Mineral evolution and mineral niches of ammonium sulfates: The case of Pastora mine, Aliseda, Spain

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ABSTRACT

The uncommon association of ammonium sulfates identified in the Pastora abandoned mine is the result of a complex mineral evolution. By means of dissolution-(re)crystallization reactions operating during long periods of time, ammonium minerals “adapt” to local spatiotemporal changes in physicochemical conditions. We found that during such an evolution, seasonal variations in temperature and humidity, the relative solubility of mineral species, and the presence of organic matter play an important role. In addition, our study shows the existence of “mineral niches” and “mineral seasonality,” which can be explained on the basis of the “mineral ecology” concept introduced by Hazen et al. (2015). Our investigation of the formation of hydrated sulfates, particularly of ammonium sulfates, might be of importance for identifying the existence of life in mineral formation environments.

Keywords: Ammoniojarosite, tschermigite, acid mine drainage, dissolution-precipitation, mineral evolution

INTRODUCTION

Even though hydrated and hydroxy sulfates are relatively common on the Earth (sub)surface, the formation of sulfate minerals bearing ammonium is rare because concentrated ammonium-solutions are quite scarce in natural environments (Dutrizac and Jambor 2000; Frost et al. 2006; Basciano 2008). Bituminous slates, hot springs, solfataras, oil-bearing shales (Kampf et al. 2016), and sites related to coal deposits, as well as their remains after mining [e.g., coal-fire gas vents (Shimobayashi et al. 2011) and burning coal dumps (BCD) (Parafiniuk and Kruszewski 2009; Masaledhani et al. 2009)], are some of the geological settings where ammonium sulfates are formed.

The occurrence of most ammonium sulfates seems to be mainly related to the weathering of sulfide minerals in a context of acid mine drainage (AMD) (e.g., Hammarstrom et al. 2005). However, the controlling factors of the precipitation and dissolution of these minerals under ambient conditions remain little known (Přikryl et al. 2007).

The interest in ammonium sulfate minerals is not limited to their environmental implications. Since the identification on Mars of hydrated magnesium and iron sulfates, i.e., jarosite (Elwood Madden et al. 2004; Klingelhöfer et al. 2004), it becomes apparent that investigations on the formation of these minerals might be useful to detect possible aqueous environments on its surface (Spratt 2015). In general terms, the occurrence of ammonium-bearing sulfates is relevant because the presence of organic matter seems to be a pre-requisite for the formation of ammonium minerals. Consequently, the detection of ammonium minerals can be considered as a circumstantial evidence of both aqueous environments and the presence of living organisms. In this regard, the abandoned Pastora iron mine has been revealed to be an outstanding natural laboratory in which numerous processes leading to the formation of a large variety of sulfate minerals can be studied (Crespo 2015; Crespo et al. 2017a, 2017b). Particularly, Pastora mine provides a unique opportunity to analyze the main factors which determine the occurrence and the spatiotemporal distribution of ammonium sulfates under changing environmental conditions.

In this paper, we present an investigation of the formation of ammoniojarosite, (NH₄)₂Fe₆(SO₄)₇(OH)₆, and tschermigite, (NH₄)₂Al(SO₄)₆·12H₂O, in Pastora mine (Aliseda, Spain) from prexistent sulfide minerals (i.e., pyrites). We found that, in the limited and to some extent controlled mineralogенetic environment of Pastora mine, the concepts of mineral evolution and mineral niches proposed by Hazen et al. (2008) are adequate to explain the generation of such minerals, which result from an intricate interplay between external (i.e., pH, temperature, relative humidity, interaction with host rocks, and the supply of ammonium from organic origin) and internal factors (i.e., differences in solubility and stability of the minerals formed).

GEOPOLITICAL CONTEXT OF PASTORA MINE

In the Sierra del Aljibe, approximately 1 km south from Aliseda (Cáceres, SW Spain), there are several goethite and hematite mineral deposits. Some of them, including the abandoned Pastora iron mine, fulfill the characteristics of gossan type ore deposits, i.e., mineral deposits originated from the weathering and oxidation of massive sulfides (mainly pyrite)