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COPPER-BEARING GLAUCONITE FROM THE WEISSLIEGENDES OF ZECHSTEIN COPPER DEPOSITS, POLAND

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A b s t r a c t. Cu-bearing glauconite is a common constituent of the top part of Weissliegendes intensely mineralized with chalcocite. It contains up to 2.02 wt.% CuO, up to 1.13 wt.% FeO, a decreased SiO_2 content, and an anomalously high content of Na_2O (over 6 wt.%) and MgO (over 7 wt.%). Electron diffraction studies suggest that the Cu-bearing glauconite is a 2M mica polytype with $a_o=5.19 \pm 0.03$, $b_o=9.00 \pm 0.05$, $c_o=19.99 \pm 0.10$ and $\beta=95.48° \pm 0.47°$. Cu-bearing glauconite has presumably formed from normal glauconite present in the Weissliegendes as a result of its reaction with Mg- and K-rich brine that was the mother solution for Cu mineralization. The formation of Cu-bearing glauconite probably preceded sulphide mineralization, being coeval with the dolomitization of Zechstein carbonates.

INTRODUCTION

In the copper-bearing Zechstein rocks of the Fore-Sudetic Monocline, glauconite is particularly abundant in organogenic carbonates, where it usually forms typical spheroidal grains. It exhibits typical optical features in reflected light (intense green internal reflections).

Spheroidal grains characteristic of glauconite have also been reported from copper-bearing sandstones, yet these forms do not show internal reflections in reflected light. This fact, as well as the intimate association of these forms with Cu sulphide mineralization, induced the present authors to carry out detailed studies of this anomalous glauconite. In view of its occurrence in forms typical of glauconite, its genesis and the copper content, it has been called „copper-bearing glauconite".

EXPERIMENTAL AND RESULTS

The chemical composition of Cu-bearing glauconite was analysed with an ARL SEMQ electron microprobe operated at an accelerating voltage of 20 kV, a sample current on ThO_2 of 11 μA, a probe current of 140 μA, and

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couting time of 100 sec. The following spectral lines and standards were used: $NaK_\alpha(NaAlSi_3O_8)$, $MgK_\alpha(MgCO_3)$, $AlK_\alpha(KAlSi_3O_8)$, $SiK_\alpha(KAlSi_3O_8)$, $SK_\alpha(FeS_2)$, $KK_\alpha(KAlSi_3O_8)$, $CaK_\alpha(CaCO_3)$, $FeK_\alpha(FeS_2)$ i $CuK_\alpha(Cu_2S)$.

When calculating the actual concentration of elements, corrections were made for absorption (Philibert 1965), fluorescence (Reed 1965) and for atomic numbers (Philibert, Tixier 1968).

Electron diffraction patterns were obtained with a Jeol JEM-100 B electron microscope operated at an accelerating voltage of 100 kV. Particles for diffraction analysis were taken under the microscope from the areas analysed by electron microprobe.

OCCURRENCE

Cu-bearing glauconite is fairly common in the top part of Weissliegendes, where it forms spheroidal grains (Phot. 1) up to 0.07 mm in size. Cu-bearing glauconite with a low Fe content coexists with chalcocite. Cu-bearing glauconite with a high Fe content or normal glauconite is separated from chalcocite by bornite. Cu-bearing glauconite differs from normal glauconite in that it shows no internal reflections in reflected light which is probably a result of the presence of Cu ions in the crystal lattice.

CHEMICAL COMPOSITION

The chemical composition of Cu-bearing glauconite (Table 1) differs widely from the composition of typical illite, glauconite or seladonite. Its characteristic features are the increased Cu content while Fe is virtually absent (Table 1, 93/B3, 93/B7), the decreased Si content, and the anomalously high Na content while the content of Mg remains high as well. The presence of Na only in the central part of the Cu-bearing glauconite grain points to its relic character (Phot. 1). The Cu content in the marginal zone of Cu-bearing glauconite (Phot. 1) is markedly lower (Ttable 1, 104/Fl, 104/Al), suggesting that Cu migrated from glauconite to Cu_2S. It can also be inferred from this fact that glauconite is earlier than chalcocite. The behaviour of Al, Si and Fe is entirely different due to the reverse direction of migration of elements trapped in Cu_2S during crystallization from Mg-rich brine, which is reflected by the high concentration of Mg in Cu-bearing glauconite (Table 1).

DIFFRACTION STUDIES

Electron diffraction was carried out on particles with a chemical composition corresponding to analysis 93/B3 (Table 1). The calculated unit cell parameters are: $a_o = 5.19 \pm 0.03$, $b = 9.00 \pm 0.05$, $c = 19.99 \pm 0.10$ and $\beta = 95.48^\circ \pm 0.47^\circ$. They suggest that the Cu-bearing glauconite under study is a 2M mica polytype.

Electron diffraction patterns (Phot. 2) show basal diffraction points of the reciprocal lattice, as well as weaker satellite points deflected, for example, by 1.5° for the $\bar{1}30$ point. Considering the fixed position of the satellites with respect to the reciprocal lattice points and their symmetry with respect to the *000* point, it is evident that it is an ordered satellite

lattice, somewhat displaced in relation to the basel lattice. Such a superstructure in Cu-bearing glauconite may be indicative of the ordering of Si and Al atoms in the tetrahedral sheet.

GENESIS OF CU-BEARING GLAUCONITE

Chalcocite that occludes the grains of Cu-bearing glauconite exhibits cracks resembling desiccation structures (Phot. 1), which are particularly pronounced on the scanning image in reflected electrons. This indicates that Cu_2S decreased in volume during crystallization, presumably due to the migration of water from partly gelatinous Cu_2S to Cu-bearing glauconite. A more plausible hypothesis, however, is that of reciprocal migration of elements: Al and Si trapped in Cu_2S (up to 2.5 wt.% Si and up to 0.5 wt.% Al in chalcocite) during precipitation from mineralized brine to Cu-bearing glauconite, and Cu and Fe from Cu-bearing glauconite to occluding chalcocite. This thesis is borne out by the markedly higher Cu content in the central parts of Cu-bearing glauconite grains (Table 1, 93/B3, 93/B7) and the considerably lower content of this element at the grain boundaries (Table 1, 104/Fl, 104/Al). The behaviour of Al and Si is opposite. The hypothesis of migration of elements between sulphides and Cu-bearing glauconite is confirmed by the bornite rim appearing as a „halo" round the Cu-bearing glauconite grain (Phot. 3).

Cu-bearing glauconite presumably formed from normal glauconite present as a primary mineral in the Zechstein Weissliegendes. This is evidenced by typical forms of occurrence of this mineral. During the reaction with Mg- and K-rich brine (mother solution for Cu), Cu and Mg were incorporated in the structure of glauconite, making it chemically similar to seladonite. Parallel to the incorporation of Mg and Cu, Fe was leached from the structure, and these processes gave rise to Cu-bearing glauconite poor in Fe. Cu-bearing glauconite is older than sulphide mineralization, this inference being borne out by the migration of elements: Al and Si to Cu-bearing glauconite, and Cu and Fe to chalcocite (Phots. 1, 3). Cu-bearing glauconite is presumably coeval with the dolomitization of Zechstein carbonates.

Electron cicroprobe studies do not provide direct evidence that Cu is incorporated in the structure of the 2M mica polytype under study. Variations in SiO_2 content (Table 1) make it conceivable that Cu is associated with chrysocolla, which is submicroscopically mixed with the 2M mica polytype. Yet, because the grains of Cu-bearing glauconite (or seladonite) are too small in size, they cannot be subjected to X-ray diffraction or infrared absorption analysis. It is worth noting, however, that variations in the Si : Al ratio (Table 1) have been observed for different grains of glauconite, this ratio being constant within the same grain (Table 1, 93/B3, 93/B7).

Electron diffraction studies were carried out on 25 glauconite pellets with a composition corresponding to analysis 93/B3 (Table 1), and none of them yielded a diffraction pattern of chrysocolla, which at the given Si : Al ratio (Table 1, 93/B3) should have the kaolinite symmetry. Moreover, the evidence against the hypothesis of Cu being incorporated in chrysocolla is provided by the fact that copper content is twice to three

times higher in places where the amount of SiO_2 is decreased by 8—10% (Table 1).

Electron diffraction patterns show distinct satellite points (Phot. 2) that form a lattice displaced with respect to the basel lattice. This type of superstructure may be associated with the ordered substitution of Cu for Al in the tetrahedral sheet. It is feasible that Cu is not an interlayer cation.

Translated by Hanna Kisielewska

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GLAUKONIT MIEDZIONOŚNY Z BIAŁYCH PIASKOWCÓW (WEISSLIEGENDES) Z CECHSZTYŃSKICH ZŁÓŻ MIEDZI, POLSKA

Streszczenie

Glaukonit miedzionośny jest pospolitym składnikiem stropowej części białego piaskowca silnie okruszcowanego chalkozynem zawiera do 2,02% wag. CuO, do 1,13% wag. FeO, obniżoną zawartość SiO_2 oraz anomalnie wysoką zawartość Na_2O (ponad 6% wag.) i MgO (ponad 7% wag.). Badania dyfrakcyjne w mikroskopie elektronowym sugerują, że badany Cu-glaukonit jest polimerfem 2M miki z $a_o = 5.19 \pm 0{,}03$; $b_o = 9{,}00 \pm 0{,}05$, $c_o = 19{,}99 \pm 0{,}10$ i $\beta = 95{,}48° \pm 0{,}47°$.

Cu-glaukonit powstał prawdopodobnie z normalnego glaukonitu obecnego w piaskowcu w reakcji z solanką bogatą w Mg i K, będącą roztworem macierzystym dla mineralizacji Cu. Wiekowo Cu-glaukonit jest prawdopodobnie wcześniejszy od mineralizacji siarczkowej, a równowiekowy z dolomityzacją węglanów cechsztyńskich.

OBJAŚNIENIA FOTOGRAFII

Fot. 1. Mikrofotografia Cu-glaukonitu ze stropowej części białego piaskowca (Weissliegendes). RL — światło odbite, REI — obraz w elektronach odbitych (szczeliny sugerują wysychanie pierwotnie kolomorficznego chalkozynu), Si, Al, K, Na, Cu, S — obrazy scaningowe rozmieszczenia pierwiastków

Fot. 2. Dyfrakcja elektronowa glaukonitu miedziowego. Orientacja uvw=*001*. Preparat 93/B3, kopalnia Rudna

Fot. 3. Obwódka bornitowa (oznaczona strzałką) w chalkozynie wokół ziarna Cu-glaukonitu. Sugeruje ona migrację Fe z glaukonitu w otaczający chalkozyn. Preparat 104/A1, strop białego piaskowca (Weissliegendes), kopalnia Rudna, światło odbite

Хенрык КУХА, Адам ПЕСТШИНЬСКИ, Анджей ВЕЧОРЕК

МЕДЬСОДЕРЖАЩИЙ ГЛАУКОНИТ В ПЕСЧАНИКАХ БЕЛОГО ЛЕЖЕНЯ ИЗ ЦЕХШТЕЙНОВЫХ МЕДНЫХ МЕСТОРОЖДЕНИЙ, ПОЛЬША

Резюме

Меденосный глауконит является распространенным компонентом кровельной части белого песчаника, интенсивно оруденелого халькозином. Он содержит до 2,02 вес. % CuO, до 1,13 вес. % FeO, пониженное количество SiO_2, а также аномально высокие количества Na_2O (свыше 6 вес. %) и MgO (свыше 7 вес. %). Дифракционные исследования в электронном микроскопе наводят на мысль, что изучаемый Cu — глауконит является полиморфической разновидностью 2M слюды с $a_o = 5{,}19 \pm 0{,}03$, $b_o = 9{,}00 \pm 0{,}05$, $c_o = 19{,}99 \pm 0{,}10$ и $\beta = 95{,}48° \pm 0{,}47°$.

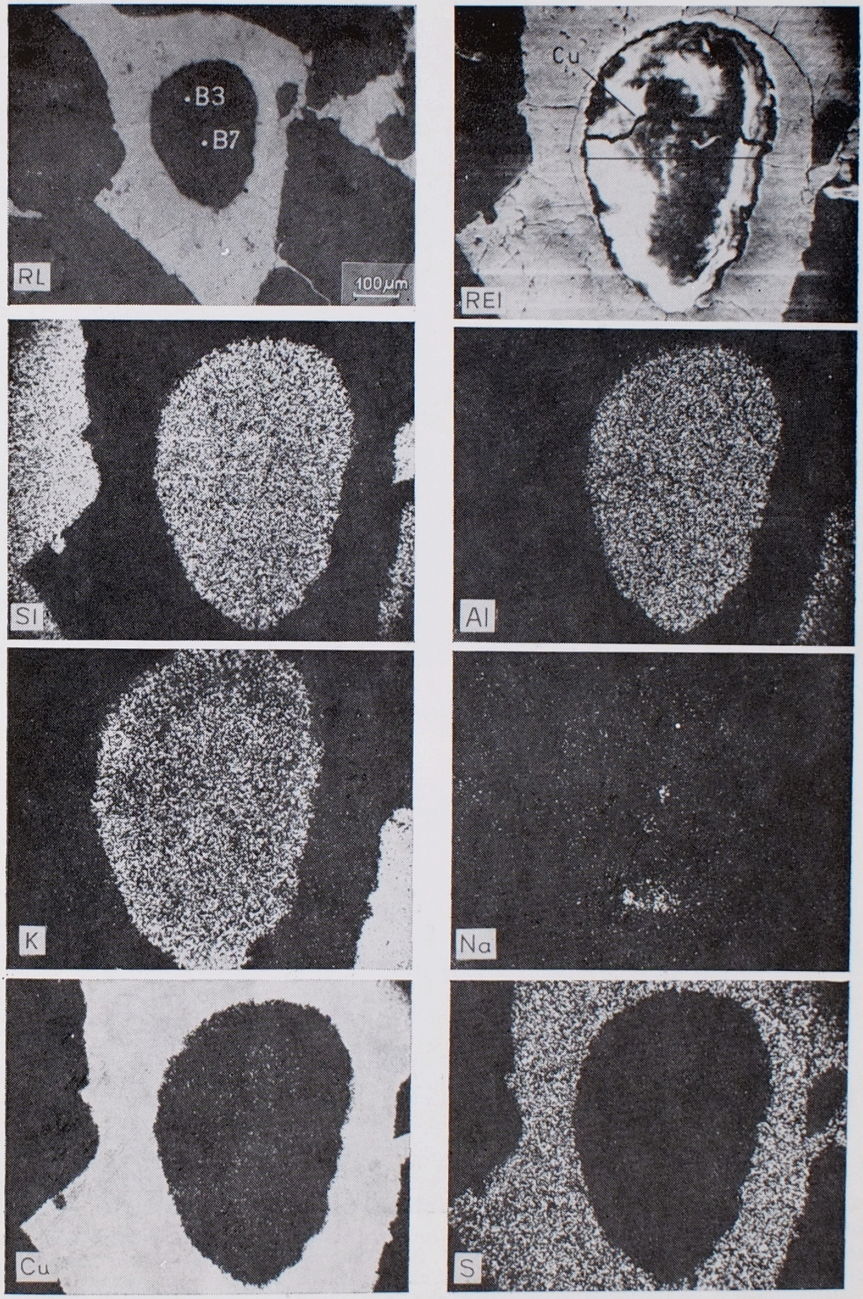
Cu-глауконит, по-видимому, образовался из содержащегося в песчанике глауконита в итоге реакции с солевыми растворами, богатыми Mg и K, являющимися материнскими растворами для Cu оруденения B возрастном отношении Cu-глауконит, по-видимому, более ранний чем сульфидное оруденение, и одного возраста с доломитизацией цехштейновых карбонатов.

ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

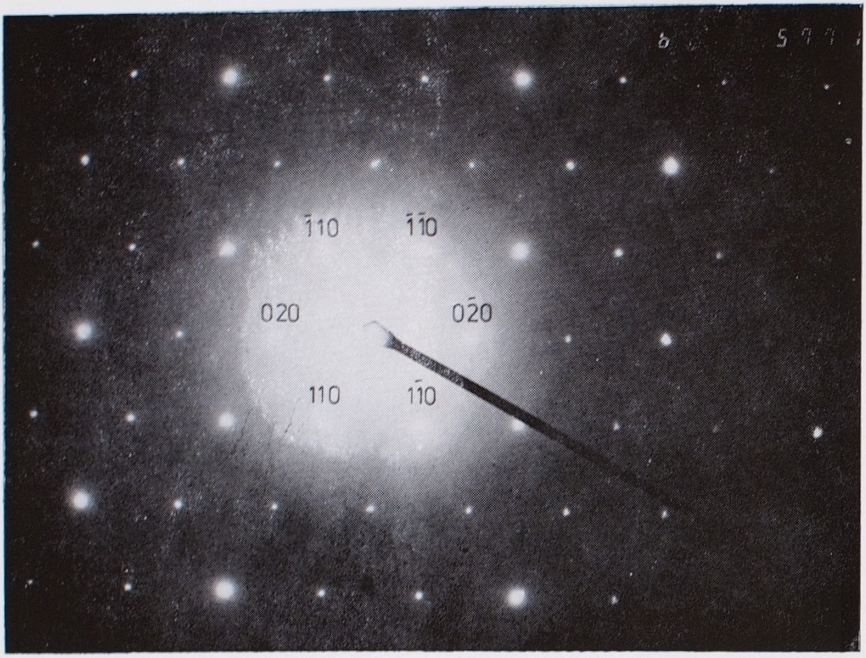
Фото 1. Микрофотография Cu-глауконита из кровельной части белого леженя
RL — отраженный свет, REI — изображение в отраженных электронах (трещины предполагают усыхание первоначально колломорфного халькозина), Si, Al, K, Na, Cu, S — электронномикроскопическое изображение размещения химических элементов

Фото 2. Электронная дифракция Cu-глауконита. Ориентировка uvw = *001*. Образец 93/B3, рудник Рудна, Польша

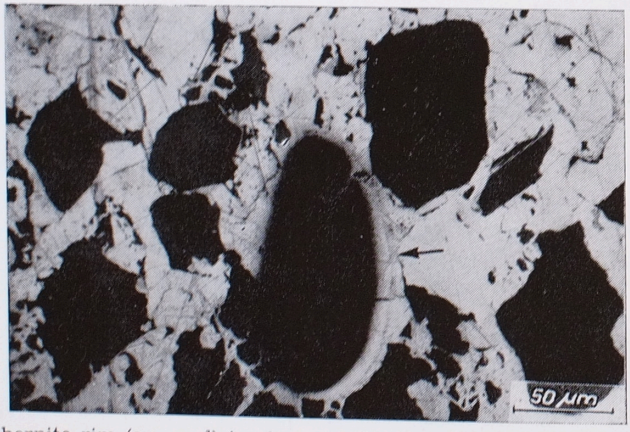
Фото 3. Борнитовая каемка (обозначенная стерлкой) в халькозине вокруг зерна Cu-глауконита. Она предполагает миграцию из глауконита в окружающий халькозин. Образец 104/A1, кровля песчаника белого леженя, рудник Рудна, отраженный свет



Phot. 1. Microphotographs of the copper glauconite from the top part of the Weissliegendes. RL — reflected light, REI — reflected electron image (cracks suggesting drying of the primary colloform chalcocite are visible), Si, Al, K, Na, Cu, S — scanning pictures of these elements. Sample 93/B3, Rudna mine, Poland



Phot. 2. Electron diffraction patern of the copper glauconite. Orientation uvw=*001*. Sample 93/B3, Rudna mine



Phot. 3. A bornite rim (arrowed) in chalcocite surrounding Cu-glauconite. The presence of the rim suggests migration of Fe from glauconite towards surrounding chalcocite. Sample 104/A1, top part of Weissliegendes, Rudna mine, reflected light