Experimental determination of barite dissolution and precipitation rates as a function of temperature and aqueous fluid composition

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Abstract

Barite dissolution and precipitation rates were investigated in closed system reactors, in which total aqueous NaCl concentrations ranged from 0 to 1.5 molal, pH from 2 to 9, and temperature from 25 to 90 °C. Measured barite dissolution and precipitation rates exhibited a reaction order of 0.2 and 1, respectively, with respect to the barite saturation state. Although these different reaction orders suggest distinctly different mechanisms for dissolution and precipitation, the rates for both processes approach equilibrium with a similar slope on a rate versus saturation state plot, consistent with the concept of micro-reversibility. Barite dissolution rate constants increase as a linear function of the square root of ionic strength but vary only slightly with pH. The dissolution rate dependence on temperature is consistent with an activation energy of 25 ± 2 kJ mol^{-1}. Barite dissolution and precipitation rates are not significantly affected by the presence of aqueous calcium, magnesium or strontium. The rates measured in the study were generated in fluids similar to those found in sedimentary basins, ocean floor sediments and oil field reservoirs so the data may provide close estimates for the reactivity of barite during a variety of natural and industrial processes.

1. INTRODUCTION

This study focuses on the dissolution and precipitation kinetics of barite (BaSO$_4$) for a number of reasons. First, barite formation provides insight into the composition and behaviour of past and present oceans. For example, the isotopic and elemental compositions of barite is used to trace past seawater chemistry, can aid in the understanding of fluid flow and sedimentary redox processes, and provide insight into past ocean productivity (Paytan and Griffith, 2007; Paytan et al., 2007; Griffith and Paytan, 2012). Although seawater is generally undersaturated with respect to barite, it is commonly found in the water column and in marine sediments (Chow and Goldberg, 1960; Wolgemuth and Broecker, 1970; Church and Wolgemuth, 1972; Chan et al., 1977; Falkner et al., 1993). Second, barite is a common precipitate in oil reservoirs and pipelines,

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where it can impede fluid flow (Vetter et al., 1982; Bezerra et al., 1990; Sorbie and Mackay, 2000; Mackay et al., 2003). It is anticipated additional data on barite dissolution and growth rates could provide insight into how to avoid such clogging. Third, barite readily dissolves and precipitates at ambient conditions (Christy and Putnis, 1993; Dove and Czank, 1995). As such, it is possible to determine barite dissolution and precipitation rates at near to identical conditions to elucidate the degree to which these two processes are linked, and if it may be possible to estimate precipitation from dissolution rates. To improve our understanding of barite reactivity at ambient conditions, we have measured its dissolution and precipitation rates in batch reactor systems. The purpose of this paper is to report these results so they can be applied to elucidate barite reactivity in natural and industrial processes.

A number of studies have explored the rates and mechanisms of barite–water interaction (Collins and Leineweber, 1956; Walton, 1963; Klein and Fontal, 1964; Mealor and Townshend, 1966; Gunn and Murthy, 1972; Symeopoulos and Koutsoukos, 1992; Murthy, 1994; Pina et al., 1998) and others have derived the reaction order of barite-fluid reactions using conductivity techniques (Nielsen, 1958, 1959; Nancollas and Purdie, 1963; Nancollas, 1968; Nancollas and Liu, 1975; Liu et al., 1976; Rizkalla, 1983; Cheng et al., 1984; Nielsen and Toft, 1984; Wat et al., 1992; van der Leeden et al., 1992; Taguchi et al., 1996) or activity methods (Bovington and Jones, 1970). Studies of barite dissolution and precipitation have also been used to provide insight into polypitting and aggregation (Dunn et al., 1999; Tang et al., 2001; Judat and Kind, 2004; Kuwahara, 2011; Jones, 2012).

Bulk barite dissolution and precipitation rates in NaCl-bearing aqueous solutions have been reported by Christy and Putnis (1993) and Dove and Czank (1995). Christy and Putnis (1993) suggested that barite dissolves via a first order reaction with respect to its saturation state and reported that there was no effect of dissolved NaCl on the rate at concentrations up to at least 0.1 molar. In addition, they concluded that barite precipitation rates increase with a second order dependence with respect to barium concentration but is pH independent. Dissolution and growth rates for barite have been extrapolated from atomic force microscopic (AFM) measurements by Higgins et al. (1998) and Godinho and Stack (2015). Other AFM studies demonstrated that factors including ionic strength and degree of reactive fluid supersaturation influence barite nucleation and crystal morphology (Bosbach et al., 1998; Risthaus et al., 2001; Kowacz and Putnis, 2008; Kowacz et al., 2010). Note, however, that AFM studies tend to generate reaction rates on a single barite surface, whereas bulk rate experiments generate a surface area averaged reaction rates for all of the barite surfaces exposed to the aqueous fluid. As such, AFM rates may not be directly comparable to corresponding bulk rates. Other studies have explored the effect of the aqueous barium to sulfate ratio and the presence of other dissolved ions on barite morphology, surface energy and reaction kinetics (Walton and Walden, 1946; Buchanan and Heymann, 1949; Benton

et al., 1993; Wong et al., 2001; Marchisio et al., 2002; Kucher et al., 2006; Kowacz et al., 2007; Steyer and Sundmacher, 2009). Granbakken et al. (1991) modeled barite dissolution and precipitation with data taken from the literature. This study builds upon these past efforts by measuring barite dissolution and precipitation rates as a function of ionic strength, pH, total mineral surface area, presence of the divalent cations such as calcium (Ca), magnesium (Mg) and strontium (Sr), the presence of barite seeds, and the initial reactive fluid Ba to SO_4 mole ratio. All experiments were performed in closed system reactor at 25, 60, and 90 °C.

2. BACKGROUND

The standard state adopted in this study is one of unit activity for pure minerals and water at any temperature and pressure. The standard state for aqueous species is taken as unit activity for the solute in a hypothetical one molal solution extrapolated to infinite dilution. Barite dissolution and precipitation can be described using:

$$BaSO_{4(barite)} = Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)} \tag{1}$$
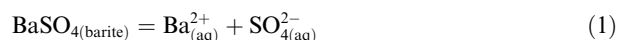
In accord with the standard state, the saturation state of the fluid with respect to barite Ω_{barite}) can be determined using:

$$\Omega_{barite} = \frac{a_{Ba^{2+}} a_{SO_4^{2-}}}{K_{barite}}, \tag{2}$$

where a_i corresponds to the activity of the subscripted aqueous species and K_{barite} refers to the equilibrium constant for Reaction (1). Thermodynamic constants and activity coefficients required to determine saturation states with Eq. (2) were generated using PHREEQC, Version 3 (Parkhurst and Appelo, 2013) together with its Pitzer database (Plummer et al., 1988). The Pitzer approach was adopted as it more accurately describes barite solubility in the high ionic strength aqueous solutions used in this study.

Dissolution and precipitation rates were obtained from closed system reactors from the slope of reactive fluid concentration versus time plots and normalised to the total mineral surface area in accord with:

$$r = \frac{M_f}{s} \frac{\partial m_i}{\partial t} \tag{3}$$

where r stands for the surface area normalised dissolution or precipitation rate, m_i signifies the concentration of ith element in the reactive fluid, t designates time, s corresponds to the total mineral surface area, and M_f represents the mass of fluid in the reactor. Surface-controlled dissolution and precipitation rates are commonly fit to the following empirical rate law:

$$r = k(\Omega - 1)^n \tag{4}$$

where k refers to a rate constant and n denotes the reaction order. The form of Eq. (4) is similar to transition state theory mineral dissolution and precipitation rate equations (Aagaard and Helgeson, 1982; Oelkers et al., 1994; Schott and Oelkers, 1995; Oelkers, 2001; Schott et al., 2009, 2012):