SOME SOLUBLE CONSTITUENTS OF METEORITES

JOHN DAVIS BUDDHUE, *Pasadena, California.*

No doubt the most frequently recognized water soluble constituent of meteorites is lawrencite ($FeCl_2$) as it is doubtless responsible for the rusty spots so frequently seen on light colored stones. Its effect on irons is all too familiar to collectors. In spite of its commonness, such determinations as we have of the amount present are almost invariably calculated from the chlorine content. Since other chlorine compounds are sometimes present, such figures are likely to be too high. The largest amount so far reported is from the Mount Eldon (Arizona), graphite mass in which W. A. Sloane[1] found 1.980%. The writer found 1.64% by extraction with alcohol but some was lost.[2]

Numerous other water soluble salts have been reported from time to time. Thus the Lancé meteorite (France) is reported to contain 0.21% sodium chloride.[3] Maskelyne reported 0.44% calcium sulphate and 4.13% calcium sulphide in the Bustee stone (Oudh, United Provinces, India), while Dancer reported 0.76% sodium sulphide, 1.58% calcium sulphate and 0.01 calcium chloride in the same stone.[4] Berzelius reported 10.3% magnesium sulphate and vitriolic nickel (presumably nickel sulphate) in Alais (France) and Roscoe found 10.91%; Scheerer found sodium chloride in the Stannern stone (Moravia); and Shepard reported the sulphates of magnesium and sodium, the chlorides of calcium and magnesium, the hyposulphites of sodium and magnesium, and soluble silica in the Bishopville stone (South Carolina).[5] He also mentions that a sulphate of iron was found in the troilite of the Cosby Creek (Tennessee) iron. Baumhauer[6] reported a water soluble substance in the Knyahinya (Ruthenia) stone which reacted with turmeric paper.

Next to lawrencite, oldhamite is probably the best known of the water soluble meteoritic minerals. This mineral is an impure calcium sulphide which was discovered in the Bustee stone by Maskelyne[7] in a part of the stone which differs in other respects from the rest. Two analyses of the little nodules showed that it consisted of calcium sulphide plus about three per cent of magnesium sulphide. Calcium sulphate and carbonate, which were also found, were doubtless alteration products. He also reported it as somewhat doubtfully present in the Bishopville meteorite.

[1] *Am. Jour. Sci.*, (5), **21,** 173 (1931).
[2] *Pop. Astron.*, **48,** 561 (1940).
[3] See Flight, *Geol. Mag.*, *n.s.* **2,** 219–222 (1875).
[4] See Flight, *Geol. Mag.*, *n.s.* **2,** 408–411 (1875).
[5] *Am. Jour. Sci.*, (2), **2,** 348 (1846); **6,** 411–414 (1848).
[6] *Archives Neerlandaissis* **7,** 146 (1872).
[7] *Brit. Assoc. Rept.*, App. **11,** 190 (1862); *Phil. Trans. London,* **160,** 195 (1870).

Borgstrom certainly found it in Hvittis (Finland); Brezina probably found it in Aubres (France); and it has been reported in Nagaya (Nogoya, Argentina?). Lacroix identified it by both optical and chemical means in the Saint-Sauveur stone (France),[8] and reported 1.15%.

Tassin found large quantities of calcium and sulphur in a fine powder derived from the Allegan (Michigan) stone.[9] Extraction with boiling water, however, gave only 0.064% of oldhamite and it could not be detected optically. According to Merrill,[10] G. Gilbert obtained CaO equivalent to 0.072% of CaS by extracting the Cullison (Kansas) stone with distilled water, and A. Blair using 1:50 HCl obtained 0.28% CaO and 0.05% SO_4. If these constituents represent original oldhamite they correspond to 0.36 and 0.45%, respectively. On the other hand the mineral could not be found present optically. Merrill[11] digested twenty-five stones with boiling water and tested the extract for calcium. The result was positive in twenty cases, doubtful in one and negative in four. In the case of Pultusk, two samples gave a positive result and a third was negative. Later, Ochansk was reported to have given a negative test.[12]

The presence of calcium is interpreted as evidence of the presence of oldhamite but since other soluble calcium salts have been reported, the value of this research is impaired by failure to test the extract for sulphide or sulphate. When one of these meteorites, Alfianello (Italy), was thoroughly washed with water and then extracted with dilute hydrochloric acid, 0.03% CaO and 0.013% S were obtained. These values are equivalent to 0.030% of additional oldhamite. Oldhamite was detected by both optical and chemical methods in the Indarch stone (Russia). Extraction with water gave 0.464% CaO which is equivalent to 0.596% CaS. Its presence in Bishopville seems to be definitely established since Merrill[13] obtained calcium equivalent to 0.67% of oldhamite by extraction with water. The author confirms this to the extent of finding a strong calcium reaction in a water extract of Bishopville, and in addition he finds an equally strong reaction for sulphate.

The writer has digested thirteen stony meteorites, and associated minerals from iron meteorites, with boiling distilled water and tested the extracts for certain ions. Ammonium oxalate was used for calcium; ammonium thiosulphate for iron; dimethylglyoxime test paper for nickel; silver nitrate for chlorine; sodium nitroprusside for sulphide;

[8] *Compt. Rend.*, **177**, 561–563 (1908).
[9] *Proc. U. S. Nat. Mus.*, **34**, 433–434 (1908).
[10] *Proc. U. S. Nat. Mus.*, **44**, 330 (1913).
[11] *Proc. Nat. Acad. Sci.*, **1**, 302–308 (1915); **14**, *1st. mem.*, 25 (1925).
[12] *Proc. Nat. Acad. Sci.*, **14**, *4th mem.*, 8 (1925).
[13] *Proc. Nat. Acad. Sci.*, **14**, *1st. mem.*, 12–13 (1925).

barium chloride for sulphate; malachite green for sulphite; and molybdate reagent plus stannous chloride for phosphate. The results are given in the accompanying Table 1.

TABLE 1

Meteorite	Ca	Fe	Ni	Cl	PO_4	S	SO_4	SO_3
Holbrook, Ariz.	++	?	–	–	++	–	++	
Richardton, N.D.	+		–	+				
Adrian, Tex. I	+		–	+	?	–		
Adrian, Tex. II	+	–	–	+	–	–		
Tyron, Nebr.	++	–	–	+++	–	–		
Gretna, Kans.	+	–	?	–	–	–	–	
Bishopville, S.C.	+++	–	–	–	–	–	+++	
Plainview, Tex.	–	–	–	–	?	–	+	–
Allegan, Mich.	–	–	–	–	+	–	?	–
Amalia Farm graphite	–	–	?	+	–	–	+	
Mt. Eldon graphite	–	+++	++	+++		–		
Canyon Diablo, troilite	–	–	?	–	?	–	?	–
Xiquipilco, troilite	–	–	?	?	+	–	+++	–

A blank indicates that the test was not made; a minus sign indicates a negative reaction; a question mark indicates a doubtful reaction; and the approximate strength of a positive result is indicated by one, two or three plus signs.

The positive results for phosphate are of interest. As far as I can determine they are the first ones to be obtained using a neutral solvent. Merrill has obtained positive results on several meteorites, but he used dilute acid and attributes the result to the solution of apatite, or a similar mineral. The Richardton, the two Adrian and the Tyron stones, apparently contain calcium chloride. (The Adrian and some of the other stones have not yet been described.) The calcium sulphate indicated in the Bishopville meteorite is probably derived from the oxidation of oldhamite.

Extraction of meteorites with organic solvents has yielded interesting results, and the origin of the organic compounds obtained is puzzling to say the least. The only definitely identifiable product however is free sulphur. Wöhler[14] obtained it from Cold Bokkeveld (South Africa), and from Kaba (Hungary). Roscoe[15] found 1.24% of free sulphur in Alais (France). Shepard[5] reported visible grains of sulphur in Bishopville and

[14] *Sitzber. Wien Akad. Wiss.*, (**1863**); *Phil. Mag.*, **25,** 319.

[15] *Proc. Lit. Phil. Soc. Manchester*, Feb. 24 (1863); *Phil. Mag.*, **25,** 319.

this was confirmed by Reichenbach.[16] Flight[17] extracted the powdered troilite of the Cranbourne (Australia) iron with carbon disulphide and obtained 0.0207% of free sulphur. Wright[18] obtained a yellow deposit when he heated Cold Bokkeveld in a vacuum. He regarded this as sulphur and states that Ramelsberg also obtained sulphur from this stone, thus confirming Wöhler's result. Dewar and Ansdell[19] found small pieces of free sulphur floating on the water they obtained by heating Orgueil (France). The sulphur reported in the last two cases may have been derived from the decomposition of some other compound, although Smith[20] obtained free sulphur from Orgueil by extraction with carbon disulphide. He also believed that he had found free sulphur in the graphite of the Cosby Creek (Tennessee), the Cranbourne (Australia), and the Smithville (Tennessee) irons.

The writer has examined all of the meteorites in the above table for free sulphur using the sensitive pyridine-caustic soda test.[21] In addition, I have examined the Cuero and Kimble Co. (Texas) stones which were kindly supplied by Dr. Virgil E. Barnes of the University of Texas; a piece of the terrestrial troilite from Del Norte Co., California, and a sample of pyrrhotite from Sudbury, Ontario. Since it is possible to make rough estimates of the amount of sulphur present when using this test I record some rather crude estimates of the percentages of free sulphur in the various samples as follows:

Specimen	Sulphur content
Cuero, Texas	None
Kimble Co., Texas	Doubtful trace
Amalia Farm graphite	0.000X%
Mt. Eldon graphite	0.000X%
Canyon Diablo troilite	0.00000X%
Xiquipilco troilite	0.00000X%
Bishopville, S.C.	1.5%
California troilite	0.00000X%
Sudbury pyrrhotite	0.0X%

All of the rest contained no free sulphur. The accuracy of these estimates is low. It is possible that they are as much as ten fold too small, except for the Bishopville stone.

[16] *Study* **13,** 364 (1865).
[17] *Phil. Trans.*, no. **171,** 893–896 (1882); *Geol. Mag., n.s.* **10,** 59–65 (1883).
[18] *Am. Jour. Sci.*, (3), **12,** 165–176 (1870).
[19] *Proc. Roy. Soc., London, Sec. A*, **40,** 549–559 (1886).
[20] *Am. Jour. Sci.*, (3), **11,** 388–393; 433–435 (1876).
[21] *Ind. and. Eng. Chem.*, (Anal. Ed.), **12,** 368 (1940).