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NATIVE COPPER IN AGATES FROM RUDNO NEAR KRZESZOWICE[2]

Abstract. The occurrence of native copper in agates from Rudno near Krzeszowice was confirmed. It is a rare mineral in these secretions. The chemical composition (low contents of admixtures) proves its crystallization at low hydrothermal temperatures (20—50°C). The relation of copper mineralization to other minerals of the agate paragenesis suggests its secondary origin. The parameters of the copper crystallization were defined as Eh 0.0—0.15 and pH 5.3—7.6 (presuming that the copper was formed in the zone of oxidation). The source of this element might be seen both in the enclosing rock and hydrothermal solutions flowing in the fault zone along the NE boundary of the Nieporaz-Brodła tectonic depression.

Key-words: native copper, agate, Poland.

INTRODUCTION

Native copper is a rare and the only native element which appears in agates. Up to now it was found only in agates from the Kamchatka-Kuril region (Russia) and from Bohemian Sudetes (Sidorov et al. 1985; Tuček 1973).

In Rudno, the village situated about 27 km NWW from Kraków, agates occur within „melaphyres" which are found at the NE boundary of the Nieporaz-Brodła tectonic depression. Those „melaphyres" form hills which are between the village and the ruins of the Tenczyn castle (Fig. 1). The specimens with native copper were found in an abandoned quarry of „melaphyres" (Fig. 1, point A), and on the neighbouring fields between the quarry and the castle, too (Fig. 1, point B).

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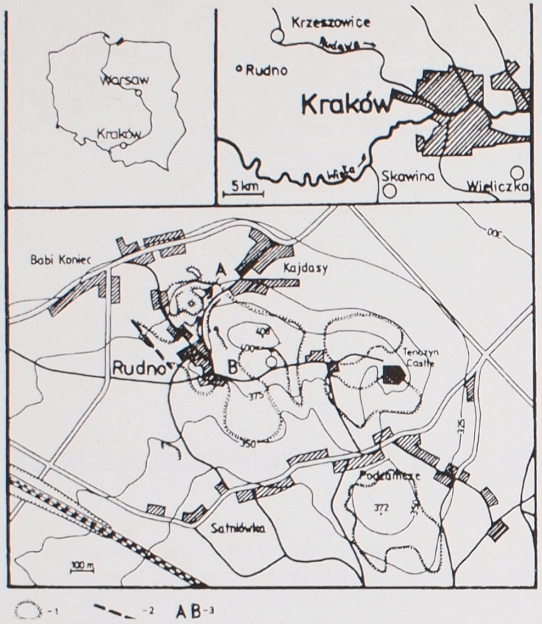

Fig. 1. The outcrops of „melaphyres" in the vicinity of Rudno after Płonczyński and Łopusiński (1992) with the localization of samples
1 — outcrops of „melaphyres"; 2 — fault; 3 — places of sampling: A — quarry, B — fields

METHODS OF INVESTIGATION

The studies leading to the identification of mineral phases were carried out using reflected light microscopy under a MeF-2 (Reichert) polarizing microscope. A Wild M 10 (Leica) stereoscopic microscope was used in the macroscopic observations and photographic documentation.

The chemical composition was defined by the method of electron-probe microanalysis. A CAMECA MS-46 microprobe was used, the parameters of current: 20 kV, 20 nA.

FORMS OF OCCURRENCE AND CHEMICAL COMPOSITION

More than 300 agate sections from private collections (Mr. K. Torbus and Mr. E. Opalski) and the collection of the author were studied. Only in 11 of them copper mineralization was observed. Native copper occurs in three forms:

— in secondary microfissures crossing agate layers obliquely (Fig. 2, A; Phot. 1);

— at the boundaries of individual agate layers (in a tree-like form) (Fig. 2, B; Phot. 2);

— as dispersed grains, independent of agate layers (Fig. 2, C; Phot. 3).

All those forms are found in the peripheries of agate amygdales. Such a mineralization was not observed in the central quartz geodes. The size of copper pockets ranges from 0.01 to 2 mm, they are irregular and of jagged edges.

The analysis of sections showed also cuprite, apart from native copper. This mineral occurs at the contact of copper and chalcedony or even replaces the former creating separate pockets (Phot. 4). The cuprite must have been formed at an Eh value higher than Eh at the stability of native copper, i.e. Eh > 0.15 (Fig. 3). It is a typical mineral which accompanies native copper in the zone of oxidation.

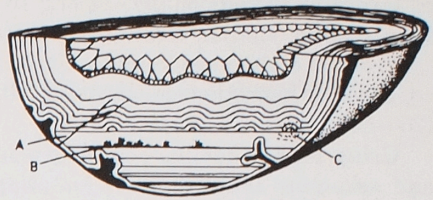

Fig. 2. The mode of occurrence of native copper in agates (explanations of points A, B, C in the text)

The chemical analysis of two samples of native copper showed its exceptional purity with regard to typical trace elements co-occurring most frequently with Cu: As, Zn, Ag, Fe, Pb. As the amount of admixtures in copper grows with the temperature of its formation, the chemical composition found is characteristic of the copper which crystallizes from hydrothermal solutions at relatively low temperatures (20—50°C) (Novgorodova 1985). The admixture of Si was found which may be caused by remnants of chalcedony left after metasomatic replacement of it by native copper.

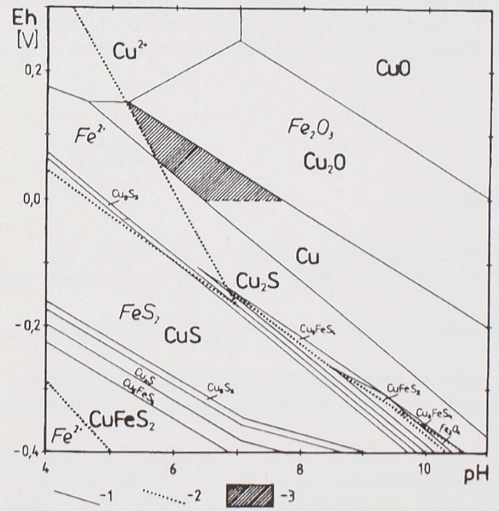

Fig. 3. Diagram of stability of mineral in the Cu–Fe–S–O–H system at the temperature of 25°C and pressure of 1 atm after Natarajan and Garrels (vide Sato 1992)
1 — boundaries of mineral phases of Cu compounds; 2 — boundaries of mineral phases of Fe compounds; 3 — field of probable crystallization of native copper in agates

DISCUSSION

The occurrence of native copper in secondary microfissures and as dispersed grains (independently of agate layers) proves its formation after the colloidal precipitation of silica which constructs chalcedon layers. Both native copper and cuprite are the last minerals of the agate paragenesis. Cuprite arose by oxidation of copper at increased Eh of environment. Mineral phases which form pigments of yellow or red colour (Fe^{3+} oxides and hydroxides) and occur in similar forms as native copper (in secondary microfissures, at the boundary

of layers or dispersionally) belong to this association. It can be assumed, that they rose in similar conditions of crystallization.

From the chemical composition (low contents of admixtures) it results that copper is of hydrothermal origin and it crystallized in relatively low temperatures (20—50°C).

Using for the comparison diagrams of the stability of Cu and Fe compounds, and assuming the crystallization temperature of 20°C (Sato 1992), the probable environments of crystallization of the native copper of Rudno can be pointed out. Hypothetic conditions of crystallization were: Eh < 0.15; pH > 5.3. Assuming that the copper was formed in near-surface condition (in the zone of oxidation) the field of the crystallization may be pointed out (Fig. 3).

The sources of copper are unknown. Copper could bee derived from enclosing rock. The average content of Cu in „melaphyres" from Rudno, which was calculated by Michałek and Żabiński (1957) amounts to 0.007 wt.%. It occurs mainly in three primary minerals: plagioclases, pyroxenes and olivines. It might be mobilized under the hypergenic conditions because its higher content was found in decomposed rock (Jaworski 1970). Copper may also be connected with hydrothermal solutions migrating near the fault zone of the NE boundary of the Nieporaz-Brodła tectonic depression (Cichoń 1982).

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REFERENCES

CICHOŃ G., 1982: Minerały wtórne w melafirach z Rudna koło Krzeszowic. *Pr. Miner.* 73.

JAWORSKI A., 1970: Przyczynek do znajomości geochemii strefy wietrzenia krakowskich skał magmowych. *Przeg. Geol.* 1, 12—20.

MICHAŁEK Z., ZABIŃSKI W., 1957: Wyniki wstępnych badań geochemicznych krakowskich skał magmowych. *Biul. IG* 115, 149—161.

NOVGORODOVA M.I., 1983: Samorodnyje metałły w gidrotermalnych rudach. Niedra, Moskwa.

PŁONCZYŃSKI J., ŁOPUSIŃSKI L., 1992: Szczegółowa mapa geologiczna Polski (1:50000), arkusz Krzeszowice.

SATO M., 1992: Persistency-field Eh-pH diagrams for sulfides and their application to supergene oxidation and enrichment of sulfide ore bodies. *Geochimica et Cosmochimica Acta* 56, 3133—3156.

SIDOROV E.G., KUTYJEW F.T., ANIKIN P.P., 1985: Samorodnaja mied w agatach Kurylo-Kamchatskoj prowincji. In: Samorodnyje metałły w postmagmaticzeskich obrazowanijach. Knih. Izdat. 72—73. Jakuck.

TUČEK K., 1973: O vyskytech ryzi medi v podkrkonosskich melafyrech (Knalezu prniho agatu s ryzi medi). *Nar. Muz., (Praha) Cas. Oddil Prirodoved.* 142 (1—4), 41—46.

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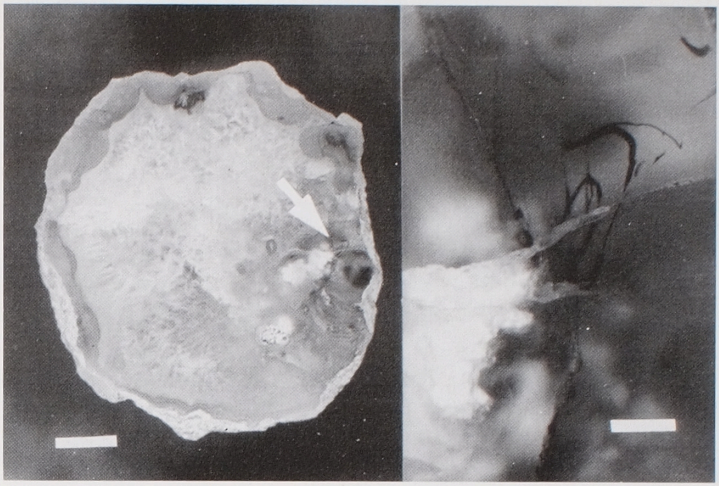
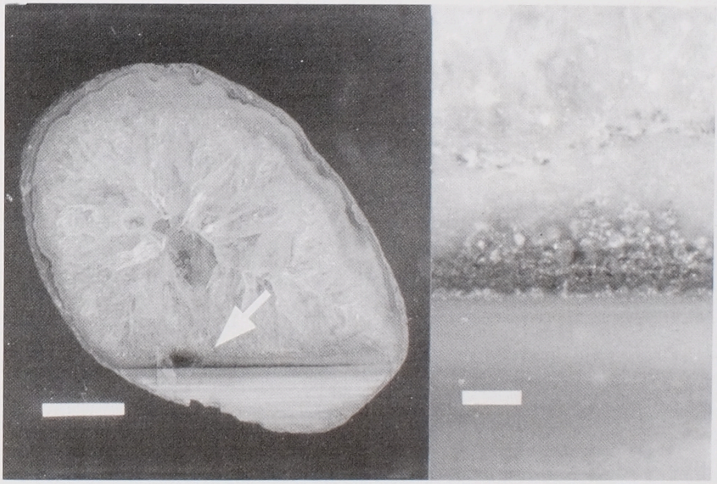
MIEDŹ RODZIMA W AGATACH Z RUDNA KOŁO KRZESZOWIC

Streszczenie

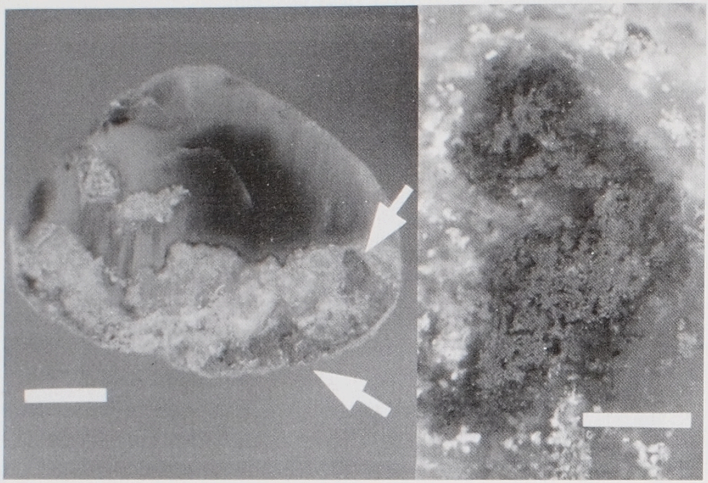
Stwierdzono wystąpienie miedzi rodzimej w agatach z Rudna koło Krzeszowic. Jest to rzadki minerał w tych sekrecjach. Skład chemiczny (mała zawartość domieszek innych pierwiastków) świadczy o jej krystalizacji w niskich temperaturach hydrotermalnych (20—50°C). Ułożenie mineralizacji miedziowej w stosunku do innych minerałów paragenezy agatowej świadczy o jej wtórnym pochodzeniu. Wyznaczono parametry środowiska powstawania miedzi (przy założeniu, że tworzyła się ona w strefie utleniania) na Eh 0,0—0,15 i pH 5,3—7,6. Źródłem tego pierwistka mogła być zarówno skała otaczająca, jak i roztwory hydrotermalne przepływające w strefie uskokowej NE granicy zapadliska Nieporaz-Brodła.



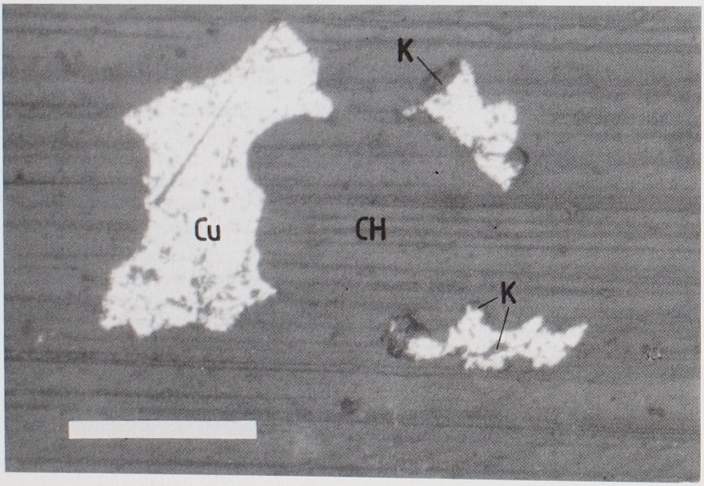
Phot. 1. Native copper in secondary microfissures. Coll. K. Torbus
A — the general form of agate (arrows show copper mineralization) (scale bar = 1 cm);
B — a fragment with mineralization (scale bar = 1 mm)



Phot. 2. Native copper at the boundary of agate layers. Coll. E. Opalski
A — the general form of agate (arrows show copper mineralization) (scale bar = 1 cm);
B — a fragment with mineralization (scale bar = 1 mm)



Phot. 3. Native copper in dispersed form. Coll. K. Torbus
A — the general form of agate (arrows show copper mineralization) (scale bar = 1 cm); B — a fragment with mineralization (scale bar = 1 mm)



Phot. 4. Native copper and cuprite in chalcedony
Cu — native copper, K — cuprite, CH — chalcedony. Reflected light, 1 nicol, scale bar = 0.1 mm