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THE ROLE OF SOLUBLE SILICA AND H₂S IN THE PROCESS OF DOLOMITIZATION

Abstract. Dolomitic breccia mineralized with sphalerite was found to occur in the bottom part of ore-bearing dolomite in the Orzel Biały Mine. Clasts of D1 dolomite are metasomatically impregnated with silica. The breccia is cemented with posterior D2 Fe-dolomite impregnated with pyrite. The close association D1 dolomite — silica and D2 dolomite — pyrite seems to suggest that the presence of soluble silica and H₂S in the solution may suppress the hydration barrier of Mg, the latter preventing direct precipitation of dolomite from the solution.

INTRODUCTION

Zn—Pb mineralization of the MVT type in Upper Silesia, Poland, occurs in ore-bearing dolomites at the contact with limestones. Ore-bearing dolomite owes its origin to the dolomitization of Triassic carbonates (Muschelkalk) in the zones where limestones grade laterally and vertically into dolostones (Pawłowska, Szuwarzyński 1979). The carbonates in question were deposited on tidal flats in the supra-, inter- and sub-tidal zones. The sedimentary structures show bedding, lamination, sedimentary and erosional discontinuities, tidal channels, and submarine flows (Pawłowska, Szuwarzyński 1979). The principal micro-components of the sediments are micrite, algae, shells and their detritus, crinoids, ooids, peloids, intraclasts and sparite. The fractionation of oxygen isotopes in the dolomites and limestones is indicative of the low-temperature process of dolomitization.

Silica appears in the limestones in the form of siliceous concretions and crusts. Similar, but somewhat smaller, forms are also present in the dolomites, in which they do not crosscut the lamination of the host rock. Abundant organic remains in the silica suggest its organic origin (Pawłowska, Szuwarzyński 1979). The amount of silica paragenetic with sulphides is insignificant (Górecka 1967), yet extensive silicification of ore-bearing dolomites has been reported from Imielin (Smulikowski 1946).

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Sulphide mineralization utilizes the original porosity-permeability of the host rock, inherited from the primary (crinoid) limestones, in which sphalerite forms spar embedding echinoderms consisting of a single Fe-dolomite crystal (Kucha — in press). However, the basic stages of mineralization use free spaces formed during diagenesis (Pawłowska, Szuwarzyński 1979), karst processes (Sass-Gustkiewicz *et al.* 1982), and in the course of mineralization itself (Kucha, Czajka 1984).

It is generally held that there are two barriers preventing direct precipitation of dolomite from the solution. One — a kinetic barrier — is the hydration of Mg and the presence of SO_4^{2-} ions in the solution. The other involves the ordering of Ca and Mg in the structure of dolomite. Therefore, the existence of Mg-calcite as the initial form is considered to be a key

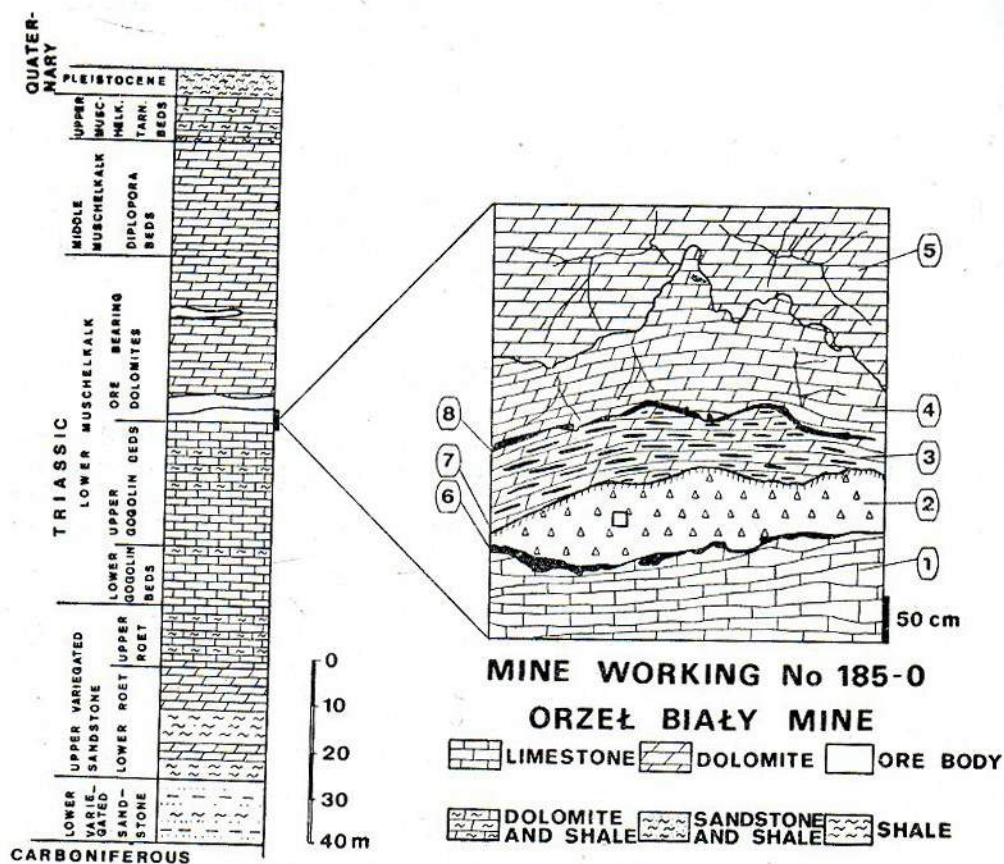


Fig. 1. General lithostratigraphic profile from Orzeł Biały Mine and a section through the deposit fragment under study

1 — dolomite underlying dolomitic microbreccia structure. It was presumably formed by replacement of Upper Gogolin Beds. In its upper part it contains 0.36 wt.% SiO_2 and 1.80 wt.% FeO ;
 2 — dolomitic microbreccia (DM) showing evidence of silicification and pyritization;
 3 — dolomite with finely dispersed and nest-like sphalerite;
 4 — dolomite with veinlike sphalerite filling up fissures owing their origin to the displacement of volume reduction from dolomitic microbreccia;
 5 — ore-bearing dolomite (average MgO and SiO_2 content — 15.92 and 0.02 wt.% resp.);
 6, 8 — intergrowths of earthy sphalerite and dolomite contouring the zone of dolomitic microbreccia;
 7 — metasomatic sphalerite in the top of dolomitic microbreccia

to the formation of dolomite, while the increase in pressure during the burying of the sediment is regarded as a factor responsible for the ordering of Ca and Mg in the crystal lattice during the transformation of Mg-calcite into dolomite (Althoff 1977).

MATERIALS AND METHODS

Investigations were carried out on samples derived from the ore-bearing dolomites and the Upper Gogolin Beds exposed in the 185—0 working in the Orzeł Biały Mine (Fig. 1). Detailed studies were carried out on dolomitic microbreccia up to 1.5 m in thickness, occurring in the bottom of ore-bearing dolomites. The breccia is underlain by dolomite with a wavy surface accentuated by a 2—20 cm thick layer made up of sphalerite, dolomite and pyrite intergrowths (Fig. 1).

The dolomitic microbreccia (DM — Figs 1, 2) consists of dolomite of two generations. D1 dolomite forms clasts varying from 1 to 15 mm in size (Fig. 2) and is cemented with fine-crystalline D2 dolomite. D1 dolomite shows evidence of silicification, exhibiting geometric parallelism to the contours of clasts (Fig. 2). The average content of SiO₂, FeO, MgO and Zn in DM is respectively 0.90, 3.60, 18.95 and 0.10 wt.%.

Dolomitic microbreccia is separated from the enclosing carbonates by a few-cm zones (crusts) of sphalerite (Fig. 1, Nos 6, 7) intergrown with dolomite and pyrite. This mixture of close-intergrown ZnS, dolomite and pyrite contours not only the dolomitic microbreccia but also the overlying dolomite (Fig. 1, No 3) mineralized with sphalerite. SiO₂ content in the sulphide crusts averages 0.68 wt.%.

Dolomite No 3 (Fig. 1) is mineralized with sphalerite which forms nests up to a few cm in size or finely dispersed forms. The average content of SiO₂, FeO, MgO and Zn is 0.25, 2.26, 18.27 and 0.51 wt.%, respectively.

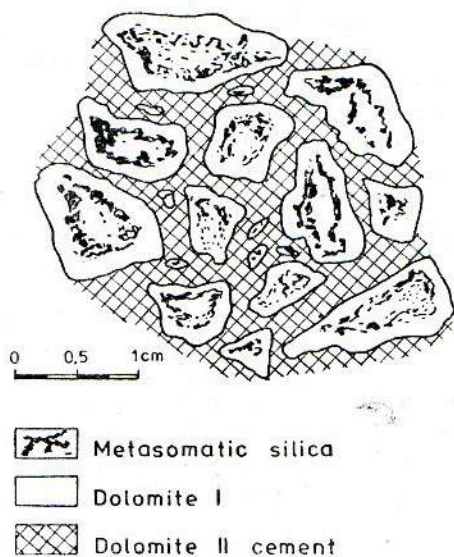


Fig. 2. Diagram showing relations between D1 dolomite clasts and chalcedony. Silica forms metasomatic banded concentrations 2—3 mm below the surface of clasts. Smaller clasts are impregnated with silica throughout their volume

Dolomite No 4 contains fissures filled up with sphalerite (Fig. 1). However, the average content of Zn does not rise above 0.19 wt.%, and that of SiO₂ is less than 0.02 wt.%. The dolomite in question may locally differ in macroscopic features from the superjacent ore-bearing dolomite (Fig. 1, No 5). Fe-dolomite (Fig. 1, No 4) may be regarded as a halo genetically related to mineralization, and the boundary between Fe-dolomite (No 4) and ore-bearing dolomite (No 5) may be discordant.

Taking into account the criterion of structure and texture alone, units No 2, 3, 6, 7 and 8 (Fig. 1) have been assigned to the dolomitic breccia under study. The breccia form so defined is from 0.15 to 3 m in thickness. Taking into consideration the chemical criterion and the lateral and vertical distribution of elements, a general lithochemical pattern of the structure discussed can be given:

i) large bodies of ore-bearing dolomites (OBD) are a first-order structure;

ii) a smaller body of Fe-dolomites occurs in the bottom of OBD, constituting a second-order structure;

iii) in the bottom part of Fe-dolomites an orebody related to the microbreccia structure is located; the orebody, together with dolomitic microbreccia, makes up a third-order structure.

The aim of this paper is to discuss the process of dolomitization only within the dolomitic microbreccia (Fig. 1).

D1 DOLOMITE — SILICA RELATION

Metasomatic silica was found in all the samples taken from the dolomitic microbreccia. Silica occurs 2—3 mm below the surface of D1 dolomite clasts (Fig. 2), usually forming a band up to a few mm thick within larger clasts. Smaller D1 dolomite clasts are impregnated with silica (Fig. 2) throughout their volume.

Microscopic studies have revealed that this silica is partly quartz and partly chalcedony. The concentrations of metasomatic silica contain numerous carbonate grains (Plates 1, 2). Larger grains generally have a composition corresponding to Fe dolomite. Smaller ones, a few μm in size, are characterized by substantial prevalence of Ca over Mg. The chemical composition of such fine grains (Table 1, No B2) shows the Mg:Ca ratio of 1:3 and may correspond to the chemical composition of primary carbonates replaced and enclosed by chalcedony. These primary carbonates would correspond in their chemical composition to high-magnesium calcite. After being enclosed in chalcedony, the carbonate relics (high-Mg calcite) were isolated, retaining their original chemical composition. From the above considerations it appears that Mg calcite could have been a precursor of D1 dolomite. Larger carbonate crystals enclosed in chalcedony also show a substantial deficiency of Mg (Table 1, No B4) when compared with larger D1 dolomite crystals occurring outside chalcedony concentrations.

Fe forms a significant admixture in D1 dolomite (Table 1). Therefore, Mg—Fe calcite can be suggested as the precursor of D1 dolomite. The transformation of Mg-calcite into dolomite is attended by a 10.5% reduction in volume (Kucha, Czajka 1984). As shown by Fig. 2, such a reduction in volume could have been responsible for the formation of local dolomitic microbreccias during dolomitization.

Table 1

Microprobe composition of minerals from dolomitic microbreccia in wt. % (upper figure) and in atomic proportion (lower figure)

Sample	MgO	SiO ₂	CaO	MnO	FeO	CO ₂ calc.	Total	Mineral
A1	20.22 0.5015	≤0.02	30.19 0.5383	0.25 0.0035	1.54 0.0214	46.86	99.06	Dolomite D1
A2	18.70 0.4638	"	30.58 0.5453	0.59 0.0083	2.74 0.0383	46.45	99.06	Dolomite D1
B1	20.41 0.5062	"	30.04 0.5357	≤0.08	3.24 0.0451	47.84	101.53	Dolomite D1
B2	0.04 0.0010	87.22	0.17 0.0030	"	0.05 0.0007		87.48	Chalcedony
B3	≤0.01	100.50	0.08 0.0014	"	0.08 0.0011		100.66	Quartz
B4	17.10 0.4241	0.31	31.00 0.5528	0.20 0.0028	5.35 0.0745	46.40	100.36	Dolomite D1
C2	19.07 0.4730	≤0.02	30.35 0.5412	0.18 0.0025	3.69 0.0514	47.01	100.30	Dolomite D2
D2	17.97 0.4458	"	30.46 0.5432	0.38 0.0054	3.80 0.0529	46.09	98.70	Dolomite D2
D4	19.18 0.4757	"	30.51 0.5440	0.29 0.0041	3.00 0.0418	46.90	99.88	Dolomite D2

The metasomatic replacement of dolomite (Mg-calcite) by chalcedony is presumably closely associated with dolomitization. Soluble silica probably formed metastable ionic complexes with Mg, which were less hydrated than pure Mg ions in the solution. In consequence, soluble silica could have acted as a catalyst of dolomitization, displacing Mg from the solution to the solid phase. This statement has been substantiated by experimental studies (Ricketts 1980). The precipitation of carbonates in hydrated silica gels gives rise to high-Mg calcites, with the possibility of their attaining the composition of dolomite. In the above experiments, the formation of high-magnesium calcite is controlled by diffusion rather than the Mg/Ca ratio in the solution (Ricketts 1980).

D2 DOLOMITE — PYRITE RELATION

D2 dolomite forms cement of the breccia consisting of D1 dolomite. However, D2 cement is also brecciated, which is only visible under the microscope. Worth noting is the fact that microbreccia made up of D2 cement is usually not cemented at all. D2 cement contains a large amount of finely disseminated pyrite (Plate 2). This pyrite is so closely associated with D2 dolomite microbreccia that a genetic relationship between dolomitization II and the formation of pyrite can be suggested.

D2 dolomite has a high Fe content (Table 1, Nos C2, D2, D4). It is feasible that pyritic Fe was extracted from dolomite, with the simultaneous

Mg substitution in its place. The reaction of carbonate Fe with H_2S results in the formation of pyrite and liberates hydrogen (Kucha, Czajka 1984; Kullerud 1967). Hydrogen ions have stronger affinity for water dipoles than Mg. Therefore, hydrogen ions could locally act a catalyst, suppressing the Mg hydration barrier and displacing Mg from the solution to the solid phase. Alternatively, the presence of H_2S may suggest the absence of SO_4^{2-} , an agent promoting the existence of hydration barrier. After the reduction of SO_4^{2-} to S^{2-} , the hydration barrier may be too weak to prevent Mg from passing to the dolomitic solid phase. The proposed mechanism seems to be very promising, as it may be applied to Zn—Pb calcites (Kucha, Wieczorek 1984), or even Zn, Pb and Fe carbonates (Kullerud 1967). They may release heavy metals during dolomitization of Mg—Zn—Pb calcites induced by the reaction with H_2S , with the simultaneous formation of sulphides.

Translated by Hanna Kisielewska

REFERENCES

- ALTHOFF P. L., 1977: Structural refinements of dolomite and magnesian calcite and implications for dolomite formation in the marine environment. *Amer. Mineral.* 62, 772—783.
- GÓRECKA E., 1967: Występowanie wolnej krzemionki w dolomitach kruszconośnych i kruszczach niecki bytomskiej. *Acta Geol. Pol.*, 17, 315—326.
- KUCHA H., CZAJKA K., 1984: Sulphide-carbonate relationships in Upper Silesian Zn—Pb deposits (Mississippi Valley type), Poland, and their genesis. *Trans. Inst. Min. Metall.* (Sect. B: Appl. earth sci.) 93, 12—22.
- KUCHA H., WIECZOREK A., 1984: Sulfide-carbonate relationships in the Navan Tara Zn—Pb deposit, Ireland. *Mineral. Deposita* 19, 208—216.
- KUCHA H., 1988: The significance of diagenesis in emplacement of stratabound Zn—Pb mineralization in carbonate sediments. In: Friedrich G., Schneider H. J., Herzig P. (Eds). Base metal sulfide deposits in volcanic and sedimentary environment. SGA publication.
- KULLERUD G., 1967: Sulfide studies. 286—321. In: Research in geochemistry, 2. New York, J. Wiley.
- LIPPMANN K., 1973: Sedimentary carbonate minerals. Springer Verlag, Berlin.
- PAWŁOWSKA J., SZUWARZYŃSKI M., 1979: Sedimentary and diagenetic processes in the Zn—Pb host rocks of Trzebieńka. 13—49. In: Pawłowska J., Chidester A. H., Wedow H. Jr. (Eds) Research on the genesis of zinc-lead deposits of Upper Silesia, Poland. Wyd. Geol., Warsaw 1979, 151 pp.
- RICKETTS B. D., 1980: Experimental investigation of carbonate precipitation in hydrated silica gels. *Jour. Sed. Petrol.* 50, 960—970.
- SASS-GUSTKIEWICZ M., DZUŁYŃSKI S., RIDGE J. D., 1982: The emplacement of zinc-lead sulfide ores in the Upper Silesian district — a contribution to understanding of Mississippi Valley-type deposits. *Econ. Geol.* 77, 392—412.
- SMULIKOWSKI K., 1946: O dolomicie z Imielna na Górnym Śląsku. *Ann. Soc. Geol. Pol.* 16.

EXPLANATION OF PHOTOGRAPHS

Plate 1

Scanning micrograph of silicified D1 dolomite. Relics of dolomite crystals and tiny relics (up to 2—3 μm) of high-Mg calcite are visible within silica. The other micrographs show: topographic image in reflected electrons, the distribution of Fe, Ca, Mg and Si

Scanning micrograph of pyrite coexisting with D2 dolomite and silica. Dolomite adjoining pyrite has a lower Fe content than dolomite grains not in direct contact with pyrite. The other micrographs show: topographic image in reflected electrons, the distribution of Fe, Ca, Mg and Si

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ROLA ROZPUSZCZALNEJ KRZEMIONKI I H_2S W PROCESIE DOLOMITYZACJI

Streszczenie

W spągowej części dolomitu kruszczonego w kopalni „Orzeł Biały” występuje zmineralizowana sfalerytem brekcja dolomitowa. Klasty dolomitu D1 są metasomatycznie impregnowane krzemionką. Brekcja scementowana jest późniejszym dolomitem Fe D2 impregnowanym pirytem. Ścisła asocjacja dolomit D1—krzemionka oraz dolomit D2—piryt może sugerować, że rozpuszczalna krzemionka oraz H_2S w roztworze mogą być czynnikami, które obniżają barierę hydratacyjną Mg, która zapobiega bezpośredniej precypitacji dolomitu z roztworu.

OBJAŚNIENIA RYCIN

Ryc. 1. Ogólny profil litostratygraficzny z rejonu kopalni „Orzeł Biały” oraz przekrój ukazujący badany fragment złoże
1 — dolomit podścielający strukturę mikrobrecji dolomitowej. Dolomit ten został przypuszczalnie utworzony przez zastąpienie górnych warstw gogolińskich (Upper Gogolin Beds). W stropowej części zawiera on 0,36% wag. SiO_2 i 1,80% wag. FeO; 2 — mikrobrecja dolomitowa (DM) z objawami sylifikacji i pirytyzacji; 3 — dolomit z drobno rozproszonym i gniazdowym sfalerytem; 4 — dolomit z żyłowym sfalerytem wypełniającym szczeliny powstałe przypuszczalnie wskutek przemieszczenia redukcji objętości ze strefy mikrobrecji dolomitowej; 5 — dolomit kruszczonego (średnia zawartość w % wag. — MgO 15,92; SiO_2 0,02); 6 i 8 — przerosty ziemistego sfalerytu i dolomitu okonturowywujące strefę mikrobrecji dolomitowej; 7 — sfaleryt metasomatyczny w stropie mikrobrecji dolomitowej

Ryc. 2. Rysunek ukazujący relacje pomiędzy klastami dolomitu D1 i chalcedonu. Krzemionka tworzy metasomatyczne wstęgowe skupienia 2—3 mm poniżej powierzchni klastów. Mniejsze klasty są przepojone krzemionką w całej objętości

OBJAŚNIENIA FOTOGRAFII

Plansza 1

Obraz skaningowy zsylikowanego dolomitu D1. W obrębie krzemionki widoczne są relikty kryształów dolomitu oraz bardzo drobne relikty (do 2—3 μm) kalcytu wysokomagnezowego. Kolejne fotografie ukazują: obraz topograficzny w elektronach odbitych, rozmieszczenie Si, Ca, Fe oraz Mg

Plansza 2

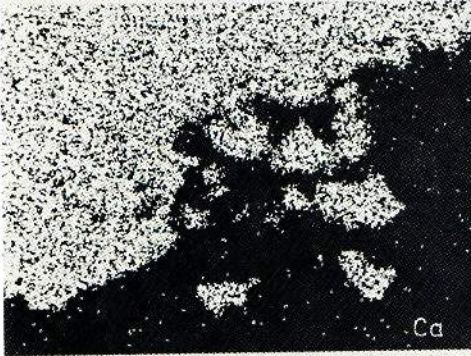
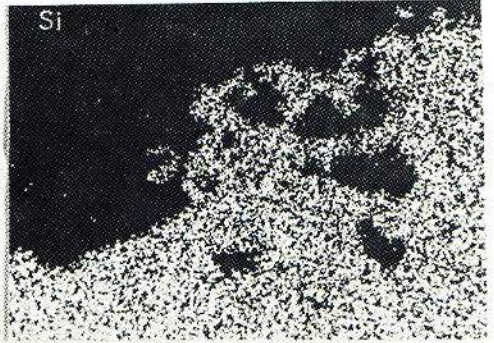
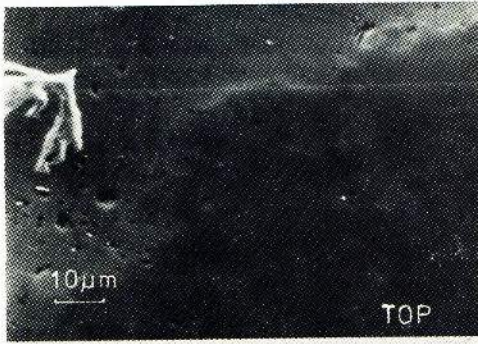
Obraz skaningowy pirytu współwystępujące z dolomitem D2 oraz krzemionką. Dolomit bezpośrednio kontaktujący z pirytem ma niższą zawartość Fe niż ziarna dolomitu nie kontaktujące się bezpośrednio z pirytem. Kolejne fotografie ukazują: obraz topograficzny w elektronach odbitych, rozmieszczenie Si, Ca, Fe oraz Mg

Хенрык КУХА, Абд Эль Монеим ОСМАН

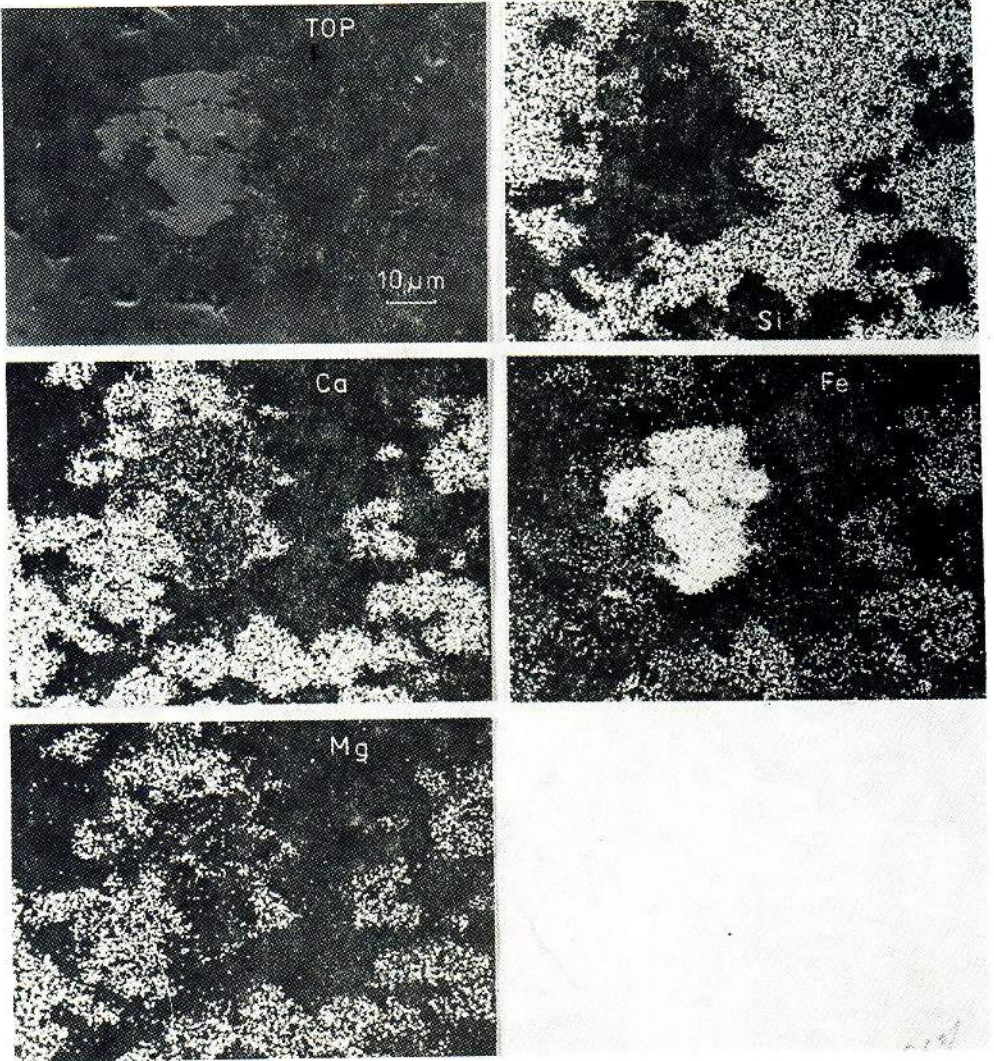
РОЛЬ РАСТВОРИМОГО КРЕМНЕЗЕМА И СЕРОВОДОРОДА В ПРОЦЕССЕ ДОЛОМИТИЗАЦИИ

Резюме

В подошве рудоносного доломита района шахты „Белый Орел” находится минерализована сфалеритом доломитовая брекчия. Класты доломита D1 метасоматически импрегнированы кремнеземом. Эта брекчия цементирована позднейшим железистым доломитом D2, импрегнированным пиритом. Тесная ассоциация доломит D1 — кремнезем и доломит D2 — пирит свидетельствует о том что кремнезем и сероводород в действующих растворах могли играть роль факторов, снижающих гидратационный барьер Mg, который не допускает непосредственного осаждения доломита из раствора.



H. KUČHA, A. E. M. OSMAN — The role of soluble silica and H_2S in the proces of dolomitization



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