

## Kraisslite and mcgovernite: new chemical data

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### Abstract

Chemical analytical data have been obtained for kraisslite and mcgovernite. Kraisslite contains both trivalent and pentavalent arsenic in the weight ratio of 3:4. Specimens from different parageneses have relatively invariant chemical compositions, which suggests some degree of ordering of Mg, Mn, and Zn. The average of five analyses yields MgO 2.6, MnO 52.0, ZnO 8.6, Fe<sub>2</sub>O<sub>3</sub> 2.0, As<sub>2</sub>O<sub>3</sub> 6.69, Al<sub>2</sub>O<sub>3</sub> 0.2, As<sub>2</sub>O<sub>5</sub> 10.35, SiO<sub>2</sub> 12.9, H<sub>2</sub>O 3.68 percent, totalling 98.9 percent, and yielding the empirical formula Fe<sub>3</sub><sup>2+</sup>Mg<sub>4</sub>Mn<sub>44</sub>Zn<sub>6</sub>(AsO<sub>3</sub>)<sub>4</sub>(AsO<sub>4</sub>)<sub>6</sub>(SiO<sub>4</sub>)<sub>12</sub>(OH)<sub>36</sub>. Ferric iron is present in both kraisslite and mcgovernite. Additional analyses of mcgovernite give the average MgO 11.5, MnO 42.2, ZnO 9.3, Fe<sub>2</sub>O<sub>3</sub> 1.7, As<sub>2</sub>O<sub>3</sub> 4.6, As<sub>2</sub>O<sub>5</sub> 12.5, SiO<sub>2</sub> 9.2, H<sub>2</sub>O 9.1 percent, totalling 100.1 percent.

### Introduction

Kraisslite and mcgovernite are both very complex magnesium manganese zinc arsenosilicates which are known only from Sterling Hill, New Jersey. Kraisslite was described by Moore and Ito (1978), who proposed the tentative formula (Mn<sub>0.89</sub><sup>2+</sup>Mg<sub>0.08</sub>Fe<sub>0.03</sub><sup>2+</sup>)<sub>24</sub>Zn<sub>4</sub>(AsO<sub>4</sub>)<sub>4</sub>(SiO<sub>4</sub>)<sub>8</sub>(OH)<sub>12</sub>. While obtaining chemical analyses of schallerite (another complex arsenosilicate composed of the same elements) for a separate study, we included samples of kraisslite and mcgovernite as control samples. Our results are at variance with existing data concerning the chemical composition of kraisslite.

### Analytical methods

The samples were chemically analyzed with an ARL-SEM-Q electron microprobe, utilizing an operating voltage of 15 kV and a beam current of 0.15 μA. The standards were manganite for Mn, synthetic ZnO for Zn, olivenite for As, and hornblende for Mg, Fe, Al, and Si. The data were corrected with a modified version of the *MAGIC-4* program.

Special attention was given to the determination of arsenic and its state of oxidation. Separate samples were used to determine trivalent and total As. Pentavalent As was calculated by difference. The trivalent As was distilled directly as the trichloride, followed by titration with iodine (Lundell *et al.*, 1951, p.

374-378). To obtain total As, FeSO<sub>4</sub>, used as the reductant, was added to the sample before distillation with HCl. The iodine solution for the titration of the distilled As was standardized against known quantities of As carried through the procedure in a manner like that used for the unknowns. The procedure was checked against solutions containing 0.5 mg/ml As, either in the trivalent or pentavalent state. Recoveries from standards of 4.00, 4.02, 4.01, 4.07 and 4.02 mg As<sup>3+</sup> were 4.00, 4.00, 4.03, 4.08 and 4.00 mg As, respectively.

We tested for reduction of pentavalent As during distillation without the reductant and it appeared to be minimal. Variation between duplicate samples of unknowns was usually 0.2 percent or less. The procedure we used is as follows: Transfer a sample containing 3-5 mg As to the distilling flask together with 175 ml HCl. For total As, also add 15 g FeSO<sub>4</sub>. With the condenser outlet immersed in 100 ml distilled water, distill over 100 ml of the acid. During this process, keep the distillate cold by means of a surrounding ice-water bath. Remove the distillate and neutralize with cold concentrated NaOH solution. One drop of methyl red will serve as a good indicator. Cool again and just reacidify with 1:1 HCl. Add 20 ml saturated NaHCO<sub>3</sub> solution, 5 ml starch, and 4-5 g solid KI. Titrate with 0.01 normal standardized iodine to the first pink endpoint. Correct the titration for a blank run on the same reagents.

### Kraisslite

Subsequent to its original description, kraisslite has been found in a number of different parageneses, indicating a broader range of associations than the original thin films and lenses. We briefly describe these parageneses for the analyzed samples, all from Sterling Hill, which remains the only locality for kraisslite. It was not determined whether or not kraisslite is in equilibrium with the associated minerals.

*NMNH 144262.* The sample consists of very thin foliae in fractures in willemite–franklinite ore which contains up to 10 percent holdenite by volume. Kraisslite occurs in contact with willemite and franklinite and also as sprays and warped foliae in massive holdenite. It was found between the 1200 and 1300 levels in the 1340 undercut pillar.

*NMNH 146199.* The sample consists of randomly oriented “booklets” of kraisslite in contact with franklinite, calcite, primary and secondary willemite, and a highly zincian adelite (containing approximately 14 percent ZnO). It was found at the 800 level in the 1220 pillar.

*NMNH 143983.* The sample consists of abundant irregular segregations of kraisslite in low-grade willemite–calcite–franklinite ore. The massive segregations of kraisslite are abundant in this material and locally comprise up to 20 percent of the ore. Kraisslite is in contact with all the minerals in this assemblage. The sample was found on the 700 level in the 1010 stope.

All samples were characterized by X-ray powder diffraction and the results are in excellent agreement with the X-ray powder diffraction patterns of the holotypes. The powder diffraction pattern of kraisslite, although similar to that of mcgovernite, is sufficiently distinct to permit unambiguous identification of the species. NMNH 137017 and 137018 are the holotype specimens for kraisslite; the former is the specimen that provided the original analysis.

### Discussion

The analytical data in Table 1 indicate a number of significant points concerning the chemical composition of kraisslite. Zinc is in tetrahedral coordination in most of the secondary minerals of Franklin and Sterling Hill. The rather constant concentration of zinc near a value of 6 Zn per cell (consistent with equipoint ranks in space group  $P6_322$ ; Moore and Ito,

1978) suggests that it may well be ordered in tetrahedral sites. Likewise, the nearly constant value of approximately 4 Mg per cell suggests that Mg may be ordered relative to Mn, but this is more problematical. The different parageneses and spatial separation of the occurrences suggest more than chance significance to these compositional similarities between samples.

Of special interest is the presence of ferric iron in kraisslite. All samples were subjected to microchemical tests which gave a positive reaction for ferric iron. Care was taken to use fresh unaltered material where possible. We note that ferric iron is present in mcgovernite as well and is also found in dixenite, which Moore and Araki (1978) have noted as being related to kraisslite. Hence, ferric iron may play some role in the crystal chemistry of kraisslite.

Of paramount significance, however, is the fact that the As exists in two oxidation states. Although Ito (in Moore and Ito, 1978) found only 0.87 percent  $As_2O_3$  and predominantly pentavalent As in kraisslite, our analytical work clearly demonstrates that the As exists in two oxidation states with  $As^{3+}:As^{5+} = 3:4$ , and is relatively constant from sample to sample, including the holotype (reanalyzed). Other minerals with As in dual roles also exist at Sterling Hill; mcgovernite was the first arsenate–silicate to be described (Palache and Bauer, 1927), and synadelphite also occurs here (Moore and Ito, 1978) in contact with kraisslite.

Calculation of the number of atoms per unit cell in kraisslite with the unit-cell dimensions and density of Moore and Ito (1978) indicates that, on initial inspection, the numbers of Si,  $As^{5+}$ ,  $Fe^{3+}$ , and Al atoms do not conform to the requirements of space group  $P6_322$ , which requires 12, 6, 4, or 2 equivalent atoms in the various sites. However, we note that the sum of  $As^{5+}$  and Si approximates 18 atoms, implying that there may be some substitutions involving these elements.

An idealized formula of  $Fe_2^+Mg_4Mn_{44}Zn_6(AsO_3)_4(AsO_4)_6(SiO_4)_{12}(OH)_{36}$  yields a calculated density of  $3.918 \text{ g/cm}^3$ , in reasonable agreement with the observed value of  $3.876 \text{ g/cm}^3$ , if we assume limited substitutions among Si and  $As^{5+}$ . This formula, however, must be considered tentative. Moore and Ito (1978) have noted streaks parallel to the  $c$  axis which suggest stacking faults in the structure. We agree with Moore and Ito that no unambiguous chemical formula can be proposed for this complex mineral in the absence of a complete crystal structure determination. Hence, the crystal chemistry of kraisslite

Table 1. Chemical analyses of kraisslite

Sample number	MgO	MnO	FeO	ZnO	Fe <sub>2</sub> O <sub>3</sub> *	Al <sub>2</sub> O <sub>3</sub>	As <sub>2</sub> O <sub>3</sub>	As <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	H <sub>2</sub> O	Total
1. Moore and Ito (1978)	2.53	51.6	1.92	8.47		0.21	0.87	17.7	13.8	3.68	100.78
2. NMNH 137017	2.3	51.4		8.0	2.2	0.2	6.48 <sup>†</sup>	10.06 <sup>†</sup>	13.2	3.68**	97.5
3. NMNH 146199	2.7	52.5		8.8	1.7	0.1	6.88 <sup>†</sup>	10.25 <sup>†</sup>	12.9	3.68**	99.5
4. NMNH 143983	2.4	53.5		8.2	1.6	0.1	6.72 <sup>†</sup>	10.74 <sup>†</sup>	13.1	3.68**	100.0
5. NMNH 137018	2.5	50.6		8.9	2.3	0.3	7.08 <sup>††</sup>	10.96 <sup>††</sup>	12.8	3.68**	99.1
6. NMNH 144262	2.9	51.8		9.1	2.1	0.1	6.99 <sup>††</sup>	10.84 <sup>††</sup>	12.5	3.68**	100.0
7. Average of 2,3,4,5,6	2.6	52.0		8.6	2.0	0.2	6.69 <sup>‡</sup>	10.35 <sup>‡</sup>	12.9	3.68	99.0
Theory***	2.66	51.5		8.06	2.63		6.53	12.64	11.90	4.08	100.0
Number of atoms per unit cell <sup>†††</sup>											
2. NMNH 137017	3.42	43.43		5.89	1.65	0.23	3.92	5.24	13.16		
3. NMNH 146199	4.01	44.36		6.48	1.27	0.11	4.16	5.34	12.87		
4. NMNH 143983	3.57	45.21		6.04	1.20	0.11	4.07	5.60	13.07		
5. NMNH 137018	3.72	42.76		6.55	1.73	0.35			12.77		
6. NMNH 144262	4.31	43.77		6.70	1.58	0.11			12.47		
Average	3.81	43.91		6.33	1.49	0.18	4.05 <sup>‡</sup>	5.39 <sup>‡</sup>	12.87		

\* Iron determined as total iron; calculated as Fe<sub>2</sub>O<sub>3</sub>.

\*\* Water taken from analysis by Ito in Moore and Ito (1978).

\*\*\* Theory for Fe<sub>2</sub><sup>3+</sup>Mg<sub>4</sub>Mn<sub>44</sub>Zn<sub>6</sub>(AsO<sub>3</sub>)<sub>4</sub>(AsO<sub>4</sub>)<sub>6</sub>(SiO<sub>4</sub>)<sub>12</sub>(OH)<sub>36</sub>.

† Oxidation state of arsenic determined as described in text.

†† Calculated from the As<sup>3+</sup>:As<sup>5+</sup> ratio derived from analyses 2, 3, and 4. Total arsenic determined by microprobe.

‡ Average of only analyses 2, 3, and 4.

††† Calculated on the basis of the unit-cell dimensions and density of Moore and Ito (1978) ( $a = 8.22$ ,  $b = 43.88 \text{ \AA}$ ,  $D = 3.876 \text{ g/cm}^3$ ).

Accuracy of data: ± 3 percent of the amount present (for microprobe analyses).

Table 2. Chemical analyses of mcgovernite

Sample Number	MgO	MnO	FeO	ZnO	Fe <sub>2</sub> O <sub>3</sub> <sup>±</sup>	As <sub>2</sub> O <sub>3</sub>	As <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	H <sub>2</sub> O	Total
1. Palache and Bauer (1927)	11.27	42.72	1.53	10.22		4.45	12.48	8.92	8.49	100.08
2. Moore and Ito (1978)	11.02	42.5	1.49	10.58		4.78	13.15	8.83	8.30	100.77*
3. NMNH R3556	11.7	39.9		9.6	1.6	4.49***	12.59***	9.2	10.92**	100.0
4. NMNH C6220-2	10.9	43.8		9.2	1.6	4.58 <sup>±</sup>	12.11 <sup>±</sup>	9.3	8.51**	100.0
5. NMNH R14830	11.6	43.5		9.1	1.7	4.65 <sup>±</sup>	12.60 <sup>±</sup>	9.3	7.55**	100.0
6. NMNH 104166	11.7	40.8		9.5	1.7	4.70 <sup>±</sup>	12.73 <sup>±</sup>	9.2	9.67**	100.0
7. NMNH 137837	11.4	42.8		9.2	1.7	4.59 <sup>±</sup>	12.46 <sup>±</sup>	9.2	8.65**	100.0
8. (Average of #3,4,5,6,7)	11.5	42.2		9.3	1.7	4.6	12.5	9.2	9.1	100.1

\* Includes 0.12 % Al<sub>2</sub>O<sub>3</sub>.

\*\* Water by difference.

\*\*\* Oxidation state of arsenic determined as described in text.

Accuracy of data ±3 percent of the amount present, for microprobe determinations.

± Determined as total iron, calculated as Fe<sub>2</sub>O<sub>3</sub>.±± Calculated from the As<sup>3+</sup>:As<sup>5+</sup> ratio 3:7 derived from analyses 1, 2 and 3.

Arsenic determined as total arsenic by electron microprobe.

might be much more complex than indicated by our analytical study.

### McGovernite

McGovernite was originally described by Palache and Bauer (1927). Its symmetry has been discussed by Wuensch (1960, 1968) and Moore and Araki (1978). Its chemical constituents are the same as those of kraisslite but are present in different ratios. We present new analyses of mcgovernite, together with those of Bauer (Palache and Bauer, 1927) and Ito (Moore and Ito, 1978), in Table 2. The analyzed samples have all been identified by X-ray diffraction.

Of special interest is the presence of ferric iron in mcgovernite, in concentrations similar to those in kraisslite, but with less variance. It is present in all samples, although not previously reported. Our determination of the oxidation states of the As substantiates the determinations by Bauer and Ito. We have calculated the ratio of  $As^{3+}:As^{5+}$  for the microprobe analyses using the 3:7 ratio determined empirically by analysis (Table 2), rather than the simpler 1:3 ratio suggested by the formula of Moore and Araki (1978).

As with kraisslite, the relative concentrations of Mg, Mn, and Zn suggest some ordering of these elements in the crystal structure. We present additional analyses as evidence of the relatively invariant composition of this mineral. We offer no chemical formula for mcgovernite; calculation of cell contents

yields results not in conformity with the space group requirements. The presence of over 1200 atoms in the unit cell, combined with the probability of complex substitutions such as are likely in kraisslite, precludes any simple formula.

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