



# Separation and characterization of pedogenic barite crystals from petrocalcic horizon materials for future isotopic and geochronological applications



Amy Brock-Hon<sup>\*</sup>, Sarah Ellen Johnston

Department of Physics, Geology and Astronomy, University of Tennessee at Chattanooga, 615 McCallie Ave. 6556, Chattanooga, TN 37403, United States

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## ABSTRACT

Although extensive work has been conducted on pedogenic barite in the petrocalcic soil horizons at Mormon Mesa, NV, further investigations are required to understand the mode and timing of its precipitation. Isolation of barite crystals from petrocalcic soil materials is an important first step, after which, crystal morphology can be examined. We sought a method to isolate barite and other heavy minerals to examine their feasibility for future isotopic and geochronological techniques. Using XRD, SEM with EDS and microprobe analyses, barite was analyzed for evidence of chemical or physical alteration after chemical separation procedures with HCl to remove carbonate and methylene iodide to separate minerals with specific gravities greater than and less than 3.3 g/mL. After separation, barite clusters were observed within the heavy mineral separates. Barite showed no remarkable signs of physical or chemical alteration after separation and small (<1 mm) clusters of barite were large enough to be hand-picked from the heavy separates. The isolation of barite from other petrocalcic soil materials is the critical first step in applying isotopic and geochronological techniques that will contribute to a better understanding of the timing and development of this unique soil system.

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## 1. Introduction

Barite, a rare pedogenic mineral in arid and semi-arid soils, is identified in late-stage petrocalcic soil horizons at Mormon Mesa, NV. Previous work utilized scanning electron microscopy of thick sections cut from indurated samples to determine barite's occurrence, morphology, and mineral associations (Brock, 2007; Brock-Hon et al., 2012; Robins et al., 2012), and computed tomography scanning to assess the 3-dimensional location of barite in these soils (Brock-Hon and Elliot, 2013). Although barite has been characterized in detail and its paleoenvironmental and paleoclimatic significance in Mormon Mesa soils is recognized, questions remain as to barite's mode (organic and/or inorganic) and timing of formation (Brock-Hon et al., 2012).

An understanding of the timing of barite formation in petrocalcic soils may result in a more detailed regional paleoclimate record over the duration of pedogenic development. Barite formation in Mormon Mesa soils is tied to  $Ba^{2+}$  and  $SO_4^{2-}$ -rich salt influx at the soil surface during more arid climates with subsequent effective precipitation events flushing these dissolved solutes into the profile to combine as barite (Brock-Hon et al., 2012; Robins et al., 2012). A chronology of barite crystallization would elucidate the timing of these key climatic events. Timing of barite crystallization in these soils would also add to our understanding of the geochemical and mineralogical development of this system. Pedogenic mineral relationships in the Mormon Mesa petrocalcic horizons reveal barite formation after induration and after

initial formation of silicate clays (Brock, 2007; Brock-Hon et al., 2012; Robins et al., 2012). Barite formation ages obtained from absolute dating would then give a refined relative timing of induration with carbonate. The potential incorporation of  $K^+$  in the barite structure (Hanor, 2000) may be advantageous for future geochronological analyses performed on individual crystals in order to specify the timing of barite formation and a relative timing of other pedogenic events.

Soil solution chemistry and mode of barite precipitation may be determined from isotopes in barite. In Mormon Mesa soils, barite's habit and its close association with fibrous silicate clay and root pores indicate that barite may be the product of organic processes (Bonny and Jones, 2008; Brock-Hon et al., 2012). Sulfur oxygen isotope analyses could be used to determine if there was an organic and/or inorganic influence on crystallization, the source of sulfur in the system, and soil environment conditions at time of crystallization (Seal et al., 2000; Thode, 1991).

Isotopic and radiometric analyses require separation of barite from other pedogenic and detrital minerals. Therefore, isolation of barite crystals from the indurated soil matrix of petrocalcic materials is a necessary first step prior to any analytical procedures. We sought a method to isolate insoluble primary and secondary grains and crystals from petrocalcic soil matrix materials to further investigate the morphology of pedogenic barite. Our goal was to employ a method for separation of barite from fibrous clays and carbonate without altering its chemistry or morphology for the future application of isotopic and radiometric analyses.

The overwhelming amount of carbonate minerals in petrocalcic horizons can be problematic for obtaining the composition of other

<sup>\*</sup> Corresponding author. Tel.: +1 423 425 4409; fax: +1 423 425 4423.  
E-mail address: [amy-brock-hon@utc.edu](mailto:amy-brock-hon@utc.edu) (A. Brock-Hon).

pedogenic minerals and detrital components, and for observing grain/crystal morphologies and surface features. Insufficient quantities of these other pedogenic minerals for in situ analysis can restrict what we know about the system's development. An incomplete assessment of detrital grain mineralogies and characteristics hinders provenance studies and can also impede geomorphic and pedogenic interpretations. The ability to isolate minerals of interest (in our case barite) would provide a means to conduct additional analytical methods on individual grains as well as view the conditions of grain/crystal surfaces (i.e. observe any surface pitting or etching as evidence for dissolution processes).

### 1.1. Barite in Mormon Mesa petrocalcic soil horizons

Petrocalcic soil horizons at Mormon Mesa, NV contain pedogenic minerals that reflect ion mobility and additions to this unique soil system over extended ( $10^6$  yr) time (Brock-Hon et al., 2012; Monger and Daugherty, 1991; Robins et al., 2012). Stage VI petrocalcic horizons at Mormon Mesa, NV contain calcium carbonate that has accumulated over the past 3–4 Ma (Brock and Buck, 2009; Machette, 1985). The carbonate has also favored the dissolution and precipitation of pedogenic minerals that reflect this evolving system (Brock, 2007; Brock-Hon et al., 2012; Robins et al., 2012). In the massive petrocalcic horizons of Mormon Mesa soils (Brock, 2007; Brock and Buck, 2009; Gardner, 1972), measured carbonate equivalences often exceed 85% (Robins et al., 2012). This carbonate fills pore spaces, limits room for crystal growth, and contributes to dissolution of primary grains (Brock-Hon et al., 2012; Reheis, 1988; Robins et al., 2012). Ions (e.g.  $\text{Si}^{4+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ) forced into solution may later recombine and precipitate as pedogenic minerals that reflect these indurated conditions. Ion contributions may also come from dust or as solutes in meteoric water at the soil surface (Reheis et al., 1995; Robins et al., 2012). Neoformed minerals can include opaline silica and fibrous silicate clays such as palygorskite and sepiolite (Brock-Hon et al., 2012; Monger and Daugherty, 1991; Robins et al., 2012). Pedogenic barite also precipitates as a result of mineral dissolution at the soil surface and through recombination of  $\text{Ba}^{2+}$  and  $\text{SO}_4^{2-}$  to form barite crystals in cracks, voids, and higher-porosity areas such as the space between fibers of silicate clays (Brock, 2007; Brock-Hon and Elliot, 2013; Brock-Hon et al., 2012; Robins et al., 2012).

The close association of barite with fibrous clay is problematic for isolation of these crystals from a bulk sample. Small (1–5  $\mu\text{m}$ ) barite crystals occur among fibers of silicate clay and with the calcite and Mg–calcite matrix (Brock, 2007; Brock-Hon et al., 2012) (Fig. 1). In cracks and around root pores, barite crystals are tabular and elongated subhedral to euhedral and range in size from 1 to 50  $\mu\text{m}$  in length (Brock-Hon et al., 2012). The use of acids such as NaOAc and HCl effectively remove calcium carbonate but not the clay fraction. When

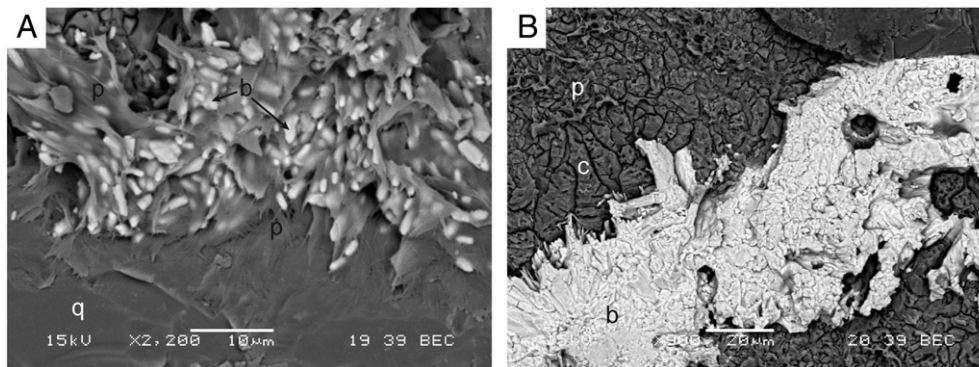
seeking to isolate barite, the intimate association between barite and clay must be addressed.

## 2. Material and methods

Two samples were obtained from each of the massive horizons of five profiles [Riverside (RI), Big Bull (BB), Logandale (LD), Hell's Kitchen (HK), Overton (OV)] and two samples were taken from the transitional horizon of the HK profile at Mormon Mesa (Brock, 2007; Brock and Buck, 2009; Brock-Hon et al., 2012). This study used indurated blocks of material collected during research associated with the Brock (2007) and Brock-Hon et al. (2012) studies from which thin sections and billets were made for detailed micromorphological investigations. These 12 samples were chosen because they had the highest observed barite counts viewed with SEM/EDS (Brock, 2007; Brock-Hon et al., 2012) and therefore had the greatest probability of containing detectable barite after separation.

Indurated blocks were crushed with a bench top ball mill to pass a 2 mm sieve and weighed. We added 50 mL of 10% HCl (by volume) to 20–50 g of powdered sample to completely remove carbonate. NaOAc is conventionally used as a mild reactant to remove carbonate and keep clays intact for identification (Rabenhorst and Wilding, 1984; Shang and Zelazny, 2008; Soukup et al., 2008). However, because the focus of this work was not on clay mineralogy, HCl was chosen for a more vigorous reaction that would stimulate the disassociation of barite and fibrous silicate clays. When the reaction was complete, samples were centrifuged for 3–4 min at 2000 rpm ( $\text{RCF} = 769 \times g$ ) using an Allegra 22 Centrifuge. The supernatant was decanted and samples were dried thoroughly before reweighing. This process of HCl addition and centrifuging was repeated until no further reaction was observed (~6 dissolution replicates). The samples were then centrifuged with ~100 mL of water and decanted 3 to 4 times to ensure that all acid residues were removed.

A standard heavy liquid separation (modified from Lindholm, 1987) was performed with methylene iodide (MeI) ( $\text{SG} = 3.30\text{--}3.33$  g/mL), to separate light minerals (quartz  $\text{SG} = 2.65$  g/mL and silicate clays = 2.0–2.15 g/mL) from heavier minerals including barite ( $\text{SG} = 4.48$  g/mL). The insoluble fraction of each sample was poured into a separatory funnel containing a small amount of MeI and additional liquid was added until the sample was completely saturated. The separatory funnel was agitated and separation proceeded for 10–15 min to allow full separation of the minerals. The heavy minerals (which sank to the bottom of the funnel) were carefully drained, and the separatory funnel agitated again. The previous steps were repeated until no heavy minerals remained; additional MeI was added when necessary. After the heavy minerals were removed, the remaining light minerals were drained onto a separate filter. Samples were washed with acetone and air-dried. Heavy separates were gently removed



**Fig. 1.** SEM backscatter image of barite in thick section samples from the Riverside (RI) profile (from Brock, 2007). Barite (b) is observed as bright white crystals. Panel (A) shows intimate association of barite with palygorskite fibers (p) adjacent to quartz grain (q). Panel (B) shows larger barite crystals filling crack. Palygorskite fibers occur with carbonate (c) matrix in this image. Note the radiating nature of the barite crystals in lower left corner of image.

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