

## CHEMICAL AND MINERALOGICAL COMPOSITION OF TWENTY TYPICAL "LIMONITES"

ROLAND BLANCHARD, *Mount Isa, Queensland, Australia.*

For many years it has been known that limonite does not exist as a mineral; that the product formerly listed in textbooks as limonite ( $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) is ferric oxide monohydrate ( $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ), existing either as goethite or lepidocrocite, with variable amounts of adsorbed and capillary water (1).

It has been known likewise that the limonitic cellular boxwork or sponge structures, which form pseudomorphously after the cleavage or fracture patterns of sulfides and certain other oxidizing minerals in nature, are composed mainly of limonitic jasper (2), even though frequently they may be so embedded in or coated over with pulverulent limonitic particles as to be nearly obscured by the latter.

Despite these more specific identifications the average person, when he hears the term "limonite" used, thinks of it as denoting the reddish, yellowish or brownish deposits formed by decomposing iron-yielding minerals in nature without regard to the individual precipitate involved; and by common consent the word, in recent years, has become accepted as a collective term for designating all supergene ferric oxide precipitates in nature which have not been more specifically identified (3). As such the term serves a convenient and highly useful purpose, especially in field work, even though it is recognized that limonite as a mineral does not exist.

The wide variations in  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$  content of limonitic jasper in the cellular pseudomorphs has not always been realized, however; nor has the extent of the admixed impurities which are present, both in the jasper, and in the granular or pulverulent product for which the term limonite, perhaps, might be more specifically reserved.

In the cellular pseudomorphs, for example,  $\text{Fe}_2\text{O}_3$  content has been found to range from 11.4% to 73.1%; the complementary  $\text{SiO}_2$  content, from 72.6% to 13.5%. Moreover, a complex, made up of various intimately intergrown, usually fine-grained, supergene gangue carbonate minerals, not infrequently takes the place of limonitic jasper in the cellular pseudomorphs, either forming directly as boxwork or, more often, building upon or replacing the limonitic jasper subsequent to the latter's formation. Where a neutralizer is abundant in the ground water, as in limestone and certain other districts, the product is common. At Broken Hill (New South Wales) such supergene gangue carbonate matter, made up of a complex comprising minute intergrowths of calcite,

magnesite, rhodochrosite and siderite in varying proportions, may be present locally in amount exceeding the limonitic jasper of the cellular pseudomorphs (4). Upon weathering it yields sufficient pulverulent hydrated ferric oxide from the decomposing siderite to make the thoroughly weathered product, in the hand specimen, virtually indistinguishable from normal gossan.

Hydrated manganese dioxide also may be present, both as a replacement constituent of the limonitic jasper and as a free precipitate. Often its colour is dark brown instead of black. As such it is not readily distinguished in the hand specimen from the limonite in which it is embedded.

Gypsum, too, sometimes serves as the interstitial binding agent for granular limonitic particles (2), itself stained the same brownish colour as the limonite, and thus often mistaken for the latter. Although less general in occurrence than the supergene gangue carbonate it is abundant in some districts, and may constitute more than 25% of a gossan.

But disregarding these occurrences, and considering only the loosely granular or pulverulent, more strictly limonitic material, many impurities still are present. In numerous districts the basic sulfate, jarosite ( $K_2O \cdot 3Fe_2O_3 \cdot 4SO_3 \cdot 6H_2O$ ), is not separately distinguished, and is commonly mistaken for and misnamed "limonite." In districts where arsenopyrite is present scorodite ( $FeAsO_4 \cdot 2H_2O$ ) is common, often effectively hidden by the more abundant limonitic matter, especially if the percentage of scorodite is low and the mineral is well dispersed. If lead minerals are present in such districts mimetite ( $3Pb_3As_2O_8 \cdot PbCl_2$ ) frequently forms, and not uncommonly weathers in part to massicot ( $PbO$ ). Both mimetite and massicot, thus derived, are widespread in Australia, occurring without necessary regard for geographic or climatic conditions, and often so minutely dispersed through the limonitic matter as to be difficult to detect in the hand specimen (5). In humid climates organic salts of iron often form conspicuous coatings along rock fractures. Most of such organic salts are unstable and eventually alter to one form or other of the ferric oxides, but while they exist they may be readily mistaken for "limonite."

These references are sufficient to show that the ferric oxide component in gossans, usually referred to as "limonite," quite generally is contaminated with admixed impurities.

To furnish an idea of the nature and extent of such impurities, Table 1 is presented. It sets forth the analyses and calculated probable mineralogical compositions of twenty typical limonitic products of diverse origin and distribution, all of which in the hand specimen had the ap-

TABLE 1  
CHEMICAL AND MINERALOGICAL COMPOSITION OF "TYPICAL" LIMONITES\* ANALYSIS

No.	Probable Mineral Composition	% P <sub>2</sub> O <sub>5</sub>	% ZnO	% Cu	% As	% Fe	% Fe <sub>2</sub> O <sub>3</sub>	% Mn	% Mn <sub>2</sub> O <sub>3</sub>	% SO <sub>2</sub>	% K <sub>2</sub> O	% CaO	% MgO	% CO <sub>2</sub>	% Al <sub>2</sub> O <sub>3</sub>	% SiO <sub>2</sub>	% Cl	% Fe <sub>2</sub> S	% Calc. based H <sub>2</sub> O	% Loss based H <sub>2</sub> O	Sub. Total	Total	Description	
1	Opuntia Limonite Ferric oxide monohydrate Silica and alumina Miscellaneous	tr	tr	tr	tr	58.2	83.23	tr	tr	1.1	tr	0.7	tr	tr	0.4	1.3	tr	tr	.45	9.36	92.59	94.29	Raw from iron mill being open-pit mined. Mount Isa Mines (Queensland) scrap heap.	
2	Supergene gangue carbonate Siderite Limonite Ferric oxide monohydrate Hydrous manganese dioxide Miscellaneous	nd	nd	nd	nd	58.3	83.35	1.9	tr	tr	tr	0.15	tr	tr	0.2	tr	tr	tr	.12	1.24	.03	92.72	91.76	Porphyritic goethite (Copper Lane stone country rock.
3	Opuntia Limonite Ferric oxide monohydrate Silica Miscellaneous	nd	nd	tr	tr	59.6	83.35	tr	tr	13.2	tr	9.2	tr	tr	tr	tr	tr	tr	tr	5.92	6.70	100.00	100.00	Pitrite granular gozosa over iron country. United Verde ore body (Arizona). Collected 1924. (Queensland) scrap heap. Iron country rock.
4	Limonite Ferric oxide monohydrate Hydrous manganese dioxide Silica and alumina Miscellaneous	nd	nd	tr	tr	56.1	81.62	2.1	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	5.80	1.38	97.22	97.22	Limonite jasper with typical drabular cracks. Alabama mine. Kimberly (Nevada). Limestone country rock.
5	Semibentonite Limonite Ferric oxide monohydrate Hydrous manganese dioxide Silica and alumina Miscellaneous	nd	0.2	tr	tr	51.99	81.39	0.1	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	1.78	3.16	100.00	100.00	Cellular pseudomorph derived mainly 85% pyrrhotite, 10% tremolite, 4% pyrite, 2% hematite. Chloritized quartzite country rock.
6	Semibentonite Siderite Limonite Ferric oxide monohydrate Silica and alumina Miscellaneous	nd	0.2	tr	tr	48.2	81.39	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	2.02	7.24	11.69	82.89	Limonite cell-filling of No. 5
7	Limonite Hematite Ferric oxide monohydrate Silica Miscellaneous	nd	tr	tr	tr	60.5	81.39	tr	tr	1.2	0.35	tr	tr	tr	tr	tr	tr	tr	tr	.31	.40	12.94	82.89	Imperfect cellular boxwork and goethite pyrite orebody. Mount Isa (Queensland). Collected 1927. Mount Isa Popojoy country rock.
8	Malachite Supergene gangue carbonate Siderite Limonite Ferric oxide monohydrate Silica and alumina Miscellaneous	nd	2.2	tr	tr	49.1	81.39	tr	tr	0.5	0.18	0.6	0.1	1.5	0.6	14.7	nd	8.9	tr	7.70	3.8	100.00	100.00	Cellular pseudomorph derived from hematite. Semipalm Springs (California). Gabho country rock.
9	Malachite Supergene gangue carbonate Siderite Limonite Ferric oxide monohydrate Silica and alumina Miscellaneous	nd	1.7	tr	tr	58.0	81.39	tr	tr	0.9	0.25	0.2	0.2	0.8	0.2	1.6	nd	11.1	tr	2.4	.21	2.74	82.89	Cellular pseudomorph derived from chalcopyrite with lesser malachite. Mount Isa Mines (Queensland). Cemented limestone country rock.
10	Malachite Supergene gangue carbonate Siderite Limonite Ferric oxide monohydrate Silica and alumina Miscellaneous	nd	0.4	tr	tr	36.7	81.39	tr	tr	tr	2.3	0.4	0.4	2.6	0.2	32.1	nd	10.1	tr	.06	.05	90.24	90.24	Cellular pseudomorph derived from chalcopyrite with lesser malachite. Mount Isa Mines (Queensland). Cemented limestone country rock.
11	Malachite Supergene gangue carbonate Siderite Limonite Ferric oxide monohydrate Silica and alumina Miscellaneous	nd	0.5	tr	tr	52.8	81.39	tr	tr	0.5	0.10	1.7	0.2	1.8	0.2	6.3	nd	0.8	tr	.07	.06	89.76	89.76	Limonite cell-filling of No. 10.
12	Malachite Supergene gangue carbonate Siderite Limonite Ferric oxide monohydrate Hydrous manganese dioxide Silica and alumina Miscellaneous	nd	0.7	tr	tr	51.1	81.39	0.1	tr	tr	0.2	0.2	0.4	0.4	0.7	13.5	nd	11.1	tr	.10	.09	100.00	100.00	Cellular pseudomorph derived from cerussite with lesser malachite. Mount Isa Mines (Queensland). Cemented limestone country rock.
13	Malachite Supergene gangue carbonate Siderite Limonite Ferric oxide monohydrate Silica and alumina Miscellaneous	0.6	tr	tr	tr	40.3	81.39	0.1	tr	tr	0.4	0.2	0.2	0.9	1.4	27.6	0.005	11.4	tr	.03	.05	81.28	81.28	Cellular pseudomorph derived from cerussite with lesser malachite. Mount Isa Mines (Queensland). Cemented limestone country rock.
14	Semibentonite Supergene gangue carbonate Siderite Limonite Ferric oxide monohydrate Hydrous manganese dioxide Silica and alumina Miscellaneous	tr	1.6	tr	tr	21.4	81.39	0.05	tr	tr	0.4	0.2	1.4	2.2	50.0	tr	tr	4.5	tr	.01	.02	100.00	100.00	Cellular pseudomorph derived from cerussite with lesser malachite. Mount Isa Mines (Queensland). Cemented limestone country rock.
15	Semibentonite Supergene gangue carbonate Siderite Limonite Ferric oxide monohydrate Silica and alumina Miscellaneous	tr	3.7	tr	tr	49.6	81.39	tr	tr	tr	0.25	tr	2.2	1.2	10.5	tr	tr	11.1	tr	.03	.05	5.70	5.70	Limonite cell-filling of No. 14.
16	Semibentonite Supergene gangue carbonate Siderite Limonite Ferric oxide monohydrate Hydrous manganese dioxide Silica and alumina Miscellaneous	0.3	0.6	tr	tr	13.3	81.39	0.02	tr	tr	0.5	0.2	1.3	1.1	72.6	tr	tr	4.3	tr	.04	.04	85.43	85.43	Cellular pseudomorph derived from cerussite with lesser malachite. Mount Isa Mines (Queensland). Cemented limestone country rock.
17	Semibentonite Supergene gangue carbonate Siderite Limonite Ferric oxide monohydrate Hydrous manganese dioxide Silica and alumina Miscellaneous	6.0	0.9	tr	tr	29.7	81.39	1.8	tr	tr	0.5	0.6	3.1	22.6	0.110	10.3	tr	10.3	tr	.34	.34	100.00	100.00	Limonite derivative from arsenical silver-lead-zinc ore, Iron Hill district, Queensland, same country rock.
18	Semibentonite Supergene gangue carbonate Siderite Limonite Ferric oxide monohydrate Hydrous manganese dioxide Silica and alumina Miscellaneous	1.6	2.3	tr	tr	17.1	81.39	1.9	tr	tr	4.9	0.3	13.8	0.4	36.7	tr	tr	6.9	tr	.07	.07	4.83	4.83	Cellular pseudomorph derived from sulfide mixture of arsenical silver-lead-zinc ore, Iron Hill district, Queensland, same country rock.
19	Chromite Supergene gangue carbonate Siderite Limonite Ferric oxide monohydrate Hydrous manganese dioxide Silica and alumina Miscellaneous (including unlocated 0.013% As, much of remainder probably is organic matter)	nd	nd	nd	0.013	8.8	81.39	2.55	2.69	tr	tr	tr	0.2	1.8	72.2	3.8	tr	7.7	tr	.23	.23	27.86	27.86	Cellular derivative from impure chromite. Tiedagan mine, North Queensland, same country rock.
20	Fluorite Supergene gangue carbonate Siderite Limonite Ferric oxide monohydrate Hydrous manganese dioxide Silica Miscellaneous	nd	tr	tr	tr	11.4	81.39	15.1	15.1	tr	35.5	0.3	29.0	nd	0.7	13.6	tr	2.1	tr	.73	.73	71.30	71.30	Cellular derivative from impure chromite. Tiedagan mine, North Queensland, same country rock.

\* Theoretical limonite, minimum and goethite maximum. Hematite probably present in all cases except No. 3. MnO is included with limonite. Jasper. Part of Al<sub>2</sub>O<sub>3</sub> probably present as siliceous associated with chromite. For convenience all Al<sub>2</sub>O<sub>3</sub> is included with limonite. Jasper. Note: Fe<sub>2</sub>O<sub>3</sub> calculated from available Fe in all cases except No. 3. MnO calculated from available Mn in all cases. Analysis by P. F. Brown; Nos. 2, 3, 4, 7, 8, 9, 10, 11, 14, 15. Analysis by P. F. Brown; Nos. 5, 6, 12, 13, 16, 17, 18, 19, 20. Miscellaneous samples mainly identified and analyzed by P. F. Brown.

pearance of, and were commonly referred to, as "limonite" in the districts in which they occurred. They have been chosen as typical from a much larger group of analyses which the author has accumulated in his work during the past twenty-five years, and represent both normal and extreme types. Calculated mineralogical compositions are based upon combined analyses and microscope examination of the powdered material. In most cases analyses were carried only to one decimal. Exceptions are  $K_2O$  and  $Cl$ . The former was determined to the nearest 0.05%; the latter, to the nearest 0.005%.

In preparing the material for analysis, detectable country rock was excluded, as was all other observed extraneous material except the hypogene quartz of Nos. 14 and 16. Hypogene quartz could not be satisfactorily removed in those two instances without detriment to the supergene material.

Supergene gangue carbonate matter comprises the fine-grained, minutely-intergrown material which either formed more or less exclusively as the boxwork of No. 20, or was precipitated as a coating upon or replacement of the previously-formed limonitic jasper mentioned on page 37. No detectable hypogene gangue carbonate is involved.

Kaolin has been observed under the microscope replacing the supergene gangue carbonate complexes, but most of the alumina of the analyses probably represents minute specks of impure clayey matter deposited by ground water. Precipitation from ground water likewise accounts for the small content of silica in cases, such as No. 2, where normally no silica would be expected.

Because under the microscope no magnesium silicate was detected in any of the specimens, all magnesia is calculated as magnesite. In small amount it was identified in the eight specimens listed as containing it.

In all cases siderite was calculated to consume  $CO_2$  remaining after requirements of calcite and magnesite (also rhodochrosite in Nos. 18 and 20) had been met. It was identified in seven of the ten specimens listed as containing it.

"Miscellaneous" comprises mainly adsorbed and capillary water. In some instances it may include organic matter, and possibly small amounts of  $CO_2$ .

Hematite was not detected in powdered material of the twenty listed specimens other than in No. 7, where it was clearly distinguished as a fine-grained co-precipitate with much more abundant goethite.

Tunell has shown that, intergrown with goethite and jarosite, hematite is not uncommon as a supergene derivative in certain of the leached disseminated copper deposits of southwestern United States (6). Its

formation in small amount by spontaneous crystallization from hydrous ferric oxide under surface conditions has been established by Raymond (7).

It is noteworthy however that, except in the disseminated copper deposits where often it forms as a partial limonitic filling of the cavities vacated by the leached sulfides, or occurs as tiny veinlets along fractures, hematite as a supergene product has been observed only rarely in the Leached Outcrop Investigation. In gossans derived from massive or semi-massive sulfides it is virtually absent.

Because of its scarcity or complete absence in most of the material listed in Table 1, it thus seems necessary to conclude, from the analyses listed in the table, that ferric oxide monohydrate may and frequently does exist in porous gossans with too low a content of adsorbed and capillary water to conform with the theoretical formula ( $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) for limonite.

The twenty products listed in the table, though in a few instances comprising extreme types, are on the whole representative of the material which, as gossan, normally passes for "limonite." They illustrate both the wide variations in composition, and extent and nature of the impurities, present in such material.

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