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MCKINSTRYITE, A NEW COPPER–SILVER SULFIDE [1]

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ABSTRACT

Mckinstryite, $Cu_{0.8+x}Ag_{1.2-x}S$, where $0 \lesssim x \lesssim 0.02$, was found on a specimen collected in 1907 at the Foster Mine, Cobalt, Ont. Mckinstryite is orthorhombic, space group *Pnam* or $Pna2_1$, $a = 14.043 \pm 0.005$ Å, $b = 15.677 \pm 0.006$ Å and $c = 7.803 \pm 0.003$ Å, $Z = 32$, specific gravity 6.61 ± 0.03. Strongest X-ray powder diffraction lines are 2.606 Å(10), 2.070 Å(7), 3.062 Å, 3.508 Å, 2.862 Å, 1.948 Å(5), 2.407 Å(4), and 2.567 Å(4).

Mckinstryite is named in honor of Hugh Exton McKinstry, 1896–1961, late Professor of Economic Geology, Harvard University.

INTRODUCTION

THE existence of a new compound of copper, silver, and sulfur was recorded by Suhr (5) and confirmed by Djurle (1), in their studies of the system Cu-Ag-S. The formula of the new compound was deduced by Djurle to be $Cu_{0.8}Ag_{1.2}S$, thus proving that it lay on the composition join Cu_2S-Ag_2S, as did the other known ternary copper-silver sulfides, stromeyerite ($Cu_{1+x}Ag_{1-x}S$), and jalpaite, ($Cu_{0.45}Ag_{1.55}S$). The phase relations and thermal stability of the new compound (identified as the β-phase, following Djurle's terminology) were reported in detail by Skinner (4), who suggested that the compound should occur as a mineral and that it might have been mistakenly identified as stromeyerite in the past. The compound has now been identified as a mineral from a specimen collected in 1907 at the Foster Mine, Cobalt, Ont., and preserved in the collections of the Geological Survey of Canada.

We propose to name the new mineral mckinstryite (măkĭnstrĭīt) in honor of the late Hugh Exton McKinstry (1896–1961), Professor of Economic Geology at Harvard University, in recognition of his many contributions to the geology and geochemistry of precious and base-metal deposits.

The name has been approved by the Commission of New Minerals and Mineral Names, IMA, with the suggestion that the spelling be changed to "mackinstryite" to avoid possible confusion in indexing. The spelling suggestion has not been accepted because we believe the possible confusions in indexing are less serious than the disservice to the scientist whose name is so casually changed. Because mineral names are not capitalized, however, the "k" should also appear in lower case.

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Small portions of the type specimens have been lodged in the collections of the U. S. National Museum and the Harvard Museum. The main specimen remains at the Geological Survey of Canada on file in the Systematic Reference Series of the National Mineral Collection.

OCCURRENCE

The type specimen of mckinstryite has been in the mineral collections of the Geological Survey of Canada for many years, designated as a specimen of stromeyerite from the Foster Mine, Cobalt, Ont. The specimen does not carry the necessary notification to clearly identify its donor. Geological Survey of Canada records indicate that it is probably the sample presented by A. P. Low in 1907 and recorded as a specimen of "stromeyerite, arsenopyrite and native silver from the Foster Mine, Cobalt" (3).

The Foster Mine is in lot 4, concession IV, Coleman township, approximately 1½ miles southeast of Cobalt, Ont. Silver was discovered on the Foster claim in 1905, and although the property has been one of the smaller producers in the area, intermittent production over the last half century has yielded more than 1.1 million ounces of silver and 435,000 pounds of cobalt, together with lesser amounts of nickel and copper.

As with many of the veins in the Cobalt district, those on the Foster property occur in Keewatin volcanics and associated interflow sediments, and in the unconformably overlying metasediments of the Cobalt Group. The Keewatin host rocks enclosed the more prolific veins.

The original location of the mckinstryite specimen within the mine workings is not known, and no records or indications exist to suggest from which of the several possible veins on the property the specimen may have come.

DESCRIPTION OF SAMPLE

The mckinstryite specimen is small, approximately 2.5 × 2.5 × 1 cm, with a coarse-grained mass of mckinstryite making up approximately one third of the volume of the sample, the remainder being a matrix of calcite and actinolite, with minor amounts of silver and arsenopyrite.

A polished section of the fraction prepared for analysis showed that the grain size of the mckinstryite ranged from 0.2 to about 3 mm in diameter and that the grains were not visibly twinned. The sample is, therefore, a coarse-grained aggregate of intergrown crystals.

The only opaque minerals present, besides those already mentioned, are minor amounts of chalcopyrite, in grains up to 1 mm in diameter, and a few laths of stromeyerite. The grain size of the mckinstryite was sufficiently coarse so that no difficulty was encountered in picking pure material for chemical analysis.

COMPOSITION

During his careful study of phases in the system Cu-Ag-S, Djurle (1) established the composition of a phase, called by him the β-phase, as $Cu_{0.8}Ag_{1.2}S$. This composition was verified by Skinner (4), who agreed with

TABLE 1

SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSIS OF MCKINSTRYITE, FOSTER MINE, COBALT, ONT. ANALYSIS BY H. W. WORTHING, U. S. GEOLOGICAL SURVEY

Element	Wt. %	Element	Wt. %	Element	Wt. %
Ag	Major	Ti	0.0002	Cr	0.0002
Cu	Major	Mn	0.0002	Ni	0.0005
Fe	0.03	Ba	0.0003	Pb	0.15
Mg	0.005	Bi	0.0007	Sn	0.0003
Ca	0.05	Co	0.003	V	0.0001

Looked for, but not found: Na, K, P, As, Au, B, Be, Cd, Ce, Ga, Ge, Hf, Hg, In, La, Li, Mo, Nb, Pd, Pt, Re, Sb, Sc, Sr, Ta, Te, Th, Tl, U, W, Y, Yb, Zn, Zr.

Results are reported in percent to the nearest number in the series 1, 0.7, 0.5, 0.3, 0.2, 0.15 and 0.1, etc., which represent mid points of internal data on a geometric scale. The assigned interval for semiquantitative results will include the quantitative value about 30 percent of the time.

Djurle that the compound did not measurably deviate from the metal/sulfur ratio of 2:1. However, neither Djurle nor Skinner specifically established the homogeneity of the β-phase on the join Cu_2S-Ag_2S.

Approximately 200 mg of carefully selected fragments of mckinstryite were submitted to chemical analysis. Semiquantitative spectroscopic analysis (Table 1) established that Cu and Ag were the only major metallic elements present. A quantitative analysis for Cu, Ag, and S, by X-ray fluorescence was then carried out by F. Cuttitta and H. J. Rose, Jr., of the U. S. Geological Survey, with the results given in Table 2. The analysis was performed by dissolving the sample in fuming HNO_3 in a sealed 25-ml volumetric flask and absorbing portion of the solution onto powdered chromatographic paper. The paper was then dried overnight at 80° C, pelletized at 80,000 psi, and analyzed directly by X-ray fluorescence. The analytic precision, established from a series of synthetic standards, is ± 1 percent of the amount present for each element. It is apparent, with Cu + Ag summing to 66.80 atom percent, and sulfur to 33.20 atom percent, that mckinstryite, like its synthetic counterpart, has a metal/sulfur ratio of 2:1 within the limits of analytical error. The formula indicated by analysis is slightly more copper-rich than $Cu_{0.8}Ag_{1.2}S$, calculating to $Cu_{0.82}Ag_{1.18}S$, indicating that the formula of mckinstryite should be written $Cu_{0.8+x}Ag_{1.2-x}S$, where $0 \lessapprox x \lessapprox 0.02$.

TABLE 2

QUANTITATIVE X-RAY FLUORESCENT ANALYSIS OF MCKINSTRYITE, FOSTER MINE, COBALT, ONT. ANALYSTS: H. J. ROSE, JR., AND F. CUTTITTA, U. S. GEOLOGICAL SURVEY

Element	Wt. %	Atom %
Cu	24.9	27.6
Ag	60.0	39.2
S	15.1	33.2
Total	100.0	100.0

Composition: $Cu_{0.82}Ag_{1.18}S$.

PROPERTIES

Mckinstryite is a steel-gray color on the newly fractured or cleaved surface, similar to stromeyerite, and becomes dark gray to black on long exposure to air. The streak is a dark steel gray. One poorly developed cleavage occurs. Fracture is subconchoidal.

The specific gravity was determined from six separate measurements on each of six fragments ranging in weight from 11 to 22 mg, using the Berman torsion balance with toluene as an immersion medium. The average for the observed specific gravity values is 6.61, with a standard deviation of ±0.03.

On a polished surface, mckinstryite has a hardness of B and a polishing hardness just slightly less than that of stromeyerite. In reflected light it is a light grayish-white color, whiter and with a slightly higher reflectivity than stromeyerite. Under crossed nicols, mckinstryite is strongly anisotropic, with gray, pale-grayish-blue and light-tan colors. The anisotropism is less pronounced than that for stromeyerite, but stronger than that for jalpaite.

Etch reactions on the polished surface, using standard etch reagents are:

HNO_3, 1:1	Positive. Etches slightly and turns gray-black.
HCl, 1:1	Negative. Slight halo around drop. Halo washes off.
KOH, 40% (by weight)	Negative. Halo around drop. Halo washes off.
KCN, 20% (by weight)	Positive. Rapid reaction with a heavy black stain produced.
$HgCl_2$, 5% (by weight)	Positive. Irridescent brown stain; forms slowly.
$FeCl_3$, 20% (by weight)	Positive. Surface blackens slowly.

The etch reactions are very similar to those for stromeyerite, and cannot be used to distinguish unambiguously between the two minerals.

The thermal stability of synthetic mckinstryite has been established by Skinner (4) who found an upper stability limit of 94.4 ± 1.5° C, at which temperature the phase transforms to a two-phase intergrowth of jalpaite plus a cation-disordered hexagonal phase of composition $(Cu_{0.96}Ag_{1.04})S$. Above 139 ± 10° C the mckinstryite composition again becomes a single phase, with the formation of a cation-disordered, face-centered-cubic compound of a high digenite type. This cubic phase, which is unquenchable, is stable up to the liquidus.

CRYSTALLOGRAPHY

Several plane surfaces, apparently cleavage planes, up to 2 × 1 mm in size, occur on the massive-looking mckinstryite sample. Fragments with these plane surfaces on were carefully flaked off and then examined by polished section and by single crystal X-ray diffraction techniques. Both methods showed that the flakes were untwinned portions of single crystals.

X-ray powder diffraction patterns were prepared by standard film methods and by a high-angle X-ray goniometer with a scintillation counter detector. The results of these efforts, together with similar data for Djurle's (1) synthetic β-phase and data collected from Skinner's (4) synthetic β-phase, are given in Table 3. These data leave no reason to doubt that the natural and

Table 3. X-ray powder diffraction data for mckinstryite ($Cu_{0.82}Ag_{1.18}S$), Foster Mine, Cobalt, Ont., and synthetic mckinstryite ($Cu_{0.8}Ag_{1.2}S$) prepared by Skinner (4), compared with those by Djurle (1) for his synthetic β-phase. d_{calc} for an orthorhombic cell, a = 14.034Å, b = 15.677Å, c = 7.803Å, space group *Pnam* or *Pna*2_1. Intensities reported as relative intensities by visual estimation. Measurements made in CuKα radiation, = 1.5418Å. N.O. = Not Observed.

		mckinstryite		synthetic mckinstryite		β-phase, Djurle (1)	
hkl	d_{calc}	d_{obs}	I	d_{obs}	I	d_{obs}	I
011	6.985	6.970	0.5	N.O.			
230	4.192	4.199	0.5	N.O.			
320	4.019	4.017	1	4.018	1	3.98	W
002	3.901	3.907	1	3.889	1	3.88	W
231	3.693	3.688	0.5	N.O.			
400	3.511	3.508	6	3.509	5	3.51	M
122	3.389	3.389	1	3.390	0.5		
150	3.060	3.062	6	3.063	6	3.058	M
312	2.944	2.945	0.5	N.O.			
430	2.914	2.913	0.5	N.O.			
250	2.863	2.862	6	2.862	5	2.867	M
322	2.799	2.797	1	2.801	1		
042,510	2.765	2.763	0.5	N.O.			
251	2.688	2.688	0.5	N.O.			
520	2.644	N.O.		N.O.		2.644	W
511,350	2.606	2.606	10	2.609	10	2.607	S
160,130	2.566	2.567	4	2.566	3	2.564	W
113	2.524	2.524	1	2.520	2	2.522	W
521	2.504	2.505	1			2.501	VW
530,351	2.472	2.472	0.5	2.470	0.5		
161,203	2.439	2.436	0.5	2.433	0.5		
213,152	2.408	2.407	4	2.405	4	2.407	M
261,432	2.335	2.333	0.5	2.331	0.5		
252	2.308	2.307	3	2.306	3	2.309	M
313	2.250	2.250	1	2.244	1		
361,522	2.189	2.188	3	2.187	2	2.190	W
352	2.166	2.167	2	2.165	2	2.166	W
350	2.136	2.137	0.5	N.O.		2.500	
403,532	2.089	2.088	2	2.086	1	2.092	W
413,243	2.071	2.070	7	2.069	7	2.070	M
640	2.009	2.009	1	2.005	1	2.010	W
641,004	1.946	1.948	5	1.947	5	1.949	M
470	1.888	1.888	2	1.885	2		
650,632,730	1.874	1.874	0.5	N.O.			
443,552,353	1.844	1.844	1	1.840	1		
224,163	1.828	1.827	0.5	N.O.			

synthetic materials possess identical structures. The similarity of spacings and intensities between some of the strong lines for stromeyerite and mckinstryite lead one to suspect that the two compounds might have certain structural elements in common.

Single-crystal X-ray diffraction studies by the Buerger precession method established that the symmetry of mckinstryite is orthorhombic, space group *Pnam* or $Pna2_1$. The cell edges determined by this method were $a = 13.99$ Å, $b = 15.66$ Å and $c = 7.80$ Å. Superstructure reflections were sought, but not found, by using very small mineral fragments and very long exposure times. Twinning effects, commonly found in complex sulfides, were not found, though the possibility of twinning by merohedry cannot be dismissed until a structural analysis is completed. Because of strong X-ray absorption effects, the measurement errors from the single-crystal photographs are large. To obtain a more precise measure of the unit cell, X-ray powder diffraction data were measured against CaF_2 as an internal standard, using a high-angle goniometer, and refined by least squares using the Evans, Appleman and Handwerker (2) program. The results of this refinement, which are to be preferred over those derived from the single crystal, are: $a = 14.043 \pm 0.005$ Å, $b = 15.677 \pm 0.006$ Å, $c = 7.803 \pm 0.003$ Å.

Stromeyerite, like mckinstryite, has an orthorhombic cell. The dimensions of the stromeyerite cell (1), are $a = 4.066$ Å, $b = 6.628$ Å, and $c = 7.972$ Å, space group *Cmcm*. The possibility of a structural relation between stromeyerite and mckinstryite is further supported by an apparent dimensional relationship between the two cells such that:

$$a_{\text{mckinstryite}}\ (14.0\ \text{Å}) \simeq 4d_{(110)\ \text{stromeyerite}}\ (13.9\ \text{Å})$$
$$c_{\text{mckinstryite}}\ (7.8\ \text{Å}) = d_{(130)\ \text{stromeyerite}}\ (7.8\ \text{Å})$$
$$b_{\text{mckinstryite}}\ (15.7\ \text{Å}) \simeq 2c_{\text{stromeyerite}}\ (15.9\ \text{Å})$$

The net defined by the (110), (130) and c of stromeyerite is very nearly orthogonal. The slight changes necessary to bring the stromeyerite and mckinstryite nets into orthogonal register could probably be accounted for by very slight changes in the general atomic positions in the mckinstryite cell, relative to stromeyerite, and consequent on the compositional difference between them. A crystal-structure investigation is proceeding and will be reported on elsewhere.

The volume of the mckinstryite cell is 1717.8 ± 0.8 Å^3. With a molecular weight for $Cu_{0.82}Ag_{1.18}S$ of 211.47 and the observed specific gravity of 6.61 ± 0.03, the calculated cell occupancy is 32.3 ± 0.3 formula units of $Cu_{0.82}Ag_{1.8}S$, indicating a Z of 32.

GEOLOGICAL SIGNIFICANCE

Although no direct geologic conclusions may be drawn from this single specimen of mckinstryite, a general observation of some significance may be drawn.

Mckinstryite breaks down above 94.4° C to a two-phase assemblage of jalpaite and a cation-disordered hexagonal compound of composition $(Cu_{0.96}Ag_{1.04})S$ (4). It would be highly fortuitous for these two compounds to be deposited in exactly the correct amounts, and in such close contact, that they would react on cooling to give large, pure masses or single crystals of mckinstryite. The presence of such a pure mass suggests very strongly that the mckinstryite from the Foster Mine was formed below 94.4° C. Mckinstryite composition becomes homogeneous again above 139° C, with the formation of a cation-disordered face-centered cubic compound (4). The compositional extent of this field is so large, however, stretching from Cu_2S to Ag_2S, that it would again be highly unlikely for an ore fluid to deposit just the precise composition that would quench to a pure mass of mckinstryite. The fact that the mckinstryite is untwinned further supports the contention that it grew below 94.4° C. Had it grown in the cation-disordered face-centered cubic field, twinning would almost certainly have occurred during the cooling process. The possibility that a complex intergrowth resulting from a higher temperature breakdown has segregated into individual coarse phases cannot, of course, be eliminated for a single specimen. Should coarse-grained, pure material be widespread, however, the argument becomes compelling.

Coexisting stably with mckinstryite are a few highly twinned crystals of silver and, on one margin of the mass, a few tiny fragments of stromeyerite, an assemblage in complete agreement with the phase diagram below 94.4° C (4). Electron microprobe analysis of the stromeyerite in a lath enclosed on both sides by mckinstryite, showed that its composition was CuAgS. The composition was definitely not copper rich, as found for many natural and synthetic stromeyerites.

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