

Bogusław BAŁ * , Witold ŻABIŃSKI *

ON THE CONTINUITY OF THE SOLID SOLUTION SERIES SMITHSONITE-SIDERITE

UKD 548.313.2:549.742.114:549.742.115

Abstract. The results of electron microprobe studies of trigonal carbonates of the series $ZnCO_3$ (smithsonite) — $FeCO_3$ (siderite) from the Cracow—Silesian Zn and Pb ore deposits have lent support to the hypothesis of continuity of this isomorphous series.

INTRODUCTION

The continuity of the isomorphous series of anhydrous trigonal zinc and iron carbonates (smithsonite-siderite) has been a subject of much discussion. The earliest studies, based on chemical analyses of Fe-smithsonites (monheimites) and Zn-siderites, led to the conclusion that there was a miscibility gap in the solid solution series of these carbonates over a certain range of Zn:Fe ratios, on the side closer to siderite (Doelter 1912, Dana et al. 1951). The highest known iron content in monheimites corresponded to the atomic ratio of Zn:Fe=0.7:1 (i.e. about 59 mol.% $FeCO_3$), while the zinc content in siderites was thought to be not greater than 2 wt.% ZnO. Some authors, however, postulated the continuity of the isomorphous series in question (Ferrari, Colla 1936; Strunz 1957).

Later on, when X-ray method was introduced to the studies of carbonates of the smithsonite-siderite series, it has been found that there exist members with the lattice constants that are intermediate relative to the respective values for pure smithsonite and siderite. Such investigations were made by Żabiński (1958) and Bał and Nieć (1979) for monheimites occurring in the Cracow—Silesian Zn-Pb ore deposits, and by Sitzia (1965) for monheimites from Montevecchio. Yet the continuity of this isomorphous series was still an open question because the cited authors did not find members showing any appreciable molecular prevalence of $FeCO_3$ over $ZnCO_3$. In 1977 Shikazono described siderites from

* Institute of Geology and Mineral Deposits, Academy of Mining and Metallurgy in Cracow (Kraków, al. Mickiewicza 30).

Japanese deposits, in which chemical analyses showed a $ZnCO_3$ content running up to 8 wt. %.

Recently, Bąk and Nieć found a new occurrence of monheimites and zinc siderites in the Bolesław mine near Olkusz, in the Cracow-Silesian Zn and Pb ore deposits. Microprobe studies of these minerals, as well as analyses of the already known monheimites from Chrzanów (Matylda mine), have thrown light on the problem of continuity of the isomorphous series under study.

MATERIALS AND METHODS

A few monheimite and zinc siderite samples from the Bolesław mine were subjected to chemical analysis and X-ray investigations. The minerals in question form fine-grained, compact aggregates of grey colour, sometimes with a greenish tinge, or thin incrustations on the walls of cavities in dolomite (dolostone), or thin veinlets cross-cutting dolostone (Bąk, Nieć 1979, 1981).

Quantitative determinations of Zn and Pb contents in the samples were carried out with classical methods. A few microprobe analyses for Zn, Fe, Mn, Ca, Mg, Pb and S were made for each sample. Electron microprobe studies were also carried out on a few samples of monheimite galmeis from Chrzanów. The latter minerals form compact, fine-grained grey or yellow-grey aggregates but, in contrast to the samples from Bolesław, they contain a substantial admixture of dolomite (Zabiński 1958). Because of this, the classical methods of analysis applied to these minerals do not allow one to make inferences as to the $ZnCO_3 : FeCO_3$ quantitative ratio. The analyses were carried out on an ARL SEMQ electron microprobe operated at an accelerating voltage of 20 kV. The samples were coated with carbon film. K_{α} spectral lines were utilized for Fe, Zn, Mn, Ca, Mg and S determinations, using the following specpure standards: Fe, Zn, Mn, Mg, CaF_2 , $CaCO_3$ and FeS_2 . Lead was determined from M_{α} line, using specpure PbS as standard.

The lattice constants a and c were determined for some samples. A powder pattern was taken for this purpose, using film technique. It was recorded with a TUR M-60 X-ray apparatus with a 114.6 mm camera, using filtered CoK_{α} radiation. The film was put asymmetrically by Straumanis-Ievins method. The distance between lines was measured with an accuracy of 0.05–0.1 mm. When calculating d_{hkl} values, corrections were made for film shrinkage and X-ray absorption in the samples.

RESULTS AND DISCUSSION

Electron microprobe data obtained for the smithsonite-siderite series have thrown new light on the continuity of this isomorphous series, as they permitted a determination of the chemical composition of single mineral grains or small grain aggregates. Classical chemical analysis, on the other hand, as well as X-ray investigations, requiring the use of a greater amount of sample, were generally able to yield only averaged data.

The results of chemical and X-ray analyses of minerals of the smithsonite-siderite series are shown in figure 1. In the upper part of the

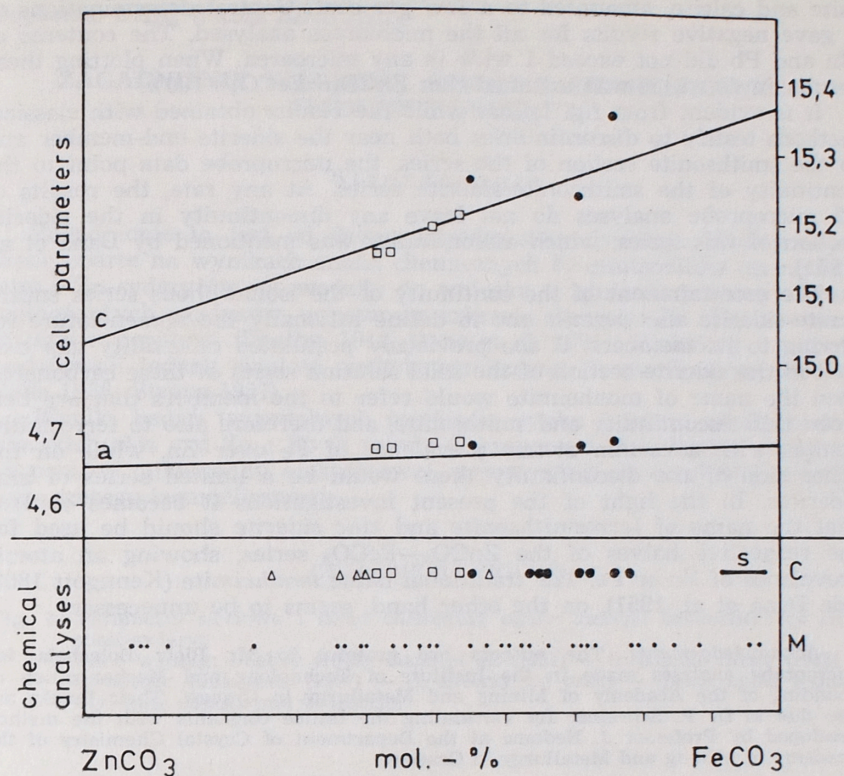


Fig. 1. Cell parameters and chemical composition of members of the isomorphous series smithsonite-siderite. After: Doelter (1912) and Dana et al. (1951) — small triangles, Sitzia (1965) — squares, Shikazono (1977) — S, present authors' data — full circles and dots. Other explanations in the text

figure are plotted the lattice constants a and c given by Sitzia (1965) and obtained by the present authors. The straight lines join the lattice constants of pure smithsonite and siderite (after Graf 1961), in accordance with Vegard's law. The a and c values for the intermediate members fall, as a rule, near these lines. It is worth noting that the effect of Zn^{2+} substitution by Fe^{2+} is considerably more pronounced for the parameter c than a . This is presumably due to the deformation of coordination polyhedra round Fe^{2+} ions as a result of Jahn-Teller effect. The elongation of octahedra round Fe^{2+} in siderite along $\bar{3}$ axis has been ascertained by Mössbauer spectroscopy (Greenwood, Gibb 1971, fide Rosenberg, Foit 1979).

The lower part of figure 1 shows the results of chemical analyses of carbonates of the $ZnCO_3-FeCO_3$ series obtained by different authors with classical methods (upper row — C) and microprobe-determined data of the present authors (lower row — M). Analyses were given only for those microareas in which the sum of $ZnCO_3$ and $FeCO_3$ contents was greater than 90 wt.%, i.e. the admixture of other minerals, mainly dolo-

mite and calcite, amounted to a few per cent. Control determinations of S gave negative results for all the microareas analysed. The contents of Mn and Pb did not exceed 1 wt.% in any microarea. When plotting these results in fig. 1, it was assumed that $ZnCO_3 + FeCO_3 = 100\%$.

It is evident from fig. 1, that while the results obtained with classical methods testify to discontinuities both near the siderite end-member and in the smithsonite section of the series, the microprobe data point to the continuity of the smithsonite-siderite series. At any rate, the results of 32 microprobe analyses do not leave any discontinuity in the siderite section of this series, which discontinuity was mentioned by Dana et al. (1951).

The ascertainment of the continuity of the isomorphous series smithsonite-siderite also permits one to define rationally the nomenclature referring to its members. If the previously postulated miscibility gap existed in the siderite section of the solid solution series of these carbonates, then the name of monheimite would refer to the members that are between this discontinuity and smithsonite, and therefore also to ferrosmithsonites with a certain atomic prevalence of Fe over Zn, while on the other side of the discontinuity there would be a limited series of zinc siderites. In the light of the present investigations it becomes obvious that the name of *ferrosmithsonite* and *zinc siderite* should be used for the respective halves of the $ZnCO_3-FeCO_3$ series, showing an atomic prevalence of Zn or Fe. The traditional name *monheimite* (Kennigott 1853, fide Dana et al. 1951), on the other hand, seems to be unnecessary.

Acknowledgements. The authors are grateful to Mr Piotr Bolechała for microprobe analyses made in the Institute of Technology and Mechanization of Founding of the Academy of Mining and Metallurgy in Cracow. Their thanks are also due to Dr P. Schreiner for calculating the lattice constants with the method developed by Professor J. Nedoma at the Department of Crystal Chemistry of the Academy of Mining and Metallurgy in Cracow.

Translated by Hanna Kisielewska

REFERENCES

- BAK B., NIEĆ M., 1979: The occurrence of monheimite in the Bolesław Zn-Pb ore deposit near Olkusz. *Miner. Polon.* 9, 1, 123-130.
- BAK B., NIEĆ M.: Występowanie monheimitu i allofanu w złożu kopalni „Bolesław” w Bukowni koło Olkusza. *Rudy i Met. Nieżel.* (in press).
- DANA J. D., DANA E. S., PALACHE C., BERMAN H., FRONDEL C., 1951: The system of mineralogy. 7th ed. Vol. 2.
- DOELTER C., 1912: Handbuch der Mineralchemie. Bd. 1. Dresden-Leipzig.
- FERRARI A., COLLA C., 1936: Soluzioni solide fra carbonati neutri romboedrici di metalli bivalenti. *Gaz. Chim. It.* 66 (*Min. Abstr.* 8, 9, 1941).
- GRAF D. L., 1961: Crystallographic tables for the rhombohedral carbonates. *Amer. Miner.* 46.
- GREENWOOD N. N., GIBB T. C., 1971: Mössbauer spectroscopy. Chapman and Hill.
- ROSENBERG P. E., FOIT F. F., 1979: The stability of transition metal dolomites in carbonate systems: a discussion. *Geoch. Cosm. Acta* 43, 951-955.
- SHIKAZONO N., 1977: Composition of siderite and the environments of formation of vein-type deposits in Japan. *Econ. Geol.* 72.
- SITZIA R., 1965: Osservazioni su alcuni ferro-smithsoniti di Montevecchio. *Symp. A. M. S. Cagliari-Iglesias.*
- STRUNZ H., 1957: Mineralogische Tabellen. III Aufl. Leipzig.
- ZABIŃSKI W., 1958: Ferrogalmei (monheimite-galmei) from Kały near Chrzanów. *Bull. Acad. Pol. Sc.* 6, 6.

Bogusław BAK, Witold ŻABIŃSKI

ZAGADNIENIE CIĄGŁOŚCI SZEREGU IZOMORFICZNEGO SMITSONIT-SYDERYT

Streszczenie

Zagadnienie to jest od dawna przedmiotem dyskusji. Najdawniejsze prace oparte na wynikach analiz chemicznych Fe-smitsonitów (monheimitów) i Zn-syderytów, prowadziły do wniosku o istnieniu przerwy w mieszalności tych węglanów, w pewnym zakresie stosunku Zn : Fe, po stronie bliższej syderytowi (Doelter 1912, Dana et al. 1951). Niektórzy z autorów postulowali jednak ciągłość omawianego szeregu izomorficznego (Ferrari, Colla 1936; Strunz 1957).

Wyniki badań trygonalnych węglanów cynku i żelaza ze śląsko-kra-kowskich złóż rud Zn i Pb (z rejonu Chrzanowa i Bolesławia), wykonane za pomocą mikroskopy elektronowej, przemawiają za ciągłością omawianego szeregu izomorficznego.

OBJAŚNIENIE FIGURY

Fig. 1. Parametry sieciowe i skład chemiczny ogniw szeregu izomorficznego smitsonit-syderyt
Dane według: Doelter (1912), Dana et al. (1951) — trójkąci, Sitzia (1965) — kwadraty, Shikazono (1977) — S, autorzy tej pracy — pełne kółka i punkty. Inne objaśnienia w tekście.

Богуслав БОНК, Витольд ЖАБИŃСКИ

ВОПРОС НЕПРЕРЫВНОСТИ ИЗОМОРФНОГО РЯДА СМИТСОНИТ-СИДЕРИТ

Резюме

Этот вопрос издавна является предметом дискуссии. Первые работы опирающиеся на химических анализах Fe-смитсонитов (монгеимитов) и Zn-сидеритов, приводили к выводу о существовании перерыва в смешиваемости этих карбонатов, в некотором пределе соотношения Zn:Fe, по стороне более близком сидериту (Doelter 1912, Dana et al. 1951). Однако некоторые авторы постулировали непрерывность рассматриваемого изоморфного ряда (Ferrari, Colla, 1936; Strunz, 1957).

Результаты исследования тригональных карбонатов цинка и железа из Силезско-Краковских месторождений руд Zn и Pb (из района Хшанова и Болеславия), выполнены с помощью электронного микроскопа говорят в пользу непрерывности рассматриваемого изоморфного ряда.

ОБЪЯСНЕНИЯ ФИГУРЫ

Фиг. 1. Параметры решетки и химический состав звеньев изоморфного ряда смитсонит-сидерит
Данные: Doelter (1912), Dana *et al.* (1951) — треугольники, Sitzia (1965) — квадраты, Shikazono (1977) — S, авторы этой работы — кружки и точки.
Другие объяснения в тексте