Artificial weathering of the ordinary chondrite Allegan: Implications for the presence of Cl⁻ as a structural component in akaganéite

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ABSTRACT

A sample of an ordinary chondrite fall, Allegan, was shown by ^{57}Fe Mössbauer spectroscopy to be unweathered. Using aerated deionized water at 25° and 0 °C, and in one case with dissolved salts added, an attempt was made to simulate meteorite weathering processes in the hot and cold desert environments where these samples accumulate. The progress of artificial oxidation was monitored by ^{57}Fe Mössbauer spectroscopy, and the final products were analyzed by neutron activation. The results confirm weathering mechanisms proposed for naturally weathered meteorites and suggest that temperature is the major factor controlling the stability of the observed oxide mineral assemblage. Akaganéite was observed as a major oxidation product in the experimentally weathered sample. This finding is interesting because it is widely accepted that β-FeOOH requires Cl⁻ for stability: The sample weathered in deionized water showed only trace amounts of Cl⁻ in both the fresh and weathered meteorite. We suggest that both Cl⁻ and OH⁻ may be effective in filling tunnel sites and that a complete solid solution is possible between these end-members. In addition, a calculated formation age of 4.59 ± 0.05 Ga and a cosmic-ray exposure age of 5.7–6.2 Ma, was derived from neutron activation analyses of the weathered sample. These ages are consistent with independent measurements made on samples of fresh Allegan, although small sample weights mean that the results should be treated with caution. However, the similar ages obtained in the weathered sample indicates that a wider spectrum of cosmochemical analyses is possible with weathered meteorites than previously thought and that congruent dissolution occurs during meteorite weathering.

INTRODUCTION

To improve our understanding of weathering processes in meteorites, we carried out artificial weathering experiments in a controlled environment using samples of the Allegan H5 ordinary chondrite (Allegan County, Michigan). Such studies potentially provide a basis for understanding the mechanisms of weathering of chondrites in the field (Bland et al. 1995, 1996a). Apart from stones observed to fall, such as Allegan, and occasional finds, most meteorites in recent years have been found in two broad geophysical environments: hot desert regions such as the Sahara and Nullarbor Plain in Australia and the cold desert of Antarctica. Numerous rare and scientifically valuable specimens were recovered from these areas. However, the great majority of samples have experienced extensive weathering during their terrestrial residency (in general this is much less in Antarctic meteorites). An improved understanding of weathering mechanisms would help determine the effect of weathering on various aspects of meteorite cosmochemistry and also differentiate genuine preterrestrial alteration from oxidation that occurred on Earth.

To this end, three experiments were conducted. One experiment to simulate weathering in the Antarctic environment, and two shorter experiments to study weathering at the higher temperatures typical of a hot desert environment.

In addition, previous experiments designed to simulate meteorite weathering do not appear to have adequately reproduced oxidation in the field and indicate that Fe-Ni is relatively resistant to weathering (Fisher and Burns 1992a). This anomalous result suggested that a more intensive study might be appropriate.

The importance of Cl in the weathering of meteorites could also be tested in our experiments. Buchwald and Clarke (1989) suggested that in Antarctic meteorites akaganéite precipitates near the reaction front around metal grains, incorporating Cl⁻ ions into ion-exchange sites, where they are retained and made available for further corrosive action or are flushed from the system. Cl is thought to be extracted from pore water by the electro-

chemical nature of the corrosion of Fe-Ni; it also may be essential for the formation of akaganéite (Post and Buchwald 1991). To test whether Cl is required in meteorite weathering, aerated deionized water was chosen to weather the meteorite sample in the experiment conducted at low temperature and also in one of the higher-temperature experiments. The other experiment, designed to simulate hot desert weathering, used water in which NaCl had been dissolved (approximately 0.2 molar solution) as a means of providing Cl⁻ ions. In this way various factors contributing to the mechanism of meteorite weathering (temperature, drainage, dissolved ions) could be evaluated and their importance assessed.

Sample preparation and experimental procedure

Weathering experiments

Samples of meteorite were ground under acetone in an agate mortar and pestle. Samples (4.0 g each) were then immersed in 20 mL aerated water: ice-water in the case of the experiment designed to simulate Antarctic weathering (the sample was held in a laboratory refrigerator) and water at room temperature for the hot desert weathering experiments. The hot-desert sample immersed in deionized water was dried under heat lamps every 24 h to mimic periodic wetting and drying in the hot desert environment. Aliquots of other samples were also periodically removed and dried. The sample immersed in salt water (0.2 molar solution) was rinsed several times in deionized water before drying completely to prevent a build-up of NaCl by evaporation. Samples from all three experiments were removed periodically and analyzed using ^{57}Fe Mössbauer spectroscopy.

The use of a finely ground starting material in our experiment inevitably leads to a loss of important structural relationships (e.g., metal and sulphide) within the sample and a destruction of porosity, both of which have a bearing on the types of alteration processes observed. Variations in grain size in this type of study and the associated variation in the available mineral surface area also have a significant effect on reactivity and dissolution rates (Hochella and Banfield 1995), as does the water-rock ratio. In addition, while hot desert meteorites experience wetting and drying through occasional storms, this clearly does not occur on a regular 24 h cycle. These factors need to be considered when interpreting our experimental results. One point in favor of this experimental approach is the large body of data on the natural weathering of ordinary chondrites (as measured by ^{57}Fe Mössbauer spectroscopy) that already exists from analyses of terrestrial age dated ordinary chondrite finds from Antarctica and hot desert regions (e.g., Bland et al. 1995, 1996a; Shinonaga et al. 1994; Burns et al. 1995), enabling a direct comparison between experimental weathering and weathering in the field.

X-ray powder diffraction

Ground samples were mounted on a standard mirror sample holder and examined using a Siemens D5000 diffractometer over $2\theta = 5–30°$. Phases were determined by comparing the samples with data from the CD-ROM database of the Joint Committee for Powder Diffraction Standards file. Although XRD is suitable for determining the crystalline phases in a sample (in general, where those phases are >5 wt%), iron oxides and oxyhydroxides are frequently too poorly crystalline to be easily resolvable. Given the small sample sizes in our study, concentrating weathering products in the form of a mineral separate was not practical. Therefore, in this study, we use XRD to support an oxide mineralogical determination by ^{57}Fe Mössbauer spectroscopy.

Mössbauer spectroscopy

Samples (0.3 g) were sandwiched between adhesive tape (about 1.25 cm^2) in a lead holder. The ^{57}Fe Mössbauer spectra were recorded at 298 K and 77 K with a microprocessor-controlled Mössbauer spectrometer using a ^{57}Co-Rh source. The drive velocity was calibrated with the same source and a metallic iron foil. Average recording time was 3 d per sample. The Mössbauer spectra were fitted with a constrained non-linear least squares fitting program of Lorentzian functions.

Mössbauer spectra of bulk meteorites are reasonably complex, as the number of Fe-containing components, particularly in weathered samples, is large. As such there is a compromise between including enough components in a fit to approximate reasonably the composition of the sample, while being aware that in adding new components the Mössbauer parameters of an individual absorption are increasingly poorly determined (Dollase 1975). In our analysis, while absorptions in individual spectra are discussed, it is felt that only by comparing spectra recorded at different velocity ranges and temperatures, and in some cases mineral separates of the same sample, is it possible to build a picture of the oxide minerals in the weathered meteorite.

Iron oxide and oxyhydroxide weathering products fall into two broad groups that may be easily distinguished in Mössbauer spectra: paramagnetic (two line, doublet absorptions) and magnetically ordered (six line, sextet absorptions). Common ferric phases that show a doublet (and similar Mössbauer parameters, in the region $\delta = 0.3–0.4$ mms⁻¹, $\Delta = 0.5–0.8$ mms⁻¹) at 298 K include lepidocrocite, small-particle goethite, akaganéite, and ferrihydrite. Magnetically ordered ferric phases at 298 K include maghemite (H = 491 kG), magnetite (two sextets at H = 491 and 458 kG), and large-particle goethite (H = 383 kG) (Childs and Baker-Sherman 1983). In cooling a sample to 77 K, some iron oxyhydroxides for which a spectral doublet is observed at 298 K are cooled below their ordering (Néel) temperature and show a magnetic hyperfine spectrum. This phenomenon (superparamagnetism) is related to particle size, such that the smaller the particles the lower the temperature at which a doublet is still observed (Kundig et al. 1966; Cohen 1976). The iron oxyhydroxides goethite (α-FeOOH) and akaganéite (β-FeOOH) both exhibit this behavior; however, the sextet

patterns observed are quite different. While goethite shows a single sextet at 495 kG, akaganéite is more complex, generally fitted to three much smaller hyperfine fields at 462, 460, and 426 kG (Childs and Baker-Sherman 1983). At 77 K, magnetite shows sextets at H = 503 and 480 kG (Banerjee et al. 1967) and maghemite at 516 kG (Childs and Baker-Sherman 1983). Lepidocrocite and ferrihydrite remain paramagnetic at 77 K. Thus, while a degree of interpretation (and caution) is required in analyzing Mössbauer spectra to derive mineralogical information in a bulk sample, by comparing spectra recorded at different temperatures, the differences in magnetic-ordering behavior and Mössbauer parameters (for some oxides and oxyhydroxides) allow us to be reasonably definitive in a mineralogical determination. This methodology was used successfully by Burns and Fisher (1994) to identify and quantify magnetite, ferrihydrite, cronstedtite, and tochilinite in CM- and CI-group meteorites.

In a study to determine reproducibility of peak areas in Mössbauer spectra of the same meteorite aliquot, we found that combined peak areas for ferric iron phases varied by 1.4% relative to the total peak area. Relative errors for calculated areas of primary phases of 12.8, 9.3, 5.6, and 8.2% were also obtained for Fe-Ni, troilite, olivine, and pyroxene, respectively (Table 1).

Cl concentration, Ar-Ar geochronology, and cosmic ray exposure age

A subsample (1.34 mg) of the weathered meteorite was wrapped in aluminum foil without further cleaning or preparation and was irradiated in the Ford Reactor at the University of Michigan. The international hornblende mineral standard, Hb3gr was used because its well-characterized Cl contents allow direct measurement of both the cosmic ray exposure age (Hennessy and Turner 1980) and the Cl concentration of the sample (Kelley et al. 1986). Upon return, the sample was loaded into a 2 mm diameter, 2 mm deep hole in an aluminum platen that was in turn loaded into a UHV laser chamber with a kovar window and baked to 120 °C overnight to remove adsorbed atmospheric argon from the sample and chamber walls. There were 14 samples for Ar isotope measurement extracted by using short 10–25 ms pulses from a focused CW Nd-YAG laser (Kelley 1995) finally resulting in total fusion of the 1.34 mg sample. Active gases were removed using Zr-Al getters and the remaining noble gases equilibrated into an MAP 215-50 static mass spectrometer with a Johnston multiplier detector. Ar isotope peak intensities were measured ten times in a sequence lasting approximately 15 min. Peak intensities were extrapolated back to the inlet time and corrected for blanks, mass spectrometer discrimination, and reactor induced interferences. Mean blank measurements during the experiment for ^{40}Ar, ^{39}Ar, ^{38}Ar, ^{37}Ar, and ^{36}Ar were 6.9, 0.03, and 0.25 $\times 10^{-12}$ cm^3 STP, respectively. The J value for this sample was 0.00415 ± 0.000021 and conversion factors used in converting Ar isotope data to Cl and Ca contents were α = 0.5424 and β = 2.45 (Kelley et al. 1986).

RESULTS

^{57}Fe Mössbauer spectroscopy

Mössbauer spectroscopy allows the relative abundance of ferric and ferrous phases in a sample to be determined, and in some cases, the nature of Fe-bearing phases to be identified. As ordinary chondrites are composed largely of Fe-bearing olivine, pyroxene, troilite, and Fe-Ni metal, Mössbauer spectroscopy has been shown to be effective in monitoring weathering in these meteorites over time and in establishing some of the mechanisms involved in meteorite weathering (Bland et al. 1996a, 1996b). Spectra recorded from unweathered ordinary chondrites typically show well-defined magnetic hyperfine structures associated with troilite (H = 306 kG) and Fe-Ni metal (H = 331 kG) as well as quadrupole split absorptions (Δ = 3.00 mms^{-1} and 2.21 mms^{-1}), characteristic of Fe^{2+} in the ferromagnesian silicates olivine and pyroxene, respectively (Ortalli and Pedrazzi 1990; Fisher and Burns 1992a).

Experiment A. This experiment was carried out over an extended period, the sample being immersed in aerated, deionized ice water for a total of 170 d. Water was changed every time an aliquot of the sample was removed for examination by ^{57}Fe Mössbauer spectroscopy (five times over the course of the experiment).

The initial Mössbauer spectrum recorded from Allegan (Fig. 1) was very similar to those recorded from the H4-H6 ordinary chondrite meteorite Noblesville (Fisher and Burns 1992a) and also from the meteorite Torino, an H6 chondrite that fell in Italy in 1988 (Ortalli and Pedrazzi 1990). Sextets associated with Fe-Ni metal (H = 338 kG) and troilite (H = 316 kG) were observed, as well as quadrupole split absorptions associated with olivine and pyroxene, respectively. The result validates the assumption that Allegan is an unweathered meteorite.

The spectrum recorded from the sample of Allegan after immersion in aerated ice water for 5 d was similar. However a new component, a doublet characteristic of paramagnetic Fe^{3+} was also identified. Because the Mössbauer parameters of iron oxyhydroxides, and hydrated ferric species are similar, the doublet (about δ = 0.36 mms^{-1}, about Δ = 0.68 mms^{-1}), may be associated with some combination of small-particle goethite, akaganéite, ferrihydrite, or lepidocrocite.

Subsequent spectra, recorded after 20, 93, and 131 d treatment showed a similar pattern, with an increasingly intense quadrupole split absorption associated with paramagnetic Fe^{3+} becoming more enhanced at the expense of primary meteoritic components.
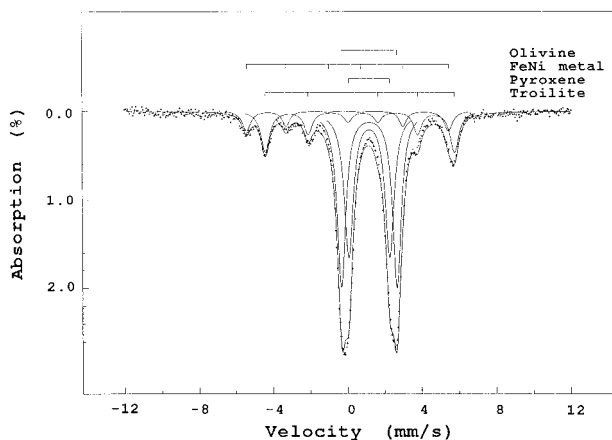
The artificial weathering of this meteorite was continued for a further 39 d to give a total of 170 d oxidation in aerated ice-water. The ^{57}Fe Mössbauer spectrum recorded at 298 K (Fig. 2) showed only a minor absorption associated with Fe-Ni alloy, and the absorptions associated with primary Fe^{2+}-containing phases were diminished. As well as an enhanced Fe^{3+} doublet, the spectrum also showed a contribution from magnetically ordered ferric phases [here fitted to three sextets (magnetic 1, 2,

TABLE 1. Reproducibility in Mössbauer spectra of meteorite samples

|		Areas (%)									
	Sample and type	1	2	3	4	5	6	7	8	9	10
	Allegan (H5) 1	9.6	18.8	37.7	34.8						
	Allegan (H5) 2	6.5	20.9	39.4	33.2						
	Allegan (H5) 3	4.9	21.3	39.6	34.2						
Mean		7.00	20.33	38.9	34.07						
Standard deviation		2.39	1.34	1.04	0.81						
Percentage error		34.14	6.60	2.68	2.37						
	Daraj 119 (L4) 1	3.1	11.1	19.6	22.0	25.2	6.8	1.0	6.0	5.3	44.3
	Daraj 119 (L4) 2	3.0	11.8	24.0	16.3	27.3	6.5	0.7	5.6	4.8	44.9
	Daraj 119 (L4) 3	2.9	13.8	23.2	16.3	26.5	6.4	0.8	5.5	4.6	43.8
Mean		3.00	12.23	22.27	18.20	26.33	6.57	0.83	5.7	4.9	44.3
Standard deviation		0.10	1.40	2.34	3.29	1.06	0.21	0.15	0.27	0.36	0.55
Percentage error		3.33	11.45	10.53	18.08	4.03	3.17	18.33	4.64	7.36	1.24
	Acfer 216 (L6) 1	4.6	9.8	40.8	25.2	15.8	1.0	1.3	0.4	1.2	19.7
	Acfer 216 (L6) 2	5.1	11.1	39.3	25.0	15.6	1.2	1.3	0.6	0.8	19.5
	Acfer 216 (L6) 3	5.0	11.0	39.8	24.7	15.7	1.2	1.4	0.7	0.8	19.8
Mean		4.9	10.63	39.97	24.97	15.7	1.13	1.33	0.57	0.93	19.7
Standard deviation		0.27	0.72	0.76	0.25	0.10	0.12	0.06	0.15	0.23	0.15
Percentage error		5.41	6.80	1.91	1.01	0.64	10.19	4.33	26.96	24.74	0.78
	Nyanga Lake 001 (H3) 1	3.2	10.6	21.7	8.3	13.9	25.5	5.5	7.1	4.3	56.3
	Nyanga Lake 001 (H3) 2	3.0	8.9	25.9	8.8	13.8	24.5	4.4	6.7	4.2	53.6
	Nyanga Lake 001 (H3) 3	3.1	9.3	23.8	8.7	13.9	25.3	4.9	7.0	4.1	55.2
	Nyanga Lake 001 (H3) 4	3.6	7.9	23.3	10.6	13.9	24.9	5.2	5.4	5.2	54.6
Mean		3.23	9.18	23.68	9.10	13.88	25.05	5.00	6.55	4.45	54.9
Standard deviation		0.26	1.12	1.73	1.02	0.05	0.44	0.47	0.77	0.51	1.13
Percentage error		8.16	12.18	7.32	11.24	0.36	1.77	9.38	11.99	11.38	2.06

Note: primary phases: 1 = Fe-Ni metal; 2 = troilite; 3 = olivine; 4 = pyroxene and secondary phases produced as a result of terrestrial oxidation; 5 = paramagnetic Fe^{3+}; 6 = maghemite; 7 = goethite; 8 = magnetite 1; 9 = magnetite 2; and 10 = all ferric phases combined.

and 3) that may be associated with maghemite and magnetite]. Magnetic (Fig. 3) and non-magnetic (Fig. 4) mineral separates of this sample were obtained, which indicated that the majority of oxide phases were associated with the magnetic (Fe-Ni metal) fraction. Spectra from the bulk sample were also recorded at 77 K (Fig. 5) and 10 K. Both were more complex, indicating that a paramagnetic Fe^{3+} species had become magnetically ordered (splitting into one or more sextet patterns) at low temperature.

The spectrum recorded at 77 K showed a well-defined magnetically ordered component (H = 327 kG) associated with troilite. Two doublets (Δ = 3.28 mms⁻¹ and 2.22 mms⁻¹) were characteristic of olivine and pyroxene. A third quadrupole split absorption was associated with paramagnetic Fe^{3+} and may indicate an oxide phase such as ferrihydrite or possibly lepidocrocite, both of which remain paramagnetic at 77 K. A significant difference between this spectra and the room temperature one was the enhanced contribution from magnetically ordered ferric
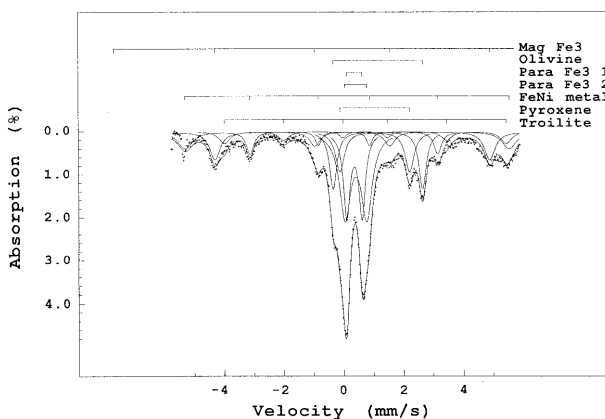

FIGURE 1. ⁵⁷Fe Mössbauer spectrum recorded at 298 K from an unoxidized sample of the Allegan, H5 ordinary chondrite fall. Suggested minerals associated with the main absorptions are also shown.
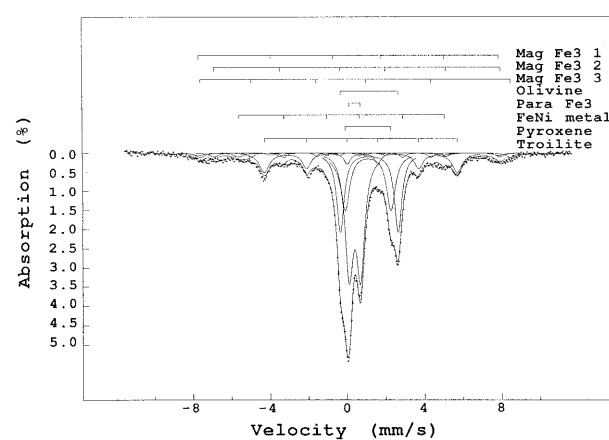
FIGURE 2. ⁵⁷Fe Mössbauer spectrum recorded at 298 K from a sample of Allegan after 170 d oxidation in aerated deionized ice water. A weak absorption associated with magnetically ordered Fe^{3+} phases is fitted to three sextets in this case.
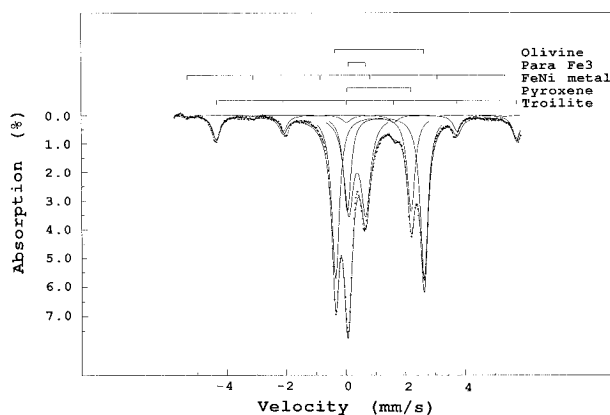
FIGURE 3. [57]Fe Mössbauer spectrum recorded at 298 K from a magnetic separate of a sample of Allegan after 170 d oxidation in aerated deionized ice water. The paramagnetic Fe^{3+} absorption is fitted to two doublets in this case.

FIGURE 4. [57]Fe Mössbauer spectrum recorded at 298 K from a nonmagnetic separate of a sample of Allegan after 170 d oxidation in aerated deionized ice water.

phases. The associated disappearance of around ⅓ of the doublet associated with paramagnetic Fe^{3+} at room temperature suggesting that a paramagnetic ferric phase had become magnetically ordered at the lower temperature. This broad absorption may be crudely fitted by a single sextet (H = 478 kG), however, it is apparent from the differences in width of the outermost peaks that a more realistic fit would include several overlapping components. In a second fit, the outer portion of this broad sextet pattern is fitted to two sextets (H = 524 and 495 kG), which may be associated with maghemite and goethite; however, the inner portion suggests the presence of an absorption with a smaller hyperfine field. Among the common ferric oxides and oxyhydroxides, only akaganéite becomes magnetically ordered at 77 K and shows a hyperfine field of <480 kG. In our spectra the interior portion of the broad magnetically ordered absorption is fitted to sextets at H = 471, 470, and 430 kG, similar to Mössbauer parameters for akaganéite at this temperature. The spectra recorded at 10 K supports this conclusion: A sextet absorption was observed in the 470–480 kG range, a hyperfine field that has been associated with akaganéite at liquid helium temperatures (Rézel and Génin 1990).

Experiment B. The room-temperature experiment was carried out over a shorter timescale, the sample being immersed in aerated water for a total of 25 d. Every 24 h the sample was dried using heat lamps (producing a temperature in the evaporating water of 56–67 °C) to simulate periodic wetting and drying in the hot desert environment.

A spectrum was recorded after a period of immersion in aerated water of 2.5 d that showed a similar suite of components as in previous spectra, including a minor doublet associated with paramagnetic Fe^{3+}.

Subsequent spectra, recorded after 13, 17.5, and 25 d showed the growth of an Fe^{3+} doublet, together with an absorption associated with magnetically ordered iron oxides and oxyhydroxides. It is interesting to compare the

weathering observed in this sample to that produced by the aerated ice water experiment at a similar stage. The proportion of paramagnetic Fe^{3+} is lower in the room-temperature experiment, although overall the contribution from ferric phases is greater than in the ice water experiment. In experiment B magnetically ordered iron oxides and oxyhydroxides contribute a greater proportion of the spectra than in experiment A. These phases did not reach a similar intensity in the ice water experiment until after 131 d of oxidation, in comparison with 13 d in experiment B.

Experiment C. This experiment was again carried out over 25 d, although in this case the sample was only dried before a Mössbauer spectrum was recorded (after 2.5, 13, 17.5, and 25 d). Before oxidation, a small quantity of NaCl was dissolved in solution (approximately 0.2 mo-
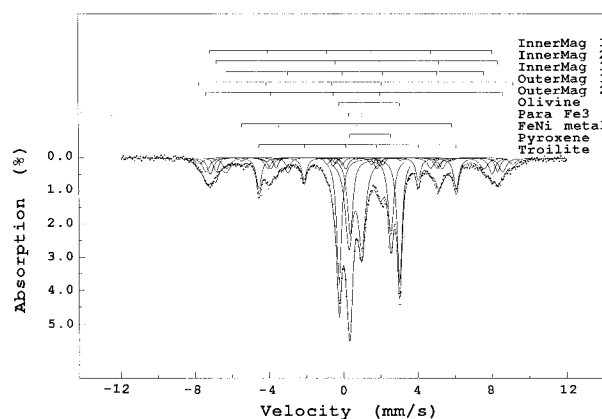
FIGURE 5. [57]Fe Mössbauer spectrum recorded at 77 K from a sample of Allegan after 170 d oxidation in aerated deionized ice water. Suggested associations for the main absorptions are also shown. While the broad magnetically ordered Fe^{3+} absorption may be fitted to a single sextet at 478 kG, differences in the widths of peaks suggest that it in fact arises from several overlapping absorptions.

TABLE 2. Ar-Ar data for individual laser analyses and calculated Ar-Ar ages

Sample	^{40}Ar	SD	^{39}Ar	SD	^{38}Ar	SD	^{37}Ar	SD	^{36}Ar	SD	$^{40}Ar/^{39}Ar$	SD	Age (Ma)	SD
1	3319.0	21.2	1.14	0.02	0.13	0.01	3.6	0.9	0.05	0.02	2901	57	4633	34
2	4110.3	28.6	1.41	0.02	0.21	0.02	14.2	1.0	0.15	0.03	2925	49	4646	29
3	895.1	3.0	0.32	0.01	0.03	0.01	0.7	0.9	0.06	0.03	2780	81	4562	49
4	1205.6	3.8	0.44	0.02	0.04	0.01	1.5	0.8	0.07	0.02	2722	106	4527	65
5	3562.2	19.5	1.26	0.02	0.22	0.02	18.5	1.0	0.17	0.03	2829	42	4591	26
6	603.5	2.6	0.21	0.01	0.07	0.01	5.1	1.0	0.05	0.02	2812	122	4581	73
7	3428.5	25.5	1.20	0.03	0.15	0.02	5.2	1.0	0.37	0.03	2848	64	4602	38
8	1051.2	3.8	0.38	0.01	0.05	0.01	4.6	0.9	0.06	0.02	2767	97	4554	59
9	237.5	1.0	0.08	0.01	0.00	0.01	1.4	0.8	0.04	0.02	3025	358	4703	198
10	2591.2	13.1	0.90	0.03	0.09	0.01	5.5	0.9	0.08	0.02	2893	110	4628	64
11	2856.2	14.8	0.97	0.03	0.21	0.02	12.5	0.9	0.26	0.03	2936	91	4653	52
12	1920.5	8.0	0.73	0.02	0.09	0.02	6.1	0.9	0.19	0.03	2614	77	4460	49
13	1534.2	3.1	0.56	0.02	0.10	0.01	8.1	0.9	0.13	0.02	2763	86	4552	52
14	2251.5	9.4	0.81	0.03	0.15	0.01	12.2	0.9	0.20	0.02	2771	88	4557	53

lar). The purpose of this was to provide Cl^- ions for incorporation into the akaganéite structure, because it has been postulated that this Cl^- ion incorporation is an important process in meteorite weathering (Buchwald and Clarke 1989).

The first ^{57}Fe Mössbauer spectrum was recorded after a period of immersion in aerated, room-temperature salt water of 2.5 d, which showed primary components (Fe-Ni alloy, troilite, olivine, and pyroxene) and a minor quadrupole split absorption ($\delta = 0.38$ mms^{-1}, $\Delta = 0.25$ mms^{-1}) associated with paramagnetic Fe^{3+}.

The spectrum recorded from Allegan after 13 d treatment was similar, however, in subsequent spectra (after 17.5 and 25 d) a minor absorption associated with magnetically ordered iron oxides and oxyhydroxides (maghemite, magnetite, and goethite) were also observed.

In summary, similar differences were observed in the Mössbauer spectra recorded from samples artificially weathered in experiment C and experiment A as observed between experiment B and experiment A. However, it is apparent that there are significant differences between the results obtained between the two room-temperature experiments, the most important of these being that the use of deionized water produced more magnetically ordered iron oxides and oxyhydroxides, while the use of salt water meant that paramagnetic Fe^{3+} species were dominant. These differences may be discussed in relation to the action of Cl^- ions, which appear to stabilize akaganéite.

X-ray powder diffraction

A sample of Allegan, weathered for 170 d under the conditions of experiment A, was analyzed by XRD. Patterns associated with olivine and pyroxene were observed. Although oxide phases were not well resolved (possibly due to poor crystallinity), peaks at $2\theta = 11.90°$, 16.99°, and 26.91° were recognized and attributed to akaganéite. The peak at $2\theta = 26.91°$ corresponds to 100% intensity, $2\theta = 26.73°$, in JCPDS-ICDD pattern 34-1266. Further resolution was not possible as the small amount of sample available did not allow mineral separation. However, taken together with the Mössbauer analyses these data suggest the presence of akaganéite.

Ar-Ar and cosmic ray exposure age

Although the purpose of this experiment was initially to measure the Cl content using neutron activation, a byproduct of the process is an Ar-Ar age for each individual laser analysis (Table 2). Precision of the individual ages is compromised because the sample was underirradiated for such an experiment leading to $^{40}Ar/^{39}Ar$ ratios close to 3000. Sample weights were also small (~1.3 mg), which may lead to a deviation from the typical mean Ca composition, and thus a non-representative sample of cosmogenic Ar (L. Schultz, personal communication). In fact, the individual Ar-Ar ages do not vary significantly from a mean of 4.59 ± 0.05 Ga (1σ error).

The isochron plot yields little information on the initial $^{40}Ar/^{36}Ar$ ratio because the quantities of ^{36}Ar are very small. The ^{36}Ar content of the present sample of Allegan is only 14% of that recorded by Ganapathy and Anders (1973). The discrepancy may be caused by underestimation of blanks during the Ganapathy and Anders experiment (blanks were two orders of magnitude higher than in the present experiment), removal of a significant solar wind component by the weathering, or only partial degassing of our sample during laser extraction.

In summary, it appears that experimental weathering has not caused significant loss of radiogenic Ar from the main K-bearing phase, plagioclase.

The exposure age can be calculated using a spallation production rate of ^{38}Ar mainly from Ca but with contributions from Fe, Ni, Ti, Cr, Mn, and K. A CRE of 5.9 Ma results from the combination of recently calculated production rates and the Ar isotope data from an unirradiated fresh sample of Allegan (Ganapathy and Anders 1973; L. Schultz, personal communication). In the present experiment, the calculation of a CRE is complicated by chemical variations between the individual laser spot analyses. However, to a reasonable approximation, the bulk composition of the meteorite (Jarosewich 1990) can be used to calculate a ^{38}Ar production rate. It may even be possible to extract further information by calculating the CRE using a production rate that assumes 40% of the Fe derived Ar was lost during weathering. Using the bulk
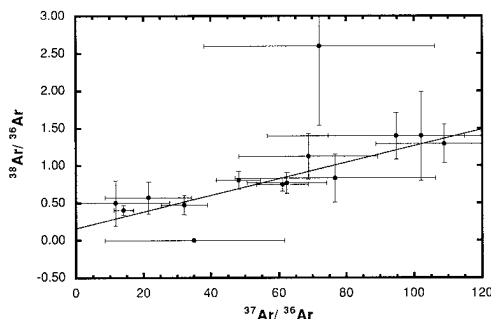
FIGURE 6. Linear regression, derived from neutron activation analysis of a sample of Allegan oxidized for 170 d in aerated ice water, yielding a gas-retention age of 4.59×10^9 y.

composition, a ^{38}Ar production rate of 3.2×10^{-8} cm³/g Ca and with only 40% of the Fe contribution, the effective production rate drops to 2.9×10^8 cm³/g Ca (Eugster and Michel 1995).

Both ^{38}Ar and ^{36}Ar are produced by spallation with a $^{38}Ar/^{36}Ar$ ratio of 1.538 that must be separated from trapped argon with a $^{38}Ar/^{36}Ar$ ratio of 0.188 (Eugster 1988). This can be achieved using a plot of $^{38}Ar/^{36}Ar$ vs. $^{37}Ar/^{36}Ar$ (^{37}Ar monitors Ca) on which the data yield an array between the spallation end-member and trapped end-member (Fig. 6). The $^{38}Ar/^{37}Ar$ ratio of the spallogenic end-member can then be calculated from the slope and intercept of the plot, and the $^{38}Ar/Ca$ ratio can be derived. The data lie on a line with the exception of one point that contains excess ^{38}Ar and may represent an Fe-rich area not weathered during the experiment. Ignoring that point, the spallation $^{38}Ar/^{37}Ar$ ratio derived from Figure 6 is 0.01148, which represents a $^{38}Ar/Ca$ ratio of 1.81×10^{-7} cm³ STP/g (Kelley et al. 1986). The $^{38}Ar/^{36}Ar$ intercept of 0.269 ± 0.078 does not coincide with the trapped composition of 0.188 and probably reflects a contribution to the ^{38}Ar budget from neutron bombardment of Cl. A CRE of 5.7 Ma results from the assumption of a bulk production rate and 6.2 Ma results from the assumption that 40% of the ^{38}Ar produced by spallation of Fe and Ni has been lost. Both results are within error of the previously derived value of 5.9 Ma. It has not been possible to detect ^{38}Ar loss unequivocally because of the scatter in the data induced by a variable contribution from neutron-induced ^{38}Ar from Cl.

Limits on chlorine concentration

The initial purpose of this experiment was to measure the Cl concentration in the weathered Allegan sample using ^{38}Ar derived from neutron bombardment of Cl. A simple maximum can be placed upon this concentration using the amount of ^{38}Ar in excess of a $^{38}Ar/^{36}Ar$ ratio of 0.188 for the bulk sample, which is 8.9×10^{-10} cm³/g, corresponding to a Cl concentration of 12 ppm (Kelley et al. 1986). However, because it has been shown that the majority of the ^{38}Ar is spallogenic, the actual concentration is lower. The $^{38}Ar/^{36}Ar$ non-spallogenic intercept (0.269)

is higher than the accepted trapped ratio (0.188) and the difference (0.081) together with the total ^{36}Ar content of the sample yields a ^{38}Ar excess of 1.14×10^{-10} cm³/g, corresponding to a Cl concentration of 1.6 ppm. These results are broadly consistent with data from Tarter et al. (1980), who found 9–14 ppm Cl in the unweathered meteorite, i.e., no Cl was introduced as a contaminant during the experimental procedure.

DISCUSSION

Implications for cosmic-ray exposure and gas-retention ages

Although our neutron activation analysis must be treated with some caution given the problems discussed previously, the similarity in formation and exposure ages in the fresh and weathered meteorite suggests that weathered meteorites may be amenable to a wider spectrum of cosmochemical analyses than previously thought. It also indicates that meteorite weathering may occur with congruent dissolution of primary phases (weathering products of Fe-Ni and troilite are easily identified in meteorite thin sections). However, silicate alteration is more subtle, possibly involving topotactic replacement along layers a few tens of angstroms wide as observed by Eggleton (1984) and Banfield et al. (1990). Mössbauer analyses of many terrestrial age dated ordinary chondrites (Bland et al. 1995, 1997) indicate that the weathering rate of silicates may be comparable to Fe-Ni and troilite oxidation. In addition, it appears that negligible atmospheric Ar must be incorporated in weathering products, a finding that is surprising given that atmospheric Kr and Xe are concentrated in hot desert meteorites (Scherer et al. 1994). It may be that this result reveals the limitations of an artificial weathering study in comparison with weathering in the field. However, further work is required to settle the question.

Weathering over time

The artificial weathering experiment performed on Allegan in aerated ice water indicated a progressive increase in the relative proportion of Fe^{3+} with time (Fig. 7a), suggesting the dissolution and oxidation of Fe^0 and Fe^{2+} in sites in primary meteoritic minerals to secondary iron oxides and oxyhydroxides during the course of the experiment. Slightly more rapid oxidation was observed during the first 20 d exposure to aerated ice-water, after which the relationship between time and oxidation appears to be approximately linear. The variation in spectral area of Fe^{3+}-containing components over time in the room temperature experiments (Fig. 7b) appears broadly similar.

Data from experimental dissolution studies generally show a similar trend to that found in Figure 7a, with an initial rapid phase of oxidation followed by linear trend. Previous studies show that experimental dissolution of freshly crushed rock and mineral grains show a transition from parabolic to linear kinetics over time (Keller et al. 1963; Luce et al. 1972; Grandstaff 1977). This observation was interpreted in terms of silicate dissolution con-
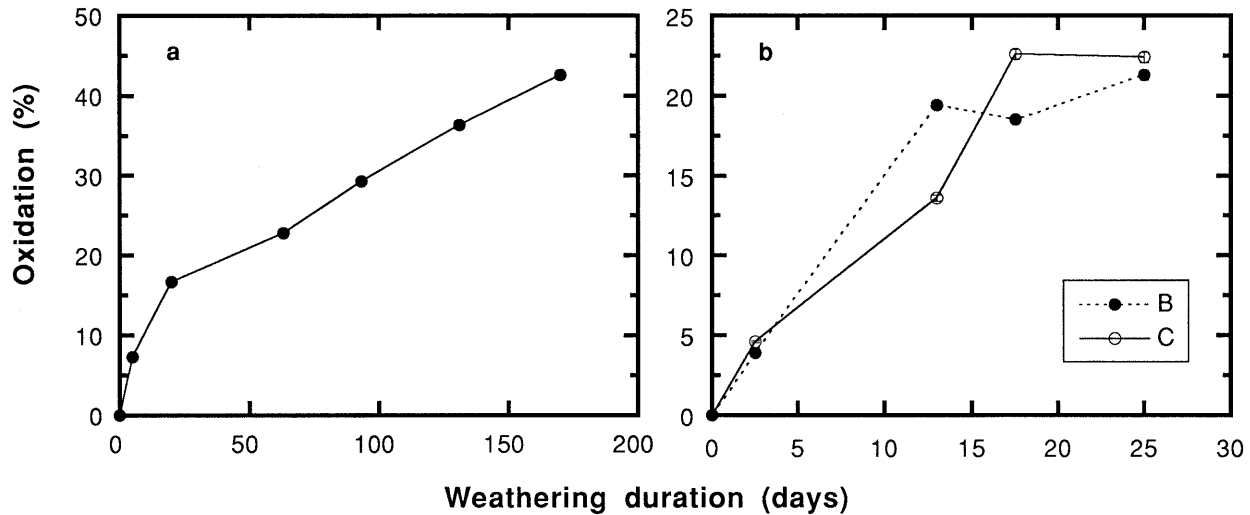
Figure 7. Total percentage oxidation, derived from Mössbauer data, against duration of weathering in days for samples weathered in ice water (**a**) and at room temperature (**b**).

trolled by diffusion through a precipitated surface layer (Helgeson 1971). However, several authors (Petrovich et al. 1976; Berner and Holdren 1977; Berner 1981; Grandstaff 1978, 1986; Petrovich 1981) argued convincingly that the high initial dissolution rate is more simply explained as an artifact of the laboratory grinding process. Grinding produces fine "dust" particles, which electrostatically adhere to surfaces. Because of their high surface area, the dissolution of fine grains is more rapid than that of the bulk material, initially producing a parabolic shaped curve. No attempt was made, in the artificial weathering experiments A, B, and C described here, to remove fine particles, thus their rapid dissolution cannot be discounted. If the initial dissolution is an experimental artifact then the true oxidation of artificially weathered meteorite samples follows an approximately linear trend over time.
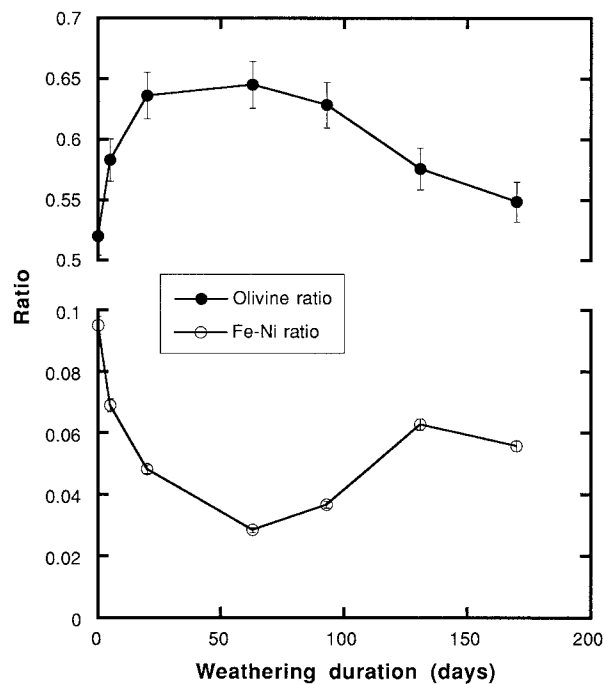
Oxidation of primary minerals

Dissolution and oxidation of individual phases within the meteorite during laboratory experiments in comparison with other minerals (Fig. 8) shows several similarities to samples oxidized in the natural environment. As observed by Gooding (1985), Buchwald and Clarke (1989), and Wlotzka (1993), Fe-Ni alloy, at least initially, appears preferentially oxidized in ordinary chondrites. In this study Fe-Ni initially showed a reduction in spectral area, relative to other primary minerals, until achieving an approximately constant ratio at a lower level. The dissolution and oxidation rates for troilite (FeS) and Fe^{2+} in sites in olivine and pyroxene appear broadly similar, which was also noted by Fisher and Burns (1992b). However, the dissolution of olivine relative to pyroxene in Allegan is variable: Pyroxene is initially weathered faster than olivine, until after about 20 d exposure to aerated ice water when the rate of dissolution for both minerals is approximately the same. Although within the error on the measurement, after this time there is a consistent trend indicating the preferential dissolution and oxidation of olivine. The initial resistance of olivine to oxidative weathering may be an artifact of the grinding process: pyroxene, with strong cleavage partings in two directions may be more easily fragmented into preferentially oxidized fine dust particles. The subsequent accelerated dis-
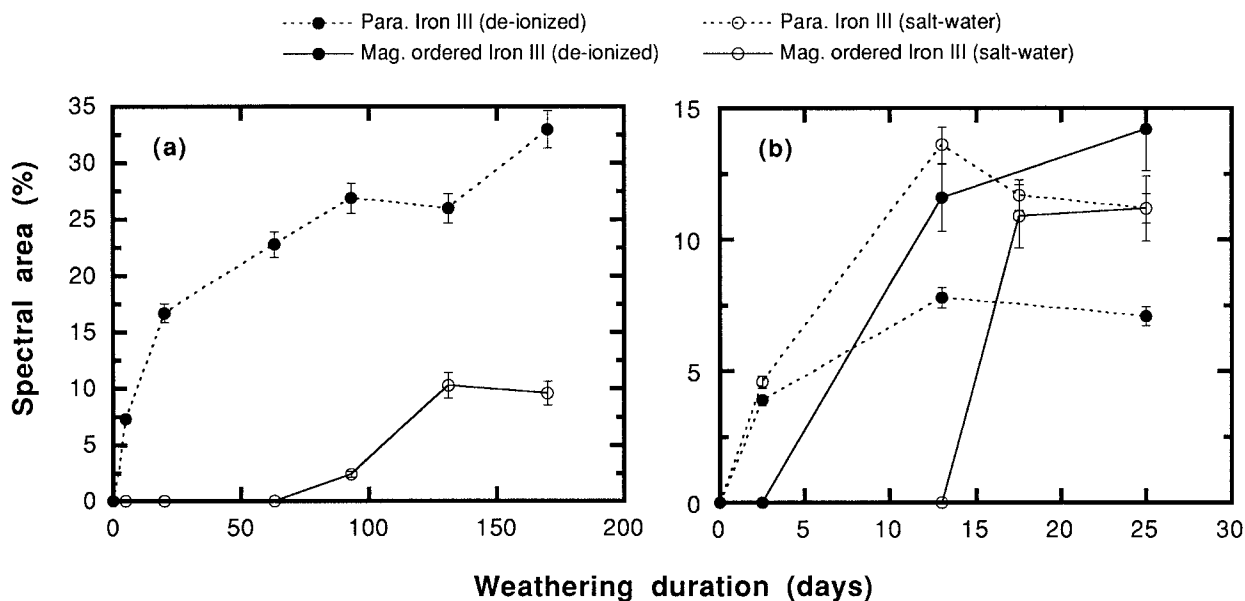

Figure 8. Ratio of percentage spectral areas of olivine against olivine plus pyroxene and Fe-Ni metal against total primary minerals, throughout the course of experiment A.

FIGURE 9. Spectral area of paramagnetic Fe^{3+} phases and magnetically ordered ferric minerals for the ice water (**a**) and room temperature (**b**) experiments.

solution of olivine relative to pyroxene is predicted by several experimental dissolution studies (Siever and Woodford 1979; Luce et al. 1972).

Corrosion products

Differences in oxidation products between experiments. Although similar weathering products were observed in the Mössbauer spectra recorded from all three experiments, their relative proportions varied substantially over time and from one experiment to another. In the case of experiment A, paramagnetic Fe^{3+} species contributed the bulk of the total ferric products (Fig. 9a), and magnetically ordered iron oxides and oxyhydroxides only appeared after oxidation had proceeded for 63 d. In contrast, Allegan weathered at room temperature showed magnetically ordered ferric species after approximately 10 d (Fig. 9b). This is significant as it indicates that the weathering experiments may have effectively mirrored oxidation in the cold- and hot-desert environments. Magnetite and maghemite (magnetically ordered iron oxides) are comparatively rare in weathered Antarctic meteorites (Buchwald and Clarke 1989) and are only observed after prolonged exposure to the polar environment. However, in meteorites from hot deserts (Bland et al. 1996a) magnetite and maghemite are common and contribute a substantial proportion of the Mössbauer spectra. The variation in the relative proportions of paramagnetic Fe^{3+} (e.g., akaganéite, lepidocrocite, small particle goethite) and magnetically ordered oxides (maghemite, magnetite, large particle goethite) in experiements A, B, and C, appears consistent with the findings of Buchwald (1989) and Buchwald and Clarke (1989). This consistency suggests that differences in oxide minerals may be due to varia-

tions in relative humidity. Akaganéite is the initial weathering product in the corrosion of meteorites, which over time and distance from the corrosion front gradually transforms to maghemite and goethite. Buchwald (1989) and Buchwald and Clarke (1989) postulated that the availability of free water may be a controlling factor in the rate at which akaganéite ages: More free water increases the rate at which Cl^- is flushed from the akaganéite structure, and thus the rate of the akaganéite-maghemite transformation. Although relative humidity is certainly an important factor, it also appears that temperature alone has a significant effect on the rates of oxide transformations. Even over the narrow temperature range in our experiments, a similar difference is observed to that seen in nature, i.e., paramagnetic Fe^{3+} (akaganéite) dominates at low temperatures whereas magnetically ordered oxides (maghemite and magnetite) contribute a greater proportion of the spectra in samples weathered at higher temperatures. Similar environmental controls on weathering products of non-meteoritic materials were identified by Schwertmann (1985).

A comparison of the two room-temperature experiments also indicates that the weathering mechanism proposed by Buchwald and Clarke (1989) may be the primary corrosion mechanism involved. The sample oxidized in salt water shows a significantly higher proportion of paramagnetic Fe^{3+}-containing species and a slightly lower proportion of magnetically ordered ferric phases than the sample oxidized in deionized water. This observation is consistent with a situation in which an increased supply of Cl^- ions enhances the range over which akaganéite is stable (and therefore limits the rate at which it transforms to goethite and maghemite). Therefore, it

appears that the artificial weathering experiments detailed in this study have effectively simulated many of the processes involved in the natural oxidation of ordinary chondrite meteorites.

Although magnetite was not definitively identified in Mössbauer spectra in this work (due to strong peak overlap with maghemite), it was identified in spectra from hot desert meteorites (Bland et al. 1996a). The stability of magnetite in meteorites weathered in hot desert environments may be related to the rapid dissolution of Fe-Ni alloy producing a local environment saturated with both Fe^{2+} and Fe^{3+} ions. Magnetite was not observed in the Mössbauer spectra recorded from weathered Antarctic ordinary chondrites (Bland et al. 1995).

Akaganéite. The weathering products identified in the Mössbauer spectra from the artificial weathering of Allegan show some similarities to the oxides and oxyhydroxides found in meteorites from hot and cold deserts (Bland et al. 1995, 1996a) and also correspond in general to those found by Buchwald and Clarke (1989) in a suite of Antarctic meteorites. However, in the case of the experimental oxidation study using deionized ice water, the presence of akaganéite is unexpected. It has been supposed that akaganéite is not true β-FeOOH, but requires Cl^- or some other large anion (e.g., F^-, Post and Buchwald 1991) to fill tunnel sites, and that without this extra species the mineral is not stable (Mackay 1960, 1962; Feitknecht et al. 1973; Chambaere and De Grave 1984). Although this assertion has been questioned and the ability of akaganéite to retain a stable crystal structure following partial substitution of Cl^- by OH^- ions has been recognized (Rézel and Génin 1990), it is commonly held that Cl^- is required for stability; indeed when the chemical formula of akaganéite is quoted it generally includes Cl^- (Keller 1970; Holm et al. 1983; Buchwald and Clarke 1989; Post and Buchwald 1991). All the previous investigations analyzed either naturally occurring akaganéite (which would have almost certainly formed in the presence of some Cl^-) or synthetic akaganéite made using Cl^-.

A comparison of Mössbauer spectra recorded at a variety of temperatures indicate the presence of akaganéite. The ^{57}Fe Mössbauer spectrum recorded at 77 K from Allegan oxidized in deionized ice water for 170 d showed sextets contributing approximately 18% of the spectral area with hyperfine parameters similar to published values for akaganéite (Childs and Baker-Sherman 1983). The presence of akaganéite was indicated by a second spectrum recorded at 10 K and suggested by XRD analysis. Akaganéite may contain between 6.9 and 3.2 wt% Cl (Johnston and Logan 1979), indicating on the order of 1% Cl in this meteorite sample. However, as described above, this meteorite was oxidized in deionized water, H5 chondrite falls are almost completely Cl-free [the Cl content of Allegan has previously been measured at 9–14 ppm (Tarter et al. 1980)], and our neutron activation analyses support the view that no additional contamination took place. This information suggests that akaganéite may

be stable without Cl^- in tunnel sites (possibly substituting OH^- as described above) and that the unique chemical environment formed during the weathering of meteorites makes akaganéite the thermodynamically stable oxide phase. We postulate that Cl^- remains the most suitable anion to fill tunnel sites; however, in exceptional circumstances where it is absent and all other factors favor akaganéite formation, akaganéite may form with OH^- alone occupying tunnel sites.

The above observation has broad implications because it is contrary to the accepted view of the formation and stability of akaganéite. It indicates that akaganéite may in fact be a true iron oxyhydroxide and that a review of the chemical formula of akaganéite and the thermodynamic conditions under which it is stable is required.

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