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HAYCOCKITE AND MOOIHOEKITE FROM TITANOMAGNETITE ORE, KRZEMIANKA, POLAND

UKD 549.332′322.08haycockit,moihockit:553.311′494(438-18Krzemianka k. Suwałk)

Abstract. Haycockite, $Cu_4Fe_5S_8$, and mooihoekite, $Cu_9Fe_9S_{16}$, were found in a titanomagnetite deposit at Krzemianka. They coexist with pyrrhotite, Ni-Co pentlandite and Ni-Co mackinawite. They presumably owe their origin to the migration of Fe between sulphide concentrations and the enclosing titanomagnetite and silicates, the process being caused by phase and chemical changes due to a drop in temperature and the sulphidization of titanomagnetite.

INTRODUCTION

The titanomagnetite deposit at Krzemianka contains dispersed sulphide mineralization in an amount of 0.5—1.5 vol.%. Oval or less commonly, irregular sulphide aggregates from 0.5 to 5 mm in size form isolated concentrations in magnetite, either alone or together with pyroxenes. The principal sulphide minerals are: monoclinic and hexagonal pyrrhotite, chalcopyrite. pentlandite, Co-pentlandite, smithite, thiospinel $(Fe,Ni)_1(Co,Ni)_2S_4$, Co-pyrite, cubanite (Kucha et al. 1977) and Ni-Co mackinawite (Kucha 1981). Chalcopyrite is also present, exhibiting in places optical anomalies corresponding to the optical properties of haycockite and mooihoekite.

Mooihoekite ($Cu_9Fe_9S_{16}$) and haycockite ($Cu_4Fe_5S_8$) were first reported from the Mooihoek deposit in Transvaal, South Africa (Cabri, Hall 1972). In reflected light, both minerals have optical features similar to those of chalcopyrite. Mooihoekite is weakly anisotropic and acquires a purple coating in air. It is tetragonal, $a=10.58$, $c=5.37$ (Cabri, Hall 1972). Haycockite is moderately anisotropic and its polished sections do not become coated even if not polished for a long time. It is orthorhombic, pseudotetragonal, $a \simeq b=10.71$, $c=31.56$ (Cabri, Hall 1972).

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EXPERIMENTAL

Optical, physical (microhardness) and chemical properties of minerals of the chalcopyrite group from Krzemianka were determined.

The chemical composition of the minerals was determined with a Cameca MS-46 electron microprobe operated at an accelerating voltage of 20 kV, a sample current on ThO_2 standard of 10 nA, and a counting time of 100 sec. The following spectral lines and standards were used: $SK_\alpha(FeS_2)$, $FeK_\alpha(FeS_2$, CoK_α, NiK_α, VK_α and $CuK_\alpha(CuFeS_2)$. The correction procedure was discussed in earlier papers (Kucha 1981).

RESULTS

The commonest copper mineral is chalcopyrite. It generally coexists with pyrrhotite and sometimes with pentlandite. It shows typical optical features, and its microhardness VHN=192.5 (Table 1) corresponds to chalcopyrite.

In reflected light, haycockite is similar in colour to chalcopyrite. In immersion it is lighter yellow than chalcopyrite. The colour of haycockite in polished section does not change even if exposed to air for a long time. It shows distinct anisotropy by which it is distinguished from chalcopyrite. No polysyntetic twinning described from the Mooihoek Farm deposit, Transvaal (Cabri, Hall 1972) has been noted.

Haycockite occurs in two parageneses. One is associated with the replacement (sulphidization) of titanomagnetite by haycockite and pyrrhotite, which are generally accompanied by small mackinawite admixtures. A characteristic feature of the sulphide assemblage in question is the presence of tiny dark spots (Phot. 1) which, as suggested by electron microprobe studies, are TiO_2 concentrations formed during the sulphidization of titanomagnetite. Sulphides representing this phase are presumably the youngest in the deposit. The haycockite grains of this paragenesis are up to 100 μm in size. The other paragenesis is associated with injected sulphide mineralization. Haycockite coexists with pyrrhotite, mooihoekite, Ni and Co pentlandite, and mackinawite rich in Ni and Co (Kucha 1981). In this paragenesis haycockite is of grain-size up to 80 μm (Phot. 2).

The microhardness of haycockite studied is VHN=255 kG/mm² (Table 1), due to which it is readily distinguishable from chalcopyrite (Cabri,

Table 1

Indentation micro-hardness VHN (kG/mm²), 50 g load, of Krzemianka haycockite, mooihoekite and chalcopyrite compared to that given by Cabri and Hall (1972)

Mineral	Cabri, Hall (1972)	Krzemianka	Number of indentations
Chalcopyrite	206	192.5 (185—210)	10
Haycockite	263	255 (245—268)	7
Mooihoekite	261	243.6 (238—255)	10

Table 2

Microprobe composition of haycockite and mooihoekite from Krzemianka, Poland, in wt. %

Sample number	Mineral	S	Fe	Co	Ni	Cu	Total
Theoret.		32.48	35.34			32.18	100.00
47K/D2		32.83	34.50		0.08	32.11	99.57
47K/F1	Haycockite	31.51	35.44	0,13	0.85	30.87	98.76
47K/F5		32.80	35.11	≤0.08	≤0.08	32.01	99.92
Theoret.		32.32	31.66			36.02	100.00
47K/F3	Mooihoekite	33.30	32.01	≤0.08	≤0.08	35.19	100.50
47K/F4		32.50	31.80			36.80	101.10

Sought for but not detected: V≤0.07.

Hall 1972). Its chemical composition is close to theoretical (Table 2). Haycockite associated with injected sulphides contains an admixture of Ni or Co (Table 2, No.47K/D2, 47K/F1)), whereas that owing its origin to the replacement of titanomagnetite (No.47K/F5) does not.

In reflected light, mooihoekite is similar in colour to chalcopyrite, but in air it gradually darkens, acquiring a purple coating. In immersion, in direct intergrowths with haycockite, it is perceptibly darker. It is weakly anisotropic, although this feature is frequently imperceptible. Mooihoekite coexists mainly with pyrrhotite, pentlandite and haycockite. No direct mooihoekite-mackinawite intergrowths have been noted. It forms grains up to 200 μm in size (Phot. 2). Its microhardness VHN=243.6 kG/mm² (Table 1). The chemical composition of mooihoekite from Krzemianka is close to the theoretical formula $Cu_9Fe_9S_{16}$ (Table 2).

DISCUSSION

The dominant copper sulphide in the Krzemianka deposit is chalcopyrite and a subordinate one — cubanite. Haycockite and mooihoekite are scarce and do not appear in any larger concentrations. They were formed in later processes, presumably associated with the chemical and phase changes of common minerals present in the deposit. The changes were produced primarily by a drop in temperature and by the exchange of components between the isolated sulphide concentrations and the enclosing titanomagnetite or silicates (Kullerud 1968). It seems that iron migration played a crucial part in these processes. The primary, magmatic mineral constituents participating in the exchange were pyrrhotite, chalcopyrite, titanomagnetite (a solid solution of magnetite and ulvöspinel) and silicates. All these processes gave rise to haycockite and mooihoekite, the minerals richer in iron than chalcopyrite.

Translated by Hanna Kisielewska

REFERENCES

CABRI L. J., HALL S. R., 1972: Mooihoeikite and haycockite, two new copper-iron sulfides, and their relationship to chalcopyrite and talhakhite. *Amer. Miner.* 57, 689—708.

KUCHA H., 1981: Electron diffraction and microprobe study of Ni-Co rich mackinawite from Krzemianka, NE Poland. *Chemie der Erde* 40, 235—240.

KUCHA H., PIESTRZYŃSKI A., SALAMON W., 1977: Geochemical and mineralogical study of sulphide minerals occurring in magnetite rocks of NE Poland. Miner. Polon. 8, 23—38.

KULLERUD G., 1968: Sulfide studies. Research in Geochemistry. Abelson Ed., v. 2, 286—321.

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HAYCOCKIT I MOOIHOEKIT Z RUD TYTANOMAGNETYTOWYCH KRZEMIANKI

Streszczenie

W złożu tytanomagnetytu w Krzemiance występują haycockit $Cu_4Fe_5S_8$ i mooikoekit $Cu_9Fe_9S_{16}$. Współwystępują one z pirotynem, pentylandytem Ni—Co i mackinawitem Ni—Co. Powstały prawdopodobnie w wyniku przemieszczenia Fe pomiędzy skupieniami siarczkowymi a otaczającym tytanomagnetytem i krzemianami. Wywołane to było przebudową fazową i chemiczną związaną ze spadkiem temperatury a także sulfidyzacją tytanomagnetytu.

OBJAŚNIENIE FOTOGRAFII

Fot. 1. Mikrofotografia haycockitu (*h*) i pirotynu (*po*) w tytanomagnetycie. Siarczki zastępują tytanomagnetyt wskutek czego zawierają dość liczne wrostki TiO_2. Słabo widoczna granica pomiędzy haycockitem a pirotynem zaznaczona została linią przerywaną. Światło odbite, imersja. Czarne, kwadratowe dziury są odciskami piramidy diamentowej mikrotrwadościomierza

Fot. 2. Mikrofotografia haycockitu (*h*) i mooihoekitu (*m*) w pirotynie (*po*). Wymienionym siarczkom towarzyszy pentlandyt (*p*). Światło odbite, imersja

Хенрык КУХА

ХАЙКОККИТ И МУЙХЕКИТ ИЗ ТИТАНОМАГНЕТИТОВЫХ РУД КШЕМЯНКИ

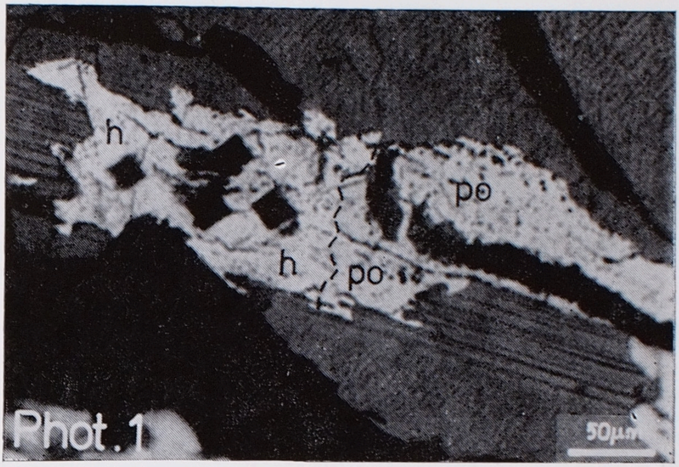
Резюме

В месторождении титаномагнетитов Кшемянка присутствуют хайккокит $Cu_4Fe_5S_8$ и муйхекит $Cu_9Fe_9S_{16}$. Они сопутствуют пирротину, Ni—Co пентландиту и Ni—Co маккинавиту. Вероятно образовались в итоге перемещения железа между сульфидными скоплениями и окружающими титаномагнетитом и силикатами. Это вызвано было фазовой и химической перестройками, связанными с понижением температуры, а также сульфидизацией титаномагнетита.

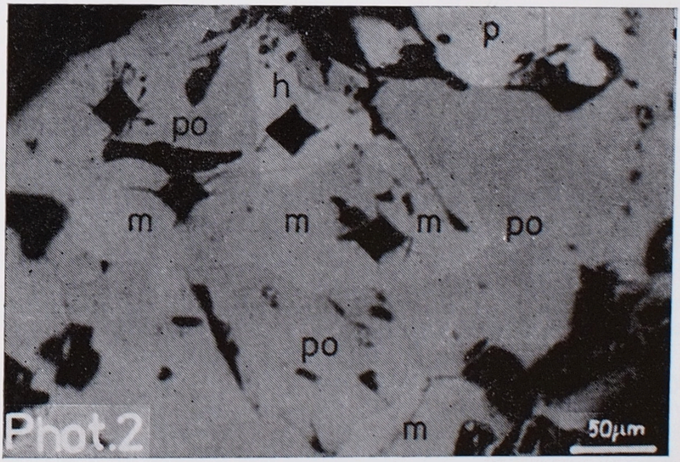
ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

Фото 1. Микрофотография хайкоккита (*h*) и пирротина (*po*) в титаномагнетите. Титаномагнетит замещается сульфидами, поэтому те содержат обильные включения TiO_2. Слабозаметная граница между хайкоккитом и пирротином подчеркнута прерывистой линией. Отраженный свет, иммерсия. Черные квадратные дырки являются оттисками алмазной пирамиды микросклерометра.

Фото 2. Микрофотография хайкоккита (*h*) и муйхекита (*m*) в пирротине (*po*). Перечисленным сульфидам сопутствует пентландит (*p*). Отраженный свет, иммерсия.



Phot. 1. Microphotograph of haycockite (*h*) and pyrrhotite (*po*) in titanomagnetite. Sulphides replace titanomagnetite, due to which they contain fairly numerous spots of TiO_2 inclusions. The indistinct boundary between haycockite and pyrrhotite is marked with a broken line. Reflected light, immersion. Black square holes are indentations of the diamond pyramid of microhardness tester



Phot. 2. Microphotograph of haycockite (*h*) and mooihoekite (*m*) in pyrrhotite (*po*). These sulphides are also accompanied by pentlandite (*p*). Reflected light, immersion.