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Evidence for hibbingite–kempite solid solution

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ABSTRACT

New occurrences of hibbingite, γ-$Fe_2(OH)_3Cl$, have been found associated with platinum-group minerals in the Noril'sk Complex, and with the Korshunovskoye iron ores of the southern Siberian platform. The Norils'k grains, which are up to 0.6 mm in diameter, are associated with the platinum-group minerals froodite, cabriite, urvantsevite and with native silver in massive pentlandite–cubanite–chalcopyrite ore. The Korshunovskoye iron ore sample in which hibbingite was found is composed of fine-grained magnetite ore associated with halite. Hibbingite, hematite and silver grains are found in cavities in halite; the reddish-brown hibbingite grains usually occur as encrustations in the cavities. The size of hibbingite and hematite grains is up to 100 μm.

Hibbingite from the Noril'sk Complex contains a significant kempite ($Mn_2(OH)_3Cl$) component; in some cases it contains over 50 mol. % Mn. These data suggest that at least a partial solid solution series exists between hibbingite and kempite. All known occurrences of hibbingite represent paragenetically late mineral assemblages. In the case of the Korshunovskoye deposits, the occurrences are associated with highly concentrated hydrothermal brines derived from the Lower Paleozoic saline sediments of the Siberian Platform cover.

KEYWORDS: hibbingite, kempite, solid solution, Noril'sk complex, Korshunovskoye iron ores, platinum-group mineral.

Introduction

NEW occurrences of hibbingite, γ-$Fe_2(OH)_3Cl$, have been found associated with platinum-group minerals in the Noril'sk Complex, and with the Korshunovskoye iron ores of the southern Siberian platform. First identified as an unnamed iron hydroxychloride in the Deep Copper Zone of the Sudbury Complex (Springer, 1989), hibbingite was characterized and named based on drill core samples from the Duluth Complex (Dahlberg, 1987; Dahlberg and Saini-Eidukat, 1991; Saini-Eidukat *et al.*, 1994). It has also been described as a terrestrial weathering product of meteorites and of archaeological artifacts (Buchwald and Koch, 1995).

In the Noril'sk samples, Fe is replaced by Mn in hibbingite. These grains contain a significant kempite ($Mn_2(OH)_3Cl$) component; in some cases over 50 mol. % Mn. The grains, which are up to 600 μm in diameter, are associated with platinum-group minerals and native silver in massive sulphide ore. In contrast, the Korshunovskoye hibbingite grains are Fe-rich, up to 100 μm in diameter, and are found in association with hematite and native silver in cavities in halite. The reddish-brown hibbingite grains usually occur as encrustations.

All known occurrences of hibbingite represent paragenetically late mineral assemblages. In the case of the Korshunovskoye deposits, the occurrences are associated with highly concentrated hydrothermal brines derived from the Lower Paleozoic saline sediments of the Siberian Platform cover. The microchemical analyses suggest that at least a partial natural solid solution series may exist between hibbingite and kempite.

Description of new occurrences

Hibbingite from the Noril'sk Complex was identified in polished sections of grab samples of massive pentlandite-cubanite-chalcopyrite ore (Fig. 1). Grains are up to 600 μm in diameter and are associated with the platinum-group minerals froodite ($PdBi_2$), cabriite (Pd_2SnCu) and urvantsevite, ($Pd(Bi,Pb)_2$) and with native silver. Textural evidence (Fig. 1*b*) indicates that the hibbingite was deposited by a vein-filling event from a Cl-bearing fluid moving through the sulphide minerals.

Hibbingite was also recognized in drill core from the Korshunovskoye iron ore deposit, located approximately 500 km to the NNE of Irkutsk city in the southern Siberian platform (Polozov *et al.*, 1995). The Korshunovskoye deposit is one of the largest of the Angara-Ilim type deposits (Dunayev, 1986). Hibbingite was found in core from drill hole no. 357 at a depth of 917 metres. The sample is composed of fine-grained magnetite ore cemented by halite. Late pyrrhotite, calcite and chlorite crystals have grown in numerous cavities. A pyrrhotite crystal of keg-like form and diameter up to 1 cm was sawn with a diamond circular saw cooled by water, and cavities filled by halite were found inside. Upon preparation of a polished section for electron microprobe investigation, individual hibbingite, hematite and silver grains were found in the halite-filled cavities (Fig. 2). Hibbingite grains usually encrust the rims of the cavities. The sizes of the reddish-brown hibbingite grains and the accompanying hematite grains are up to 100 μm.

Mineral chemistry

A summary of analyses of fresh hibbingite from the Duluth, Sudbury, and Noril'sk Complexes and from the Korshunovskoye deposit is presented in Table 1 and on Fig. 3, which shows that grains in the Noril'sk samples contain a significant kempite ($Mn_2(OH)_3Cl$) component; in some cases over 50 mol. % Mn. The composition of a kempite from California reported in Palache *et al.* (1951) contains 0.92 mol. proportion kempite, but since no analysis for Fe is provided (and the deficiency could well be made up by Mg or some other element), the questionable nature of this analysis has been indicated on Fig. 3. The data suggest that at least a partial solid solution exists between kempite and hibbingite. Synthesis by Laverat *et al.* (1973) of the complete range of compounds with the generalized formula $(Fe,Mn)_4(OH)_6Cl_2$-nH_2O supports the existence of such a natural solid solution series.

Duluth Complex and Korshunovskoye hibbingite grains in polished sections were exposed to

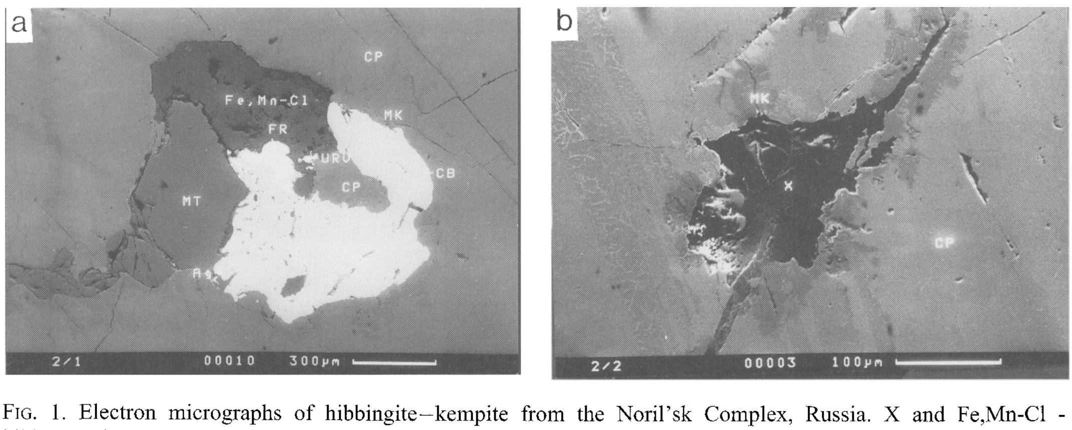

FIG. 1. Electron micrographs of hibbingite–kempite from the Noril'sk Complex, Russia. X and Fe,Mn-Cl - hibbingite-kempite; Fr - froodite; MT - magnetite; MK - mackinawite; URV - urvantsevite; CB - cabbriite; CP - chalcopyrite; Ag - Silver.

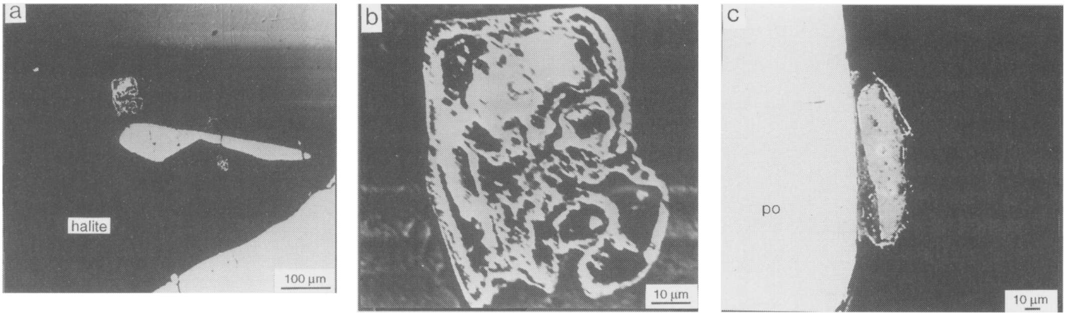

FIG. 2. Electron micrographs of hibbingite from the Korshunovskoye iron ore deposit, Russia. (*a*) Hibbingite in halite, adjacent to sulphide. (*b*) Enlargement of convoluted grain of hibbingite in halite. (*c*) Hibbingite adjacent to pyrrhotite (po).

atmosphere and analyzed. In the case of the Korshunovskoye sample, the original mineral had been analysed first during spring 1992, immediately after polished section preparation, and again during the winter of 1995–1996 after storage in a dessicator. Reanalysis shows that, with time, the chlorine content of the grains decreases from approximately 17 wt.% to approximately 6 wt.% concomitant with a small increase in iron. This is consistent with Springer's (1989) observation of the formation of akagenéite ($Fe_8(O,OH)_{16}Cl_{<2}$; Post and Buchwald, 1991) in Sudbury hibbingite.

Mode of formation

The occurrences of hibbingite from the Korshunovskoye and Noril'sk deposits are distinct from those found in the Duluth and Sudbury Complexes because of their formation inside sulphide grains. As seen in Fig. 1*b*, Noril'sk sulphide contains a fracture through which Cl-bearing fluids traveled to deposit the hibbingite-kempite. Serpentinization occurred in both the Duluth and Korshunovskoye deposits, and Cl may play an important role in this process (Rucklidge and Patterson, 1977; Miura *et al.*, 1981); however, the genetic relation of serpentinization to hibbingite formation is not established for the Korshunovskoye occurrence as it is for the Duluth Complex occurrence. Rather, the youngest ore-genesis stage of the Korshunovskoye deposit is associated with highly concentrated hydrothermal brines derived from the Lower Paleozoic saline sediments of the Siberian Platform cover. A similarity among all known occurrences of hibbingite is that they represent paragenetically late mineral assemblages.

Synthesis of related compounds by Laverat *et al.* (1973) suggests that natural Co-bearing varieties of hibbingite may also exist. The existence of the related Mg-bearing mineral korshunovskite ($Mg_2Cl(OH)_3$-nH_2O; Malinko *et al.*, 1983) indicates that similar Fe, Mn or other divalent metal analogues to korshunovskite may also be found.

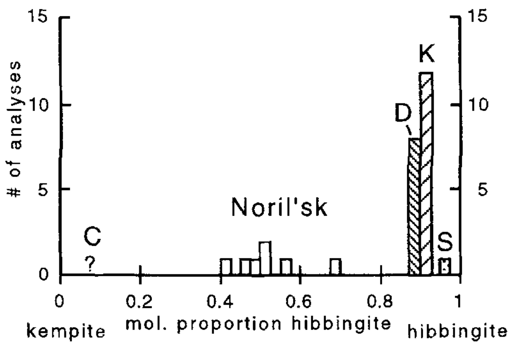

FIG. 3. Histogram showing range of measured hibbingite–kempite compositions. C - California (Palache *et al.*, 1951), D - Duluth Complex, K - Korshunovskoye, S - Sudbury Complex (Springer, 1989).

Conclusions

The following conclusions may be drawn from this study:

(1) Considerable variation exists in natural hibbingite composition; over 50 mol. % kempite component was measured in hibbingite from the Noril'sk Complex. These data suggest that at least

TABLE 1. Mineral analyses of hibbingite from the Korshunovskoye and Noril'sk deposits, in comparison with analyses from the Duluth and Sudbury Complexes, and with kempite from California

wt. %	Duluth ave.	Sudbury	Noril'sk 1	Noril'sk 2	Noril'sk 3	Noril'sk 4	Noril'sk 5	Noril'sk 6	Noril'sk 7	Noril'sk ave	Korsh ave	Kempite
Fe	49.02 (1.29)	53.90	28.50	38.40	29.20	23.30	27.60	25.40	30.90	29.04 (4.8)	51.38 (0.97)	n.a.
Mn	1.49 (0.28)	n.a.	26.90	17.20	26.60	31.90	28.80	29.90	25.80	26.73 (4.7)	0.11 (0.02)	50.59
Mg	2.62 (0.37)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a. 0.30	(0.26) n.a.	
Cl	17.39 (1.13)	18.20	17.00	17.10	17.30	17.10	17.10	17.10	17.30	17.14 (0.11)	17.00 (0.76)	16.41
(OH)*	29.92 (1.90)	27.90	27.60	27.30	26.90	27.70	26.50	27.60	26.00	27.09 (0.65)	31.20 (0.87)	21.40
Atoms												
Fe	1.76	1.93	1.02	1.38	1.05	0.83	0.99	0.91	1.11	1.04	1.84	n.a.
Mn	0.05	n.a.	0.98	0.63	0.97	1.16	1.05	1.09	0.94	0.97	0.00	1.84
Mg	0.22	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.02	n.a.
SUM +	2.04	1.93	2.00	2.00	2.01	2.00	2.04	2.00	2.05	2.01	1.87	1.84
Cl	0.98	1.03	0.96	0.96	0.98	0.96	0.96	0.96	0.98	0.97	0.96	0.93
(OH)	3.52	3.28	3.25	3.21	3.16	3.26	3.12	3.25	3.06	3.18	3.67	3.03
n	8	1								7	12	1

Notes: Duluth data from Sairn-Eidukat *et al.* (1994); includes 0.10 wt.% Si. Sudbury analysis from Springer (1989). Noril'sk analyses by N. Rusdashevsky using a LINK 10000 EDS analyser at Mechanobr Institute for Physical and Chemical Research, St. Petersburg. Korshunovskoye analyses by Olga Belozerova in the Institute of Geochemistry SB RAS using a JEOL Superprobe-733 electron microprobe analyser and the following standards: almandine (Mn), pyrope (Fe), chlorine-bearing apatite (Cl). Analysis conditions are: accelerating voltage 15 kV, current 20 nA, beam diameter 1.5–2 μm. Kempite analysis from Palache *et al.* (1951). n.a. - not analysed. * by difference.

a partial solid solution exists. This prediction can be tested by measurement of the cell parameters.

(2) Synthesis of related compounds by Laverat *et al.* (1973) suggests the possible existence of natural Co-bearing varieties of hibbingite. The existence of the related Mg-bearing mineral korshunovskite indicates that Fe, Mn or other divalent metal analogues to korshunovskite may also be found.

(3) All occurrences of hibbingite found to date show that it is paragenetically among the last minerals to form. In the Duluth Complex, clear textural evidence exists for the alteration of hibbingite to iron oxides such as hematite and goethite.

(4) Reanalysis of hibbingite from the Korshunovskoye deposit which was exposed to atmosphere agrees with re-analysis of Duluth Complex hibbingite, and suggests that after Cl-loss an intermediate breakdown product of hibbingite is akagenéite.

Acknowledgements

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