Strontianite composition and physical properties

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Abstract

Microprobe analyses indicate that strontianites from 12 localities lie essentially along the $CaCO_3$–$SrCO_3$ join between $Sr_{0.968}Ca_{0.029}$ and $Sr_{0.753}Ca_{0.244}$ with Ba and Pb present at the 2500–3600 ppm and the 100–600 ppm levels respectively. Lattice parameters vary regularly across the join, with d_{132} giving the best indirect measurement of $SrCO_3$ content: mole percent $SrCO_3$ (±0.95) = $-2116.24 + 1162.84$ (d_{132} Å). Densities range from 3.78 for $SrCO_3$ to 3.59 for $Sr_{0.753}Ca_{0.244}CO_3$, with values in excess of 3.78 indicating that the Ba–Pb contents are present in more than trivial amounts. Abundant submicroscopic twinning precluded measurement of optical properties.

Introduction

An interest in the strontianite occurrences in the lower Paleozoic carbonate rocks of the Appalachian Mountains revealed the need for a simple method of compositional determination. While there are several studies dealing with physical properties of synthetic strontianites (Holland *et al.*, 1963; Froese and Winkler, 1966; and Chang, 1965, 1971), no work has been done to test their applicability to natural material. In the present study we have examined the range of chemical variation of 12 strontianites and the relationships between chemical composition and some physical properties.

Experimental procedures

The samples examined in this study are listed in Table 1. Other data from the literature used in establishing the determinative curves are from Swanson *et al.* (1954), Holland *et al.* (1963), and De Villiers (1971). The 12 strontianites listed in Table 1 were analyzed with an ARL electron microprobe, using the EMPADR VII computer program (Rucklidge and Gasparrini, 1969) for data reduction. Standards used for the elements were synthetic $SrCO_3$ (Sr), calcite (Ca), witherite (Ba), and cerussite (Pb). Carbon was obtained by calculating the number of carbon atoms according to the relation C = Sr + Ca + Ba + Pb. As

the standards and unknowns are of similar compositions, Sr and Ca should be accurate to about 2 percent of the amount present. No problem was encountered in the detection of Ba and Pb, although their relative error is probably much higher because of the counting statistics and problems in estimating the backgrounds. The number of cations listed in Table 1 are given to four decimal places to prevent round-off errors in the calculations.

Unit cell parameters were determined from packed mounts of powdered strontianite, using spinel (a = 8.0833 Å) as an internal standard. These were run on a Norelco diffractometer at 0.25° 2θ/min, using monochromatized CuK_α radiation. Each sample was scanned at least once with increasing and decreasing 2θ. All peaks were measured at two-thirds peak height and indexed with reference to the data of Swanson *et al.* (1954). The least-squares program of Appleman and Evans (1973) was used to refine the lattice parameters. Four decimal places were retained on the cell edges to prevent round-off errors in the calculations.

Densities were determined with the use of a Berman torsion balance, using toluene, corrected for temperature, as a displacement liquid. The densities of Table 1 are averages of several determinations made on two to four different pieces per sample. As most of the strontianites occur as tufts of small acicular crystals, care was taken that air did not remain trapped between the fine crystals.

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TABLE 1. Crystal and chemical data for strontianites

	1	2	3	4	5	6	7	8	9	10	11	12	13
SrO	60.17	58.33	64.75	56.20	61.52	60.19	56.39	63.78	61.63	68.14	64.15	57.39	70.19
CaO	7.26	8.12	3.36	9.85	6.34	7.13	9.08	4.20	6.11	1.09	4.45	9.76	–
PbO	0.05	0.03	0.09	0.04	0.04	0.01	0.03	0.02	0.04	0.08	0.09	0.07	–
BaO	0.31	0.37	0.32	0.32	0.30	0.35	0.36	0.26	0.39	0.29	0.31	0.31	–
CO_2*	31.33	31.24	30.23	31.68	31.16	31.24	31.17	30.44	31.07	29.86	30.82	32.12	29.81
Total	99.13	98.09	98.74	98.08	99.37	98.93	97.03	98.70	99.24	99.46	99.82	99.65	100.00

Number of ions on the basis of 1 CO_3

	1	2	3	4	5	6	7	8	9	10	11	12	13
Sr	0.8153	0.7926	0.9094	0.7531	0.8378	0.8178	0.7681	0.8895	0.8420	0.9685	0.883ℓ	0.7586	1.0000
Ca	0.1817	0.2040	0.0873	0.2438	0.1598	0.1791	0.2286	0.1081	0.1544	0.0287	0.1134	0.2385	–
Pb	0.0004	0.0002	0.0006	0.0003	0.0003	0.0001	0.0002	0.0001	0.0003	0.0005	0.0006	0.0004	–
Ba	0.0028	0.0034	0.0030	0.0029	0.0027	0.0032	0.0033	0.0025	0.0036	0.0028	0.0028	0.0027	–
d_{132} meas.	1.8891	1.8879	1.8984	1.8830	1.8922	1.8905	1.8850	–	–	1.9017	1.8954	–	1.9065
d_{132} calc.	1.8897	1.8881	1.8985	1.8839	1.8916	1.8906	1.8853	1.8954	1.8922	1.9022	1.8957	1.8861	1.9062
a, Å	5.0841(8)**	5.0834(7)	5.0984(7)	5.0746(17)	5.0881(6)	5.0854(9)	5.0763(15)	5.0944(7)	5.0888(11)	5.1028(14)	5.0936(6)	5.0789(8)	5.1059(7)
b, Å	8.3317(14)	8.3211(17)	8.3759(14)	8.3005(26)	8.3389(12)	8.3361(20)	8.3059(26)	8.3602(16)	8.3440(22)	8.3992(15)	8.3619(12)	8.3154(17)	8.4207(13)
c, Å	5.9847(10)	5.9806(9)	6.0115(9)	5.9687(25)	5.9920(7)	5.9869(13)	5.9743(22)	6.0012(9)	5.9917(11)	6.0197(11)	6.0027(8)	5.9716(9)	6.0319(11)
V, Å³	253.51(5)	252.97(6)	256.71(5)	251.41(11)	254.24(4)	253.80(7)	251.90(11)	255.59(6)	254.42(7)	258.00(7)	255.66(5)	252.20(6)	259.35(6)
$\rho_{meas.}$	3.63	3.59	3.73	3.59	3.64	3.66	–	3.71	–	3.77	–	–	–
$\rho_{calc.}$	3.646	3.626	3.718	3.598	3.663	3.645	3.610	3.706	3.668	3.771	3.700	3.594	3.780

*Calculated to give $C = Sr + Ca + Ba + Pb$.
**The estimated standard errors are given in parentheses and refer to the last decimal place(s).
1 Faylor Quarry, Winfield, Union County, Pennsylvania (Lapham and Geyer, 1972)
2 Salem Rock Company Quarry, Dublin, Pulaski County, Virginia (Dietrich, 1960)
3 Drensteinfrut, Minster district, Westphalia, Germany (Harder, 1964)
4 Belton Quarry, East Stone Gap, Wise County, Virginia (Mitchell and Pharr, 1961)
5 Mud Hills, Barstow, San Bernardino County, California (Knopf, 1918)
6 Clay Center, Ottawa County, Ohio (Morrison, 1935; Howard, 1959)
7 Frazer Duntile Quarry, Clyde Avenue, Ottawa, Ontario (Sabina, 1968)
8 Drensteinfrut, Minster district, Westphalia, Germany (Harder, 1964)
9 Saalfeld, Thuringia, Germany (No reference available)
10 Silbertaal, Germany (No reference available)
11 Minerva Mine, Cave in Rock, Hardin County, Illinois (Grawe and Nackowski, 1949; Weller, Grogan and Tippie, 1952)
12 South Pittsburg, Marion County, Tennessee (No reference available)
13 Johnson Matthey Spec. pure $SrCO_3$

Spindle stage work on what appeared to be optically untwinned material yielded almost identical β and γ values. Checking the grains by X-ray single crystal techniques showed the presence of submicroscopic twinning on (110). In general, the refractive indices were found to increase with increasing Ca content and are approximated by lines drawn between the refractive indices of synthetic $SrCO_3$, $\alpha = 1.517$, $\beta = 1.663$, $\gamma = 1.667$ (Swanson et al., 1954) and aragonite, $\alpha = 1.5300$, $\beta = 1.6810$, $\gamma = 1.6854$ (Mülheim, 1888, in Palache et al., 1951).

Results and discussion

Results of the study are summarized in Table 1. The microprobe analyses show the strontianites examined to be essentially a solid solution along the $SrCO_3$–$CaCO_3$ join, with Ca substituting for Sr up to about 25 mole percent. Older analyses of CaO content of strontianites in Palache et al. (1951) indicated values as high as 7.36 weight percent, well within the extreme values found in this study. Recent strontianite analyses, many only partial, also fall within the range of the samples in this study, excepting for the 11 percent CaO content found by Mitchell and Pharr (1969) for the Belton Quarry strontianite. An analysis of material from the same quarry (#4) shows a slightly lower CaO content, 9.85 percent, closer to the lower of the two values they reported. In the past, there was a question as to whether many of these high-calcium contents were due to admixture of $CaCO_3$. The microprobe and X-ray results presented here suggest that this is not the case.

The limited compositional range of strontianite coexisting with a $CaCO_3$ phase suggests an immiscibility gap in the system $CaCO_3$–$SrCO_3$. Holland et al. (1963) precipitated strontianite and aragonite from aqueous solutions at 96°C and demonstrated the existence of an immiscibility gap between 40 and 70 mole percent $SrCO_3$. Strontianite is thought to be a very low-temperature mineral, most likely crystallizing at or near 100°C (Helz and Holland, 1965). Its occurrence in open vugs and veins suggests crystallization at very low pressures, probably at most equal to the hydrostatic pressure of the ground water. The range of strontianite compositions found in this study falls within the compositional limits indicated by Holland et al. (1963) and predicted from the work of Chang (1965) for conditions coinciding with natural conditions.

The samples studied exhibit very limited sub-

TABLE 2. Equations for strontianite composition from cell parameters and density

Equation	e.s.d.	Correlation Coefficient
mole % $SrCO_3$ = $-2116.24 + 1162.84$ $(d_{132}, Å)$	± 0.95 (mole % $SrCO_3$)	0.9928
= $-3886.02 + 702.03$ $(a_o, Å)$	± 2.37	0.9523
= $-1746.35 + 219.41$ $(b_o, Å)$	± 1.00	0.9919
= $-2156.62 + 373.83$ $(c_o, Å)$	± 2.26	0.9585
= $-734.63 + 3.219$ $(v, Å^3)$	± 0.79	0.9949
= $-367.47 + 123.18$ (ρ_{nat})	± 0.29	0.9988
= $-381.35 + 127.33$ (ρ_{syn})	± 0.45	0.9985

stitution of Ba and even less of Pb. Other strontianite analyses rarely indicate the presence of these elements, reflecting either the minor role these play or, in the case of Ba, coprecipitation with Sr in the wet-chemical analysis. The most Ba- and Pb-rich strontianite reported is from the Suiza mine (De Villiers, 1971), which contains 3.71 mole percent $BaCO_3$ and 0.10 mole percent $PbCO_3$. These are an order of magnitude greater than the Ba and Pb contents of the samples of this study.

The minor role of Ba in strontianite is not the result of unavailability, for several strontianite specimens in this study have barite matrices. The same type of argument could be made for Pb, but associated Pb minerals are less common and not as intimate. Complete solid solutions on the $SrCO_3$–$BaCO_3$ and $SrCO_3$–$PbCO_3$ joins have been synthesized at high temperatures and pressures (Cork and Gerhard, 1931; Chang, 1965; Chang and Brice, 1972), but an immiscibility gap at lower temperatures is still possible. The ionic radius of Sr (~ 1.30) is similar to that of Pb (1.33), whereas the size difference with Ba (1.47) is nearly the same as that with Ca (1.18), for nine-coordinated ions according to Shannon and Prewitt (1969). On this basis, an immiscibility gap with $BaCO_3$ is conceivable (Chang, 1965). Immiscibility with $PbCO_3$ is less likely, and the lack of intermediate compositions may be the result of the rarity of solutions enriched in both Pb and Sr.

The samples in Table 1 lie essentially on the $SrCO_3$–$CaCO_3$ join, and their cell dimensions are consistent with those of synthetic strontianites. The relation of Sr–Ca content with the various cell parameters for strontianite is summarized in Table 2. The d-spacing of the 132 peak has been suggested as a good indirect measure of strontianite composition (Froese and Winkler, 1966). Results for this parameter using calculated d_{132} are also presented in Table 2

and in Figure 1. Measured values of d_{132} are listed in Table 1 for comparison. From the estimated standard deviations and correlation coefficients of Table 2, it would appear that measurement of either d_{132}, b, or V are equally suitable for indirectly determining $SrCO_3$ content. However, measurement of d_{132} using an internal standard is most appealing for its simplicity.

The relationships between composition and the calculated densities for synthetic strontianites and the natural strontianites of this study are included in Table 2 and shown in Figure 2. Calculated densities were used because of the difficulties in measuring densities. For comparison, Table 1 contains the measured densities which compare favorably with the calculated densities.
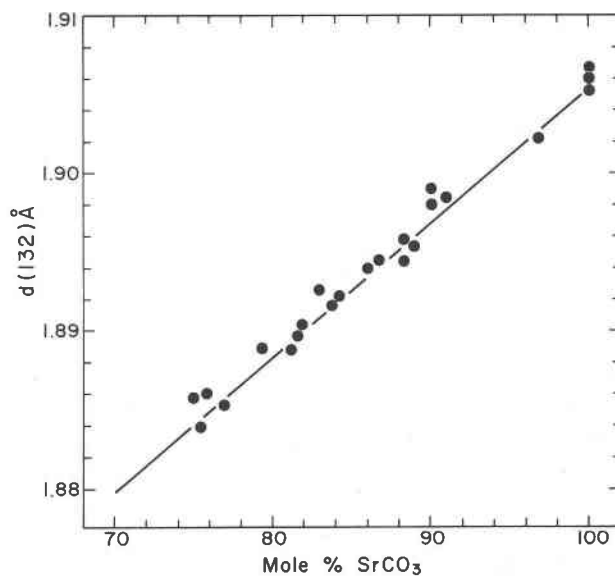

FIG. 1. Calculated values of d_{132} plotted against mole percent $SrCO_3$ content. The line is the regression line of Table 2 calculated for these spacings and compositions.
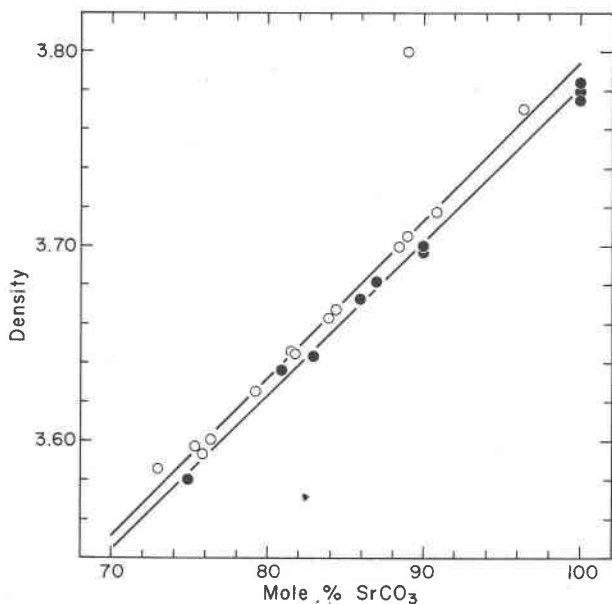
FIG. 2. Calculated values of density plotted against mole percent SrCO₃ content. Solid circles are synthetic strontianites and open circles natural strontianites. Regression lines are given by the equations in Table 2, the lower for synthetic strontianites, the upper for natural strontianites.

The natural strontianites yield somewhat higher densities than the synthetic strontianites as a result of their Ba and Pb contents. The Ba- and Pb-rich Suiza mine strontianite plots well above both curves in Figure 2. In contrast to the cell dimensions, density is very sensitive to the presence of these elements. If strontianite composition is determined using one of the cell parameter spacings, a check on density will give an indication whether Ba and Pb are present in significant amounts or not.

Acknowledgments

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