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ON THE GENESIS OF GRAPHITE FROM MAGNETITE ROCKS OF KRZEMIANKA (NE POLAND)

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Abstract. Physico-chemical studies of graphite from Krzemianka have revealed that it owes its origin to a specific electrochemical process involving the oxidation of pyrrhotite and the reduction of CO_2 to graphite. This is evidenced by an S admixture in siderite and graphite, and a high (0.30%) Fe admixture in graphite. Also a 0.40 wt. % content of Cu in siderite shows that it formed as a result of the replacement of the primary, magmatic sulphide assemblage consisting, among other minerals, of pyrrhotite and chalcopyrite group.

INTRODUCTION

The anorthosites and norites (Juskowiak, 1973) occurring in north-eastern Poland were found to contain rich ore mineralization which was described in several papers (Siemiątkowski, 1970; Kucha, Piestrzyński 1976; Kucha *et al.* 1977, 1979). The oxide assemblage is represented by magnetite, titanomagnetite, ilmenite, ulvöspinel, spinel-hercynite series, and hematite. Corundum, anatase, siderite and graphite appear as subordinate minerals (Kucha, Piestrzyński, 1976). The sulphide assemblage consists of pyrrhotite, smithite, thiospinel, pentlandite, cobalt pentlandite, pyrite, cobalt pyrite, marcasite, chalcopyrite, cubanite, mackinavite and the talnakhite group.

The presence of graphite is associated with the later processes operating within the magmatic massif. The mineral assemblage accompanying graphite contains hexagonal pyrrhotite, presumably thiospinel, magnetite and siderite. Siderite was described by Siemiątkowski (1976) as calcite.

In the authors' opinion, two graphite parageneses can be distinguished in the deposit. One consists of graphite coexisting with siderite in basic plagioclases, mainly in labrador. The other paragenesis is represented by pyrrhotite which is

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replaced by siderite with the deposition of reaction products, secondary magnetite, cobalt pentlandite and graphite. These two parageneses would correspond to the four distinguished previously by Siemiątkowski (1976).

EXPERIMENTAL

Electron microprobe investigations were carried out on a Cameca MS-46 microanalyser, using the following standards and spectral lines: S $K_{\alpha}(FeS_2)$, Ca $K_{\alpha}(CaF_2)$, V K_{α}, Mn K_{α}, Fe $K_{\alpha}(FeS_2)$, Ca K_{α}, Ni K_{α} and Cu K_{α}. The instrument was operated at an accelerating voltage of 20 kV, a probe current of 150 µA and a sample current of 10 nA, using ThO_2 standard. Counting time was 100 sec.

Electron micrographs were recorded with a JEM 100B transmission microscope operated at 100 kV. Samples for diffraction were picked under the optical microscope from 10 × 10 µm areas. Electron diffraction patterns were obtained not only for graphite but for siderite and labrador as well.

RESULTS

The main forms of graphite occurrence in the basic magnetite rocks of Suwałki were reported by Siemiątkowski (1976), who distinguished four graphite parageneses. In accordance with the hypothesis of genesis of this graphite advanced by the present authors, it is suggested to reduce the number of parageneses to two:

a. Graphite or graphite with siderite occurring as fine-grained aggregates (Phot. 2) and veinlets in labrador. The length of graphite veinlets varies from a dozen or so to several dozen µm, and their thickness is generally not more than a few µm. Sometimes cracks up to 5 µm in thickness are encountered, partly filled with pyrrhotite, or pyrrhotite and chalcopyrite, and graphite. The graphite aggregates displaying compact, feathery or rosette textures and intergrown by siderite (Phot. 2) vary from 10 to 150 µm in size, averaging 30 – 50 µm. When cataclastic processes began to operate, the cracks in labrador were capillary in nature, which caused the imbibition of the products and substrates of chemical reactions and their filling with graphite and siderite.

Table 1

Electron diffraction pattern of graphite from Krzemianka (NE Poland)

Graphite from Krzemianka		Graphite (Andrews *et al.* 1971)
d	*hkl*	*d*
2.14	*100*	2.13
2.05	*101*	2.03
1.56	*103*	1.54
1.24	*110*	1.23
1.15	*112*	1.15
1.03	*200*	1.05
0.81	*210*	0.80

b. The other paragenesis (Phot. 1) consists of hexagonal pyrrhotite (Tab. 2, A6) with smithite inclusions (Tab. 2, A1, A2). Both these minerals are replaced by siderite (Tab. 2, A3) with the deposition of secondary, stoichiometric magnetite (Kucha, Piestrzyński, 1976), cobalt pentlandite (Tab. 2, A5, A7) and graphite (Tab. 2, A4). The existence of graphite (Tab. 1) and siderite in this paragenesis was confirmed by electron

diffraction studies (Phot. 4).

Magnetite and siderite form as the product of oxidation of pyrrhotite (Phot. 1). Microscopic studies at high magnifications revealed the presence of small inclusions of pyrrhotite in magnetite, pyrrhotite and magnetite in siderite, and siderite in magnetite. The inclusions are not more than 4 µm in size. It seems, therefore, that magnetite arose in the first stage of oxidation of pyrrhotite while siderite and graphite formed in the second stage of this process. In some cases, a change in the Fe:S ratio was recorded by electron microprobe at the hexagonal pyrrhotite – magnetite interface. It is feasible that this is due to the formation of a transitional phase, thiospinel Fe_3S_4, in the course of oxidation.

The evidence substantiating the advocated hypothesis of graphite origin is provided by the sequence and spatial distribution of the minerals belonging to this paragenesis. Pyrrhotite is coated with a magnetite rim 10 – 20 µm in thickness (Phot. 1). A 15 – 30 µm thick reaction rim of siderite accretes in turn on Fe_3O_4 (Phot. 1). Small (up to a few µm) magnetite relics are commonly embedded in siderite, which testifies to the replacement of Fe_3O_4 by $FeCO_3$. The outer (younger) part of the siderite rim contains fine graphite platelets. A layer of reaction graphite of a thickness 20 – – 40 µm forms in turn on siderite. (The thickness of reaction rims can be greater than given if the sample surface intersects the boundary of the accreting minerals at an angle other than 90°).

Tabela 2

Chemical composition of minerals building up paragenesis the pyrrhotite, magnetite, syderite and graphite

No	S	Ca	V	Mn	Fe	Co	Ni	Cu	Total	Atomic proportions	Mineral
A_1	38.2		⩽0.07	0.07	60.5	⩽0.09	0.40	⩽0.08	100.07	$(Fe_{9.75}Ni_{0.06})_{9.81}S_{11}$	smythite
A_2	40.5				59.8	⩽0.09	0.60	⩽0.08	100.85	$(Fe_{9.32}Ni_{0.08})_{9.40}S_{11}$	smythite
A_3	0.06	1.90	⩽0.07	0.07	43.0		⩽0.06	0.40			syderite
A_4	0.03	⩽0.03	⩽0.02	⩽0.02	0.30		⩽0.03	⩽0.04			graphite
A_5	32.6				47.7	9.8	10.0		100.10	$(Fe_{6.72}Ni_{1.34}Co_{1.31})_{9.37}S_8$	pentlandite
A_6	39.0				61.5	0.15	⩽0.07		100.65	$(Fe_{9.96}Co_{0.02})_{9.98}S_{11}$	hex. pyrrhotite
A_7	33.7				26.3	19.6	20.5		100.19	$(Fe_{3.59}Ni_{2.66}Co_{2.54})_{8.79}S_8$	pentlandite

DISCUSSION

The coexistence of pyrrhotite (pentlandite, uncommonly chalcopyrite), magnetite, siderite and graphite in the Krzemianka deposit indicates that both oxidation and reduction processes were involved in their genesis. The oxidation of pyrrhotite (possibly through thiospinel) gives rise to magnetite, which in turn is replaced by siderite. From the point of view of the electrochemical theory (Marx, 1971), pyrrhotite could be regarded as an electronegative mineral acting as catode on which specific, surficial adsorption of CO_3 ions takes place under the natural conditions. The actual electrochemical process would involve reduction and the formation of siderite with a Cu admixture. A graphite monolayer would form on siderite, constituting a catalyzing substrate for the successive reduction $-CO_2 \rightarrow CO \rightarrow C$. The growth of graphite on the surface of siderite crystals proves the rightness of the thesis concerning the formation of a graphite monolayer (Phot. 3). The presence of Cu and S admixtures (Tab. 2), as well as high (0.30 wt. %) iron content (Tab. 2) and traces of sulphur in siderite, further substantiates the hypothesis of graphite genesis advanced by the present authors.

When considering the genesis of graphite, the formation of graphite through decomposition of siderite with the deposition of magnetite at 400 – 600°C, which process was documented by laboratory experiments (French, Rosenberg, 1965), was also taken into account. However, the spatial distribution and percentages of the paragenesis constituents, i.e. of pyrrhotite, magnetite, siderite and graphite, testify explicitly to the electrochemical process as understood by Marx (1971).

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O GENEZIE GRAFITU Z MAGNETYTOWYCH SKAŁ KRZEMIANKI, PÓŁNOCNO-WSCHODNIA POLSKA

Streszczenie

Przeprowadzono badania grafitu występującego w złożu magnetytowym Krzemianki, na terenie północno-wschodniej Polski. Analizy chemiczne w mikroobszarze wykonano na mikroanalizatorze Cameca MS-46, badania dyfrakcyjne przy zastosowaniu mikroskopu elektronowego transmisyjnego JEM 100B.

Wyróżniono dwie paragenezy grafitu. Pierwsza to grafit współwystępujący z syderytem w zasadowych plagioklazach. Grafit ten narasta w postaci monowarstwy na powierzchni kryształów syderytu. Drugą paragenezę stanowi pirotyn zastępowany przez syderyt z wydzieleniem produktów reakcyjnych: magnetytu, pentlandytu kobaltowego i grafitu. Obserwacje mikroskopowe wskazują, że grafit ten powstał w wyniku procesu elektro-chemicznego związanego z: utlenieniem pirotynu, utworzeniem syderytu (poprzez specyficzną, powierzchniową adsorpcję jonów CO_3) i kolejną redukcję $CO_2 \rightarrow CO \rightarrow C$.

Obecność domieszek Cu i S w syderycie oraz wysoka zawartość Fe i ślady S w graficie popierają wysuniętą tezę genezy grafitu z Krzemianki.

OBJAŚNIENIA FOTOGRAFII

Fot. 1. Typowa parageneza grafitu złożona z pirotynu i smithytu (biały) zastąpionego przez magnetyt (jasnoszary). Te trzy minerały są z kolei zastępowane przez syderyt (ciemnoszary). Grafit zaznaczony jest linią kropkowaną, smithyt linią kreskowaną. A2 – A6 punkty analizy w mikroobszarze (tab. 2)

Fot. 2. Grafit (jasnoszary) i syderyt (szary) otoczony przez labrador (szary)

Fot. 3. Obwódka grafitu (jasnoszary) na powierzchni kryształu syderytu (szary) otoczona przez labrador (ciemnoszary)

Fot. 4. Elektronogram grafitu z Krzemianki, północno-wschodnia Polska

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О ГЕНЕЗИСЕ ГРАФИТА ИЗ МАГНЕТИТОВЫХ ПОРОД КШЕМЯНКИ (СЕВЕРО-ВОСТОЧНАЯ ПОЛЬША)

Резюме

Были проведены исследования графита, выступающего в месторождении магнетита Кшемянки на территории северо-восточной Польши. Рентгеновские микро анализы были выполнены микроанализатором Камеца МС-46, дифракционные исследования — с использованием электронного микроскопа IEM 100B.

Были выделены два парагенезиса графита. Первый — это графит, выступающий совместно с сидеритом в основных плагиоклазах. Этот графит выступает в форме монослоя на поверхности кристаллов сидерита. Другой парагенезис прелставлен пиротином, замещенным сидеритом с выделением продуктов реакции: магнетита, кобальтового пентландита и графита. Наблюдения под микроскопом показывают, что этот графит возник в результате электрохимического процесса, связанного с: окислением пиротита, образованием сидерита (посредством специфической, поверхностной адсорбции ионов CO_3) и последовательного восстановления $CO_2 \rightarrow CO \rightarrow C$.

Наличие примесей Cu и S в сидерите и большое содержание Fe и следы S в графите поддерживают выдвинутую гипотезу генезиса графита из Кшемянки.

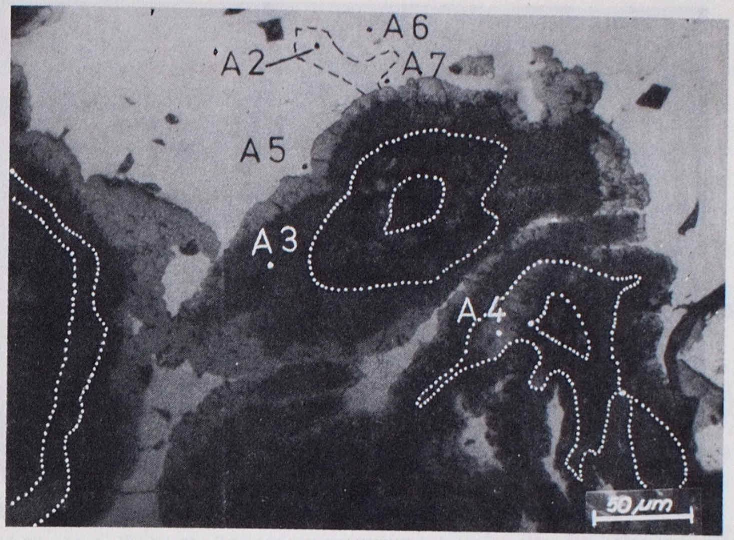
ОБЪЯСНЕНИЕ ФОТОГРАФИЙ

Фот. 1. Типичный парагенезис, состоящий из пиротита и смитита (белого), замещенного магнетитом (светлосерым). Эти три минерала в свою очередь замещаются сидеритом (тёмносерый). Графит, обозначенный пунктирной линией, смитит — штриховой линией. A2—A6 пункты анализа микрополя (таб. 2)

Фот. 2. Графит (светлосерый) и сидерит (серый) в окружении лабрадора (серый)

Фот. 3. Ободок графита (светлосерый) на поверхности кристалла сидерита (серый), окруженный лабрадором (тёмносерый)

Фот. 4. Электронограмма графита из Кшемянки, северо-восточная Польша



Phot. 1. A typical graphite paragenesis builded up with hexagonal pyrrhotite and smithite (white) replaced by magnetite (light grey). These three minerals then are replaced by siderite (dark grey). Graphite is marked by spot-line, smithite by dotted line. A2—A6 points of microprobe analyses (Tab. 2)

Phot. 2. Graphite (light grey) — siderite (grey) surrounded by labrador (grey)

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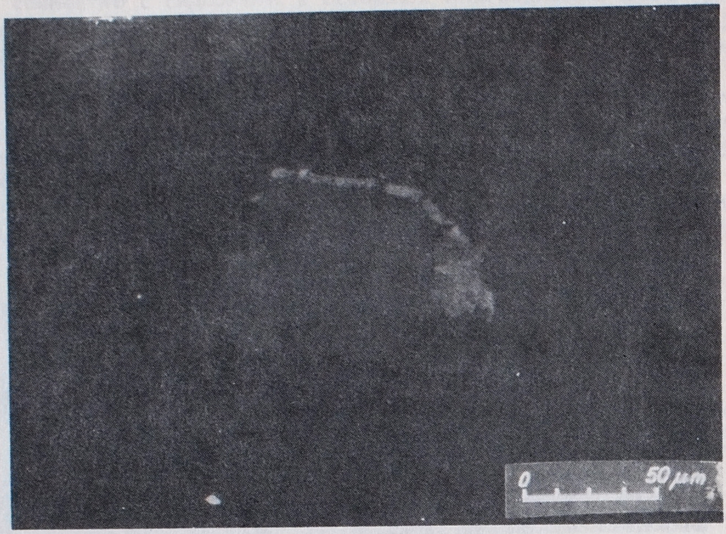

Phot. 3. A graphite rim (light grey) on the surface of siderite crystal (grey) surrounded by labrador (dark grey)

Phot. 4. Electron diffraction pattern of graphite from Krzemianki, NE Poland (uvw = *001*)