

Witherite composition, physical properties, and genesis

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Abstract

Microprobe analyses of 17 natural witherite specimens from various localities show substitution of strontium (up to 11 mole percent), lesser amounts of calcium (< 1 mole percent) and no detectible lead. Most witherites contain less than 4 mole percent Sr and 0.5 mole percent Ca. Lattice parameters and density vary regularly with composition in the entire range. The equation, equivalent mole percent $\text{SrCO}_3 (\pm 1.1) = -1102.58 (d_{220}, \text{A}) + 2515.74$, can be used to determine the approximate composition of witherite-strontianite solid solutions for $X(\text{SrCO}_3) \leq 11$. A plot of mean ionic radius vs. cell volume for natural witherites lies above the plane connecting the pure end-members BaCO_3 - SrCO_3 - CaCO_3 , suggesting a small positive excess volume of mixing.

Calcium substitution is limited to minor amounts because of the miscibility gap between witherite and orthorhombic $\text{CaBa}(\text{CO}_3)_2$, alstonite. The limited Sr substitution and negligible Pb substitution, however, are believed to depend upon the composition of the pre-existing sulfate (barite) from which witherite forms and the disequilibrium behavior of low-temperature solutions (<200°C) that crystallize orthorhombic carbonates.

Introduction

This work is part of a systematic study of the chemistry and physical properties of the orthorhombic carbonates. The probable conditions and mechanisms of witherite genesis are examined in order to explain the limited chemical composition of natural witherites.

Experimental procedures

The 17 witherite samples examined in this study are listed in Table 1.² In addition to the literature summarized by Palache *et al.* (1951) and Deer *et al.* (1962), other data used in the following discussions of witherite compositions are from Frank-Kamenetskii (1948), Gvakhariya (1953), De Villiers (1971), and Sidorenko (1947).

The witherite samples were analyzed on an auto-

mated ARL SEMQ microprobe at 15 kV and 10 nanoamps, employing Bence-Albee methods of data reduction. Standards included synthetic BaCO_3 (Ba) and SrCO_3 (Sr) and natural calcite (Ca) and cerussite (Pb). The carbon content was obtained by calculating the number of carbon atoms according to the relation $C = \text{Sr} + \text{Ca} + \text{Ba} + \text{Pb}$. No elements other than Ba, Sr, and Ca could be detected with a Kevex X-ray energy-dispersive unit. With standards and unknowns of similar compositions, Ba analyses should be accurate to about 2 percent of the amount present. The relative errors for Sr and Ca are higher because of counting statistics and the problem of estimating background counts for minor elements.

Unit-cell parameters were determined from smear mounts of powdered witherite using a Picker powder diffractometer. Scans at the rate of 0.5°/min were made with monochromatized $\text{CuK}\alpha$ radiation using BaF_2 ($a = 6.1978\text{A}$) as an internal standard. All peaks were measured at one-half peak height and indexed according to the data of Swanson *et al.* (1954). The least-squares program of Appleman and Evans (1973) was used to refine the cell parameters.

Densities of several samples were determined with

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²To obtain a copy of Table 1, order Document AM-79-100 from the Business Office, Mineralogical Society of America, 2000 Florida Ave., NW, Washington, DC 20009. Please remit \$1.00 in advance for the microfiche.

a 2 ml pycnometer, using toluene (corrected for temperature) as the displacement medium. Several measurements were made for each sample and were averaged.

Sample (2), Table 1, was synthesized from J. T. Baker reagent grade BaCO₃ Lot 418067 at 550°C and 1 kbar. This sample served as a standard for microprobe analysis.

Results

Results of the study are given in Table 1. Because of the compositional similarity of the majority of samples, Table 1 has been abridged in Table 2 to include representative compositions. The microprobe analyses show substitutions of up to 11 mole percent SrCO₃, less than 1 mole percent CaCO₃, and no measurable substitution of lead. Sample 19 is the most strontium-rich of the witherites studied or reported in the literature. Higher calcium contents have been reported (Sidorenko, 1947) but were attributed to the presence of calcite inclusions. The analyses of with-

Table 2. Crystal and chemical data for witherites

	4	13	18	19
PbO	0.00	0.00	0.00	0.00
CaO	0.08	0.11	0.24	0.02
SrO	0.68	1.72	3.26	6.06
BaO	77.15	76.58	75.00	72.10
CO ₂ *	22.50	22.78	23.10	23.28
Total	100.41	101.19	101.60	101.46
Number of ions on the basis of 1 CO ₃				
Pb	0.0000	0.0000	0.0000	0.0000
Ca	0.0028	0.0037	0.0081	0.0008
Sr	0.0129	0.0320	0.0599	0.1104
Ba	0.9844	0.9644	0.9320	0.8888
M.I.R.***	1.4672	1.4639	1.4580	1.4521
V _c , Å ³	303.93(6)	302.87(9)	301.32(10)	300.38(6)
a _c , Å	5.312(.7)	5.305(1)	5.297(2)	5.293(1)
b _c , Å	8.999(1)	8.890(2)	8.877(3)	8.861(2)
c _c , Å	6.428(1)	6.421(2)	6.408(2)	6404(1)
d ₂₂₀ calc.	2.2807	2.2779	2.2745	2.2722
d ₂₂₀ meas.	2.2807	2.2777	2.2750	2.2721
ρ _{calc.}	4.29	4.28	4.27	4.24
ρ _{meas.}	4.31	4.28	4.26	4.22

*Calculated to give C = Ba + Sr + Ca + Pb

**The estimated standard errors are given in parentheses and refer to the last decimal place(s).

***Mean ionic radius

4 Anglesarke, Lancashire, England NMNH #103262

13 Settingstone Mine, Northumberland, England

18 Arkhyz, Caucasus, USSR

19 Cassiar District, British Columbia NMC#34999

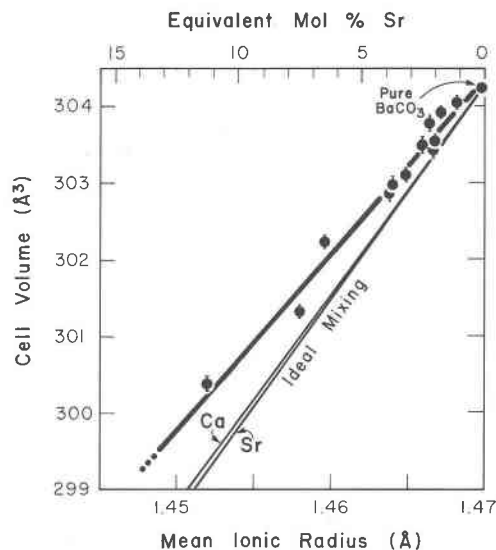


Fig. 1. Plot of cell volume and mean ionic radius for witherite samples in Table 1. Because the calcium contents of the witherites are small, the mean ionic radius is also given in terms of the equivalent mole percent SrCO₃ substitution in witherite. The ionic radii for nine-coordinated Ba²⁺ (1.47Å), Sr²⁺ (1.31Å), and Ca²⁺ (1.18Å) are from Shannon (1976). The unit-cell volumes used to draw the ideal mixing lines are BaCO₃, 304.24Å³ (Swanson and Fuyat, 1953), CaCO₃, 226.85Å³ (Swanson *et al.*, 1954), and SrCO₃, 259.35Å³ (Speer and Hensley-Dunn, 1976).

erites in this study show a mean of 3.3 mole percent Sr and 0.3 mole percent Ca, comparable to the natural witherite compositions in the literature.

The unit-cell parameters exhibit a small, systematic variation between the extreme witherite compositions (Table 2). Unit-cell volume varies nearly linearly with mean ionic radius over the compositional range (Fig. 1). If there were ideal mixing in the Ba-Sr and Ba-Ca solid solutions, the samples should lie on the lines joining end-member orthorhombic carbonates in plots of cell volume vs. ionic radius. However, the witherite samples lie above the ideal mixing lines (Fig. 1), suggesting a positive excess volume of mixing in this compositional range. The excess volume may result from the large barium atoms preventing the structure from contracting around the smaller Sr and Ca ions when they are present in small amounts.

The approximate Sr content of witherite can be determined indirectly, using Figure 1, because Ca is a minor constituent. A simpler method is to use the single *d*₂₂₀ spacing of witherite. The equation derived by linear regression is

$$\text{equiv. mole percent Sr CO}_3(\pm 1.1) = -1102.58 (d_{220}, \text{Å}) + 2515.74$$

The 220 reflection, rather than the 132 peak used for other orthorhombic carbonates, was chosen because of its intensity, sharpness and the lack of interfering peaks.

Table 2 contains measured and calculated densities, which compare favorably. Density was found to vary linearly with the mean atomic mass of the cations in the sample (Fig. 2a), fitting a linear regression equation

$$\text{mean cation atomic mass} = 86.48 (\rho) - 235.01$$

which can be recast as

$$\text{equiv. mole percent SrCO}_3(\pm 1) = -173.9 (\rho) + 748.9$$

This equation differs from the regression line for the calculated density of synthetic orthorhombic carbonates of the group IIa cations: Ca, Sr, Ba, and Ra (Fig. 2b). Although over the range of the end-member group IIa carbonates these cations show a linear relationship, in detail they exhibit a larger deviation than expected for the errors in cell volume and atomic mass determination. Other metal cations that form orthorhombic carbonates, Sm, Eu, and Pb, lie well above both lines. These possess suitable sizes and valences to form orthorhombic carbonates, but they are heavier atoms than the group IIa cations.

Discussion

Natural witherite examined in this study and reported in the literature shows only a limited compositional range; only Sr substitutes for Ba in significant amounts.

Barium has been rarely reported in analyses of cerussite and aragonite above trace amounts (Palache *et al.*, 1951, p. 194–196; Deer *et al.*, 1962, p. 319–322). Speer and Hensley-Dunn (1976) and Speer (1976) found that Ba is present in only minor amounts (<3600 ppm) in strontianite. These results combined with the witherite analyses from Table 1 and from the literature show that the orthorhombic carbonates exhibit strong bimodal distributions on the CaCO_3 – BaCO_3 , SrCO_3 – BaCO_3 , and PbCO_3 – BaCO_3 joins. The rarity of intermediate compositions in the orthorhombic carbonates must be either a result of a crystal-chemical factor, such as a miscibility gap, or a reflection of the fluid composition, or the mechanisms by which witherite crystallizes.

Experimental work on the CaCO_3 – BaCO_3 join by Terada (1953), Chang (1965, 1971), Boström *et al.* (1969), and Chang and Brice (1972) has demonstrated the presence of a miscibility gap between

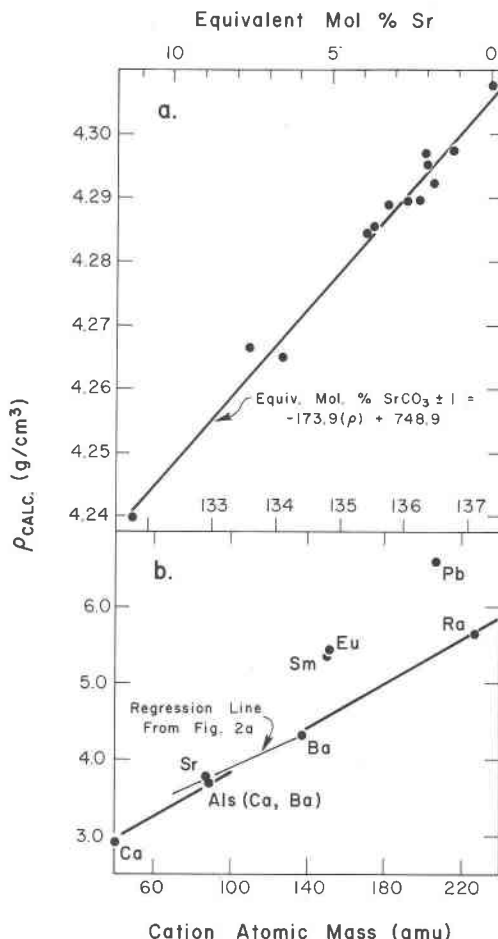


Fig. 2. (a) Plot of calculated densities vs. mean atomic mass for cations of witherite samples in Table 1. Because the calcium contents of the witherites are small, the mean atomic mass is also given as equivalent mole percent SrCO_3 substitution in witherite. (b) Plot of the calculated densities and atomic mass for cations of the orthorhombic carbonates. Unit-cell volumes used to calculate the densities in addition to those used in Figure 1 are alstonite (als), 267.3Å^3 (Sartori, 1975); EuCO_3 , 259.10Å^3 (Mayer *et al.*, 1964); SmCO_3 , 260.72Å^3 (Asprey *et al.*, 1964); RaCO_3 , 335.3Å^3 (Wiegel, 1977, p. 370–371), and PbCO_3 , 269.61Å^3 (Swanson and Fuyat, 1953). The calculated densities of witherite samples in Table 1 fall along the line from Fig. 2a.

witherite and alstonite, $\text{CaBa}(\text{CO}_3)_2$, for a wide range of temperatures, pressures, and fluid compositions. This miscibility gap accounts for the limited substitution of Ca for Ba in witherite. Complete or nearly complete solid solutions have been found in the SrCO_3 – BaCO_3 system by Cork and Gerhard (1931), Terada (1953), Chang (1965, 1971) and Chang and Brice (1972) and in the system PbCO_3 – BaCO_3 by Boström *et al.* (1969) and Chang and Brice (1972) over a similar range of conditions. The ionic

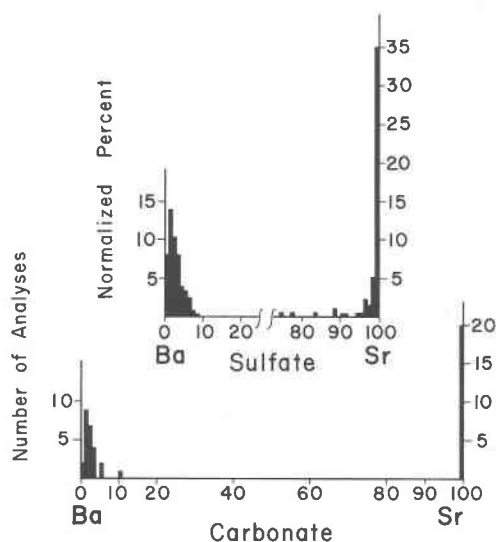


Fig. 3. Frequency distribution of observed barite-celestine compositions and witherite-strontianite compositions. The sulfate data are from Hanor (1968) who normalized the 2293 barite and 77 celestine analyses so that each set of data represents 50 percent of the total. The 20 strontianite analyses are from Speer and Hensley-Dunn (1976) and Speer (1976). The 24 witherite analyses are from this study, as well as Frank-Kamenetskii (1948), Gvakhariya (1953), Deer *et al.* (1962), De Villiers (1971), and Sidorenko (1947).

radii of Pb^{2+} (1.35Å) and Sr^{2+} (1.31Å) for nine-coordinated ions (Shannon, 1976) are nearly the same, and these ions could be expected to behave similarly with regard to solid solutions with Ba^{2+} (1.47Å). In contrast, Ca^{2+} (1.18Å) is much smaller than Pb^{2+} or Sr^{2+} , which may account for the miscibility gap along the Ba-Ca join. The difference in ionic radii between Ba and Pb or Sr is nearly the same as between Ca and Sr as well as between Ca and Pb, where miscibility gaps have been found (Holland *et al.*, 1963; Chang, 1965, 1971; Boström *et al.*, 1969; Chang and Brice, 1972). Nevertheless, the experimental work indicates the possibility of complete solid solutions on the BaCO_3 - SrCO_3 and BaCO_3 - PbCO_3 joins and suggests that the causes of the limited witherite compositions lie in its genesis.

The bimodal composition of the orthorhombic carbonates has its analogue in the orthorhombic sulfate minerals, especially the (Ba,Sr) SO_4 system, which has received the most attention and is reviewed by Hanor (1968). Disequilibrium between the aqueous solution and the (Ba,Sr) SO_4 crystals, which behave as an unreactive precipitate, permits fractional precipitation between the less soluble BaSO_4 and the more soluble SrSO_4 . This results in a geochemical separation of the two elements and a paucity of intermediate sul-

fate compositions. Hanor (1968) termed this "inert behavior." More recently Thorstenson and Plummer (1977) have explained this behavior of two-component solid phases as "stoichiometric saturation" and have interpreted the cause as "low-temperature kinetic problems."

Orthorhombic carbonates are known to form at low temperatures where these kinetic problems may occur. In lead-zinc-barite-fluorite deposits where witherite has formed from barite, the filling temperatures of fluid inclusions in barite have been reported as 150°-70°C (Brown, 1967), 130°-50°C (Sawkins, 1966), and 150°-115°C (Hayase *et al.*, 1977). Presumably the witherite formed at temperatures at the low end of the range, after formation of barite.

The mechanism of witherite formation may also be an important control of its chemistry. Witherite is commonly thought to occur when barite is altered by the action of carbonated waters (Weller *et al.*, 1952; Holland, 1967; Helz and Holland, 1965). Based on the association and texture of the many witherite occurrences in Great Britain, Hancox (1934) postulated that in all instances the witherite was produced in this way. Strontianite is similarly believed to form from a pre-existing sulfate, celestine, while cerussite has been noted to form from anglesite. Figure 3 is a frequency distribution of naturally-occurring Ba-Sr sulfates and carbonates. The carbonate and sulfate compositions have a similar distribution, suggesting that the geochemical separation of Ba and Sr that occurred in the sulfate system at low temperatures was preserved when the carbonates formed from the sulfates. This is possible since the sulfate-to-carbonate reaction for each cation takes place under different conditions of $a(\text{CO}_3)/a(\text{SO}_4)$ in the mineralizing fluid (Barton, 1957; Gundlach, 1959). The low reaction temperatures of carbonate formation would probably prevent any carbonate-sulfate or carbonate-carbonate solid equilibration. So the composition of witherite may primarily reflect the geochemical separation of cations in the sulfate system preserved by lack of reequilibration in the carbonates as a result of "inert behavior." It could be concluded that witherite formed from pre-existing barite should have a Sr content similar to the barite. The histogram in Figure 3 suggests that this is generally true. In two specific instances, Frank-Kamenetskii (1948) and Sidorenko (1947) found this to hold for deposits which they studied.

Thermodynamic calculations for equilibrium conditions would predict that during the alteration of

barite to witherite, these two coexisting phases should have differing Sr contents. The equilibrium constant for the exchange reaction



indicates a strong partitioning of Sr into the carbonate phase during alteration. Figure 4 summarizes the calculations showing the compositions of coexisting sulfates and carbonates for three temperatures. These calculations were made for $P = 1$ atm, assuming ideal solid solution in the carbonate and sulfate phases and using the free energies of formation from Robie and Waldbaum (1968). The results suggest that as witherite forms from barite, witherite preferentially takes up Sr, and the two minerals become increasingly Ba-rich until the barite is consumed and the carbonate phase reaches the initial bulk composition of the sulfate. Under disequilibrium conditions, the distribution of Ba and Sr between the coexisting mineral pairs during alteration of barite to witherite could have several possibilities. In order to predict the compositions of the coexisting mineral phases, disequilibrium would necessitate considering separately the controls and deviation from equilibrium of the dissolution mechanism of the sulfate and precipitation mechanism of the carbonate. This would be instead of combining them as in the equilibrium case by exchange reaction 1.

Figure 4 shows that the equilibrium partitioning of Ba and Sr between carbonate and sulfate phases makes coexisting barite-witherite pairs potential geothermometers. But since natural witherite forms at low temperatures where disequilibrium is a good possibility, equilibrium between the two solids would need to be demonstrated. In addition, since natural witherite and barite have nearly end-member compositions, the pairs will plot on the narrow limb of a diagram such as Figure 4. Compositional determinations and calibration of the geothermometer would have to be exceptionally accurate in order to reduce the error in temperature estimates to acceptable levels.

A barite-witherite pair from the Cassiar District, B.C., from which sample (19) was taken, was examined in this study. The locality and geology of the occurrence is given by Woodcock and Smitheringale (1957). The barite is almost entirely replaced by witherite and contains less than 0.02 mole percent Sr, whereas the coexisting witherite contains 11 mole percent Sr. If this represents a system closed with respect to Ba and Sr, the barite cannot be at its original

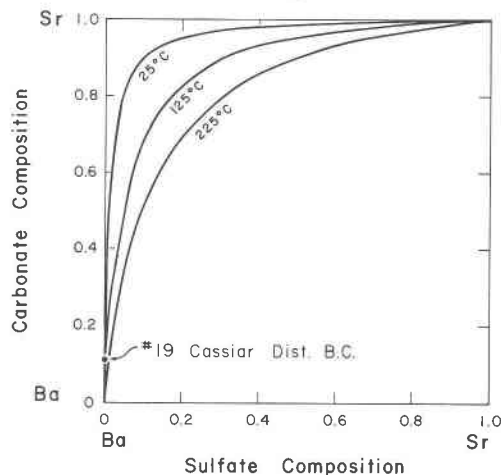


Fig. 4. Calculated distributions of Sr and Ba between witherite-strontianite and barite-celestine solid solutions at different temperatures. The plotted point represents the compositions of coexisting witherite and barite from the Cassiar District, British Columbia (sample 19).

composition. Rather the barite must have been selectively depleted in Sr. This barite-to-witherite alteration pair would then follow the expected equilibrium behavior. This barite-witherite pair is plotted in Figure 4.

Summary

The limited composition of witherite results from a miscibility gap along the Ca join with alstonite and low-temperature kinetic problems preventing the reequilibration of witherite, aqueous fluid and earlier-precipitated Pb and Sr carbonates, cerussite, and strontianite. The orthorhombic carbonate compositions may be largely inherited from precursor sulfate minerals and reflect similar disequilibrium processes in the sulfate system. These disequilibrium geochemical separations are governed by the differing solubilities of Ba, Sr, Ca, and Pb carbonates and sulfates from which the carbonates form. As sulfates react with carbonated waters, each nearly end-member sulfate is converted to a carbonate under different conditions. The equilibrium constant of the barite-witherite exchange reaction predicts that under equilibrium conditions the Sr preferentially partitions into the carbonate phase during the conversion of sulfate to carbonate. This is confirmed in one instance and suggests that the most Sr-rich witherite should be found as the early alteration products of Sr-bearing barites. However, because witherite forms at such low temperatures, disequilibrium is likely,

and other barite-to-witherite alteration pairs may exhibit different compositional behavior.

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References

- Appleman, D. E. and H. T. Evans, Jr. (1973) Job 9214: Indexing and least-squares refinement of powder diffraction data. *Natl. Tech. Inf. Serv., U. S. Dept. Commerce, Springfield, Virginia, Document PB-216 188*.
- Asprey, L. B., F. H. Ellinger and E. Staritzky (1964) Compounds of divalent lanthanides—preparation, optical properties, and crystal structure. In K. S. Vorres, Ed., *Rare Earth Research II*, p. 10–20. Macmillan, New York.
- Barton, P. B. (1957) Some limitations on the possible composition of the ore-forming fluid. *Econ. Geol.*, 52, 333–353.
- Boström, K., J. Hanor, J. Blankenburg and R. Glaccum (1969) Some subsolidus phase relations in the system $\text{BaCO}_3\text{--CaCO}_3\text{--PbCO}_3$ at 500°C. *Ark. Mineral. Geol.*, 5, 47–53.
- Brown, J. S. (Ed.) (1967) Genesis of stratiform lead–zinc–barite–fluorite deposits. *Econ. Geol. Monogr.* 3.
- Chang, L. L. Y. (1965) Subsidiary phase relations in the systems $\text{BaCO}_3\text{--SrCO}_3$, $\text{SrCO}_3\text{--CaCO}_3$, and $\text{BaCO}_3\text{--CaCO}_3$. *J. Geol.*, 73, 348–368.
- (1971) Subsidiary phase relations in the aragonite-type carbonates: I. The system $\text{CaCO}_3\text{--SrCO}_3\text{--BaCO}_3$. *Am. Mineral.*, 56, 1660–1673.
- and W. R. Brice (1972) Subsidiary phase relations in aragonite-type carbonates: II. The systems $\text{CaCO}_3\text{--SrCO}_3\text{--PbCO}_3$ and $\text{CaCO}_3\text{--BaCO}_3\text{--PbCO}_3$. *Am. Mineral.*, 57, 155–168.
- Cork, J. M. and S. L. Gerhard (1931) Crystal structure of the series of barium and strontium carbonates. *Am. Mineral.*, 16, 71–77.
- Deer, W. A., R. A. Howie and J. Zussman (1962) *Rock-Forming Minerals, Vol. 5, Non-silicates*. Wiley, New York.
- De Villiers, J. P. R. (1971) Crystal structure of aragonite, strontianite, and witherite. *Am. Mineral.*, 56, 758–767.
- Frank-Kamenetskii, V. A. (1948) Witherite from barite veins in the northern Caucasus (Arkhyz and Dzhalankol). *Chem. Zentr.*, I, 144. (extracted from *Chem. Abstracts*, 44, 7191, 1950).
- Gundlach, H. (1959) Untersuchungen zur Geochemie des Strontians auf hydrothermalen Lagerstätten. *Geol. Jahrb.*, 76, 637–712.
- Gvakhariya, G. V. (1953) A barite–witherite association. *Sobshcheniya Akad. Nauk Gruzinskoi, SSSR*, 14, no. 5, 267–272. (extracted from *Chem. Abstracts*, 49, 2956, 1955).
- Hancox, E. G. (1934) Witherite and barytes. *Mining Mag.*, 51, 76–79.
- Hanor, J. S. (1968) Frequency distribution of compositions in the barite–celestite series. *Am. J. Sci.*, 53, 1215–1222.
- Hayase, K., G. R. Mas and A. L. Bengochea (1977) Synthesis of barium–strontium sulfate solid solution and some considerations on the genesis of barite–celestite deposits in Neuquen Province, Argentina. *J. Japan. Assoc. Min. Pet. Econ. Geol.*, 72, 93–102.
- Helz, G. R. and H. D. Holland (1965) The solubility and geologic occurrence of strontianite. *Geochim. Cosmochim. Acta*, 29, 1303–1315.
- Holland, H. D. (1967) Gangue minerals in hydrothermal deposits. In H. L. Barnes, Ed., *Geochemistry of Hydrothermal Ore Deposits*, p. 382–432. Holt, Rinehart, and Winston, New York.
- , M. Brocsik, J. Munoz and U. M. Oxburgh (1963) The coprecipitation of Sr^{2+} with aragonite and Ca^{2+} with strontianite between 90° and 100°C. *Geochim. Cosmochim. Acta*, 27, 957–977.
- Mayer, I., E. Levy and A. Glasner (1964) The crystal structure of EuSO_4 and EuCO_3 . *Acta Crystallogr.*, 17, 1071–1072.
- Palache, C., H. Berman and C. Frondel (1951) *Dana's System of Mineralogy*, Vol. 2, 7th edition. Wiley, New York.
- Robie, R. A. and D. R. Waldbaum (1968) Thermodynamic properties of minerals and related substances at 298.15°K (25°C) and one atmosphere (1.013 bars) pressure and high temperatures. *U. S. Geol. Surv. Bull.* 1259.
- Sartori, F. (1975) New data on alstonite. *Lithos*, 8, 199–207.
- Sawkins, F. J. (1966) Ore genesis in the North Pennine orefield, in the light of fluid inclusion studies. *Econ. Geol.*, 61, 385–401.
- Shannon, R. D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.*, A32, 751–767.
- Sidorenko, A. V. (1947) The genesis of witherites of the western Kopet-Dag. *C. R. (Dokl.) Acad. Sci. URSS*, 55, 149–151.
- Speer, J. A. (1976) Pennsylvania minerals: II. Strontianite. *Mineral. Record*, 7, 69–71.
- and M. L. Hensley-Dunn (1976) Strontianite composition and physical properties. *Am. Mineral.*, 61, 1001–1004.
- Swanson, H. E. and R. K. Fuyat (1953) Standard X-ray diffraction powder patterns. *Natl. Bur. Stand. Circ.* 539, Vol. II.
- , ——— and G. M. Ugrinic (1954) Standard X-ray diffraction powder patterns. *Natl. Bur. Stand. Circ.* 539, Vol. III.
- Terada, J. (1953) Crystal structure of the Ba, Sr and Ca triple carbonate. *J. Phys. Soc. Japan*, 8, 158–164.
- Thorstenson, D. C. and L. N. Plummer (1977) Equilibrium criteria for two-component solids reacting with fixed composition in an aqueous phase—example: the magnesium calcites. *Am. J. Sci.*, 277, 1203–1223.
- Weller, J. M., R. M. Grogan and F. R. Tippie (1952) Geology of the fluorite deposits of Illinois. *Illinois State Geol. Surv. Bull.* 76.
- Wiegel, F. (1977) Radium. In K. Swars, Ed., *Gmelins Handbuch der Anorganischen Chemie, Ergänzungsband 2*. Springer-Verlag, New York.
- Woodcock, J. R. and W. V. Smitheringale (1957) Fluorite–witherite deposit at Lower Liard Crossing, British Columbia, The Geology of Canadian Industrial Mineral Deposits. *Commonwealth Mining and Metallurgical Congress*, 6th, Vancouver, 244–247.

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