

## Corrosion of Fe-Ni alloys by Cl-containing akaganéite ( $\beta$ -FeOOH): The Antarctic meteorite case

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### ABSTRACT

A suite of 12 iron and 8 stony meteorites from various environments and locations in Antarctica was studied, representing a range of compositions, metallographic structures, and degrees of weathering. Polished sections of meteoritic metal with adhering corrosion products were examined microscopically, with the electron microprobe and SEM, and were used as samples for X-ray diffraction examination. The major corrosion products are Cl-containing akaganéite (up to 5 wt% Cl) and goethite, with minor amounts of lepidocrocite and maghemite. Cl is not native to the meteorites but, owing to the electrochemical nature of the corrosion of Fe-Ni alloys, is attracted from the snow and ice, or rocky soil, environment that contains low amounts of Cl. Akaganéite precipitates near the reaction front, incorporating  $\text{Cl}^-$  ions into ion-exchange sites, where they may be retained, made available for further depassivating, corrosive action, or become flushed from the system. With time and distance from the reaction surface, akaganéite ages and transforms to mainly goethite and maghemite. It is again argued that lawrencite ( $\text{FeCl}_2$ ) is not a mineral in meteorites. In the stormy Antarctic, wind-blown terrestrial particles may become attached to the weathering products on the meteorite and in time themselves decompose, delivering terrestrial ions to the meteorite corrosion system. The ions may move a significant distance from the surface, and in particular Cl may be found along almost invisible cracks in the deep interior. Trace-element work and age determinations ( $^{36}\text{Cl}$ ) should take this problem into account.

### INTRODUCTION

Meteorites are our most accessible samples of extraterrestrial bodies. They provide us with direct evidence of early planetary system processes, along with information on many subsequent interactions throughout their complex histories prior to and after arrival on the Earth. They fall randomly in terms of both time and geographic distribution. Our life-supporting atmosphere laden with oxygen and moisture, however, is hostile to these intruders from the less reactive environment of space. Corrosive processes begin as a meteorite enters the atmosphere and continue until nothing remains that is recognizable. The metallic phases that are present in all but a few meteorites are among the first to show obvious effects of terrestrial weathering. Two Fe-Ni alloys, kamacite (low-Ni Fe-Ni, bcc) and taenite (high-Ni Fe-Ni, fcc), are the main metallic minerals present, and they are gradually converted to rust. Understanding this corrosion process has obvious implications for developing strategies to terminate, or at least minimize deterioration that continues when these scientifically important materials are incorporated into research and exhibit collections. For these and other reasons, we have undertaken a comprehensive

study of iron-meteorite corrosion in all terrestrial environments. Although a number of recent papers have considered various aspects of the weathering of stony meteorites, little attention has been given to iron meteorites since the works of Buddhue (1957), White et al. (1967), Faust et al. (1973), and Buchwald (1977).

Early in our studies it was realized that Cl-containing akaganéite is a mineralogical key to the understanding of the corrosion of meteoritic metal and that its role is most clearly demonstrated by the comparatively simple association of corrosion products that develops on meteorites retrieved after long exposures to the cold and low-humidity environment of Antarctica (Buchwald and Clarke, 1988). The process that emerges and overcomes passivation barriers includes anodic metal going into solution,  $\text{Cl}^-$  ions that originate from the terrestrial environment moving to the reaction surface to maintain charge balance, and Cl-containing akaganéite precipitating at the reaction surface. Over time, the initial corrosion products undergo an aging process that converts them to mainly goethite. This same process is also responsible for the corrosion of the metal particles in Antarctic chondrites, stony meteorites containing from 6 to 15 wt% metal. Preliminary indications are that Cl-containing akaganéite

TABLE 1. Characterization of selected Antarctic meteorites

Name*	Mass (kg)	Type	Bulk composition**		State of corrosion	Age† (10 <sup>3</sup> yr)
			wt% Ni	wt% P		
ALH A77283	10.5	IA, coarse octahedrite	7.33	0.22	3	110 ± 70
ALH A77289	2.19	IA, coarse octahedrite	6.84	0.21	2	170 ± 70
ALH A78252	2.79	IVA, fine octahedrite	9.33	0.17	1	360 ± 70
ALH A81013	17.8	IIA, hexahedrite	5.52	0.27	1	
ALH 84165	0.10	IIIA, medium octahedrite	7.76	0.14	0	
DRP A78009	138.1	IIB, coarsest octahedrite	6.59	0.34	3	
EET 83390	0.02	(IA), octahedrite	7 <sup>‡</sup>	0.2 <sup>‡</sup>	3	
GRO 85201	1.40	IIIA, medium octahedrite	8.59	0.23	0	
ILD 83500	2.52	IVB, ataxite	18.9	0.28	2	~3000
NEP 642614	1.07	IA, coarse octahedrite	7.26	0.20	1	
PGP A77006	18.9	IA, coarse octahedrite	7.27	0.20	2	90 ± 70
Y 75105	0.02	IIA, hexahedrite	5.26 <sup>§</sup>	0.25 <sup>‡</sup>	0	

\* Allan Hills (ALH), Derrick Peak (DRP), Elephant Moraine (EET), Grosvenor Mountains (GRO), Inland Forts (ILD), Neptune Mountains (NEP), Purgatory Peak (PGP), Yamato Mountains (Y).

\*\* E. Jarosewich, analyst. Remainder is Fe with ~1% total Co, S, Cr, C, etc.

† Nishiizumi (1984) and Nishiizumi et al. (1987).

‡ Our estimate.

§ Kracher et al. (1980).

plays an important role in the weathering of essentially all meteoritic metal, and we suspect that in the corrosion of other ferrous metals under similar circumstances, this mineral plays a role that has not been previously recognized.

### METEORITE SPECIMENS

After preliminary examination of corrosion products on 40 iron meteorites from a variety of environments, we focused our attention on a suite of 12 Antarctic irons. Collected between 1964 and 1986, they represent a variety of compositions and metallographic structures, different environments within Antarctica, and separations by large distances on the continent (Table 1). The Allan Hills, Elephant Moraine, Grosvenor Mountains, and Yamato Mountains meteorites were found on either bare ice or in an ice and rock moraine, generally at altitudes of 1600–2000 m (Yoshida et al., 1971; Yanai, 1976; Cassidy, 1980; Clarke et al., 1981; Clarke, 1982a). The Derrick Peak meteorites were found on a ridge and on a side of Derrick Peak, a mountain protruding above Heather-ton Glacier in the Britannia Range (Kamp and Lowe, 1982; Clarke, 1982b, 1984). The Inland Forts specimen was found partially within soil at Inland Forts on the south slope of the Asgard Range above Taylor Glacier (Clarke, 1989). The Neptune Mountains meteorite was found on glacial debris about 30 m above the ice on a nunatak in the central Neptune Range (Buchwald, 1975). The Purgatory Peak meteorite was recovered from the base of the mountain in the Victoria Dry Valley (King et al., 1980; Clarke, 1982a). Common to these specimens is that they were found completely or largely exposed on the ice, on rock surfaces, or on soil. Great care was taken to prevent contamination or deterioration of specimens during collection and transport to curatorial facilities, and they have received special attention within these facilities. Background on the field and curatorial programs that

provided the specimens is given by Marvin and Mason (1980, 1982, 1984) and Marvin and MacPherson (1989).

Table 1 provides total specimen weights, chemical and structural classification, and bulk Ni and P values. The severity of corrosion is also evaluated on a scale from 0 (no corrosion) to 4 (destructive corrosion), a scale similar to but different in detail from the scale used for Antarctic stony meteorites (Lipschutz, 1982). The final column reports terrestrial ages (Nishiizumi, 1984; Nishiizumi et al., 1987).

### EXPERIMENTAL METHODS

Regions with interfaces between metals and oxides or oxide fragments were selected for examination that included microscopic identification on polished sections, electron microprobe and scanning electron microscope (SEM-EDAX) analysis on these same sections, and X-ray powder-diffraction studies of oxide isolated from selected sections. Polished sections were made in the standard way: cutting with tap-water-cooled carborundum blades, followed by wet-grinding with garnet grit, and wet polishing with diamond and finally Al<sub>2</sub>O<sub>3</sub> paste. In order to establish that Cl was not introduced by the use of tap water, control sections were prepared without its use from corrosion products that had not been previously exposed to tap water. Dry cutting and coarse grinding were followed by petroleum-lubricated fine grinding and polishing with diamond paste. Akaganéite in these sections contained comparable levels of Cl and convinced us that Cl was not introduced or moved during our sample preparation. However, it would be reasonable to expect that in procedures such as abrasive-wire sawing, where long cutting times and large amounts of tap water are involved, a slight modification of the mobile Cl concentration in akaganéite is possible.

Chemical data were obtained with an ARL SEMQ electron microprobe with six fixed spectrometers for Si, Al,

TABLE 2. Oxide weathering products of Antarctic iron meteorites

Name	Structure	General formula	Formula wt% Fe	Observed range (wt%)		
				Fe	Ni	Cl
Akaganéite	hollandite	$\beta$ -FeOOH	62.9	39–60	0.5–19	0.3–5.4
Goethite	diaspore	$\alpha$ -FeOOH	62.9	41–61	1.0–8.0	<0.2
Lepidocrocite	boehmite	$\gamma$ -FeOOH	62.9	45–60	0.5–11	<0.2
Maghemite	cubic spinel	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	69.9	58–63	0.4–7.0	<0.1

Fe, Mg, Ca, and K, and three adjustable spectrometers set for Ni, P, and Cl, or for Co, Na, and S, operated at 15 kV and 0.025-mA sample current on brass. Magnetite and Kakanui hornblende were used for Fe standards (Jarosewich et al., 1980), and synthetic Ni-Fe alloys were used for the Ni standards. Values for Ni in the oxides were corrected by using the MAGIC-IV program.

Photographs and additional chemical data by energy-dispersive X-ray analysis were obtained using a Philips SEM-EDAX operated at 20-kV accelerating voltage.

Samples for X-ray diffraction analyses were dispersed with acetone onto a low-background quartz slide, and data were collected with a Scintag automated diffractometer system, operated under the following conditions: 0.03° step size, 2- and 4-mm divergent slits, 0.3- and 0.5-mm receiving slits, Ge detector, CuK $\alpha$  radiation,  $\lambda = 1.54091$  Å, 45 kV, 40 mA, and a 1.0°/min scan rate.

#### CORROSION ASSEMBLAGES

Corrosion assemblages on iron meteorites that have so far been retrieved from Antarctica are much less extensive than those that have been observed on many specimens found in temperate and tropical environments. Corrosion on the exterior surfaces of those selected for study is typical and normally consists of a relatively thin layer of oxides, less than 1 mm thick. More severe corrosion develops on under-surfaces, in cleavages, or in fissures within the meteorite.

Akaganéite, goethite, lepidocrocite, and maghemite are the four minerals that constitute the bulk of the corrosion products observed. They are listed in Table 2 by name, structure type, and general formula. Also given is the formula weight percent of Fe and the observed ranges in weight percent for Fe, Ni, and Cl as determined by electron microprobe. Low Fe totals were observed on all four of the oxides and are due mainly to the presence of water of hydration and to irregularities of surfaces caused by the presence of voids in the oxide. For this reason, analytical data are presented to no more than two significant figures. The oxides also contain Ni in varying amounts as a consequence of derivation from an Fe-Ni alloy. Akaganéite contains significant amounts of Cl, and small amounts of Cl were occasionally observed in goethite and lepidocrocite.

Observations on specific meteorites are summarized in Table 3. The major and accessory weathering products are given for each meteorite, along with the range in Ni, Cl, and S for the major product. Also noted are other

elements that were observed in the oxides and foreign mineral grains that were present.

Akaganéite is rust colored, and its powder is orange to brownish. It is grayish blue in polished section, is softer than maghemite and magnetite, and is often rich in shrinkage cracks, like dried mud. It may contain a significant content of adsorbed water, and this is particularly evident when the electron-microprobe beam is kept on a spot. Within 2–10 min, 5–10 wt% H<sub>2</sub>O may be lost, as is indicated by an increase with time in Fe counts. In polarized light, akaganéite is microcrystalline, with orange to reddish internal reflections that are intermediate between those of goethite and lepidocrocite, appearing subdued like a coke fire in a fireplace.

Akaganéite is observed in various relationships in Antarctic iron meteorites. It fills corrosion pits 0.5–2 mm across on the surface, and in the interior it loosely cements cracks as a disordered and microcracked oxide. Akaganéite is usually in contact with as yet uncorroded metal, whereas goethite, maghemite, and lepidocrocite are often found as oxide intergrowths or as coatings on or between other oxides. Our data show (Tables 2 and 3) that natural akaganéite is rich in Cl. In a given meteorite oxide, the Cl content may vary from the limit of detection (0.1 wt%) to several weight percent, as analyzed by the electron microprobe. There is both a large-scale variation among different parts of the meteorite and a small-scale variation, for example, within the akaganéite-goethite filling of an extended crack, due to varying proportions of these two minerals. Most of the Cl is located in the akaganéite, whereas a few tenths of a percent may be present in goethite and lepidocrocite. Cl is apparently absent in maghemite (Table 2).

The Cl content of akaganéite is highest near its interface with metal or in the deep interior when it is a crack filling. In a typical crack filled with akaganéite, 100  $\mu$ m wide at the surface and narrowing to 5  $\mu$ m at a depth of 15 mm, Cl ranges from 0.1 wt% at the surface to 4.9 wt% near the bottom of the crack. The Cl concentrates where corrosion is currently active, and levels of 4–5 wt% are typical at these locations.

Lepidocrocite is sometimes observed coating exterior surfaces and in internal cracks. It has clearly been transported in solution and deposited as botryoidal layers, or it forms laminated bands 5–50  $\mu$ m thick, sometimes enveloping foreign particles such as quartz and feldspar grains.

Although our efforts focus on iron meteorites, we have

**TABLE 3.** Corrosion products and nonmeteoritic minerals on Antarctic iron meteorites

Name	Weathering products		Major oxide composition Range in wt%			Elements introduced into oxides	Foreign minerals
	Major	Accessory	Ni	Cl	S		
ALH A77283	akaganéite	goethite	0.5–5.5	0.7–2.5	nd	Ca, K	
ALH A77289	akaganéite	goethite	1.8–6.0	0.3–3.4	nd	Mg, Ca, Al	
ALH A78252	akaganéite	goethite	1.5–8.5	0.3–5.0	nd	Mg, Si	quartz, olivine, zeolite
ALH A81013	akaganéite	goethite	0.9–4.5	0.7–1.6	0.2–0.7	Al, Mg, Ca, (S)	
ALH 84165	akaganéite	lepidocrocite	1.8–12	0.4–1.5	0.1–1.9	Al, K, (S)	
DRP A78009	akaganéite	goethite, lepidocrocite	1.0–5.6	0.8–4.5	0.2–0.5	Si, Ca, Mg, (S)	calcite,* quartz
EET 83390	akaganéite	goethite, maghemite, lepidocrocite	1.0–13	0.3–2.5	0–2.0	Mg, Al, K, (S)	
GRO 85201	akaganéite	goethite, maghemite, lepidocrocite	0.4–12	0.6–2.4	nd	Al, K, Si	feldspar
ILD 83500	akaganéite		1.2–16	0.4–3.0	0–0.4	Mg, Ca, Al, Na, (S)	calcite,* quartz
NEP 642614	akaganéite	goethite, maghemite	2.2–19	0.4–3.6	nd	Ca, Mg, Al	
PGP A77006	goethite	akaganéite, maghemite, lepidocrocite	1.0–5.0	<0.2	<0.2	Si, Al, Mg, Ca, K, (S)	orthoclase, plagioclase, calcite,* olivine, quartz, amphibole
Y 75105	akaganéite	goethite	1.5–4.7	0.4–5.4	nd	Mg, K, Al	

Note: nd = not determined.

\* Identified in vugs and veins.

also examined the corrosion of metal particles in polished thin sections of a suite of 8 chondritic meteorites from Antarctica. Both H- and L-group meteorites of petrographic grades 4–6 (Van Schmus and Wood, 1967), and of weathering classes B and C (Lipschutz, 1982), are included. Specimens selected are from the Allan Hills, the Elephant Moraine, and the Taylor Glacier, and they were collected during the 1976 through 1982 field seasons. Their names, total weights, classifications, their range in akaganéite wt% Cl, Ni, and Na, and their terrestrial ages are given in Table 4. In general the same relationships between oxides and metals developed for iron meteorites are observed in association with the metal particles in these stony meteorites. Metal particles are in the millimeter and smaller size range and constitute varying amounts of the specimen. Average metal content for observed-fall H-group chondrites is 18 wt%, and for L-group chondrites 7.4 wt% (Mason, 1965). A by-product of these chondrite studies was black and white photographs illustrating important relationships; photographic equivalents of iron meteorites are difficult to obtain without resorting to color photography.

Conversion in place of chondritic kamacite to akaganéite is illustrated by SEM back-scattered electron photographs (Fig. 1) and semiquantitative chemical data. In specimen EET 82602, a kamacite particle containing approximately 6 wt% Ni is partly converted to akaganéite (Fig. 1a). The enclosing silicates appear not to have been disturbed, indicating that akaganéite has directly replaced kamacite without significant volume change. Assuming that akaganéite consists only of Fe, Ni, and Cl, the analyzed area (Fig. 1a) contains 5.5 wt% Ni and 3.1 wt% Cl. A more advanced state of weathering, also without distortion in the silicate relationships, has converted a network of kamacite to essentially akaganéite in EET 82604 (Fig. 1b). A 20 × 25 μm area of akaganéite in this association contained 5.0 wt% Ni, 4.4 wt% Cl, 0.5 wt% S, assuming that it consisted only of these elements and Fe. These associations suggest that H<sub>2</sub>O, Cl<sup>-</sup>, and O<sub>2</sub> moved through earlier-formed corrosion oxides to react with kamacite and that Fe and some of the Ni were removed so that the less dense akaganéite could replace kamacite on an equal volume basis.

An akaganéite-goethite vein penetrating a chondrule in

**TABLE 4.** Akaganéite in association with metal grains in Antarctic chondrites

Name*	Mass (kg)	Type	Weathering	Akaganéite compositions Range in wt%			Age** (10 <sup>3</sup> yr)
				Cl	Ni	Na	
ALH A76009	407	L6	B	0.3–2.3	2.1–7.4	<0.1	
ALH A77004	2.2	H4	C	<0.2	1.7–4.6	<0.1	170 ± 70
ALH A77285	0.3	H6	C	0.2–1.8	2.7–6.7	<0.1	220 ± 70
ALH A79002	0.2	H6	C	0.3–3.9	1.9–4.7	<0.1	
EET 82602	1.8	H4	B	0.2–3.3	2.0–5.3	nd	
EET 82604	1.6	H5	B/C	0.5–3.2	1.7–5.9	nd	
EET 82606	1.0	L6	B	0.4–3.4	1.8–19	nd	
TYR 82700	0.9	L4	B	0.6–4.2	2.5–5.5	nd	

\* Allan Hills (ALH), Elephant Moraine (EET), Taylor Glacier (TYR).

\*\* Nishiizumi (1984).

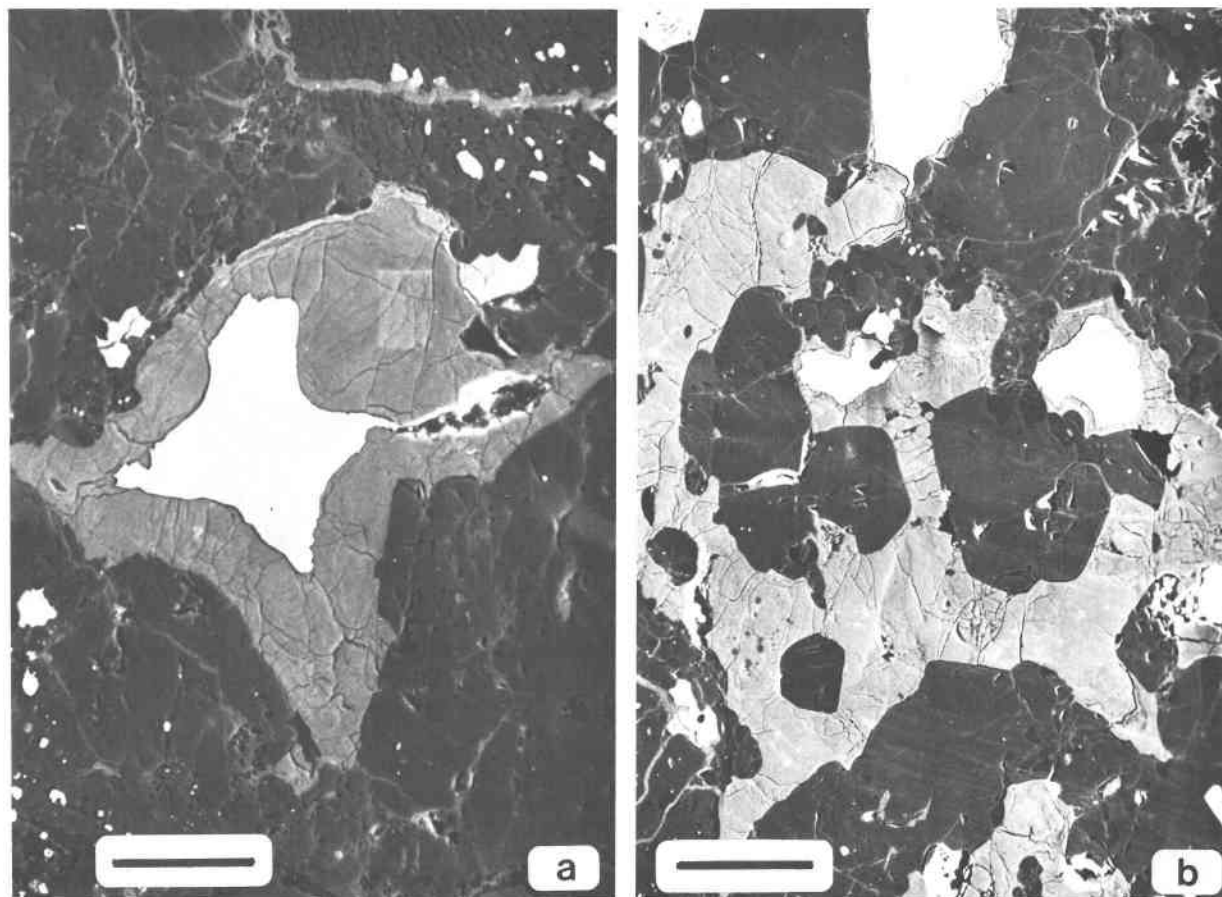


Fig. 1. Backscattered-electron images of akaganéite replacing metal in polished thin sections of Antarctic chondrites. (a) EET 82602 (H4), akaganéite (gray) replaces kamacite (white). Various silicates surround the akaganéite, and a thin akaganéite-goethite-filled horizontal crack is at the upper right. The lighter gray rectangle at the upper right of the akaganéite field is an area analyzed by SEM-EDAX. The network of cracks in the akaganéite is typical. Scale bar = 0.05 mm. (b) EET 82604 (H5), a network of kamacite (white) largely replaced by akaganéite (gray). Darker minerals are silicates. Scale bar = 0.1 mm.

EET 82602 demonstrates deposition of these weathering products by solutions moving into a crack (Fig. 2). A semiquantitative analysis of a  $10 \times 10 \mu\text{m}$  area, again ignoring  $\text{H}_2\text{O}$  and  $\text{O}_2$ , found mainly Fe, 5.5 wt% Ni, 0.9 wt% Cl, 0.4 wt% S, 1.1 wt% Al, 3.1 wt% Mg, 2.6 wt% Si, and 0.6 wt% Ca, suggesting that parts of the adjacent troilite and silicates were dissolved and incorporated in the akaganéite-goethite filling.

Troilite and silicate associations may also be invaded by akaganéite veins (Fig. 3a). Analysis indicates that Ni, Cl,  $\text{H}_2\text{O}$ , and possibly Fe were moved along cracks to react with the troilite and silicates to produce akaganéite. A semiquantitative analysis of a small area, neglecting again the light elements, indicated major Fe, 2.9 wt% Ni, 4.1 wt% Cl, and 3.0 wt% S. Growth contours that are readily recognized under the microscope in these veins are suggestive of growth by solution transport.

An interface between metal and chlorapatite in EET 82606 (Fig. 3b) reveals that a thin strip of the metal has been replaced by akaganéite, but there appears to be no

indication of the still distinct boundary of the chlorapatite having been affected. Clearly demonstrated in this association is the dependence of akaganéite composition on the composition of the metal from which it formed. The somewhat thicker akaganéite in the bottom half of Figure 3b formed by replacement of part of the adjacent kamacite field and retains the approximately 18:1 Fe:Ni ratio of the kamacite. Analyses in this akaganéite area were all close to 5 wt% Ni, 90 wt% Fe, and 4 wt% Cl, ignoring  $\text{H}_2\text{O}$  and  $\text{O}_2$ . The akaganéite in the top of the picture formed from taenite with an entirely different Fe:Ni ratio of about 4:1. Consequently, this akaganéite is very rich in Ni, averaging 19 wt% Ni, 76 wt% Fe, and 4 wt% Cl, by the same analytical procedure.

## DISCUSSION

### Cl and Ni in akaganéite

Akaganéite is geologically a rather rare mineral that was first described as a weathering product from the Jap-

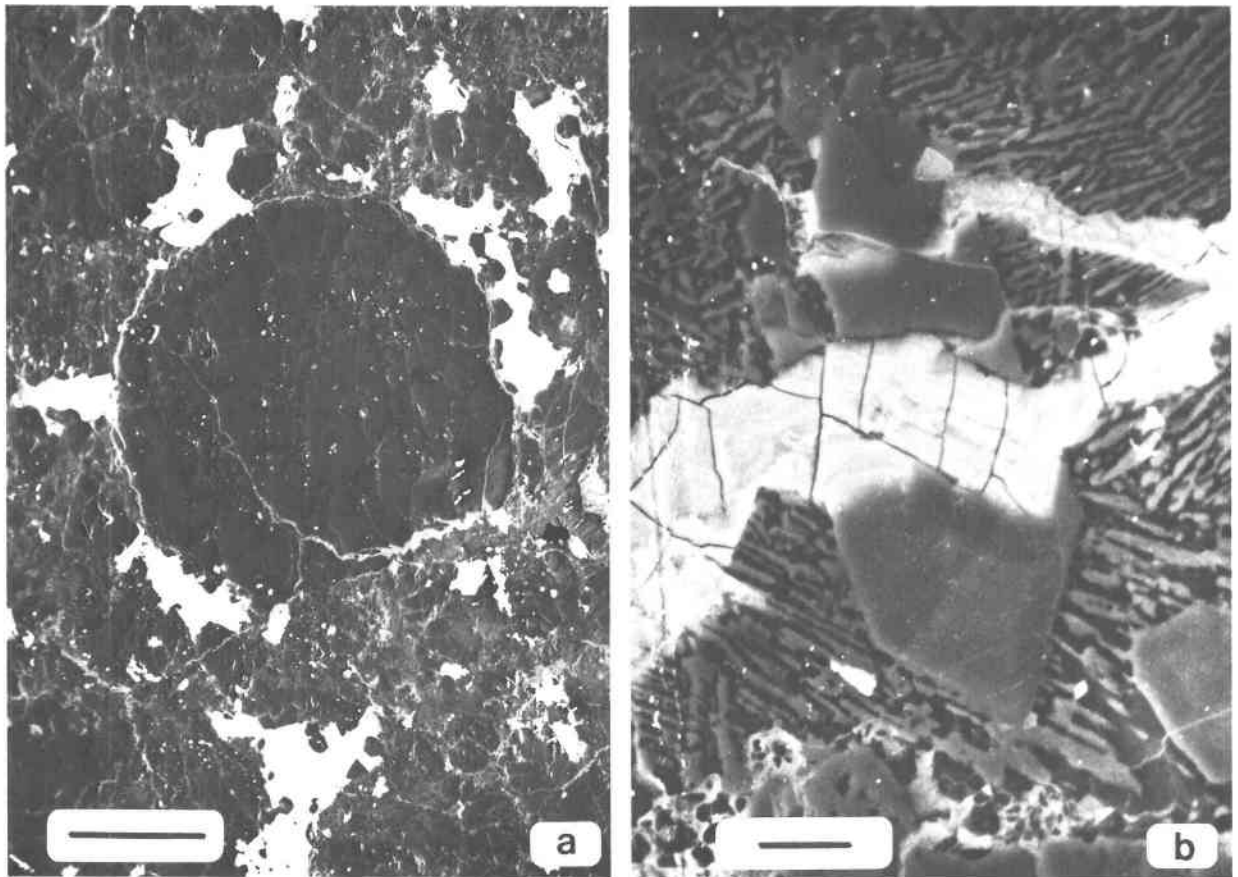


Fig. 2. Backscattered-electron images of a chondrule in EET 82602 (H4). (a) A section through a silicate chondrule (dark) partially surrounded by kamacite (white), with slightly weathered kamacite also in the silicate matrix. A vein of akaganéite-goethite penetrates the chondrule from its lower right to the upper left. Thin veins of akaganéite-goethite also border the chondrule. Scale bar = 200  $\mu\text{m}$ . (b) Enlargement of lower right area of akaganéite-goethite vein (white to light gray) penetrating the chondrule silicates (dark). Scale bar = 10  $\mu\text{m}$ .

anese limonite mine Akagané (Mackay, 1962). It was noted as a corrosion product on a few iron meteorites by Marvin (1963), who identified it in X-ray powder photographs. Akaganéite (Table 2) has the idealized formula  $\beta\text{-FeOOH}$  and has long been known from synthetic work (Mackay, 1960).

An important point for corrosion of ferrous metal is akaganéite's ability to host Cl in its structure, synthetic material having been reported to contain from 1.3 to 6.4 wt% Cl (Keller, 1970). Many authors have noted that it easily adsorbs water, 2–20 wt%, particularly when crystals are fine or the crystallinity is poor. Synthetic akaganéite has an exchange capacity,  $\text{Cl}^-$  and  $\text{OH}^-$  being rather easily exchanged. By repeat washing with water, synthetic akaganéite with 5.4–6.3 wt% Cl was shown to lose 21–36 wt% of its Cl (Keller, 1970). The unusual properties of this iron oxide are best accounted for by the formula proposed by Keller,  $\text{Fe}_8[(\text{O},\text{OH})_{16}(\text{Cl},\text{OH})_{<2}]$ , where 8  $\text{FeOOH}$  formula units are arranged in a monoclinic cell as in hollandite (J. E. Post and V. F. Buchwald, manuscript in preparation) and where  $\text{Cl}^-$  occupies some but

not all of the tunnel sites, making it rather easy for Cl to enter or leave the structure.

Akaganéite may also accommodate Ni in its structure. In the present study, up to 19 wt% Ni was observed, although 3–5 wt% Ni was the normal amount because most of the akaganéite has formed from kamacite. Its X-ray diffraction pattern typically gives broad peaks, undoubtedly as a result of very small crystal size. This is consistent with earlier observations (Mackay, 1962; Keller, 1970) on synthetic akaganéite by TEM (transmission electron microscopy) of crystals averaging  $2500 \times 250 \text{ \AA}$  with a maximum length of 5000  $\text{ \AA}$ . It has, therefore, not been possible to identify changes in lattice parameters due to Fe:Ni ratio variations. The roles of both  $\text{Cl}^-$  and Ni in the akaganéite structure will be discussed in detail elsewhere (J. E. Post and V. F. Buchwald, manuscript in preparation).

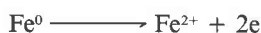
#### Corrosion mechanism

The corrosion mechanism of meteoritic metal in the Antarctic environment is in large part an electrochemical

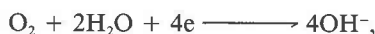


reaction that produces akaganéite as the initial product. Sources of the required potential difference to drive corrosion cells are the normal components of meteoritic metal and structural cracks. The major phase is generally kamacite (bcc Fe containing 4–7 wt% Ni), with minor amounts of the accessory minerals taenite (fcc Fe with 25–40 wt% Ni), schreibersite [(Fe,Ni)<sub>3</sub>P], and troilite (FeS) providing interfaces of differing chemical potential. These interfaces, as well as cracks, are sites where O<sub>2</sub> and electrolytes invade the metal. The result is that anodic kamacite goes into solution, electrons pass through metal to the cathode where O<sub>2</sub> (and sometimes H<sup>+</sup>) is reduced, and akaganéite precipitates. It appears that in the Antarctic deep freeze, such reactions may take place without liquid water, evidently requiring a much extended time owing to low coefficients of diffusion in ice and in oxides.

In simplest form and using conventional half-reactions, the process may be expressed as follows. Metal (Fe<sup>0</sup>) is oxidized at the anode



and O<sub>2</sub> is reduced at the cathode



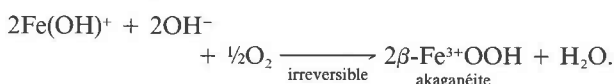
or, alternatively, H is reduced at the cathode



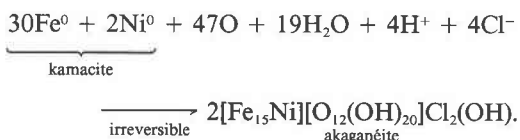
Combining the first two equations



This is followed under oxidizing conditions by the formation of akaganéite



In order to represent the degradation of meteoritic metal more realistically, we have adopted a variant of Keller's formula (Keller, 1970) for akaganéite, [Fe<sub>15</sub>Ni][O<sub>12</sub>(OH)<sub>20</sub>]Cl<sub>2</sub>(OH). It satisfies structural constraints, is in charge balance (Fe is assumed to be Fe<sup>3+</sup>, and Ni is Ni<sup>2+</sup>), and contains 55.9 wt% Fe, 3.9 wt% Ni, and 4.7 wt% Cl—amounts that have been commonly observed in this study. The reaction may then be expressed as

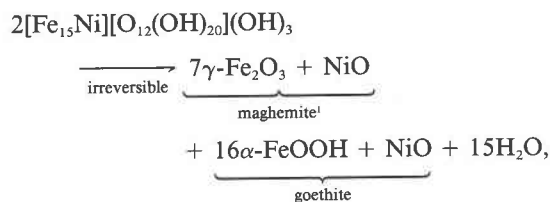


This reaction results in the formation of akaganéite as a replacement for kamacite. Little Ni or Fe is leached from the corrosion product, and Cl is derived and accumulated, even from environments where it is present in very low concentrations. Three factors appear to be important in explaining this dramatic accumulation of Cl:

the electrochemical nature of the corrosion reaction, the high ionic mobility of Cl<sup>-</sup>, and the size of the Cl<sup>-</sup> ion that allows it to fit into the tunnel sites of akaganéite and stabilize its structure.

The electrochemical requirement is that anions move to the anode, the surface where Fe<sup>0</sup> goes into solution, to maintain charge balance and that electrons flow through metal to the cathode where anions are produced. Chloride ions are apparently attracted to the vicinity of the corrosion front preferentially, their high ionic mobility undoubtedly being an important contributing factor. At the corrosion front, Cl<sup>-</sup> decomposes any passivating iron oxide film on the metal surface and often gives rise to pitting attack. Under these conditions, a Cl-containing akaganéite forms and encloses any taenite, troilite, or schreibersite located in the corrosion zone as passive minerals. Only much later in corrosion development, a stage rarely observed in Antarctic meteoritic metal, do these minerals disintegrate, usually in the order given, schreibersite, being able to survive in the corrosion products for a surprisingly long time.

Slowly in the Antarctic environment, but more rapidly in temperate climates, Cl<sup>-</sup> in akaganéite is exchanged with OH<sup>-</sup>, and Cl<sup>-</sup> is released into solution to move again to the corrosion front or to be flushed from the system. The akaganéite left behind will approach the composition [Fe<sub>15</sub>Ni][O<sub>12</sub>(OH)<sub>20</sub>](OH)<sub>3</sub> and, having lost its Cl, becomes unstable. Under conditions of modest heating and/or seasonal changes in temperature and humidity, it decomposes according to a reaction such as



a reaction that may be termed the aging of akaganéite. The products, typically maghemite and goethite, may for as yet unknown reasons occur in widely varying proportions. They are intimately intergrown on the micrometer scale, but may be distinguished in polished section (maghemite is brownish and harder and therefore stands out in relief). They contain most or all of the Ni and Fe that were previously in the akaganéite. Very little loss by leaching is observed in these early corrosion stages. The great terrestrial age of some of the meteorites studied (Tables 1 and 4) combined with the limited development of aging products when compared with temperate and trop-

<sup>1</sup> In this work we have observed a cubic spinel that may be either maghemite (γ-Fe<sub>2</sub>O<sub>3</sub>) or magnetite (Fe<sub>3</sub>O<sub>4</sub>). It contains Ni and has an X-ray diffraction pattern that may be interpreted as that of either Ni-substituted maghemite or Ni-substituted magnetite. Data are insufficient to distinguish between the two possibilities, so we have labeled all of the observed spinel material as maghemite.

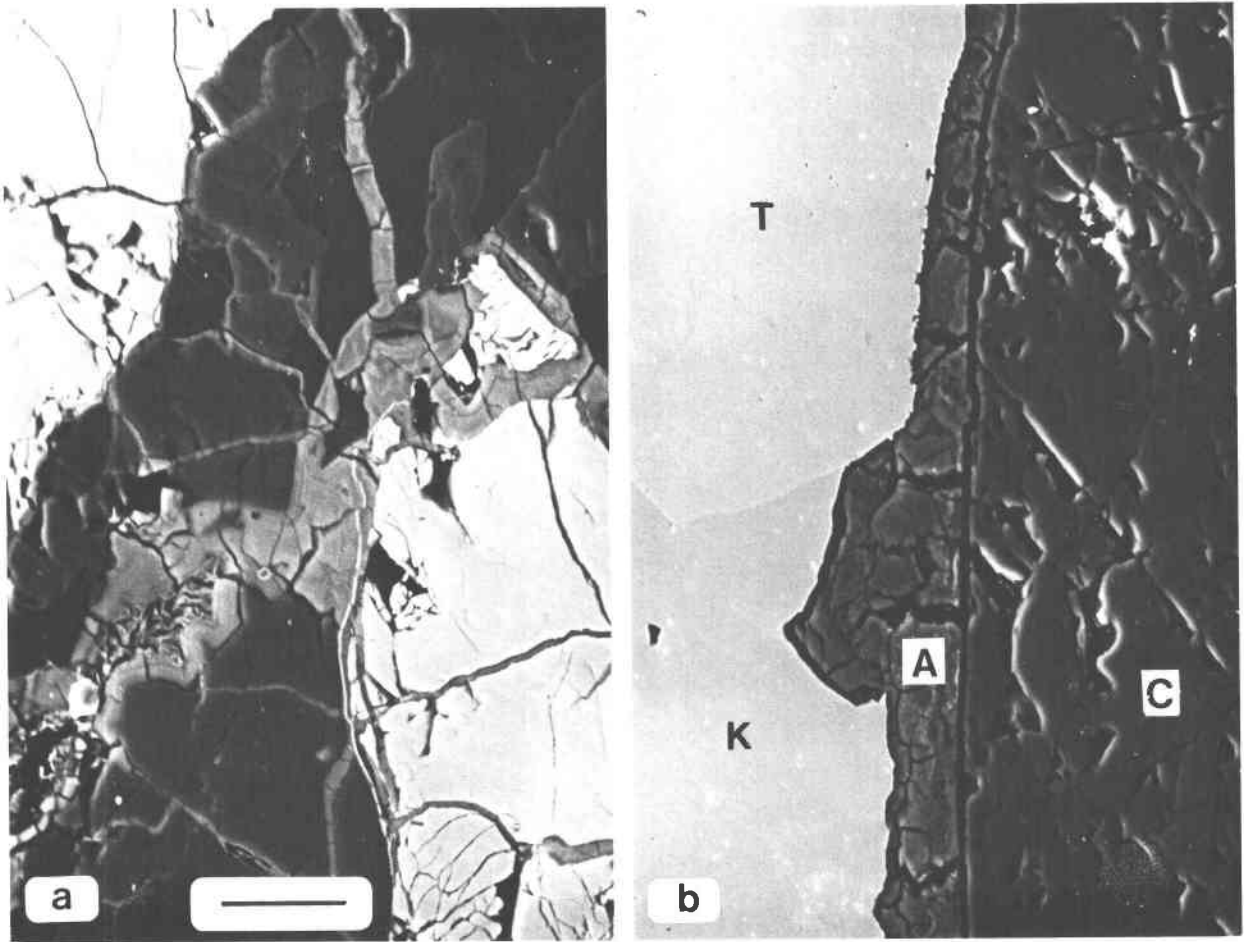


Fig. 3. Backscattered-electron images of akaganéite associations in EET 82606 (L6). (a) Akaganéite-goethite veins (dark gray) through troilite (light gray) and silicates (dark). Growth contours in akaganéite are typical of transport reactions. Scale bar = 25  $\mu\text{m}$ . (b) Taenite (T) and kamacite (K) in contact with a thin band of akaganéite (A) invading metal at a previous interface between metal and chlorapatite (C). Scale as in (a). See text for further discussion.

ical occurrences, suggests that aging is much slower in the Antarctic environment.

#### Source of Cl

What is the source of the Cl that plays this important role in the formation of the corrosion product akaganéite in Antarctic meteorites? Chlorapatite is the only well-characterized Cl-containing mineral that occurs in iron meteorites (Buchwald, 1975, 1984). Although chlorapatite may contain as much as 5 wt% Cl, it is sporadically dispersed in comparatively rare silicate-containing inclusions that could not possibly supply the amount of Cl that is observed. Three other possibilities remain: the metal itself, the mineralogical chimera lawrencite, or introduction from the terrestrial environment by the mechanism outlined above.

Although it is not the interpretation given by Berkey and Fisher (1967), they nevertheless have persuasively

shown that the metal of iron meteorites contains little Cl. Their neutron-activation analyses show very low levels of Cl in unweathered metal and suggest an upper limit of 10 ppm Cl (probably very high). As akaganéite replaces kamacite in approximately equal volumes, Cl must be introduced from some other source to provide the high levels that are observed.

The mineral lawrencite ( $\text{FeCl}_2$ ) has a long and controversial history that will be treated in detail elsewhere. The name has been used commonly in the meteoritic literature, particularly in reference to Cl-containing, semiliquid efflorescences associated with the corrosion of meteoritic metal. Jackson (1838) first reported Cl in meteorites in the severely corroded Lime Creek iron meteorite find. His claim that the Cl was indigenous to the meteorite was countered promptly in an insightful paper by Shepard (1842). Jackson and Hayes (1844) answered with what appears to have been an overpowering, even if by modern



eyes largely unresponsive, rebuttal. Later J. Lawrence Smith (1855, 1874, 1877) reported observing the "protochloride of iron" in the solid state in the Tazewell and Smith's Mountain iron meteorites. Insufficient chemical and physical data were given to characterize the material with any certainty, but the idea of an iron chloride mineral became accepted. Daubrée (1877) introduced the name lawrencite to honor the discoverer, and later Smith (1883) used the term himself. The name has been accepted by modern authorities, sometimes with equivocation, and continues to be used despite the lack of even a minimal description of natural material in the literature (Buchwald, 1977). In the course of this work we have examined a number of dried residues from typical "lawrencite" occurrences, and in every case an akaganéite X-ray diffraction pattern has been obtained (Buchwald and Clarke, 1988).

The presence of Cl in iron meteorite finds is real, of course, the older literature having been reviewed by Cohen (1903). Recently it has been shown (Buchwald, 1975, 1977, 1986) for iron meteorites found embedded in temperate-zone soils that the Cl is introduced from the groundwater to which these meteorites have been long exposed. During exposure, Cl—along with O<sub>2</sub> and H<sub>2</sub>O—decomposes the Fe alloy. The corrosion mechanism outlined above expands on this earlier work and explains the accumulation of Cl in terms of akaganéite. Cl accumulation apparently begins as the meteorite lands, and akaganéite continues to play a role in corrosion as long as metal remains.

Antarctic meteorites add a new dimension to this picture, as many of them have never been buried in soil. For example, the Allan Hills meteorites, found on the wind-swept bare ice fields at an altitude of about 2000 m, contain akaganéite with up to 5.0 wt% Cl. This Cl was apparently introduced from the snow and ice of the Antarctic environment. Unfortunately, Cl analyses of the ice in contact with the meteorites are unavailable, but concentrations may well be in the low ppm range as was found by Heumann et al. (1987) and Mulvaney et al. (1988) for sea-shelf locations. The annual average temperature at the Allan Hills is low (−30 °C), and precipitation is low and difficult to measure. The meteorites have presumably spent most of their residence time on Earth within the ice, being eventually exposed by the strong katabatic winds out of the South that remove surface snow and evaporate the upper part of the snow and ice fields. The ultimate source of the low levels of Cl in the snow and ice is probably largely sea spray from the oceans, with an increment of hydrogen chloride exhalations from volcanic action. The Cl is carried as either an aerosol or a gas over the snow and ice fields, where a portion is incorporated in newly formed snow and ice deposits (Duce et al., 1973; Heumann et al., 1987; Shaw, 1988). Cl may also be concentrated in the residual ice surface, being preferentially left behind as ice sublimates.

Concern over the ozone layer, among other reasons, has made the halogen geochemistry of Antarctica a topic of

much current interest. Irregularities in halogen abundances have been noted in both Antarctic meteorites and rocks (Dreibus and Wänke, 1983; Dreibus et al., 1985; Heumann et al., 1987). Although our findings do not speak directly to these anomalies, the weathering mechanism proposed is an obvious source of Cl contamination for metal-containing meteorites. Weathering-product akaganéite accumulates Cl, perhaps in part from decomposing chlorapatite in some meteorites, but certainly in the main from the local environment. The process apparently has a high Cl<sup>-</sup> ion specificity. A highly mobile anion is required to provide charge balance at the metal interface, bringing large numbers of Cl<sup>-</sup> ions to the region of akaganéite formation. The ionic radius of the Cl<sup>-</sup> ion fits the requirements for tunnel-site occupancy in the akaganéite structure and is incorporated in it and becomes localized. This ionic selectivity provides a rationale for unexpected halogen-abundance relationships. Under these circumstances, one would not expect to see a relationship between the sea spray-derived component of the Cl present in akaganéite and Na and K. Interpretations of isotopic data, such as <sup>36</sup>Cl age determinations, could also be affected.

#### Antarctic environmental factors

The areas where Antarctic meteorites have been found are notoriously stormy. Wind velocities are frequently more than 20 m/s, and under these circumstances, blowing mineral grains and ice crystals become mild abrasives. This is probably why we have not yet seen an Antarctic iron meteorite with a heavy corrosion scale. Meteorites from temperate latitudes often display coatings several millimeters to centimeters thick, whereas Antarctic iron meteorite coatings rarely exceed 1 mm and are usually only 0.1 mm thick. The severe winds combined with corrosive processes in Antarctica produce distinctive specimen-surface morphologies. Corrosion preferentially attacks kamacite, and since abrasive particles in due time remove most of the akaganéite, iron meteorites often show a pronounced surface relief. On the surface of Allan Hills A77283, for example, the more resistant taenite lamellae stand in relief, displaying a delicate Widmanstätten pattern and revealing the internal octahedral structure of the meteorite (Clarke et al., 1981). On Derrick Peak A78009 and other specimens of that fall, the effect is even more dramatic: the large, hard schreibersite crystals protrude as irregular, bronze-colored knobs 0.5–5 mm above the rust-colored surface, an effect that is unknown from any other iron meteorite (Clarke, 1982b). The reason is, no doubt, that the rate of abrasion due to wind-carried particles is significantly greater than the rate of corrosion-product accumulation.

The absence of liquid water because of the low Antarctic temperatures is an obvious limitation to corrosion development. The meteorites, however, are dark colored, and they do absorb heat during limited periods of exposure to the Sun's radiation. Specimens found on the ice on sunny days have, on occasion, been observed to be in

contact with tiny pools of water. Schultz (1986) measured the internal temperature of a stony meteorite lying on the blue ice surface of the Allan Hills and found that on 2 austral summer days of the 21 the experiment ran, temperatures were just above the freezing point of water. Our observation, mentioned above, of botryoidal lepidocrocite in some corrosion assemblages strongly suggests that liquid water is sometimes present. Marvin (1980) identified hydrated magnesium carbonates and sulfates in white surficial deposits on Antarctic stony meteorites. The deposits were explained as formed from salts leached from the meteorites by liquid water produced from snow on sun-warmed meteorite surfaces.

### Introduced elements and minerals

As may be seen from the last two columns of Table 3, foreign elements and minerals have been incorporated into the akaganéite corrosion assemblages. Even in the interior of the Antarctic ice cap, wind-transported mineral grains from eroded nunataks are apparently ubiquitous and may adhere to the corroding meteorite, ultimately to be cemented to it by growing iron oxides. Most particles are quartz, in the 10 to 100- $\mu\text{m}$  range, but olivine, feldspar, amphibole, and zeolite grains have also been observed.

On decomposing, the mineral grains release small amounts of Al, Si, Ca, and K, which may become incorporated into the growing akaganéite or into later-forming lepidocrocite. The amounts of these elements are generally low, on the order of a few tenths of 1 wt%, but occasionally, as in Purgatory Peak A77006, the concentrations in akaganéite reach 1.1 wt% Mg and 0.2 wt% Al. S, probably as sulfide, is also present in akaganéite, usually in the range of 0.1–1.0 wt%. S has been put in parentheses in Table 3 because it probably is not a foreign ion but may originate from decomposition of troilite in the meteorite. P is sometimes present in akaganéite, usually in the range of 0.1–1.0 wt%, but occasionally reaching the 5 wt% level. This is to be expected, however, as most iron meteorites contain appreciable amounts of schreibersite. On penetrating the atmosphere, sulfides and phosphides located at the surface melt preferentially and solidify to very fine grained multicomponent eutectics in the fusion crust. These components are the first to be attacked by corrosion and are responsible for the occasional high P and S concentrations of akaganéite in the initial stages of corrosion. Later, most of the P and S are leached out if liquid water is available.

### Terrestrial age and location

In a general way, one would expect that the degree of weathering reflects the terrestrial age of the meteorite. That this is not the case is demonstrated by the age determinations of Nishiizumi (1984) and Nishiizumi et al. (1987), given in Tables 1 and 4. We agree with Nishiizumi's conclusion that the terrestrial age in the Antarctic is a composite of two unknowns, the time buried in the ice and the time exposed on the surface. Corrosion rates

for meteorites either buried or exposed are unknown. It is reasonable to assume, however, that rates at the surface are higher and that this is where most of the corrosion takes place.

We observed no correlation between the location and the severity of corrosion except for the exposed mountain-side location for the Derrick Peak specimens mentioned above. We did note, however, that foreign substances were more pronounced on meteorites found among rock debris in the mountain ranges than on those from the blue ice fields of the Allan Hills. Some specimens were visibly affected on the surface, having yellowish or whitish incrustations. On such specimens, such as Derrick Peak, Inland Forts, and Purgatory Peak, calcite was identified in veinlets and vugs, deposited together with lepidocrocite or introduced into cracks of akaganéite. The presence of calcite as crystalline veinlets is further documentation of the sporadic presence of liquid water.

### CONCLUSIONS

Akaganéite, previously regarded as a rare mineral, is in reality a significant corrosion product of the Fe-alloy phases in Antarctic meteorites. Work in progress suggests that it is equally important in the corrosion process of metal-bearing meteorites in all environments. Akaganéite's particular importance derives from its crystal structure that readily incorporates  $\text{Cl}^-$  ions attracted to the corrosion front and from its small crystal size that greatly enhances its water adsorption capacity.  $\text{Cl}^-$  ions positioned in the tunnel sites of akaganéite are readily released under moist conditions to move again to the akaganéite- $\text{Fe}^0$ -interface region, where they serve to depassivate the  $\text{Fe}^0$  and reinitiate corrosion. Invading akaganéite may again incorporate the  $\text{Cl}^-$  ions, providing a reservoir of corrosive agent following just behind the reaction front.

Purer forms of akaganéite typically contain 4–5 wt% Cl, but, as it is often intergrown with Cl-free goethite on a microscopic scale, microprobe analyses often yield somewhat lower Cl values (0.3–4 wt%). Akaganéite forms in situ by replacement of metal and contains Ni when formed from meteorites. The Ni level reflects the composition of the phase from which it formed, having Fe/Ni ratios of about 16 when formed from kamacite and about 4 when formed from taenite. On aging, akaganéite loses Cl and decomposes in situ to intimate intergrowths of goethite and maghemite that retain the Ni of the akaganéite. On a given meteorite, therefore, akaganéite will be located at the actively corroding interface, while goethite and maghemite will be found nearer the surface as "dead" oxides. Lepidocrocite is occasionally found as crusts and fillings, deposited on or in the other oxides after deposition from solution.

Cl apparently starts accumulation on meteoritic metal surfaces upon landing. Over time, very small amounts of Cl are sufficient to destroy large iron bodies, because of its quasi-catalytic role in the corrosion reaction. Our ob-

servations demonstrate that the Antarctic environment is sufficiently rich in Cl, be it ultimately from air-borne sea spray or from volcanic action (Antarctica has one active volcano, Mount Erebus, on Ross Island), to corrode meteoritic metal. Although the Antarctic ice may well contain Na as well as Cl, it is the anion that is both selectively attracted to the metal surface and incorporated into the precipitating akaganéite. There is no site for the large Na cation in the corrosion products. Precipitating akaganéite and lepidocrocite may entrap windblown mineral particles from eroding mountain ranges. These particles slowly decompose and provide foreign ions that become incorporated in the various corrosion products.

Considering only bulk composition, all iron meteorites would be expected to be equally susceptible to corrosion. Variations in structure and their associated mineralogical relationships are, however, responsible for important differences. The electrochemical potentials established between kamacite, taenite, schreibersite, and troilite account for differing levels of corrosive activity. A meteorite rich in large-angle grain boundaries (IIB, IIIA) or in inclusions (IA) is more exposed to corrosion attack than homogeneous, coarse-grained meteorites (IIA) or heterogeneous, but inclusion-poor duplex meteorites (IVB). The fusion crust on iron meteorites, being largely magnetite, will be noble relative to the bulk meteorite and will enhance the attack on metal immediately below the fusion crust. Although time must be a factor in the amount of corrosive activity to which a given specimen is exposed, the complexities of individual residence histories do not lead to a recognizable correlation between degree of weathering and terrestrial age.

The reason for the alarming breakdown of some meteorites in museum collections is that akaganéite resides in the interfaces between uncorroded metal and inactive iron oxides. Moisture provided by ambient humidity slowly penetrates the oxides and reinitiates active corrosion under what may appear to be a benign crust. Suddenly, what appeared to be a substantial meteoritic mass crumbles. Protective measures include flushing Cl from the crust and reducing oxygen and humidity levels. There is no need to resort to the doubtful mineral lawrencite to explain the corrosion of meteoritic metal. Phenomena previously attributed to lawrencite by some authors are readily explained by the well-characterized mineral akaganéite.

The Antarctic meteorites preserve the initial steps in the degradation of meteorites. Because the temperature most of the time is far below the freezing point and because the air is very dry, the decomposition of akaganéite to other minerals such as goethite, maghemite, and magnetite is inhibited. The full decomposition of akaganéite may, however, be studied on meteorites recovered from more temperate climates.

The specificity of the Cl accumulation process in metal corrosion must be considered in studies that involve Cl elemental and isotopic abundances. Geochemical rela-

tionships that might be expected under other circumstances may not hold where corroded metal is involved.

A final conclusion is that the corrosion mechanism proposed here and developed from studies of Antarctic meteoritic metal has much broader implications for ferrous metal corrosion. Work in progress convinces us that this mechanism is fundamental to meteoritic metal corrosion in all environments. Preliminary studies suggest its importance for archeological ferrous metals and for structural metal under some circumstances.

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