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Coprecipitation in the Barite Isostructural Family: 1. Binary Mixing Properties

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Abstract—This study attempts to provide a theoretical evaluation of coprecipitation and fundamental data of binary mixing properties in the barite isostructural family. Mixing properties of binary solid solutions in the barite isostructural family were derived from evaluation of coprecipitation experiments and partitioning coefficients reported in the literature. The Margules parameters, W , for these binary systems correlate well through the relationship,

$$W - 0.003875(\Delta\bar{G}_{n,M^{2+}}^{\circ} - \Delta\bar{G}_{n,Tr^{2+}}^{\circ}) = 1262\Delta V + 30$$

where $\Delta\bar{G}_n^{\circ}$ denotes the non-solvation contribution to the standard partial molal Gibbs free energy of formation for the major (M^{2+}) and trace (Tr^{2+}) aqueous ions, and ΔV is the molar volume mismatch between the two substituting end-members

$$\left(\Delta V \equiv \frac{(V_{TrSO_4}^{\circ} - V_{MSO_4}^{\circ})^2}{V_{TrSO_4}^{\circ}} \right),$$

and V° is the molar volume of end-member components. From this correlation, Margules parameters for the $BaSO_4$ - $TrSO_4$ and $SrSO_4$ - $TrSO_4$ binary systems, for which no experimental data are available, were estimated. Tr here stands for trace divalent metals and includes Cu^{2+} , Co^{2+} , Zn^{2+} , Fe^{2+} , Mn^{2+} , Eu^{2+} , Cd^{2+} , Ca^{2+} , Sr^{2+} , Pb^{2+} , and Ra^{2+} . These estimated mixing properties allow predictions of miscibility gaps for the $BaSO_4$ - $TrSO_4$ and $SrSO_4$ - $TrSO_4$ binaries, and partitioning coefficients for Tr^{2+} between barite or celestine and aqueous solutions. Copyright © 2004 Elsevier Ltd

1. INTRODUCTION

Coprecipitation is typically defined as the simultaneous removal of both the tracer and carrier constituents from an aqueous solution without regard to the specific mechanisms involved. Coprecipitation is potentially important to many environmental issues, such as acid mine drainage, radionuclide immobilization in fouled waste repositories, metal contaminant transport at industrial and defense sites, metal concentrations in aquatic systems, and wastewater treatment technology. While mechanisms of coprecipitation may vary in each case and may include surface adsorption, ion-exchange, surface precipitation (e.g., Zhu, 2002), occlusion, and solid solutions, this paper deals with the formation of solid solutions. The environmental significance of coprecipitation (solid solutions) hinges on the solubility of a minor constituent in a solid solution that is greatly reduced in comparison to the solubility of its pure solid (Drever, 1988, 1992; McIntire, 1963; Morel, 1983; Sposito, 1984; Stumm and Morgan, 1981, 1996). Metal concentrations of environmental concern, such as Ra, Pb, Zn, Co, Ni, Cd, As, and Cr, are typically at or below parts per million, at which level contaminants are usually far below the solubility limits of the pure solids in which they are a major constituent, such as $RaSO_4$, $PbCO_3$, $Ni(OH)_2$, or $Cr(OH)_3$. Hence, solubility limits of pure solids generally do not control the fate and transport of these contaminants. However, contaminants can be incorpo-

rated into precipitating common solids forming a solid solution in which they are only a trace or minor component (coprecipitation), and can be controlled at much lower concentrations than the solubility of pure solids.

Examples where coprecipitation reactions occur at or near the Earth surface abound, as solids precipitated in pristine and contaminated geological environments are seldom pure. For example, $RaSO_4$ co-precipitates with $BaSO_4$ (barite) in uranium mill tailings (Paige et al., 1993), in uranium mill waste waters (Sebesta et al., 1981), and with (Ba, Sr) SO_4 scale as Naturally Occurring Radioactive Material (NORM) during oil and gas production (Fisher, 1995; Gray, 1993; Smith, 1987; White, 1992). Uranium may coprecipitate with calcite during the weathering of uranium deposits (Leslie and Percy, 1993; Percy et al., 1995), and Zn, Cd, Co, Ba, and a host of radionuclides also coprecipitate with calcite (Curti, 1999; Reeder, 1996). Cm^{3+} and Eu^{3+} coprecipitate with powellite ($CaMoO_4$) during the corrosion of high-level nuclear waste glass (Bosbach et al., 2002). A class of common and important coprecipitation reactions involves iron and manganese oxyhydroxides (Cornell and Schwertmann, 1996; Hem and Lind, 1991). Laboratory experiments show that Al (Shulze and Schwertmann, 1984; Wolska and Schwertmann, 1993), Cr (Manceau et al., 1992; Schwertmann et al., 1989), Mn, Ni, and Co (Cornell, 1991; Stiers and Schwertmann, 1985), UO_2^{2+} (Bruno et al., 1995; Duff et al., 2002), and Cu^{2+} , Zn, and Cd (Gerth, 1990) can substitute for Fe^{3+} in goethite, Cr^{3+} and Fe^{3+} coprecipitate to form an amorphous solid solution (Amonette and Rai, 1990; Sass and Rai, 1987). Jarosite solid solutions are found to

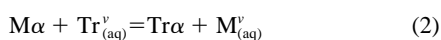
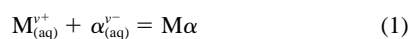
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precipitate in acid mine drainage environments (Alpers et al., 1989).

The mechanisms of coprecipitation are often a challenge to identify, and this subject is undergoing intense and active research (see e.g., Duff et al., 2002). For different solids or systems of interest, the mechanisms may be different. The present communication deals with the coprecipitation data of Ra^{2+} , Ba^{2+} , Pb^{2+} , Sr^{2+} sulfates and Ba^{2+} chromate, which all reports indicate are crystalline solid solutions. Based on these data, a correlation trend was delineated so that binary mixing properties, for which no experimental measurements are available, can be estimated. The term *coprecipitation* is used to describe the formation of these crystalline solid solutions, in which the tracer component substitutes for the carrier component, but also includes the corresponding dissolution reaction.

2. THERMODYNAMIC BASIS OF COPRECIPITATION

The precipitation of a binary solid solution phase, $(M, \text{Tr})\alpha$, from an aqueous solution (coprecipitation) can be represented by the reactions,



where M (e.g., Ba^{2+} in $(\text{Ba}, \text{Ra})\text{SO}_4$) represents the major or carrier metal with a valence of $^{++}$ in the solid phase of concern and Tr (e.g., Ra^{2+} in $(\text{Ba}, \text{Ra})\text{SO}_4$) represents the trace metal that substitutes for M . The symbol α indicates the remaining composition of the solid phase, e.g., SO_4^{2-} . The mass action equations that describe reactions (1) and (2) can be written as,

$$K_1 = \frac{a_{M\alpha}}{a_{\alpha^{v-}} a_{M^{v+}}} \quad (3)$$

$$K_2 = \frac{a_{\text{Tr}\alpha} a_{M^{v+}}}{a_{M\alpha} a_{\text{Tr}^v}} \quad (4)$$

where K represents the equilibrium constant, and a_i the activity of the i th solid component and aqueous species.

The activity-composition relationship of the solid component is as follows,

$$a_{M\alpha} = X_{M\alpha} \lambda_{M\alpha} \quad (5)$$

$$a_{\text{Tr}\alpha} = X_{\text{Tr}\alpha} \lambda_{\text{Tr}\alpha} \quad (6)$$

where X and λ denote the mole fraction and rational activity coefficients for end-member components, respectively. The activity coefficients for the end-member components can be calculated using the regular and subregular (Margules) solution models (Ganguly and Saxena, 1987; Thompson, 1967). For a binary system consisting of M - Tr , the regular solution model equations give,

$$RT \ln \lambda_{M\alpha} = W(1 - X_{M\alpha})^2 \quad (7)$$

$$RT \ln \lambda_{\text{Tr}\alpha} = W(1 - X_{\text{Tr}\alpha})^2 \quad (8)$$

where R denotes the gas constant ($1.987 \text{ cal/mol K}^{-1}$); and T denotes the temperature in degrees Kelvin. W is the Margules parameter, which can be thought of as the energy necessary to

interchange one mole of the $\text{Tr}\alpha$ with one mole of $M\alpha$ in the mixture without changing composition (Anderson and Crerar, 1993). W is independent of composition, but is a function of T and pressure (P). The subregular solution model equations are,

$$RT \ln \lambda_{M\alpha} = (1 - X_{M\alpha})^2 [2W_{21} - W_{12}] X_{M\alpha} + W_{12} X_{\text{Tr}\alpha} \quad (9)$$

$$RT \ln \lambda_{\text{Tr}\alpha} = (1 - X_{\text{Tr}\alpha})^2 [2W_{12} - W_{21}] X_{\text{Tr}\alpha} + W_{21} X_{M\alpha} \quad (10)$$

where W_{12} and W_{21} represent Margules parameters in the subregular model. The regular solution model is a special case of the subregular solution model for $W_{12} = W_{21}$. A regular solution model obeying Eqn. (7) and (8) is the simplest form, which works for most binary non-electrolyte solutions (Ganguly and Saxena, 1987; Garrels and Christ, 1965). The subregular model, or asymmetrical regular solution model, can be viewed as two different regular solution models from the two dilute ends (Ganguly and Saxena, 1987).

The activity-composition relationship for a ternary system can be expressed as (Prigogine and Defay, 1954),

$$RT \ln \lambda_1 = [W_{12} X_2^2 + W_{13} X_3^2 + (W_{12} - W_{23} + W_{13}) X_2 X_3]$$

$$RT \ln \lambda_2 = [W_{12} X_1^2 + W_{23} X_3^2 + (W_{12} - W_{13} + W_{23}) X_1 X_3]$$

$$RT \ln \lambda_3 = [W_{13} X_1^2 + W_{23} X_2^2 + (W_{13} - W_{12} + W_{23}) X_1 X_2] \quad (11)$$

where W , with the numerical subscripts, denotes binary interaction parameters in the respective binary systems (for example: 1= RaSO_4 ; 2= BaSO_4 ; 3= SrSO_4 , and W_{12} designates the binary RaSO_4 - BaSO_4).

Implicit in Eqn. (11) are the assumptions that the binary systems are regular (symmetrical) solutions and that ternary interactions are negligible. The latter assumption is somewhat customary for mineral solid solutions since ternary data are generally lacking (Ganguly and Saxena, 1987).

3. BINARY SOLID SOLUTIONS IN THE BARITE ISOSTRUCTURAL FAMILY

There are several isostructural minerals and crystalline solids in the barite group, including RaSO_4 , barite (BaSO_4), celestine (SrSO_4), hashemite (BaCrO_4), and anglesite (PbSO_4) (Gaines et al., 2000; Smyth and Bish, 1988). The structure has a space group Pnma . In the barite structure, the sulfate forms regular tetrahedra and the divalent metals are coordinated with 12 oxygens that belong to 7 different sulfate groups (Fig. 1). A complete solid solution series exists between barite and celestine, and barite and RaSO_4 , although natural barites seldom contain more than a few percent Sr or Pb (Doerner and Hoskins, 1925; Gaines et al., 2000; Hanor, 2000). Substitution of SeO_4^{2-} into barite is also found (Gaines et al., 2000).

Although the focus of this study is on the mixing properties of solid solutions, standard state properties for end-member solid phases and aqueous species are involved in the derivation because excess properties are derived from the subtraction of standard state and ideal mixing properties from the measurable quantities. Thus, the solid solution properties are not isolated properties, but they should be internally consistent with the standard state properties for the end-members and aqueous

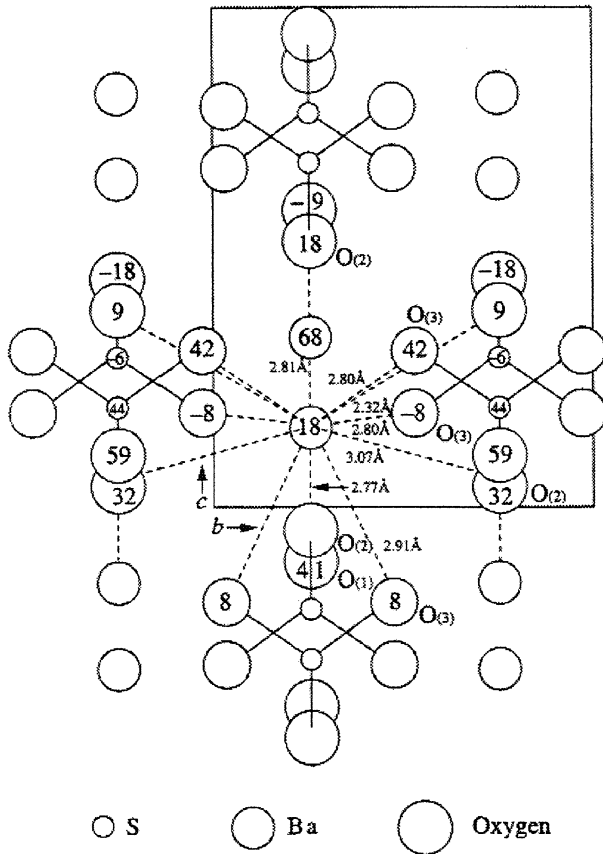


Fig. 1. The barite structure perspective view down the c axis. After Gaines et al. (2000).

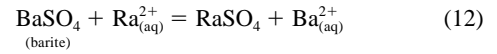
species involved in the derivation. These properties are extracted from experimental data or are estimated when experimental data are not available.

Two types of end-members in the barite isostructural family solid solutions are considered. The first type includes divalent metal sulfates and chromates, for which their pure solids physically exist and have the barite crystalline structure. For these end-members, such as BaSO_4 , SrSO_4 , RaSO_4 , PbSO_4 , and BaCrO_4 , the standard states are defined as unit activity for the pure end-member component at the temperature and pressure of interest (Raoultian standard state, Fig. 2a). These end-members can both be carriers and tracers. A second type of end-member is $\text{Tr}\alpha$ for which pure solids do not exist or have a crystalline structure different from barite. This usually involves an incompatible Tr^{v+} with respect to M^{2+} . For example, CaSO_4 commonly substitutes into the barite and celestine structures, but pure CaSO_4 has a different crystalline structure (anhydrite) from barite. A Henrian standard state (Ganguly and Saxena, 1987) is defined for these end-members, as unit activity for hypothetical pure end-members with barite structure extrapolated along the Henry's law slope from the infinite dilution region (Fig. 2b). With such definitions for $\text{Tr}\alpha$ and $\text{M}\alpha$, the activity coefficients for both end-members are unity in the dilute region where Henry's law is obeyed (Ganguly and Saxena, 1987). The standard state for water is unit activity of pure

water. For aqueous species other than H_2O , the standard state is unit activity of the species in a hypothetical one molal ideal solution referenced to infinite dilution at the temperature and pressure of interest.

3.1. The BaSO_4 - RaSO_4 Binary

The coprecipitation of Ra - BaSO_4 can be described by the reaction



The equilibrium constant, K , for the above reaction can be calculated from the relation

$$K = \exp(-\Delta G_R^\circ/RT) \quad (13)$$

where ΔG_R° stands for the standard state molal Gibbs free energy of reaction (12).

The standard state thermodynamic properties used to calculate K are tabulated in Table 1. A considerable range of ΔG_f° values for barite exists in the literature (Glushko et al., 1979; Helgeson et al., 1978; Wagman et al., 1982). The value of -325563 cal/mol is chosen from Helgeson et al. (1978) be-

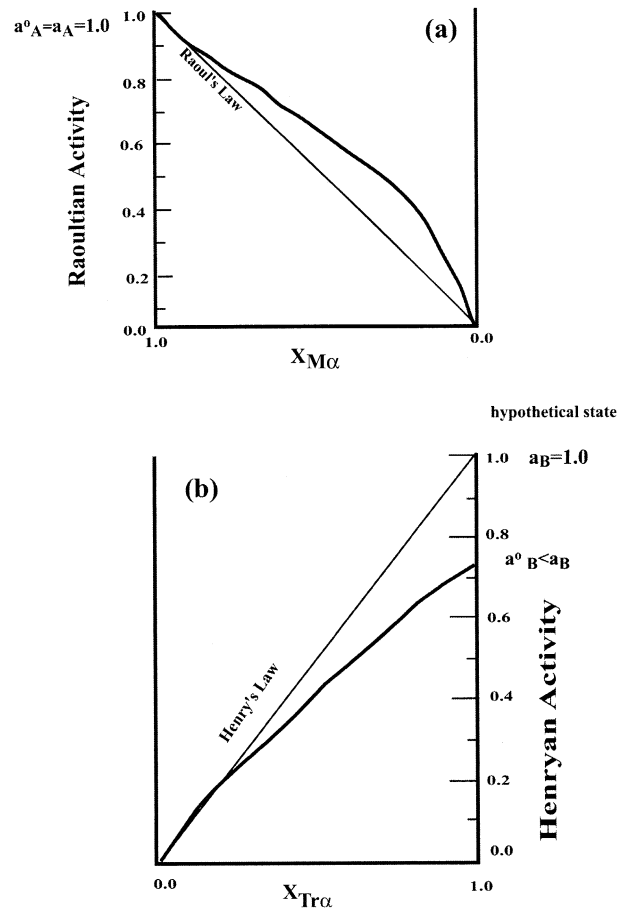


Fig. 2. Schematic diagrams illustrate the two standard states for solid solution end-members.

Table 1. Standard state thermodynamic properties* used in this study.

Species name	Formula	log K_{sp}	Space group ^f	ΔG_f° cal mol ⁻¹	V° cm ³ mol ⁻¹	r^h Å
barite	BaSO ₄	-9.99 ^a	Pnma	-325,563 ^a	52.10	
	RaSO ₄	-10.38 ^b	Pnma	-326,290 ^b	55.35	
anglesite	PbSO ₄	-7.97 ^b	Pnma	-194,510 ^b	47.98	
celestine	SrSO ₄	-6.63 ^c	Pnma	-320,700 ^b	46.371	
hashemite	BaCrO ₄	-9.76 ^c	Pnma		55.55	
SO ₄ ²⁻				-177,930 ^d		
CrO ₄ ²⁻				-173,940 ^d		
Ra ²⁺ (aq)				-134,200 ^d		1.70
Ba ²⁺ (aq)				-132,730 ^d		1.61
Pb ²⁺ (aq)				-5,710 ^d		1.49
Sr ²⁺ (aq)				-133,720 ^d		1.44

* at 25°C and 1 bar.

^a Helgeson et al. (1978).

^b Sverjensky and Molling (1992).

^c Nordstrom et al. (1990).

^d Shock and Helgeson (1988).

^e Rai et al. (1988).

^f Gaines et al. (2002).

^g Molar volumes from Symth and Bish (1988), unless otherwise indicated. For hashemite from MinCryst on-line database.

^h Shannon-Prewitt effective ionic radii in 12 coordination.

cause it is consistent with solubility measurements of Blount (1978) as well as the ΔG_f° values for Ba²⁺ and SO₄²⁻ ions from Shock and Helgeson (1988), which we use in our aqueous speciation model (see Zhu, this issue). The ΔG_f° values for RaSO₄(c) in the literature are all based on the same solubility measurements (cited by Langmuir and Riese, 1985). We chose the value of -326290 cal/mol selected by Sverjensky and Molling (1992), again for consistency with ΔG_f° for related aqueous ions. A K value of 2.56 for reaction (12) is calculated using these data.

The equilibrium constant, K , also can be defined as

$$K = \frac{\left(\frac{X_{\text{RaSO}_4} \lambda_{\text{RaSO}_4}}{X_{\text{BaSO}_4} \lambda_{\text{BaSO}_4}}\right)}{\left(\frac{m_{\text{Ra}^{2+}} \gamma_{\text{Ra}^{2+}}}{m_{\text{Ba}^{2+}} \gamma_{\text{Ba}^{2+}}}\right)} \quad (14)$$

where X_i and λ_i are the mole fractions and rational activity coefficients for the components in the solid solution, respectively, and m_i and γ_i are the molality and activity coefficients of the aqueous ions Ra²⁺ and Ba²⁺, respectively. Rewriting Eqn. (14), we have,

$$K = K_D (\lambda_{\text{RaSO}_4} / \lambda_{\text{BaSO}_4}) / (\gamma_{\text{Ra}^{2+}} / \gamma_{\text{Ba}^{2+}}) \quad (15)$$

where K_D is the Henderson and Kracek (1927) partition coefficient

$$K_D = \frac{(X_{\text{RaSO}_4} / X_{\text{BaSO}_4})}{(m_{\text{Ra}^{2+}} / m_{\text{Ba}^{2+}})} \quad (16)$$

Because Ra²⁺ usually has dilute concentrations in barite for the environmental problems of concern, Raoult's law is probably obeyed for the BaSO₄ component. Hence, $\lambda_{\text{BaSO}_4} \approx 1.0$.

The activity coefficient for the trace component (the tracer), λ_{RaSO_4} , is calculated in the following manner. Doerner and Hoskins (1925) conducted exchange reactions in very dilute solutions (HCl 0.0053 *N*), in which ionic complexation can be neglected and the ionic activity coefficient ratios ($\gamma_{\text{Ra}^{2+}} / \gamma_{\text{Ba}^{2+}}$)

are close to unity. They found a $K_D = 1.8$ (p.675). From the equation

$$K = K_D \cdot \lambda_{\text{RaSO}_4} \quad (17)$$

we have calculated $\lambda_{\text{RaSO}_4} = 1.5$. This value corresponds to a regular solution interaction parameter, W , of about 210 cal/mol (see Eqn. 8).

3.2. The SrSO₄-RaSO₄ and PbSO₄-RaSO₄ Binaries

Through derivations similar to those in Section 3.1, we calculated W from the partitioning coefficients for SrSO₄-RaSO₄ and PbSO₄-RaSO₄. To ensure internal consistency of thermodynamic properties, the log K values for the exchange reactions



and



were calculated from the standard state Gibbs free energy of formation listed in Table 1. Using the distribution coefficient values of 280 for SrSO₄ and 11 for PbSO₄ from the earlier work of Goldschmidt cited by Langmuir and Riese (1985), yields Margules parameters (W) of 1772 and 1869 cal/mol for the SrSO₄-RaSO₄ and PbSO₄-RaSO₄ binary, respectively.

3.3. SrSO₄-BaSO₄ Binary

Despite the large amount of work done on this binary, results of solubility measurements and derived mixing properties are conflicting and equivocal (see Glynn, 2000 for review). Felmy et al. (1993) fitted a W value of 478 cal/mol to their solubility data, while Galinier et al. (1989) derived a W value of 956 cal/mol. Glynn (1990) gave a value of 1386 cal/mol. The W

value for SrSO₄-BaSO₄ is also derived in this study from the experimental distribution coefficient provided in McIntire (1963), using the standard state Gibbs free energy listed in Table 1 and the same assumption of unit activity coefficients for the carrier and approximate unit activity coefficient ratios for the aqueous metal ions. A W value for the SrSO₄-BaSO₄ binary is 1413 cal/mol at 18°C. Becker et al. (2000) made calculations of mixing properties using molecular methods. Prieto et al. (1997) conducted experiments on SrSO₄-BaSO₄, and found compositional zoning.

3.4. PbSO₄-BaSO₄, BaSO₄-BaCrO₄, and BaCrO₄-RaCrO₄ Binary

A W value of 1600 cal/mol was estimated by Glynn (1990) for the BaSO₄-PbSO₄ binary from reported compositional ranges of natural barite (20% Pb maximum reported and hence perceived miscibility gaps). However, McIntire (1963) gave a K_D of 0.026, from which a W of -593 cal/mol is calculated using the solubility products, K_{sp} , listed in Table 1. An experimental distribution coefficient of 1.1 was given by McIntire (1963) for the binary solid solution BaSO₄-BaCrO₄ corresponding to the exchange reaction



Using the K_{sp} from Rai et al. (1988), a W of -370 cal/mol was calculated for the binary BaSO₄-BaCrO₄ solution. Henderson and Kracek (1927) measured a K_D of 15.5 for fractional precipitation of Ba-RaCrO₄. The constant K_D over a wide compositional range (Ba:Ra weight ratio from 10⁻⁹ to 10⁻² in barite) indicates that the solid solution is ideal (McIntire, 1963).

4. A SEMI-EMPIRICAL CORRELATION FOR MARGULES PARAMETERS

In solid solutions with isovalent substitutions, deviation from ideal mixing comes from both the differences in ionic radii of the substituting ions and the differences in other intrinsic ionic characteristics such as electronegativity, crystal field effects, electron configuration, and polarity of the ions (Ganguly and Saxena, 1987; Urusov, 1975). We can define the excess Gibbs free energy ΔG^{excess} of a solid solution as being composed of two terms:

$$\Delta G^{\text{excess}} = \Delta G_{\text{elastic}}^{\text{excess}} + \Delta G_{\text{ionic}}^{\text{excess}} \quad (21)$$

For a symmetrical binary regular solution we have,

$$\Delta G^{\text{excess}} = WX_{M\alpha}X_{Tr\alpha} \quad (22)$$

where W denotes the interaction parameter and X_i denotes the mole fraction of the binary end-member components of the solid solution (M, Tr) α . It follows that,

$$W^{\text{excess}} = W_{\text{elastic}}^{\text{excess}} + W_{\text{ionic}}^{\text{excess}} \quad (23)$$

The first term is related to differences in the sizes of substituting ions, and the second term describes differences in ionic properties other than the size.

The effects of the differences in ionic radii have been described by the elastic theory (Greenwood, 1979). For a solid

solution (M, Tr) α , the strain energy for one mole of a component Tr α into an infinite elastic continuum of component M α was described by (Ganguly and Saxena, 1987),

$$\omega_{Tr\alpha} = \frac{2}{3} \hat{\mu}_{M\alpha} C_{M\alpha} \frac{(V_{Tr\alpha}^o - V_{M\alpha}^o)^2}{V_{Tr\alpha}^o} \quad (24)$$

where $\hat{\mu}$ is the shear modulus of M α , and $C_{M\alpha}$ is defined as

$$C_{M\alpha} = \frac{3\Psi_{Tr\alpha}}{3\Psi_{Tr\alpha} + 4\hat{\mu}_{M\alpha}} \quad (25)$$

where Ψ denotes the effective bulk modulus of Tr α in the solid solution and V^o stands for the molar volume of end-member components. Note, in the above equation, that the volume term is second order.

The role of ionic properties other than the size in the mixing properties of a solid solution is well illustrated by Davis and Navrotsky (1983) using the example of the NaCl-AgCl solid solution. Although the ionic sizes for the two cations are close (1.02 Å for Na⁺ and 1.15 Å for Ag⁺ from Shannon 1976), the bonding characteristics of the two ions are significantly different since Ag⁺ is a transition metal and Na⁺ is an alkali metal. A large positive heat of mixing is found for this solid solution.

In light of the above argument, a correlation that considers both size misfit and the bonding differences in substituting ions is presented here. The correlation is formulated as

$$W' = a\Delta V + b \quad (26)$$

where W' is the adjusted Margules parameter. The volume mismatch term, ΔV , is defined by (Ganguly and Saxena, 1987; Greenwood, 1979)

$$\Delta V \equiv \frac{(V_{Tr\alpha}^o - V_{M\alpha}^o)^2}{V_{Tr\alpha}^o} \quad (27)$$

W' is defined as

$$W' \equiv W - \beta(\Delta\bar{G}_{n,M^{v+}}^o - \Delta\bar{G}_{n,Tr^{v+}}^o) \quad (28)$$

where $\Delta\bar{G}_n^o$ denotes the non-solvation contribution to the standard partial molal Gibbs free energy of formation of the aqueous ions (Helgeson et al., 1981). β is an empirically derived parameter.

The adjustment of W to W' in Eqn. 28 is intended to account for the differences in bonding characteristics of substituting ions that are not reflected in the differences in ionic radii. This formulation follows the Sverjensky linear free energy correlations for isostructural crystalline solid families (Sverjensky and Molling, 1992).

The parameters a , b , and β for the binary solid solutions in the barite isostructural family were obtained from multiple linear regression analysis. The W values derived and discussed in the preceding section were used together with the $\Delta\bar{G}_n^o$ values from Sverjensky and Molling (1992) or computed from Shock and Helgeson (1988) to calculate W' values. The molar volumes for the end-members are listed Table 1. Molar volumes of end-members, for which experimental data are lacking or which are hypothetical, are estimated from the correlation for the barite isostructural family derived in this study,

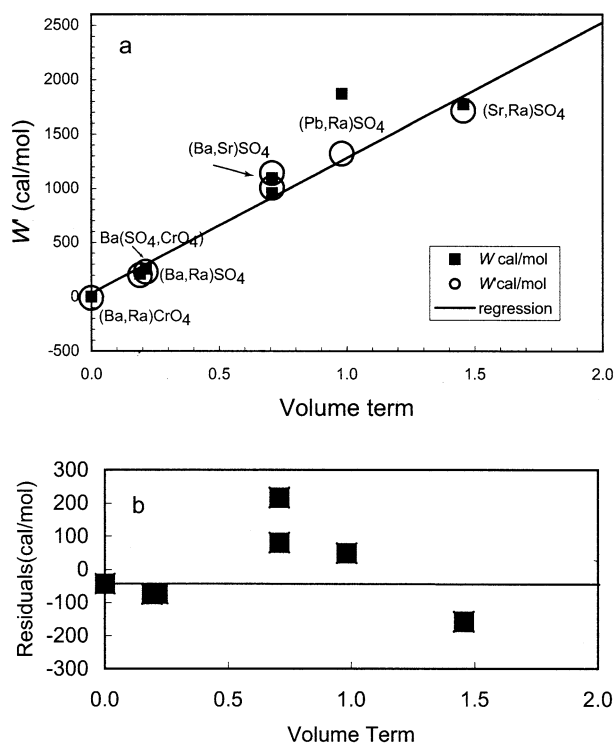


Fig. 3. (a) Correlations between the modified Margules parameter with volume mismatch for binaries in the barite isostructural family. The line is from multiple linear regression. The reported values for the BaSO₄-PbSO₄ binary and some values for the BaSO₄-SrSO₄ binary were excluded from the regression. See discussion in the text; (b) Residuals between the predicted and experimental/natural assemblage binary excess properties.

$$V^o = \left(\frac{0.6024}{4} \right) [(19.46616 - 4.19322r(\text{XII})) \times ((1.40 + r(\text{XII}))^3)] \quad (29)$$

where $r(\text{XII})$ is the Shannon-Prewitt effective ionic radius with 12-coordination (Shannon, 1976). The correlation for this relationship is excellent ($R^2 = 1.0$). The differences between measured and calculated molar volumes are only 0.12, 0.05, 0.07 cm³/mol for barite, celestine, and anglesite, respectively. This regression scheme followed Zhang et al. (1991).

Multiple linear regression analysis following Eqn. (26) and (28) resulted in the following correlation

$$W - 0.003875(\pm 0.001219)(\Delta \bar{G}_{n,M^{2+}}^o - \Delta \bar{G}_{n,T^{2+}}^o) = 1262(\pm 129)\Delta V + 30(\pm 93) \quad (30)$$

The correlation is excellent, with $R^2 = 0.97$ (Fig. 3a) and the intercept is close to zero. If both the size and ionicity are adequately taken into account in the regression, the intercept should be zero.

Various forms of correlations have been explored to predict Margules parameters for binary solid solutions (Davis and Navrotsky, 1983). The introduction of the W' term appears to improve the correlation for those substituting ions with different characteristics. For example, a large correction is made for

Pb²⁺ (a transition metal) substitution of Ra²⁺ and Ba²⁺, both alkaline earth elements (~500 cal/mol for both). The $\Delta \bar{G}_n^o$ term is negligible, as expected, for substitutions between alkaline earth metals. Blundy and Wood (1994) found excellent correlation for crystal-melt partitioning coefficients based on ionic radii and elastic properties of the crystalline sites. However, they noted exceptions for transition metals-alkaline earth substitutions, which, in light of what is found in this study, may be attributed to the lack of "ionicity" corrections.

The second order term for the volume mismatch used in this study also improves the correlation and apparently is more in accord with the elastic theory than the first order term or ionic radii-based terms used previously (see review by Davis and Navrotsky, 1983). However, the current formulation does not take into account Goldschmidt's "polarity rule" that it is easier for smaller ions to substitute for larger ions than the reverse.

The regression residuals between measured and predicted W values are within ± 300 cal/mol (Fig. 3b). This is a significant advancement over previous studies, which generally have an accuracy of about ± 1500 to 2500 cal/mol (e.g., Davis and Navrotsky, 1983). The correlation formula developed in this study (Eqn. 26 and 28) appears to work for halides and metal oxides with rocksalt type structures as well (Zhu, unpublished data).

Various schemes of regression were experimented with in this study. The high correlation described above was obtained by excluding the W values for (Ba,Pb)SO₄ binary and some estimates for the (Ba, Sr)SO₄ binary. For the former, there is a large disparity (2100 cal/mol) between the W value from Glynn (1990) and that calculated from McIntire (1963). The Glynn (1990) value of 1600 cal/mol was estimated from the perceived miscibility gap of 20% Pb in natural barite. Whether there is a complete solid solution in the BaSO₄-PbSO₄ series remains controversial (see Hanor, 2000 for a discussion). Additionally, the value of -593 cal/mol is calculated from an experimental partitioning coefficient cited by McIntire (1963). W estimates from perceived miscibility gaps are very inaccurate (Glynn, 2000).

The mixing properties for the BaSO₄-SrSO₄ binary, a geologically and environmentally significant solid solution, are still controversial (see Glynn, 2000; Hanor, 2000, for detailed discussions of the occurrence and experimental data sets). It appears that the experimental data from Galinier et al. (1989) and Starke (1964), cited by Hanor, (2000) are consistent with the correlation among W values of other binaries (Fig. 3a). McIntire (1963) cited the experimental partitioning coefficient measured by Goldschmidt, in which Ba²⁺ is the tracer. It is difficult to argue for a subregular solid solution model based on that value alone. Felmy et al. (1993) conducted careful experiments. However, it is troubling that their derived value does not fit well in the correlation.

5. APPLICATIONS

The high degree of correlation in Eqn. (30) permits prediction of the Margules parameter, W , for binary solid solutions, for which there are no experimental data. For estimating W values, the molar volumes for fictitious Tr SO₄ end-members with barite structure were estimated from Eqn. (29). For small

Table 2. W values* for binary solid solutions in the barite isostructural family.

Tracer	Carrier	W cal mol ⁻¹	Method	W'
RaSO ₄	BaSO ₄	210 ^a	exptl	197
RaSO ₄	SrSO ₄	1772 ^b	K_D	1711
RaSO ₄	PbSO ₄	1869 ^b	K_D	1318
SrSO ₄	BaSO ₄	478 ^c	exptl	526
SrSO ₄	BaSO ₄	956 ^d	exptl	1004
BaSO ₄	SrSO ₄	1444 ^e	exptl, K_D	1396
SrSO ₄	BaSO ₄	1092 ^f	exptl K_D	1140
PbSO ₄	BaSO ₄	-593 ^e	exptl, K_D	-56
PbSO ₄	BaSO ₄	1600 ^g	mis gap	2138
BaCrO ₄	BaSO ₄	257 ^e	exptl, K_D	228
RaCrO ₄	BaCrO ₄	0 ^e	exptl	-13

* at 25°C and 1 bar.

^a Doerner and Hoskins (1925).^b Langmuir and Riese (1985).^c Felmy et al. (1993).^d Galinier et al. (1989).^e McIntire (1963).^f Starke (1964).^g Glynn (1990).

divalent ions, radii of 12 coordination (fictitious) were estimated from the linear extrapolation of radii of lower coordination numbers (from Shannon, 1976). $\Delta\bar{G}_r^\circ$ values were taken from Sverjensky and Molling (1992). The W values were then calculated from Eqn. (30). Tables 3 and 4 list the W values for the BaSO₄-TrSO₄ and SrSO₄-TrSO₄ binaries. Tr here includes Ni²⁺, Mg²⁺, Cu²⁺, Co²⁺, Zn²⁺, Fe²⁺, Mn²⁺, Eu²⁺, Cd²⁺, Ca²⁺, and Pb²⁺. Figure 4 shows the activity-composition relationships in the BaSO₄-SrSO₄, BaSO₄-RaSO₄, BaSO₄-PbSO₄, and SrSO₄-PbSO₄ binaries. Eqn. (5), (6), (7), and (8) are used for the calculations.

The positive values of W indicate more energetic repulsion between Tr and Ba²⁺ or Tr and Sr²⁺, $\lambda_i > 1$, and positive deviation from Raoult's Law. Large positive values of W can lead to immiscibility and exsolution. Negative W values (e.g., (Ba, Pb)SO₄ and (Sr, Pb)SO₄ binary) indicate an energy preference for the two end-members to associate in the solution, which can produce intermediate compounds (Anderson and

Table 3. Predicted W and K_D values for the BaSO₄-TrSO₄ binaries.

M^{2+}	r_M^{2+} (Å)	V° cm ³ mol ⁻¹	W cal mol ⁻¹	$\ln K_{ex}$	$\ln K_D^*$ $X_{Tr\alpha} = 0.01$	$\ln K_D^*$ 0.05
Cu ²⁺	1.21	38.54	5289	-33.44	-42.19	-41.47
Co ²⁺	1.22	38.87	5062	-33.52	-41.90	-41.21
Zn ²⁺	1.2	38.21	5843	-32.97	-42.63	-41.84
Fe ²⁺	1.23	39.20	4782	-30.60	-38.51	-37.87
Mn ²⁺	1.25	39.87	4310	-27.11	-34.24	-33.66
Eu ²⁺	1.42	45.64	1123	-7.19	-9.05	-8.90
Cd ²⁺	1.31	41.88	2619	-17.44	-21.77	-21.42
Ca ²⁺	1.34	42.90	2420	-16.17	-20.17	-19.85
Sr ²⁺	1.44	46.37	876	-7.73	-9.18	-9.06
Pb ²⁺	1.49	48.05	-78	-4.68	-4.55	-4.56
Ra ²⁺	1.7	55.36	285	0.89	0.42	0.46

* Only applicable in the case that the aqueous Tr^{2+} and M^{2+} are dominant and their activity coefficient ratio close to unity.Table 4. Predicted W and K_D values for the SrSO₄-TrSO₄ binaries.

M^{2+}	r_M^{2+} (Å)	V° cm ³ mol ⁻¹	W cal mol ⁻¹	$\ln K_{ex}$	$\ln K_D^*$ $X_{Tr\alpha} = 0.01$	$\ln K_D^*$ 0.05
Ni ²⁺	1.11	35.27	3810	-28.83	-35.14	-34.62
Mg ²⁺	1.16	36.90	2863	-28.55	-33.28	-32.90
Cu ²⁺	1.21	38.54	1323	-25.71	-27.90	-27.72
Co ²⁺	1.22	38.87	1253	-25.80	-27.87	-27.70
Zn ²⁺	1.2	38.21	1717	-25.24	-28.08	-27.85
Fe ²⁺	1.23	39.20	1128	-22.88	-24.74	-24.59
Mn ²⁺	1.25	39.87	959	-19.38	-20.97	-20.84
Eu ²⁺	1.42	45.64	30	0.54	0.49	0.49
Cd ²⁺	1.31	41.88	129	-9.71	-9.92	-9.91
Ca ²⁺	1.34	42.90	332	-8.44	-8.99	-8.95
Pb ²⁺	1.49	48.05	-386	3.05	3.69	3.64
Ba ²⁺	1.61	52.22	905	7.73	6.23	6.35
Ra ²⁺	1.7	55.36	1931	8.62	5.43	5.69

* Only applicable in the case that the aqueous Tr^{2+} and M^{2+} are dominant and their activity coefficient ratio close to unity.

Crerar, 1993). In this case, $\ln \lambda_i$ is negative and $\lambda_i < 1$, indicating a negative deviation from Raoult's Law (Swalin, 1972; see Fig. 4). The corrections for the "ionicity," ($W'-W$), are negligible with Ca²⁺, Ba²⁺, Sr²⁺, and Eu²⁺ for Ba²⁺ or Sr²⁺ substitutions, and about 400 cal/mol with Be²⁺ and 250 cal/mol with Mg²⁺ for Ba²⁺ and Sr²⁺ substitutions. However, for transition metals, Ni²⁺, Cu²⁺, Co²⁺, Zn²⁺, Fe²⁺, Mn²⁺, Cd²⁺, and Pb²⁺ for Ba²⁺ or Sr²⁺ substitutions, the corrections are significant and generally >500 cal/mol.

Miscibility gaps were calculated from these estimated W values, and are shown for some SrSO₄- and BaSO₄-TrSO₄ binaries in Figure 5. As a rule of thumb, a W value larger than ~1100 cal/mol results in a miscibility gap at 25°C (Glynn, 2000). From these miscibility gaps, the maximum amounts of Tr^{2+} that can be structurally incorporated into barite and celestine can be calculated.

However, the W values or miscibility gaps can only tell us compatibility between the tracer and carrier, or the deviation from ideality in the solid solution, but they alone cannot tell us how much a tracer will be incorporated into the carrier. The tendency for partitioning of a trace constituent into a solid or an aqueous solution can be shown in the Henderson and Kracek partition coefficients, K_D , as defined by Eqn. (16) for radium partition between barite and an aqueous solution. Overall, the partitioning coefficients are influenced by three factors, defined by the three terms on the right hand side of the following equation (McIntire, 1963):

$$\ln K_D = \ln \left(\frac{K_{sp}^{M\alpha}}{K_{sp}^{Tr\alpha}} \right) + \ln \left(\frac{\gamma_{Tr^{2+}}}{\gamma_{M^{2+}}} \right) + \frac{W(1 - X_{Tr\alpha})^2}{RT} \quad (31)$$

where the first term on the right shows the "intrinsic" factor or the tendency of $Tr\alpha$ to form in the aqueous solution with respect to the host and is quantified by the ratios of the solubility products of the end-members. The second term shows the influences by the differential aqueous speciation or complexation of the tracer and carrier ions and ratios of activity coefficients. Note the link between the Henderson and Kracek partition coefficient and K_{sp} in Eqn. (31), as defined in Eqn.

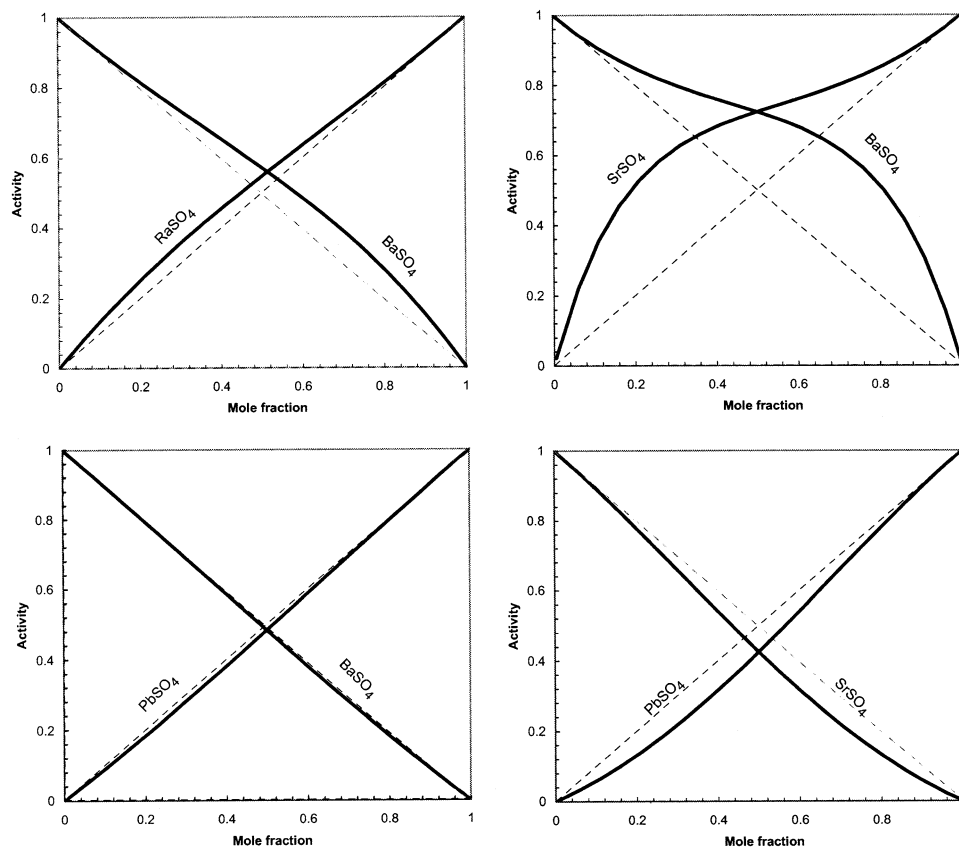


Fig. 4. Calculated activity-composition relationships for binaries in the barite isostructural family.

(16), requires the concentrations of Tr^{v+} and M^{v+} to be the “free” aqueous ions, not the total molality of aqueous Tr^{v+} and M^{v+} ions when the ion association model is used. The third term in Eqn. (31) quantifies the effects of the non-ideality of the solid solution for incorporation of trace amounts of Tr^{v+} into $M\alpha$. Note $\lambda_{M\alpha} \approx 1.0$ in solid solutions with dilute $Tr\alpha$, partly because of our choices of standard states (see Fig. 2).

With the W values in hand, the partition coefficients between barite or celestine and the aqueous solution can be calculated from expressions similar to Eqns. (15) and (16) for cases in which the divalent aqueous ion is dominant and the activity ratios of the aqueous carrier and tracer ions are approximate to unity. The equilibrium constants for the exchange reactions for Tr^{2+} (Eqn. 2) were calculated from solubility products for MSO_4 listed in Table 1 and $TrSO_4$ end-members. The latter were calculated from the standard state Gibbs free energy of formation for the fictitious $TrSO_4$ end-members predicted by Sverjensky and Molling (1992), standard molal Gibbs free energy of formation for aqueous Tr^{2+} and M^{2+} ions as listed in Sverjensky and Molling (1992), and for sulfate in Table 1. Table 3 and 4 list the K_D values for a mole fraction of 1 and 5% substitution with the tracer. Note the K_D values are a function of solid compositions.

The calculated partition coefficients show that $TrSO_4$ with lower solubility than the hosts, are favorably partitioned into the solid with respect to the aqueous solution. Thus, Ra^{2+} is favorably partitioned into barite and celestine, and Ba^{2+} , Pb^{2+} ,

and Eu^{2+} are favorably partitioned into celestine with respect to aqueous solution. For soluble $Tr\alpha$, little Tr^{2+} can be partitioned into $M\alpha$ even though Tr^{2+} and M^{2+} may be “compatible.” The relative contributions from the first and second term in Eqn. (31) to K_D are illustrated in Figure 6.

For the partitioning between barite and aqueous solutions, the sequence of partitioning into barite, from favorable to unfavorable, is Ra^{2+} , Pb^{2+} , Eu^{2+} , Sr^{2+} , Ca^{2+} , Cd^{2+} , Mn^{2+} , Fe^{2+} , Zn^{2+} , Co^{2+} , Cu^{2+} , Mg^{2+} , Ni^{2+} , and Be^{2+} . Gaines et al. (2000) summarized that up to 6% of $CaSO_4$ can enter into $BaSO_4$, and a minor substitution of Fe^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+} , and Hg^{2+} occurs in natural barite. Due to the smaller size of Sr^{2+} , the formation of solid solutions with smaller divalent metals is more likely. The predicted sequence of partitioning into celestine, from favorable to unfavorable, is Ra^{2+} , Pb^{2+} , Eu^{2+} , Sr^{2+} , Ca^{2+} , Cd^{2+} , Mn^{2+} , Fe^{2+} , Zn^{2+} , Co^{2+} , Cu^{2+} , Mg^{2+} , Ni^{2+} , and Be^{2+} .

6. CONCLUDING REMARKS

“Minerals are invariably solid solutions” (Garrels and Christ, 1965). The incorporation of trace elements into major or common minerals has been studied extensively, primarily as a way of investigating temperatures and fluid compositions in sediment diagenesis, ore deposits, igneous and metamorphic rocks, and trace metal cycling in geological systems and processes. The interest in coprecipitation has been renewed in recent years

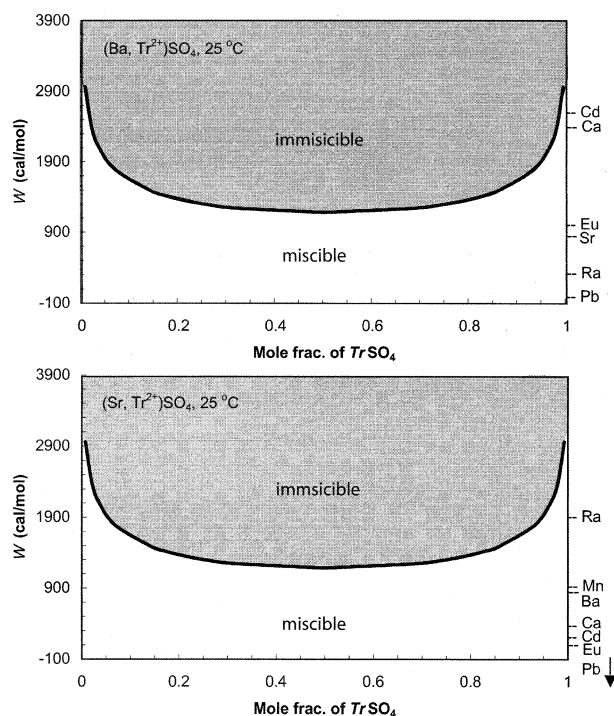


Fig. 5. Calculated miscibility gaps at 25°C. The intersects between the solid curve and W values (vertical axis) show the miscibility gaps (shaded area) for the respective metals labeled on right. For example, in the lower diagram, extending a line from the W value of 1931 cal/mol labeled Ra (radium) from right to the left covering the whole mole fraction of RaSO_4 from 0 to 1, and this line corresponds to a horizontal tie-line drawn at a fixed temperature in the conventional T - X binary phase diagram. The shaded segment of the line, about between 5 and 95% RaSO_4 , is the miscibility gap. In other words, at 25°C and 1 bar, celestine can incorporate up to 5% RaSO_4 , and RaSO_4 can incorporate up to 5% for the SrSO_4 .

because of the potential environmental significance of trace contaminants in solids. However, the prevailing approach to the coprecipitation problem is the use of partitioning coefficients, which are empirical and phenomenological parameters, seldom applicable outside in the range of conditions under which they are measured.

A comprehensive or integrated approach to this topic should include aqueous speciation and complexation, standard state and mixing thermodynamic properties of the solids and solid solutions, and precipitation and dissolution kinetics. However, excess thermodynamic properties for many important solid solutions are lacking. As shown for the barite isostructural family in this study, as well as reviews by Glynn (2000) and Hanor (2000), the available experimental data and analyses of natural minerals were obtained over a long period of time, span a wide range of qualities, and often conflict with each other. This study attempts to provide a theoretical evaluation of coprecipitation and fundamental data of binary mixing properties in the barite isostructural family. Although the approach present in this study is an improvement over the prevailing use of partitioning coefficients and the ideal solid solution assumption in environmental and geological studies, the results are

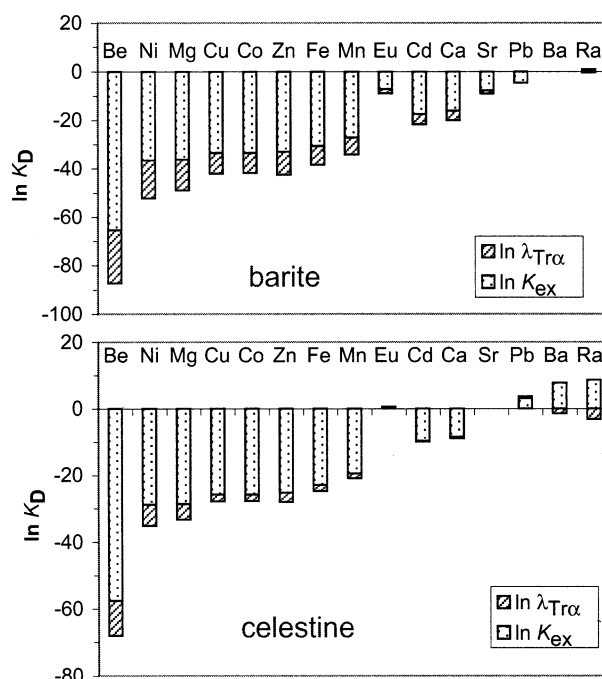


Fig. 6. Relative contributions to the partition of Tr^{2+} between barite or celestine and an aqueous solution. See Eqn. 31 for reference. K_{ex} stands for the equilibrium constant for (exchange) reaction (2) and is equal to $\left(\frac{K_{\text{sp}}^{M\alpha}}{K_{\text{sp}}^{\text{Tr}\alpha}}\right)$.

preliminary. Careful experiments are needed to study these important solid solutions.

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