 sites. We hypothesize that this rock postdates the formation of the original lunar crust; that is, it is genetically distinct from the plagioclase-rich lunar crust.

In categorizing the postulated rock types, we have relied on chemical characteristics. Because most highland samples are modified by collisional processes, even whole crystalline igneous rocks (for example, samples 68415, 62295, and 14310) may have crystallized from pools of liquid produced during major collisions. We recognize that the cataclastic textures of highland rocks suggest that the dispersion or variance within chemical groupings is at least partially due to mechanical mixing. Nevertheless, we maintain that the chemical and isotopic characteristics of some major rock types have not been obliterated during the early bombardment of the lunar surface. The existence of macroscopic samples consisting of almost pure plagioclase—for example, sample 60025 and rocks with highly regular large-ion lithophile (LIL) element patterns such as the KREEP basalts [lunar rocks with basaltic major element composition accompanied by high and distinctive concentrations of K, rare-earth elements (REE), and P] —are a priori evidence in support of this assertion.

Some of the distinguishing chemical characteristics of lunar rock types are summarized in Figs. 1 through 3. The FeO, MgO, and Al_2O_3 contents of all major lunar rock types recognized to date are summarized in Fig. 1. The FeO/MgO ratio of mare basalts distinguishes them from both terrestrial and other lunar basalts (*4*). Two rocks with Al_2O_3, FeO, and MgO concentrations intermediate between those of typical mare basalts and those of the highland rocks (samples 14053 and 14072) are also noted. The bulk of the data summarized in Fig. 1 applies to plagioclase-rich rocks that contain 15 or more percent (by weight) Al_2O_3. These rocks can be divided into three distinct groups: (i) group 1, KREEP basalts with 15 to 20 percent Al_2O_3 and with FeO/MgO ratios close to unity; (ii) group 2, anorthositic rocks, including anorthosites, gabbroic anorthosites, and anorthositic gabbros, with more than 25 percent Al_2O_3 and FeO/MgO ratios that are, in general, similar to those of the KREEP basalts; and (iii) group 3, rocks with 20 to 25 percent Al_2O_3 and with a rather wide range of FeO and MgO concentrations which have systematically lower FeO/MgO ratios than either of the previous groups. All the specimens in group 3 have relatively high Cr_2O_3 contents (0.1 to 0.18 percent) and TiO_2 contents that fall in the range from 0.6 to 1.0 percent. Several crystalline specimens in this group are distinguished by the occurrence of spinel. Olivine is also abundant in some of these rocks, for example, sample 62295 (*5*). Some exceptions to this rather simple major element classification can be noted immediately—in particular, KREEP samples like sample 14310, which have higher Al_2O_3 contents and different Sr/Yb and Sr/Eu ratios. These differences may be explained if we postulate the addition of plagioclase with low Eu and Sr contents to typical KREEP basalt (*6, 7*).

The chemical characteristics of the KREEP basalts and the highly aluminous rocks in group 3 are further com-

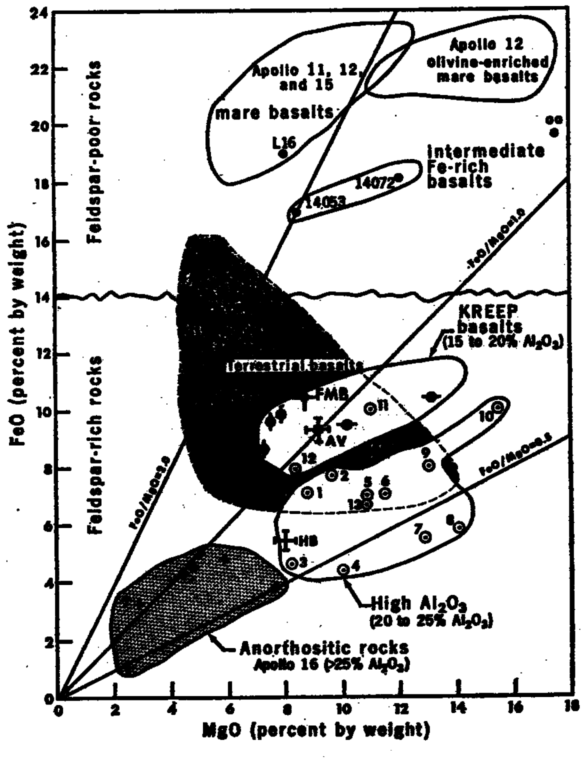

Fig. 1. The FeO, MgO, and Al_2O_3 contents of different lunar rock types: +, rocks with more than 25 percent Al_2O_3; ⊙, rocks with 20 to 25 percent Al_2O_3; ⧫, Apollo 15 KREEP basalts; -●-, Apollo 16 KREEP basalts; *AV*, mean KREEP composition from broad-beam microprobe analyses of individual fragments; *HB*, "highland basalt" (*15*); *FMB*, mean composition of Fra Mauro basalt glasses; *GG*, Apollo 15 green glass; *L16*, Luna 16 basalt. Points labeled 1, 2, 3, . . . correspond to samples 66095, 61156, 60335, 61016 (dark), 14073, 14083 (light), 15273,4,2, 62295, 22007, 15445,17, 22006, 14310, and 15273,4,3, respec-and .15273,4,3, respec-from (*2, 4, 15, 18, 19*), and our unpublished results.

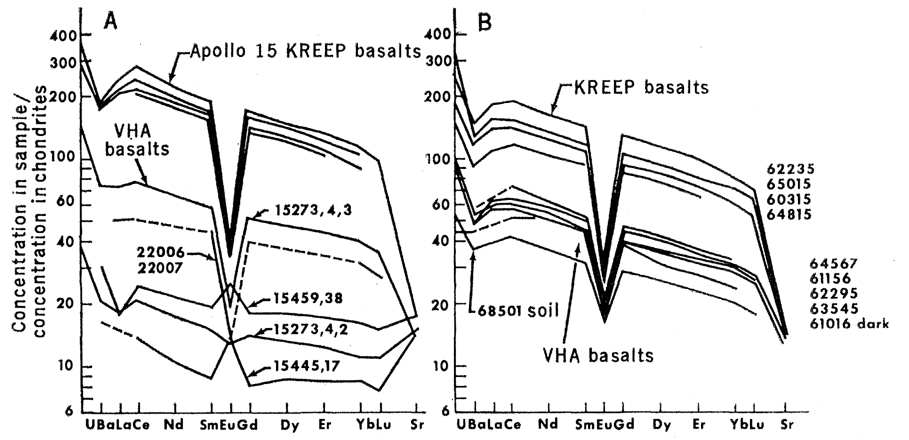

Fig. 2. Abundances of LIL elements in KREEP and VHA basalts: (A) Apollo 15 and Luna 20 samples; (B) Apollo 16 samples. Values for Luna 20 samples 22007 and 22006 are from (*18*); other data are from (*9*, *20*), and our unpublished data. All data are normalized to chondrite values given by Bansal *et al.* (*9*). The normalizing values used for U and Sr are 0.011 and 11 parts per million, respectively.

pared in Fig. 2. The concentrations for the LIL elements (REE, U, Ba, and Sr) are illustrated in terms of abundances normalized to values for chondrites. Both the relative abundances and the absolute concentrations of these elements for six of the rocks with 20 to 25 percent Al_2O_3 [samples 61156, 62295, 61016 (dark), 63545, 15273,4,3, and 22007] are essentially identical. The trace element characteristics of a few samples in this group—for example, samples 15273,4,2, 15459,38, and 15445,17—indicate that they have quite different origins. In addition, samples 60335 and 66095 have Y, Zr, Th, Nb, and K abundances similar to those of the group containing sample 61156 (*2*). The relative abundances of the trivalent REE in the six samples listed above are remarkably similar to those of the KREEP basalts. Only the Sm/Eu and Sr/Eu ratios are distinctly different. The Sm/Eu ratio of the highly aluminous rocks is about half that of the KREEP basalts, and the Sr/Eu ratio is almost twice that of the KREEP basalts. The general characteristics of this LIL element abundance pattern—in particular, the relatively constant Sr and Eu concentrations—along with the systematic fractionation of these elements from other LIL elements is most plausibly explained in terms of the partial melting of a plagioclase-rich source material (*4*, *8*). On the basis of the combined LIL element and major element characterization of seven fragments from three lunar sites, we conclude that most of the rocks in group 3 are from an independent magma type derived by the partial melting of a plagioclase-rich source material. We will tentatively designate rocks chemically similar to sample 61156 as very high Al_2O_3 (VHA) basalts.

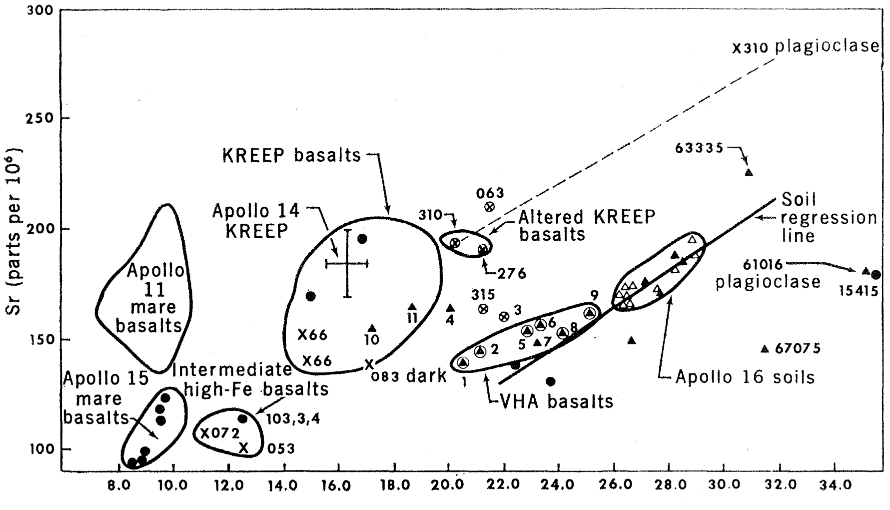

Fig. 3. The Al_2O_3 and Sr contents of some lunar rocks and soils: △, Apollo 16 soils; ▲, Apollo 16 rocks; Ⓐ, VHA basalts, mainly Apollo 16 samples; × and ⊗, Apollo 14 samples; ●, Apollo 15 samples. Numbers with three or more digits refer to appropriate generic sample numbers. The numbers 1, 2, 3, . . . designate sample numbers 62295, 61016,79 (dark), 14083 (light), 65015, 61156, 61016,143, 15273,4,3, 66095, 60335, 60315, and 62235, respectively. The parameters of the regression line are: $Sr = 8112\ Al_2O_3 - 45.369$ with a regression coefficient of 0.93. Data are from (*2*, *6*, *12*, *20*, *21*), and our unpublished results.

The postulated existence of this VHA basalt magma at the Apollo 16 site suggests a reexamination of the major element correlations observed for the soil samples from this site. The unusually precise chemical correlation among many elements and the known occurrence of KREEP basalts, breccias, and anorthosites at this site have led to the suggestion that the soil consists of a mixture of KREEP basalt and anorthosite or gabbroic anorthosite (*2*, *9*). The correlation of Al_2O_3 with CaO, FeO, and MgO clearly indicates that one end-member of the soil at this site is extremely rich in plagioclase. Figure 3 illustrates the Al and Sr contents of both soil and rock samples from this site. It is quite clear that the Sr/Al regression line for Apollo 16 soils does not pass through the Sr and Al concentrations of KREEP basalts. Furthermore, the Sr/Al ratios of anorthosites from this site are quite variable. The major element correlations, along with the Sr/Al regression plotted here, suggest that the Sr content of typical anorthosite from the Apollo 16 site must be relatively high. We suggest that it is most significant that the Sr/Al ratio of the VHA basalts from the Apollo 16 site is much more consistent with that of the soil regression or mixing line than with the Sr/Al ratio of KREEP basalts. It appears that, if the Apollo 16 soils are a mixture of two end-members, then the VHA basalts approximate the low Al_2O_3 end-member. The LIL abundance patterns of VHA basalts and typical Apollo 16 soil samples shown in Fig. 2B are remarkably similar. The concentrations of these elements in the soil and in VHA basalts suggests that more than half of some of the soils may be made up of VHA basalts. We suggest that such basaltic rocks may underlie most of the Cayley Plains west of the Apollo 16 landing site.

Finally, we mention an observation based on the x-ray fluorescence experiment of Adler *et al.* (*10*) that supports our hypothesis; they have demonstrated that the region west of Descartes between 3°E and 13°E, along with several other highland areas, has mean Al/Si concentration ratios ranging from 0.57 to 0.59 and mean Mg/Si concentration ratios ranging from 0.21 to 0.26. These preliminary data suggest that the average Al_2O_3 concentration for large regions within the highlands is between 22 and 23 percent. These values are quite similar to those of the VHA basalts. The Mg/Si ratios of these regions are somewhat lower than those of the VHA basalts. Nevertheless, we suggest that the orbital x-ray fluorescence concentrations for some regions of the highlands correspond much more closely to those of the VHA basalts than to those of anorthosite or gabbroic anorthosite.

The chemical characteristics of highland rocks outlined here suggest several constraints on the petrogenesis of these rocks:

1) The large Eu and Sr anomalies of this rock type indicate that the Al-rich character probably cannot be ascribed to the addition of plagioclase to a less aluminous liquid if this plagioclase is typical in having relatively low REE concentrations and high Sr and Eu concentrations [see, for example (*7, 11, 12*)]. This constraint is quite general. It is applicable to both igneous differentiation processes that may have gone on during the formation of the primitive crust and to mechanical mixing of different rock types during the subsequent evolution of the lunar crust. More specifically, the FeO/MgO ratios and LIL element contents of the KREEP basalts and the VHA basalts preclude the formation of the VHA basalts by the mixing of plagioclase with KREEP basalt.

2) The close association of the VHA basalts and the anorthositic rocks may suggest to some that these rocks are complementary products of the same magmatic sequence. If this is so, the Eu and Sr anomalies require that the parent liquid for these two rock types had a Al_2O_3 content in excess of 25 percent. In essence, this scheme assumes that the Eu and Sr fractionation from the trivalent REE results from the removal of plagioclase, along with some olivine or pyroxene, or both, from an unknown parent liquid. This hypothesis is essentially untestable unless the characteristics of this parent liquid are specified. If its LIL element pattern is assumed to be unfractionated relative to that of chondrites (*7*), the liquid must have contained 27 to 29 percent Al_2O_3 in order to crystallize sufficient plagioclase to produce the observed Eu and Sr abundances in a residual liquid with 22 percent Al_2O_3. If one assumes that the LIL elements in the hypothetical parent liquid are already fractionated, the petrogenesis of one magma type is based on the postulation of arbitrary characteristics for another unobserved magma. The assumption that the VHA basalts are an independent magma type appears to us to be a simpler explanation of the observed chemical characteristics.

3) Finally, the formation of KREEP basalt from VHA basalt by fractional crystallization is also very unlikely. Such extensive differentiation implies significant changes in the Cr_2O_3 content of the residual liquid due to the precipitation of spinel or pyroxene. In fact, the Cr_2O_3 content of the KREEP basalts is somewhat higher (0.12 to 0.18 percent) than that of the VHA basalts. In addition, the genetic association of KREEP and VHA basalts requires that they be spatially associated. The most plausible interpretation of the Al/Si ratios inferred from the x-ray fluorescence experiment (*10*) and the K, U, and Th contents inferred from the gamma-ray experiment (*13*) indicates that some areas of the moon contain abundant amounts of VHA basalts and very small amounts of KREEP basalts, whereas other lunar areas contain large amounts of KREEP basalts and very small amounts of VHA basalts. We suggest that the evidence presented here argues against the derivation of KREEP basalts from the VHA basalts.

We have investigated the simple hypothesis that the VHA basalts and the KREEP basalts are both products of partial melting from the same starting material, the former being formed by 7 to 12 percent partial melting and the latter involved in 0.5 to 2 percent partial melting. This hypothesis explains the Eu and Sr anomalies and the Eu/Sr ratios. It fails to explain the nearly identical slopes of the LIL abundance patterns, suggesting that a more complex origin of these two rock types is required. Perhaps relatively small differences such as the occurrence or nonoccurrence of melilite in the source of these liquids can have a significant effect on the abundance patterns of the trivalent REE. If melilite occurs in the source of the VHA basalts, it may retain the trivalent REE in the source region more effectively than diopside, which has been proposed as the main site for REE elements in the source of KREEP basalts (*4*). In conclusion, we suggest that both selenological evidence and chemical data indicate that the VHA basalts originated independently of the Al-rich crust and of the KREEP basalts.

Moreover, the identification of the VHA basalts with the compositional group designated "low-K Fra Mauro basalts" (*14*), "highland basalt" (*15*), or the "high alumina basalt" of Prinz *et al.* (*16*) is tenuous. The Al_2O_3, FeO, and MgO contents of the low-K Fra Mauro basalts are well within the range defined for the KREEP basalts. Both the Al_2O_3 content and the FeO/MgO ratio of the high alumina basalt defined by Prinz *et al.* (*16*) are intermediate between those of KREEP basalt and those of the VHA basalts identified here. The composition of "highland basalt," plotted in Fig. 1 as *HB*, is almost midway between the mean values observed for anorthositic rocks and those given here for the VHA basalts. This compositional relation suggests the possibility that the glass particles designated "highland basalt" may originate from a mechanical mixture of two major highland rock types, that is, anorthosite and VHA basalt.

We emphasize that knowledge of the LIL element abundance patterns has been essential in the characterization of the rock types discussed here. When such data are lacking, it is difficult to make meaningful comparisons between different lunar rock types.

We have chosen the chemical name "very high alumina basalts" with the awareness that it may be replaced by a more distinctive name as more details about this rock type emerge. Equivalent mineralogical or conventional rock names—for example, allivalite (*17*) or spinel troctolite—may be appropriate for some of the individual specimens in the category described here.

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References

1. T. A. Mutch, *Geology of the Moon* (Princeton Univ. Press, Princeton, N.J., 1970); N. J. Trask and J. F. McCauley, *Earth Planet. Sci. Lett.* **14**, 201 (1972); C. A. Hodges, *U.S. Geol. Surv. Map I-748* (1972); D. E. Wilhelms and J. F. McCauley, *U.S. Geol. Surv. Misc. Geol. Invest. Map I-703* (1971).
2. Apollo 16 Preliminary Examination Team, *Science* **179**, 23 (1973).
3. Apollo Field Geology Investigation Team, *ibid.*, p. 62.
4. P. W. Gast, *Moon* **5**, 121 (1972).
5. S. O. Agrell, personal communication.
6. W. I. Ridley, R. Brett, R. J. Williams, H. Takeda, R. W. Brown, *Geochim. Cosmochim. Acta* **1** (Suppl. 3), 159 (1972).
7. N. J. Hubbard, P. W. Gast, C. Meyer, L. E. Nyquist, C. Shih, H. Wiesmann, *Earth Planet. Sci. Lett.* **13**, 71 (1971).
8. P. W. Gast and N. J. Hubbard, *ibid.* **10**, 94 (1970); N. J. Hubbard and P. W. Gast, *Geochim Cosmochim. Acta* **2** (Suppl. 2), 999 (1971).
9. B. M. Bansal, S. E. Church, P. W. Gast, N. J. Hubbard, J. M. Rhodes, H. Wiesmann, *Earth Planet. Sci. Lett.* **17**, 29 (1972).
10. I. Adler *et al.*, in *Apollo 16 Preliminary Science Report* (*NASA SP-315,* National Aeronautics and Space Administration, Washington, D.C., 1973), pp. 19-1 to 19-14.
11. H. Wakita and R. A. Schmitt, *Science* **170**, 969 (1970).
12. C. C. Schnetzler and J. A. Philpotts, *Geochim. Cosmochim. Acta* **2** (Suppl. 2), 1101 (1971).
13. A. E. Metzger, J. I. Trombka, L. E. Peterson, R. C. Reedy, J. R. Arnold, *Science* **179**, 800 (1973)
14. A. M. Reid, J. Warner, W. I. Ridley, R. W. Brown, *Meteoritics* **7**, 395 (1972).
15. A. M. Reid, W. I. Ridley, R. S. Harmon, J. L. Warner, P. R. Brett, P. Jakes, R. W. Brown, *Geochim. Cosmochim. Acta* **36**, 903 (1972).
16. M. Prinz, E. Dowty, K. Keil, T. E. Bunch, *ibid.*, in press.

→ G. M. Brown, *Phil. Trans. Roy. Soc. London Ser. B* **240**, 1 (1956).

18. J. C. Laul and R. A. Schmitt, *Geochim. Cosmochim. Acta*, in press.
19. H. J. Rose, Jr., F. Cuttitta, C. S. Annell, M. K. Carron, R. P. Christian, E. J. Dwornik, L. P. Greenland, D. T. Ligon, Jr., *ibid.* **2** (Suppl. 3), 1215 (1972).
20. B. M. Bansal, P. W. Gast, N. J. Hubbard, L. E. Nyquist, J. M. Rhodes, C. Y. Shih, H. Wiesmann, in *Lunar Science—IV, Houston, March 1973*, J. W. Chamberlain and C. Watkins, Eds. (Lunar Science Institute, Houston, 1973), p. 48; W. I. Ridley, N. J. Hubbard, J. M. Rhodes, B. Bansal, H. Wiesmann, C. Shih, *J. Geol.*, in press.

21 W. Compston, H. Berry, M. J. Vernon, B. W. Chappell, M. J. Kaye, *Geochim. Cosmochim. Acta* **2** (Suppl. 2), 1471 (1971).

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Anomalous Heat Capacities of Supercooled Water and Heavy Water

Abstract. *Emulsification makes it possible to supercool water to the homogeneous nucleation temperature. Accordingly, the heat capacities of water and deuterium oxide have been determined from the respective equilibrium melting points to −38° and to −34°C, respectively. Two methods, drift calorimetry and differential scanning calorimetry, have been used. Both methods reveal a striking rise in the constant-pressure heat capacity below −20°C. This indication of an apparently cooperative behavior should serve to test current theories of water, most notably perhaps, the pair potential model of Ben-Naim and Stillinger. Some implications of possible meteorological significance are mentioned.*

One of the most fundamental thermodynamic properties of water, its heat capacity, has not, to our knowledge, been reported for temperatures much below 0°C. Since an understanding of the relation between thermal energy and "geometrical" structure is vital to an understanding of the nature of water, and since measurements made on supercooled water in capillaries have shown that structural anomalies become more pronounced with decreasing temperature (*1–3*), we have sought to measure the constant-pressure heat capacity, C_p, of this substance to the lowest possible temperatures.

It is possible to study gram-sized samples of clean water to ~ −20°C under certain circumstances. Hallett has reported viscosities obtained from measurements on bulk water to −23.8°C (*4*). Accurate measurements at temperatures much lower than this are made possible by the use of samples of water so small that the chances of heterogeneous nucleation are greatly reduced. Such samples may be examined individually, as in the capillary studies of water density (*1–3*), or en masse, as in studies of emulsified water (*5, 6*). Particularly stable emulsions, in which water can be held without crystallizing for long periods at temperatures approaching the homogeneous nucleation temperature, −40°C, have been developed by Rasmussen and MacKenzie (*5*). These emulsions have proved very suitable for low-temperature heat capacity studies; they are made by dispersing water in heptane supersaturated with sorbitan tristearate (Span 65), one of a number of commercially available water-insoluble surfactants (*7*). Water droplet diameters in the range 1 to 5 μm are readily achieved with a standard blender.

Emulsions containing 40 to 50 percent water (by volume) have been used in both of the heat capacity studies presented in this report. Two different calorimetric methods were used. At the Cryobiology Research Institute, the total heat capacity of the calorimeter chamber containing the emulsion was determined by conventional drift calorimetry. The differences in heat capacities between supercooled water and ice were calculated at 5°C intervals. At Purdue University, data were obtained by differential scanning calorimetry (DSC); both the Perkin-Elmer DSC-1B and the more recent and much-refined DSC-2 instruments have been employed. In DSC measure-

Table 1. Heat capacities of water and deuterium oxide (in calories per mole per degree Celsius).

Temperature (°C)	C_p (water)					C_v (water) (av. DSC)	C_p (deuterium oxide)	
	Av. DSC-1B	DSC-2	Av. of the two DSC's	Drift calorimeter	Bulk water (DSC)		Av. DSC-2	Drift calorimeter
4						18.1	20.3	21.0
0	18.3	18.3	18.3	17.7	18.4			21.0
− 3	18.2	18.0	18.1	17.6	18.3	18.0	20.1	21.1
− 8	18.1	18.0	18.0	17.5	18.2	17.9	20.5	20.9
− 13	18.1	18.2	18.1	17.5	19.0	17.9	21.2	21.4
− 18	18.3	19.0	18.6	17.8	18.9	18.0	22.0	22.3
− 23	18.8	20.1	19.5	18.8		17.9	24.2	24.4
− 28	19.3	22.5	20.9	21.0		17.8	26.3	29.2
− 33	22.1	25.1	23.6	25.0		17.7	30.9	
− 38	27.0	28.9	28.0			17.8		