Rapid Growth of Magnesium-Carbonate Weathering Products in a Stony Meteorite from Antarctica

A. J. T. JULL, S. CHENG, J. L. GOODING, M. A. VELBEL

Nesquehonite, a hydrous magnesium carbonate, occurs as a weathering product on the surface of the Antarctic meteorite LEW 85320 (H5 chondrite). Antarctic meteorites have resided on the earth for periods of 10^4 to 10^6 years, but the time needed for weathering products to form has been uncertain. Isotopic measurements of $\delta^{13}C$ and $\delta^{18}O$ indicate that the nesquehonite formed at near freezing temperatures by reaction of meteoritic minerals with terrestrial water and carbon dioxide. Results from carbon-14 dating suggest that, although the meteorite has been in Antarctica for at least 3.2×10^4 to 3.3×10^4 years, the nesquehonite formed after A.D. 1950.

WEATHERING PRODUCTS HAVE been observed on many Antarctic meteorites (*1–4*), but their consequences for cosmochemical analyses have remained poorly understood, and their time of formation has not been quantitatively evaluated. Weathering products are typically in the form of "rust," or hydrated iron oxides and hydroxides; however, sulfates and carbonates have also been observed. Most workers have presumed that weathering proceeds slowly in the cold, dry Antarctic environment (*5*). Most Antarctic meteorites have been exposed to terrestrial conditions for 10^4 to 10^5 years (*6, 7*), and small increments of weathering can accumulate into measurable effects. Many specimens are, however, remarkably well preserved. Characterization of terrestrial weathering effects is crucial to studies of Antarctic meteorites (*3–5, 8, 9*) to distinguish the effects of terrestrial alteration from primary features.

The procedure for classifying the weathering of Antarctic meteorites is based on the amount of rust visible to the unaided eye; weathering categories "A," "B," "C" indicated "minor," "moderate," and "severe" amounts of rust. However, other forms of terrestrial alteration, which do not involve the formation of rust, can also occur. The most obvious and widely noted of these alterations are white powders or efflorescences on the surfaces of meteorites (*4*). Although occurring on less than 5% (fewer than 100) of the samples, the white deposits are conspicuous and can be readily analyzed. The white deposits indicate that some combination of post-fall elemental redistribution and terrestrial contamination of the meteorites has occurred. Characterizing these deposits is therefore needed to understand the nature and magnitude of weathering effects in Antarctic meteorites.

Earlier work on the white, powdery deposits was limited to a few descriptive mineralogical studies on eight meteorites (*1–3, 9*) and demonstrated that the deposits consist predominantly of various magnesium carbonates and sulfates. Yabuki *et al.* (*1*) identified the white material on Yamato 74371 as nesquehonite [ideally, $Mg(HCO_3)(OH) \cdot 2H_2O$]. In a study of seven Allan Hills meteorites, Marvin (*2*) identified several evaporite minerals, including hydromagnesite, epsomite, starkeyite, gypsum, and nesquehonite. Similar alteration products formed on different classes of meteorites, including chondrites, two carbonaceous chondrites, and one ureilite.

In this report, we describe magnesium carbonates formed on the Antarctic H5 chondrite Lewis Cliff 85320 (LEW 85320), using a variety of analytical methods. This meteorite specimen had a mass of 110 kg and is amongst the largest meteorites that have been recovered from Antarctica. In the field, an unusual abundance of white efflorescent weathering products was observed on the fusion crust of the meteorite (*10*). When the sample was unpacked at Houston, about 1.0 g of the white material was removed, but during storage of the main specimen under dry nitrogen at room temperature, additional material formed during a 9-month period. The mass of precipitate collected from the second crop was 0.4 g.

Aliquots (100 mg) were taken from both crops of salt and subdivided for mineralogical and isotopic analyses. Minerals were identified by powder x-ray diffractometry and with a scanning electron microscope (SEM) combined with an energy-dispersive x-ray spectrometer (EDS). The first salt crop (sample 40), a pure white powdery aggregate, produced an excellent x-ray diffraction (XRD) pattern with 26 peaks above background at 2° to 60° two-theta (Table 1). Eleven peaks correspond to peaks reported for synthetic nesquehonite (*11*), and all but one have also been reported for natural nesquehonite (*1*). Some of the peaks, however, might also be attributable to other hydrous magnesium carbonate accessory minerals such as hydromagnesite [$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$] or barringtonite ($MgCO_3 \cdot 2H_2O$). One anomalous peak, at a *d*-spacing of 1.03 nm, is quite weak relative to the nesquehonite peaks and probably represents a trace of the hexahydrate, "hydrophase II" [$Mg_5(CO_3)_4(OH)_2 \cdot 6H_2O$] (*11*). Under the SEM, aggregates from sample 40 revealed two distinctive morphologies: elongate, lath-like prisms, 5 to 10 μm wide by 30 to 60 μm long, and thin curved sheets. The elongate habit is characteristic of nesquehonite, whereas the wispy habit may represent hydromagnesite or "hydrophase II" (*11*). The second salt crop (sample 22), a salt-and-pepper-textured powder, produced low XRD peak intensities (two strong and six weak peaks), most likely because of poor crystallinity but, perhaps, because of contamination by fusion crust from the meteorite. We attributed all observed peaks to nesquehonite. Under the SEM, the morphology of the second crop resembled that of the first, except that the bulk of the Mg-rich material in the second crop did not have crystal faces and was fractured in places. We inferred that this anhedral material was the crystalline phase responsible for the nesquehonite XRD peaks in the second crop, because it made up most of the sample. Thin superposed depos-

Table 1. X-ray diffraction data for meteoritic and terrestrial nesquehonite. Peaks at *d*-spacings (*d*) for two-theta >48° are not reported. JCPDS data for terrestrial nesquehonite (*27*).

LEW 85320, 22		LEW 85320, 40		JCPDS 20-669	
d (nm)	*I**	*d* (nm)	*I*	*d* (nm)	*I*
		1.03	5		
0.651	85	0.651	100	0.648	100
		0.582	5		
		0.490	2	0.491	12
		0.446	2		
		0.413	4		
0.385	100	0.386	93	0.385	75
0.359	31	0.357	16	0.359	8
0.323	42	0.323	12	0.323	20
0.303	35	0.303	30	0.303	30
		0.298	6		
0.278	58	0.278	11	0.277	10
0.262	38	0.262	13	0.262	55
0.2252	46	0.251	21	0.251	6
		0.247	4		
		0.234	2	0.234	20
		0.217	9	0.217	2
		0.202	8	0.202	8
0.193	31	0.192	19	0.192	16

*Intensity (*I*) normalized to 100 for the most intense peak.

A. J. T. Jull, National Science Foundation Accelerator Facility for Radioisotope Analysis and Department of Geosciences, University of Arizona, Tucson, AZ 85721.
S. Cheng, Department of Geosciences, University of Arizona, Tucson, AZ 85721.
J. L. Gooding, National Aeronautics and Space Administration, Johnson Space Center, Planetary Science Branch, Houston, TX 77058.
M. A. Velbel, Department of Geological Sciences, Michigan State University, East Lansing, MI 48824.

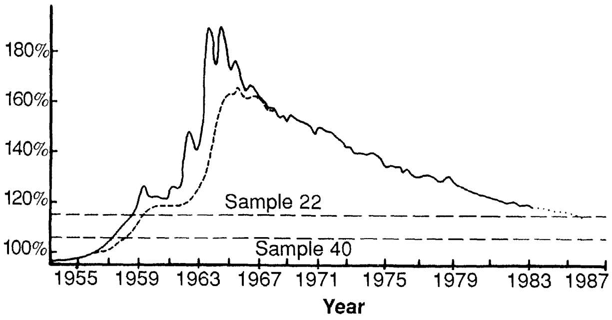

Fig. 1. Atmospheric ^{14}C levels since A.D. 1955 showing the effect of bomb ^{14}C. The 100% level is the expected atmospheric value when the fossil fuel ^{14}C depression has been removed. The levels of ^{14}C for both sample 40 (Antarctica) and 22 (Antarctica and Houston) are indicated by the horizontal dashed lines. Northern Hemisphere data are shown with a solid curve and Southern Hemisphere data with a dashed curve. The dotted curve is an extrapolation to recent times.

its of wispy material were identical to those in sample 40.

We analyzed samples of the weathering-product material to determine its ^{14}C activity with accelerator mass spectrometry (AMS). Aliquots (15 mg) were dissolved in phosphoric acid (85%) to liberate carbon dioxide, which was collected and reduced to graphite over iron at 600°C with standard procedures (*12, 13*). The graphite was pressed into a target holder, mounted in the accelerator ion source, and analyzed for ^{14}C by AMS (*14*). The activity of ^{14}C in the magnesium carbonate was similar to that for contemporary atmospheric carbon and can be expressed in terms of the percent difference from modern A.D. 1950 carbon (Table 2). Atmospheric ^{14}C activities after A.D. 1950 were elevated because of the production of ^{14}C by atmospheric nuclear weapons testing (*15, 16*) (Fig. 1). The large change in the ^{14}C levels since A.D. 1950 allows accurate dating of minerals that incorporated ^{14}C during the last 30 years. Both samples of the LEW 85320 nesquehonite have ^{14}C activities at post-bomb levels. The ^{14}C content in the original salt (sample 40) suggests that the mineral was formed or last equilibrated with atmospheric carbon in A.D. 1955 to 1959, whereas the ^{14}C content in the second crop of salt (sample 22) is consistent with incorporation of A.D. 1986 atmospheric CO_2. We analyzed a whole-rock chip from the fusion-crusted exterior of the meteorite (but free of visible salt) to determine its cosmogenic ^{14}C activity, using the methods described by Jull and Donahue (*17*) and Jull *et al.* (*18*). The gas released above 500°C contained 1.07 decays per minute (dpm) per kilogram of ^{14}C normalized to the rock weight (dpm/kg); this value is consistent with a terrestrial age of about 32,000 to 33,000 years ago, if a saturated activity of between 50 and 60 dpm/kg (*17, 18*) is assumed. Blank samples from Antarctic meteorites with long ^{81}Kr terrestrial ages (*19*) and terrestrial quartz give equivalent apparent ages of greater than 45,000 years. The level of 1.07 dpm/kg may be the result of a small residue of carbonate contamination in that the total carbon content of 112 ppm is higher than that observed for most other Antarctic samples (*18*).

Table 2. Isotopic compositions of LEW 85320 (H5) samples; PDB is the ^{13}C isotope ratio relative to Pee Dee Belemnite in parts per mil; SMOW is the ^{18}O isotope ratio relative to Standard Mean Ocean Water in parts per mil.

Sample number (all LEW)	^{14}C (activity or percent of modern values)	^{13}C (PDB)	^{18}O* (SMOW)
85320,55†	1.07 ± 0.09 dpm/kg (112 ± 10 ppm total C)		
85320,40‡	105.9 ± 1.0%	+5.40	+9.39
85320,22§	117.3 ± 1.0%	+4.28	+11.35

*If fractionation appropriate for calcite is assumed. †Whole-rock chip (0.5 g) from outer 0.5 to 1 cm; rusty but without visible salt. ‡Salt found in field; sampled upon receipt at Johnson Space Center, July 1986. §Salt that appeared on meteorite during curation, July 1986 to March 1987.

For stable isotope analysis, we heated the weathering products to 150°C in a vacuum to remove water of crystallization. We evolved CO_2 using 100% H_3PO_4 and analyzed the gas using a VG 602D mass spectrometer (Table 2). Measured $\delta^{13}C$ values of +4.3 to +5.4 per mil are consistent with the carbon having originated from atmospheric CO_2 that has formed bicarbonate under near-freezing conditions (*20*). The $\delta^{18}O$ values are too isotopically heavy for the carbonate to have been in equilibrium with ice [typically about −45 to −34 per mil (*21, 22*)] in this region of Antarctica. Instead, the values suggest that the carbonate formed from water at about 0°C and with a $\delta^{18}O$ isotope composition of about −25 per mil. This value is heavy for water from Antarctic ice and suggests that the process for forming the weathering products may be more complex than simple precipitation of carbonate from meltwater and dissolution of atmospheric CO_2. The water may have become heavier because of kinetic effects during diffusion or Raleigh distillation of water during drying. Similar conclusions have been suggested by Grady *et al.* (*23*).

Formation of evaporite efflorescences requires either remobilization of elements in the meteorite or addition of elements from the terrestrial environment (*4, 5*). Ordinary chondrites consist predominantly of olivine and pyroxene, with varying abundances of Ni-Fe metal and sulfides, but with little indigenous water and carbon. The occurrence of hydrous magnesium carbonate alteration products implies that H_2O and C have been added to the meteorite during weathering; the source of Mg is problematical. If Mg was derived from the meteorite, reactions involving ferromagnesian silicate minerals would be required. A plausible reaction involving olivine is

$$\begin{aligned}(Fe_xMg_{1-x})_2SiO_4 &+ (8 - 5x)H_2O \\ &+ 2(1 - x)CO_2 + (0.5x)O_2 \\ \rightarrow 2(1 - x)&Mg(HCO_3)(OH) \cdot 2H_2O + \\ &(2x)FeOOH + H_4SiO_4 \qquad (1)\end{aligned}$$

where x is the mole fraction of fayalite in the olivine. This reaction should be thermodynamically favored because, for olivine in equilibrated H chondrites ($x = 0.18$), the value of log K (298 K) is 32. Reaction 1 occurs as $CO_2(g)$ combines with water to form $H_2CO_3(aq)$, which dissociates to give $H^+(aq)$ and $HCO_3^-(aq)$. The $H^+(aq)$ drives olivine hydrolysis, liberating $Mg^{2+}(aq)$, which reacts with $HCO_3^-(aq)$ and $H_2O(l)$ to form nesquehonite. Oxygen oxidizes Fe^{2+}, which reacts with $H_2O(l)$ to form goethite, with release of dissolved silicon that might coprecipitate with goethite as sialic rust (*3, 5*). Similar reactions involving pyroxene are also plausible, but under freezing conditions, olivine may be more susceptible to weathering (*5*). Mobilization of oxygen in the water originating from melted ice or in thin surface films at subfreezing temperatures (*3, 5*) might give rise to heavier oxygen than would be expected from typical Antarctic ice.

Superposition of euhedral nesquehonite on the fusion crust indcates that the salt formed after the meteorite fell. Isotopic results also suggest that the original (sample 40) nesquehonite formed under Antarctic conditions. Ming and Franklin (*11*) synthesized nesquehonite at temperatures as low as 4°C. Schultz (*24*) experimentally determined that temperatures in the interior (2 cm depth) of a sample of the Allende (CV3) meteorite, exposed to Antarctic conditions, reached 5°C on wind-free days during austral summer, even though the air temperature never exceeded −11°C during the study period. Thus, insolation heating of meteorites in Antarctica is sufficient to raise the temperature of meteorite interiors to depths of several centimeters above the freezing point of pure water. At such temperatures, nesquehonite may form directly from the resultant solutions. Therefore, the observed mineralogy and morphology of the nesquehonite and current knowledge of nesquehonite stability are both consistent with direct formation of nesquehonite under Antarctic conditions. The formation of additional nesquehonite during curation of the meteorite can be understood as continued outward migration and evaporation of the saline solutions formed in Antarctica.

Antarctic meteorites have been on the earth for on the order of 10^4 to 10^6 years and have apparently been transported great distances by glaciers (*25, 26*). Whether chemical weathering of meteorites occurred during their encasement in ice or only after they were exposed to the atmosphere on stranding surfaces has been uncertain (*5*). Results for nesquehonite from LEW 85320 suggest that, at least for salt formation, weathering may be sufficiently rapid that most observable effects can develop in tens of years rather than over thousands of years. Rapid formation of nesquehonite suggests, but does not prove, that most weathering phenomena occur after exhumation of the meteorites from deep-glacial ice. In the simplest interpretation, ages of magnesium carbonate weathering products on Antarctic meteorites would indicate the times elapsed since surface exposure of the meteorites. The amount of rust on a surface alone cannot be used as a reliable indicator of the state of preservation of meteorites. The correlation between degrees of weathering and terrestrial-residence ages might evade detection if reliance is placed solely on the rust index.

REFERENCES AND NOTES

1. H. Yabuki, A. Okada, M. Shima, *Sci. Pap. Inst. Phys. Chem. Res. Jpn.* **70**, 22 (1976).
2. U. B. Marvin, *Antarct. J. U.S.* **15**, 54 (1980).
3. J. L. Gooding, *Proc. Lunar Planet. Sci. Conf.* **12**, 1105 (1981); *Geochim. Cosmochim. Acta* **50**, 2215 (1986).
4. M. A. Velbel, *Meteoritics*, in press.
5. J. L. Gooding, in *International Workshop on Antarctic Meteorites, Lunar and Planetary Institute Technical Report, 86-01*, J. O. Annexstad, L. Schultz, H. Wanke, Eds. (Lunar and Planetary Institute, Houston, 1986), p. 48.
6. K. Nishiizumi, *ibid.*, p. 71.
7. L. Schultz, *ibid.*, p. 80.
8. J. L. Gooding, S. A. Wentworth, M. E. Zolensky, *Geochim. Cosmochim. Acta* **52**, 909 (1988).
9. U. B. Marvin and K. Motylewski, *Lunar Planet. Sci. XI*, 669 (abstr.) (1980).
10. J. L. Gooding, *Antarct. Meteor. Newslett.* **9**, 22 (1986); P. Englert, personal communication.
11. D. W. Ming and W. T. Franklin, *Soil Sci. Soc. Am. J.* **49**, 1303 (1985).
12. P. J. Slota, A. J. T. Jull, L. J. Toolin, *Radiocarbon* **29**, 303 (1987).
13. A. J. T. Jull, D. J. Donahue, T. W. Linick, L. J. Toolin, *ibid.* **28**, 191 (1986).
14. T. W. Linick, A. J. T. Jull, L. J. Toolin, D. J. Donahue, *ibid.*, p. 522.
15. T. W. Linick, thesis, University of California, San Diego (1976).
16. I. Levin *et al.*, *Radiocarbon* **27**, 1 (1985).
17. A. J. T. Jull and D. J. Donahue, *Geochim. Cosmochim. Acta* **52**, 1309 (1988).
18. ———, T. W. Linick, in preparation.
19. M. Freundel, L. Schultz, R. C. Reedy, *Geochim. Cosmochim. Acta* **50**, 2663 (1986).
20. W. G. Mook, J. C. Bommerson, W. H. Styerman, *Earth Planet. Sci. Lett.* **22**, 169 (1974).
21. G. Faure and D. Buchanan, *Antarct. J. U.S.*, in press.
22. S. Epstein, R. P. Sharp, A. J. Gow, *Science* **168**, 1570 (1970).
23. M. M. Grady, E. K. Gibson, I. P. Wright, C. T. Pillinger, *Lunar Planet. Sci. XIX*, 409 (abstr.) (1988).
24. L. Schultz, *Meteoritics* **21**, 505 (1986).
25. W. A. Cassidy, E. Olsen, K. Yanai, *Science* **198**, 727 (1977).
26. E. L. Fireman and T. Norris, *Proc. Lunar Planet. Sci. Conf.* **12**, 1019 (1981).
27. Joint committee on powder diffraction standards (JCPDS), *Mineral Powder Diffraction File* (International Center for Diffraction Data, Swarthmore, PA, 1980).

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Herbicide Resistance in Transgenic Plants Expressing a Bacterial Detoxification Gene

DAVID M. STALKER,* KEVIN E. MCBRIDE, LORRAINE D. MALYJ

The herbicide bromoxynil (3,5-dibromo-4-hydroxybenzonitrile) is a photosynthetic (photosystem II) inhibitor in plants. A gene, *bxn*, encoding a specific nitrilase that converts bromoxynil to its primary metabolite 3,5-dibromo-4-hydroxybenzoic acid, was cloned from the natural soil bacterium *Klebsiella ozaenae*. For expression in plants, the *bxn* gene was placed under control of a light-regulated tissue-specific promoter, the ribulose bisphosphate carboxylase small subunit. Transfer of this chimeric gene and expression of a bromoxynil-specific nitrilase in leaves of transgenic tobacco plants conferred resistance to high levels of a commercial formulation of bromoxynil. The results presented indicate a successful approach to obtain herbicide resistance by introducing a novel catabolic detoxification gene in plants.

ADVANCES IN GENETIC ENGINEERING of plants have allowed the development and transfer of agronomically important traits such as viral resistance, insect resistance, and herbicide resistance. These traits allow transfer of single dominant genes that exhibit a rapidly discernible phenotype. Herbicide resistance can be achieved by at least three different mechanisms: overproduction of a herbicide-sensitive biochemical target; structural alteration of a biochemical target, resulting in reduced herbicide affinity; or detoxification-degradation of the herbicide before it reaches the biochemical target inside the plant cell. Resistance obtained by the first two mechanisms has been developed for the herbicides glyphosate (*1, 2*), atrazine (*3*), the sulfonylureas (*4*), and phosphinothricin (*5*). A report describing the transfer to plants of a *Streptomyces* gene encoding a phosphinothricin acetyltransferase (*6*) resulted in phosphinothricin-resistant plants, establishing detoxification by conjugation as a viable strategy. Two advantages of a detoxification-degradation mechanism, as opposed to altering a biochemical target, are that specialized compartmentation of the detoxifying activity is not required and that greater herbicide resistance can be achieved with lower levels of detoxifying enzyme. Disadvantages include the potential toxicity of one or more metabolites and the possibility that detoxifying activities might react with endogenous plant compounds to impair plant function.

We have been interested in the nitrile-containing broadleaf herbicide bromoxynil (3,5-dibromo-4-hydroxybenzonitrile), a potent photosystem II (PSII) inhibitor. Although the actual chloroplast-localized biochemical target is not well defined, there is evidence that bromoxynil acts by binding a component of the quinone-binding protein complex of PSII, inhibiting electron transfer (*7, 8*). It has further been suggested that a low-affinity binding site within this complex exists in the 32-kD polypeptide (*9, 10*). Bromoxynil has a very short half-life in the environment, as microbial populations and tolerant plant species can convert the cyano moiety of bromoxynil to the corresponding amide and acid derivatives (*11–13*). A natural soil isolate, *Klebsiella ozaenae*, has been identified that transforms bromoxynil to 3,5-dibromo-4-hydroxybenzoic acid, releasing ammonia (*14*). This reaction (Fig. 1) is carried out via a bromoxynil-specific nitrilase. The nitrilase gene (*bxn*), which is plas-

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Calgene, 1920 Fifth Street, Davis, CA 95616.

*To whom correspondence should be addressed.