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A survey of the signal stability and radiation dose response of sulfates in the context of adapting optical dating for Mars

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ABSTRACT

The Martian landscape is currently dominated by eolian processes, and eolian dunes are a direct geomorphic expression of the dynamic interaction between the atmosphere and the lithosphere of planets. The timing, frequency, and spatial extent of dune mobility directly reflects changing climatic conditions, therefore, sedimentary depositional ages are important for understanding the paleoclimatic and geomorphologic history of features and processes present on the surface of the Earth or Mars. Optical dating is an established terrestrial dosimetric dating technique that is being developed for this task on Mars. Gypsum and anhydrite are two of the most stable and abundant sulfate species found on the Earth, and they have been discovered in Martian sediments along with various magnesium sulfates and jarosite. In this study, the optical dating properties of various Ca-, Mg-, and Fe-bearing sulfates were documented to help evaluate the influence they may have on in-situ optical dating in eolian environments on Mars. Single-aliquot regenerative-dose (SAR) experimental procedures have been adapted to characterize the radiation dose response and signal stability of the Martian sulfate analogs. Jarosite was dosimetrically inert in our experiments. The radiation dose response of the Ca- and Mg-sulfates was monotonically increasing in all cases with characteristic doses ranging from ~100 to ~1000 Gy. Short-term signal fading also varied considerably in the Ca- and Mg-sulfates ranging from ~0% to ~40% per decade for these materials. These results suggest that the OSL properties of Ca- and Mg-sulfates will need to be considered when developing protocols for in-situ optical dating on Mars, but more enticingly, our results foreshadow the potential for gypsum to be developed as a geochronometer for Mars or the Earth.

1. Introduction

Various hydrous and anhydrous sulfate minerals have been identified on the surface of Mars from research conducted on meteorites, and via a suite of remote instruments on the surface or orbiting Mars [1]. The occurrence of sulfates on Mars is important because hydrated sulfates form in the presence of water – either by precipitation from aqueous solution, evaporation of surface water, or through hydrothermal processes – thus indicating that Mars once had a watery past [2]. Today, eolian processes dominate the cold, dry landscape of Mars. Therefore, sulfates and other surface sediments originating from and previously influenced by aqueous processes, are currently being redistributed by eolian transport.

Eolian transport provides the optimal conditions for optical dating and the technique has been used successfully to make absolute age determinations for numerous terrestrial eolian deposits (reviewed in Refs. [3,4] and many others). Optical dating is an established terrestrial dosimetric dating technique that has been proposed for use in constraining the chronology of geomorphic features and surface processes on Mars [5,6]. Since optical dating is applied almost exclusively to silicates on the Earth, and surface sediments on Mars are anticipated to be a mixture of various minerals, including sulfates, an understanding of the OSL properties of sulfate minerals will be critical in order to adapt optical dating techniques for use on Mars. We report here the results of a survey of the dosimetric signal stability and radiation dose response for a variety of sulfate minerals thought to be present on the surface of Mars.

1.1. Sulfates on Mars

Mg- and Ca-sulfates, which constitute the second major class of hydrated minerals on Mars after hydrous phyllosilicates, have

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been mapped by ESA's OMEGA instrument and detected by the NASA Mars Exploration Rovers (MERs), Spirit and Opportunity [1,2,7–9]. This confirmed the observations made by Viking and Pathfinder, which both detected sulfate (as inferred from SO_3) in relatively high concentrations in Martian surface sediments [10]. The most predominant Ca-sulfates on Mars are inferred to be gypsum, anhydrite, and bassanite. Mg-sulfates, which include primarily kieserite and hexahydrite, but also epsomite and starkeyite, are more abundant than Ca-sulfates in some regions of Mars [1,11]. Jarosite, detected using Mössbauer spectroscopy and the Mini-TES instrument on the MERs, is a ferric hydroxide sulfate found at Meridiani Planum [1,12–14].

Data collected at Gusev crater from a wide range of landed and orbital instruments suggests that the subsurface regolith at Gusev crater consists of more than 20 wt% sulfate deposits, including primarily Mg-sulfates with minor abundances of Ca-sulfates and trace Fe-sulfates [11]. Mini-TES spectra of outcrops in Meridiani Planum that are aqueous in origin identified a mineralogic composition of 15–30% by volume Mg- and Ca-sulfates with only minor jarosite [13]. Meridiani also contains bedrock with a high abundance of sulfur, which is preserved in sedimentary structures [1,15]. Though Mg- and Ca-sulfates are predominant in this region, the detected abundances of jarosite never exceeded 5% by volume or ~10 wt%, which was confirmed by Mössbauer spectroscopy [14]. Mg- and Ca-sulfates were confirmed by the APXS results and the overall sulfate abundance in the outcrops is 25% by volume [1,15]. The presence of jarosite has been cited as mineralogical evidence for aqueous processes on Mars, probably under acid-sulfate conditions [14].

Gypsum has also been identified by OMEGA in the northern circumpolar dunes, with a decrease in abundance continuing westward from Chasma Boreale [16]. Gypsum signatures were found in the Olympia Undae sand sea by NASA's CRISM orbital spectrometer as well [17,18]. These gypsum signatures are stronger on the dune crests, and decrease in concentration in a clockwise, downwind direction along the circumpolar dunes suggesting a dynamic eolian process is controlling the gypsum distribution [17,19].

1.2. *Studies of the optical dating properties of Martian sediment analogs*

As a terrestrial dating method, optical dating is routinely conducted on quartz and feldspars [3,4]. These silicates could be thought of as the "primary geochronometers" for optical dating on Mars. However, because sulfates are wide-spread on Mars, have abundances ranging as high as 40 wt% [13], and mineralogical separation for an in-situ optical dating instrument will likely be limited or precluded, it is important to examine the optical dating properties of sulfate minerals thought to occur on Mars.

In-situ optical dating of eolian sediments on Mars was first proposed by Lepper and McKeever [20] in 1998. Since that time, several studies examining the basic OSL properties of silicate analogs for Martian surface materials including the Martian soil simulant JSC Mars-1 [5], prepared silicate mineral mixtures [21], and volcanic rocks [22] have been reported. In addition, efforts aimed at developing OSL measurement procedures for use with Mars analog materials have been conducted (reviewed in Ref. [23]). An estimate of the saturation doses for gypsum and anhydrite were included in an investigation by Jain et al. [22]. They report a saturation dose of >6000 Gy for gypsum and ~2500 Gy for anhydrite using a blue-OSL/UV measurement combination. The dose response data are based on analysis of one aliquot for each mineral so variability/reproducibility of the saturation dose value cannot be evaluated. In addition, the sulfate samples were heated repeatedly to 260 °C during the dose response experiment. Since gypsum begins losing structural water at temperatures as low as 70 °C and is completely converted into anhydrite at 180 °C, repeated heat treatments to 260 °C would have transformed their only gypsum aliquot to anhydrite.

The information gained in this survey of basic optical dating properties of sulfate minerals can be used to address two basic questions: (1) How will the presence of sulfates in Mars surface deposits influence optical dating of the primary geochronometers, and (2) can any of the sulfates serve as potential geochronometers for optical dating? In addition, the data reported here can provide impetus for more detailed studies of the specific minerals.

2. Materials/samples

A variety of synthetic sulfates including gypsum, anhydrite, hexahydrite, kieserite, and jarosite, as well as two natural gypsum samples were examined in this study (Table 1). The naturally occurring samples are described further in this section. The natural sample referred to as "Pierre Shale" gypsum (PSG) in this study is a secondary precipitate from the Pierre Shale Formation. The Pierre Shale Formation, originally deposited in a shallow sea environment, contains veins and seams of gypsum [24]. These veins and seams of gypsum are dissolved by groundwater and then re-crystallized as cm-scale, transparent-yellow, secondary gypsum crystals [25]. The sample (PSG) was collected as single crystals, with no significant inclusions, from a weathered outcrop along St. Hwy. 32 in Barnes Co., North Dakota. The crystals were gently ground by hand into sand-sized grains using a mortar and pestle.

Table 1
Sample information.

Mineral	Symbol used	Chemical formula	Physical form	Source	Nominal purity
Gypsum	WSG	$CaSO_4 \cdot 2H_2O$	Natural granular fine sand	White Sands National Monument[a]	$>97\%$
Gypsum	PSG	$CaSO_4 \cdot 2H_2O$	Natural single crystal	Weathered outcrop of Pierre Shale, Barnes Co., ND[b]	n/a
Gypsum	SGP	$CaSO_4 \cdot 2H_2O$	Synthetic powder	Alpha Aesar®	99%
Anhydrite	ANH	$CaSO_4$	Synthetic powder	Alpha Aesar®	99%
Hexahydrite	HEX	$MgSO_4 \cdot 6H_2O$	Synthetic granular coarse-sand	Sunmark™ OTC epsom salt[c]	n/a
Kieserite	SKS	$MgSO_4 \cdot H_2O$	Synthetic powder	Steve Chipera, Los Alamos National Laboratory	$>99\%$
Jarosite	JAR	$(K,H_3O)Fe_3(OH)_6(SO_4)_2$	Synthetic powder	Jerry Bigham and Sandy Jones, Ohio State University[d]	n/a

[a] Sample collected by and permission to use provided by David Bustos, W.S.N.M.
[b] Sample collected as single crystals by Lepper.
[c] XRD analysis conducted; peak structure dominated by hexahydrite with limited, minor peaks associated with epsomite.
[d] Hydronian-jarosite; some limited substitution of H_3O^+ for K^+.