The Cerargyrite Group (holohedral-cubic silver haloids).

By G. T. PRIOR, M.A., F.G.S. and L. J. SPENCER, M.A., F.G.S.

Assistants in the Mineral Department of the British Museum.

[Read February 4, 1902.]

Historical Introduction.—As given in modern text-books, the holohedral-cubic silver haloids occurring as minerals include the following species: the pure chloride, chlorargyrite, AgCl.; the pure bromide, bromargyrite, AgBr; the intermediate embolite, Ag(Cl,Br), containing chlorine and bromine in varying proportions; and iodobromite, containing all three halogens in a definite ratio corresponding to the formula 2AgCl.2AgBr.AgI.

The terms hornsilver (used by Gesner as far back as 1565) and cerargyrite (Beudant, 1832) are usually taken as referring only to the pure chloride. As regards their signification, however, they are equally applicable to all of the above species, and in lack of chemical analyses were certainly so applied in the past. Thus Breithaupt, after the discovery of the bromide and chloro-bromide of silver by Berthier in 1841 and 1842, remarks that many of the specimens of 'Hornerz' in the Werner Museum having a greenish colour probably contained bromine. The new bromide and chloro-bromide, together with the chloride of silver, were included by Breithaupt in the genus 'Cerargyrites.' In the present note we propose to so far revive this idea as to refer to all the holohedral-cubic silver haloids under the general name of cerargyrite.

To the chloro-bromide analysed by Plattner in 1849, and having the chemical composition expressed by the formula 3AgCl.2AgBr, Breithaupt gave the name embolite. That he regarded embolite as a definite species with this particular composition is evident from the fact that to two other chloro-bromides, described by him in 1859 and showing different proportions of the two halogens, he gave the distinct specific

names megabromite (4AgCl.5AgBr) and microbromite (3AgCl.AgBr). Later analyses of chloro-bromides by Beck, Munro, Wood, and Field led to still other formulae, so that in 1886 it was pointed out by Welch that of fourteen published analyses, four corresponded more or less closely to 3AgCl.2AgBr, two to 5AgCl.2AgBr, and one to AgCl.AgBr, while seven called each for a separate formula. It has been recognized therefore that in these chloro-bromides the proportion of chloride and bromide may vary considerably. Embolite thus ceases to be a very definite species, since it may pass indefinitely, on the one hand into chlorargyrite, and on the other into bromargyrite.

It is one of the objects of the present paper to show that in the case of silver haloids containing all three halogens this history of embolite is repeating itself. Just as embolite was at first considered to have a fixed, definite chemical composition, so has the iodobromite, from Dernbach in Nassau, described by A. von Lasaulx in 1877¹, been regarded in the text-books as a mineral with the definite formula 2AgCl. 2AgBr.AgI.

Lasaulx claimed that iodobromite was the first mineral to be described as containing all three halogens. In 1869, however, F. A. Moesta² published an analysis of a chloro-bromide of silver from Chili showing a small percentage (1.73) of iodine in what would otherwise be described as an embolite. Previous to this, in 1853, Damour³ had detected iodine in two specimens of olive-green silver bromide from Huelgoat, Brittany; and Dufrénov in 1856 in his treatise mentions the isomorphous replacement of some of the chlorine by icdine in chlorargyrite from the same locality. Dufrénoy was thus led to consider the existence of a cubic silver iodide as probable, and even described 4 as such some bright yellow crystals on a specimen from Chañarcillo in the Muséum d'Histoire Naturelle in Paris; but as no chemical analysis was made of the crystals, it is probable that they contained all three halogens (see analysis of orange-yellow crystals of silver haloid from Chañarcillo on p. 179 below). More recently, in 1888, after the discovery of the silver ores of Broken Hill, A. Liversidge pointed out⁵ that 'all the New

¹ Zeits. Kryst. Min., 1877, vol. i, pp. 506-7; Neues Jahrb. Min., 1878, pp. 619-23 (Abstract in this Magazine, vol. ii, p. 237).

² Ueber das Vorkommen der Chlor-, Brom- und Jodverbindungen des Silbers in der Natur (Ein Beitrag zur Kenntniss der geologischen und bergbaulichen Verhältnisse). Marburg, 1870, 47 pp., 4 plates. (Also as Habilit.-Schrift, Marburg, 1869.)

³ Ann. des Mines, 1853, ser. 5, vol. iv, p. 332.

* Traité de Minéralogie, 2nd edition, 1856, vol. iii, pp. 452, 460.

⁵ Journ. and Proc. Roy. Soc. N.S.W., 1888, vol. xxii, p. 365.

South Wales silver chloride specimens' which he had examined 'contain iodine, some only traces, and others a fair percentage.'

In the present paper are given the results of qualitative and quantitative analyses made on very carefully selected material, showing that the chloride, bromide and iodide of silver may occur together in isomorphous mixtures in very varying proportions besides the particular one found by Lasaulx in iodobromite. Accordingly iodobromite, just as embolite, ceases to be a definite species. If the name were retained it might be applied to isomorphous mixtures of chloride, bromide and iodide of silver in which the three halogens are all present in fair amount; but since the name is a particularly misleading one, as suggesting that the mineral only contains iodide and bromide, we propose to refer to the varieties of the cerargyrite group which contain all three halogens as iodiferous embolites or briefly *iodembolites*.

Qualitative examination of Cerargyrites.—In order to test the present method of classification of the silver haloids a qualitative chemical examination was made of thirty-two specimens in the British Museum collection labelled chlorargyrite, bromargyrite, and embolite.

The method of analysis consisted in decomposing the mineral in the usual way by means of zinc and sulphuric acid, so that the silver was deposited and the halogens passed into solution as zinc salts. A portion of this solution was tested for iodine by the addition of one or two drops of a saturated solution of nitrous acid in sulphuric acid, and then for bromine (after the removal of the iodine dissolved in carbon bisulphide) by addition of chlorine water. Another portion of the solution was tested for chlorine by adding either potassium permanganate, or lead peroxide and acetic acid, boiling until all bromine and iodine were expelled, and treating with silver nitrate to precipitate the chlorine. As a confirmatory test a third portion of the original solution was treated with silver nitrate, and the resulting precipitate tested as to its solubility in ammonia.

The result of the qualitative examination given in the following table, showed that none of the specimens labelled bromargyrite consisted of *pure* bromide of silver, that many so-called chlorargyrites contained much bromine, and that many of the specimens referred to embolite contained iodine in varying amounts besides the chlorine and bromine.

176

Number.	Locality.	Colour.	Chlorine.	Bro- mine.	Iodine.
Chlorargy- rites :	Johanngeorgenstadt S. America Copiapo, Chili Chili Taltal, Chili	colourless " greenish-yellow tinge greenish tinge	much ,, ,, ,, ,,	none 77 77 77 77	none 13 29 39 39
Embo- lites :—					
34665 34293 34295 32133 44464 34811 A. G. 11 37086 A. G. 8 65398 65397 37087	Dolcoath mine, Cornwall " Chañarcillo " 'Peru' Copiapo, Chili S. America Broken Hill Plateros, Mexico	greenish-grey pale greenish-grey greenish-grey "" pale greenish-grey greenish-grey	much "" some much "" "" very little	some " little some much some little some little " much	NODE)))))))))))))))))))
Iodembo- lites :—					
83458 76235 71538 80678 64379 85484 64376 84822 83825 44459 35842 36280 53925 46189 40661	Broken Hill ,, ,, ,, ,, ,, ,, ,, ,, ,,	pale greenish-grey pale greenish-yellow greenish-yellow orange-yellow greenish-yellow orange-yellow orange-yellow orange-yellow pale greenish-yellow	some ,, ,, ,, ,, ,, ,, much some ,, ,, ,, ,, ,, ,, ,, ,, ,, ,	some "" " " " little some " " little some little some " " " " " " " " " " " " " " " " " " "	very little little very little little much little much some " little some

IODEMBOLITES.

Four of the specimens which the qualitative examination had shown to contain all three halogens were selected for more detailed investigation and quantitative analysis. The following description of the physical characters applies mainly to the three first well-crystallized specimens (A, B, C).

Physical Characters.- The crystals on all three specimens, although differing considerably in chemical composition, are very similar in general appearance. The faces are bright and smooth, but not perfectly plane, so that only approximate measurements can be obtained on the The angles measured agree closely enough with cubic goniometer. angles, and the only forms present are the cube $a\{100\}$ and octahedron o{111}. On the Broken Hill specimens a few of the crystals are twinned according to the spinel-law. The colour of the crystals of two specimens (A and B) is bright orange-yellow, that of specimen C is greenish-yellow; but this is soon altered to green on exposure to light. The crystals are translucent, and only small fragments allow of the passage of sufficient light for examination under the polarizing microscope. Small crystals which have not been distorted are optically isotropic, but when bent are feebly birefringent with undulose extinction. The mineral is very tough and sectile. The hardness is 24. Fragments are readily flattened when pressed with a knife-blade and leave no mark (streak) on paper. The fracture is uneven to sub-conchoidal, and no cleavage could be developed in the directions of the faces of the cube, octahedron or rhombic dodecahedron.

Method of Analysis.—For the analysis only crystallized material was taken, on which no iodyrite could be seen. Any calcite, oxide of iron and native silver were removed by digestion in dilute nitric acid; clayey material and some of the smaller garnets were removed by washing in a stream of water, after which the material was carefully picked out under the lens and examined under the microscope.

In all the analyses the mineral in small fragments was decomposed by means of zinc and sulphuric acid. The silver was collected, washed and dissolved in nitric acid, any insoluble residue (quartz or, in the case of the Broken Hill specimens, minute garnets) being separated at this stage and weighed. The total silver was then precipitated as chloride and weighed. The solution containing the halogens as zinc salts was transferred to a separator and treated with a few drops of a saturated solution of nitrous acid in sulphuric acid. The liberated iodine was dissolved in carbon bisulphide, and the solution collected on a moist filter, washed and titrated with sodium thiosulphate. The sodium thiosulphate solution was standardized by means of pure iodine dissolved in potassium iodide, which was treated in the separator with carbon bisulphide, collected on a filter, and washed in precisely the same way as the iodine solution in the analyses. For the determination of the chlorine and bromine, the indirect method was adopted of precipitating

with silver nitrate, weighing the combined silver chloride and bromide, and then converting wholly into chloride by reducing with zinc and sulphuric acid, dissolving the silver in nitric acid and reprecipitating with hydrochloric acid.

The results thus obtained are given under I, but as a check there are also given under I (a) the results of the more indirect calculation of the percentages of the chlorine and bromine from the weights of the total silver and iodine, together with the weight of the mineral used in the analysis. In each case the two results show a fairly close agreement. The atomic weights used were Ag=108, Cl=35.5, Br=80, I=127.

A. Specimen (No. 36280) from Chañarcillo, Chili.

The matrix of this specimen is a crystalline limestone which in places is ferruginous, argillaceous, or quartzose, with patches of red hydrated oxide of iron. Embedded throughout are small particles of native silver. Cavities in the mass are lined with crystals of calcite, and on these rest the bright orange-yellow cubo-octahedra of iodembolite, the largest of which are about 7 mm. across. The same cavities also sometimes contain aggregates of small indistinct crystals of pale sulphur-yellow iodyrite, which in places rest upon the orange-yellow cubo-octahedra.

Result of analysis (G. T. P.):---

						I.	I (a).
	Ag		•			60.37	60.37
	CĨ	•				7.11	6.95
	\mathbf{Br}	•		•	•	22.35	22.29
	I		•	•	•	10.39	10.39
						100.22	100.00
This corr	espon	ds 1	to :				
	AgC	l			•	28.72	28.38
	AgBi		•	•		52.53	52.39
	AgI				•	19.23	19.23
	-					100.48	100.00

Weight of mineral used = 0.8645 (after deducting 0.0081 insoluble). I = 0.0863; AgCl corresponding to total silver = 0.6949; AgCl + AgBr after separation of iodine = 0.7025; AgCl equivalent to AgCl + AgBr = 0.5950 gram.

Approximate formula: 5AgCl.7AgBr.2AgI.

Specific gravity (weight of 1 cc. at 23°C.)=6.17.

B. Specimen (No. 83825) from Broken Hill, New South Wales.

This specimen consists of a large crumbly, but closely set mass of arborescent native silver, the branches of which are encrusted with bright but minute and indistinct crystals of silver¹. This is abundantly encrusted with small bright cubo-octahedra of the orange-yellow iodembolite, with which are associated numerous minute reddish garnets, a few angular fragments of quartz sometimes with a bluish opalescence, and a yellow clayey material. Often the crystals of iodembolite are nothing more than hollow shells of material around the native silver, from which the mineral has no doubt been derived. These shells contain in their interior a loose granular aggregate of minute crystals, occasionally distinguishable under the microscope as cubooctahedra, and, as far as can be seen, with the same characters as the enclosing shells and larger crystals, with which they are no doubt identical. Minute reddish garnets are sometimes completely embedded in the crystals of iodembolite.

This and the following specimens showed no iodyrite in association with the iodembolite, while on almost all other specimens of a similar character from Broken Hill it is present. Usually in these cases the pale yellow iodyrite rests on the darker yellow cubic mineral, though sometimes the reverse is the case.

Result of analysis (G. T. P.) :---

180

				I.	I (a).
Ag .	•	•	•	56-93	56.93
Cl	•			1.96	1.70
\mathbf{Br}	•	•		32.22	32.60
Ι			•	8.77	8.77
				99.88	100.00
This correspon	ndi	s to):—	-	
AgCl	•		•	7.93	7.16
AgBr	•	•		75.78	76.61
AgI	•	•		16 ·23	16.23
				99.89	100.00

Weight of mineral used = 0.9311 (after deducting 0.0116 insoluble). I = 0.0816; AgCl corresponding to total silver = 0.7043; AgCl + AgBr after separation of iodine = 0.7789; AgCl equivalent to AgCl + AgBr = 0.6120 gram.

Approximate formula: 5AgCl.40AgBr.7AgI. Specific gravity (weight of 1 cc. at 18°C.)=6.31.

¹ These crystals of silver are rarely suitable for goniometric measurement, but on one of them the forms $a \{100\}, d \{110\}, and \{10.8.0\}$ were determined. The form $\{10.8.0\}$ does not appear to have been previously recorded on native silver: measured to $a (100), 16\frac{1}{9}^{\circ}$ to 17° ; calculated $(100): (10.8.0) = 16^{\circ} 42'$ (L. J. S.).

C. Specimen (No. 84822) from Broken Hill, New South Wales.

This specimen consists almost wholly of a cellular aggregate of greenishyellow cubo-octahedra of iodembolite. As in the specimen last described these crystals are often only hollow shells of material. The faces of the cube have a drusy or tesselated appearance, owing to the grouping of smaller crystals in parallel position. Brownish garnets occur abundantly embedded in the crystals of the iodembolite. Minute grains of garnet are sometimes aggregated into curious angular forms, of a flesh-pink colour, suggestive of pseudomorphs, or at first sight somewhat resembling crystals of marshite. Psilomelane and limonite are also present in small amount.

Result of analysis (G. T. P.) :---

			I .	\mathbf{I} (a).
Ag			67.28	67.28
Cl	•		14.36	14.14
\mathbf{Br}			15.85	16.23
Ι.	•	•	2.35	2.35
			99.84	100.00

This corresponds to :---

AgCl		58.04	57.17
AgBr		37.24	38.48
AgI .	•	4.35	4.35
		99.63	100.00

Weight of mineral used = 0.7409 (after deducting 0.0166 insoluble). I = 0.0174; AgCl corresponding to total silver = 0.6623; AgCl + AgBr after separation of iodine = 0.7059; AgCl equivalent to AgCl + AgBr = 0.6406 gram.

Approximate formula: 20AgCl.10AgBr.AgI. Specific gravity (weight of 1 cc. at 23°C.)=5.82.

D. Specimen (No. 83458) from Broken Hill, New South Wales.

This specimen represents what appears to be the commonest type of silver haloid from Broken Hill. It is a large cellular or coralloidal mass, evidently a pseudomorph after wiry native silver, as suggested also by the associations of specimen B. The surface of the branches and wires has a drusy aspect, but no definite crystalline form can be distinguished. The colour is pale greenish-grey. The material is tough and sectile. The hardness is $2\frac{1}{2}$. Associated minerals, present in only very small amount, are psilomelane, limonite and small brown garnets.

Result of analysis (G. T. P.):-

	-		I.	I (a).
Ag.	•	•	66.91	66.91
Cl .	•	•	13.20	13.18
Br .			19.71	19.75
Ι		•	0.16	0.16
			99.98	100.00
This corresponde	s to	:—	-	
AgCl		•	53 .36	53.28
AgBr	•		46-33	46.43
AgI .	•	•	0 29	0.29
			99.98	100.00

Weight of mineral used = 1.2565 (after deducting 0.0045 gram insoluble). I = 0.0020; AgCl corresponding to total silver = 1.1170; AgCl + AgBr after separating 10dine = 1.2525 gram.

Approximate formula: 3AgCl.2AgBr.

Specific gravity (weight of 1 cc. at 17° C.)=5.66.

CONCLUSIONS.

Collecting together for convenience of comparison the foregoing results, we have :---

				A.	<i>B</i> .	<i>C</i> .	D.
AgCl	•	•		28.72	7.93	58.04	53.36
AgBr			•	52.53	75.73	37.24	46.33
AgI	•	•	•	19.23	16.23	4.35	0.29
Sp. gr.				6.17	6.31	5.82	5.66

These analyses, together with those of other authors, show that the chloride, bromide and iodide of silver can form isomorphous mixtures in very varying proportions. In the case of the chloro-bromides where the limiting members of the series both crystallize only in the cubic (holohedral) system, there is no reason to doubt that isomorphous mixture may take place in any proportion whatever. With the chloro-bromo-iodides the case is different, since the pure iodide, as it occurs in nature and at temperatures below 146° C., is crystallographically distinct from the chloride and bromide. In the latter case it is conceivable that there may be a limit to the amount of iodide which can enter into isomorphous mixture with the chloride and bromide, and that when this limit is passed the excess of iodide will crystallize out as hexagonal iodyrite. In this connexion therefore it is of interest to recall the fact

182

already mentioned that of the four specimens of iodembolite analysed, iodyrite occurs only in association with the one from Chañarcillo in which the largest percentage of iodine (10.39) was found: iodyrite also occurs in association with the 'iodobromite,' from Dernbach, which contains a still larger percentage of iodine (15.05).

In order if possible to settle this point, some fusion experiments were made with mixtures of silver chloride, bromide and iodide in varying molecular proportions¹, in the same way as that previously employed in the case of miersite (this vol. p. 43). The result of these experiments appeared to indicate that the limiting amount of iodide which could enter into isomorphous mixture with the chloride and bromide was reached for mixtures of the three in about equal molecular proportions (Cl: Br:I=1:1:1), for in mixtures containing a less proportion of iodide there was no separation of iodyrite on solidification and cooling after fusion, but in mixtures containing a greater proportion of iodide small specks of doubly refractive iodyrite became more numerous as the proportion of iodide increased.

Sometimes, in the presence of a large excess of silver iodide, fine Iamellar intergrowths of isotropic and birefringent material are seen, thus indicating that iodyrite may form intimate intergrowths with holohedral-cubic silver haloid in the same way that it does with miersite (this vol. p. 44). This further implies that at temperatures above 146° C. the amount of iodide which is capable of entering into the isomorphous mixture may exceed to any extent the limit given above. As in miersite, it would thus be possible to have natural crystals of cerargyrite containing an excess of silver iodide as an intimate intergrowth of iodyrite. In none of the natural crystals examined by us is, however, the limit exceeded, for there is no separation of iodyrite when they are fused and again cooled.

The natural crystals of cerargyrite and artificial mixtures in various proportions of silver chloride, bromide and iodide (the last not being in excess), as well as the pure chloride and bromide, all behave in much the same way when fused and again cooled on a microscope slide. They all show the same prominent crystalline structure marked out by two sets of rods and bars, and are isotropic or only feebly birefringent. This fusion method is therefore of no help for purposes of distinguishing the different kinds of cerargyrite.

¹ G. F. Rodwell has determined the specific gravity, melting point and coefficient of expansion of such artificial mixtures (Proc. Roy. Soc., 1876, vol. xxv, p. 292; Phil. Trans., 1883 (1882), vol. clxxiii, p. 1189).

In view of the fact that in the holohedral-cubic silver haloids the chloride and bromide can form isomorphous mixtures in indefinite proportions, and that the iodide can also enter into isomorphous mixture with them in a very varying though limited amount, the present system of classification into a number of arbitrary and apparently disconnected species appears somewhat unsatisfactory. We propose therefore to include all the holohedral-cubic silver haloids under the common groupname of cerargyrite and to use the names 'chlorargyrite,' 'bromargyrite,' 'embolite,' and 'iodembolite' to indicate sub-species depending on varying proportions of chloride, bromide and iodide.

The horny character is common to the whole group, and, as previously mentioned, the name hornsilver was not originally applied merely to the pure chloride, for some of the characters in the older text-books (colour, &c.) attributed to cerargyrite show that at any rate chlorobromides, as well as pure chloride, were included. Portions of these old descriptions, however, appear to have been handed down with too little discrimination, so that they now figure in modern text-books as characterizing the pure chloride. For this reason some of the characters, such as colour and specific gravity, for the sub-species chlorargyrite, embolite and bromargyrite require a certain amount of revision.

As regards colour, the result of the qualitative examination given in the table on p. 177, together with that of the quantitative analyses, suggests that the absolutely pure chloride is colourless or grey, that embolites are mainly greenish-grey, that a decided yellow colour is only apparent when the mineral contains an appreciable amount of iodide, and that when the latter is in large amount (near 20%) the colour is distinctly orange-yellow.

As regards specific gravity, the value 5.552 for chlorargyrite given in the text-books dates back to the time of Mohs (1824). A determination was therefore made of the specific gravity of the pure chlorargyrite, (No. 54819) from the Florida mine, Taltal, Chili, in which the qualitative examination had shown the absence of bromine and iodine. The result of the determination made on 0.6516 gram of material was 5.556 (G. T. P.) as the weight of 1 cc. at 14° C. The specific gravities for embolite, 5.81 to 5.43 of Domeyko, and 5.53 of Yorke, should no longer appear in text-books, as they are obviously too low.

The hardness of 1-1.5 given for chlorargyrite and embolite is too low, for we find that all the specimens which we have examined scratch gypsum with ease, but do not scratch calcite; the hardness is therefore $2\frac{1}{2}$.

184

The crystal-forms given in the text-books also require confirmation. The forms {211} and {221}, for example, have evidently been copied through Hausmann (1847) from Lévy (1837), who however gives {411} and {441}. On the several crystals examined by us only the cube and octahedron are developed.

The general characters of the Cerargyrite Group may now be summarized as follows:---

Holohedral-cubic. Common forms, the cube, $a\{100\}$, and octahedron, $o\{111\}$. Twinning rare; twin-plane o(111).

Cleavage, none. Fracture, uneven to sub-conchoidal. Tough and sectile. Hardness $= 2\frac{1}{2}$. Specific gravity, variable, depending on chemical composition.

Lustre, resinous to adamantine. Translucent. Colour, variable, and depending on chemical composition, but in all cases altered on exposure to light (differing in this respect from iodyrite and miersite). Optically isotropic.

Chemical composition, Ag(Cl,Br,I), the relative amounts of the isomorphous constituents, Cl, Br and I, varying considerably. On this variation the following *sub-species* are based :---

Chlorargyrite, AgCl. Grey or colourless. Sp. gr.=5.556. Bromargyrite, AgBr. Greenish-grey. Embolite, Ag(Cl,Br). Greenish-grey. Iodembolite, Ag(Cl,Br,I). Greenish-yellow to orange-yellow.

The results of the present investigation on the silver haloids and a previous investigation by one of us on marshite, miersite and iodyrite (this vol. pp. 38-53. See also p. 188 in this number) show that silver iodide may crystallize under one or other of the following four conditions. At temperatures below 146° C. (assuming atmospheric pressure) pure silver iodide crystallizes as rhombohedral iodyrite, while above this temperature tetrahedral-cubic crystals (type (b), this vol. p. 46) are formed: it may also enter, to a certain extent, into isomorphous mixture with holohedral-cubic silver chloride and bromide; or again, with copper iodide, it may form tetrahedral-cubic crystals of the double salt 4AgI.CuI.

The silver haloids at present known to occur as minerals may therefore be classified under the three main species :---

Cerargyrite, Ag(Cl,Br,I), holohedral-cubic. Iodyrite, AgI, hemimorphic-rhombohedral. Miersite, 4AgI.CuI, tetrahedral-cubic.