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INVESTIGATING CO-OCCURRENCES OF GYPSUM VEINS AND MAGNESIUM SULFATES IN THE RIO PUERCO NECKS REGION AS A GEOCHEMICAL PROXY FOR SULFATE ORIGIN ON MARS

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Abstract—In Gale crater on Mars, abundant secondary calcium (Ca) and magnesium (Mg) sulfate minerals are common as veins and cement in the sedimentary strata of Mount Sharp. However, the climate and source of aqueous sulfate (SO_4^{2-}) during their formation are not well understood. Our $\delta^{34}S$ analysis of surficial deposits in the Rio Puerco necks region show that oxidation of bedrock sulfides with negative $\delta^{34}S$ (-37 to -6‰) leads to abundant formation and co-occurrence of Ca-sulfate veins and Mg-sulfate-rich salt with similar negative $\delta^{34}S$ values (-33 to -13‰). Additionally, the negative $\delta^{18}O$ values of SO_4^{2-} (-7 to +3‰) and gypsum hydration water (-9 to +1‰) are consistent with local meteoric precipitation, implying their origin from shallow water-rock interactions. Our geochemical comparisons between the Rio Puerco necks region and Gale crater strongly suggest the importance of sulfide weathering and short-lived water activity under a dry climate in the past on Mars.

INTRODUCTION

Secondary sulfate (SO_4^{2-}) minerals commonly form on or near the surface, particularly in dry climates where high evaporation rates enhance precipitation of dissolved ions out of water, including salts enriched in SO_4^{2-} (e.g., Warren, 2006). The SO_4^{2-} ions in aqueous systems may come from multiple atmospheric, volcanic, and bedrock sources, but the main input (~70–90%) is typically from chemical weathering of S mineralization in the bedrock, such as sulfide oxidation and/or evaporite dissolution (e.g., Berner and Berner, 2012; Szynkiewicz et al., 2019). In the semiarid region of the Rio Puerco necks, oxidation of bedrock sulfides within the Mancos shale and Gallup sandstone involves widespread formation of various secondary sulfate minerals in the form of soil cement and efflorescent precipitation (Szynkiewicz et al., 2014). Typically, Mg-sulfate salts are found on higher elevations in close proximity to in situ sites of sulfide (pyrite) weathering, while Ca-and Na-sulfates are more common in lower elevations of ephemeral drainages and are associated with longer groundwater flow paths. Recent field investigations by our group have also identified widespread co-occurrences of gypsum veins in places where Mg-sulfate formation is abundant on or near the surface. However, it is unclear why the gypsum mainly precipitates in the Mancos shale fractures as veins and the Mg-sulfates are more common in the soil cement and/or as efflorescent salts.

Similar co-occurrences of Mg-sulfate cements and Ca-sulfate veins enriched in gypsum, bassanite, and anhydrite have been detected on Mars in Gale crater, investigated by the Curiosity rover (e.g., Vaniman et al., 2018; Rampe et al., 2020; Gasda et al., 2022). However, the sources of aqueous SO_4^{2-} and climate conditions for abundant sulfate mineral formation in Gale crater have not been addressed by many previous studies. This is in part because accurate measurements of minor S minerals (e.g., sulfides) are challenging with existing analytical tools on the Mars rovers and because past climate conditions are poorly constrained for Mars. Consequently, terrestrial field studies such as those in the Rio Puerco necks region are needed to address the existing knowledge gap in understanding fluid and SO_4^{2-} sources as well as climate conditions for the secondary sulfate mineral formation on Mars.

In this report, we discuss the fluid sources and climate conditions for abundant formation of various sulfate minerals in the Rio Puerco necks region using field observation and stable isotope tracers ($\delta^{34}S$, $\delta^{18}O$).

BACKGROUND

The Rio Puerco watershed is located along the east-southeast margin of the Colorado Plateau and along a transition zone with the Rio Grande rift in northern New Mexico, and it is covered by Permian- through Tertiary-age continental and marine sandstones, shales, coals, mudstones, and carbonate rocks (Wilks, 2005). In the studied region of the Rio Puerco necks, the most abundant strata are the Mancos shale and Gallup sandstone of Upper Cretaceous age. These strata are generally horizontal, often faulted, and eroded into broad valleys flanked by mesas and mountains (Fig. 1). The Gallup sandstone units tend to crop out in small cliffs (or canyon walls), whereas the Mancos shale units form undulating mounds (Phippen and Wohl, 2003). The climate of the region is semiarid, with average annual precipitation (snowfall and monsoon rains) ranging from 102 cm in high northern mountain areas (3,445 m asl) to

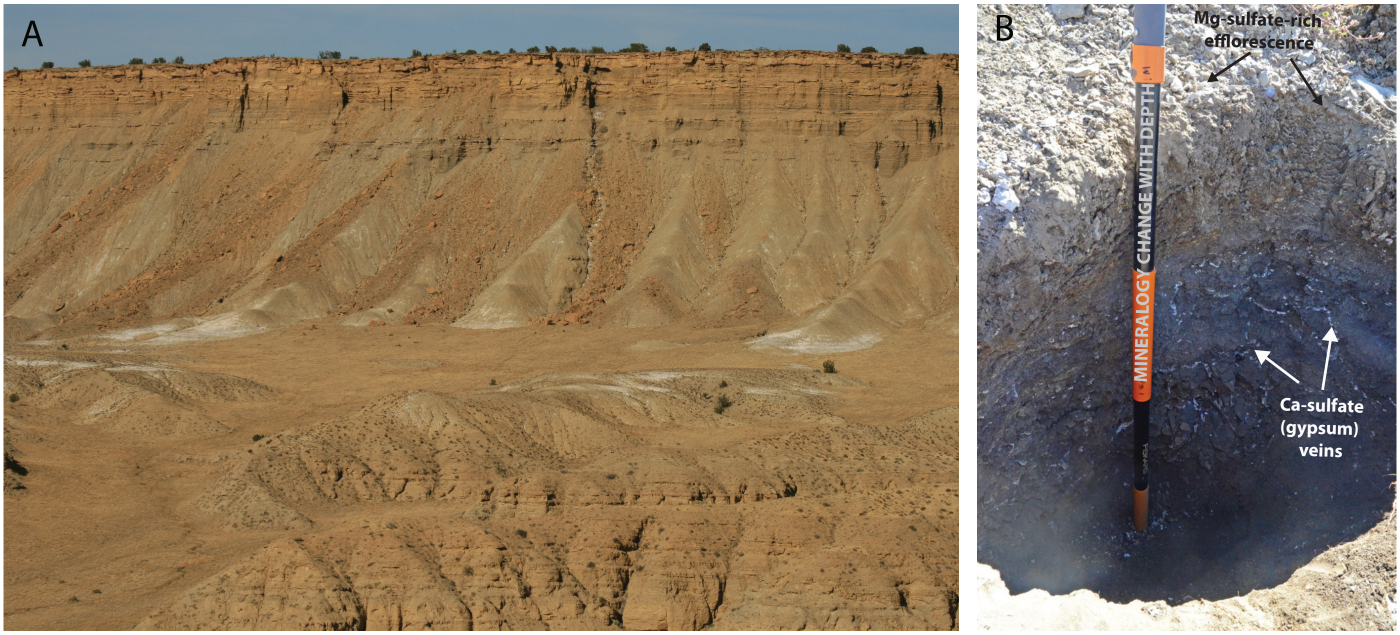

FIGURE 1. (A) Examples of sulfate-rich efflorescence (white color) near the Cerro De Santa Clara neck. (B) Co-occurrences of Mg-sulfates (efflorescence and cement on/near the surface; black arrows) and Ca-sulfate veins (white arrows) in the Mancos shale.

28 cm in lower elevations to the south (1,440 m asl; Phippen and Wohl, 2003). On average, the source rocks undergo physical erosion at integrated rates of ~100 m Ma^{-1}, but chemical denudation rates are only ~1.4 m Ma^{-1} (Bierman et al., 2005).

Secondary sulfate minerals are widespread in the Rio Puerco necks region. Under modern semiarid conditions, they are formed either as efflorescent salts and/or soil cement found on erosional hill slopes, steep and fractured canyon walls/cliffs, on mounds, and in topographic depressions of valley floors (Fig. 1A; Szynkiewicz et al., 2014). Based on quantitative XRD analysis of 23 samples using a Siemens D500 diffractometer with JADE full-pattern fitting (Szynkiewicz et al., 2014), they are mostly composed of hydrated Mg-sulfates (starkeyite, hexahydrite; totaling up to 84 wt%), Ca-sulfate (gypsum; up to 99 wt%), Na-sulfate (thenardite; up to 93 wt%), and Mg-Na-sulfates (blödite, konyaite; up to 17 wt%). Additionally, local patches of yellow Fe-K sulfate (jarosite; up to 93 wt%) can be found in small topographic depressions. Generally, hydrated Mg-sulfates (starkeyite, hexahydrite) are more abundant in the weathered sandstone/shale horizons of the steep, fractured walls/cliffs, whereas Na-sulfates (thenardite) are more common in the foothills, valley floors, and streambeds. Additionally, abundant networks of gypsum veins are common in the Mancos shale (Fig. 1B) and within fractured canyon walls/cliffs of the Gallup sandstone.

ISOTOPE RESULTS

Previous study has shown that sulfide weathering (oxidation) of the Mancos shale and Gallup sandstone with negative $\delta^{34}S$ (-37 to -6‰, n = 38) is an important source of aqueous SO_4^{2-} in the Rio Puerco watershed (Szynkiewicz et al., 2014). As a result, the secondary sulfate minerals precipitating as efflorescent salts and/or soil cement show comparable negative $\delta^{34}S$ values (-33 to -13‰, n = 74). These differ from atmospheric and marine evaporite-derived SO_4^{2-}, with higher $\delta^{34}S$ values of 0 to +10‰ and +17 to +18‰, respectively (Krouse and Grinenko, 1991). Our new isotope analyses of gypsum veins found along canyon walls of the Gallup sandstone and in □1-m-deep trenches dug within the Mancos shale yielded similar negative $\delta^{34}S$ values (-32 to -13‰, n = 44), suggesting the same sulfide-derived SO_4^{2-} origin as the sulfate salts present in the sulfate salts and soil cement.

The $\delta^{18}O$ of SO_4^{2-} extracted from soil cement and gypsum veins showed similar ranges of -5 to +3‰ (median -2‰, n = 28) and -7 to +1‰ (median -3‰, n = 44), respectively, which were comparable to the $\delta^{18}O$ of gypsum hydration water, -9 to +1‰ (median -5‰, n = 42). These, in turn, were in good agreement with the $\delta^{18}O$ variations of modern precipitation in central New Mexico (Sharp, 2017). Additionally, the $\delta^{18}O$ of SO_4^{2-} in the gypsum of three trenches dug in the Mancos shale significantly decreased with depth (-2 to -7‰, -3 to -6‰, +6 to - 2‰; n = 5 per trench), suggesting strong evaporation of shallow groundwater near the surface during SO_4^{2-} formation in the Mancos shale. Conversely, the $\delta^{18}O$ of canyon veins in the cliff/surface exposures of Gallup sandstone showed a narrower range and more negative values of -7 to -3‰ (n = 7), implying that gypsum precipitation from infiltrated meteoric water is less affected by surface evaporation.

INITIAL CONCLUSIONS

Field examination of gypsum vein occurrences in the Mancos shale suggests a pedogenic origin, as they show heterogenous distribution, mainly filling shallow fractures originating from bedrock weathering with more abundant gypsum formation near the surface. This is corroborated by higher $\delta^{18}O$ values of gypsum in the upper parts of the studied trenches that likely resulted from increased evaporation of meteoric fluids near the surface. While the canyon/cliff veins of Gallup sandstone exhibited greater spatial distribution in both vertical and horizontal directions, suggesting possible diagenetic origin, the similar δ^{34}S and δ^{18}O values as in the trench gypsum from the Mancos shale suggest more recent origin from the infiltration of meteoric precipitation.

The distinctive negative δ^{34}S values consistent with the local bedrock suggest that sulfide weathering is a major SO_4^{2-} source for the gypsum veins and Mg-rich sulfate efflorescence and in soil cement. Additionally, the similar δ^{18}O of sulfates in veins, efflorescence salt, and soil cement are consistent with the δ^{18}O of local meteoric precipitation, implying their primary formation under modern, semiarid conditions. It is likely that lower solubility of Ca-sulfate minerals in water enhances gypsum precipitation during fluid flow through bedrock fractures of Mancos shale and Gallup sandstone. Conversely, Mg-sulfates have higher solubility in water; thus, they more commonly form in soil cement/efflorescence near zones with sulfide weathering on or near the surface where water quickly evaporates due to the dry climate. With increasing groundwater flow paths, Mg dissolved in water is typically consumed for clay formation and/or ion exchange with the host rock. This, in turn, could explain the shift from Mg- toward Ca- and Na-sulfate-rich mineralogy in the efflorescence at lower elevations previously reported by Szynkiewicz et al. (2014).

According to in situ XRD and orbital analyses, abundant co-occurrences of Mg- and Ca-sulfates are common in Gale crater and other places on Mars such as Mawrth Vallis and Valles Marineris (e.g., Chojnacki and Hynek, 2008; Rampe et al., 2020; Bishop et al., 2023). They show many similarities to the secondary sulfate occurrences in the Rio Puerco necks region, strongly suggesting the importance of sulfide weathering and short-lived water activity under a dry climate in the past on Mars.

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Stone-masonry cabin likely built by Hispanic farmers during 1880–1950. The cliffs across the Rio Puerco are capped by the Dalton-Hosta sandstone tongue. The impressive Cabezon neck stands on the left. View is to the east.