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A comparison of standard thermodynamic properties and solubility data for baryte, $Ba^{2+}_{(aq)}$ and $SO_4^{2-}_{(aq)}$

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ABSTRACT

The thermodynamic solubility product for baryte, determined at standard conditions, from data in commonly used compilations, was compared with published experimental solubility products for baryte and with the solubility products from databases used by the *PHREEQC* geochemical speciation code and *MultiScale*, which is often used by oil companies to predict or describe baryte scaling. The values in the various databases agree well with experimental data ($10^{-10.05}$–$10^{-9.96}$; Melcher, 1910; Neuman, 1933; Templeton, 1960; Davis and Collins, 1971; Blount, 1977; Felmy *et al.*, 1990), which agree within uncertainty with the values presented in the compilations of Robie *et al.* (1979), Wagman *et al.* (1982), Lide (2005), Raju and Atkinson (1988), as well as Nordstrom and Munoz (1994), whose values have the least uncertainty. In solutions of 50% seawater mixed with 50% reservoir formation waters, the data predict baryte supersaturation, both at standard temperature and at the temperatures expected in the reservoir, completely consistent with field observations. This provides confidence that the Pitzer approach for activity correction and the database is valid for investigations of baryte precipitation rates in high ionic strength solutions.

Introduction

BARIUM (Ba^{2+}) is common in silicate minerals and is released to solution during weathering (Kastner, 1999; Hanor, 2000). Sulfate (SO_4^{2-}) is the most stable and most abundant sulfur species in oxidizing environments (Ivanov, 1981). Consequently, Ba^{2+} and SO_4^{2-} concentrations exceed baryte ($BaSO_4$) solubility, resulting in its formation in a variety of environments such as in sedimentary basins, at seafloor hydrothermal vents and in anthropogenic environments (Hanor, 2000). Surface seawater is supersaturated with respect to calcite (Mackenzie and Andersson, 2013) but is typically undersaturated with respect to baryte (Chow and Goldberg, 1960). Baryte approaches saturation as depth increases (Wolgemuth and Broecker, 1970). Although surface seawater is undersaturated, it often contains pelagic baryte particles, some of which are interpreted to have formed *in situ*, where the saturation state locally exceeds its solubility product (Hanor, 2000). The presence of baryte in sediments provides information about the geological processes that occurred during sedi-

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mentation (Griffith and Paytan, 2012) and the biogeochemical cycles that controlled concentration and behaviour (von Allmen *et al.*, 2010). Sometimes, baryte occurs as a result of human activity, most notably during petroleum production. For oil production, seawater is often injected into reservoirs but where pore solutions contain dissolved barium, the increase in sulfate concentration that results from seawater injection, precipitates baryte (Jordan *et al.*, 2008). Baryte scaling can completely block pore throats, decreasing permeability and in some cases, destroying the reservoir.

Several sets of thermodynamic property data for baryte and aqueous barium and sulfate have been compiled since the 1930s (Latimer *et al.*, 1933; Helgeson, 1969; Robie *et al.*, 1979; Wagman *et al.*, 1982; Raju and Atkinson, 1988; Nordstrom and Munoz, 1994; Robie and Hemingway, 1995; Lide, 2005) and a number of geochemical speciation codes are also available that include databases with baryte solubility constants (Crawford, 1999). One example is the open-access computer code *PHREEQC*, which features its own database as well as databases from other sources (Parkhurst and Appelo, 2013). Another licensed computer code, designed specifically for predicting scaling in the oil industry, is *MultiScale* (Scale Consult, 2006).

TABLE 1 (*contd. opposite*). Summary of compiled published stadard-state thermodynamic properties for baryte (BaSO$_4$) and the free ions barium (Ba^{2+}) and sulfate (SO$_4^{2-}$).

Reference	BaSO$_{4(s)}$			Ba$^{2+}_{(aq)}$		
	S^o (J·mol^{-1}K^{-1})	ΔH_f^o (kJ·mol^{-1})	ΔG_f^o (kJ·mol^{-1})	S^o (J·mol^{-1}K^{-1})	ΔH_f^o (kJ·mol^{-1})	ΔG_f^o (kJ·mol^{-1})
Helgeson (1969)				12.6[*e]	−538.35[*e]	
Robie *et al.* (1979)	132.21[a] ±1.68	−1473.19[b] ±2.00	−1362.19[b] ±2.60	9.60[b] ±1.70	−537.64[b] ±0.24	−560.74[b] ±0.24
Wagman *et al.* (1982) and Lide (2005)	132.2	−1473.2	−1362.2	9.6	−537.64	−560.77
Raju and Atkinson (1988)	132.2[b]	−1473.19[b]	−1362.31[b]	9.6[b]	−537.71[b]	−560.93[b]
Nordstrom and Munoz (1994)	128.6[c] ±2.0	−1468.3[c] ±2.5	−1356.3[c] ±2.6	8.4[f] ±2.0	−532.5[f] ±2.5	−555.4[f] ±2.6
Robie and Hemingway (1995)	132.2[d] ±1.6	−1473.6[d] ±2.0	−1362.5[d] ±2.6	8.40[f] ±1.00	−532.5[f] ±2.0	−555.4[f] ±2.0

Standard state: 298.15 K, 1 bar and assuming unit activity and 1 molal ionic strength. Reference state for elemental barium and sulfur (orthorhombic) for ΔH_f^o and ΔG_f^o is zero at standard state and for S^o is zero at absolute zero temperature. S^o: absolute standard molar entropy; ΔH_f^o: standard enthalpy of formation; ΔG_f^o: standard Gibbs free energy of formation; ΔS_r^o: change in standard entropy of the reaction; ΔH_r^o: change in standard enthalpy of the reaction; ΔG_r^o: change in Gibbs free energy of the reaction; log K: logarithm of the thermodynamic solubility product.
Values given in *italic* were calculated in the present study.
Approach a: calculated change in Gibbs free energy of the reaction using the entropy and enthalpy of the reaction: $\Delta G_r^o = \Delta H_r^o - T\Delta S_r^o$, where $\Delta H_r^o = \Delta H_{f,Ba}^o + \Delta H_{f,SO_4}^o - \Delta H_{f,BaSO_4}^o$; $\Delta S_r^o = S_{Ba}^o + S_{SO_4}^o - S_{BaSO_4}^o$.
Approach b: calculated change in Gibbs free energy of the reaction using formation Gibbs free energy of the reactants and the product: $\Delta G_r^o = \Delta G_{f,Ba}^o + \Delta G_{f,SO_4}^o - \Delta G_{f,BaSO_4}^o$.
Thermodynamic solubility of baryte was determined using: log K = $- \Delta G_r^o/(\ln(10)RT)$, where T represents the standard temperature, 298.15 K and R is the molar gas constant, 8.3144621(75) J·mol^{-1}K^{-1} (NIST, 2014).
±: expanded uncertainty at the 95% confidence level.
*: converted from the original data in cal mol^{-1}deg^{-1} with a thermochemical calorie 4.184 J.
Data from: [a] Kelley and King (1961); [b] Parker *et al.* (1971); [c] Nordstrom and Munoz (1994); [d] DeKock (1986); [e] Latimer (1952); [f] Busenberg and Plummer (1986); [g] Wagman *et al.* (1968); [h] Cox *et al.* (1989).

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Traditionally, the thermodynamic solubility product at standard state serves as the basis for extrapolation to other conditions. Furthermore, modelling of mineral dissolution and precipitation rates relies on equations that incorporate the difference between actual activities and those expected at equilibrium (Palandri and Kharaka, 2004). Small deviation and inconsistency in reported values for stability are often amplified when one seeks to model more complex systems. Thus, an internally consistent and accurate set of thermodynamic data is required, especially for extrapolating from standard conditions to solutions at reservoir temperature and the ionic strength of seawater or formation water.

The aims of this study were to: (1) assess published thermodynamic data for baryte and the

Thermodynamic properties

Six thermodynamic compilations that include the thermodynamic properties for baryte, free barium and sulfate ions at standard conditions (1 bar, 298.15 K and assuming unit activity and 1 molal ionic strength) are summarized in Table 1 (all uncertainties in this work are reported with two standard deviations). All these data sets were derived from experimental and theoretical studies, where the sources have been indicated in the table footnotes.

Free barium ion, Ba²⁺

Free barium ion, Ba^{2+}

The only experimental data available for the entropy of free barium is from Brown *et al.*

TABLE 1 (*contd.*).

| SO_4^{2-} (aq) | | | BaSO$_{4(s)}$ = Ba^{2+}(aq) + SO$_4^{2-}$(aq) | | | | | |
| | | | a | | | | b | |
S^o (J·mol^{-1}K^{-1})	ΔH_f^o (kJ·mol^{-1})	ΔG_f^o (kJ·mol^{-1})	ΔS_r^o (J·mol^{-1}K^{-1})	ΔH_r^o (kJ·mol^{-1})	ΔG_r^o (kJ·mol^{-1})	Log K	ΔG_r^o (kJ·mol^{-1})	Log K
20.1*[g]	−909.27*[g]	−744.63*[g]	−99.6*	25.7*	55.38	−9.70		
20.00[g] ±1.70	−909.27[g] ±0.24	−744.63[g] ±0.24	−102.6 ±3.0	26.3 ±2.0	56.9 ±2.2	−9.96 ±0.39	56.8 ±2.6	−9.95 ±0.46
20.1	−909.27	−744.53	−102.5	26.3	56.9	−9.97	56.9	−9.97
20.1[b]	−909.27[b]	−744.54[b]	−102.5	26.2	56.8	−9.95	56.8	−9.96
18.5[h] ±0.4	−909.3[h] ±0.4	−744.0[h] ±0.4	−101.7 ±1.0	26.5 ±0.5	56.9 ±1.8	−9.97 ±0.32	57.1 ±1.8	−10.00 ±0.32
18.5[h] ±0.8	−909.3[h] ±0.8	−744.0[h] ±0.8	−105.3 ±2.0	31.8 ±3.0	62.4 ±3.0	−10.93 ±0.53	63.1 ±3.4	−11.05 ±0.59

free barium and sulfate ions at standard-state conditions and compare them with published experimental solubility data and with the solubility constants used in the databases of speciation models; and (2) to suggest the most consistent and accurate parameters for the Ba^{2+}–SO$_4^{2-}$–H$_2$O system that can be used as a reliable starting point for geochemical speciation calculations and for predicting solubility relationships in pure systems. Finally, we used the data to predict the saturation state for sulfate minerals from solutions formed of seawater mixed with formation water, from several reservoirs where baryte scaling had been observed under field conditions.

(1936). The entropy of barium was originally obtained (9.2 J·mol^{-1}·K^{-1}) from the heat of the dissolution, measured on high-purity barium chloride dihydrate utilizing high-purity solids. Later recalculations by Latimer *et al.* (1938) and Kelley and King (1961) derived the same value (9.6 ± 1.2 J·mol^{-1}·K^{-1}).

For the Ba^{2+} enthalpy of formation, two experimental values are available: Fitzgibbon *et al.* (1973) and Cordfunke *et al.* (1990). Fitzgibbon *et al.* determined enthalpy using calorimetry (−535.3 ± 1.7 kJ·mol^{-1}) in a solution of Ba^{2+} made from high-purity metal. Cordfunke *et al.* calculated the enthalpy of Ba^{2+}

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(-534.75 ± 1.74 kJ·mol^{-1}) using their measured enthalpy of formation for barium chloride as well as the thermodynamic properties for the chloride ion from Cox *et al.* (1989). The value (-537.64 kJ·mol^{-1}) compiled by Parker *et al.* (1971) and Wagman *et al.* (1982) is close to the experimental data reported by Fitzgibbon *et al.* (1973) and Cordfunke *et al.* (1990).

The values for entropy and enthalpy for Ba^{2+} published by Helgeson (1969) were taken from Latimer (1952). These values are higher than those of the other data sets (Table 1).

Finally, a new set of thermodynamic properties for Ba^{2+}, derived from solubility data of witherite, BaCO$_3$, were proposed later by Busenberg and Plummer (1986). They fitted the equilibrium constant of witherite to experimental solubility data between 278 K and 353 K, using recalculated thermodynamic data from carbonate species presented by Busenberg *et al.* (1984).

Free sulfate ion, SO$_4^{2-}$

Based on many experimental studies, the entropy of sulfate was reported by Latimer *et al.* (1938; 18.4 ± 4.2 J·mol^{-1}·K^{-1}) and, later, by Cox *et al.* (1989; 18.50 ± 0.40 J·mol^{-1}·K^{-1}). These values agree within uncertainty.

The entropy of sulfate from Wagman *et al.* (1968) is greater than that from Cox *et al.* (1989) and also agrees with the above values within uncertainty.

The enthalpy of formation of sulfate from the six compilations of thermodynamic properties agrees within the uncertainty with the experimental value determined by Johnson and Sunner (1963; -909.34 ± 0.45 kJ·mol^{-1}).

Baryte, BaSO$_4$

The only experimental data available for baryte entropy were published by Latimer *et al.* (1933). They used vacuum bomb calorimetry to measure the heat capacity on high-purity solids and originally obtained a value of 131.84 ± 0.07 J·mol^{-1}·K^{-1}. This value was later extrapolated to standard conditions by Kelley and King (1961; 132.2 ± 0.8 J·mol^{-1}·K^{-1}) using the third law of thermodynamics, which states that the entropy for a pure crystal at absolute zero temperature should be zero. Later estimates by DeKock (1986), which included Latimer *et al.* (1933) and higher-temperature heat-capacity measurements and considered two independent baryte formation reactions from the elemental

species (Ba$_{(s)}$, O$_{2(g)}$, S$_{(g)}$ or S$_{(s)}$), resulted in the same value as that estimated by Kelley and King (1961).

For the enthalpy of baryte, the first published value is from Latimer (1952; -1465.2 kJ·mol^{-1}). Parker *et al.* (1971) included this value in their compilation and extrapolated from high-temperature data to a standard-state value of -1466.5 kJ·mol^{-1} but no information about newer experimental studies was provided. Later, Robie *et al.* (1979) and DeKock (1986) adjusted this value slightly (-1473.2 kJ mol^{-1}). Recently, Majzlan *et al.* (2002) determined the enthalpy of formation using high-temperature oxide melt calorimetry. They obtained values for: synthetic baryte, -1459.7 ± 3.7 kJ·mol^{-1}, Colorado natural baryte, -1464.2 ± 3.7 kJ·mol^{-1}, and South Carolina natural baryte, -1464.9 ± 3.7 kJ·mol^{-1}. Values for the two natural samples agree within uncertainty with data presented by Nordstrom and Munoz (1994).

From thermodynamic properties for the barium ion (Busenberg and Plummer, 1986) and solubility measurements, Nordstrom and Munoz (1994) obtained values (S^o: 128.6 J·mol^{-1}K^{-1}; ΔH_f^o: -1468.3 kJ·mol^{-1}) that are lower than those obtained calorimetrically (S^o: 132.2 J·mol^{-1}K^{-1}; ΔH_f^o: -1473.2 kJ·mol^{-1}) by the other compilations from Table 1.

Solubility data

There are many values for the thermodynamic solubility product for baryte. However, some are based on recalculation from data previously published in compilations (Egorov and Titova, 1962; Sillén and Martell, 1964; Khodakovsky *et al.*, 1966; Malinin *et al.*, 1969; Smith and Martell, 1976; Monnin and Galinier, 1988; Kaasa, 1998), and in reports of experiments at temperatures other than 298.15 K (Uchameyshvili *et al.*, 1966; Schulien, 1987; Jiang, 1996). The results of work at non-standard conditions are not reviewed here.

Table 2 presents the thermodynamic solubility product for baryte extrapolated to infinite dilution from solubility measurements conducted at standard temperature and pressure. Although a variety of methods has been used, the values determined (log K: -10.05 to -9.96) are in surprisingly good agreement, where the total difference is only 19%. For the more recent studies, which use more accurate techniques for determining aqueous ion concentrations, all are within the limits of experimental error.

TABLE 2. Published experimental thermodynamic solubility product for baryte extrapolated from solubility data to standard-state conditions: 1 bar, 298.15 K and pure water, i.e. ionic strength (IS = 0).

Reference	Analytical method	Activity coefficient estimation approach	log K
Melcher (1910)	Conductivity	Pitzer ion interaction	−10.00[a]
Neuman (1933)	Conductivity	Linear relationship between solubility and square root of the ionic strength	−10.04
Templeton (1960)	Spectroscopy	Debye-Hückel	−9.96
Davis and Collins (1971)	Liquid scintillation	Linear relationship between solubility and square root of the ionic strength	−9.96
Blount (1977)	X-ray fluorescence	Extended Debye-Hückel	−9.98
Felmy et al. (1990)	ICP-AES	Pitzer ion interaction	−10.05±0.05[b]*

[a]: calculated in this study using a mean activity coefficient for $BaSO_4$ of 0.970, which is estimated using *PHREEQC* Version 3 using the Pitzer.dat.
[b]: accepted value derived from $NaClO_4$ electrolyte background.
ICP-AES: Inductively coupled plasma-atomic emission spectroscopy.
*: Later documentation on the NONLIN software developed by Felmy gives uncertainties as 1 standard deviation. We assume that the uncertainty in Felmy et al. (1990) is reported at that level.

Comparison of the thermodynamic properties and solubility data

The Gibbs free energy and the thermodynamic solubility product for baryte dissolution, $BaSO_{4(s)}$ = $Ba^{2+}_{(aq)}$ + $SO_4^{2-}_{(aq)}$, were calculated for each compilation presented in Table 1 using two approaches: from the entropy and enthalpy data (a), and from the Gibbs free energy of formation (b). The values for baryte using both approaches, from the compilations of Robie et al. (1979), Wagman et al. (1982) and Lide (2005), Raju and Atkinson (1988) and Nordstrom and Munoz (1994) agree with each other within their uncertainty because, with the exception of the Nordstrom and Munoz (1994) compilation, they originate from the same sources. They also agree with the thermodynamic solubility product determined experimentally from solubility measurements (Fig. 1). The estimates of Helgeson (1969) are slightly higher (−9.70), whereas calculations from the data of Robie and Hemingway (1995) result in significantly lower values (−10.93 and −11.05).

Helgeson (1969) was a pioneer in using computer modelling to estimate consistent sets of thermodynamic properties from experimental data for a large number of different elements and systems to get the overall best fits. His estimate for baryte is reasonably close to the experimental

values but is still off by a quarter of an order of magnitude. Although the sulfate data from Helgeson (1969) are similar to those presented by Robie et al. (1979), he obtained a higher log K because his enthalpy estimate for barium was too high.

Robie and Hemingway (1995) attempted to improve their data by incorporating updated thermodynamic properties for Ba^{2+} from Busenberg and Plummer (1986), resulting in values that are lower than those reported from other work. Recently, Wolery and Sutton (2013) identified discrepancies for the barium properties between the compilations from Robie et al. (1979) and Robie and Hemingway (1995) but they did not explain the origin of the discrepancies. Robie and Hemingway (1995) did not assess the internal consistency of the data set with baryte and sulfate. Consequently, the solubility product determined from their data is lower than that of Robie et al. (1979). The solubility-data deviations are larger than those from calorimetric measurements so the uncertainty associated with the Ba^{2+} data reported by Robie and Hemingway (1995) is greater than that reported by Robie et al. (1979).

The compilation from Robie et al. (1979), derived from calorimetric measurements, is reliable and consistent but contains larger uncertainties than the Nordstrom and Munoz
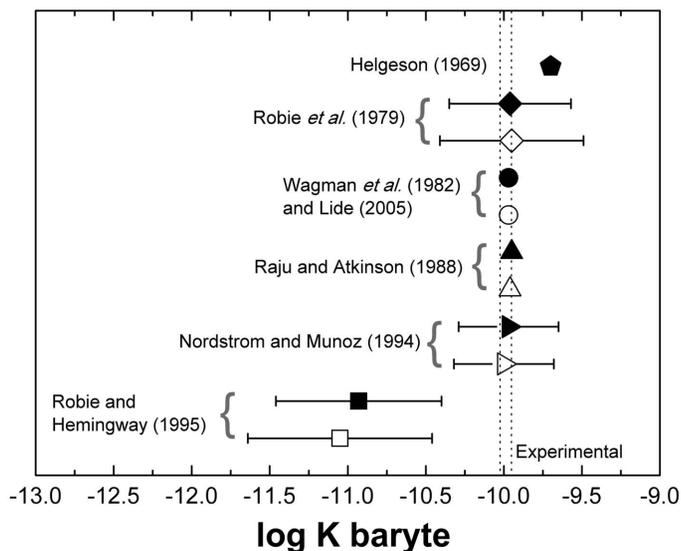
FIG. 1. Calculated log K for baryte solubility at the 95% confidence limit, determined from the Gibbs free energy of reaction, derived from two approaches: (a) from enthalpy and entropy (filled symbols); and (b) from Gibbs free energy of formation (open symbols). Values from Helgeson (1969), Wagman *et al.* (1982), Lide (2005) and Raju and Atkinson (1988) were reported without uncertainty. The double dotted vertical bar represents the range of experimental values for the logarithm of the thermodynamic solubility product for baryte (log K: -10.05 to -9.96).

(1994) compilation which has also been updated with Ba^{2+} data from Busenberg and Plummer (1986) and the baryte data were adjusted with calculations from barium and sulfate thermo-dynamic properties and baryte solubility. Nordstrom and Munoz used a combination of thermodynamic data derived from a variety of experimental methods and generated a consistent data set for the baryte system after assessing the internal consistency of the newer and previously existing data.

Geochemical speciation databases

For the baryte system, eight of the nine *PHREEQC* databases (Parkhurst and Appelo, 2013; Version 3; i.e. amm.dat, llnl.dat, minteq.dat, minteq.v4.dat, phreeqc.dat, pitzer.dat, sit.dat and wateq4f.dat), include the species: Ba^{2+}, $BaOH^+$, SO_4^{2-} and HSO_4^-. The database iso.dat does not include any Ba^{2+} species. The *MultiScale* database includes Ba^{2+}, SO_4^{2-} and HSO_4^- (Scale Consult, 2006; Version 8).

The origin of the thermodynamic data included in the databases for the common speciation codes is often difficult to track. For wateq4f.dat, the equilibrium constant for baryte dissolution (log K:

-9.97), the change in standard enthalpy of the baryte reaction (ΔH_r^o: 26.57 kJ·mol^{-1}) and the analytical expression for the temperature depen-dence have all been adopted from Nordstrom *et al.* (1990), which is based on data reported by Blount (1977). Three other *PHREEQC* databases, amm.dat, phreeqc.dat and pitzer.dat, also use log K = -9.97.

For llnl.dat, sit.dat, minteq.dat and minteq.v4.dat, it was not possible to track the origin of the baryte data. In these databases, log K is similar but not the same, -9.9711, -9.97, -9.976 and -9.98. The first three, llnl.dat, sit.dat and minteq.dat, have ΔH_r^o close to 26.57 kJ·mol^{-1}, presented by Nordstrom *et al.* (1990), with values of 25.9408 kJ·mol^{-1}, 26.46 kJ·mol^{-1} and 26.28 kJ·mol^{-1}. Minteq.v4.dat, however, uses a lower ΔH_r^o value, 23 kJ·mol^{-1}. In conclusion, all of the databases associated with *PHREEQC* have very similar log K for baryte dissolution at standard temperature but at non-standard temperature, the log K using minteq.v4.dat would differ markedly. For example, at 373.15 K, calculations with wateq4f.dat and minteq.v4.dat result in log K = -9.53 and -9.17, respectively.

The *MultiScale* speciation code does not feature a specific log K at 298.15 K for the

baryte dissolution reaction such as those associated with *PHREEQC*. Rather, it uses only an analytical expression for the temperature dependence adopted from Kaasa (1998), which is based not only on data from Blount (1977) but also on data from Templeton (1960), Jiang (1996) and Malinin *et al.* (1969). Malinin *et al.* (1969) calculated a larger value (−9.72) than Templeton (1960; −9.96) even though they used the same data source. Blount (1977) pointed out that Malinin *et al.* (1969) overcorrected their values by changing the ion-size parameter (å) at high temperature. The empirical equation used by Kaasa (1998) is the same as *PHREEQC* but with different analytical coefficients. The log K calculated at standard temperature using the Kaasa (1998) expression and *MultiScale* code results in the same value (−9.93), which differs slightly from most of the data in the thermodynamic compilations (Table 1) and those produced from experiments (Table 2) but still agrees within uncertainty.

Application of thermodynamic properties to other sulfate minerals

Anhydrite ($CaSO_4$) is a common mineral in evaporite deposits, precipitated from highly saline brine and celestite ($SrSO_4$) and often coexists with baryte (Hanor, 2000). To evaluate the robustness of the data in the compilations by Robie *et al.* (1979) and Nordstrom and Munoz (1994), values for these minerals were calculated using the thermodynamic data for the minerals and for the free ions, Ca^{2+} and Sr^{2+}. Values calculated at standard-state conditions for anhydrite, using data from Robie *et al.* (1979) are: log K = −4.15 ± 0.79, from enthalpy and entropy (a) and log K = −4.12 ± 0.76 from Gibbs free energy (b). Using data from Nordstrom and Munoz (1994), these are log K = −4.41 ± 0.34 from enthalpy and entropy (a) and log K = −4.41 ± 0.32 from free energy (b). Calculated values for celestite, with data from Robie *et al.* (1979) are log K = −6.51 ± 0.78, derived from a and log K = −6.46 ± 0.70, from b. With data from Nordstrom and Munoz (1994), log K = −6.63 ± 0.20 (a) and log K = −6.63 ± 0.26 (b). The results agree within uncertainty with the experimental thermodynamic solubility products, for $CaSO_4$, log K = −4.62 ± 0.03 and for $SrSO_4$, log K = −6.50 ± 0.05, which were reported by Smith and Martell (1976) and with all the *PHREEQC* databases for anhydrite

and celestite, with one exception, i.e. the llnl.dat (log K: −5.6771) for celestite. The uncertainty determined with data from the Robie *et al.* (1979) compilation is greater than that obtained with the data of Nordstrom and Munoz (1994).

Sulfate-mineral solubility predictions in reservoir conditions

The thermodynamic properties of the free ions and the sulfate minerals published by Nordstrom and Munoz (1994) allow us to evaluate the likelihood of precipitation from solutions where composition is known. During oil recovery, seawater, which contains sulfate, is injected into a reservoir where the formation waters often contain barium (Jordan *et al.*, 2008). The present authors used the thermodynamic data to predict solubility for baryte, celestite and anhydrite, for a selection of reservoir fluids. We set the calculations to mix seawater with formation water in equal proportions. Figure 2 shows phase diagrams for the Ba^{2+}–Ca^{2+}–SO_4^{2-} and Sr^{2+}–Ca^{2+}–SO_4^{2-} systems using previously published data, for the temperature of the formation water as well as at standard temperature (data from Yuan *et al.*, 1994). We also predicted solubility and plotted stability diagrams for seawater mixtures with formation water from several other producing reservoirs in the North Sea Basin. In all cases, baryte precipitation was predicted in 50:50 mixtures of seawater and formation water, in horizons where field evidence indicated baryte formation.

It is not possible to plot all of the data on one set of diagrams. For each formation water, new diagrams are required because the differences in composition and ionic strength significantly shift the solubility limits. As temperature increases, the baryte stability field decreases, whereas the fields for anhydrite and celestite increase, as expected, from the value of the ΔH_r^o for dissolution of these phases (Table 1). From the activities (a_x) derived from the *PHREEQC* geochemical speciation program, and using the pitzer.dat database, we made diagrams to represent the mixed water for conditions where temperature was 298 K and above 350 K. Figure 2 shows that the waters are highly supersaturated with respect to baryte, marginally supersaturated with respect to celestite and undersaturated with respect to anhydrite. The calculations made with the Pitzer database predict a significant thermodynamic drive for baryte precipitation when sea water mixes with forma-
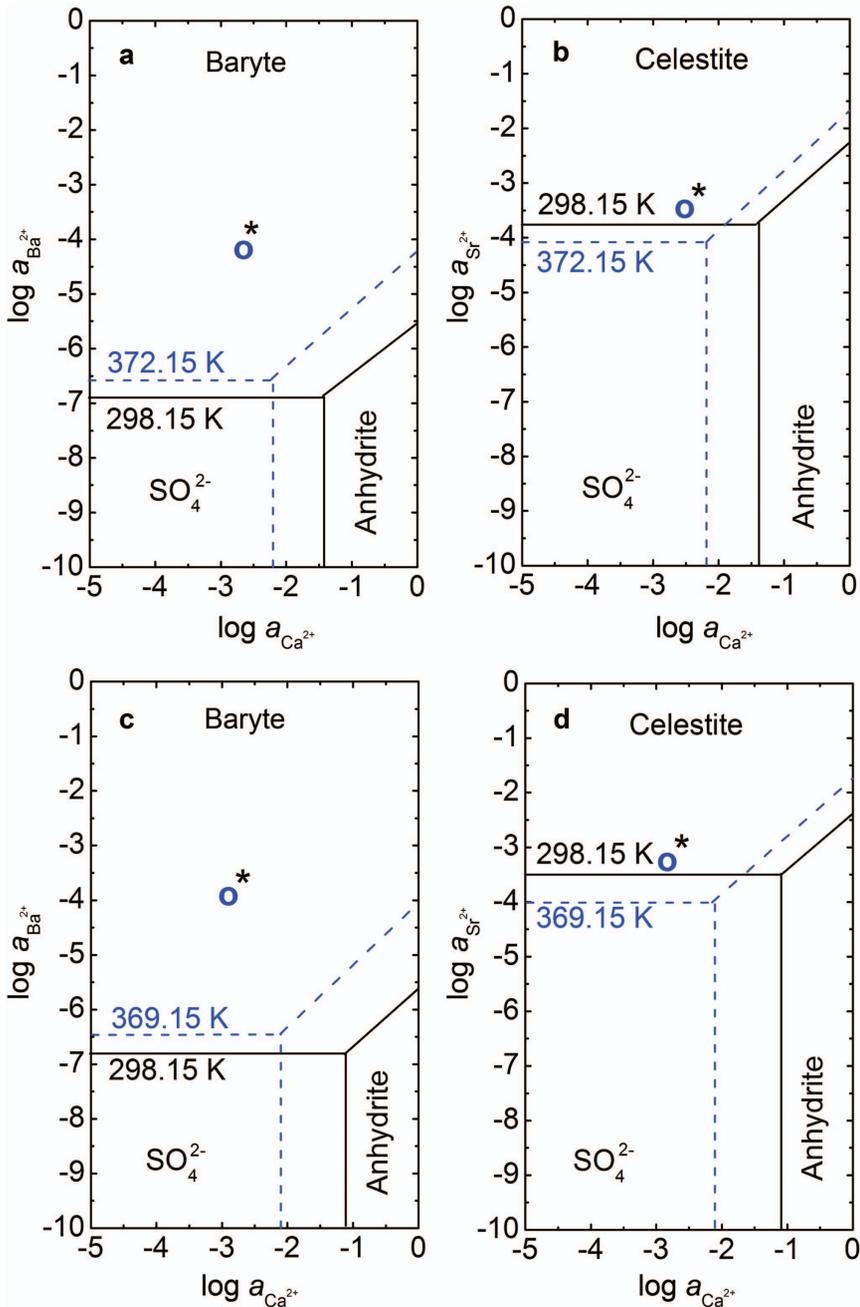
FIG. 2. Activity-activity diagram for the Beryl and Forties Field: (*a*) The Ba^{2+}–Ca^{2+}–SO_4^{2-} and (*b*) the Sr^{2+}–Ca^{2+}–SO_4^{2-} systems at atmospheric pressure, 298.15 K (with log $a_{SO_4^{2-}}$ = −3.011) and 372.15 K (with log $a_{SO_4^{2-}}$ = −2.975) for a solution of equal portions of seawater and Beryl Field formation water. The bold star represents the mixed water composition at 298.15 K (c) and the blue open circle at 372.15 K. (*c*) and (*d*) Similar diagrams for the same systems with solubility predicted for temperatures of 298.15 K (with log $a_{SO_4^{2-}}$ = −3.157; bold star) and 369.15 K (with log $a_{SO_4^{2-}}$ = −3.088; blue open circle) for a solution of equal portions of seawater and Forties Field formation water (data from Yuan *et al.*, 1994).

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tion water, which is completely consistent with the field observations.

Conclusions

More recent experimental studies using modern methods for determination of aqueous concentrations report a thermodynamic solubility product for baryte of $10^{-10.05}$ to $10^{-9.96}$ at standard conditions. These values agree with those calculated from thermodynamic properties compiled by Robie *et al.* (1979), Wagman *et al.* (1982), Lide (2005), Raju and Atkinson (1988) as well as Nordstrom and Munoz (1994), whose values have the smallest uncertainty.

Thermodynamic solubility for baryte at standard conditions from *PHREEQC* databases: amm.dat, llnl.dat, minteq.dat, minteq.v4.dat, phreeqc.dat, pitzer.dat, sit.dat and waterq4f.dat, agrees with the more recent experimental data.

The data predict baryte precipitation when seawater is mixed with formation water from a number of reservoirs, reflecting observations in the field. This consistency of the thermodynamic data for high-salinity solutions at typical reservoir conditions indicates that the data can be combined with Pitzer calculations of activity coefficients and used for further experiments where rates of reaction will be examined.

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