

RIGID-BODY CHARACTER OF THE SO₄ GROUPS IN CELESTINE, ANGLÉSITE AND BARITE

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ABSTRACT

The crystal structures of natural celestine (Sr_{1.00})SO₄, anglesite (Pb_{0.99}Sr_{0.01})SO₄, and barite (Ba_{0.99}Sr_{0.01})SO₄ have been refined in space group *Pbnm* utilizing rotating anode, Mo X-ray diffraction data from single crystals. Unit-cell parameters for celestine are *a* 6.8671(7), *b* 8.3545(8), and *c* 5.3458(6) Å, for anglesite, *a* 6.9549(9), *b* 8.472(1), and *c* 5.3973(8) Å, and for barite, *a* 7.154(1), *b* 8.879(2), and *c* 5.454(1) Å. Structural data are presented for these sulfates with greatly improved precision over previous studies owing to high peak-to-background intensity ratios and precise analytical absorption corrections. The final model *R*(*F*) values are 0.025, 0.041, and 0.019, for celestine, anglesite, and barite, respectively. The average bond-distance from divalent cation to the nearest twelve oxygen atoms is 2.827(1) Å in celestine, 2.864(5) Å in anglesite, and 2.951(2) Å in barite. The average sulfur-to-oxygen bond distance is 1.475(2) Å in celestine, 1.476(6) Å in anglesite, and 1.476(2) Å in barite. The sulfate tetrahedra in each structure show very similar distortions that are attributed to the bonding of the various oxygen atoms to the divalent cations, which is similar in each structure. Thus, the different metal cations do not seem to affect the size or shape of the sulfate tetrahedra. An analysis of the displacement parameters suggests that the SO₄ groups behave as rigid molecular units, with an apparent shortening of the S–O bonds of 0.008–0.010 Å.

Keywords: sulfates, celestine, anglesite, barite, X-ray-diffraction data, rigid-body motion.

SOMMAIRE

Nous avons affiné la structure cristalline d'échantillons naturels de célestine (Sr_{1.00})SO₄, anglésite (Pb_{0.99}Sr_{0.01})SO₄, et barite (Ba_{0.99}Sr_{0.01})SO₄ dans le group spatial *Pbnm* par diffractométrie avec anode rotative, rayonnement MoK α , sur cristaux uniques. Les paramètres réticulaires des trois minéraux sont: *a* 6.8671(7), *b* 8.3545(8), et *c* 5.3458(6) Å (célestine), *a* 6.9549(9), *b* 8.472(1), et *c* 5.3973(8) Å (anglésite), et *a* 7.154(1), *b* 8.879(2), et *c* 5.454(1) Å (barite). Les données structurales pour ces trois sulfates sont établies avec une précision nettement améliorée par rapport aux données antérieures à cause d'un rapport d'intensité de pic à bruit de fond plus grand et des corrections pour l'absorption analytique plus précises. Les affinements ont convergé à un résidu *R*(*F*) de 0.025, 0.041, et 0.019, pour la célestine, l'anglésite, et la barite, respectivement. Dans la même séquence, la distance moyenne entre le cation bivalent et les douze atomes d'oxygène les plus proches est 2.827(1), 2.864(5), et 2.951(2) Å, respectivement, tandis que la distance moyenne entre soufre et oxygène est 1.475(2), 1.476(6), et 1.476(2) Å, respectivement. Les tétraèdres SO₄ dans chaque structure font preuve de distorsions très semblables; elles seraient dues aux liaisons entre cations bivalents et atomes d'oxygène, qui sont semblables dans les trois minéraux. Les différents cations ne semblent donc pas influencer la dimension des tétraèdres de sulfate. Une analyse des paramètres de déplacement fait penser que les groupes SO₄ se comportent comme agencements moléculaires rigides, avec un raccourcissement apparent de la longueur des liaisons S–O de 0.008 – 0.010 Å.

(Traduit par la Rédaction)

Mots-clés: sulfates, célestine, anglésite, barite, diffraction X, mouvement d'un agencement rigide.

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INTRODUCTION

The isostructural divalent metal sulfide minerals *celestine* (SrSO_4), *anglesite* (PbSO_4), and *barite* (BaSO_4) are simple structures of moderately high symmetry that present an opportunity to study the detailed geometry of the sulfate tetrahedron in a group of geologically significant minerals. Miyake *et al.* (1978) concluded that there is a possible systematic variation in the geometry of the sulfate tetrahedron with field strength of the divalent metal cation in these structures, although the sulfate tetrahedra in their refinements were statistically identical. The presence of the heavy divalent metal in these structures makes it difficult to determine the positions of the light elements with high precision by X-ray diffraction, because of strong absorption effects and the small relative contribution of the oxygen atoms to total scattering. However, instrumentation and methodologies for X-ray diffraction have improved over the past 20 years. Consequently, we have undertaken new refinements of celestine, anglesite, and barite using a high-intensity Mo

X-ray source and analytical absorption corrections, with the intention of determining the positional and thermal parameters of the atoms with increased precision. Of particular interest is the possibility of systematic variation in geometry of the sulfate group among these structures.

BACKGROUND INFORMATION

Celestine and barite are the most abundant strontium and barium minerals, respectively, in the Earth's crust, and are the principal commercial sources of strontium and barium. It has been proposed that 13% of the strontium and 37% of the barium in the planet have fractionated into the crust (Anderson 1989). Both minerals have similar parageneses; they occur in hydrothermal veins and as secondary minerals in sedimentary environments. Anglesite, a minor ore of lead, typically occurs in the oxidized portion of hydrothermal lead deposits as an alteration product of galena and also as a primary mineral in some low-temperature oxidized hydrothermal deposits.

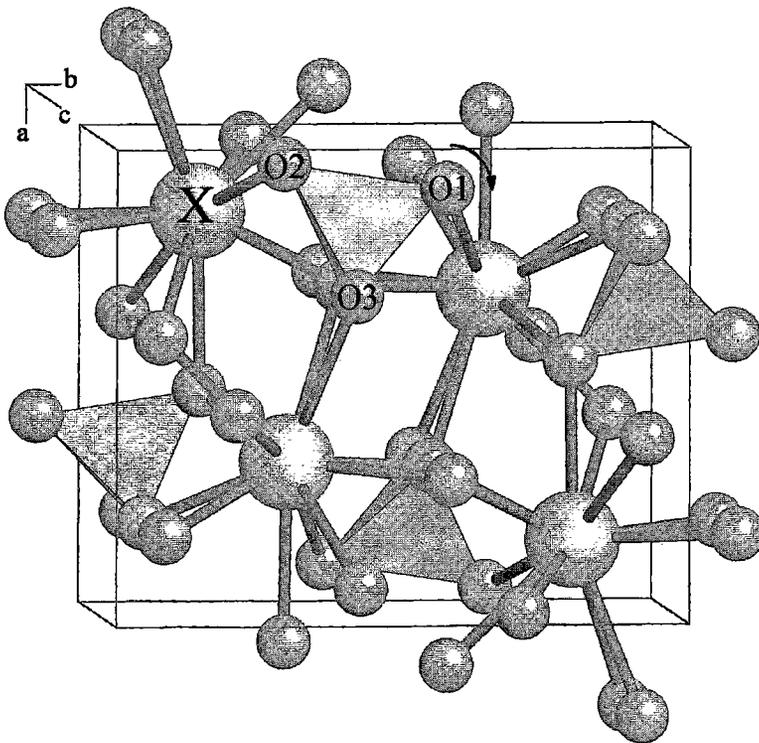


FIG. 1. An illustration of the structure of barite. The SO_4 groups are indicated by tetrahedra, with large spheres representing the X cation, and smaller spheres representing the O atoms. The arrow near the O(1) atom demonstrates the rotational aspect of the SO_4 groups as the size of the X cation increases. The principal thermal motion of the sulfate group is a rotation (libration) about an axis normal to this illustration, consistent with rigid-body character of the group.

The structure of celestine, anglesite and barite, first determined by James & Wood (1925), is orthorhombic (*Pbnm*), with four formula units per cell (Fig. 1). The divalent cation, the sulfur, and two of the three oxygen atoms (O1 and O2) lie on the mirror plane, and the third oxygen (O3) is in a general position. The coordination number of the metal cation to oxygen has been demonstrated to be twelve (Hawthorne & Ferguson 1975) for Sr in celestine from a bond-strength *versus* bond-valence analysis (Brown 1981). The four-coordinated sulfur lies in a slightly distorted tetrahedron of O atoms.

Previous structural studies of these minerals (Sahl 1963, Garske & Peacor 1965, Colville & Staudhammer 1967) were motivated, in part, by a desire to determine if the geometries of the SO₄ groups were the same in all three structures. This is complicated by the technical difficulty of refining accurate positions of the oxygen atoms in the presence of heavy, strongly absorbing atoms such as Sr, Pb, and Ba. Hawthorne & Ferguson (1975) and Hill (1977) reported that the SO₄ groups in all three structures display identical geometries, and that Sr and Ba appear to be 12-coordinated, on the basis of bond-strength sums. Hill (1977) also noted that the O1 and O2 atoms show considerably larger thermal motion than the O3 atom. As O1 and O2 are constrained to lie on a mirror plane in space group *Pbnm*, he attempted to refine their positions as split atoms and in a lower symmetry space-group, but no improvement was observed. Hill (1977) concluded that the larger thermal motion of O1 and O2 over O3 occurs because only one atom of Ba is within 3.0 Å of either O1 or O2, whereas three atoms of Ba are within 2.91 Å of O3, thus effectively constraining its motion. Miyake *et al.* (1978) reported refinements of all three isostructural species in order to clarify their structural relations and to obtain S–O force constants for a comparison with observed vibrational frequencies. They concluded that the geometries of the SO₄ groups are consistent with a systematic variation with field strength of the divalent metal ion, although we note that their tetrahedron geometries are statistically identical. We have performed new refinements of celestine, anglesite, and barite using a high-intensity Mo X-ray source and analytical absorption corrections with the intention of determining the positional and thermal parameters of the atoms with increased precision.

EXPERIMENTAL

For these experiments, single crystals of celestine, anglesite, and barite were chosen from the University of Colorado mineral collection. For the purpose of obtaining high-quality data with a rotating anode X-ray source, crystal quality was checked using the X-ray precession method. It was observed during this procedure that many of the celestine samples from sedimentary environments show complex mosaic structures. A cleavage fragment of transparent, colorless celestine (locality unknown) of dimensions 200 × 230 × 250 μm

was found to be of excellent quality. Similarly, we chose a crystal of barite measuring 100 × 120 × 150 μm from Cortez, Colorado (No. 2485), and a sample of anglesite from Monteponi, Sardinia, Italy (No. 4696) measuring 150 × 150 × 230 μm. In each case, the crystal chosen for data collection was a nearly equant, rectangular cleavage fragment taken from colorless bulk sample. Electron-microprobe chemical analyses indicate near end-member compositions. For celestine, the analysis totaled 99.28 wt.% and yielded (Sr_{1.003}Pb_{0.001}Ca_{0.005})(SO₄)_{0.999}. For anglesite, the analysis totaled 99.58 wt.% and yielded (Pb_{0.987}Sr_{0.006}Cd_{0.003})(SO₄)_{1.001}. For barite, the analysis totaled 100.47 wt.% and yielded (Ba_{0.986}Sr_{0.007}Cd_{0.001})(SO₄)_{1.002}.

For the purpose of comparison, we collected each dataset identically. Each specimen was mounted on a Siemens P4 automated diffractometer equipped with an 18 kW, Mo rotating-anode generator operating at 50 kV and 250 mA. The crystals were optically centered in the goniometer, and their orientation determined from a rotation photograph. For each crystal, unit-cell parameters were determined from the positions of 25–35 low-angle reflections (9° ≤ 2θ ≤ 26°) that were automatically centered in both positive and negative 2θ space to eliminate zero-point errors. The incident-beam monochromator in this type of instrument always has a slight effect on the effective wavelength of the undifferentiated Kα₁ and Kα₂, so that the Kα_{mix} wavelength is determined by centering a standard spherical crystal of corundum before and after each cell refinement. This procedure consistently gives unit-cell parameters that are in agreement with those refined from differentiated Kα₁ high-angle reflections and generally reproducible to within 1σ. The structure parameters were refined using the SHELXTL refinement package (Sheldrick 1990), with starting positions from Miyake *et al.* (1978).

TABLE 1. UNIT-CELL CONSTANTS AND DATA-COLLECTION PARAMETERS FOR CELESTINE, ANGLSITE AND BARITE

Parameter	Celestine	Anglesite	Barite
<i>a</i> (Å)	6.8671(7)	6.9549(9)	7.1540(14)
<i>b</i> (Å)	8.3545(8)	8.4723(11)	8.8790(18)
<i>c</i> (Å)	5.3458(6)	5.3973(8)	5.4540(11)
cell volume (Å ³)	306.69(6)	318.03(8)	346.44(3)
Molar volume (Å ³ /Z)	76.67	79.51	86.61
Scan type	0–2θ	0–2θ	0–2θ
Scan range (°2θ)	2–80	2–80	2–80
Scan width (°2θ)	1.5	1.5	1.2
Mean (I/σ)	29.84	21.43	36.47
No. Reflections			
(+h, +k, ±l)			
Total	2,164	2,241	2,448
Unique	1,022	1,057	1,154
Unique and F _o > 2σ	921	870 (>3σ)	1,121
R _{int} (data merging)	0.010	0.044	0.008
wR(F)	0.023	0.038	0.020
R(F)	0.025	0.041	0.019
Goof	1.43	2.02	1.98

Unit-cell and data-collection parameters are summarized in Table 1.

Prior to absorption correction, the refinements resulted in $R(F)$ values of 0.047, 0.060, and 0.038 for celestine, anglesite, and barite, respectively. The calculated X-ray absorption coefficients for our samples of celestine, anglesite and barite are 173.0 cm^{-1} , 535.3 cm^{-1} and 119.1 cm^{-1} , respectively. This corresponds, for example in anglesite, to a maximum X-ray transmission factor of 7.3%. Analytical absorption corrections were performed on each crystal using the measured dimensions and indices of each cleavage face and the absorption algorithm of SHELXTL. After absorption correction, the models converged to $R(F)$ values of 0.025, 0.041, and 0.019 for celestine, anglesite, and barite, respectively. Additional model statistics are also given in Table 1. No reflections with $I/\sigma > 2$ were arbitrarily omitted from these structure refinements. Final position and displacement parameters are reported in Table 2. Nearest-neighbor distances, polyhedron volumes, and distortion parameters of the tetrahedra are given in Table 3. Electrostatic site-potentials were calculated according to the procedure outlined by Smyth (1989) and are also presented in Table 2. A table of structure-factors is available from the Depository of Unpublished

Data, CISTI, National Research Council, Ottawa, Ontario, Canada K1A 0S2.

RESULTS AND DISCUSSION

The calculated standard deviations in the positional and displacement parameters and interatomic distances are less than one-third of those previously reported; the current results thus represent a significant improvement in precision. The improved precision and the use of nearly identical experimental methods for the refinements facilitate comparison of structural details among the three structures.

In the structure of the barite-group sulfates, each large divalent cation ($X = \text{Sr}, \text{Pb}, \text{Ba}$) has traditionally been assigned coordination to the nearest 12 oxygen atoms, solely on the basis of bond distances. There is a natural gap in $X\text{-O}$ separation that occurs after the twelfth O atom, with the thirteenth closest O atom over 0.5 \AA further away. Furthermore, with a 12-coordinated X cation, we find that all O atoms are 4-coordinated and formally charge-balanced. However, because there is considerable distortion in the SO_4 groups and a large range of $X\text{-O}$ distances, such a charge balance should be interpreted cautiously. In their study of the structure

TABLE 2. FINAL POSITION AND ATOMIC DISPLACEMENT PARAMETERS FOR CELESTINE, ANGLESITE, AND BARITE

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	$B_{\text{eq}}(\text{\AA}^2)^*$	Elec.Pot. (V)
Celestine											
Sr	0.15818(3)	0.18395(2)	0.25	0.01005(9)	0.00757(9)	0.01681(11)	0.00026(6)	0.0	0.0	0.906(4)	-20.72
S	0.18505(7)	0.43797(6)	0.75	0.00797(20)	0.00762(19)	0.00896(20)	-0.00014(14)	0.0	0.0	0.647(9)	-69.76
O(1)	0.0923(3)	0.5952(2)	0.75	0.0195(9)	0.0119(7)	0.0299(11)	0.0084(6)	0.0	0.0	1.61(4)	32.84
O(2)	0.0418(3)	0.3071(2)	0.75	0.0126(7)	0.0161(7)	0.0210(9)	-0.0066(6)	0.0	0.0	1.31(3)	30.86
O(3)	0.3107(2)	0.4222(1)	0.9744(2)	0.0138(5)	0.0156(5)	0.0116(5)	-0.0011(4)	-0.0040(4)	0.0006(4)	1.080(2)	30.24
Anglesite											
Pb	0.16716(5)	0.18798(4)	0.25	0.02194(15)	0.01293(15)	0.02321(17)	0.00110(11)	0.0	0.0	1.530(7)	-20.33
S	0.1849(2)	0.4358(2)	0.75	0.0124(6)	0.0096(6)	0.0088(6)	-0.0003(5)	0.0	0.0	0.81(3)	-69.63
O(1)	0.0946(11)	0.5915(8)	0.75	0.025(3)	0.014(3)	0.035(4)	0.008(2)	0.0	0.0	1.9(2)	32.76
O(2)	0.0424(9)	0.3072(9)	0.75	0.015(2)	0.022(3)	0.025(3)	-0.008(2)	0.0	0.0	1.6(1)	30.93
O(3)	0.3090(6)	0.4189(5)	0.9726(10)	0.0195(17)	0.0192(20)	0.0129(15)	-0.0024(13)	-0.0057(12)	0.0016(18)	1.36(8)	30.21
Barite											
Ba	0.15842(2)	0.18453(2)	0.25	0.01025(8)	0.00843(8)	0.01298(8)	-0.00048(3)	0.0	0.0	0.835(4)	-19.35
S	0.19082(9)	0.43749(7)	0.75	0.0091(2)	0.0084(2)	0.0093(2)	0.00033(16)	0.0	0.0	0.705(9)	-69.66
O(1)	0.1072(4)	0.5870(3)	0.75	0.0266(12)	0.0131(8)	0.0280(12)	0.0105(8)	0.0	0.0	1.79(5)	32.57
O(2)	0.0498(3)	0.3176(2)	0.75	0.0117(9)	0.0209(10)	0.0202(10)	-0.0067(6)	0.0	0.0	1.39(4)	31.14
O(3)	0.3118(2)	0.4194(2)	0.9704(2)	0.0149(5)	0.0149(5)	0.0103(5)	-0.0020(4)	-0.0028(4)	0.0008(4)	1.05(2)	30.27

* Equivalent isotropic temperature factor, $B_{\text{eq}} = \frac{8\pi^2}{3} \sum_{i=1}^3 U_{ii}$.

TABLE 3. NEAREST-NEIGHBOR DISTANCES, BOND ANGLES, AND DISTORTION PARAMETERS IN COORDINATION POLYHEDRA FOR CELESTINE, ANGLESITE, AND BARITE

Parameter	mult.	celestine	anglesite	barite
X - O1	(1)	2.523(2)Å	2.609(7)Å	2.780(3)Å
X - O2	(1)	2.635(2)	2.610(6)	2.800(3)
X - O3	(2)	2.645(1)	2.654(5)	2.807(2)
X - O3	(2)	2.689(1)	2.733(5)	2.813(2)
X - O3	(2)	2.814(1)	2.910(4)	2.906(2)
X - O2	(2)	2.974(1)	3.009(3)	3.072(1)
X - O1	(2)	3.260(1)	3.271(4)	3.317(2)
<X - O>	(12)	2.827(1)	2.864(5)	2.951(2)
<i>the (SO₄)²⁻ tetrahedra</i>				
S - O1	(1)	1.459(2)	1.460(7)	1.456(3)
S - O2	(1)	1.471(2)	1.473(7)	1.467(2)
S - O3	(2)	1.484(1)	1.487(5)	1.490(2)
<S - O>	(4)	1.475(2)	1.476(6)	1.476(2)
O(1)-S-O(2)		112.2(1)°	112.3(2)°	112.3(4)°
O(1)-S-O(3)	(2)	109.5(1)	109.7(1)	109.7(2)
O(2)-S-O(3)	(2)	108.9(1)	108.7(1)	108.6(2)
O(3)-S-O(3)		107.9(1)	107.6(1)	107.8(4)
O(1) - O(2)		2.432(3)Å	2.435(10)Å	2.427(3)Å
O(1) - O(3)	(2)	2.403(2)	2.409(8)	2.409(3)
O(2) - O(3)	(2)	2.403(2)	2.403(7)	2.403(3)
O(3) - O(3)		2.400(2)	2.403(11)	2.404(3)
Poly. Vol. (Å ³)		1.643	1.650	1.648
*Ang. Var (°)		2.11	2.48	2.56
*TQE		1.0005	1.0005	1.0006

*Calculated tetrahedral angle variance and quadratic elongation after Robinson *et al.* (1971).

of celestine, Hawthorne & Ferguson (1975) computed bond-strength sums after the method of Brown (1981) and verified this assignment of coordination number for Sr in celestine. They found that the average deviation from the ideal bond-valences around the O atoms in celestine is 0.04 valence units (*vu*). Hill (1977) concluded that all 12 Ba-O bonds in barite were also significant.

Bond-strength sums were calculated using the method of Brown (1981) from the refined data. For celestine, these calculations yielded Sr = 2.03 *vu*, S = 5.90 *vu*, and 1.96, 1.93, and 2.02 *vu* for O1-O3, respectively. For anglesite, they gave Pb = 2.17 *vu*, S = 5.81 *vu*, and 1.96, 1.98, and 2.01 *vu* for O1-O3, respectively. And for barite, they gave Ba = 2.29 *vu*, S = 5.88 *vu*, and 1.97, 2.02, and 2.09 *vu* for O1-O3, respectively. These results are consistent with a coordination number of twelve.

The sulfate tetrahedra in these structures show similar and significant distortions (Table 3), with the S-O1 distance being the shortest, and S-O3, the longest. In all three structures, the O1-O3, O2-O3, and O3-O3 edges are short and very similar, whereas the O1-O2

edge, which lies in the mirror plane, is long. Miyake *et al.* (1978) calculated the polyhedron force constants in celestine, anglesite, and barite, and studied the relative effects of the metal cations on the sulfate tetrahedra. In barite, for example, they suggested that in order to reduce the barium - sulfur repulsive forces, the two equivalent O(3) atoms move closer to barium. Such a displacement acts to distort the sulfate tetrahedra, because each oxygen atom in the tetrahedron would not be bound to sulfur with equal strength. Indeed, Miyake *et al.* (1978) reported that the O(3)-S-O(3) bond angle for all three structures is less than 109°, with relatively long S-O bond distances, whereas the O(1)-S-O(2) is greater than 109°, with relatively short S-O bond lengths. They also reported that the average S-O bond distance is affected by the metal cation, and decreases in the order PbSO₄, BaSO₄, and SrSO₄. However, the shortening of the average S-O bond distances reported by Miyake *et al.* (1978) is well within their standard deviations and thus is not significant.

In the current study, we observe very similar distortions of the sulfate tetrahedra among these structures, with the average O(3)-S-O(3) bond angle being 107.8(1)°, whereas the average O(1)-S-O(2) bond angle in the three structures is 112.3(1)°. However, the average S-O bond distances, as well as the distortions, in the current refinements are statistically identical among the structures, with <S-O> = 1.475(2) Å, 1.476(6) Å, and 1.476(2) Å for celestine, anglesite, and barite, respectively. Thus, in contrast to previous studies and with greatly improved precision, we observe no significant variation in the sulfate tetrahedra in the presence of different metal cations with respect to distances and distortions (Table 3).

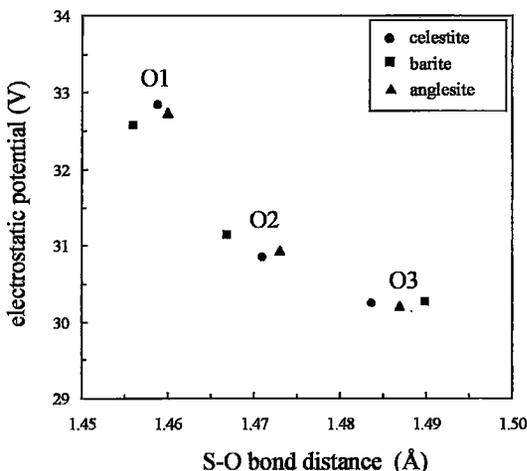


FIG. 2. Plot of the calculated electrostatic potential (V) versus S-O bond length (Å) in the sulfate tetrahedra of celestine, barite, and anglesite.

Electrostatic site potentials (Table 2) were calculated on the basis of a nominal valence point-charge model (Smyth 1989). Oxygen-site potentials are plotted *versus* S–O distance for the three oxygen sites in each structure in Figure 2. Because of the very high potential gradients around the hexavalent sulfur atom, oxygen potentials are very sensitive to the S–O distance, and therefore require high-precision refinements in order to obtain reliable values. Average oxygen-site potentials are useful predictors for oxygen isotope fractionation (Smyth & Clayton 1988). The average oxygen-site potentials for these structures are virtually identical at 31.05, 31.03, and 31.06 V for celestine, anglesite, and barite, respectively. This finding indicates that the oxygen isotope fractionation of the three phases relative to quartz should be nearly identical.

Miyake *et al.* (1978) used Urey–Bradley force field functions to calculate force constants of the SO_4 groups in these minerals. They obtained an average value of the S–O bond stretching force constant of 6.20 md/Å. This indicates that the strength of the S–O bond is of the same order as the Si–O bond, if we accept the value of 7.24 md/Å obtained by Lasaga & Gibbs (1987) for the SiO_4 group that was computed with quantum *ab initio* methods. In general, the values derived from quantum calculations are 15% too large, so an adjusted Si–O force constant of 6.15 md/Å is slightly smaller than for the S–O bond. In fact, Hill *et al.* (1994) demonstrated that force constants, f , vary monotonically with bond length, R , as $f = c/R^n$, where c and n are constants. This result implies that the S–O bonds in our study should be stronger than the Si–O bond, consistent with $\langle R(S-O) \rangle = 1.476 \text{ \AA}$ compared with $\langle R(Si-O) \rangle = 1.615 \text{ \AA}$. We therefore expect the SO_4 tetrahedra within the barite-group structures to behave as rigid units (see Fig. 1), since all SiO_4 groups behave as rigid molecular units (Downs *et al.* 1990, Bartelmehs *et al.* 1995). Further, if the displacement parameters of an SiO_4 group in a given structure do not indicate rigid-body motion, then either the structure has some intrinsic static or dynamic disorder, or the quality of the refinement data may be suspect (Downs *et al.* 1990, Bartelmehs *et al.* 1995).

Given that the SO_4 group should be at least as tightly bound as the SiO_4 group, then the same rigid-body criteria should hold for sulfates. Analysis of the SO_4 groups in our study indicates that they are quite rigid (Table 4). The values for Δz^2_{SO} are the differences in the mean-

square displacement amplitudes of S and O along the S–O bond. In a perfectly ideal rigid body, these values should be zero, since the displacement of each atom along the bond would be equal to each other, as if a rigid rod were separating the atoms. Downs *et al.* (1990) suggested that if $|\Delta z^2_{SiO}|$ is less than 0.00125, then the Si–O bond could be considered rigid. The values computed for the S–O bonds are all less than 0.00020, consistent with rigid-body behavior of the S–O bonds. It is also important for the O–O contact to be rigid in order for the entire tetrahedron to be considered rigid and for the O–S–O angles to not actively vibrate. The values for Δz^2_{OO} also indicate very rigid O–O contacts, though Δz^2_{OO} for anglesite is significantly larger than for the other structures. This is probably an artifact of the dominating scattering of the Pb atom in anglesite and not a consequence of increased bending activity of the O–S–O angle. Passing the criteria for rigid-body behavior is consistent with a lack of positional disorder and the high quality of the present datasets. None of the previous refinements of these mineral structures indicate rigid-body behavior.

The rigid-body motions of the SO_4 groups were then subjected to a TLS (translation, libration, and screw motions) analysis using the computer program TLS developed by Downs *et al.* (1992). The results of the analysis are presented in Table 4. This analysis demonstrates that the translational component of rigid-body motion is represented almost entirely by the displacement parameters of the S atom, and that the 2:1 difference in sizes of the isotropic displacement factors between O and S arises because the O atoms are undergoing additional motion due to libration. The libration angle of the SO_4 group is rather large for a crystal at room conditions, in the order of 7–8°, consistent with long, weak X–O bonds weakly constraining libration motion of the SO_4 group. Such large librational displacements are similar to those in low-density silica framework structures like cristobalite at room conditions, with typical librations of SiO_4 groups of 3–4°. As a result of the TLS analysis, the $R(S-O)$ distance can be corrected for the effects of thermal motion. The corrected mean values, given in Table 4, show an increase of 0.008–0.010 Å from the uncorrected values.

The observation of Hill (1977) concerning the relative sizes of the displacement ellipsoids, *i.e.*, that the isotropic displacement factors of O(1) and O(2) are larger than for O(3), still holds in our datasets. The rigid-body analysis indicates that this is a consequence of the orientation of the libration axis. The major axis of libration for the asymmetric unit S tetrahedron is oriented along the unit direction [0.142 0.018 0].

Finally, with comparable crystallographic data from all three structures, we can also examine the systematics of the barite structure as it changes with the occupant of the X site. The cell volume increases linearly with the average $\langle R(X-O) \rangle$, and the SO_4 tetrahedra rotate about a line perpendicular to the mirror plane and

TABLE 4. RIGID-BODY ANALYSIS OF THE SO_4 GROUPS IN CELESTINE, ANGLESITE, AND BARITE

Parameter	Celestine	anglesite	Barite
$\Delta z^2_{SO} (\text{\AA}^2)$	-0.00018	0.00012	-0.00016
$\Delta z^2_{OO} (\text{\AA}^2)$	0.00082	0.00165	0.00069
B_{eq} due to translation	0.60	0.74	0.63
Libration Angle (°)	7.39	8.18	7.30
Corrected $\langle R(SO) \rangle$ (Å)	1.483	1.486	1.484

through the sulfur position. In Figure 1, an arrow is drawn near one of the O(1) atoms to illustrate the direction of rotation of the tetrahedron as the size of the X cation increases. We examined the variation of $R(X-O)$ versus the average value, $\langle R(X-O) \rangle$. Though the same trend also exists for the variation of $R(X-O)$ versus cell volume, the variation of $\langle R(X-O) \rangle$ better indicates the role of chemical substitution. Each topologically equivalent X-O bond length was regressed against $\langle R(X-O) \rangle$ for the three structures, and the slope and intercepts are plotted against each other in Figure 3. Negative values for the intercept, $R_0(X-O)$, reflect the regression condition that when $\langle R(X-O) \rangle$ is zero, then some bonds must be longer than zero, and some must be shorter. This plot illustrates that as the size of the X cation increases, the shorter X-O bonds tend to increase at a substantially greater rate than the longer X-O bonds, resulting in a more regular coordination. This seems to be consistent with the proposal that increasing X-O repulsion with increasing X-cation radius has a greater effect on the shorter bonds. The result is that the SO_4 tetrahedra rotate as a function of X-cation radius. Interestingly, the rotation of the tetrahedra with change in composition is in the same direction as the main thermal libration (Fig. 1).

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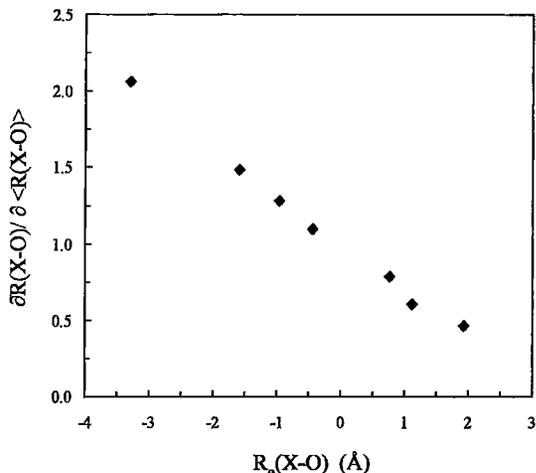


FIG. 3. A plot of the variables obtained in the regression of $R(X-O)$ against the average X-O bond length, $\langle R(X-O) \rangle$. The intercept is $R_0(X-O)$, and the slope is $\partial R(X-O) / \partial \langle R(X-O) \rangle$. The plot illustrates that as the X cation radius increases, the shorter bond-lengths tend to increase at a faster rate than the longer bonds. The linear trend of these data demonstrates that the rotation of the SO_4 tetrahedra is a function of cation size.

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