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Zincian dolomites and associated carbonates from the Waryński mine, Poland: An AEM investigation

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ABSTRACT

Zincian carbonates from the oxidized zone of the Waryński mine, Upper Silesia, Poland, a Pb-Zn ore deposit, were analyzed by AEM techniques. Compositions lie in the system $CaCO_3$-$MgCO_3$-$(Fe,Mn)CO_3$-$ZnCO_3$ within three one-phase areas of $CaCO_3$-rich, dolomite, and $CaCO_3$-poor solid solutions similar to those in the system $CaCO_3$-$MgCO_3$-$FeCO_3$ (Rosenberg, 1967). Dolomite solid solutions extend from $CaMg(CO_3)_2$ to at least 72 mol% $CaZn(CO_3)_2$ and have electron-diffraction patterns consistent with the $R\bar{3}$ dolomite structure. The extent of solid solution is greater toward $CaZn(CO_3)_2$ than toward $CaFe(CO_3)_2$ in the system $CaCO_3$-$MgCO_3$-$FeCO_3$ at higher temperatures. However, neither of these end-members has been observed in nature or synthesized. $CaCO_3$-poor solid solutions approach the system $FeCO_3$-$ZnCO_3$ whereas $CaCO_3$-rich solid solutions are close in composition to the $CaCO_3$ end-member.

Analyses of carbonates from the Waryński mine and from Tsumeb, Namibia (Garavelli et al., 1982), as well as inferences from experimental studies (Goldsmith, 1983) suggest that the dolomite end-member $CaZn(CO_3)_2$ may be stable at low temperatures.

INTRODUCTION

Phase relationships in the system $CaCO_3$-$MgCO_3$-$ZnCO_3$ and the extent of Zn substitution for Mg in the dolomite structure are long-standing problems in the geochemistry of the carbonates. Advances in our knowledge of this system have come slowly because of the rarity of these carbonates in nature and because of the almost complete lack of experimental data.

Dolomites containing significant amounts of Zn were first described from Tsumeb, Namibia, by Hurlbut (1957), but Ca in these dolomites was partially replaced by Pb. More recently, several Zn-rich, Pb-free dolomites have been described from the same locality (Garavelli et al., 1982). A carbonate approaching $CaZn(CO_3)_2$ in composition and showing evidence of cation ordering consistent with the dolomite space group, $R\bar{3}$, was identified, characterized, and named minrecordite. It occurs within a zone of oxidation with dioptase, $CuSiO_2(OH)_2$, and, therefore, is thought to have crystallized at low temperature.

Although a thorough study of the system $CaCO_3$-$ZnCO_3$ has never been attempted, some data at 600 and 750 °C have been published (Goldsmith and Northrup, 1965). Subsolidus relations are similar to those in the system $CaCO_3$-$FeCO_3$ in that extensive immiscibility exists and an ordered compound was not observed. However, the maximum thermal stability of $CaZn(CO_3)_2$, may lie below 600 °C (Goldsmith, 1983).

Experimental data are not available for the system $CaCO_3$-$MgCO_3$-$ZnCO_3$, but on the basis of octahedral distortion, Rosenberg and Foit (1979) predicted that the extent of substitution of Zn for Mg in the dolomite structure is greater than that for Fe^{2+}. Thus, considering all lines of evidence, a dolomite composition approaching end-member $CaZn(CO_3)_2$ is probably stable at a maximum temperature that lies below 600 °C. However, much more data are required to define phase relations in the ternary system.

In 1959, Zabiński described a zincian dolomite with a Zn/Mg ratio close to unity from the Waryński mine, near Bytom, Upper Silesia, Poland; the zincian dolomite occurred in an assemblage with calcite, smithsonite, goethite, and gypsum. The fine grain-size of the minerals in this assemblage precluded separation of zincian dolomite for purposes of characterization. Identification was based on X-ray powder diffraction and chemical analyses of bulk samples after leaching to remove smithsonite and gypsum. In a later study (Jasieńska and Zabiński, 1972), electron-microprobe analyses confirmed the chemical composition of zincian dolomite inferred earlier and revealed that Zn is unevenly distributed in dolomite grains. Zincian dolomite occurs on grain rims and in the cement between grains, suggesting that it formed during the final stages of dolomitization. Electron-microprobe analyses of discrete dolomite grains were obtained, but the resolution was not adequate to provide analyses of zones within grains.

A sample of the zincian dolomite–bearing assemblage

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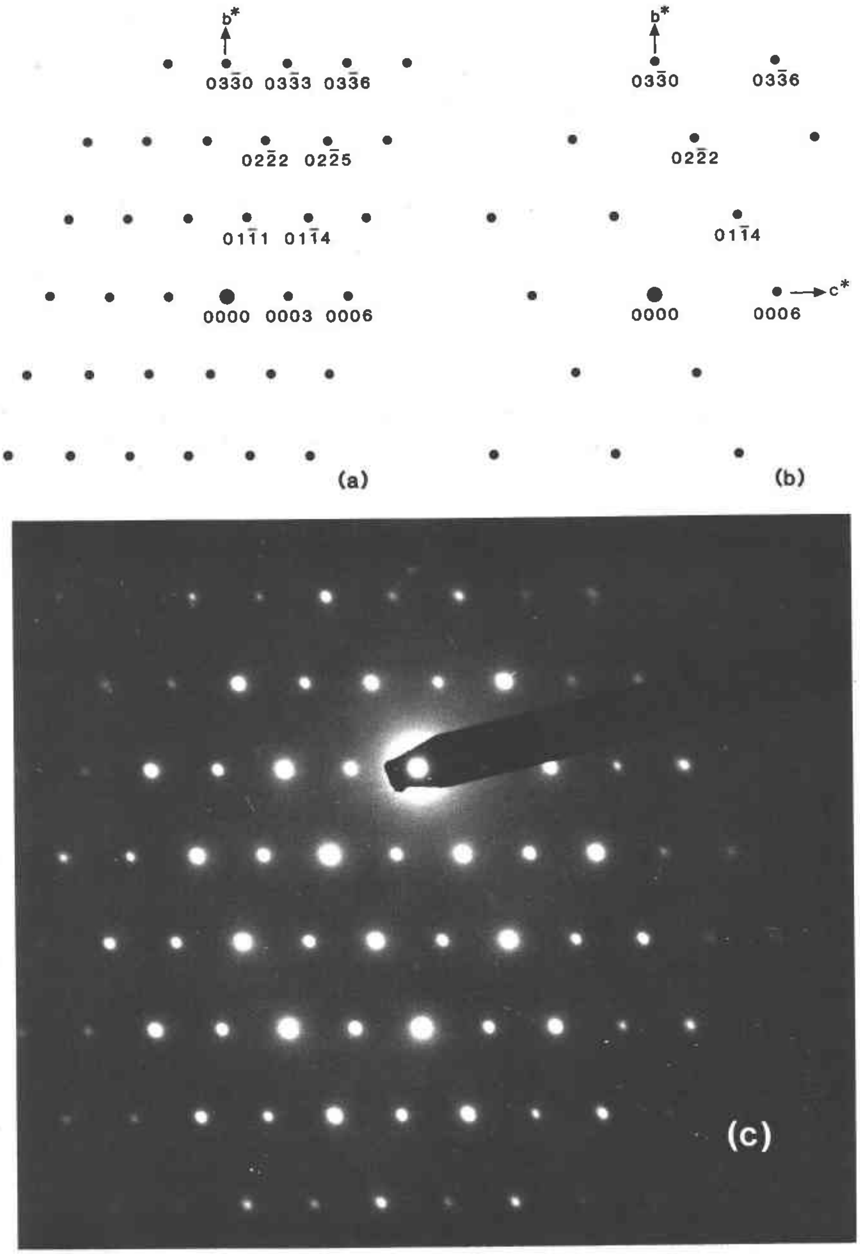

Fig. 1. Electron-diffraction patterns. (**a**) Schematic [100] diffraction pattern from the dolomite structure, space group $R\bar{3}$. The absences 0001, 0002, $01\bar{1}0$, $02\bar{2}0$, etc. are due to rhombohedral lattice. (**b**) Schematic [100] diffraction pattern from the calcite structure, space group $R\bar{3}c$. Absences additional to those in Fig. 1a occur for reflections $h\bar{h}0l$ when l is odd. They are the result of c-glide planes parallel to $\{11\bar{2}0\}$ planes. (**c**) $\langle 100 \rangle$ diffraction pattern obtained from a zincian dolomite grain of composition (mol%) 49% CaCO$_3$, 20% MgCO$_3$, 0% MnCO$_3$, 2% FeCO$_3$, and 29% ZnCO$_3$. The pattern corresponds to Fig. 1a rather than 1b, showing that the space group is $R\bar{3}$.

was obtained for analysis by means of analytical electron microscopy (AEM) through the kindness of Dr. W. Zabiński, Institute of Geology and Mineral Deposits, Academy of Mining and Metallurgy, Krakow, Poland. It was anticipated that this investigation would test predictions of the extent of Zn substitution for Mg in the dolomite structure and provide a further insight into phase relations in the system CaCO$_3$-MgCO$_3$-ZnCO$_3$.

Procedures

Although the sample was received as a fine powder, the crystals were too thick for "thin specimen" analysis (Lorimer, 1987). Therefore, the sample was ground lightly under ethanol and air-dried before it was deposited from a distilled water suspension onto C-covered grids. Inasmuch as textural relationships were destroyed by grinding, the coexistence of phases and their compositions in successive zones could not be determined. Further studies in which grains are mounted in an epoxy resin and thinned by ion milling would be of interest and may be possible if suitable samples can be obtained.

Isolated crystals transparent to the electron beam (100 kV) in the TEM mode were selected for AEM analyses. Elemental ratios were determined using a Philips EM400T electron microscope equipped with an EDAX energy-dispersive X-ray detector, following procedures reviewed by Lorimer (1987). The analyses (60-s live time) were quantified using proportionality constants that had previously been obtained for Mg, Ca, Fe, and Mn from well-characterized silicate standards (Cliff and Lorimer, 1975) and for Zn from a homogenized Al-Zn-Mg alloy. The total relative errors in elemental analyses have been calculated at the 2σ confidence level based on X-ray (Gaussian) counting statistics and assuming an error of ±2% in the proportionality constant (Lorimer, 1987). For typical Ca- and Zn-rich analyses, the relative error is approximately ±3.0% for Ca, ±4.7% for Mg, ±11.1% for Mn, ±6.1% for Fe, and ±3.2% for Zn.

Electron diffraction was used to determine whether the zincian carbonates with Ca/(Zn + Mg + Fe + Mn) ratios approximating unity have the ordered dolomite structure, space group $R\bar{3}$ or the calcite structure, space group $R\bar{3}c$. The c glide in the calcite space group leads to systematic absences for reflections of the type $h\bar{h}0l$ when l is odd.[1] However, because of the double diffraction that occurs with electrons in samples of any significant thickness, the only zone axis that will show the absence or presence of the relevant reflections, and thus of the c-glide plane, is ⟨100⟩ (Figs. 1a, 1b).

Because only a small amount of sample was available, X-ray diffractometry was not attempted in this study. X-ray powder-diffraction data for this material was published in an earlier study (Zabiński, 1959).

RESULTS AND IMPLICATIONS

Semiquantitative, preliminary AEM analyses were carried out in order to identify the minerals present in the sample. A great many of the grains were found to be rhombohedral cleavage fragments, presumably carbonates. Most of these crystals have compositions lying in the system $CaCO_3$-$MgCO_3$-$MnCO_3$-$FeCO_3$-$ZnCO_3$, although end-member $CaCO_3$ and $ZnCO_3$ were also observed. Gypsum, an unidentified calcium silicate, and Fe-rich, formless masses, thought to be goethite, are present in small proportions.

One hundred crystalline grains with compositions in the system $CaCO_3$-$MgCO_3$-$MnCO_3$-$FeCO_3$-$ZnCO_3$ were analyzed quantitatively using AEM techniques. Based on their chemical compositions, 65 of these analyses are thought to represent dolomites, 21 calcites, 8 siderites, and 6 smithsonites.

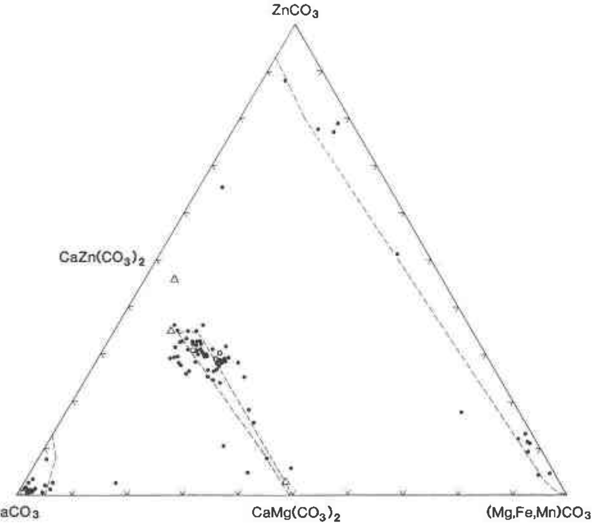

Fig. 2. Compositions of zincian carbonates in the system $CaCO_3$-$(Mg,Fe,Mn)CO_3$-$ZnCO_3$. Solid circles, Waryński mine, single analysis; open circles, Waryński mine, two coincident analyses; open squares, Waryński mine, four coincident analyses; open triangles, Tsumeb, Namibia (Garavelli et al., 1982); broken lines, one-phase areas in the system $CaCO_3$-$MgCO_3$-$FeCO_3$ at 450 °C (Rosenberg, 1967).

Electron-diffraction patterns of typical compositional analogues of dolomite were found to be consistent with the dolomite structure. Three grains containing more than 20 mol% $ZnCO_3$ were tilted in reciprocal space until the ⟨100⟩ zone axis was parallel to the electron beam. All three showed the same pattern. The diffraction pattern in Figure 1c was obtained from a grain with a composition of 49 mol% $CaCO_3$, 20 mol% $MgCO_3$, 0 mol% $MnCO_3$, 2 mol% $FeCO_3$, and 29 mol% $ZnCO_3$. It is identical to the pattern in Figure 1a and can, therefore, be indexed as belonging to the $R\bar{3}$ (dolomite) rather than the $R\bar{3}c$ (calcite) space group.

Carbonate compositions in the five-component system expressed in terms of the end-members $CaCO_3$, $(Mg,Fe,Mn)CO_3$, and $ZnCO_3$ are shown in Figure 2 along with the boundaries of the one-phase areas in the system $CaCO_3$-$MgCO_3$-$FeCO_3$ at 450 °C (dashed lines; Rosenberg, 1967). Most of the analyses lie within or close to these one-phase areas, suggesting that subsolidus relations in the system $CaCO_3$-$(Mg,Fe,Mn)CO_3$-$ZnCO_3$ are similar to those in the system $CaCO_3$-$MgCO_3$-$FeCO_3$. Both systems are dominated by three one-phase areas of $CaCO_3$-rich, dolomite, and $CaCO_3$-poor solid solutions, separated by extensive two-phase areas. The Fe and Zn analogues of dolomite, $CaFe(CO_3)_2$ and $CaZn(CO_3)_2$, have not been observed. The few analyses that lie between one-phase areas are thought to represent mixtures of two phases.

The compositional analogues of dolomite are also

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[1] Throughout this paper we have used the hexagonal cell a = 4.82 Å, c = 16.03 Å, as reported for minrecordite by Garavelli et al. (1982).

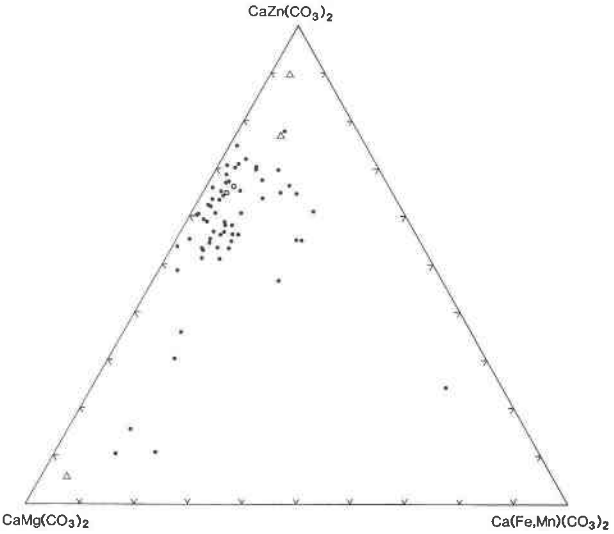

Fig. 3. Compositions of zincian dolomites on the dolomite plane $CaMg(CO_3)_2$-$Ca(Fe,Mn)(CO_3)_2$-$CaZn(CO_3)_2$. Symbols as in Fig. 2.

shown on the plane $CaMg(CO_3)_2$-$CaFe(Mn)(CO_3)_2$-$CaZn(CO_3)_2$ (Fig. 3). Many of these compositions are close to the join $CaMg(CO_3)_2$-$CaZn(CO_3)_2$, $FeCO_3$ being a minor component. Furthermore, there is no obvious relationship between Fe and Zn content. $MnCO_3$ is a minor to trace component in all of the carbonates from the Waryński mine; the Fe/Mn ratio in the dolomitic compositions is greater than 4.0 in 77% of the analyses.

Inasmuch as many of the dolomites from the Waryński mine lie close to the system $CaCO_3$-$MgCO_3$-$ZnCO_3$, further comparison with the system $CaCO_3$-$MgCO_3$-$FeCO_3$ is possible (Fig. 2). Like the ferroan dolomites (Goldsmith et al., 1962; Rosenberg, 1967), the zincian dolomites appear to form a series of solid solutions extending toward, but not reaching $CaZn(CO_3)_2$. The dolomite analysis with the highest $ZnCO_3$ content has the composition 53.62 mol% $CaCO_3$, 6.22 mol% $MgCO_3$, 1.39 mol% $MnCO_3$, 2.68 mol% $FeCO_3$, and 36.11 mol% $ZnCO_3$. Thus, the zincian dolomite solid-solution series appears to extend from $CaMg(CO_3)_2$ to at least 72 mol% $CaZn(CO_3)_2$. Furthermore, many of the zincian dolomites also contain excess $CaCO_3$; however, some are Ca-deficient perhaps because of the substitution of some Mn for Ca, the presence of small admixtures of a siderite-smithsonite solid solution within analyzed grains, and/or analytical error.

Despite the existence of a complete series of solid solutions between $MgCO_3$ and $FeCO_3$ (Rosenberg, 1963), Mg is absent or present in small proportions in the $CaCO_3$-poor analyses whereas it is concentrated relative to Fe in the dolomites. The $CaCO_3$- poor analyses (Fig. 2) are Fe rich and approach the binary system $FeCO_3$-$ZnCO_3$. Although there is only one analysis intermediate between siderite and smithsonite, analyses of siderite-smithsonite solid solutions from a Pb-Zn deposit in the same district as the Waryński mine suggest that a complete series of solid solutions probably exists in the system $FeCO_3$-$ZnCO_3$ (Bak and Zabiński, 1981). The $CaCO_3$-rich solid solutions lie close to the $CaCO_3$ end-member and the analogous one-phase area in the system $CaCO_3$-$MgCO_3$-$FeCO_3$ (Fig. 2).

DISCUSSION

The zincian dolomites from the Waryński mine occur in the zone of oxidation of a Pb-Zn ore deposit where they formed as a result of metasomatic alteration of preexisting dolomites under supergene conditions (Zabiński, 1980). Minrecordite and associated zincian dolomites from Tsumeb, Namibia, formed under similar conditions (Garavelli et al., 1982), although apparently not from preexisting dolomites by replacement of Mg by Zn. Crystallization temperatures of the zincian dolomites and the siderite-smithsonite solid solutions reported by Bak and Zabiński (1981) must have been low.

The chemical compositions of three monomineralic zincian dolomites from Tsumeb (Garavelli et al., 1982) are also shown in Figures 2 and 3 (triangles). The two more magnesian samples lie within the compositional series from the Waryński mine whereas the sample richest in Zn (minrecordite; 92 mol% $CaZn(CO_3)_2$) is separated from all other zincian dolomites by a compositional gap. Analytical data are required to close this compositional gap and, thereby, confirm minrecordite as a single-phase member of a continuous dolomite solid-solution series. The zincian dolomite series could then be extended with confidence to at least 92 mol% $CaZn(CO_3)_2$.

Even if the minrecordite composition is disregarded, the extent of solid solution from $CaMg(CO_3)_2$ toward $CaZn(CO_3)_2$ at low temperatures equals or exceeds the extent toward $CaFe(CO_3)_2$ at relatively high temperatures (Fig. 2). This is in accord with predictions based on octahedral distortion in transition-metal dolomites by Rosenberg and Foit (1979). Furthermore, by analogy with ferroan dolomites (Rosenberg, 1967; Anovitz and Essene, 1987), the extent of this solid solution may be expected to increase at higher temperatures. Thus, if end-member $CaZn(CO_3)_2$ is not stable at low temperatures, it may become stable at high temperatures. However, as pointed out by Goldsmith (1983), the stability of $CaZn(CO_3)_2$ may have an upper temperature limit.

If the calcites from the Waryński mine coexisted in equilibrium with the zincian dolomites, then the solubility of Zn in calcite also approximates that of Fe at higher temperatures (Fig. 2; Rosenberg, 1967). This inference is in possible conflict with the preliminary experimental results of Goldsmith and Northrup (1965) at 600 and 750 °C, which show Fe to be more soluble than Zn in the calcite structure.

Analyses of carbonates from the Waryński mine along with those from the Tsumeb deposit, Namibia (Garavelli et al., 1982), suggest that the dolomite end-member $CaZn(CO_3)_2$ may be stable at low or elevated temperatures, but more evidence is required to confirm this inference. If minrecordite (92 mol% $CaZn(CO_3)_2$) is a single-phase member of a continuous dolomite solid-solution series, then the stability of the end-member $CaZn(CO_3)_2$ would be highly likely, but its stability limits and phase relations would still require investigation. Because Zn-rich dolomites are rare in nature, an experimental investigation of stability relationships in the system $CaCO_3$-$MgCO_3$-$ZnCO_3$ would be desirable.

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