



Review

The stability of sulfate and hydrated sulfate minerals near ambient conditions and their significance in environmental and planetary sciences

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ABSTRACT

Sulfate and hydrated sulfate minerals are abundant and ubiquitous on the surface of the Earth and also on other planets and their satellites. The humidity-buffer technique has been applied to study the stability of some of these minerals at 0.1 MPa in terms of temperature–relative humidity space on the basis of hydration–dehydration reversal experiments. Updated phase relations in the binary system $\text{MgSO}_4\text{--H}_2\text{O}$ are presented, as an example, to show how reliable thermodynamic data for these minerals could be obtained based on these experimental results and thermodynamic principles. This approach has been applied to sulfate and hydrated sulfate minerals of other metals, including Fe (both ferrous and ferric), Zn, Ni, Co, Cd, and Cu.

Metal–sulfate salts play important roles in the cycling of metals and sulfate in terrestrial systems, and the number of phases extends well beyond the simple sulfate salts that have thus far been investigated experimentally. The oxidation of sulfide minerals, particularly pyrite, is a common process that initiates the formation of efflorescent metal–sulfate minerals. Also, the overall abundance of iron-bearing sulfate salts in nature reflects the fact that the weathering of pyrite or pyrrhotite is the ultimate source for many of these phases. Many aspects of their environmental significance are reviewed, particularly in acute effects to aquatic ecosystems related to the dissolution of sulfate salts during rain storms or snow-melt events.

Hydrous Mg, Ca, and Fe sulfates were identified on Mars, with wide distribution and very large quantities at many locations, on the basis of spectroscopic observations from orbital remote sensing and surface explorations by rovers. However, many of these findings do not reveal the detailed information on the degree of hydration that is essential for rigorous interpretation of the hydrologic history of Mars. Laboratory experiments on stability fields, reactions pathways, and reaction rates of hydrous sulfates likely to be found on Mars enhance our understanding of the degrees of hydration of various sulfates that should currently exist on Mars at various seasons and locations and during various atmospheric pressure and obliquity periods. Two sets of systematic experiments were described; one on hydrous Mg sulfates and the other on hydrous Fe^{3+} sulfates. Also, their implications to Mars sulfates mineralogy were discussed.

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1. Introduction

Simple hydrated metal–sulfate salts, such as epsomite (MgSO₄·7H₂O), coquimbite (Fe₂³⁺(SO₄)₃·9H₂O), and halotrichite (Fe²⁺Al₂(SO₄)₄·22H₂O), where one or more cations combine with sulfate and a number of waters of hydration, have received an explosion of scientific attention over the past one to two decades. Two main reasons are responsible for this focused attention. First, they form at the surface of the Earth through the weathering of sulfide minerals, where they can sequester or store metals and acidity in a highly soluble form during dry periods; these minerals can dissolve readily during rain events or spring snow melt, causing acute toxic events such as fish kills downstream (Nordstrom, 2009). Second, spectral data from satellites orbiting Mars or more recently from rovers on the Martian surface have identified magnesium and iron sulfate salts as important constituents of the Martian soil, where they likely play important roles in the hydrologic cycle of the planet and represent clues in the search for evidence of life on the planet (Squyres et al., 2004). Similarly, orbital remote sensing studies of other planets and their satellites, such as the Jovian moon Europa, have indicated the presence of these phases elsewhere in the solar system (Chou and Seal, 2003a; Dalton et al., 2012).

The crystallography, geochemistry, and environmental significance of sulfate and hydrated sulfate minerals, which are abundant and ubiquitous in the lithosphere of Earth and also on other planets and their satellites, were last reviewed comprehensively over a decade ago (i.e., Alpers et al., 2000). In 2000, information on the stability of sulfate and hydrated sulfate minerals and their thermodynamic and kinetic properties were lacking due to limited experimental observations and reliable measurements. Thus, one of the greatest obstacles to improving of understanding of the behavior of these minerals in both terrestrial and extraterrestrial environments was the lack of reliable thermodynamic data for these phases and the lack of adequate kinetic data for the rates of reactions among these phases.

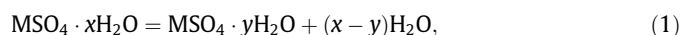
The purpose of this review paper is to summarize recent laboratory studies related to the thermodynamic and kinetic properties of this group of minerals as they relate to surface environment on Earth and Mars. Temperature and relative humidity (RH) are master variables that determine the stability of many of these minerals under a range of conditions. The humidity-buffer technique, which has formed the basis of much of the recent experimental research on these phases, is described (Chou et al., 2002). This paper also summarizes the occurrences of metal–sulfate minerals in terrestrial settings, particularly those associated with mining. Experimental studies related to the stability and reaction rate of these phases under conditions relevant to Mars and its hydrologic cycle are described.

These minerals present a number of challenges in terms of preservation from the time of collection in the field to the time of analysis and characterization due to their rapid rates of hydration, dehydration, and oxidation for those containing ferrous iron and other reduced elements. A review of these topics is beyond the scope of this paper. Instead, the reader is referred to recent comprehensive studies by Frost et al. (2006) and Hyde et al. (2011) for pertinent information. Furthermore, less soluble and reactive simple sulfate minerals such as anglesite (PbSO₄) and barite (BaSO₄), and hydroxysulfates such as schwertmannite (Fe³⁺O₈(OH)_{8–2x}·(SO₄)_x·nH₂O where 1 ≤ x ≤ 1.75), jarosite ((K, Na, H₃O)Fe₃³⁺(SO₄)₂(OH)₆), and alunite ((K, Na)Al₃(SO₄)₂(OH)₆), among others, are beyond the scope of this review and are only mentioned as needed for completeness in describing mineral assemblages despite their geologic importance.

2. The humidity buffer technique

The humidity-buffer technique was based on the isopiestic method, which was widely used for the determination of solvent activity of nonvolatile solutions (e.g., Pytkowicz, 1979; Clegg and Whitfield, 1991; Barthel et al., 1998). The humidity-buffer technique was developed by Polyanskii et al. (1976) for the study of ion-exchange resins, and later used by Malinin et al. (1977), Chou et al. (2002), Jerz and Rimstidt (2003), Vaniman et al. (2004), Vaniman and Chipera (2006), Kong et al. (2011a), Wang et al. (2009, 2011), and Chou and Seal (2003a, 2003b, 2004, 2005a, 2005b, 2007) for the stability studies of metal sulfate and hydrated metal sulfate minerals. This technique has also been used for mineral characterization (Anderson et al., 2007), monitoring phase transition in real-time (Peterson and Grant, 2005), and development of microanalytical techniques (Hyde et al., 2011). After comparing the humidity-buffer technique with the gas-flow-cell method, which was designed by Parkinson and Day (1981) to control precisely the RH for plant growth experiments, Chou et al. (2002) preferred the humidity-buffer technique for their mineral stability studies because of better temperature control and more precise reversibility.

For the hydration–dehydration reaction of the sulfate minerals of a divalent metal M:



$$\begin{aligned} \Delta G_r^\circ &= -RT \ln K = -(x - y)RT \ln(a\text{H}_2\text{O}) \\ &= -(x - y)RT \ln(f\text{H}_2\text{O}/0.1) \\ &= -(x - y)RT \ln[(f^* \text{H}_2\text{O}/0.1) \cdot (\%RH)/100], \end{aligned} \quad (2)$$

where x and y are the numbers of water molecules per formula of the minerals, ΔG_r[°] is the standard Gibbs free energy of reaction for

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