THE CRYSTAL STRUCTURE OF FERROAN ZINCIAN RHODOCHROSITE

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ABSTRACT

Roentgenographic and thermal analysis of this new variety proved that it is a Mn-Fe and Zn carbonate isomorphous with $MnCO_3$.

Specific gravity and refractive indices have been determined.

We have studied samples of a new variety discovered by and obtained from Eng. Victorio Angelelli. This mineral has been found in Capillitas, Catamarca, Argentine Republic.

Its chemical analysis, checked against the chemical analysis of rhodochrosite found in the same place, is shown in Table 1. The results of

TABLE 1

	Ferroan zincian rhodochrosite	Rhodochrosite
MnO	29.80%	57.23%
FeO	13.93	trace
ZnO	14.88	—
CaO	3.13	2.41
CO_2	37.45	39.68
MgO	trace	1.23
H_2O	0.20	—
Insol. acid	trace	Insol. H_2SO_4 0.15
Total	99.39	100.70

TABLE 2. CHEMICAL ANALYSIS INTERPRETED AS CARBONATE MOLECULES

	Mol weight	Ferroan zincian rhodochrosite		Rhodochrosite
		%	Mol. conc.	%
$MnCO_3$	114.94	48.25	0.42	92.8
$FeCO_3$	115.86	22.45	0.194	trace
$ZnCO_3$	125.39	22.96	0.183	—
$CaCO_3$	100.09	5.59	0.056	4.3
$MgCO_3$	84.33	trace		2.6
Total		99.25		99.7

this analysis are significant if we consider the new mineral as being a mixture of carbonates. Table 2 shows that in this mineral two molecules of manganese carbonate appear to be associated with one molecule of zinc carbonate and one of iron carbonate. In other words, in a better accordance with the concept of crystalline molecules, four carbonate

(a) Rhodochrosite

(b) Ferroan zincian rhodochrosite

FIG. 1. ROTATION PHOTOGRAPHS

groups appear to be associated with two manganese atoms, one zinc atom, and one iron atom.

This simple relation suggests an isomorphous compound of rhodochrosite in which a regular substitution of the metallic ions has taken place. In order to verify this assumption, we have determined its physical constants, x-ray crystalline structure, and differential thermal analysis, and compared the results so obtained with those obtained from the pure and mixed carbonates.

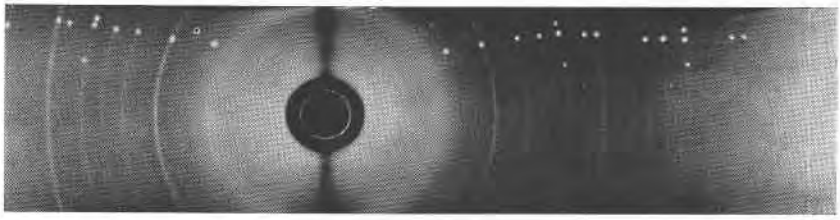
R. G. Wayland (1) has studied the composition, specific gravity, and refractive indices of different samples of rhodochrosite from Butte, Montana, giving variation diagrams of those properties in connection with their composition. But all of them have very small amounts of zinc carbonate. The consequence is that these results do not provide us with any significant information.

Nevertheless, we have tried the Wayland criteria in our study of this new mineral.

Crystal Structure

Rotation patterns were obtained of rhodochrosite and the new mineral in order to obtain information relating to the manner of growth of the

(a) Rhodochrosite



(b) Ferroan zincian rhodochrosite

Fig. 2. Powder photographs

crystals. The results were as follows. Although the rhodochrosite pattern showed very sharp spots, which indicates that this mineral has a definite crystalline orientation (Fig. 1*a*) the new mineral showed discontinuous and almost complete rings which shows an irregular growth of crystals (Fig. 1*b*). We have also tried the Hull-Debye powder method, in order to find any possible difference between the two samples (Fig. 2). The results indicate a complete identity between the crystalline structures of the two minerals.

Table 3 shows the results obtained with three samples of ferroan zincian rhodochrosite and one of rhodochrosite, checked against the values calculated from Bragg's data (2) for a rhombohedral lattice with $a=5.84$ Å; $\alpha=47°\ 20'$, space group $D_{3d}^{6}=R\bar{3}c$.

Patterns were obtained with CoKα radiation in a 50 mm. radius camera. Table 3 shows a very good correspondence of the new mineral and rhodochrosite spacings.

This correspondence of the spacings and the sharpness of the lines in the powder pattern contribute strongly to the hypothesis that the

TABLE 3

hkl	*d* (obs.)					*d* (cal.)
	Ferroan zincian rhodochrosite				Rhodochrosite	
	Sample 1	Sample 2	Sample 3	Average		
110	3.613	3.637	3.594	3.614	3.600	3.598
211	2.820	2.809	2.788	2.806	2.794	2.806
110	2.363	2.357	2.377	2.366	2.341	2.355
210	2.152	2.145	2.139	2.144	2.144	2.135
200	1.979	1.975	1.977	1.977	1.961	1.964
220	1.810	1.802	1.798	1.803	1.804	1.799
332	1.751	1.745	1.737	1.744	1.744	1.751
$\bar{2}10$ $2\bar{1}1$	1.519	1.515	1.506	1.513	1.512	1.527 1.506
310 433	1.439	1.434	1.430	1.434	1.435	1.450 1.427
320 $\bar{2}11$	1.366	1.362	1.357	1.365	1.366	1.376 1.353

mineral is isomorphous with rhodochrosite. If we take into account the (211) and (322) lines, which are the strongest in the carbonate's patterns, we see that the corresponding spacings for Mn, Fe and Zn carbonates are: 2.81, 2.81 and 2.71 for (211) and 1.75, 1.745 and 1.685 for (322), respectively.

So small a difference suggests the possibility of a wider reflection in the case of a mixture of those carbonates with no possible resolution, and, consequently, no possible evidence of the presence of the three carbonates.

Nevertheless, a pattern of a mixture of equal parts of rhodochrosite ($MnCO_3$) and siderite ($FeCO_3$) shows sharp pairs of reflections. Consequently, this new mineral which shows no resolution, appears to be not a mixture of carbonates, but an isomorphous form of rhodochrosite.

The case of dolomite, in which half of the Ca ions of calcium carbonate has been substituted for Mg ions, is well known. This substitution is accompanied by a lowering in the crystal symmetry. In our case, as the atomic numbers of Mn, Fe and Zn ions are not substantially different

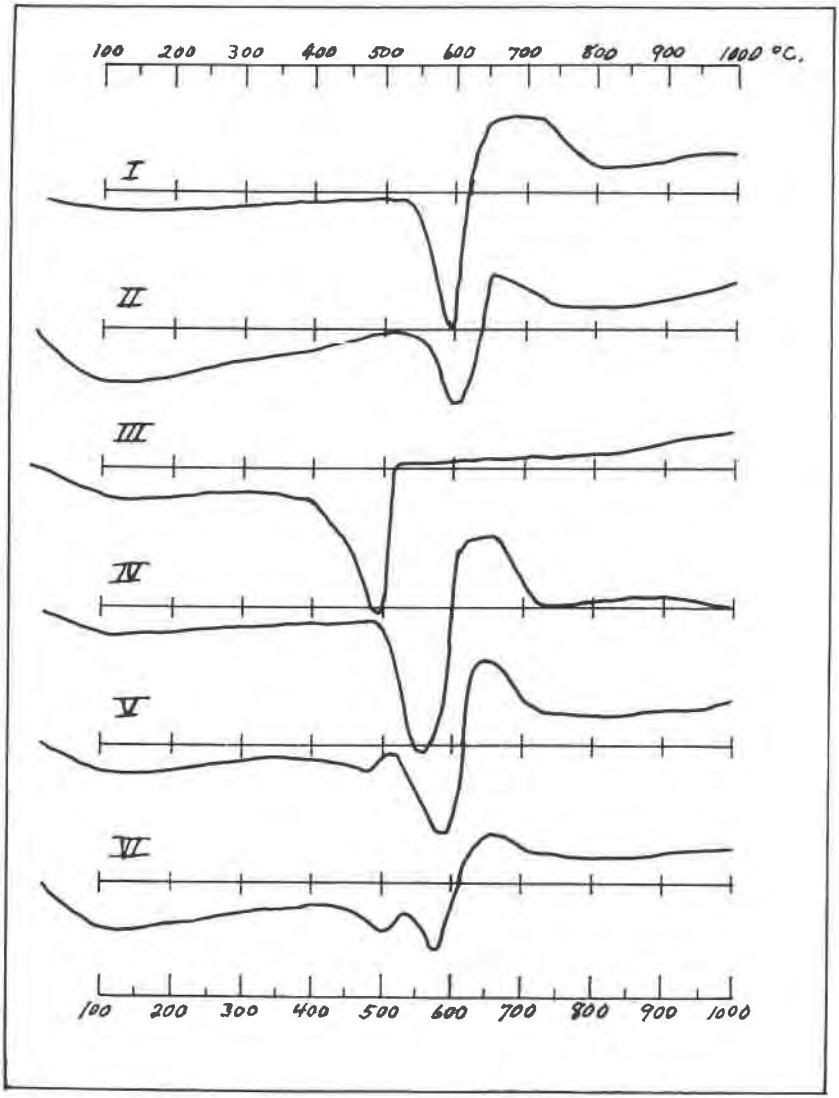


FIG. 3. Thermal differential analyses

Curve I—New Mineral.
Curve II—Rhodochrosite
Curve III—Smithsonite
Curve IV—Siderite
Curve V—50% $MnCO_3$+25%$ZnCO_3$+25%$FeCO_3$
Curve VI—50% curve II+25% curve III+25% curve IV.

(25, 26, and 30), such an effect would be so weak as not to be detectible in the intensity distribution in its pattern reflections.

Differential Thermal Analysis

We have carried out differential thermal analysis following the technique developed by different authors during recent years (3). We made use of an electric furnace with a quartz muffle in which we used, on a refractory support, a nickel disk (37 mm. diameter and 15 mm. height) as a sample holder, with three holes of 7 mm. diameter. The first of them keeps the hot terminal of a chromel-alumel couple in calcined alumina. Its e.m.f. is determined by means of a potentiometer circuit, in order to know the instantaneous temperature of the furnace. The second and third holes contain the terminals of a differential chromel-alumel thermocouple with calcined alumina and sample studied, respectively.

An identical nickel disc covers the first, with three holes through which the thermocouple terminals emerge, in order to avoid the effect of radiant heat on the samples. The e.m.f. on the differential thermocouple was recorded in a Brown Electronic Recorder with 0–10 mV scale which is connected in series with a constant e.m.f. of 4 mV in order to keep the needle in a central position on the scale, and so to record endothermic and exothermic peaks.

The heating rate was about 10° C. per minute. The temperature read on the potentiometer was noted in the record for each 50° approximately. Thermal curves are shown in Fig. 3. The new mineral (curve 1) is characterized by a large endothermic peak ranging from 530° to 620° with a maximum from 590 to 600°, characteristic of all the carbonates, and a large exothermic peak with a maximum ranging from 660 to 730° C.

The rhodochrosite (curve 2) is quite similar, with an endothermic peak with a maximum from 590 to 605 °C. and a sharp exothermic peak with a maximum at 650–660° C. Smithsonite (curve 3) shows the endothermic maximum peak at a lower temperature (490–500° C.) and no maximum in the exothermic one. Siderite (curve 4) shows the endothermic maximum at 560° C and an exothermic peak with a maximum ranging from 625° to 770° C.

These last three curves are in complete agreement with those mentioned in the bibliography (4). We have analyzed, for comparison, a mixture of $MnCO_3$ 50%, $FeCO_3$ 25% and $ZnCO_3$ 25%; which is the composition of the new material. The curve so obtained is shown as curve 5. It shows two endothermic maxima at 460° and 580°, respectively, and one exothermic maximum at 640° C.

It must be noted that the same result is obtained by adding half of the ordinates of curve 2 ($MnCO_3$), with the fourth part of the ordinates of

curves 3 and 4 ($ZnCO_3$ and $FeCO_3$). We concluded that the observed reactions in the mixture correspond to the addition of the individual reaction of each component, without any secondary reactions between them.

We may also state that the new variety is a single substance, and not a mixture of carbonates. Half of the Mn ions of the rhodochrosite have been substituted by Fe and Zn ions in equal parts.

Refractive Indices

We have determined the refractive index by means of the Pulfrich refractometer, obtaining a value: $n_0 = 1.836$. The computation, according to Wayland's criterion, by adding the products of concentrations and refractive indices of each carbonate, gives a value $n_0 = 1.807$ which differs by 0.029 from the observed value.

This computation has no justification; we have preferred to compute the molar refractions M.R. in accordance with the expression:

$$\text{M.R.} = \frac{(n^2-1)}{(n^2+2)} \frac{M}{d} \qquad \text{(Lorentz Lorenz).}$$

M being the molecular weight and d the density for each of the carbonates, and then adding the products of these M.R. by concentrations. The value so obtained for the refractive index is: $n_0 = 1.827$ which differs only by 0.009 (0.5%) from the observed value.

Better results are obtained by adding the ionic refractivities, following J. A. Wasastjerna. By means of numerical values tabulated by W. L. Bragg (2), the value $n_0 = 1.838$ has been obtained, which only differs by 0.1% from the observed one.

Density

The theoretical value of rhodochrosite's density as calculated for a rhombohedral lattice of $a = 5.84$ Å, $\alpha = 47° 45'$ (Wyckoff's values (5)) with two molecules per unit cell is: $D_{calc} = 3.819$ g/cm³.

The computation from Bragg's results (2) provides us with a slightly higher value: $D'_{calc} = 3.874$ g/cm³.

These results are much higher than those observed by other authors. R. G. Wayland gives the following references: W. E. Ford: D = 3.70 (1917); Brentano and Adamson: D = 3.47 to 3.67 (1929); T. Anderson (6) in 1934 gives the observed value: D = 3.6333 g/cm³.

We have determined the density of Capillitas rhodochrosite and obtained the value: $D_{obs} = 3.665$ g/cm³.

By applying the values of Wayland and taking into consideration its

composition, its density would be: $D_w = 3.627$ g/cm.^{3} the difference being 0.038, which is about 1%.

In the case of the new variety, we have determined the density and calculated its theoretical value, on the basis of the dimensions of the cell. We have also calculated the value corresponding to a mixture of carbonates, according to Wayland, and the value obtained by checking with the observed value for the rhodochrosite, taking into consideration the substitution of metallic ions, which raises the mean molecular weight from 114.94 to 117.78. The results are:

Mean density of new mineral	$D_{obs} = 3.762$ g./cm.^{3}
Unit cell calculated	$D_{theory} = 3.913$ g./cm.^{3}
Calculated according to Wayland	$D_w = 3.832$ g./cm.^{3}
Calculated by ion substitution	$D_{calc} = \frac{3.665 \times 117.78}{114.94} = 3.756$ g./cm.^{3}

It is evident that the last value is in better agreement with the observed one. Nevertheless, we believe that the density value is not especially significant, because we are dealing with minerals, and not with individual crystals.

Summary

We have studied the mineral described by Angelelli as ferroan zincian rhodochrosite, from Capillitas, Catamarca, Argentine Republic.

From the interpretation of chemical analysis, x-ray diffraction, and thermal differential analysis, it is a triple Mn, Fe, Zn carbonate, isomorphous with $MnCO_3$ (rhodochrosite). Its formula is: $(Mn, Fe, Zn)CO_3$.

The dimensions of the unit cell differ slightly from those of rhodochrosite, and are: rhombohedral lattice, $a = 5.84$ Å, $\alpha = 47° 45'$.

Its refractive index is $n_0 = 1.836$ and its density $D = 3.762$ g/cm.^{3}

Acknowledgment

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