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ZINCIAN AND PLUMBIAN DOLOMITE FROM TSUMEB, SOUTH-WEST AFRICA*

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ABSTRACT

Five specimens of zincian-plumbian dolomite from Tsumeb, South-West Africa are described. Chemical analyses give a range in percentage of ZnO from 3.23 to 8.74 and of PbO from 0.58 to 4.96. DTA analyses show a progressive decrease in the temperature of the first endothermic reaction with increasing percentage of ZnO and a decrease in the temperature of the second endothermic reaction with increasing percentage of PbO. Because of several variables the indices of refraction, specific gravity and unit cell dimensions show a much less regular variation with change in composition.

INTRODUCTION

Through the kindesss of Dr. B. H. Geier and Dr. G. Söhnge of the Tsumeb Corporation, five specimens of dolomite from Tsumeb, South-West Africa were made available for study. Assays made at the mine laboratory showed that the dolomite contained appreciable amounts of zinc. Lead was also present and in two specimens in significant amounts. Only traces of zinc have heretofore been found in dolomite, with the exception of a dolomite from Blieberg, Carinthia which according to Gintl (1877) contained 1.57 per cent ZnO. In a paper describing tarnowitzite and plumbocalcite from Tsumeb, Siegl (1936) mentions a plumbodolomite from Kreuth, Carinthia, but no analysis nor description of the mineral is given. Until now this appears to be the only locality of a plumbian dolomite.

Although all of the dolomite specimens came from the 30 level and are associated with oxidized ore minerals, they differ in their physical appearance and show considerable differences in their chemical analyses. In Table 1 they are numbered from 1 to 5 and hereafter will be referred to by number.

CHEMICAL COMPOSITION

All the specimens with the exception of #5 have visible impurities intimately disseminated through them. In order to separate the dolomite from the associated minerals, the samples were ground to minus 200 mesh and a separation made with methylene iodide. The method proved fairly effective with the exception of #2 in which, after separation, could be seen tiny particles of malachite attached to the dolomite fragments.

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TABLE 1. APPEARANCE AND ASSOCIATION OF DOLOMITE

1. Flesh colored, massive; associated with chalcocite, native copper and limonite.
2. White, massive; associated with malachite and limonite.
3. Light gray, porous crystalline crusts; associated with malachite, native copper and limonite.
4. Pink, massive and in crystalline aggregates and individual rhombohedrons; associated with malachite.
5. Flesh-colored crystalline crusts; free of other minerals.

The copper reported in the analysis of #2 is, therefore, assumed to be due to malachite. The copper reported in the other analyses may also be due to malachite in particles too small to be detected.

To make the analyses conform to the dolomite type formula, $AB(CO_3)_2$, it is necessary to group Zn, Fe and Mn with Mg in the B positions rather than with Ca in the A position. Moreover, the closer

TABLE 2. CHEMICAL ANALYSES OF ZINCIAN PLUMBIAN DOLOMITE*

	1	2	3	4	5
CaO	29.33	27.74	27.77	29.74	28.13
MgO	18.30	17.78	14.34	15.03	14.78
ZnO	4.48	3.23	8.74	6.80	8.31
FeO	0.44	0.66	0.12	0.18	2.16
MnO	0.41	0.27	0.09	0.30	0.27
CoO	0.10	—	—	0.53	0.10
CuO	0.06	1.73	0.15	0.97	0.09
PbO	0.58	3.75	4.96	0.70	1.06
CO_2	45.58	43.95	43.56	45.48	44.32
H_2O	—	—	—	—	0.27
Insol.	0.69	0.94	—	—	0.40
Total	99.97	100.05	99.51	99.73	99.89
	Molecular Percentages				
$CaCO_3$	49.88	29.30	50.27	52.21	49.49
$MgCO_3$	43.28	43.87	36.10	36.71	36.19
$ZnCO_3$	5.24	3.95	10.89	8.22	10.00
$FeCO_3$	0.58	0.92	0.17	0.25	3.27
$MnCO_3$	0.55	0.38	0.12	0.41	0.37
$CoCO_3$	0.14	—	—	0.70	0.12
$CuCO_3$	0.08	—	0.19	1.20	0.10
$PbCO_3$	0.25	1.68	2.26	0.30	0.46

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approach of Zn, Fe and Mn in ionic size to Mg than to Ca argues for such a grouping. Also, on the basis of ionic size Pb is considered to substitute for Ca rather than Mg. For analyses 1 and 5 the formula can be written, $(Ca, Pb)(Mg, Zn, Fe, Mn, Co)(CO_3)_2$, giving almost exactly a 1:1 ratio of the elements in the A and B positions. However, in analyses 2, 3 and 4 there is a slight excess of Ca^{++} plus Pb^{++} over the amount required in the A position. In these there is presumably a substitution of Ca^{++} for Mg^{++} and the formula can be written, $(Ca, Pb)(Mg, Zn, Fe, Ca, Mn, Co)(CO_3)_2$.

Differential Thermal Analyses

Differential thermal analyses were made in air of the analyzed specimens. The thermal curves are reproduced in Fig. 1 together with a curve for dolomite from Binnenthal, Switzerland.

The equipment used in the thermal study was manufactured by the Robert L. Stone Co., Austin, Texas. The samples were ground to minus 60 plus 200 mesh and the temperature increased at a uniform rate of 10° per minute with a resistance of 400 ohms.

The curves show the two endothermic peaks characteristic of the dolomite structure. The first peak of the Binnenthal dolomite is at 815° C. Haul and Heystek (1952) list 12 DTA analyses of dolomite as reported by seven investigators. These data show the first peak has been variously reported from 770°–825° C. The first endothermic reaction of dolomite is due to the decomposition of the $MgCO_3$ layers in the structure and the temperature at which it takes place is influenced by the cations that have been substituted in the Mg^{++} positions. Kulp, Kent and Kerr (1951) point out that in ankerite the greater amount of Fe^{++}, the lower the temperature of the first endothermic peak. According to them a Mg:Fe ratio of 5:1 reduces this peak temperature from 815° C. (dolomite, iron free) to 760° C. Frondel and Bauer (1955) show that in kutnahorite a ratio of Mg:Mn = 1:13 lowers the temperature of the first reaction to 774° C.

Zn substituting for Mg in the dolomite structure causes a greater effect. Mg:Zn = 10:1 reduces the temperature of the first endothermic peak to about 740° (specimen 2). Increasing amounts of Zn tend to further lower the temperature of this reaction but the trend is not linear as in ankerite (Kulp, Kemp and Kerr, 1951). In specimen #3 with Mg:Zn = 3.3:1, the peak temperature of the first reaction is 725° C. In these zincian dolomites the situation is complicated by cations other than Mg^{++} and Zn^{++}. In #5 the presence of 3.27 per cent $FeCO_3$ can be detected in the thermal curve by its oxidation to Fe_2O_3 and CO_2. The amount of Fe^{++} in the other samples is so small that its presence is not recorded by the thermal analyses.

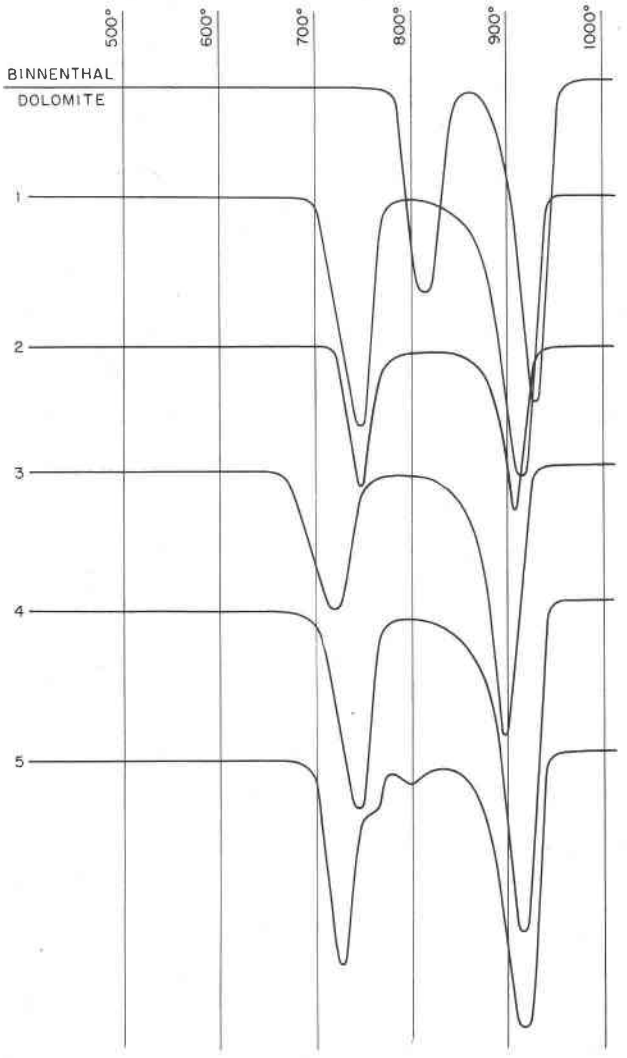

FIG. 1. Differential thermal analysis curves of zincian-plumbian dolomite.

There is no evidence that the temperature and amplitude of the second endothermic peak, that associated with the decomposition of the $CaCO_3$ layers, is affected by the presence of Zn. However, there appears to be a rough correlation between the amount of Pb and the temperature of the second endothermic peak. This peak in the Binnenthal dolomite (lead free) is at 940° C. In sample #1 with 0.25 mole per cent $PbCO_3$ it is at 925° C.; and in sample #3 with 2.26 mole per cent $PbCO_3$ at 895° C. In a similar manner the presence of lead in calcite lowers the tempera-

ture of the endothermic peak. According to Beck (1950) the peak temperature of the single endothermic reaction of Iceland spar is at 1,005° C. whereas in plumbian calcite from Bleiberg, Corinthia with 23 per cent $PbCO_3$, it is at 925° C.

Physical and Optical Properties

The refractive indices as measured by the immersion method are given in Table 3. Also given in the table are values for nO calculated from the indices of refraction of $CaCO_3$, $MgCO_3$, $ZnCO_3$, $FeCO_3$, $PbCO_3$ and $MnCO_3$, taken in the ratios of the analyses of Table 2. The specific gravities were obtained by use of the Berman microbalance and checked by suspension in methylene iodide. Specific gravities were calculated from the specific gravities of the end members taken in the ratios of the analyses. In both indices of refraction and specific gravity there is fairly good agreement between measured and calculated values.

Table 3. Tsumeb Zincian-Plumbian Dolomite

Indices of Refraction and Physical Properties

	Specimen No.				
	1	2	3	4	5
Measured					
nO	1.690	1.698	1.703	1.699	1.700±0.0005
nE	1.520	1.519	1.520	1.519	1.521±0.001
Calculated					
nO	1.690	1.693	1.701	1.696	1.700
Specific Gravity					
Measured	2.90	2.93	3.08	2.93	2.95
Calculated	2.91	2.97	3.07	2.94	3.01
Color	flesh colored	white	gray	pink	flesh colored
Hardness	4	3½	3½	3½	4
Fluorescence	red	none	none	none	red

The color of specimen #4, a vivid pink, is undoubtedly due to the presence of cobalt (0.53 per cent CoO). Furthermore, the flesh color of specimens #1 and #5 may also be due to the small amount (0.10 per cent CoO) of cobalt.

X-ray Study

X-ray powder photographs were taken of the five specimens of zincian dolomite and of the Binnenthal dolomite for comparison. The *d* spacing of $10\bar{1}4$ and 0006 and unit cell dimensions listed in Table 4 show only slight correlation with composition. Specimens 3, 4 and 5 with greater amounts of $ZnCO_3$ have slightly larger unit cells than specimens 1 and 2.

TABLE 4. AXIAL RATIOS OF TSUMEB ZINCIAN-PLUMBIAN DOLOMITE

	d-10$\bar{1}$4	d-0006	c_0	a_0	c_0/a_0
1	2.889	2.665	15.990	4.806	3.327
2	2.885	2.668	16.008	4.804	3.332
3	2.899	2.679	16.074	4.808	3.343
4	2.894	2.683	16.098	4.816	3.343
5	2.892	2.675	16.050	4.814	3.334
Binn. dolomite	2.887	2.670	16.007	4.804	3.330

EVALUATION OF DATA

In the normal solid solution series involving two or three end-members, there can usually be shown a progressive change in the physical constants with change in the relative amounts of the substituting ions. This is true in minerals of the dolomite structure-type, $AB(CO_3)_2$, when one or two substituting cations occupy the B position. However, in the dolomite from Tsumeb, the situation is complicated not only by having as many as four elements substitute in the B position, but also having Pb substitute in the A position.

Attempts to plot specific gravity, index of refraction and d spacings against composition showed marked deviations from progressive change. Only in the differential thermal analyses is there a general correlation with composition. This is undoubtedly due to the fact that DTA separates from one another the effects due to substitution in the A positions from substitution in the B positions.

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