



Solubility product of siderite (FeCO_3) as a function of temperature (25–250 °C)

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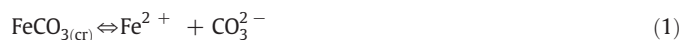
ABSTRACT

The solubility of natural siderite was investigated from 25 to 250 °C in 0.1 mol kg⁻¹ NaCl aqueous solutions using a hydrogen–electrode concentration cell, which provided continuous *in situ* measurement of hydrogen ion molality. Iron(II) was analyzed by a revised Ferrozine–spectrophotometric method. The obtained apparent solubility products ($K_{\text{sp-siderite}}$) were extrapolated to infinite dilution to generate the solubility products ($K_{\text{sp}^{\circ}\text{-siderite}}$), allowing calculation of the thermodynamic properties of siderite. Of all the temperature functions tested, the equation giving a reliable fit of our data in the investigated temperature range (25–250 °C) has the following form: $\log_{10} K_{\text{sp}^{\circ}\text{-siderite}} = a + b \cdot (T/K) + c \cdot (T/K)^{-1} + d \cdot \log_{10} (T/K)$ with: $a = 175.568$, $b = 0.0139$, $c = -6738.483$ and $d = -67.898$. Based on this equation and its first and second derivatives with respect to T , we were able to derive values for the Gibbs energy of formation: $\Delta_f G_{298.15}^{\circ} = (-680.71 \pm 2)$ kJ mol⁻¹, enthalpy of formation: $\Delta_f H_{298.15}^{\circ} = (-749.59 \pm 2)$ kJ mol⁻¹, entropy: $S_{298.15}^{\circ} = (109.54 \pm 2)$ J mol⁻¹ K⁻¹ and heat capacity: $C_{p,298.15}^{\circ} = (83.26 \pm 2)$ J mol⁻¹ K⁻¹ of siderite (uncertainties are 3σ). The values of $\Delta_f G_{298.15}^{\circ}$ and $\Delta_f H_{298.15}^{\circ}$ are in very good agreement with the values reported by Robie et al. [Robie, R.A., Haselton, H.T. Jr., Hemingway, B.S., 1984. Heat capacities and entropies of rhodochrosite (MnCO_3) and siderite (FeCO_3) between 5 and 600 K. *Am. Mineral.* 69, 349–357] and Chai and Navrotsky [Chai, L., Navrotsky, A., 1994. Enthalpy of formation of siderite and its application in phase equilibrium calculation. *Am. Mineral.* 79, 921–929], respectively. The density model [Anderson, G.M., Castet, S., Schott, J., Mesmer, R.E., 1991. The density model for estimation of thermodynamic parameters of reactions at high temperatures and pressures. *Geochim. Cosmochim. Acta* 55, 1769–1779] reproduced correctly our experimental data and allowed the extrapolation of the siderite solubility product up to 350 °C by using our values of the Gibbs energy and enthalpy of formation of siderite combined with its entropy and the heat capacity equation given by Robie et al. [Robie, R.A., Haselton, H.T. Jr., Hemingway, B.S., 1984. Heat capacities and entropies of rhodochrosite (MnCO_3) and siderite (FeCO_3) between 5 and 600 K. *Am. Mineral.* 69, 349–357].

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1. Introduction

Iron is the fourth most abundant metal on Earth occurring in a variety of rock and soil minerals in oxidation states (II) and (III). Under anoxic conditions, the concentration of ferrous iron (Fe(II) or Fe^{2+}) is frequently controlled by the ferrous carbonate, siderite ($\text{FeCO}_{3(\text{cr})}$), according to a reaction that can be expressed as:



Siderite is commonly found in hydrothermal veins associated with fluorite, galena and barite and as concretions in shales and sandstones (Mozley, 1989; Munoz et al., 1999; Munoz et al., 2005). Siderite has also been identified in extraterrestrial materials, such as meteorites

(Romanek et al., 1994; Valley et al., 1997; Treiman and Romanek, 1998) and interplanetary dust particles (Keller et al., 1994). Siderite formation is known to be facilitated by both mesophilic and thermophilic iron reducing bacteria (e.g., Zhang et al., 2001), and has been interpreted to be microbially mediated in many natural environments (see Mortimer and Coleman, 1997).

Lately, siderite has also been mentioned as potential CO₂ mineral trapping in numerous computer simulations of CO₂ geological sequestration (e.g., Johnson et al., 2002; Xu et al., 2003; Palandri and Kharaka, 2005; Palandri et al., 2005; Zerai et al., 2006). This was confirmed in supercritical CO₂–brine–rock experiments performed at 200 °C by Kaszuba et al. (2005) and in the study of Palandri et al. (2005). Glauconitic, arkosic and illitic sediments are discussed in these previous studies for their potential to trap CO₂ in siderite, ankerite ($\text{CaFe}(\text{CO}_3)_2$), calcite (CaCO_3), magnesite (MgCO_3) or eventually dawsonite ($\text{NaAlCO}_3(\text{OH})_2$). However, these sediments, in particular Fe(II)-bearing glauconitic beds, are generally of limited thickness and geographical occurrence as oppose to other iron-rich sediments (including redbeds), which in addition present great

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Table 1
Literature values of the siderite solubility product K_{sp}° -siderite (Eq. (1)).

t (°C)	$\log_{10}K_{sp}^{\circ}$ -siderite	References
30	-10.46	Smith (1918)
30	-10.55	Recalculated value from the data of Smith (1918) (see text)
17	-10.12	Singer and Stumm (1970)
22.5	-10.22	
25	-10.24	
30	-10.25	
20	-10.40	Bardy and Péré (1976)
50	-11.20	Reiterer et al. (1981), Extrapolated to infinite dilution by Bruno et al. (1992)
25	-10.60	Calculated by Robie et al. (1984) from Smith (1918) and Langmuir (1969)
30	-11.11	Braun (1991)
40	-11.27	
50	-11.88	
60	-12.43	
70	-12.31	
80	-12.57	
25	-10.80	Bruno et al. (1992)
25	-10.77	Greenberg and Tomson (1992)
43	-10.94	
62	-11.03	
83	-11.25	
94	-11.42	
25	-10.90	Silva et al. (2002)
25	-10.93	Ptacek and Reardon (1992)
25	-11.03	Ptacek and Blowes (1994)
25	-11.03	Jensen et al. (2002) dried crystals
25	-10.43	Jensen et al. (2002) wet crystals

thickness and high porosity and permeability. As iron must be in its ferrous oxidation state to precipitate into carbonate minerals, sedimentary Fe(III) requires a reductant, which may be organic matter, sulfur dioxide (SO₂) or hydrogen sulfide (H₂S) (see for example, Palandri et al., 2005; Palandri and Kharaka, 2005). Nevertheless, in order to model CO₂ mineral trapping in these geological reservoirs, it is essential to know precisely the solubility product and thermodynamic properties of siderite (this paper) and its dissolution/precipitation rates (see Golubev et al., 2009-this issue).

A number of previous studies have focused on the determination of the solubility product of FeCO_{3(cr)} at low temperature (<90 °C), various ionic strengths (from 0.1 to 1.0 mol kg⁻¹ NaClO₄ or 0.1 to 5.5 mol kg⁻¹ NaCl medium) and CO₂ pressure from 0.01 to 0.93 bars (e.g., Smith, 1918; Singer and Stumm, 1970; Bardy and Péré, 1976; Reiterer et al., 1981; Braun, 1991; Bruno et al., 1992; Greenberg and Tomson, 1992; Ptacek and Reardon, 1992; Ptacek and Blowes, 1994; Jensen et al., 2002; Silva et al., 2002). A summary of literature values for the solubility product of Eq. (1) is given in Table 1 and the values are reported as a function of reciprocal temperature in Fig. 1. It can be seen from this figure that the values at 25 °C are dispersed, ranging from 10^{-11.03} to 10^{-10.24}. Few values are also available for temperature greater than 30 °C, including the data of Reiterer et al. (1981) (50 °C), Braun (1991) (30–80 °C) and Greenberg and Tomson (1992) (25–94 °C), with large scatters among the values obtained from one set to the other. The standard state thermodynamic properties of siderite at 298.15 K, 1 bar are tabulated in a number of thermochemical data compilations (Wagman et al., 1982; Robie and Hemingway, 1995). Most of them are reported in Table 2, including, at absolute temperature T , the Gibbs energy of formation $\Delta_f G_{298.15}^{\circ}$, the enthalpy of formation $\Delta_f H_{298.15}^{\circ}$, the entropy $S_{298.15}^{\circ}$ and the heat capacity C_p° . Robie et al. (1984) measured the heat capacity of siderite by adiabatic calorimetry from 5 to 380 K, and by differential scanning calorimetry in the temperature range 350–550 K. The heat capacity and entropy reported by these authors at 298.15 K are 82.44 ± 0.10 J mol⁻¹ K⁻¹ and 95.47 ± 0.15 J mol⁻¹ K⁻¹, respectively. Note that this value of the heat capacity was deduced by Robie et al. (1984) from a

smoothed regression of the heat capacity data corrected for deviations from exact stoichiometry of the solid, which differed from the value that can be calculated at the same temperature from Eq. (2) below (82.25 J mol⁻¹ K⁻¹), also reported by Robie et al. (1984) and Robie and Hemingway (1995):

$$C_p^{\circ} / \text{J mol}^{-1} \text{K}^{-1} = 257.38 - 0.04620 \cdot (T / \text{K}) - 3081.9 \cdot (T / \text{K})^{-0.5} + 1.523 \cdot 10^6 \cdot (T / \text{K})^{-2} \quad (2)$$

Chai and Navrotsky (1994) determined the enthalpy of formation of siderite at 25 °C by drop calorimetric measurements of enthalpies of decomposition of FeCO_{3(cr)} at 978 and 1075 K. The value of $\Delta_f H_{298.15}^{\circ} = -750.60$ kJ mol⁻¹ obtained by these authors is in good agreement with Helgeson et al. (1978). However, the literature values of the standard enthalpy of formation differ by more than 10 kJ mol⁻¹ (see Table 2). Recently, Preis and Gamsjäger (2002) performed a critical evaluation of solubility data and enthalpy of formation of siderite and gave a new optimized value of $\Delta_f H_{298.15}^{\circ} = -752.00$ kJ mol⁻¹. They also provided support for the validity of the properties of Fe²⁺ in the survey performed by Parker and Khodakovskii (1995).

In this study, we measured the solubility products of Eq. (1) from 25 to 250 °C in 0.1 mol kg⁻¹ NaCl aqueous solutions using a hydrogen-electrode concentration cell (HECC) and re-evaluated the thermodynamic properties of siderite from these solubility measurements.

2. Materials and methods

2.1. Starting solutions and materials

All solutions were prepared from reagent grade chemicals and distilled deionized water (resistivity 0.18 MΩ m). For the test solution,

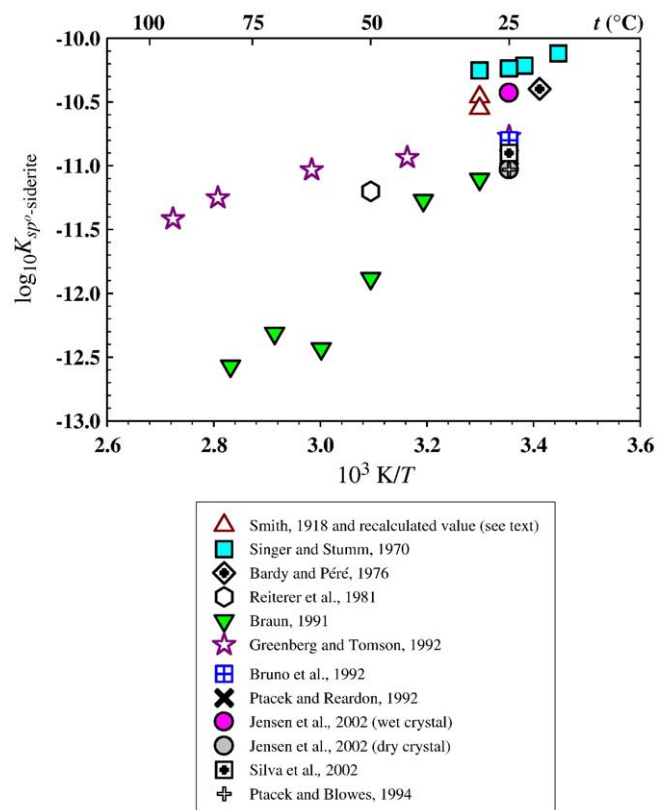


Fig. 1. $\log K_{sp}^{\circ}$ -siderite values from the literature as a function of the reciprocal of temperatures.

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