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WEATHERING OF STONY METEORITES IN ANTARCTICA.

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Introduction. Weathering produces undesirable physical, chemical, and isotopic changes that might disturb the records of cosmochemical evolution that are sought in meteorites. As partial compensation, though, weathering of meteorites in an icy "regolith" offers, by analogy, insight into processes of rock alteration that have probably operated on icy planetary bodies such as comets, asteroids, satellites of the Jovian planets, and planet Mars. For Antarctic geoscience, weathering effects in meteorites might be "marker horizons" that contain information about histories of Antarctic ice sheets.

Meteorites are physically disintegrated by crack-propagation phenomena, including ice riving and secondary-mineral riving, and are probably abraded by wind that is laden with ice crystals (on open ice sheets) or dust particles (if downwind from moraines). Chemical weathering proceeds by oxidation, hydration, carbonation, and solution and produces a variety of secondary minerals and mineraloids. Weathering proceeds at rates that are slower than in temperate climates but produces effects that may be distinctively different from those in non-Antarctic meteorite finds.

Differential Weathering Under Freezing Conditions. In general, the rates and styles of both physical and chemical weathering vary with the availability of liquid water, which controls solution, transportation, and precipitation processes. Minerals show differential susceptibilities to chemical attack that, to a first approximation, are correlated with values of the Gibbs free-energy changes that can be calculated for pertinent decomposition reactions. Because ice and vapor, rather than liquid, are the dominant forms of water in the Antarctic meteorite collection areas, differential weathering might be even more pronounced in Antarctica than in temperate latitudes.

Liquid water can survive in porous rocks at < 273 K either as "unfrozen" capillary water or as undercooled planar films on mineral surfaces [1]. It can be estimated (method of [2]) that for particle sizes and porosities that apply to stony meteorites, thermodynamically "liquid" water (> 15 molecular layers thick) should be expected at temperatures as low as 263-264 K (Fig. 1) although at deep-ice temperatures (250 K) unfrozen water thicknesses should be < 5 molec-
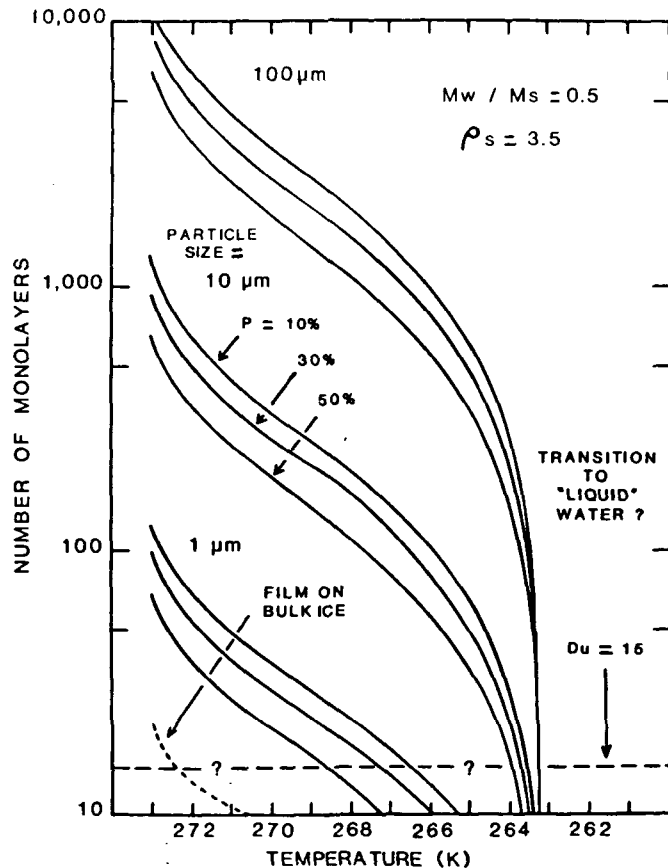

Figure 1.

Estimated thickness of "unfrozen" water layers in wet stony meteorites (water/rock mass ratio = 0.5) as a function of temperature, particle size, and porosity (P).

ular layers. Unfrozen water would form brines on hygroscopic phases (e.g., lawrencite) and, thereby, extend its own stability to even lower temperatures. Therefore, rust mantles on metal particles, which apparently form in liquid water [3], might develop while meteorites are ostensibly "frozen." The ability to nucleate ice from undercooled water varies significantly among minerals [1,4] and it might be expected that effective nucleators, which can immobilize water by freezing, should be less susceptible to weathering than are ineffective nucleators, which are less capable of immobilizing water. As shown in Fig. 2, a grid formed by conventional chemical-thermodynamic and

ice-nucleation parameters might be useful in quantifying the relative susceptibilties of minerals to chemical weathering under "hydrocryogenic" (cold water) conditions. Fig. 2 was constructed by calculating a "thermodynamic" ordinate and an "ice-nucleation" abscissa. For each mineral, the thermodynamic parameter represents the range of values obtained for the equilibrium constants of oxidation, hydration, and carbonation reactions for one mole of mineral reactant at the normal triple point of water. The ice-nucleation parameter represents the minimum crystallographic misfit, $/\delta/$, between the most favorable plane in the mineral substrate and the basal plane of the condensate, ice Ih, and is a measure of the favorability for epitaxial overgrowth of ice on the mineral. Although other determinative factors exist, the temperature at which a mineral can nucleate ice from undercooled water varies inversely with $/\delta/$ [5].
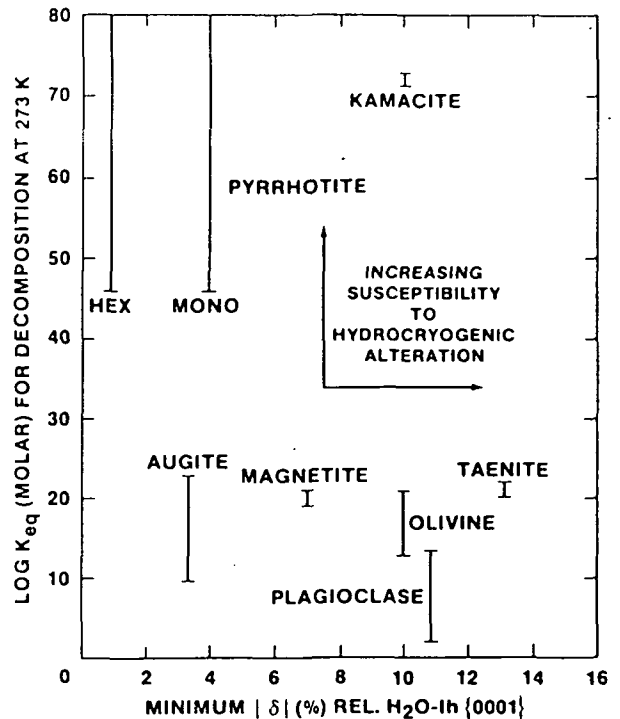

Figure 2.

Prediction of relative susceptibilities of meteoritic minerals to weathering under Antarctic conditions. Note that the x-axis parameter is unique to weathering under freezing conditions.

The relative susceptibilities of Fe-rich minerals to Antarctic weathering, as predicted in Fig. 2, are generally consistent with observations. Namely, pyrrhotite (or troilite) is less susceptible than is Ni-Fe metal, taenite is less susceptible than is kamacite, and silicates are less susceptible than are sulfides and metal. However, two less obvious predictions are also inherent in Fig. 2. First, due to its large value of $/\delta/$, plagioclase might be of similar or greater susceptibility to hydrocryogenic alteration than are pyroxene and olivine. Second, because of large values of both K_{eq} and $/\delta/$, glasses should be especially susceptible to weathering. Ignoring ice-nucleation effects (e.g., as in temperate-latitude weathering), plagioclase should possess a low susceptibility because of its low values for K_{eq}, relative to mafic silicates. However, under hydrocryogenic conditions, the susceptibility of plagioclase might be similar to that of olivine, because of the $/\delta/$ parameter (Fig. 2). Because the expected decomposition products of plagioclase (secondary aluminosilicates, carbonates, and oxides) would not be rusty in appearance, weathering of plagioclase could be easily overlooked during casual inspection of Antarctic meteorites. In the case of glasses, their higher susceptibilities relative to crystalline phases, as measured by

the K_{eq} parameter, would be further accentuated by their high (and effectively incalculable) $/\delta/$ values that result from the absence of long-range order in the glass structures. For example, the calculated thermodynamic coordinate for basalt glass (log K_{eq} = 15-30) indicates that it is more susceptible to chemical weathering than is augite. Although a meaningful value of $/\delta/$ cannot be calculated for basalt glass, it would undoubtedly be a very large number that would plot far to the right of augite in Fig. 2. In any case, the poor ice-nucleation properties of basalt glass have been confirmed experimentally. Under otherwise identical conditions, powdered basalt glass nucleated ice from undercooled water at a temperature that was 5.7 K lower than for the nucleation of ice by powdered augite [6]. A similar argument can be made for differences in susceptibility between plagioclase and plagioclase glass (e.g., maskelynite). Therefore, among the silicate portions of meteorites, glassy components should be the most susceptible to chemical weathering. It should be kept in mind that the overall susceptibility to weathering of a meteorite will be a function of the relative susceptibilities of its mineral components. Therefore, the wide range of phase compositions among meteorites should lead to a wide range in overall susceptibilities to weathering among meteorites.

Mineralogy of Weathering Products. Some samples, especially fusion-crusted surfaces, show clear evidence for etching (incongruent dissolution) of primary mineral grains and nearby deposition of secondary precipitates in voids and fractures, thereby confirming the role of liquid water during weathering of the Antarctic specimens (Fig. 3). "Metallic rust" is composed of oxidized Fe, Ni, and various amounts of S, Cl, and water whereas "sialic rust" is an Fe-rich, hydrous material that includes major to minor concentrations of Si, Al, and other lithophiles [3,7]. Metallic rust commonly occurs as veins and as mantles on Ni-Fe metal or troilite although sialic rust is typical of achondrites, especially in association with mafic silicates and spinels. Sulfates and carbonates occur both independently and along with other weathering products [3,8].

Figure 3.

SEM photomicrograph of a smectite-like clay mineraloid (SMEC) grown in a fracture in fusion crust of Antarctic shergottite EETA79001. Secondary mineral(oid)s contribute to disintegration of Antarctic meteorites through crack propagation. Scale bar is 10 μm.

Aluminosilicates, which may include clay minerals and zeolites, are abundant as decomposition products of glass and plagioclase in basaltic achondrites [3,7]. Rust can act as a pore-filling cement in a manner analogous to diagenetic cements in terrestrial sandstones. However, at tips of microcracks, specific-volume increases that accompany deposition of secondary mineral(oid)s cause widening of fractures and rock disintegration as exemplified by polygonal fracture patterns and pluck pits in fusion crust. Also, migration of water-soluble salts to free surfaces, with subsequent removal by wind abrasion, comprises a subtle but significant process of mass loss from the meteorites.
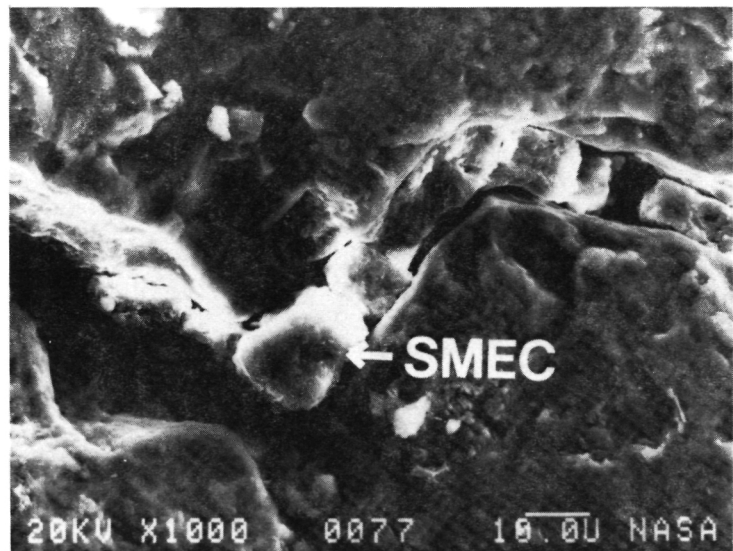
"Glacial" Weathering vs. "Periglacial" Weathering. The most likely time for exposure of a meteorite to liquid water should occur when a meteorite resides at a free surface (i.e., an ice/atmosphere or moraine/atmosphere interface) and is exposed to solar radiant heating. Such exposure can occur shortly after fall of the meteorite, before the rock is incorporated into the glacier, or after emergence of the rock from the glacier at a zone of ablation and accumulation. For convenience, weathering at a free surface (top of glacier or moraine) can be defined as "periglacial" whereas possible weathering during encasement in ice can be defined as "glacial." In the general case where a meteorite falls, is incorporated into a glacier, and then emerges again at a later time, the "glacial" weathering interval would lie between a "first periglacial" and a "second periglacial" weathering period.

Obviously, physical disintegration of a meteorite is not likely to be important as long as the meteorite is encased in ice. However, the existence of "unfrozen" water, as discussed above, might support initiation of chemical weathering during the first periglacial or glacial period that would set the trend for accelerated physical and chemical decomposition during the second periglacial period. From the standpoint of Antarctic geoscience, it would be desirable to recognize and quantify both glacial and periglacial weathering effects in each meteorite. Combined with data on terrestrial residence ages, data on the glacial and periglacial weathering histories of meteorites might reveal the histories of the ice sheets and the mechanisms by which meteorites are transported and concentrated. Important evidence that bears directly on this question occurs in ALH82102 (H5) which was found emerging from ice but which was already significantly rusted, even on its most deeply submerged side. However, it remains to be determined whether the rust in ALH82102 developed during the first periglacial or the glacial period of the meteorite's terrestrial history.
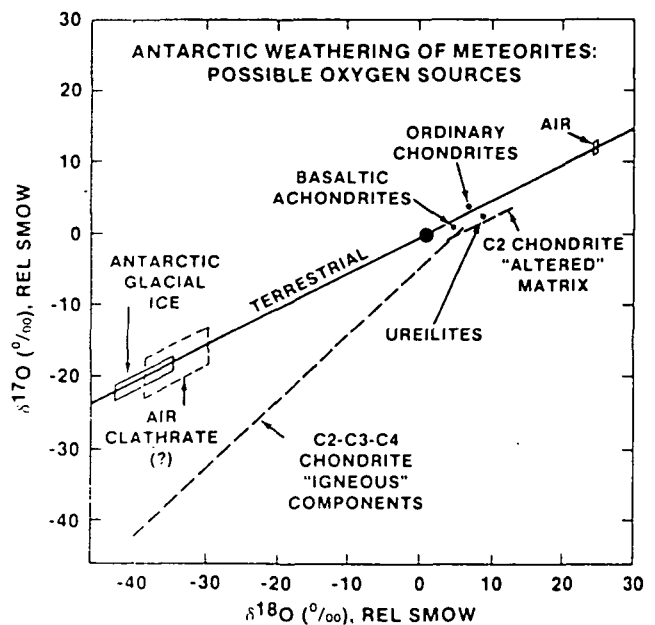

Figure 4.

Possible sources of interference in oxygen isotopic analyses of meteorites found in Antarctica. Large filled circle is SMOW and other points are for fresh, non-Antarctic meteorites [21]. The air clathrate composition is an estimate.

Detailed hydrogen, carbon, and oxygen stable-isotopic studies of weathered meteorites might provide one means of distinguishing glacial from periglacial weathering effects. During periglacial times, weathering probably depends on melted snow or ice as the principal source of water and on the atmosphere as the source of O_2 and CO_2. During glacial times, though, volatiles required for weathering might be derived from gas bubbles or clathrate ices that form in the ice at depths of 900-1300 m [9]. Trapped gas possesses atmospheric values of elemental and isotopic abundances, except for possible CO_2 enrichments and slightly positive values of $\delta^{15}N$ [10]. However, air clathrate should be significantly enriched in O_2 relative to air [11] and, by analogy with methane hydrate [12], H_2O in air clathrate should possess a higher $^{18}O/^{16}O$ ratio than that in free water, probably with values in the range between ice ($\delta^{18}O$ = - 35-43 o/oo) and air ($\delta^{18}O$ = + 23-24 o/oo) (Fig. 4). Therefore,

oxygen isotopic compositions of weathering products will depend upon relative contributions of oxygen from glacial ice, air clathrate, and air, as well as identities of the reactive species (i.e., O_2, H_2O, CO_2). From Fig. 4, it is clear that uptake of only small amounts of Antarctic oxygen from any of the three suspected reservoirs would be sufficient to perturb the oxygen isotopic compositions of meteorites.

"Weatherometers." A definitive correlation between degree of weathering and terrestrial residence age has not yet been found but may simply reflect absence of a quantitative scale for weathering, especially with regard to distinguishing glacial from periglacial weathering effects. Differential susceptibilities of meteoritic minerals to chemical weathering prevents application of a single weathering index to all types of meteorites. Although a single, "universal" weatherometer might not be possible, development of one or more weatherometers for each of the major groups of stony meteorites (carbonaceous chondrites, ordinary chondrites, eucrites, etc.) would represent a major element of progress toward deducing the terrestrial histories of the Antarctic meteorites. The most useful weatherometers should be relatively rapid, utilize modest quantities of samples, yet produce quantitative results that can be calibrated against other measurable parameters. A combination of x-ray diffractometry, reflectance spectrophotometry, and differential thermal analysis was previously found to be useful in quantifying relative degrees of weathering among small bulk samples of chondrites [3] and much more work along those lines is needed. Other petrographically-oriented weatherometers that should be investigated include rust haloes on metal particles (ordinary chondrites) and hydration rinds on glasses (unequilibrated chondrites and basaltic achondrites), both of which are expected to grow in thickness (at constant temperature) at log-linear rates, as previously demonstrated by studies in the fields of corrosion science and archeological obsidian dating, respectively. Indeed, little real utilization of weathering effects in meteorites as Antarctic geoscience tools can be made until quantitative weatherometers are discovered and calibrated.

Cosmochemical Interferences. Elemental fractionations clearly occur during weathering because compositions of some weathering products are very different from those of their progenitors. Although untreated aliquots that are isochemically weathered at the scale of sampling may appear undisturbed in bulk analyses (e.g., INAA), disturbances may become apparent in analyses that depend upon mineralogical, ion-exchange, or leachate separations (e.g., RNAA, radiochronometry) or gas extractions (e.g., noble gas studies) because phase locations, abundances, and site-retentivities of analyte species are subject to change by weathering. Fractionation of K from Na and of K from Ca are typical of aluminosilicate weathering products (Fig. 5), suggesting that other alkali/alkaline-earth fractionations (e.g., Rb/Sr) might also be important. In view of the unusual Eh-pH stability fields of Ce- and Eu-based species relative to other species based on rare-earth elements (REE)[13], fractionated REE patterns, and especially "Ce anomalies" [14], might reflect variable Eh-pH conditions during hydrocryogenic weathering. At least some of the Eh-pH conditions that favor REE fractionation should also favor magnetite (rather than hematite or goethite) formation during oxidation of Fe-bearing silicates. Therefore, absence of reddish rust from a sample might not guarantee that the sample was free of trace-element fractionations.

    Meteorites can acquire trace-element contamination from atmospheric aerosols as demonstrated by contents of anthropogenic [137]Cs [15]. Because

137Cs has been a significant environmental pollutant only since the advent of atmospheric tests of nuclear weapons, its distribution among Antarctic meteorites might vary greatly with the periglacial "weathering ages" of the meteorites (i.e., lengths of time spent in contact with polluted air, ice or snow). Trace-element analyses of Antarctic meteorites should be screened for possible effects of weathering or aerosol contamination before new "cosmochemical" effects are reported.

Isotopic fractionations wrought by weathering are poorly understood because so few meteorites have been deliberately studied from that point of view. However, disturbances of both oxygen istopic systems [16] and K-Ar systems [17] have been reported for some analyses of Antarctic meteorites. Because some gas-absorbent weathering products (e.g., aluminosilicates and oxides) do not thermally decompose until > 1100 K, their volatile releases might trangress into temperature intervals that are assigned to "indigenous meteoritic" components in many analyses of cosmogenic volatiles. In fact, extraneous Ar trapped in weathering products has been blamed for an anomalously old 39Ar-40Ar age (4.6-4.9 Gy) obtained for ALHA76001 (L6) [18].

Trace-element and isotopic disturbances can be minimized by careful sample selection [e.g., 19], although much more work is needed before effects of the Antarctic environment on cosmochemical analyses are fully understood.
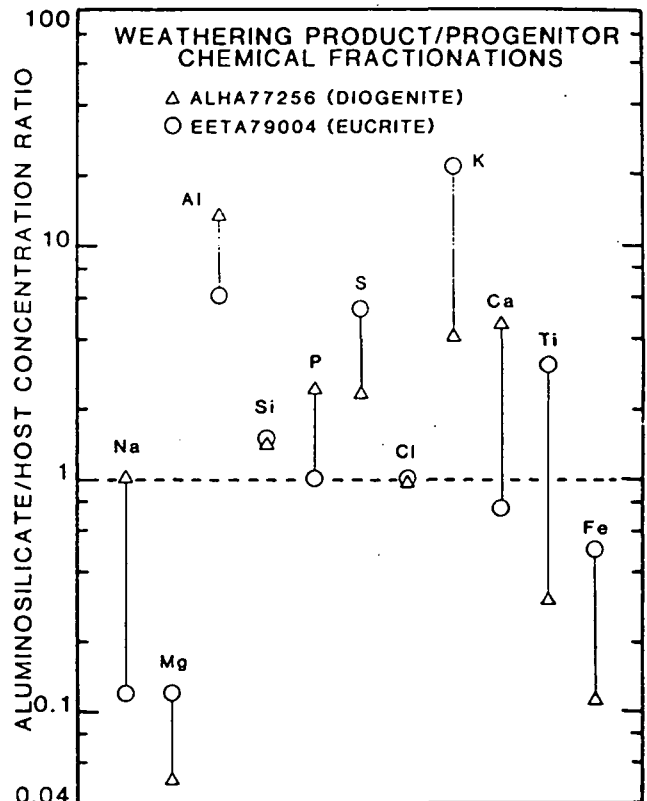

Figure 5.

Elemental fractionations in aluminosilicate weathering products relative to their hosts in Antarctic meteorites.

Martian and Cometary Analogs. Antarctic alteration of meteorites has occurred on timescales (10^4-10^6 y) that are unachievable in laboratory experiments but which approach those that are meaningful for planetary evolution. Accordingly, weathering of basaltic achondrites, especially shergottites, might be an excellent analog for weathering on Mars [20]. Furthermore, although pre-terrestrial alteration effects in carbonaceous chondrites are usually interpreted in terms of "hydrothermal" (hot water) processes on an asteroid or comet, remarkably similar features have evolved terrestrially in some Antarctic meteorites by phenomena that are clearly "hydrocryogenic" [4,7]. Therefore, terrestrially formed oxide, clay and salt minerals in Antarctic meteorites should be studied for possible petrogenetic insights into alteration processes on meteorite parent bodies. Furthermore, work toward quantifying weathering effects in Antarctic meteorites might provide insight into methods for quantifying pre-terrestrial aqueous alteration effects that occur in carbonaceous and other highly unequilibrated chondrites.

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