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Compositions of Silver Halides from the Broken Hill District, New South Wales

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ABSTRACT. Some 320 specimens of silver halides from the Broken Hill field, New South Wales, held in the collections of the Australian Museum have been examined. On the basis of colour and habit variations, 42 specimens were selected for analysis. Contrary to previous suggestions, compositions of individual specimens are highly variable and reflect a complex crystallisation history. Bromargyrite has been detected for the first time away from the Broken Hill main lode horizon. Compositions are discussed in terms of the lacunar nature of the appropriate phase diagrams; natural material is shown to reflect compositions of synthetic phases prepared at about 25°C. No obvious relationship between composition and physical properties could be detected for the chlorargyrite-bromargyrite series. This highlights the difficulties of visual identifications.

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The Broken Hill orebody is one of the world's greatest silver-lead-zinc deposits, yet the details of the formation of its oxidised zone are sketchy. The deposit is renowned for its silver halide minerals, which formed the basis of the deposits wealth in its early years. Considerable amounts of bromide and iodide minerals are present, but their extent and relationships to the more common mineral chlorargyrite, AgCl, are not well described. The present work was undertaken to rectify this gap in our knowledge, as part of a larger research programme aimed at developing a fuller understanding of the chemical processes responsible for mineral formation in supergene base metal ores. It is hoped that this will lead to new exploration methods for such deposits and to better extraction processes.

Noteworthy silver halide minerals at Broken Hill, NSW, appear in the oxidised sections of the main lode horizon (Birch *et al.*, 1982; Liversidge, 1886, 1891, 1894; Prior & Spencer, 1902; Smith, 1926) in the Consols Mine (Plimer, 1982) and in the many small silver mines scattered throughout the Broken Hill Block (Stevens, 1980). All three halides were represented in

the Broken Hill lode: chlorargyrite (AgCl) bromargyrite (AgBr) and the AgI dimorphs iodargyrite and miersite, (end-member compositions are shown). In the main lode, no chlorargyrite (*sensu stricto*) was found (Smith, 1926); it was really bromian chlorargyrite (*var. embolite*), sometimes bearing minor iodine (*var. iodembolite*). Material approaching pure AgCl in composition was only recorded from the Consols Mine and from surrounding deposits in the Broken Hill Block.

A brief comment on nomenclature is warranted here. Birch et al. (op. cit.) have suggested ranges of compositions for the silver halides but these have no IMA currency. With respect to AgCl-AgBr solid solutions, when Cl and Br predominate, phases are referred to as bromian chlorargyrite and chlorian bromargyrite, respectively. Embolite is a varietal name corresponding to a member of the AgCl-AgBr solid solution series. The term *iodembolite* has been used to distinguish similar phases containing, or supposed to contain, significant amounts of iodine. Where mention is made of phases containing all three halogens investigated here, the dominant halide, determines the mineral nature and other halide descriptors are arranged in order of decreasing mol fractions. Thus, bromian iodian chlorargyrite has Cl>Br>I.

Chlorargyrite and bromargyrite form a complete solid solution. Nevertheless, bromargyrite is the rarest of halides from Broken Hill and until this study was unrecorded outside the main lode horizon (Birch *et al.*, *op. cit.*). Complete solid solution of AgI in AgCl and AgBr does not occur at room temperature. Both chlorargyrite and bromargyrite are face-centred cubic and miersite, the body-centred cubic AgI analogue, is unstable with respect to its hexagonal dimorph iodargyrite at ambient temperatures (<146°C). However, the miersite lattice is stabilised at room temperature by solid solution of CuI at amounts greater than about 1 mol% (Barth & Lunde, 1926; Quercigh, 1914; Rolsten, 1961; Spencer, 1901). Complete solid solution exists between miersite and marshite, CuI.

These results were confirmed by Barclay & Jones (1971) in a study of silver halides from Broken Hill and environs, held in the Tate Museum of the University of Adelaide, South Australia. They used X-ray fluorescence methods for the determination of iodine and the application of Vegard's Law to determine chlorine:bromine ratios in minerals, as compared to prepared standards of known composition. Vergard's Law relates the systematic change of unit cell parameters to variations of composition. They also investigated the extent of solid solution AgI in AgCl and AgBr.

While their results broadly agreed with those of earlier workers, several points are raised here. First, their analyses gave constant compositions, or at least average compositions. The question raised is whether large crystals of silver halides, formed over considerable time, would have constant composition; some masses are centimeters in size and compositional variation would be expected to be in line with varying groundwater chemistry (Williams, 1990). Secondly, no attempt was made to relate analyses with physical characteristics of hand specimens. Smith (1926) made several observations relating to apparent comparisons to physical properties such as hardness, sectility and colour. Finally, determinations of the limits of solid solution of AgI in AgCl and AgBr were at odds with other published work (Chateau, 1959a,b,c) and when plotted on an appropriate phase diagram iodine contents of bromian chlorargyrite nowhere approached the solid solution limit in spite of the fact that silver iodides are abundant at Broken Hill intergrown with and growing on the Ag(Cl, Br) phases.

We therefore have determined the compositions of silver halide specimens from Broken Hill and nearby mines using modern SEM EDS X-ray methods, and have related these to the appearance of the minerals (descriptions of colour variations are given in Birch *et al., op. cit.*). Further, we show that these analyses, as well as those of earlier workers lend support to the conclusions of Chateau (*op. cit.*), on the limits of solid solution of the silver halides.

Experimental

Over 320 specimens of silver halides from the Broken Hill, NSW district are held in the collections of the Australian Museum, Sydney, NSW. Each was examined and characterised before 42 were selected for analysis to cover noted physical differences. Most material came from the Broken Hill deposit; two specimens were from the Broken Hill Consols Mine and 11 were from other mines.

The sectility of the halides helped in their preparation for analysis. Samples were pressed in a stainless steel infra-red disc press to give flat surfaces for analysis. No X-ray diffraction measurements were carried out on the silver iodides. Analyses of all identified silver halides (as well as material contained in chlorargyrite and bromargyrite) showed no detectable copper in them. During preparation other phases were not removed from the silver halides, as was done by Barclay & Jones (*op. cit.*). They needed to purify their samples prior to Xray diffraction measurement; we gained more information by preparation of the whole specimen (*vide infra*).

Specimens were mounted on double sided tape and carbon coated. They were analysed using an Hitachi SEM (model S2500) fitted with the LINK Dispersive System (EDS) AN1000. A 15 kV accelerating voltage was used with a 1 mA beam current. For each analysis spot, 50 second counts were taken using a focused beam. Normally, some 10-12 spot analyses were made for each sample, guidance for which was taken from the brightness of areas detected in back-scattered radiation images. The equipment was calibrated using the VKa peak and analytically pure, laboratory reagent grade AgCl, AgBr and AgI standards were run concurrently with each batch of analyses. Analysed secondary mineral standards used embolite (BM83458) and iodargyrite (BM84810); numbers in brackets refer to British Museum (Natural History) specimen numbers. Count rates were found to deteriorate on AgI (especially) and other halide standards after several analytical runs, thus requiring repolishing of standards at frequent intervals.

Raw analytical data and SEM-BSE photomicrographs for every spot analysis have been deposited with the Australian Museum, and are available upon request. Elements below a 2σ detection limit are ignored. Several point analyses were made of included accessory minerals such as cerussite. The majority of the analysis of halides approximate well to AgX compositions, although depth of penetration of the electron beam may result in some composites. Extreme high and low totals probably reflect topographic features of the specimen surface, although relative highs of silver analyses versus halides, for example, reflect the presence of native silver in some specimens.

In this discussion, the halide data are normalised to 100% with respect to AgCl+AgBr+AgI and are so reported in the tables below, with a cut-off at a mol fraction of 0.01; this has been chosen as a reasonable limit (i.e., the 1 mol% level) although some analytical data go beyond it. Comparison with other published data on the system shows this cut-off choice does not limit the data or its interpretation.,

Results and discussion

General compositions and attributions. Barclay & Jones (*op. cit.*) suggest that the silver halides of Broken Hill are homogeneously disordered. This would be a natural assumption by extrapolation of their work on the relationship of the compositions of the various solid solution phases to Vegard's Law. This study shows that while their overall limits of solid solution are broadly correct, some natural silver halides from Broken Hill are chemically inhomogeneous; others do have relatively constant composition.

This is illustrated by samples D18759 and D35986 in Tables 1 and 2. The former is an iodian chlorian bromargyrite (iodembolite), and the latter a bromian chlorargyrite (embolite). Some variation in composition is obvious from the spot analyses, but is not particularly marked. Nevertheless, this differs from specimen D10481 (Table 1), which on bulk analysis is a bromian chlorargyrite. However, one of the spot analyses corresponds to bromargyrite and compositions vary from $AgCl_{0.86}Br_{0.14}$ to $AgCl_{0.21}Br_{0.79}$. Thus, chemical variation of embolites cannot be inferred from X-ray powder diffraction measurements. This is not at all surprising. The large masses of silver halides in some specimens could not reflect formation solutions of constant composition since they must have crystallised over a considerable time. Because groundwater compositions are continually changing, the halide composition will reflect that fluctuation in the first order. Thus, the silver halide crystals even millimetres in size would have variable composition reflecting groundwater geochemistries prevailing. All of the analysed silver halides show this variability to different extents.

It should be noted that casual observations of hand specimens are not particularly reliable guides to composition. By way of example, specimen D24260 (Table 1) is labelled as iodargyrite (Table 2). It is a yellow-grey massive material, but the yellowness is not related to the presence of iodine, which was undetected in spot analysis. By way of contrast, bromian chlorargyrite or chlorian bromargyrite *versus* iodine-rich phases are easily distinguished by using back-scattered X-ray images.

Specimens D34811 and D23904 (Table 1) demonstrate the limits of solid solution of the silver halides, in that separate phases are present. In D34811, two phases are apparent in hand specimen (Table 2). The yellow-green phase corresponds to an iodian bromian chlorargyrite near the limit of iodide substitution (vide infra). The yellow crystals coating this phase are chlorian iodargyrite with a trace of bromine in one spot analysis. D23904 similarly gave some spot analyses consistent with an iodian embolite and four others corresponding with chlorian iodargyrite or pure iodargyrite. What is significant is that D34811 has clearly identifiable yellowgreen embolite masses dusted by iodargyrite. In contrast, D23904 appears in hand specimen to be a single phase in terms of colour. Only detailed analysis can reveal the admixture of several phases.

Iodembolites. Iodembolite was a term given to bromian chlorargyrite bearing a small amount of iodine. It was apparently distinguished from *embolite* (or simple bromian chlorargyrite) by its greenish to orangeyellow colour, and hardness and sectility differences (Birch *et al., op. cit.*). Twelve specimens from the Australian Museum, labelled "iodembolite", have been analysed. Visual methods used to distinguish such silver halides are unreliable.

D23904 and D18759 (Tables 1 and 2) were both labelled "embolite". The former, even though including an AgI phase, bears considerable iodine and would fit its name. However, the latter is clearly an iodian chlorian bromargyrite. Both are waxy, yellowish green to green halide. Analyses of the remaining ten *iodembolites* are given in Table 3. Most were yellowish green or green, some purple or greenish brown and others were black as a result of photochemical alteration of the surface.

Three groups of analysis are evident. The first (D25918, D28196, D29303 and D29383) corresponds to bromian chlorargyrite with no iodine detected, although one spot analysis in D29383 corresponds to chlorian iodargyrite. Other analyses in D29383 place it close to bromargyrite. Four analysis (Table 3) correspond to halides in which small amounts of iodine are occasionally determined (D20648, D25951, D26980 and D28194). In D20648, pure iodargyrite and bromian iodargyrite are present as well, as separate phases. As no iodine was detected in a number of spot analyses for this specimen (and for D29383), the iodide phase probably crystallised during a separate mineralising event. Otherwise, the bromian chlorargyrite would be saturated with iodide. Finally, two iodembolites, D30448 and D31586 (Table 3), contain more iodine and it was found in most of the spot analyses. Both these phases appear to be homogeneous in lacking separate AgI (see descriptions of iodembolite in Table 2).



Fig. 1. Compositions of all silver halide specimens (spot analyses) from the Broken Hill main lode horizons (filled circles), together with the average data (crosses) for specimens analysed by Barclay & Jones (op. cit.). No locality data were provided for the latter specimens. The dashed line joins the experimentally determined limits of solid solution of AgI in AgCl and AgBr at 25°C (Chateau, op. cit.).

Embolite. Bromian chlorargyrite is most commonly associated with Broken Hill (Birch et al., op. cit.). Thirteen Australian Museum samples have been analysed in this study (Tables 1 and 4). Relating compositions, colour, association, etc. (Table 2) has proved just as problematic as for *iodembolites*. In some cases the names would appear to be interchangeable. Colours vary from purple-brown to yellow, greenish yellow and green.

The two embolite analyses in Table 1 illustrate this point. D35986 has an ideal composition for the mineral, but two halide phases are present. Purplebrown material is coated by a second generation of waxy, green, reticulated halide. No significant compositional difference between the two generations of bromian chlorargyrite could be detected. By way of contrast, D34811 also carries two distinguishable halide phases, yellow iodian bromian chlorargyrite (iodembolite) coated with minute, canary yellow crystals of iodargyrite. Remaining analyses of "embolites" reveal that they are either bromian chlorargyrites alone, or with minor amounts of iodine

in substitution. Analyses are not indicative of homogeneous materials, with bromine mol fractions varying from 0.2 to 0.4. Some analyses more closely approach bromargyrite. One spot analysis in D29370 indicates patches of chlorian bromargyrite embedded in bromian chlorargyrite. Attention is drawn here to specimen D36399. Coronadite gossan forms the matrix, on which greenish-yellow, crystalline halide is coated with masses of a later, bright yellow phase. The two are obviously the result of separate mineralising events with the greenish material corresponding to approximately AgCl_{0.7}Br_{0.3} with a trace of iodine in one analysis, and the bright yellow material to AgI with trace amounts of chlorine. Similarly, in D35996 and D34495, chlorian bromian iodargyrite is embedded in a groundmass of green *embolite* veinlets in kaolin.

Other attributions. Bromyrite (bromargyrite) is a rare mineral from the oxidised zone of the Broken Hill orebody (Birch et al., op. cit.; Barclay & Jones, op. cit.), although silver halides within the embolite range sometimes show spot analyses corresponding to



Fig. 2. Compositions of silver halides as reported in Figure 1 for specimens collected from deposits remote from the Broken Hill main lode horizons.

bromargyrite (sensu stricto). Reference to Table 1 reveals that confusion remains concerning visual identification of bromargyrite. Specimen D18759 is an iodian chlorian bromargyrite but was labelled "bromyrite" and relabelled "iodembolite" (Table 2). While it is gratifying to report another true bromargyrite from Broken Hill, it shows the problems of unchecked attribution. One of the four analysed specimens (Table 5; D46338) is purportedly a bromargyrite. It is yellow, but is an iodian bromian chlorargyrite. None of the spot analyses approaches the attribution, but the iodine contents of the solid solution series in this case are significant. Comments on colour identification of bromargyrite (Birch et al., op. cit.) need modification in the light of the analytical data presented here.

Specimens labelled "cerargyrite" (chlorargyrite) are similarly bedevilled by mis-attribution since such specimens contain significant bromine and iodine. It was previously reported that specimens from the Broken Hill Consols Mine approach the end member in composition (Barclay & Jones, *op. cit.*; Birch *et* al., op. cit.; Plimer, op. cit.). D10481 (Table 1) and D26168 (Table 5) are *embolites*, the latter with a trace of iodine. Analyses of *cerargyrites* from the Broken Hill Consols Mine (Table 5) also reveal incorrect attribution. D28184 is an unexceptional *iodembolite* while D28185 contains significant iodine and bromine. This gives no support to the contention that the Consols Mine halides are more chlorine-rich than those derived from the main lode horizons.

Aside from pieces or fragments of gossan included in the silver halides, native silver and fragments or crystals of cerussite, PbCO₃, are also encountered. Some point analyses are worthy of comment. In a few specimens, isolated grains give high lead **and** chlorine values, but low silver. They could not be attributed to cerussite but may correspond to phosgenite, Pb₂CO₃Cl₂, a mineral reported in the district only from the Broken Hill Consols Mine (Birch *et al., op. cit.*; Plimer, *op. cit.*) There it was found with cerussite, vanadinite, Pb₅(VO₄)₃Cl, and chlorargyrite. Alternatively, the grains might be cotunnite (PbCl₂), the Pb(II) oxy- or hydroxychlorides laurionite or paralaurionite, (PbOHCl), mendipite (Pb₃O₂Cl₂) or other related species (Edwards *et al.*, 1992). These grains were, however, too small to separate for X-ray identification. Thus a careful search for these halide specimens, now underway, may turn up such species new to Broken Hill.

In the main lode (vide infra), silver iodide is common as inclusions or intergrowths with bromian chlorargyrite (unlike specimens in the surrounding district). This may only be revealed in the backscattered electron images of prepared specimens, as confirmed by subsequent analysis. Two modes of occurrence or patterns of halide distribution are noted. The first concerns AgI associated with bromian chlorargyrite of low iodine content, with the AgI formed in an earlier separate mineralising event and simply enclosed by the later, iodine-deficient phase (see D20648). Alternatively, where AgI is detected together with iodian bromian chlorargyrite with elevated iodine content, the two phases grew together as a result of the hosting bromian chlorargyrite phase reaching the limit of solid solution with silver iodide (see D34811).

Silver halides from other Barrier Range deposits. Halides from mines distant from the main Broken Hill orebody are analysed in Table 6 and described in Table 7. Individual spot analyses are shown in Figure 2.

Many of the observations on halides from the Broken Hill main lode are mirrored in these specimens. Compositional variation is, for example, quite pronounced. Samples D30480, D30482 and D30484 are all from the Model Republic Mine at Purnamoota. D30480 is an iodian bromian chlorargyrite of constant composition around AgCl_{0.60}Br_{0.35}I_{0.05}. While all these are iodembolites, the other specimens have quite variable iodide contents and chloride mol fractions vary from 0.54 to 0.84. Specimen D35460 from the Caledonian Mine, Purnamoota is more varied. Five spot analyses correspond to bromian chlorargyrite or iodembolite. However, one analysis corresponds to an iodian chlorian bromargyrite indicating that some of the mass crystallised from an aqueous solution with elevated bromide activities. This analysis represents the first report of a bromargyrite in the Broken Hill Block, away from the Broken Hill main lode.

All other samples analysed correspond to bromian chlorargyrite (*embolite*) or *iodembolite*, little different to those from the main lode. However, in some support of the observation by Smith (1926) that chlorargyrite was typical of the Consols Mine and others outside the main lode area, one spot analysis from the Maybell North Mine, Mount Gipps, gave the highest proportion of chloride amongst other material analysed in this study, $AgCl_{0.90}Br_{0.10}$.

Reference to Figure 2 shows that analyses of halides from outside mines are comparable to those from the Broken Hill lode, in terms of Cl:Br ratios. One noticeable difference is less iodine in the more remote localities, although crystals of pure AgI are found in gossans from Little Darling Creek, Mookaie Hill and Mulga Springs (N. Gray and P.A. Williams, unpublished results).

Finally for this group of halides, mention should be made of mineral inclusions other than gossan pieces (as in D35460). Cerussite occurs in samples from the Maybell North and Day Dream Mines. Some alteration to native silver is detected in D18719; native silver is pronounced in hand specimen. Two spot analysis of an inclusion in D30480 from the Model Republic Mine correspond to pure Ag₂S; although it is not known whether the sulfide phase is primary or secondary, it clearly alters to the halide.

Limits of solid solution in the silver halides. Reference to Figures 1 and 2 shows that silver halides from the Broken Hill field are quite variable in chloride:bromide:iodide ratios, both in the main lode horizons and more remote localities. Chlorargyrite is the dominant species, as might be expected given normal geochemical distributions (Williams, *op. cit.*) that suggest compositions with Cl>Br>I would dominate. However, the high amounts of Br and I in the silver halide suites from Broken Hill and environs are both noteworthy and unexplained. Groundwater chemistries compatible with observed compositions of mineral suites must have prevailed.

Aside from this, it is worth examining the extent of solid solution in the silver halides, both from analysis and laboratory studies of synthetic materials. Barclay & Jones (op. cit.) investigated the limits of solid solution of AgI in the AgCl and AgBr. Unfortunately, their report appears to be in error because of computational matters and other, unconstrained variables. The latter centre about the fact that the solid solution experiments performed were not conducted at constant temperature (at least as reported in the literature). Furthermore the limits of solid solution of AgI in the other silver halides, as reported in the appropriate figure, reflect weight percent values, rather than mol percent values, as represented. Recalculation of their data gives limits of solid solution of AgI in the other halides of $AgCl_{0.93}I_{0.07}$ and $AgBr_{0.65}I_{0.35}$. Even with these corrections, we cannot apply them to our considerations as they correspond to undefined temperatures.

Good sense is made of their analytical data, in relation to the work of Chateau (*op. cit.*). He determined limits of solid solution among the silver halides for different reasons to those considered for naturally occurring phases. His results give the extent of solid solution of AgI in AgCl and AgBr as 5 and 31 mol percent, respectively, at 25° C. He also noted that AgCl and AgBr solution in AgI was much more restricted, amounting to less than about 5 mol percent (Chateau, 1959b,c) even at temperatures up to 70° C. These results are not too different to those of Barclay & Jones (*op. cit.*), who did not specify the temperatures of their experiments.

Extrapolation of solid limits of AgI in AgCl-AgBr solutions (i.e., the ternary system) is not based on

detailed experimental study. However, we can connect the end member solid solution limits (AgI in AgCl or AgBr) as a guide, as shown in Figures 1 and 2. This relationship closely matches compositions of naturally occurring phases. All of the reported analyses for iodian bromian chlorargyrite and bromargyrite analogues fall below the line; substituted silver iodides are observed as separate phases when more iodide was apparently available in mineralising solutions. This accords with the analytical data reported here for specimens which consist of admixtures of ternary phase and AgI.

We note that a temperature of 25°C would most likely correspond to conditions prevailing when these halides were formed; lower temperatures would serve to lower the limits of AgI substitution in AgCl-AgBr solutions. Higher temperatures would, by accommodating more extensive solid solution, not favour the compositions we have found.

Finally, we stress that the silver halides analysed here are anything but homogeneous. These species are substantial masses of largely crystalline material. Therefore they most probably crystallised over an extended period. This explains why the halides are so heterogeneous; groundwater compositions would fluctuate in composition and the chemical nature of the solid phase simply reflects those changing groundwater chemistries.

Detailed examination of spot analyses reveals such changing patterns, in a way that the figures, being an amalgamation of all data, do not. First, the tables show that for many spot analyses, iodine was not detected or was present in only trace amounts. In some specimens, iodine is present in uniformly high amounts. Localised reaction chemistry could explain that, but patterns of AgBr substitution in AgCl are more subtly complex. In individual specimens, zones corresponding to, roughly AgCl_{0.75}Br_{0.25}, with negligible iodine contents, are part of a single phase of varying composition juxtaposed with zones with approximate composition $AgCl_{0.65}Br_{0.35}$. The latter most frequently contain more iodine. As zones of these compositions are found in many specimens, these patterns of substitution probably represent particular mineralising events. Similarly, the bromargyrite phases belong to yet another, separate mineralising episode. Nevertheless, these minerals are very heterogeneous in composition and this may be overlooked if they are examined by methods related to Vegard's Law properties or if they are classified by physical properties and attributes.

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SUPPLEMENTARY MATERIAL. Descriptions of all of the specimens examined, non-normalised analytical data and back-scattered images showing point analysis locations have been deposited with the Collection Manager of the Mineralogy and Petrology Section, Australian Museum.

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No. ^a	Composition ^b														
D18759	Cl	8	11	9	8	10	12	10	11	10	11	10	8		
	Br	86	83	82	83	84	80	82	81	80	81	83	82		
	Ι	6	6	9	9	6	8	8	8	10	8	7	10		
D35986 ^c	Cl	67	67	67	68	72	65	68	67	70	68	66	68		
	Br	33	33	33	32	28	35	32	33	30	32	34	32		
D10481 ^d	Cl	69	86	85	55	72	62	30	79	60	68	75	67		
	Br	31	14	15	45	28	38	70	21	40	32	25	33		
D34811	Cl		1		1	1		1	1	1	63	65	65		
	Br					1					26	25	24		
	Ι	100	99	100	99	98	100	99	99	99	11	10	11		
D23904 ^e	Cl	63	65	63	68	65	65	65	66						
	Br	30	28	30	28	29	30	27	26	2					
	Ι	7	7	7	4	6	5	8	8	98	100	100	100		
D24260 ^f	C1	69	71	73	75	67	72	73	71	67	67	72	81		
	Br	31	29	27	25	33	28	27	29	33	33	28	19		

 Table 1. Compositions derived from spot analyses of selected specimens of silver halides from Broken

 Hill.

^a Australian Museum specimen number. ^b Compositions expressed in mol% terms; thus, the first analysis for D18759 corresponds to $AgCl_{0.08}Br_{0.86}I_{0.06}$. For specimen descriptions see Table 2. Where no number is reported in the Table, the halogen was not detected during analysis; traces of As detected. ^c Traces of Pb, As, Fe detected. ^d Traces of P detected. ^e Traces of As detected. ^f Traces of Pb, P, As detected.

Table 2. Specimen descriptions for silver halides from the Broken Hill main lode and the Broken Hill Consols Mine.^a

- D18759 LABEL: No.682 Iodembolite changing into native silver, Proprietary, Broken Hill. LABEL: Iodembolite and native As (*sic*), Broken Hill.
 COMMENTS: On the first label, the word "bromyrite" is crossed out and replaced by the word "iodembolite." Sample consists of massive green halide altering to native silver, accompanied by some soft orange clay.
 D35986 LABEL: Embolite on matrix, Broken Hill, NSW.
 Comment: Ferruginous, manganiferous gossan cementing quartz chips and fragments coated by purple-brown halide, then by later greenish halide in worm-like masses. Both halides were analysed but could not be distinguished.
- D10481 LABEL: Cerargyrite on kaolin, Broken Hill, NSW.
- COMMENTS: Green halide masses and veinlets in massive kaolinite.
- D34811 LABEL: Embolite, Broken Hill, NSW. COMMENTS: Yellowish halide with minor iron oxyhydroxides with later bright yellow dusting of second generation halide. The latter is iodargyrite, by analysis.
- D23904 LABEL: Iodembolite, Broken Hill, NSW.
- COMMENTS: Waxy, yellow-green halide globules to 2 mm on porous, hematite gossan.
- D24260 LABEL: Iodargyrite, Broken Hill, NSW.
- COMMENTS: Waxy, yellow-green, massive halide.
- D25918 LABEL: Iodembolite with cerussite, Proprietary Mine, Broken Hill, NSW. COMMENTS: Halides altered by light exposure to black masses on massive cerussite associated with orange iron oxyhydroxides. Cerussite inclusions were detected in the prepared samples.
- D28196 LABEL: Iodembolite, Proprietary Mine, Broken Hill, NSW. COMMENTS: Well-crystallised yellow-green halides associated with minor iron oxyhydroxides; crystals of bromian chlorargyrites to 2 mm.
- D29303 LABEL: Iodembolite in kaolin, Block 11, Proprietary Mine, Broken Hill, NSW. COMMENTS: Massive white kaolinite matrix bearing small red garnet crystals is impregnated with green halide masses and veinlets; this material was analysed. An open vugh in the specimen contained large (to 5 mm) halide crystals, some of which were coated with a second generation of bright yellow powdery halide.
- D29383 LABEL: Iodembolite, Broken Hill, NSW. COMMENTS: Stalactitic coronadite with later purple halide crystals to 4 mm. X-ray map showed bright patch of AgI and another of a Pb-rich phase.

D20648 LABEL: Iodembolite with smithsonite, Broken Hill, NSW. COMMENTS: Minor coronadite with clays and iron oxides accompany the bulk of the specimen which consists of an intergrowth of "teardrop" and crystallised smithsonite, cerussite (minor) and yellow-green halide; the smithsonite was last to crystallise. LABEL: Iodembolite with iodyrite, Proprietary Mine, Broken Hill, NSW. D25951 COMMENTS: Bright yellow crystalline masses of halide coated by later greenish-yellow to brown colloform halide. Analyses do not distinguish between the different coloured phases; the specimen is dusted by later iron oxyhydroxides. D26980 LABEL: Iodembolite, Broken Hill, NSW. Comment: Specimen consists of aggregates of cerussite crystals and some massive cerussite cemented by later yellow-green halide in crystals to 3 mm. X-ray map shows cerussite inclusions in halide. D28194 LABEL: Iodembolite, Proprietary Mine, Broken Hill, NSW. COMMENTS: Ferruginous gossan coated with purple-grey material and waxy, green halide masses. D30448 LABEL: Iodembolite on matrix, Broken Hill, NSW. COMMENTS: Matrix is rotten, oxidised garnet sandstone containing quartz fragments and siliceous iron-rich gossan bearing yellow crystals of halide on more open, vughy areas and yellow-green masses in cavities; some filiform masses to 1 cm coat the specimen. LABEL: Iodembolite, Broken Hill, NSW. D31586 COMMENTS: Slug of halide varying in colour from green to yellow and then to purple-brown. LABEL: Embolite, Broken Hill, NSW. D29370 COMMENTS: Matrix is a fine-grained, cerussite-rich, banded material after garnet sandstone coated and impregnated by greenish brown, arborescent masses of halide. LABEL: Embolite on kaolin, Broken Hill, NSW. D30466 COMMENTS: Specimen consists of masses of waxy, green halide crystals to 7 mm impregnating a mass of kaolinite bearing minor Mn oxides. LABEL: Embolite in kaolin, Broken Hill, NSW. D30481 COMMENTS: Dense, Grey, banded halide associated with minor Fe-stained clay. D30360 LABEL: Embolite, Broken Hill, NSW. COMMENTS: Specimen consists of a massive and reticulated crystalline cerussite nodule bearing yellow-green halide crystals in cavities; minor limonite coatings invest parts of the specimen. D31665 LABEL: Embolite with cerussite and malachite, Broken Hill, NSW. COMMENTS: Massive cerussite is coated by later purple-grey halide crystals to 2 mm; malachite crystal plates are scattered across both phases. D36399 LABEL: Embolite, Broken Hill, NSW. COMMENTS: Matrix of coronadite gossan is coated with yellow-green halide crystals and separate, bright yellow halide masses; both halide phases were analysed separately. D35996 LABEL: Embolite in kaolin, Broken Hill, NSW. COMMENTS: Veinlets of green halide invest massive kaolinite. D33111 LABEL: Broken Hill, NSW. COMMENTS: Unidentified green copper mineral coats mass of green halides bearing later native copper; base of specimen bears a bright, apple-green species and minor iron oxyhydroxides. LABEL: Embolitedendroids, Proprietary Block 14 Mine, Broken hill, NSW (Presented Block 14 Ltd). D32138 COMMENTS: Green dendroidal sheet of halide dusted with powdery blue copper mineral (unidentified). D29066 LABEL: Embolite with iodyrite in kaolin, Broken Hill, NSW. COMMENTS: Massive, yellow-green halide. D34495 LABEL: Embolite, colloform arborescent masses, Broken Hill, NSW. COMMENTS: Yellow to greenish brown colloform masses of halide associated with minor clays. LABEL: Bromyrite, Broken Hill, NSW. D46338 COMMENTS: Aggregates of yellow to bright yellow halide crystals to 3 mm on orange ferruginous gossan. D26168 LABEL: Cerargyrite in kaolin with malachite, Broken Hill, NSW. COMMENTS: Green halide masses in kaolinite with red garnets; later dusting of malachite. D28184 LABEL: Cerargyrite, Consols Mine, Broken Hill, NSW. COMMENTS: Slug of purple-grey halide with minor quartz inclusions; some halide is crystalline. D28185 LABEL: Cerargyrite with bromyrite and silver-chloro-antimoniat (sic) in limonite, Consols Mine, Broken Hill, NSW. COMMENTS: Matrix is a ferruginous gossan bearing some compact hematite masses one side of the specimen bears bright yellow halide crystals; the other (analysed) was coated with yellowish green halide crystals to 1.5 mm.

^a In order of discussion in text; in the Table, "Label:" refers to the specimen description on the Australian Museum label (*verbatim*).

No.						C	ompos	ition						
D25918 ^b	C1	65	61	66	67	68	64	61	64	81	62			
	Br	35	39	34	33	32	36	39	36	19	38			
D28196 ^c	C1	80	66	84	83	68	65	68	73	63	66			
	Br	20	34	16	17	32	35	32	27	37	34			
D29303 ^d	Cl	60	60	57	67	67	67	65	66	68	69			
	Br	40	40	43	33	33	33	35	34	32	31			
D29383 ^e	C1	63	50	52	62	63	78	65	66	61	52	62	2	
	Br	37	50	48	38	37	22	35	34	39	48	38		
	Ι												98	
D20648	C1	54	78	74	71	77	70	78	74	82	71			
	Br	42	22	26	29	22	29	22	26	18	29			1
	Ι	4				1	1					100	100	99
D25951 ^b	Cl	61	63	60	64	65	67	80	67	64	66	63		
	Br I	39	37	40	36	35	33	20	33	36	34	36 1		
D26980 ^e	Cl	78	79	67	61	65	79	61	71	66	76	-		
	Br	22	20	33	39	35	21	39	29	34	24			
D28194 ^e	Cl	64	64	60	65	72	63	76						
	Br	36	36	40	33	26	37	34						
	Ι				2	2								
D30448 ^c	Cl	57	64	61	68	64	59	69	63	66	58	64		
	Br	41	26	37	32	36	39	30	37	34	39	36		
	Ι	2		2			2	1			3			
D31586 ^f	Cl	57	64	61	60	50	47	54	62	62	60	60	67	
	Br	43	34	39	38	46	39	39	38	35	38	38	32	
	Ι		2		2	4	14	7		3	2	2	1	

Table 3. Compositions of *iodembolites* from Broken Hill.^a

^a Analyses are reported in the same way as in Table 1. ^b Traces of As, Pb, Fe detected. ^c Traces of Pb, Fe detected. ^d Traces S, As, Fe, detected. ^e Traces Fe, As detected. ^f Traces Pb, S, P, As, Fe detected.

Table 4. Analyses of embolites from Broken Hill.^a

No.							Analy	ses					
D29370 ^b	C1	60	62	61	63	66	74	66	61	76	19		
	Br	40	38	39	37	34	26	34	39	24	81		
D30446 ^c	Cl	71	70	77	76	76	67	76	81	75	67	76	67
	Br	29	30	23	24	24	33	24	19	25	33	24	33
D30481 ^d	Cl	64	66	66	68	61	61	68	71				
	Br	36	34	34	32	39	39	32	29				
D30360 ^d	Cl	64	65	64	67	64	72	59	64	63	65		
	Br	30	35	36	32	36	28	41	36	37	35		
	Ι	6			1								
D31665	C1	63	63	64	68	65	69	66	68	64	67		
	Br	37	36	36	30	35	31	34	32	33	33		
	Ι		1		2					3			
D36399 ^e	Cl	67	67	68	73	63	65	63	65	71	62	68	64
	Br	33	33	32	27	37	35	36	35	29	38	32	36
0	Ι							1					
D36399 ^f	C1				1	1		1					
	Ι	100	100	100	99	99	100	99	100	100	100		

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D35996g	C1	67	66	73	67	69	63	78	67	62	61	2	6	
D 33770*	Br	31	34	27	33	31	37	22	33	38	39	2	3	
	Ι	2										98	91	
D33111 ^h	Cl	60	63	68	64	64	70	66	67	61	53	66	65	
	Br	40	37	32	36	36	30	34	33	39	44	34	35	
	Ι										3			
D32138 ^c	Cl	56	79	80	73	57	85	81	64	77	55	56	60	
	Br	42	21	15	27	42	15	19	32	23	45	43	40	
	Ι	2		5		1			4			1		
D29066 ⁱ	C1	50	60	62	60	67	60	50	53	53	51	44	59	
	Br	41	32	34	35	28	34	41	40	39	36	40	36	
	Ι	9	8	4	5	5	6	9	7	8	13	16	5	
D34495 ^c	C1	63	68	63	64	63	65	63	57	67	67	2	3	
	Br	37	32	37	36	37	34	36	43	32	33	3	4	
	Ι						1	1		1		95	93	

^a Analyses are reported in the same way as in Table 1. ^b Traces Fe, As detected. ^c Trace As detected. ^d Traces As, S, Fe detected. ^e Greenish yellow phase; traces Cu, As, Fe detected. ^f Bright yellow phase; traces Pb, As detected. ^g Traces Pb, As detected. ^h Traces Pb, As, Fe detected. ⁱ Trace Fe detected.

Table 5.	Analytical	data	for	miscellaneously	attributed	samples	from	Broken	Hill,	including	the	Broken	Hill
Consols	Mine. ^a												

No.							Analy	ses					
D46338 ^b	Cl	60	57	57	53	56	57	58	68	° 56	66		
	Br	32	35	34	37	35	34	32	31	35	33		
	Ι	8	8	9	10	9	9	10	1	9	1		
D26168 ^c	Cl	72	76	63	65	60	77	77	72	66	65		
	Br	28	24	37	35	40	22	23	28	34	35		
	Ι						1						
D28184 ^d	Cl	75	68	86	70	70	70	78	70	84			
	Br	25	30	14	28	30	29	21	30	16			
	Ι		2		2		1	1					
D28185 ^d	Cl	55	56	55	56	55	55	60	50	45	50	56	
	Br	43	43	44	43	44	43	40	46	45	45	41	
	Ι	2	1	1	1	1	2		4	10	5	3	

^a Analyses reported as in Table 1. ^b Trace S detected. ^c Traces Pb, Cu, S, As detected. ^d Consols Mine; traces Pb, As, S, Fe detected.

No.							Analys	ses						
D30482 ^b	Cl	84	83	64	61	79	66	64	71	57	60	67	65	
	Br	16	17	31	35	21	34	36	29	41	37	30	32	
	Ι			5	4					2	3	3	3	
D30480 ^c	C1	65	61	59	62	61	64	60	56	59	60			
	Br	30	35	36	34	35	31	36	39	37	35			
	Ι	5	4	5	4	4	5	4	5	4	5			
D30484	Cl	61	66	66	56	67	65	67	54	66	66	72	68	
	Br	38	31	30	42	31	30	28	45	31	31	26	30	
	I	1	3	4	2	2	5	5	1	3	3	2	2	

Table 6. Silver halide analyses from deposits remote from the Broken Hill orebody.^a

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D35460 ^d	Cl	62	43	56	64	61	69						
	Br	38	53	43	36	36	31						
	Ι		4	1		3							
D28186 ^d	Cl	59	59	72	64	67	64	66	62	67	65	66	68
	Br	40	41	28	33	29	33	32	38	31	32	32	30
	Ι	1			3	4	3	2		2	3	2	2
D18714 ^e	Cl	74	71	66	79	71	77	75	72	70	70	76	73
	Br	26	29	34	21	29	23	25	28	30	29	24	27
	Ι										1		
D18719 ^f	C1	73	70	64	67	70	63	61	66	60	57	63	76
	Br	27	30	35	32	30	37	38	33	40	43	37	24
	Ι			1	1			1	1				
D18724 ^g	Cl	67	67	63	67	65	63	67	61	71	65	73	61
	Br	33	33	37	33	35	37	33	39	29	35	27	39
D18712	C1	76	78	85	76	62	84	82	75	85	76	68	66
	Br	24	22	15	24	38	16	18	25	15	24	32	34
D18720 ^h	C1	62	67	66	81	57	74	75	79	66	90		
	Br	38	33	34	19	43	26	23	21	34	10		
	Ι							2					
D18721	Cl	64	60	64	57	65	65	58	62	58	65	58	75
	Br	36	40	36	43	35	35	42	37	42	35	42	25
	Ι								1				

^a Analyses reported in same way as in Table 1. ^b Traces Pb, As, P, Fe detected. ^c Traces Pb, S, Fe, As detected; see text re inclusions. ^d Traces Fe, As detected. ^e Trace of Pb detected. ^f Traces Pb, As detected. ^g Traces of Fe detected. ^h Traces P, As, Fe detected.

Table 7.	Specimen descriptions for silver halides collected remote from the Broken Hill main lode.
D30482	LABEL: Model Republic Mine, Purnamoota, NSW. COMMENTS: Purple halide slug
D30480	LABEL: Embolite (slug), Model Republic Mine, Broken Hill, NSW, Purnamoota. COMMENTS: Grey-purple halide slug with minor coatings of hematite and yellow iron oxyhydroxides.
D30484	LABEL: Model Republic Mine, Purnamoota, NSW. COMMENTS: Purple halide slug.
D35460	LABEL: Silverhalide weighing lbs, Caledonian Mine, Purnamoota, Broken Hill District, NSW.
	COMMENTS: Sawn mass of purple-grey halide containing patches of days and ferruginous gossan fragments.
D28186	LABEL: Cerargyrite in azurite, War Dance mine, Purnamoota, Barrier Ranges, NSW. COMMENTS: Block of azurite with vuglus containing azurite crystals some of which has altered to later malachite. The azurite is veined and coated in parts by later greenish
D18714	LABEL: Embolite, Lily mine, Thackaringa, NSW. COMMENTS: Purple halide slug with minor copper straining and attached mica flakes on surface
D18719	LABEL: Iodembolite with native silver, Bobby Burns Mine, Appolyon Velly, Barrier Range, NSW.
D18724	COMMENTS: Sawn specimen of compact, ferruginous gossan containing large masses of green halide, some of which has been altered to native silver. LABEL: Embolite with cerussite, Day Dream mine, Barrier Range, NSW. COMMENTS: Specimen matrix is massive, ferric oxyhydroxide-coated cerussite with rough, angular cavities containing green halide masses and infrequent malachite
D18712	LABEL: Cerargyrite, Black Bird mine, near Silverton, NSW.
D18720	LABEL: Embolite, Maybell North, Mt. Gipps, Barrier Range, NSW.
D18721	LABEL: Cerargyrite, Maybell North Mine, M. Gipps, Barrier Range, NSW. COMMENTS: Mass of grey-purple to green halide coated with minor clays and iron oxyhydroxides on a decomposed schist base.

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