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**THE REPLACEMENT OF RUTILE BY CHALCOCITE
IN THE ZECHSTEIN COPPER ORES
OF THE FORE-SUDETIC MONOCLINE**

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Abstract. The phenomenon of replacement of rutile by sulphides, encountered in the top part of white copper-bearing sandstones, is a result of TiO_2 alteration under the influence of a reducing environment. This alteration is caused by the presence of an Fe admixture in the crystal lattice of rutile. Fe ions are extracted in the presence of sulphide ion, entering into the crystal lattice of bornite and chalcocite of anomalous compositions. Rutile is partly dissolved and recrystallizes within sulphide grains in the directions imposed by their crystal lattices, or occurs as a mixture of TiO_2 , clayey substance and carbonates.

INTRODUCTION

The processes of decomposition of titanium minerals in reducing environments have been reported from the copper deposits of Zaire (Cailteux, Dimanche 1973; Bartholome et al. 1973), uranium deposits in sandstones (Adams et al. 1974), and from present-day sediments (Carrol 1960). The source material is ilmenite, and the reaction products are rutile or leucoxene, haematite or pyrite and bornite.

The processes of metasomatic replacement of terrigenous minerals, e.g. of rutile, by sulphides have been observed in the top part of white copper-bearing sandstone (Banaś et al. 1979). Rutile occurs there in insignificant amounts as a component of the heavy fraction of white sandstones (Nemec et al. 1978). The mechanism of its replacement is worth studying in view of the considerable stability of this mineral under the near-surface conditions.

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EXPERIMENTAL

Samples to be investigated were collected from the top part of white sandstone in the Rudna mine.

The chemical composition of minerals was analysed with an ARL SEMQ electron microprobe operated at an accelerating voltage of 20 kV and a sample current of about 15 nA. The following lines and standards were used: TiK_{α} (100% Ti), FeK_{α} (Cu_5FeS_4 and 100% Fe), CuK_{α} (Cu_2S , Cu_5FeS_4 , 100% Cu), SK_{α} (FeS_2).

Electron diffraction was carried out with a JEM 100B electron microscope operated at an accelerating voltage of 100 kV. The measurement accuracy of the interplanar spacing was 0.75–1.0%. The grains for investigation were taken from the areas analysed previously with the microprobe.

MICROSCOPIC STUDIES

Three forms of the occurrence of TiO_2 substance were observed in reflected light. The first type is represented by terrigenous, well-rounded grains, sometimes of a fine-crystalline structure, showing low reflectance and bright internal reflections (Plate I).

The second type consists of tabular or acicular TiO_2 inclusions in sulphide minerals, from some to a dozen or so micrometers in thickness, up to several dozen micrometers in length, oriented in accordance with the crystallographic directions of sulphides. There are generally relics of undecomposed rutile in their immediate vicinity. The optical features of this substance are hard to determine because of the size of inclusions. Electron diffraction studies confirmed the presence of rutile in these two types of substance.

Lastly, TiO_2 substance occurs in the form of intergrowths with clay minerals and carbonates. It is presumably an amorphous variety of TiO_2 , characterized by low reflectance and barely perceptible bright, sometimes brownish, internal reflections.

The replacement of terrigenous rutile usually proceeds from the grain boundaries (Plate I). Sometimes the replacement is directional, the fine chalcocite veinlets being arranged along the crystallographic planes of rutile (Plate II). The final product of the process is rutile relics in the chalcocite mass, contouring the shape of a destroyed grain, or myrmekitic intergrowths of sulphides and TiO_2 .

DISCUSSION

From the above studies it appears that rutile is replaced by chalcocite (Plate I, II). Yet in view of the considerable chemical stability of this mineral, it is difficult to account for this type of reaction in thermodynamic terms (Garrels, Christ 1965). Since TiO_2 forms many polymorphs, it was necessary to examine both the primary grains with the optical features of rutile and the products of its reaction with chalcocite (Plate II). Electron diffraction studies have shown that both the primary forms (Plate I, Table 1, analysis 93/ G_1) and the secondary lamellae arranged

along the crystallographic planes of half- and quarter-bornite are made up of rutile.

Electron microprobe studies have revealed the presence of an insignificant admixture of Fe (0.5%) in the terrigenous grains of rutile (Table 1, Plate I). The characteristic, diffuse contour of Fe distribution compared with Ti, Cu and S ones testifies to the migration of this element towards the surrounding sulphide grain (Plate I). This migration could proceed along certain crystallographic directions (e.g. 110 cleavage planes), or by way of diffusion through the crystal lattice in conformity with the migration gradient. Such processes were described by Temple (1966), who noticed that under oxidizing conditions pseudorutile converted into rutile with the precipitation of Fe. This statement is supported by the ordered distribution of chalcocite inclusions (Plate I). The process of replacement presumably proceeds along the lattice planes containing Fe atoms.

It has been found that the extraction of Fe admixture from rutile is caused about by the reducing environment, and specifically by the presence of S^{2-} ion (Bartholome et al. 1973).

The products of the replacement of terrigenous TiO_2 are recrystallized rutile with a lower Fe content (0.17% — Table 1, analysis 93/ D_1) and sulphides of anomalous compositions (Table 1). It seems that at a minimum amount of extracted iron there formed anomalous "quarter-bornite" $Cu_{5.75}Fe_{0.25}S_4$ (Table 1, no 93/ G_2 and 93/ F_2), whereas when this amount was somewhat greater, anomalous "half-bornite" $Cu_{5.5}Fe_{0.5}S_4$ was formed, having half the stoichiometric content of iron (Table 1, no 93/ G_1).

It is possible that Plate I represents the initial stage of TiO_2 replacement by sulphides, while phot. 2

Table 1
Chemical composition of chalcocite, rutile and their reaction products

Sample No	Fe	Cu	S	Si	Ti	Ca	Al	Nb	Na	K	Σ	Remarks
93/ G_1	4.70	8.00	2.00	0.54	33.43	0.31	0.49	0.10	≤ 0.04	≤ 0.03		rutile corroded by chalcocite
93/ F_1	1.31	37.46	8.95	0.45	20.83	0.14	0.36	≤ 0.05	1.15	0.10		myrmekite structure of bornite and rutile "half-bornite"
93/ D_4	4.84	66.75	21.50	≤ 0.04	6.06	≤ 0.03	0.03	≤ 0.05	≤ 0.04	≤ 0.03		rutile
93/ D_2	0.50	2.67	0.58	≤ 0.04	49.50	0.36	0.51	0.09	0.43	≤ 0.03		chalcocite
93/ D_1	0.17	1.18	≤ 0.04	0.33	54.00	0.09	0.32	0.10	0.43	≤ 0.03	100.43	"quarter-bornite"
93/ D_3	0.15	79.56	20.72	≤ 0.04	≤ 0.06	≤ 0.03	≤ 0.02	≤ 0.05	≤ 0.04	≤ 0.03	100.08	"quarter-bornite"
93/ G_2	2.27	75.50	22.31	≤ 0.04	0.13	≤ 0.03	≤ 0.02	≤ 0.05	≤ 0.04	≤ 0.03		
93/ F_2	3.91	72.96	22.42	≤ 0.04	0.09	0.05	0.07	≤ 0.05	≤ 0.04	≤ 0.03	99.34	"quarter-bornite"

illustrates the final stage in which both the relics of undecomposed rutile and the lamellae of rutile recrystallized in the lattice of chalcocite are present. This fact indicates that TiO_2 has migrated at very short distances.

Studies of the opaque fraction of heavy minerals from the white sandstones have revealed the presence of an insignificant amount of ilmenite (Nemec et al. 1978). It is feasible that the rutile studied is the product of its diagenetic transformation although microscopic investigations have not shown the participation of ilmenite in the discussed processes of replacement.

Translated by Hanna Kisielewska

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ЗАМЕЩЕНИЕ РУТИЛА ХАЛЬКОЗИНОМ В ЦЕХШТЕЙНОВЫХ МЕСТОРОЖДЕНИЯХ МЕДНЫХ РУД

Резюме

В прикровельной части белых меденосных песчаников наблюдаются проявления замещения рутила сульфидами меди, главным образом халькозином. Микроскопические исследования в отраженном свете показали, что существуют три формы субстанции TiO_2 ; терригенные зерна, игольчатые включения в сульфидах меди и прорастание субстанции TiO_2 с глинистыми минералами и карбонатами.

Терригенные зерна рутила замещаются халькозином вдоль плоскости сети содержащей атомы Fe. Наличие железа в структуре рутила подтверждается исследованием микрозондом (таблица 1, планшет I). Ионы Fe экстрагируются в восстановительной среде в присутствии иона S^{2-} (Bartholme et al. 1973) и входят в состав борнита и халькозина с аномальными составами (таблица 1). Рутил является растворенным и рекристаллизуется в зернах сульфидов согласно с их кристаллографической решеткой или как смесь TiO_2 , глинистого вещества и карбонатов. Вторичный рутил содержит менее Fe (таблица 1), анализ 93(D₁). Его наличие подтвердилось дифракционными исследованиями с помощью электронного микроскопа. Планшет I представляет начальную стадию замещения TiO_2 сульфидами, а планшет II завершающий этап, в котором имеются с одной стороны реликты неразложившегося первичного рутила, а с другой — включения рутила рекристаллизованного в решетке халькозина.

ОБЪЯСНЕНИЯ СНИМКОВ

- Планшет I Метасоматическое замещение терригенных зерен рутила халькозином вдоль плоскостей раздела и (или) плоскостей сети с железом. Вокруг зерна рутила видна метасоматическая оторочка четверть-борнита. Таблица 1, 93/G₂, Препарат 93/G₁ и G₂, TOP — картина в отраженных электронах, Cu, Si, S, Fe — сканировые картины перечисленных элементов, 1, 2 — места химических анализов
- Планшет II Завершающая стадия замещения Fe-носного рутила халькозином. Рекристаллизованный очищенный из железа рутил образует включения согласно с кристаллической ориентировкой сульфидов. Препарат 93/D₁, 2, 3 и 4, TOP — картина в отраженных электронах, Cu, Ti, S, Fe — сканировые картины перечисленных элементов 1, 2, 3, 4 — места химических анализов

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ZASTĘPOWANIE RUTYLU PRZEZ CHALKOZYN W CECHSZTYŃSKICH ZŁOŻACH RUD MIEDZI

Streszczenie

W stropowej części białych piaskowców miedzionośnych zaobserwowano przejawy zastępowania rutylu przez siarczki miedzi, głównie chalkozyn. Badania mikroskopowe w świetle odbitym wykazały istnienie trzech form występowania substancji TiO_2 : ziarn terrygenicznych, igielkowych wrostków w siarczках miedzi i przerostów substancji TiO_2 z minerałami ilastymi i węglanami.

Terrygeniczne ziarna rutylu są zastępowane przez chalkozyn wzdłuż płaszczyzn sieciowych zawierających atomy Fe. Obecność żelaza w strukturze rutylu wykazały badania w mikroobszarze (Tab. 1, Plansza I). Jony

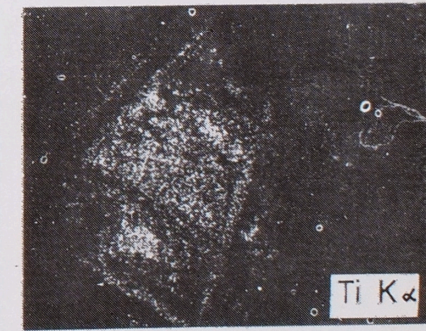
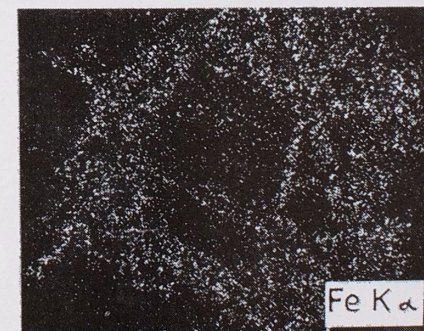
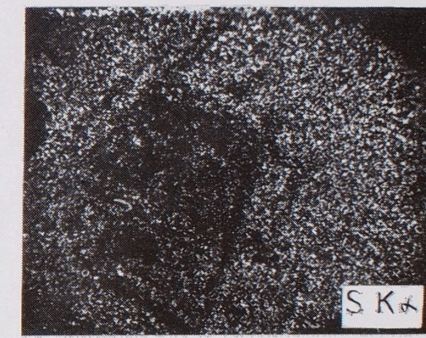
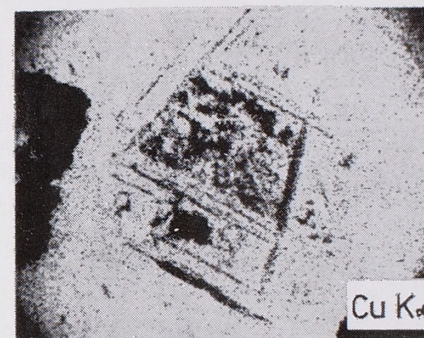
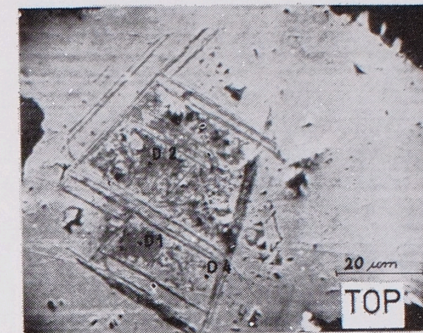
Fe są ekstrahowane w środowisku redukcyjnym w obecności jonu S^{2-} (Bartholome et al. 1973) i wchodzi w skład bornitu i chalkozynu o anomalnych składach (Tab. 1). Rutyl jest rozpuszczany i rekrytalizuje w ziarnach siarczków zgodnie z ich siecią krystalograficzną lub jako mieszanina TiO_2 , substancji ilastej i węglanów. Wtórny rutyl posiada niższą zawartość Fe (Tab. 1, analiza 93/D₁). Jego obecność została potwierdzona badaniami dyfrakcyjnymi w mikroskopie elektronowym.

Plansza I przedstawia początkowe stadium zastępowania TiO_2 przez siarczki, natomiast Plansza II etap końcowy, w którym obecne są zarówno relikty nierozłożonego rutylu pierwotnego jak i lamele rutylu rekrytalizowanego w sieci chalkozynu.

OBJAŚNIENIA FOTOGRAFII

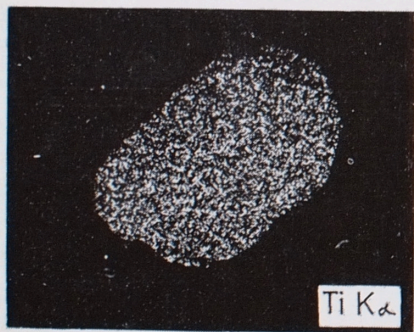
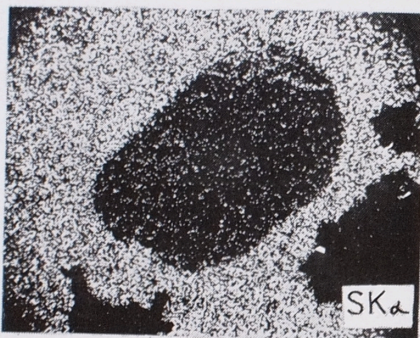
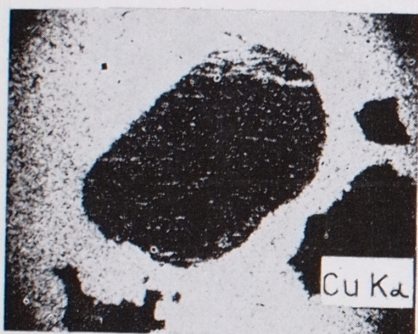
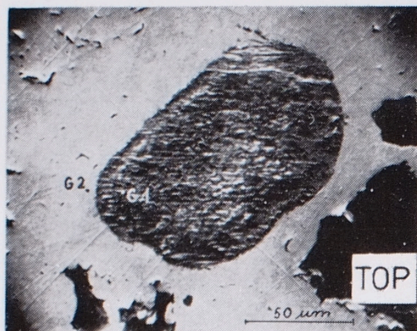
Plansza 1 Metasomatyczne zastępowanie terygenicznych ziarn rutylu przez chalcokozyn wzdłuż płaszczyzn podzielnosci i (lub) płaszczyzn sieciowych obsadzonych żelazem. Wokół ziarna rutylu występuje metasomatyczna obwódka ówierc-bornitu (Tab. 1, 93/G₂). Preparat 93/G₁ i G₂, TOP — obraz w elektronach odbitych, Cu, Ti, S, Fe — obrazy scannin-gowe wymienionych pierwiastków, 1, 2 — miejsca analizy chemicznej w mikroobszarze

Plansza 2 Końcowe stadium zastępowania Fe-nośnego rutylu przez chalcokozyn. Zrekrystalizowany, oczyszczony z żelaza rutyl tworzy lamele zgodne z orientacją krystalograficzną siarczków. Preparat 93/D_{1, 2, 3 i 4}, TOP — obraz w elektronach odbitych, Cu, Ti, S, Fe — obrazy scannin-gowe wymienionych pierwiastków, 1, 2, 3, 4 — miejsca analizy chemicznej w mikroobszarze



Final stage of chalcocite replacement of Fe-bearing rutile. The iron-refined rutile lamellae are recrystallized and oriented within the sulphide lattice. Sample 93/D, TOP — reflected electron image, Cu, Fe, S, Ti — scanning images of the elements, 1, 2, 4 — spots of microprobe analyses

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Chalcocite metasomatic replacement of terrigenous rutile alongside parting and/or Fe-enriched crystallographic planes. Around the rutile grain a rim of a "quarter-bornite" (Tab. 1, 93/G₂) is produced. Sample 93/G,
 TOP — reflected electron image, Cu, Ti, S, Fe — scanning images of the elements,
 1, 2 — spots of microprobe analyses,

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