THE AMERICAN MINERALOGIST, VOL. 52, JULY–AUGUST, 1967

SECONDARY MINERALS PRODUCED BY WEATHERING OF THE WOLF CREEK METEORITE

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ABSTRACT

Specimens of the Wolf Creek iron meteorite have been almost completely altered to secondary minerals by weathering. The specimens are a mixture of goethite and nickelian maghemite with small amounts of jarosite, apatite, lipscombite, a nickel serpentine, and two new minerals—reevesite,[1] $Ni_6Fe_2(OH)_{16}CO_3 \cdot 4H_2O$ (the nickel analog of pyroaurite), and cassidyite,[1] $Ca_2(Ni, Mg)(PO_4)_2 \cdot 2H_2O$ (the nickel analog of collinsite). The phosphate minerals have been formed by the weathering of the phosphide schreibersite.

INTRODUCTION

The Wolf Creek crater in Western Australia (19°11′S, 127°48′E) was first reported by Reeves and Chalmers (1949). It was observed from an aircraft in June 1947 by Reeves and two companions during an aerial survey, and was reached on the ground two months later. It was independently located and its meteroritic origin suspected by Guppy and Matheson early in 1958 when they were preparing a geological map of the region from air photographs. In November 1948 the crater and its surroundings were mapped by a geological party from the Commonwealth Bureau of Mineral Resources (Guppy and Matheson, 1950). Subsequent accounts of the crater have been published by Cassidy (1954) and McCall (1965), and LaPaz (1954) described some of the meteoritic material collected by Cassidy.

Henderson and Mason visited the crater in 1963 while on an expedition sponsored by the National Geographic Society, and collected the specimens on which this paper is based. We investigated the geology of the crater and our observations corroborated the published accounts. However, we disagree with McCall (1965, p. 988 and Fig. 36) that the quartzite on the crater rim is solid outcrop, the result of "gentle updoming" (p. 989). Our observations indicate that the rim quartzite is completely overturned. The surface of crater mound itself and the ground for about 400 yards from the base of the mound consist of laterite. This laterite is well exposed in the interior crater walls. It forms the crest of the crater rim at the lowest points (in the south and southwest sections); elsewhere it is capped by quartzite. The lower surfaces of the quartzite have an iron oxide varnish, frequently with laterite cemented to them; we believe this is the original contact between the laterite and the quartzite, in-

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[1] Approved in advance of publication by the Commission on New Minerals and Mineral Names, IMA.

verted by the "flip-over" or folding outward of the rocks as a result of the meteorite impact. The regional geology shows 50 feet of Tertiary laterite underlain by quartzite below a coating of desert sand. Quartzite and laterite in normal succession are exposed in low outcrops about a mile west of the crater; between this area and the laterite surface around the crater mound, the ground is covered with sand and vegetation.

THE METEORITES

The most remarkable feature of all the meteoritic material that has been collected at the Wolf Creek crater is its extremely weathered nature. The specimens consist entirely or almost entirely of iron oxides. We have cut up some forty masses, including one weighing about 250 kg, and have found only a few metal particles, mostly microscopic in size, and with occasional crystals of schreibersite, the latter partly or completely altered to phosphate minerals.

The extremely weathered state of the meteoritic material might be explained by one or more of the following factors:

1. The meteorite landed long ago, giving ample time for weathering and oxidation. The crater is presumably post-Miocene, since it disrupts a surface laterite believed to be of that age. The good state of preservation of the crater argues for a rather young age, but erosion in this desert country of low relief is very slow. McCall says "The morphological state of the crater probably limits the possible age to Pliocene or at the very latest Plio-Pleistocene."
2. The meteorite contained a considerable amount of lawrencite $(Fe,Ni)Cl_2$, which led to rapid decomposition.
3. The extreme shocking of the meteorite material by the impact made it peculiarly susceptible to weathering.

The recent discovery of small masses of unaltered nickel-iron, not at the crater itself but about 4 km to the southwest (Taylor, 1965), suggests that the third factor may be the most significant one. The unaltered metal has the structure of a medium octahedrite, and contains 8.6 percent Ni. On the other hand, absolute proof is lacking that the specimens obtained by Taylor and those from the crater itself belong to one and the same meteorite. It is not impossible, although certainly improbable, that they represent two different falls at different times.

In a few of the cut specimens sparsely disseminated metallic particles are visible. Analysis of one with the microprobe gave 21.3 percent nickel. The high nickel content probably results from selective enrichment during weathering.

The weathered meteorites are made up almost entirely of goethite and maghemite, with accessory amounts of jarosite, a nickel serpentine, apatite, lipscombite, reevesite (the nickel analog of pyroaurite), and cassidyite (the nickel analog of collinsite). A little opal, presumably introduced by terrestrial waters, was found in some cavities. Chalmers (in Reeves and Chalmers, 1949) and McCall (1965) state that hematite is present in these weathered meteorites; however, we have not found any. LaPaz (1954) recorded "a considerable amount of bright yellowish-green zaratite"; however, all the green secondary material examined here was a nickel serpentine. Notes on the individual minerals follow.

MINERALOGY

Goethite: This mineral is the major constituent of the weathered Wolf Creek meteorites. In thin sections it is reddish-brown and translucent. Microprobe analyses show that it contains small and varying amounts of nickel, the amount of NiO ranging from 0.7 to 1.3 percent. Cobalt was also detected, in amounts up to 0.3 percent CoO.

Maghemite: This mineral is present in lesser amount than goethite, but it is intimately mixed with it and renders these weathered meteorites quite magnetic. Many of the individual meteorites show strong polarity. Microprobe analyses show that the maghemite contains nickel in considerably greater amount than the goethite; the amount is variable and ranges up to a miximum of 8.7 percent NiO. Cobalt can also be detected in small amounts, ranging up to a maximum of 0.6 percent CoO. The mineral gives a good spinel-type X-ray powder photograph, but the high-angle lines are diffuse, probably because of small crystallite size or variable composition or both. The unit cell edge is 8.36 Å, intermediate between that of Fe_3O_4 (8.391 Å) and γ-Fe_2O_3(8.339 Å). Mossbauer analysis (E. Sprenkel-Segal, pers. comm.) shows that essentially all the iron is in the ferric state. The mineral can be described as a nickelian maghemite.

Reevesite: This mineral occurs as bright yellow fine-grained aggregates lining cavities and cracks in the weathered meteorites. In thin sections it is clear golden-yellow, stained brown in places by minute grains of goethite. The individual crystallites are hexagonal platelets up to 0.1 mm in diameter and 0.02 mm thick. The refractive indices are $\omega = 1.735$, ϵ about 1.65 (ϵ is difficult to measure directly and has been estimated from the birefringence).

The X-ray powder photograph is closely comparable with that of pyroaurite, $Mg_6Fe_2(OH)_{16}CO_3 \cdot 4H_2O$. Qualitative analysis showed nickel and iron as major constituents, and the presence of carbonate. These data indicate that the ideal formula of reevesite is $Ni_6Fe_2(OH)_{16}CO_3 \cdot 4H_2O$, which requires 51.6 percent NiO and 18.4 percent Fe_2O_3. Microprobe analyses confirmed nickel and iron as major constituents, and showed about 0.2 percent CoO and no detectable magnesium. Nickel and iron varied inversely in different areas of the mineral, higher nickel

TABLE 1. X-RAY POWDER DATA FOR REEVESITE FROM WOLF CREEK, WESTERN AUSTRALIA; 11.46 CM DIAMETER CAMERA, Fe-Kα RADIATION. INDEXED ON A UNIT CELL HAVING $a=6.15$ Å, $c=45.61$ Å

hkl	$d_{calc.}$	$d_{obs.}$	I	hkl	$d_{calc.}$	$d_{obs.}$	I
0 0 6	7.602	7.63	100	1 3 4	1.465	1.463	5
0.0.12	3.801	3.80	73	2.0.26	1.465		
1 1 6	2.851	2.82	12	2.2.12	1.425	1.426	6
2 0 2	2.645	2.65	6	0.2.28	1.390	1.389	2
0 2 4	2.593	2.60	81	0.1.32	1.377	1.378	3
0 2 7	2.465	2.47	28	1.2.26	1.323	1.325	4
2 0 8	2.413	2.41	17	4.0.10	1.278	1.280	6
0.2.10	2.300	2.30	61	2.0.32	1.257	1.257	1
2.0.14	2.062	2.06	8	0.4.14	1.233	1.236	1
0.2.16	1.946	1.946	48	4.0.16	1.206	1.208	1
2 1 7	1.923	1.924	6	0.4.20	1.150	1.151	1
2.0.20	1.732	1.731	20	3.2.16	1.123	1.123	1
0.2.22	1.636	1.635	15	2.0.38	1.094	1.094	1
1.1.24	1.617	1.623	15	1.3.28	1.094		
2 2 0	1.537	1.537	33	5 0 2	1.064	1.064	1
0.1.29	1.508	1.508	34		1.064	1.064	1
1.2.20	1.509			1.3.31	1.042	1.043	1
1 3 1	1.476	1.477	4	2 4 1	1.006	1.006	1

corresponding to lower iron and vice versa. The maximum nickel content, calculated as the oxide, is 52.1 percent NiO and the corresponding amount of iron oxide is 18.1 percent Fe_2O_3, close to the ideal formula.

Reevesite is hexagonal—rhombohedral; the unit-cell dimensions are $a=6.15$ Å, $c=45.61$ Å, $c/a=7.416$. The X-ray powder pattern is presented in Table 1.

The calculated density for the ideal formula of reevesite is 2.78. The actual density could not be measured accurately because of the impossibility of separating pure material, but centrifuging samples in acetone-methylene iodide mixtures indicated a density close to 2.80.

Since pyroaurite has a hexagonal dimorph, sjögrenite, the material was carefully examined for a possible hexagonal dimorph of reevesite. This was not found, but if it were present in small amount admixed with reevesite it could go undetected.

The mineral is named reevesite in honor of Dr. Frank Reeves, who was responsible for the discovery of the Wolf Creek meteorite crater in 1947. The original material is deposited in the collections of the U. S. National Museum.

Cassidyite: This mineral occurs as thin crusts and small spherules in cavities and cracks in the weathered meteorites. The color ranges from pale green to bright green evidently reflecting a variable nickel content. In thin section it is colorless and finely fibrous in structure. The refractive indices evidently vary somewhat with the nickel content: $\alpha = 1.64 - 1.65$, $\gamma = 1.67 - 1.68$, $\gamma - \alpha = 0.025$; the fibrous crystals are length-slow.

The X-ray powder photograph is closely comparable with that of collinsite, $Ca_2(Mg,Fe)(PO_4)_2 \cdot 2H_2O$. Microprobe analyses showed that the calcium and phosphorus contents are very uniform, but nickel and magnesium vary inversely. The mean of a number of analyses is CaO $= 32.3$ percent, $P_2O_5 = 39.2$ percent; NiO ranged from 6.4 percent to 16.2 percent, MgO from 5.7 to 2.2 percent. Iron was not detectable, but a small amount of cobalt, equivalent to 0.4 percent CoO is present. With more than about 8 percent NiO the atomic proportions of nickel exceed those of magnesium; if collinsite is defined as a mineral containing $Ca_2Mg(PO_4)_2 \cdot 2H_2O$ as its major component, and cassidyite as the isostructural mineral with $Ca_2Ni(PO_4)_2 \cdot 2H_2O$ as its major component, then the material from Wolf Creek contains both nickelian collinsite and magnesian cassidyite. The type collinsite from Francois Lake, British Columbia can be more precisely characterized as a ferroan collinsite.

TABLE 2. X-RAY POWDER DATA FOR CASSIDYITE FROM WOLF CREEK, WESTERN AUSTRALIA; 11.46 CM DIAMETER CAMERA, Fe-Kα RADIATION. INDEXED ON A UNIT CELL HAVING $a = 5.71$ Å, $b = 6.73$ Å, $c = 5.41$ Å, $\alpha = 96°49.5'$, $\beta = 107°21.5'$, $\gamma = 104°34.9'$

hkl	$d_{calc.}$	$d_{obs.}$	*I*	*hkl*	$d_{calc.}$	$d_{obs.}$	*I*
010	6.371	6.26	13	$\bar{2}02$	2.230	2.23	38
001	5.046	4.98	13	$\bar{1}\bar{2}2$	2.108	2.11	22
$\bar{1}10$	4.800	4.87	13	$1\bar{3}1$	2.085	2.08	28
$\bar{1}01$	4.460	4.47	15	$\bar{2}\bar{1}2$	2.057	2.05	21
$\bar{1}\bar{1}1$	3.532	3.49	38	$1\bar{2}2$	1.977	1.993	24
$1\bar{1}1$	3.233	3.23	65	$\bar{2}30$	1.961	1.961	23
101	3.125	3.13	48	$\bar{3}11$	1.898	1.913	10
$0\bar{2}1$	2.992	3.03	95	$\bar{1}\bar{3}1$	1.864	1.862	18
$\bar{2}01$	2.717	2.73	16	$0\bar{3}2$	1.824	1.824	27
$\left\{ \begin{matrix} 1\bar{2}1 \\ \bar{1}21 \end{matrix} \right\}$	$\left\{ \begin{matrix} 2.690 \\ 2.689 \end{matrix} \right\}$	2.70	100	$\bar{3}20$	1.761	1.753	32
				003	1.682	1.689	33
$\bar{1}02$	2.653	2.67	79	$\bar{3}\bar{1}1$	1.664	1.660	46
$0\bar{1}2$	2.535	2.54	21	$\bar{2}\bar{3}1$	1.529	1.530	23
021	2.470	2.47	21				

Cassidyite is triclinic; the unit-cell dimensions are $a = 5.71$ Å, $b = 6.73$ Å, $c = 5.41$ Å, $\alpha = 96°49.5'$, $\beta = 107°21.5'$, $\gamma = 104°34.9'$. The spacings and intensities of the lines in the X-ray powder pattern are given in Table 2.

The density of cassidyite has not been directly measured, because of the small amount available and the difficulty in freeing it from adhering goethite and reevesite. From the unit-cell dimensions and the composition, the calculated density of $Ca_2Mg(PO_4)_2 \cdot 2H_2O$ is 2.96 and that of $Ca_2Ni(PO_4)_2 \cdot 2H_2O$ is 3.26. From these data the density of natural cassidyite is 3.1–3.2.

Cassidyite is named in honor of Dr. William A. Cassidy, who mapped the Wolf Creek crater in 1953. Type material of this mineral is deposited in the collections of the U. S. National Museum.

Lipscombite: This mineral occurs as dull green crusts lining lath-shaped cavities which were originally schreibersite crystals. Occasionally a little schreibersite remains. The refractive index is about 1.86, and the birefringence is low, 0.01 or less; dispersion is strong, and in thin section the mineral shows anomalous bright blue interference colors. It is weakly pleochroic, yellow-green to green. The unit cell dimensions are $a = 7.33$ Å, $c = 12.76$ Å, $c/a = 1.741$ in good agreement with the data of Lindberg (1962). Microprobe analyses show iron and phosphorus as major components; the mineral contains about 0.9 percent NiO and 0.1 percent or less of CoO and MgO. It is remarkable that the weathering of schreibersite, a nickel-rich mineral, has resulted in an almost nickel-free iron phosphate. Possibly nickel is not readily accepted in the lipscombite structure, or the nickel remained in solution when the lipscombite was deposited. The pale color of the Wolf Creek material suggests that it is essentially a ferric phosphate with little or no ferrous iron.

This is the second record of lipscombite as a mineral, the first being a manganoan lipscombite described by Lindberg (1962) as a secondary mineral in the Sapucaia pegmatite, Brazil.

Other minerals. Other minerals found in small amounts within the weathered Wolf Creek meteorites include jarosite (as small crystals in cavities which probably held troilite), apatite, opal, and a nickel serpentine. X-ray and microprobe examination show that the latter mineral is the nickel analog of clino-chrysotile; Dr. George Faust will describe it in detail and name it.

DISCUSSION

The physicochemical conditions accompanying the weathering of the Wolf Creek meteorites resulted in complete or almost complete conversion of the iron to the ferric state (mainly into goethite and maghemite), whereas the nickel was oxidized to the bivalent state. Some of the nickel originally taken into solution was reprecipitated by residual nickel-iron, judging by the high nickel content of the occasional residual metal particles in contrast to the nickel content of the original meteorite (8.6 percent, according to Taylor, 1965). Much of the nickel was precipitated as nickelian maghemite, and some as goethite. However, a considerable part must have been carried away in solution, since the weathered specimens contain much less total nickel than the original meteorites (assuming Taylor's specimens are representative). This behavior can be understood in terms of the different properties of nickel and iron in aqueous solutions. Iron in aerated solutions readily oxidizes to the ferric state and precipitates as ferric hydroxide even at low pH, about 2–3. Nickel is not oxidized beyond the bivalent state under conditions of weathering, and does not precipitate as a hydroxide until the pH is about 7. Hence nickel is much more stable in solution under weathering conditions than is iron, and can thus be removed by circulating water. The solutions that attacked the Wolf Creek meteorites were probably quite acid from the decomposition of troilite in the meteorites.

A remarkable feature of these weathered meteorites, and one not fully understood, is that they appear to be "pseudomorphs" of the original metal fragments. Whereas pieces of manufactured iron, and native iron such as that from Disko Island, usually disintegrate on weathering by the flaking-off of successive layers of oxide, the Wolf Creek meteorites seem to have remained intact. The great expansion accompanying oxidation has apparently been accommodated without disrupting the specimens. Individual specimens have a "breadcrust" surface, and a system of radial cracks. When such specimens are cut in half they frequently show a small cavity at the center (sometimes lined with reevesite). A possible factor in the preservation of the Wolf Creek specimens is the entire absence of frost in this tropical region. Certainly in a temperate climate freezing and thawing in winter would probably soon disintegrate such specimens.

Acknowledgments

We would like to express our appreciation to the National Geographic Society for its financial support of the expedition on which this material was collected. We are indebted to Mr. Charles Fiori for his assistance with the electron microprobe analyses, to Dr. D. Appleman for providing computer refinement of the cell dimensions of reevesite and cassidyite, and to Dr. George Faust for his help in characterizing the nickel serpentine.

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Manuscript received, August 20, 1966; accepted for publication, December 1, 1966.