Proposed Origin of the Burns Formation (Meridiani Planum, Mars) by Erosion, Reworking, and Diagenetic Alteration of a Grasberg-like Precursor

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Abstract

The sulfate-rich sandstones of the Burns formation investigated by the Opportunity rover on Meridiani Planum, Mars, are directly underlain by the fine-grained sedimentary rocks of the Grasberg formation. It was recently shown that, except for differing amounts of MgO and SO₃, the Burns and Grasberg rocks have nearly identical chemical compositions, suggesting both units are genetically related. Here, quantitative models demonstrate that the chemical composition of the Burns formation can be accurately reproduced by addition of MgO and SO₃ to a Grasberg-like precursor, along with small amounts of Ni. Based on this result, a new scenario is proposed for the origin of the Burns formation: (1) deposition of fine-grained airfall deposits with composition similar to the Grasberg rocks; (2) induration of the deposits, resulting in materials that closely resemble the current Grasberg formation in composition and texture; (3) erosion into sand-sized particles, which are then reworked by eolian and fluvial processes to form the bedding features observed in the Burns rocks; (4) infiltration of the deposits by one or more generations of groundwater, resulting in diagenetic alteration that included local element redistribution, dissolution/recrystallization of minerals, cementation, and formation of hematite spherules; (5) evaporation of groundwater at some point during diagenesis enriched the Burns sediments in MgO and SO₃, with greater amounts accumulated closer to the surface. This scenario fully accounts for the chemical composition of the Burns sandstones as well as their sedimentary and diagenetic features, while invoking only a known sediment source and sedimentary/diagenetic processes widely observed on Mars.

1. Introduction

The Burns formation on Meridiani Planum consists of sulfate- and hematite-rich sandstones with prominent bedding features indicative of deposition by eolian and fluvial processes. As one of the few places on Mars that have been examined in detail by rovers, the Burns sandstones are a keystone for interpretations of sediment sources and depositional mechanisms on Mars, for understanding of diagenetic alteration of martian sediment deposits, and for the evolution of environmental conditions at the surface of the planet. Investigation of the Burns rocks also offers potential insights into the origin of the layered sulfate-rich deposits that are widespread geologic features across Mars (e.g., Gaillard et al., 2013; Ehlmann and Edwards, 2014). Unraveling the processes involved in the formation of the Burns sandstones is therefore a critical component to understanding the early geologic history of Mars.

Given the limited amount of mineralogic information available for the Burns rocks, their chemical composition provides what is perhaps the most fundamental set of data that can be used to interpret the source of the sediments and their subsequent diagenesis. It was recognized very early in the Opportunity rover mission that the rocks currently have a chemical composition which closely resembles martian basalts with the addition of a sulfur component (e.g., Squyres et al., 2004, 2006; Clark et al., 2005; McCollom and Hynek, 2005). Accordingly, scenarios that have been proposed to explain the origin of the sandstones have largely focused on environments and processes that allow sulfur-bearing and basalt-derived components to be combined at some stage during formation of the rocks.

Over the years, a number of different models have been proposed to account for the chemical composition of the Burns rocks. Most of these models, however, can be categorized into two general types, as illustrated in Figure 1. One type of model (Fig. 1a) proposes the Burns rocks represent mixtures of two end-members consisting of (a) Mg-, Fe-, and Ca-sulfate salts and (b) chemically altered basalt depleted in Mg, Fe, and Ca (referred to hereafter as the "sulfur-plus-cations" model; Squyres et al., 2006; Hurowitz and Fischer, 2014). This chemical model is generally portrayed in the context of a broader overall scenario for the origin of the Burns sandstones, which will be referred to here as the "sedimentary-evaporite" scenario. In this scenario, the sulfate and altered basalt components are combined through evaporation of groundwater on the margins of playa lakes, and these materials then eroded into sulfate-cemented siliciclastic sand-sized grains that were transported by wind and water to be deposited at their present location (Squyres et al., 2004, 2006; McLennan et al., 2005; Grotzinger et al., 2005, 2006; and others). Following deposition, it is thought that the sands were diagenetically modified during multiple episodes of groundwater infiltration (McLennan et al., 2005), ultimately resulting in the sandstones observed by Opportunity.

The second type of proposed chemical model ("sulfur-only"; Fig. 1b) infers that the composition of the rocks is accounted for by addition of a sulfur component to pristine martian basalt, likely as sulfuric acid derived from an atmospheric or volcanic source (McCollom and Hynek, 2005; Tréguir et al., 2008; Berger et al., 2009; Niles and Michalski, 2009; McCollom, 2018). In these models, the sulfur component is added to the basalt component without any accompanying cations or input of elements other than S and O (thus, "sulfur-only"). Geochemical mass-balance calculations indicate that either of these two types of models can potentially account for the observed chemical compositions of the Burns rocks (McCollom, 2018). However, of these two types, the sulfur-only model is found to provide a much simpler and more straightforward pathway to explain the current chemical composition of the Burns rocks.



Here, a new alternative chemical model is proposed for the Burns sandstones that involves diagenetic addition of MgO and SO_3 to materials having an initial elemental composition similar to that of the underlying Grasberg formation (Fig. 1c). Motivation for this model largely derives from a recent study which showed that, except for differences in the abundances of MgO and SO_3 , the Burns and Grasberg rocks have nearly identical chemical compositions (McCollom and Hynek, 2021). This similarity in chemical compositions implies that the original sediments for the two formations likely came from closely related sources, or maybe even the same source.

Using analyses of compositional trends and a quantitative geochemical model, we show that the chemistry of the Burns rocks can be closely reproduced by addition of MgO and SO_3 to sediments having an initial

composition similar to that of the Grasberg formation. This finding leads us to further propose a novel scenario for the origin of the Burns formation sandstones that involves erosion, reworking, and diagenetic alteration of materials that initially had a chemical composition and morphology similar to (or identical to) the existing Grasberg rocks. This new scenario implies a distinctly different depositional and diagenetic history for the Burns formation than previously favored scenarios, with very different implications for sediment sources, diagenetic processes, and environmental conditions on the surface of early Mars.

This communication begins with a brief overview of the Burns and Grasberg formations. We then present an analysis of the evidence for diagenetic mobility of chemical elements in these formations, followed by description of the proposed model for diagenetic addition of MgO and SO₃ to the Burns sediments. Finally, we outline our proposed scenario for the origin of the Burns sandstones, which we refer to here as the "diagenetic scenario" to differentiate it from other proposed scenarios.

2. Overview of the Burns and Grasberg formations

The Burns formation consists of sandstones whose framework is thought to be composed of sulfate-cemented siliciclastic sand grains (Fig. 2) (Squyres et al., 2004, 2006; Grotzinger et al., 2005). The ubiquitous presence of sedimentary structures that includes cross-bedding, planar laminations, and festoon cross-laminations indicates the sands were deposited at their current location by a combination of eolian and aqueous processes (Grotzinger et al., 2005, 2006). Following deposition, the sediments underwent diagenetic alteration that included precipitation of isopachous cements, formation of hematite spherules, and dissolution of some minerals leaving behind tabular-shaped voids (Fig. 2a inset; McLennan et al., 2005). Multiple episodes of groundwater infiltration may have been involved in producing the observed diagenetic features (McLennan et al., 2005). The hematite-bearing Burns sandstones are a regional unit that covers a large area ($^{-4} \times 10^{5}$ km²) and may have been even larger in the past (Hynek and Di Achille, 2017).



Burns formation rocks are highly enriched in sulfate, containing between 17 and 28.6 wt% SO₃ (Clark et al., 2005). The remaining chemical elements have a composition that closely resembles typical martian basalt (Squyres et al., 2004, 2006; McCollom and Hynek, 2005, 2006; McCollom, 2018). The Burns rocks displayed very little variation in their chemical composition across the rover traverse of more than 16 km (Fig. 1). One exception, however, is that a subset of nine Burns rocks have anomalously low abundances of MgO and SO₃, which has been widely attributed to partial loss of Mg-sulfate minerals during diagenesis (e.g., Clark et al., 2005; Hurowitz and Fischer, 2014; McCollom, 2018).

Opportunity was not equipped with instrumentation to directly determine the mineralogy of the Burns rocks. However, their mineral composition can be constrained to some extent from other observations (with considerable uncertainty). Based on the bulk chemical compositions and data from the miniature thermal emission (mini-TES) and Mössbauer spectrometers onboard the rover, model mineral compositions include ~30-40% siliciclastic components (possibly including plagioclase, pyroxenes, and nontronite or other

phyllosilicates), 15-25% amorphous silica and/or glass, 5-10% hematite plus other Fe-oxides/oxyhydroxides, and ~30-40% Mg-, Fe-, and Ca-bearing sulfate minerals including natrojarosite, together with minor chloride and phosphate components (Clark et al., 2005; McLennan et al., 2005; Glotch et al., 2006b; Glotch and Bandfield, 2006; Morris et al., 2006).

The Burns formation is directly underlain by the Grasberg formation, first encountered when the rover arrived at the rim of Endeavour crater (Fig. 3; Crumpler et al., 2015; Mittlefehldt et al., 2018). On the Endeavour rim, the Grasberg formation is a thin (~2 m) unit that consists of fine-grained sedimentary rocks, which appear in outcrop as light-toned, flat-lying polygonal blocks (Fig. 3d,f). Outcrops of the Grasberg formation form a distinctive bench which surrounds promontories such as Cape York on the crater rim (Fig. 3a,b). Although Opportunity only investigated exposures of the Grasberg on the western rim of Endeavour, outcrops of similar appearance are present around the crater (Grant et al., 2016) suggesting that the unit is regional in extent. The Grasberg formation has been divided into upper and lower units, with much of the lower unit covered by unconsolidated dark-toned materials that made observations of the underlying bedrock difficult (Fig. 3g).

Bedrocks of the Grasberg formation have a homogenous morphology and lack distinct bedding or other sedimentary structures like those that are ubiquitous in the Burns formation, including the Burns rocks that lie immediately above the Grasberg contact (Fig. 3e,f,g). Individual grains in the Grasberg bedrocks were too small to be resolved by the microscopic imager on Opportunity ($<100 \ \mu m$) and are thus much finer-grained than the sands that compose the Burns formation rocks (0.1-1 mm diameter). The fine-grained textures and lack of bedding features suggests that the Grasberg sediments were originally emplaced as an airfall deposit derived from an impact or volcanic source (Crumpler et al., 2015; Mittlefehldt et al., 2018).

Geochemically, the rocks from the Grasberg formation have moderately high sulfur contents (SO₃ = 6.3 to 13.1 wt.%), albeit they are substantially less enriched in S than the Burns formation (17-28.6 wt.% SO₃). Compared to the Burns formation, the measured compositions of the Grasberg rocks have lower MgO, MnO, and Ni contents and higher SiO₂, K₂O, FeO, TiO₂, and Zn (Crumpler et al., 2015; Mittlefehldt et al., 2018). However, when normalized to the same MgO, SO₃ and MnO contents, the remaining elements have essentially identical abundances in both the Grasberg and Burns formations (McCollom and Hynek, 2021). This close similarity in chemical compositions suggests that the sediments comprising the two units may have come from closely related sources, or maybe even the same source, with subsequent mobilization of MgO, SO₃, and MnO accounting for the observed differences in their present compositions.

Little information is available on the mineralogical composition of the Grasberg rocks, in part because the mini-TES and Mössbauer spectrometers were no longer operating when the rover reached Endeavour. The relatively high SO₃ contents of Grasberg rocks indicates that sulfate minerals are likely to be present, but the identity of these minerals is undetermined. Centimeter-scale gypsum veins are widespread in the lower unit (Fig. 3g), but it is unclear whether gypsum is present in the surrounding bedrocks. Visible-near infrared (VNIR) spectra indicate that the Grasberg rocks contain higher amounts of red hematite than the Burns formation, but the gray hematite spherules that are ubiquitous in the Burns formation are absent from the Grasberg (Farrand et al., 2014).



3. Data sources

Chemical compositions of rocks from the Burns and Grasberg formations used for this study were downloaded from the Planetary Data System (PDS) website in October, 2014, and August, 2018, with one additional Grasberg sample (Ogallala) taken from Mittlefehldt et al. (2021). The chemical compositions of rocks were obtained using the Alpha Particle X-ray Spectrometer (APXS) mounted on the arm of the Opportunity rover (Rieder et al., 2003, 2004; Gellert et al., 2006), and processed using the method, fit program, and calibration parameters described in Gellert et al. (2006). Chemical compositions for other rocks that are included in the figures for context were either downloaded from PDS or derived from literature sources as described in the Supplemental Materials. All data used in the study as well as diagrams based on those data are included as a supplemental spreadsheet (Supplemental Dataset1). To avoid confusion, the names assigned to APXS targets in the PDS database are used in this communication, even though different names have been used for some of the same targets in other published studies.

To avoid contributions from surface deposits and alteration, only those Burns samples that were abraded with the rock-abrasion tool (RAT; Gorevan et al., 2003) are used in the analysis, with the exceptions of Callitris and CapeFairweather1. The latter two samples were either only brushed with the RAT (Callitris) or analyzed untreated (CapeFairweather1), but are included in the data compilation because they represent Burns samples that are adjacent to the contact with the underlying Grasberg formation. Despite not being abraded with the RAT, the compositions of these two targets are similar to the abraded Burns samples, and images of the targets show little evidence for contamination from surface debris or alteration of the bedrock (McCollom and Hynek, 2021). Because only a relatively small number of targets from the Grasberg formation were analyzed by Opportunity, the analysis includes both RAT abraded and brushed Grasberg samples. However, these samples form a coherent group with similar composition and appear to be a reasonable representation of the composition of the bedrock without any significant surface contribution (see McCollom and Hynek, 2021). Furthermore, images of the brushed Grasberg targets show very little surface debris and no obvious evidence of alteration (McCollom and Hynek, 2021).

4. Investigating diagenetic mobilization of MgO and SO_3 in the Burns formation

4.1. Geochemical trends in the Burns and Grasberg formations

The major element compositions of the Burns formation rocks analyzed by Opportunity were nearly uniform in composition across the rover's entire traverse from Eagle crater to Endeavour crater (Fig. 1; McCollom, 2018). One notable exception, however, is that a subset of nine rocks have significantly lower-than-average MgO and SO₃ abundances. These rocks were first encountered in Endurance crater, where rocks exposed deep within the crater's interior were found to have anomalously low abundances of MgO and SO₃ (Fig. 4; Clark et al., 2005). Subsequently, rocks with similarly low MgO and SO₃ contents were identified for Burns rocks in the interior of Victoria crater (Squyres et al., 2006) and just above the contact with the underlying Grasberg formation (McCollom and Hynek, 2021). Heretofore, the trend of decreasing MgO and SO₃ at depth within Endurance and Victoria craters has generally been attributed to partial removal of Mg sulfate minerals from the deeper deposits during diagenesis (Clark et al., 2005; Niles and Michalski, 2009; Hurowitz and Fischer, 2014; McCollom, 2018; McCollom and Hynek, 2021). However, loss of MgO and SO₃ does not appear to be a unique interpretation, and alternative explanations have been proposed (e.g., Amundson et al., 2008; Amundson, 2018).



The samples at depth within Endurance crater also exhibit relatively high abundances of several elements, including Si, Al, Na, and K (Fig. 4). However, mass balance calculations indicate that the higher abundances for this group of elements can be explained by passive enrichment in their relative abundances owing to the lower amounts of MgO and SO₃ without any need to invoke mobilization or differences in sediment composition (McCollom, 2018; Amundson, 2018). The abundances of Ca and Fe exhibit variable abundances with no discernible trend as a function of depth in Endurance (Fig. 4), which is potentially attributable to localized redistribution during diagenesis with no net transfer into or out of the formation (McCollom, 2018).

Because Ti is essentially immobile in a broad range of geologic environments, element: TiO_2 ratios provide a useful tool for assessing the extent of mobilization by aqueous fluids. Element: TiO_2 ratios have been used to assess mobilization of elements by fluids in a variety of martian settings, with anomalously higher ratios indicating enrichment in a particular element and lower ratios indicating loss of the element (e.g., Ming et

al., 2008; Ruff et al., 2014; Zolotov and Mironenko, 2016; Yen et al., 2017a; Hausrath et al., 2018; McCollom, 2018; Amundson, 2018). Element: TiO_2 ratios can be effected by processes other than element mobilization, but there is no indication that these other factors have contributed to variations in element: TiO₂ ratios in the Burns or Grasberg formations (McCollom, 2018; McCollom and Hynek, 2021). For instance, heavier Ti-bearing minerals can be physically sorted and separated from silicate minerals during eolian or fluvial transport, resulting in variations in element: TiO₂ ratios within sedimentary deposits (e.g., Fedo et al., 2015). However, Ti abundances in the Burns rocks exhibit strong positive linear correlations that converge on the origin for both Si and Al, and the Grasberg rocks plot on the same trend (Supplemental Fig. S1). These trends are inconsistent with the negative correlations that would be expected if sorting during transport had separated Ti-bearing minerals from siliciclastic components. Variations in element: TiO_2 ratios can also arise from variability in TiO_2 abundance of the sediments as they are deposited (e.g., Sheldon and Tabor, 2009; Sharma et al., 2013). But, when adjusted for differing amounts of MgO and SO_3 , the abundance of TiO_2 is constant within analytical error for all Burns and Grasberg samples (McCollom and Hynek, 2021). Furthermore, element: TiO₂ ratios for many elements are nearly uniform across the Burns formation, including Si, Al, Na, K, Mn, P, and Cr (McCollom, 2018). Consequently, there is no indication that there were significant variations in TiO_2 abundance of the sediments when they were initially deposited. Thus, it appears that element: TiO₂ ratios are an accurate indicator of the relative mobility of individual elements in the Burns and Grasberg formations.

Measured element: TiO_2 ratios in the Burns and Grasberg rocks are displayed in Figure 5 as a function of relative depth. To allow for better interpretation of general trends, the compositions of Burns rocks in this and other diagrams have been separated into four categories: (1) rocks encountered along the rover's traverse along the surface, rocks exposed within the walls of (2) Endurance and (3) Victoria craters, and (4) rocks located just above the contact with the underlying Grasberg contact (i.e., Callitris and CapeFairweather1). Also, to facilitate comparison, the relative depths of rocks exposed within Victoria crater are plotted next to those from within Endurance crater based on similarities in depth below the crater rim and physical appearance; however, the actual stratigraphic relationship of these materials is uncertain. Some studies have hypothesized that Victoria crater lies stratigraphically above Endurance crater (e.g., Squyres et al., 2009; Hayes et al., 2011) and that Opportunity traversed downward through a stratigraphic section more than 100 m deep as it drove towards Endeavour crater (Edgar et al., 2014). However, the available geologic evidence for this is equivocal since there are no continuous exposures of bedding over long distances between the craters or any other features (e.g., marker beds) that would allow stratigraphic relationships to be established along the rover's traverse. Therefore, it is equally plausible that the entire Burns formation consists of a relatively thin (<20 m) unit uniformly draped on top of existing topography. In the latter case, rocks exposed within Victoria and Endurance would be at an approximately equivalent stratigraphic depth. In any event, the Burns rocks found just above the Grasberg contact along the rim of Endeavour crater presumably lie at an even greater depth in the formation than those exposed within Endurance and Victoria craters, although how much deeper is unclear.

As seen in Fig. 5, both MgO:TiO₂ and SO₃:TiO₂ decrease with depth in Endurance crater, which is especially evident in the samples exposed in the deepest part of the crater below the Wellington contact (Fig. 1b). In addition, the deepest samples that have the lowest MgO and SO₃ levels also have relatively low Ni:TiO₂ ratios, suggesting that mobilization of Ni may have been coupled to that of Mg. Coupled mobilization of Ni and Mg would be consistent with the inferred Ni enrichment of Mg-sulfate minerals on Mars (vanBommel et al., 2016; Yen et al., 2017b). As observed in Endurance, the deepest samples in Victoria crater also exhibit low MgO:TiO₂, SO₃:TiO₂, and Ni:TiO₂ ratios. Moreover, the Burns rocks closest to the Grasberg contact also exhibit low ratios for these same elements (Figs. 5a, 5b, and 5k).

Nearly all samples from within Endurance and Victoria craters have FeO:TiO₂ and CaO:TiO₂ ratios that are lower than the average for samples measured along the surface traverse (Figs. 5g & 5h). However, there is no clearly discernible trend in the FeO:TiO₂ and CaO:TiO₂ data as a function of depth like that observed for MgO and SO₃. Consequently, these variations may reflect small-scale heterogeneities or localized redistribution of Fe and Ca on the scale of centimeters rather than significant net transport into or out of the formation, consistent with other evidence for localized mobilization of these elements during diagenesis (e.g., formation of hematite spherules; McCollom, 2018).



Chlorine abundances in Burns formation rocks have a bimodal distribution, with one group of samples having abundances around 0.6 wt.% and a second group with ~1.6 wt.% Cl (Clark et al., 2005; McCollom, 2018). These values translate to Cl:TiO₂ ratios of ~0.4 and ~2.0, respectively (Fig. 5m). Notably, nearly all of the Burns samples with higher Cl abundances are found at depth within Endurance and Victoria craters, with a transition in Endurance crater that occurs near the Whatanga contact (Fig. 5m).

The remaining elements, including Si, Al, Na, K, Cr, Mn and P, all exhibit element: TiO_2 ratios that are nearly constant throughout the formation with no discernible difference between the samples at depth and those at the surface. The constant ratios suggest that this group of elements was essentially immobile throughout diagenesis (McCollom, 2018). Constant ratios could also arise if the same amount of an element was added to or removed from all samples, but this seems to be a much less likely possibility.

The Grasberg rocks that immediately underly the Burns formation on the rim of Endeavour crater have even lower MgO:TiO₂ and SO₃:TiO₂ ratios than the Burns rocks, as well as lower Ni:TiO₂ ratios than all Burns rocks except for Callitris and CapeFairweather1 (Figs. 5a, 5b, and 5k). Most Grasberg rocks also have lower MnO:TiO₂ and P₂O₅:TiO₂ ratios than the Burns rocks, although the two Burns samples immediately above the contact have similarly low MnO:TiO₂ ratios (Fig. 5j) and a couple of Grasberg samples have P₂O₅:TiO₂ ratios similar to the Burns rocks (Fig. 5l). With few exceptions, element:TiO₂ ratios for all other major elements in the Grasberg rocks are within the range of the Burns samples, reflecting the close similarity in chemical composition between the two formations (McCollom and Hynek, 2021).

The Grasberg rocks exhibit a range of $Cl:TiO_2$ ratios that is similar to the Burns formation, but too few samples are available to determine if this range is representative of the formation as a whole. It is worth

noting, however, that the two Grasberg analyses with the highest $Cl:TiO_2$ ratios ("Grasberg1 brush RAT brush" and "Grasberg3 brush RAT offset") were obtained on targets immediately adjacent to one another on the same outcrop, and the Cl levels in these adjacent samples were substantially higher than any other analyzed Grasberg rocks (including those samples that were not treated in any way by the RAT prior to analysis which were not included in this study; McCollom and Hynek, 2021). In addition, the two targets with elevated Cl have higher Na than any other Grasberg samples and also have higher amounts of these elements than any Burns samples. Consequently, it is possible that the elevated Cl and Na in these two Grasberg targets may represent a local enrichment in Cl-bearing salts, with most of the formation having substantially lower amounts of these elements.

4.2. Interpretation of element mobility during diagenesis of the Burns and Grasberg formations

The chemical trends shown in Figure 5 allow several inferences to be made concerning element mobility in the sedimentary rocks on Meridiani Planum. First, the systematic variations in MgO and SO₃with depth in the Burns rocks strongly suggests that these elements were mobilized during diagenesis (Figs. 5a and 5b; Clark et al., 2005; Niles and Michalski, 2009; Hurowitz and Fischer, 2014; McCollom, 2018; McCollom and Hynek, 2021). If, as the data suggest, the initial sediments that form both the Grasberg and Burns formations came from a related source with similar chemistry (McCollom and Hynek, 2021), then the even lower MgO and SO₃ levels in the Grasberg rocks can be viewed as continuation of the same trend as that observed for the Burns rocks (Figs. 5a and 5b).

The lower abundances of MgO and SO₃ at depth within Endurance and Victoria craters has conventionally been attributed to partial loss of these components from the deeper deposits during diagenesis (Clark et al., 2005; Niles and Michalski, 2009; Hurowitz and Fischer, 2014; McCollom, 2018; McCollom and Hynek, 2021). Here, we propose an alternative model whereby the Burns sediments initially had much lower abundances of MgO and SO₃ that were similar to those of the Grasberg formation, and were subsequently enriched in these components during diagenesis. The mechanism for this enrichment would presumably involve evaporation of Mg- and sulfate-bearing groundwater. Nickel would be transported along with Mg and precipitate as a component of Mg-sulfate minerals during evaporation, accounting for the similar trends for Ni and MgO in the rocks (Figs. 5a and 5k). Alternatively, the precipitation of Mg- and Ni-bearing sulfate salts could have resulted from freezing of upwelling groundwater in the shallow subsurface (e.g., Marion et al., 2008) followed by gradual sublimation of the residual water ice.

In this proposed model, the lower MgO, SO₃, and Ni abundances observed for the Grasberg rocks would represent the pristine composition of both formations, with all Burns rocks becoming significantly enriched in these components during diagenesis. Precipitation of greater amounts evaporite minerals closer to the surface would then account for the variation of MgO, SO₃, and Ni with depth in Endurance and Victoria craters (Figs. 5a, 5b, and 5k), rather than transport of these components out of the deeper deposits. Thus, this model would simultaneously account for both the differences in composition between the Burns and Grasberg formations and for the increasing abundances of MgO, SO₃, and Ni in the shallower samples.

If the original sediments that formed the two units initially had similar compositions, then the lower $MnO:TiO_2$ and $P_2O_5:TiO_2$ ratios in the Grasberg rocks relative to the Burns must also be accounted for (Figs. 5j and 5l). Potentially, the generally higher abundances of Mn and P in the Burns rocks relative to the Grasberg could be accounted for either by diagenetic enrichment of the Burns rocks in Mn and P or by depletion of these elements in the Grasberg rocks. Of course, it's also possible that the original sediment sources for the Burns and Grasberg formations initially had different abundances of Mn and P; however, this appears to be a much less likely explanation given the close similarity in abundances of the other elements (McCollom and Hynek, 2021). That is, it seems unlikely that that the Mn and P abundances would be radically different in the sediment sources for the two units when nearly all other elements are almost identical.

In the case of Mn, Ming et al. (2015) noted that the Grasberg rocks have FeO:MnO ratios that are substantially higher than is typical for martian crust (Fig. 6), and they proposed that the elevated ratios are attributable to partial removal of Mn by aqueous fluids during diagenesis. Removal of Mn would also account for the lower MnO: TiO_2 ratios in the Grasberg rocks (Figs. 5j and 6). If this explanation is valid, the higher MnO: TiO_2 ratios observed for most Burns rocks may represent the original composition of the sediments, and the Grasberg deposits would presumably have had similar ratios prior to the loss of Mn during diagenesis.



Alternatively, the lower MnO:TiO₂ ratios of the Grasberg formation may represent the pristine composition, which would then require that the entire Burns formation was enriched in Mn during diagenesis in order to explain the higher ratios in that unit. This possibility would also require that the original sediment source for both units had substantially higher FeO:MnO and lower MnO:TiO₂ ratios than is observed for most martian basalts or estimated for the average martian crust (Fig. 6b). However, this does not appear to be an unreasonable requirement given that many of the sedimentary rocks of the Murray formation in Gale crater examined by the Curiosity rover have FeO:MnO and MnO:TiO₂ values similar to those of the Grasberg (Fig. 6b). Unless there has been widescale transport of Mn out of the Murray rocks (for which there appears to be little evidence), their relatively high FeO:MnO and low MnO:TiO₂ ratios must reflect a sediment source that is depleted in Mn relative to most martian basalts and to the average martian crust.

On balance, it appears that the simpler explanation for the data is that the Grasberg sediments initially had Mn levels similar to that of most Burns rocks, but some of this Mn was lost from the Grasberg rocks during diagenesis as proposed by Ming et al. (2015). This explanation would be consistent with the similarity of the FeO:MnO and MnO:TiO₂ ratios in the Burns rocks to those of martian basalts and to average martian crust (Fig. 6b). It would also be consistent with the nearly uniform MnO:TiO₂ ratios throughout the Burns formation (excepting the two rocks adjacent to the Grasberg contact; Fig. 5j). If substantial amounts of Mn had been added to the Burns deposits during diagenesis as required by the alternative explanation, it is difficult to imagine that all of the deposits were enriched by the same amount of Mn as would be required to explain the uniform MnO:TiO₂ ratios in the Burns rocks. Whether or not the inferred loss of Mn might be related to the process that enriched the Burns rocks in MgO and SO₃ is unclear and requires further study.

On this topic, it is worth noting that the two Burns rocks immediately above the Grasberg contact, Callitris and CapeFairweatther1, have FeO:MnO and MnO:TiO₂ ratios that are lower than the rest of the Burns samples, but similar to those of the underlying Grasberg rocks (Figs. 5j and 6a). This would imply that any diagenetic loss of Mn that occurred in the Grasberg rocks extended into the base of the Burns formation, at least in the region of the Endeavour crater rim explored by Opportunity. Furthermore, it would imply that the Mn loss took place after the Burns sediments were already emplaced (McCollom and Hynek, 2021).

Previously, McCollom et al. (2018) argued that P was immobile throughout deposition and diagenesis of the Burns formation. This inference was based on: (1) the limited variability in both the abundance of P and the P:Ti ratios in the Burns rocks (Fig. 51), and (2) the close similarity of the P levels and P:Ti ratios in the Burns rocks to those of most martian basalts. If the original sediments for both the Burns and

Grasberg formations had similar compositions and P was immobile during diagenesis of the Burns, then the lower P_2O_5 :TiO₂ ratios observed for most Grasberg rocks (Fig. 51) would have to be attributed to partial removal of P or to variation in source sediment composition. Alternatively, the higher P_2O_5 :TiO₂ ratios in the Burns formation could be explained by mass transfer of P into the Burns sediments during diagenesis, enriching the amount of P in the sediments from an initial composition that was similar to the Grasberg rocks. However, as for Mn, this would require that P was added in almost uniform amounts to the Burns deposits to account for the limited variability in P_2O_5 and P_2O_5 :TiO₂, which seems less likely.

Lastly, the bimodal distribution of Cl indicates that it was likely mobilized to some extent during diagenesis. Of course, this is not surprising given the high solubility of Cl-bearing minerals and evidence for mobilization of Cl elsewhere on Mars. However, the extent of mobilization of Cl into the deposits, as well as its possible relationship with the inferred enrichment in MgO and SO_3 , is not immediately evident.

All but two of the Burns samples with high abundances of Cl are found at depth within Endurance and Victoria craters (Fig. 5m). One of the exceptions is LemonRind, where the analyzed target has the appearance of alteration rind or coating of a fracture surface (Supplemental Fig. S2). LemonRind has a much higher Cl content than the immediately adjacent target (Fruitbasket_Strawberry) where abrasion by the RAT appeared to penetrate the materials analyzed at LemonRind. Thus, the high Cl contents of Lemon-Rind appear to represent a localized enrichment, perhaps caused by fluid flowing within a fracture. The other exception is the target BlackShoulder_Abraded, encountered on the plains north of Murray Ridge on the rim of Endeavour crater. Images of this target are less clear (Supplemental Fig. S2), but it could also represent a rind or fracture coating.

Notably, the transition from lower to higher Cl contents in the samples within Endurance crater appears to coincide with the Whatanga contact (Figs. 1a and 5m). The shift from lower to higher Cl coincides with a transition from lighter to darker tone in the exposures of bedrocks in the crater walls (Supplemental Fig. S3). The rocks below the contact have rougher surfaces with more cavities, and the darker tone is largely attributable to the accumulation of dark surface materials within these cavities rather than a darker color of the underlying bedrock itself. The contact has been interpreted as possibly representing the capillary fringe of a groundwater table, with recrystallization of cements in the saturated materials below the contact leading to the difference in morphology and surface texture (Grotzinger et al., 2005). In Victoria crater, the transition from lower to higher Cl contents with depth also appears to coincide with a transition from lighter- to darker-toned bedrock exposures (Supplemental Fig. S3).

These observations suggest that the elevated Cl contents for the bedrocks exposed at depth within Endurance and Victoria craters could be attributable to precipitation of Cl-bearing minerals as the groundwater table lowered and the capillary fringe retreated into the subsurface. Whether or not this inferred Cl enrichment is associated with enrichments in MgO and SO₃ is unclear at this time. It is worth noting, however, that the transition from lower to higher Cl appears to occur at a shallower depth (near the Whatanga contact; Fig. 5) than the transition from higher to lower MgO and SO₃(near the Wellington contact). One possible explanation to explain these trends that might be worth exploring in future studies is that the MgO and SO₃ enrichments were caused by evaporation of fluids in a rising water table and wicking towards the surface, while the more soluble Cl-salts precipitated as the groundwater retreated back into the subsurface.

4.3. Geochemical model for enrichment of the Burns formation in Mg, SO_3 , and Ni

To test whether the inferred diagenetic enrichment of the Burns formation in MgO, SO₃, and Ni can account for the chemical compositions of the rock samples analyzed by Opportunity, a quantitative mass-balance model was constructed to simulate addition of these components to a Grasberg-like precursor (Fig. 7). The model calculations involved addition of MgO, SO₃, and Ni in increments to materials that were assumed to have an initial composition equivalent to the average of the Grasberg formation samples. Following the addition of each increment, the abundances of all elements were renormalized to total 100 wt%. The resulting model predicts trends of increasing abundances for MgO, SO₃, and Ni, while the relative abundances of all other (immobile) elements progressively decrease owing to passive dilution by the addition of increasing amounts of MgO, SO₃, and Ni (Fig. 7). The model calculations are included in the accompanying spreadsheet (Supplemental Dataset1), where interested readers can vary the input parameters to examine how different input parameters effect model predictions.

It was assumed for this initial model that Mn and P were not transported into the Burns sediments along with MgO, SO₃, and Ni, but were instead partially removed from the Grasberg by a separate diagenetic process not explicitly incorporated into the model. To account for the presumed higher Mn concentrations in the original sediments relative to their current abundance in the Grasberg rocks, it was assumed that both units originally had an MnO:TiO₂ratio similar to that currently observed in the Burns rocks. This assumption leads to an estimated MnO abundance of 0.43 wt% in the original sediments. Additionally, it was assumed that the two RAT-abraded Grasberg samples that have the highest P_2O_5 :TiO₂ ratios approximates the pristine composition of the sediments prior to the inferred loss of P. For simplicity, mobilization of Cl was not considered in this initial model. Although mobilization of Cl may well be linked to the inferred enrichment in MgO and SO₃, exploring this possibility would require much more elaborate modeling strategies than employed here, and therefore must await subsequent studies. Again, readers can modify the model calculations in the accompanying spreadsheet to explore alternatives to these assumptions.



During development of the model, it was observed that addition of the MgO and SO₃ in a 1:1 molar ratio did not result in compositional trajectories that passed through the Burns MgO data. Therefore, the MgO:SO₃ ratio was varied in the model, and a ratio equal to 0.65 was found to provide the closest approximation to the Burns data overall based on visual inspection. Since Mg-sulfate minerals generally have a MgO:SO₃ equal to one, this result would imply that the evaporating diagenetic fluids precipitated greater amounts of SO₃ than could be accounted for by precipitation of Mg-sulfate minerals alone. The excess of SO₃ could be explained if additional cations were extracted from the sediments as they reacted with the evaporating groundwater and were subsequently incorporated into precipitation of sulfate minerals. For instance, reaction of pyroxene in

the sediments with SO_4 -bearing groundwater could result in precipitation of sulfate minerals together with amorphous silica (e.g., McCollom et al., 2013), as illustrated by the generalized reaction:

(Mg, Fe, Ca) Si O_3 [augite] + SO₄²⁻ + H⁺ + H₂O \rightarrow MgSO₄H₂O [kieserite] + FeSO₄H₂O [szomolnokite] + CaSO₄2H₂O [gypsum] + SiO_{2(am)} [amporphous silica](1)

where the exact stoichiometry would depend on the composition of the dissolving pyroxene. The result of such reactions would be incorporation of sulfate from the fluid without additional enrichment of the sediments in Mg or other cations. The model results shown in Figure 7 also assume Ni is added at a Ni:SO₃ ratio of 0.00233.

Results of the mass-balance model are displayed in Figure 7, with the red arrows representing model predictions for how the abundances of individual elements should evolve with increasing addition of MgO, SO₃, and Ni. As seen in the figure, this simple model provides a very close fit to the observed Burns formation data for most elements, especially for the group of elements whose relatively constant element:TiO₂ ratios indicate that they have been immobile during diagenesis (i.e., Si, Al, Na, K, Ti, and Cr, see Fig. 5; McCollom, 2018). The model also captures the general trend of the P_2O_5 data for the Burns rocks, albeit the trend is offset to somewhat lower P_2O_5 abundances (Fig. 7l). Furthermore, the model accurately reproduces the MnO data for most Burns samples (Fig. 7k), provided the assumed higher Mn abundance is representative of the original sediments. The two Burns samples adjacent to the Grasberg contact lie well below the predicted MnO trend, but this could potentially be explained by loss of Mn from these samples during diagenesis similar to that inferred for the Grasberg.

The model also reproduces the general trends of higher MgO and lower FeO and CaO for the Burns rocks compared to the Grasberg (Figs. 7g, 7h, and 7i). However, the abundances of these elements in the Burns rocks are highly variable among samples and do not exhibit consistent trends as a function of SO_3 like that observed for most other elements (Fig. 7). A likely explanation for the scatter of Mg, Fe, and Ca around the predicted model trends is that they were affected by additional processes during diagenesis, which probably involved localized redistribution (\tilde{s} scale of centimeters) of these elements during mineral dissolution and reprecipitation (McCollom, 2018). The inferred localized redistribution of Mg, Fe, and Ca would be consistent with the abundant evidence for formation of hematite spherules and late-stage sulfate cements (Squyres et al., 2004, 2006; McLennan et al., 2005; Grotzinger et al., 2005).

It is also worth noting that, for most elements, the compositional trajectories predicted by the diagenetic model correspond very closely to linear regression lines fit to the Burns data as a function of SO_3 (Supplemental Fig. S4). The close agreement between the model predictions and the independently calculated regression lines provides further support for the argument that the diagenetic model accurately replicates the observed chemical compositions of the Burns rocks. For Fe, Ca and Mn, the regressions provide a poor fit to the data and the predicted model trajectories do not correspond particularly well to the calculated regression lines (Supplemental Fig. S4). However, given the evidence that additional diagenetic process had a large effect on the distribution of these elements, neither a close correlation with SO_3 nor a close match between model predictions and the regressions would necessarily be expected.

4.5. Comparison with previously proposed geochemical models

Any proposition of a new model naturally raises questions about how it compares with other models proposed to explain the same data. Accordingly, in this section we compare our new diagenetic model with others that have been proposed to account for the chemical composition of the Burns formation, including the sulfurplus-cations and sulfur-only chemical models (Fig. 1). We also briefly address a sulfide mineral oxidation model for the Burns formation that has been proposed by some authors (Zolotov and Shock, 2005; Dehouck et al., 2012).

Advocates of sulfur-plus-cations models have so far provided only rudimentary details of their chemical model, which to date consist only of demonstrating that the measured compositions of the Burns rocks lie on mixing lines between two endmembers projected onto element-ratio diagrams (Fig. 8; Squyres et al.,

2006; Hurowitz and Fischer, 2014). Squyres et al. (2006) proposed that the chemical composition of the Burns rocks could be accounted for by a mixture of two endmembers composed of: (1) chemically altered martian basalt depleted by about 55% in Σ (Fe + Mg + Ca), and (2) a mix of Mg-, Fe- and Ca-sulfate minerals deposited by evaporating fluids. As shown in Figure 8a (modified after Figure 3 in Squyres et al., 2006), the Burns rocks fall close to a mixing line between the specified endmembers (black line) when plotted in the dimensions of Al₂O₃/(FeO+MgO+CaO) versus SO₃. The comparison shown in this diagram is the only criteria used by Squyres et al. (2006) to support their chemical model. Neither the proportions of cations removed from the basalt precursor nor those added in as sulfate precipitates are specified, and no compositional information on the endmembers is provided beyond the constraint that they possess element ratios consistent with the mixing line.



Also portrayed in Figure 8a by the red arrow is the calculated trajectory of rock compositions for diagenetic addition of MgO and SO₃to a Grasberg-like precursor as proposed here, projected onto the same parameter space as the Squyres et al. (2006) diagram. As seen in the figure, the diagenetic model provides a comparably good match to the observed Burns data as the Squyres et al. (2006) model. The sample that deviates the most from the predicted diagenetic trajectory is MacKenzie_Campbell, which has the highest wt.% Al₂O₃ of any Burns sample and accounts for its position above the predicted trajectory. The anomalously high Al₂O₃ of this sample suggests a localized enrichment in Al-bearing minerals, either in the original materials or during diagenesis.

Hurowitz and Fischer (2014) proposed a similar two-endmember mixing model for the Burns rocks, but with somewhat different element ratios used to constrain the endmembers (Fig. 8b). Hurowitz and Fischer (2014) defined the endmembers in terms of two element ratios, $Al_2O_3/(FeO+MgO+CaO+Na_2O+K_2O)$ and SiO_2/SO_3 , and estimated endmember compositions by fitting mixing models to the measured ratios of the Burns rocks. Hurowitz and Fischer (2014) considered two separate fits that either: (a) included the subset of Burns samples with the lowest MgO and SO₃ abundances, or (b) excluded them on the presumption that these components were partially removed during diagenesis.

As seen in Figure 8b, the fits of Hurowitz and Fischer (2014) accurately reproduce the chemical compositions of the Burns rocks when portrayed in this parameter space. Their preferred mixing model that excludes the low MgO and SO₃ samples constrains the groundwater-derived component to have high SO₃ together with little or no SiO₂ or Al₂O₃, while the siliciclastic component has an Al₂O₃/(FeO+MgO+CaO+Na₂O+K₂O)

ratio between 0.15 and 0.18 and contains no more than a few wt% SO_3 (Fig. 1b). These authors noted that, on the siliciclastic component end, the inferred mixing lines extend through compositional fields for cation-conservative alteration of Adirondack class basalts by sulfur-bearing fluids and for soils analyzed by the Opportunity and Spirit rovers, which could potentially provide some insight into the source of the siliciclastic component (Fig. 8b).

For the dimensions portrayed in Figure 8b, the diagenetic model proposed here closely parallels the mixing model of Hurowitz and Fischer (2014). This is not totally unexpected, however, since the proposed diagenetic model is essentially a two-component mixing model with Grasberg-like materials and MgO-SO₃ precipitates as endmembers. The endmembers of the diagenetic model proposed here are consistent with the constraints derived by Hurowitz and Fischer (2014), and the compositions of the Grasberg rocks lie close to the extension of their mixing line to the inferred composition of the siliciclastic component. Again, the sample that deviates the greatest amount from the trends defined by both models is MacKenzie_Campbell, whose anomalously high Al_2O_3 abundance causes it to fall above the predicted lines in this parameter space.

Thus, the proposed diagenetic model appears to be generally consistent with the mixing model calculated by Hurowitz and Fischer (2014), although those authors interpret the mixing to take place in an entirely different context than proposed here. Hurowitz and Fischer (2014) interpret the mixing as occurring on the margins of a playa lake, where evaporating fluids precipitate multi-cation sulfates and mix with siliciclastic materials to account for the measured compositions of the Burns rocks. Conversely, the diagenetic model here involves addition of only a single cation, and invokes addition of the evaporite component during diagenesis rather than before deposition. Nevertheless, the convergence between the proposed diagenetic model (with compositions predicted independent of the measured compositions of the Burns samples) and the mixing model of Hurowitz and Fischer (which is derived through a fit to the measured compositions of the Burns rocks) provides additional confirmation that the diagenetic model accurately reproduces the Burns data.



Another perspective comparing these two types of models is provided in Figure 9, which shows the somewhat curious observation that total cation concentrations are nearly uniform across all Burns samples independent of their SO₃ abundance. This invariance is illustrated by linear regressions of the Burns data, which are essentially horizontal lines (Fig. 9). If substantial amounts of cations were transported into the Burns precursor materials along with the sulfur component as suggested in the model proposed by Squyres et al. (2006), the Burns data should display a positive correlation between Σ (FeO + MgO + CaO) and SO₃, which is not observed in the data (dashed blue arrows in Fig. 9). The only way that the observed trend in the Burns data could possibly be reconciled with the cation-plus-sulfur model is if there were substantial losses of cations and SO₃ from some samples during diagenesis along with gains in others, producing a trend that deviates from the expected positive correlation (see McCollom, 2018). In addition, it can be seen Figure 9 that Grasberg data fall even farther from the expected trajectory for the cations-plus-sulfur model. Consequently, the cation-plus-sulfur model cannot account for the close chemical similarity of the Grasberg

and Burns formations unless there was an even more extensive loss of cations from the Grasberg during diagenesis. Although possible, this reconciliation of cations-plus-sulfur models with the observed data would require much more extensive mobilization of cations during diagenesis than required by sulfur-only models (McCollom, 2018) or the model proposed here. On the other hand, the proposed diagenetic model readily accounts for the observed trends in total cations in the Burns rocks as well as their similarity to the Grasberg rocks (Fig. 9).

With respect to the sulfur-plus-cations models, it is also worth emphasizing that although these models reasonably reproduce the Burns data when portrayed in the parameter spaces depicted in Figure 8, they have much greater difficulty in reproducing the data when examined from more comprehensive perspectives. Indeed, a major strength of the diagenetic model proposed here is that it is capable of accounting for the full suite of elemental compositions, and not just a couple of element ratios (e.g., Figs. 7, 8, and 9). As described in detail by McCollom (2018), sulfur-plus-cation models can only be reconciled with trends in the abundances of elements in the Burns rocks relative to SO_3 and TiO_2 if there was extensive mobilization and internal redistribution of Fe, Ca, and Mg during diagenesis at a scale far greater than that required in other types of models (e.g., Fig 9; see McCollom, 2018, for additional examples). This diagenetic remobilization would be in addition to the alteration of precursor basalt-derived materials required to make these models compatible with the measured compositions of the Burns rocks (e.g., Figs. 1a and 8). While plausible, these constraints result in cation-plus-sulfur models that are far more complex than other models proposed to explain the same data (McCollom, 2018), including the one proposed here.

Furthermore, siliciclastic components that might seem to be compatible with two end-member mixing models when examined only from the perspective of element-ratio plots can be seen to be incompatible when investigated in greater detail. For example, martian soils and altered Adirondack class basalts might appear to be plausible endmembers when portrayed in simple element-ratio diagrams like those shown in Figure 8 (Squyres et al., 2006; Hurowitz and Fischer, 2014). Yet, they are clearly eliminated as possible endmembers when examined in a broader context. Addition of a sulfur-rich component to martian soils or to altered Adirondack basalt cannot feasibly account for the measured amounts of Si, K, Ti, and P in the Burns sediments because the abundances of this suite of elements are far too low in these proposed precursors (Supplemental Fig. S5; McCollom, 2018). When the full suite of elements is considered, the only martian materials identified to date that actually have a close chemical affinity to the Burns sediments are the Irvine class basalts in Gusev crater (McCollom and Hynek, 2021).

The other category of previously proposed chemical models ("sulfur-only") invokes addition of only an oxidized sulfur component (i.e., sulfuric acid, sulfate, or sulfite) to pristine basalt to account for the composition of the Burns rocks (Fig. 10; McCollom and Hynek, 2005; Tréguir et al., 2008; Berger et al., 2009; Niles and Michalski, 2009). Depending on the model, the sulfur component is proposed to come from either an atmospheric or volcanic source. For elements other than MgO, predicted compositional trajectories for addition of sulfur to pristine basalt are very similar to those of the diagenetic model; however, the trajectories for sulfur-only models extend from a pristine basalt composition with little or no SO_3 rather than from the Grasberg (Fig. 10; see McCollom, 2018). Note that the elemental trajectories for the sulfur-only model pass close to the Grasberg samples, so this type of model could potentially explain the composition of that unit as well (McCollom and Hynek, 2021).



For MgO, sulfur-only models require that the pristine basalt initially had a substantially higher abundance of MgO than either the Burns or Grasberg formations, and that some of this MgO was subsequently removed from a subset of samples during diagenesis (McCollom, 2018). Consequently, the primary differences between the sulfur-only models and the diagenetic model proposed here are assumptions concerning the MgO content of the initial sediments and whether some of this MgO was gained or lost during diagenesis (along with SO_3). If the Grasberg rocks formed through sulfur-only addition to the same basaltic precursor as the Burns, even greater diagenetic loss of MgO and SO_3 would be required to account for their current composition (i.e., they fall even further from the sulfur-only trajectory in Fig. 10g; McCollom and Hynek, 2021).

While both the sulfur-only model and the one proposed here make somewhat similar predictions for most elements, the diagenetic model appears to more accurately reproduce the slope of the trends in elemental compositions of the Burns rocks as a function of SO₃than the sulfur-only model (Fig. 10). The predicted trajectories for the diagenetic model are slightly steeper than those of the sulfur-only model because the addition of MgO along with SO₃ leads to greater dilution of the remaining elements, and the resulting trajectories more closely reproduce the linear trends observed in the Burns data for many elements including Si, Al, K, Na, Ti and Cr. We would argue, therefore, that the diagenetic model provides a somewhat better explanation for the chemical data.

As an additional note, advocates of the sulfur-plus-cations models have asserted that the addition of a sulfur component alone to pristine basalt cannot possibly explain the chemistry of the Burns rocks because this would produce chemical compositions that conform to horizontal trends when portrayed on diagrams like those shown in Figure 8 (Squyres et al., 2006; Hurowitz and Fischer, 2014). However, McCollom (2018) demonstrated that this assertion is incorrect because it fails to take into account mobilization of Mg, Fe, and Ca during diagenesis. When diagenetic mobility of these cations is accounted for, nearly all of the variation along the vertical axes in Figure 8 is eliminated and it becomes evident that the sulfur-only models can readily explain the data (McCollom, 2018). Furthermore, since the diagenetic model proposed here is also consistent with the data when plotted in the parameter space of Figure 8, it is evident that these types of element-ratio diagrams on their own are not suitable to discriminate among the alternative models.

Another alternative type of chemical model proposes that the sulfates present in the Burns sandstones are formed through oxidation of pyrite or other sulfides (Zolotov and Shock, 2005; Dehouck et al., 2012). It appears doubtful, however, that this type of model is compatible with the chemical composition of the Burns rocks. In order to explain the high sulfate contents of the Burns formation, the precursor would need contain > 12 wt% pyrite or other sulfide minerals (Dehouck et al., 2012), which in turn would require a substantial enrichment in Fe or other metallic elements to account for the sulfides (~8 wt% or more). The Burns rocks do not appear to have any significant enrichment in metallic elements compared to typical martian basalts, so a sulfide mineral-rich precursor does not appear to be tenable. Nevertheless, oxidation of sulfide minerals may well have contributed to other sulfate-rich deposits on Mars.

5. Proposed scenario for formation of the Burns sandstones

The success of the diagenetic model in accounting for the chemical composition of the Burns rocks leads us to propose a new overall scenario for the origin of the Burns formation sandstones. In this section, we first provide a brief overview of the scenario, followed by more detailed discussion of several of the components involved. We propose the following scenario to explain the origin of the sandstones:

1) Deposition of fine-grained airfall materials with a chemical composition similar to the Grasberg rocks and derived from a closely related source (or possibly the same source). 2) Moderate induration of the fine-grained sediments then forms friable mudrocks similar in texture and composition to the current Grasberg rocks. 3) The indurated sediments then eroded into sand-sized particles, followed by local transport, reworking, and deposition of the sand at its present location. Transport was primarily by eolian processes, but with fluvial transport driven by emerging groundwater active for brief intervals in isolated locations. These processes were responsible for the bedding structures currently observed in the rocks. 4) Infiltration of the sand deposits by one or more generations of groundwater, leading to diagenetic effects that include dissolution and recrystallization of minerals, formation of hematite spherules, localized element mobilization and redistribution, and cementation. 5) At some point during sediment deposition and groundwater infiltration, evaporation of groundwater enriched in dissolved Mg and $SO_4^{2^-}$ results in precipitation of sulfate minerals and increased abundances of MgO and SO₃ in the sediment deposits, with higher amounts precipitated closer to the ground surface. 6) Late-stage diagenetic processes remove Mn and P from the Grasberg as well as Mn from the bottom of the Burns formation, accounting for the lower levels of MnO and P₂O₅ in those deposits.

5.1. Original source and deposition of sediments

The proposed scenario assumes that the sediments which eventually became the Burns formation were initially deposited as fine-grain airfall deposits derived from an impact or explosive volcanic eruption. Deposition as volcanic ash would be consistent with the geologic context of the Meridiani region (Hynek et al., 2002, 2003). Hynek and Phillips (2008) noted that the depositional processes for the broader Meridiani region led to coherent bedding traceable over hundreds of km that conform to the regional slope. Hynek et al. (2003) used rudimentary particle fallout plus global circulation models to show that airfall from the Tharsis region could easily be carried to Meridiani Planum, and would be one possible source for airfall deposits. More recently, large craters in Arabia Terra (north of Meridiani) have been classified as volcanic calderas that could have potentially supply substantial amounts of ash to Meridiani and even Gale crater (Michalski and Bleacher, 2013). A large impact could also supply the fine-grained materials, although it is not clear that it could supply sufficient volume of homogenous materials to account for the entire regional extent of the Burns formation (Hynek and Phillips, 2008).

Presumably, the initial fine-grained sediments had a basaltic provenance, although the materials may have been altered to some extent at their source locale prior to being transported to Meridiani Planum. When normalized to similar S contents, the Grasberg and Burns rocks have chemical compositions that are very similar to the Irvine class basalts in Gusev crater (McCollom and Hynek, 2021). This is demonstrated, for instance, by hierarchical cluster analysis based on chemical composition where the Irvine basalt from Gusev is found to cluster together with the Grasberg and Burns samples in a coherent group that is distinctly separate from other martian basaltic rocks. Therefore, Irvine may serve as a proxy of the basaltic precursor to the sediments that became the Grasberg and Burns formations.

The proposed scenario assumes that the original fine-grained sediments were already enriched to some degree

in S before being deposited on Meridiani. The RAT abraded and brushed Grasberg samples have an average SO_3 content of 9.2 wt%. Some of this SO_3 could have been added during diagenesis, and it is also possible that more recent alteration of the exposed bedrock surface added some SO_3 . However, it seems likely that these sources were minor contributors and that the initial sediments contained at least several wt% SO_3 . Many other martian basalts and sedimentary rocks measured in situ by rovers have comparable SO_3 levels. For instance, the sedimentary rocks of the Murray formation in Gale crater have an average SO_3 content of 6.2 wt%, and the basalts in Gusev crater have an average SO_3 content of 5.3 wt% (these averages exclude Murray samples associated with gypsum veins and Gusev samples that are extensively altered with highly elevated S abundances; see Supplemental Dataset1).

The source of the elevated S contents in the original sediments is unclear at this time. One possibility is that it is indigenous to the basaltic precursor through crystallization from a sulfur-rich magma. Many of the martian basalts analyzed in situ by rovers contain several percent SO_3 (see Supplemental Dataset1), although it is currently unclear to what extent this represents the original rocks rather than secondary alteration. Another possibility is that the basaltic precursor initially had much lower S contents, but was subsequently enriched in S through acid-sulfate alteration through reaction with sulfuric acid derived from an atmospheric or volcanic source. This alteration might have occurred, for instance, through fumarolic activity on the flanks of a volcano (e.g., McCollom et al., 2013) or by melting of ice deposited on top of volcanic ash or cinders (e.g., Niles and Michalski, 2009; Kite et al., 2013; Niles et al., 2017). Low water:rock ratios during this process could account for the addition of SO_3 without significant loss of cations from the basaltic precursor. Nevertheless, it is conceivable that the high solubility of Mg-sulfate salts resulted in the removal of some Mg from the basaltic materials during this process, resulting in the relatively low MgO contents of the Grasberg sediments compared to most martian basalts. These sulfur-enriched basaltic materials would then have been transported to Meridiani Planum by repeated explosive eruptions.

The results of a preliminary two-stage geochemical model that includes alteration of a basaltic precursor prior to deposition of the source materials at Meridiani Planum are shown in Figure 11 (see Supplemental Dataset1 for calculations). In this model, the basalt initially has a composition very similar to the basaltic Irvine target in Gusev crater (Supplemental Table S1). Alteration of the basalt, most likely under waterlimited acid-sulfate conditions, adds SO_3 while removing MgO. All other elements remain largely unchanged during this initial stage. Magnesium is highly mobile under acid-sulfate conditions, and is typically the first major cation to be removed as acid-sulfate alteration progresses (e.g., McCollom et al., 2013). This initial stage of alteration results in materials that have a Grasberg-like chemical composition, which were then transported to Meridiani. Following deposition, addition of MgO and SO_3 to the Burns sediments during diagenesis then accounts for their current composition. More detailed geochemical modeling will be needed to test the feasibility of this model and possible alternatives, but these preliminary calculations outline a complete and plausible pathway to attain the chemical composition of the Burns formation.

Although we favor an airfall source for the initial sediments, an alternative possibility is that the fine-grained materials first accumulated as wind-blown dust trapped within ice deposits and then were left behind when the ice sublimated (Niles and Michalski, 2009; Kite et al., 2013). Sulfuric acid present in the ice, derived from an atmospheric source, could have altered to materials to some degree and enriched them in SO_3 (Niles et al., 2017). Meltwater from overlying snow deposits could also have promoted recrystallization of sulfate salts within the deposits as they accumulated, cementing them to the point where they could later erode into sand-sized particles.



5.2. Inducation and erosion into sand-sized particles

Following deposition, the proposed scenario presumes that the fine-grained sediments became moderately indurated and were then eroded into sand-sized grains. This would require that the indurated materials were sufficiently coherent to form sand-sized grains when eroded, yet friable enough that they would erode. The materials that eroded may have been less-well lithified than the current Grasberg formation, but otherwise would have had similar texture and composition. Sand-size aggregates of clays and other minerals ("pebbles") form in arid terrestrial environments and maintain their structure through transport and re-deposition (Bowler, 1973; Magee, 1991; Müller et al., 2004; Wright and Marriott, 2007). In some cases, sulfate- and chloride-rich salts or carbonates hold these aggregates together. Some terrestrial deposits composed of mud aggregates have textures that appear similar to that of the Burns sandstones (e.g., Supplemental Fig. S6).

If the fine-grained source materials had undergone acid-sulfate alteration prior to deposition at Meridiani, recrystallization of sulfate- and chloride-bearing minerals may have facilitated cohesion of the siliciclastic components and enabled the formation and transport of sand-sized aggregates. Recrystallization of sulfates and chlorides could have been promoted by water percolating into the fine-grained airfall deposits, either from a rising groundwater table or through melting of overlying snow and ice deposits (e.g., Kite et al., 2013).

5.3. Transport and deposition

A number of studies have examined the prominent cross-bedding and other sedimentary structures in the Burns formation sandstones (e.g., Grotzinger et al., 2005, 2006; Edgar et al., 2012). These studies document that the sands were deposited primarily by eolian processes, with evidence for fluvial transport in a few isolated locations. In the scenario proposed here, sulfate-cemented siliciclastic sand grains derived from erosion of a Grasberg-like precursor are inferred to have been reworked by mostly eolian processes and redeposited at their current location, resulting in the cross-bedding and laminations documented in previous studies. In some isolated locations, emerging groundwater facilitated the transport of some sand deposits and formation of fluvial bedforms, as proposed by Grotzinger et al. (2005, 2006).

5.4. Diagenesis and MgO-SO₃ enrichment

There is extensive evidence for diagenesis of the Burns sandstones as documented in detail by McLennan

et al. (2005) and other studies. Among the more prominent diagenetic features observed in the rocks are the formation of hematite spherules, dissolution of minerals leaving behind tabular-shaped voids, and development of isopachous cements (Fig. 1). The Whatanga contact in Endurance crater (Fig. 1) has also been interpreted as marking the upper extent of recrystallization of minerals by diagenetic fluids (Grotzinger et al., 2005). The gradation in MgO and SO₃ abundances with depth in Endurance and Victoria craters has generally been inferred to be a diagenetic process as well, although it has hitherto been attributed to removal of Mg-sulfates at depth (Clark et al., 2005; Niles and Michalski, 2009; Hurowitz and Fischer, 2014; McCollom, 2018; McCollom and Hynek, 2021) or to deep weathering of the sediments by meteoritic water (Amundson et al., 2008; Amundson, 2018). There has been considerably less study of diagenetic impacts on the Grasberg formation; however, the unit contains numerous post-depositional gypsum veins (Mittlefehldt et al., 2018) and there is geochemical evidence for diagenetic mobilization of Mn (Ming et al., 2015; McCollom and Hynek, 2021).

It has been proposed that the diagenetic features found in the Burns sandstones may be attributable to two or more generations of groundwater infiltration (McLennan et al., 2005). Hydrologic models suggest that Meridiani Planum was a locus for groundwater upwelling from large-scale crustal aquifers on Mars (Andrews-Hanna et al., 2007, 2010; Andrews-Hanna and Lewis, 2011), and Meridiani is also proposed to have been an area that received high amounts of snowmelt on early Mars (Kite et al., 2013). Consequently, fluids could have infiltrated the Burns sediments from both above and below at various times during its early history.

The scenario proposed here does not appear to be incompatible with any of the diagenetic features or processes inferred by previous studies. The main difference in diagenetic processes proposed here is that MgO and SO₃ are inferred to be added to the Burns sediments during diagenesis. Presumably, this would have involved evaporation of fluid during one of the episodes of groundwater infiltration, leaving behind MgO and SO₃. Alternatively, freezing of Mg-rich groundwater could also lead to precipitation of Mg-sulfates and other minerals (e.g., Marion et al., 2008).

Given the high solubility of Mg-sulfate minerals, sulfate-bearing fluids migrating through martian aquifers can be expected to accumulate relatively high concentrations of Mg. While it is possible that the fluids also transported and deposited some small amounts of Fe and Ca into the Burns rocks along with Mg, the geochemical data do not allow for significant net addition or removal of these elements from the formation as a whole (Figs. 5 and 7; McCollom, 2018). Furthermore, the data strongly indicate that many elements, including Si, Al, Na, K, and Cr were not mobilized to any discernible degree during diagenesis, and therefore were not added to the sediments during the inferred enrichment in Mg. More detailed geochemical modeling may allow further constraints to be placed on the composition of the evaporating fluid and its source.

One thing that can perhaps be inferred at this time about the fluid that added the MgO and SO₃ to the Burns deposits is that it was more likely to come from upwelling groundwater rather than from precipitation at the ground surface. Fluids infiltrating the sand deposits from above (for example, through melting of snow deposits; Kite et al., 2013) would be expected to initially contain very little or no Mg, and would leach Mg from the rocks as they percolated downwards until they became saturated with respect to Mg-sulfate minerals. This would produce a trend where the deposits had lower MgO abundance towards the top and increasing MgO with depth, opposite to the trend observed in the Burns rocks (Fig. 5a). Still, this possibility may warrant further study since the Mg-depleted deposits produced by downward-percolating fluids could have been removed from the top of the unit since erososion of at least a meter of the Burns formation is indicated by the lag deposits of hematite accumulated at the surface (Squyres et al., 2004).

It is possible to make an estimate of the minimal amount of evaporating fluid that would be required to account for the inferred diagenetic enrichment in Mg. At near freezing temperatures, the stable form of Mg-sulfate would be epsomite (MgSO₄*7H₂O), which has a solubility product (K_{sp}) at low temperatures (0-25degC) equal to ~3 (Steiger et al., 2011). Assuming an activity of water equal to 0.9 and neglecting activity coefficients for dissolved Mg and sulfate, the K_{sp} can be approximated as:

$$K_{\rm sp} \approx \left[{\rm Mg}^{2+} \right] \left[{\rm SO}_4^{2-} \right] \left({0.9} \right)^7 \approx 3 \left({{\rm mole} \over {\rm kg}} \right)^2.(2)$$

If we further assume that Mg and SO₄ were present in the solution in the same proportions as they precipitate in the diagenetic model, then $[SO_4^{2-}] = 1.55[Mg^{2+}]$ and Eq. 2 reduces to $[Mg^{2+}]^2$ [?] 4.04 (mole/kg)² or $[Mg^{2+}]$ [?] 2.0 M. Addition of approximately 32-72 g Mg per kg rock would be needed to account for enrichment of the Burns rocks relative to the Grasberg, corresponding to 0.8-1.8 moles Mg (see Supplemental Dataset1).

Thus, evaporation of less than 1 kg of groundwater saturated with respect to epsomite could account for the required enrichment of Mg in each kg of Burns rocks. If the Burns formation was originally 20 m thick and has a density of 2,500 kg/m³, this would correspond to evaporation of an equivalent water column of <50 m. This figure is much smaller than the amount of groundwater upwelling at Meridiani predicted by hydrologic models (2.5-17 km; Andrews-Hanna et al., 2007). Groundwater flow models that include geochemical and mineralogical constraints have called into question the feasibility of the large fluid fluxes predicted by the hydrologic models (Kite and Melwani Daswani, 2019), but could perhaps be compatible with the much smaller fluxes required to support the diagenetic model proposed here.

It has been noted many times that the presence of natrojarosite in the Burns rocks inferred from Mossbauer spectroscopy requires acidic conditions (e.g., Klingelhofer et al., 2004; Elwood Madden et al., 2004; note that this mineral is typically referred to in the literature as "jarosite," which strictly speaking refers only to the K-rich endmember, but in actuality the mineral at Meridiani is probably an Al-bearing natrojarosite; Morris et al., 2006; McCollom et al., 2014). Groundwater migrating through martian crust is not expected to be acidic, since any source of acidity in the fluid would be rapidly buffered by fluid-rock interactions in the aquifer. However, the near-surface fluids could have become acidified through oxidation of ferrous Fe-bearing components as proposed by Hurowitz et al. (2010). Alternatively, if the original airfall materials had undergone acid-sulfate alteration at the source location, natrojarosite could have already been present when the fine-grained sediments were initially deposited at Meridiani Planum and then survived through subsequent diagenesis. The rapid decomposition of minerals from the alunite-jarosite group in laboratory experiments has led to suggestions that the natrojarosite in the Burns rocks would have rapidly decomposed if exposed to aqueous fluids for any substantial period of time after their formation (e.g., Elwood Madden et al., 2004, 2009). However, the persistence of minerals from this group in porous sandstones for millions of years suggests that they may be much more stable in natural settings than generally thought (e.g., Potter-McIntyre and McCollom, 2018).

More study will be required to evaluate the timing of the proposed MgO and SO₃ enrichment relative to other diagenetic processes. Sedimentary features in the Burns formation indicate that the sediments may have been saturated with water during some intervals while they were being deposited, at least in the lower parts of the formation (Grotzinger et al., 2005, 2006). Evaporation of fluids during these intervals could have added MgO and SO₃ at an early stage. Alternatively, the enrichment may not have occurred until a much later stage, more-or-less simultaneous with other diagenetic features such as precipitation of isopachous cements and creation of the tabular-shaped voids. One intriguing possibility is the that the isopachous cements, whose precipitation evidently post-dated the formation of the hematite spherules (McLennan et al., 2005), might represent Mg-sulfate minerals precipitated from late-stage evaporation or freezing of infiltrating groundwater.

6. Discussion

6.1. Origin of the Burns formation

The recent recognition that the chemical compositions of the Burns and Grasberg formations are nearly identical is a strong indication that the origins of the two formations are closely linked (McCollom and Hynek, 2021). The alternative possibility that these two formations had entirely independent sediment sources which just happened to have the same chemical composition and yet were deposited immediately adjacent to one another would be a rather remarkable coincidence, and stretches credibility. Therefore, any proposed scenario for the origin of the Burns formation must now account for its relationship to the Grasberg formation.

The new scenario proposed here for the origin of the Burns sandstones accounts for all of the most salient

features of the rocks while invoking only a known sediment source and processes that are recognized to be widespread across Mars. Moreover, it offers an explanation for the close similarity of its chemical composition to the Grasberg formation, which would be problematic to explain in the context of other proposed scenarios for the Burns rocks. The new scenario offers a simpler pathway to explain the principal observations of the Burns rocks and requires fewer assumptions than other proposed scenarios, and we argue that it warrants further investigation and testing against other proposed alternatives. If valid, the proposed diagenetic scenario would have substantial implications for the origin of sedimentary rocks on Meridiani Planum and across Mars, for interpretations of the widespread sulfate-rich deposits on the planet, and for surface environmental conditions on early Mars. The scenario would also provide new insights into diagenetic processes in martian sediments that may be particularly relevant as the Curiosity rover approaches rocks on Mount Sharp that are enriched in the Mg-sulfate mineral kieserite (Milliken et al., 2010; Sheppard et al., 2020; Rapin et al., 2021).

While our description of the proposed scenario refers to "Grasberg-like" materials as a precursor to the Burns formation, it is possible that the Grasberg formation itself may be the last vestiges of the materials that eroded to become the Burns formation. If this is the case, then the origins and geologic histories of the two units would be even more closely linked, which would directly contradict previous proposals that the two formations are separate units with distinctly different origins (Crumpler et al., 2015; Mittlefelhdt et al., 2018; Bouchard and Jolliff, 2018). Moreover, although Mittlefelhdt et al. (2021) suggests that the stratigraphic status of the Grasberg formation is uncertain, the scenario proposed here would connect the two units stratigraphically and temporally, with the Grasberg being emplaced immediately below and preceding deposition of the Burns sands. In this respect, the proposed scenario is consistent with the stratigraphic relationships inferred by Crumpler et al. (2015; Fig. 3).

The diagenetic scenario also implies that the original source of sediments for both units were airfall deposits, likely volcanic ash. If, so, these deposits could be related to other ashfall deposits identified across the equatorial regions of Mars as first proposed by Hynek et al. (2003). That work showed that the voluminous Medusae Fossae Formation on the opposite side of the planet from Meridiani Planum was likely derived from volcanic airfall from Tharsis. Similar layered deposits west of Meridiani thicken as they approach the Tharsis complex, implying a possible similar origin. Alternatively, Michalski and Bleacher (2013) argued for past regional supervolcano eruptions as a possible source for the widespread layered materials stretching from Meridiani Planum to Gale crater.

Fracture-filling deposits in the rocks that immediately underly the Grasberg and Burns formations may provide some supporting evidence for the inferred diagenetic alteration. During inspection of rocks from the Shoemaker formation (which lies directly beneath the Grasberg rocks on the rim of Endeavour crater; Fig. 3), Opportunity's wheels fortuitously uncovered two rocks, named Pinnacle Island and Stuart Island, which have white- and red-toned mineral deposits coating fracture surfaces (Fig. 12). These deposits were subsequently found to be enriched in Mg, Ni, SO₃, Mn, and P (Arvidson et al., 2016), the very same set of elements that are inferred to have been mobilized during diagenesis of the Burns and Grasberg formations. Consequently, these two rocks may record the groundwaters that led to diagenesis of the overlying rocks, and provide further support for the inferred mobilization of this suite of elements.



One question that naturally arises from the proposed scenario is why the Burns rocks became enriched in MgO and SO₃ while the Grasberg rocks did not. A likely explanation for this is that the finer-grained Grasberg rocks would have had much lower porosity and permeability than the sands that compose the Burns formation. This would provide much less opportunity for evaporating fluids to precipitate MgO and SO₃. Of course, this would not preclude localized enrichments along fracture surfaces in the Grasberg formation similar to those observed in the Pinnacle Island and Stuart Islands samples (Fig. 12), but these would have been very difficult for the rover to detect.

6.2. Implications for other diagenetic processes and sulfur inputs

The scenario proposed here may also provide some new insights into the origin of other enigmatic diagenetic features of the Burns rocks. For instance, many of the Burns rocks were observed to contain tabular-shaped voids (e.g., Fig. 13a). The shape of the voids suggests dissolution of preexisting minerals during diagenesis (McClennan et al., 2005), but the identity of the dissolved minerals and timing of their dissolution remain uncertain. One possible explanation for these voids that would be consistent with the scenario proposed here is that they represent dissolution of gypsum crystals incorporated into the sands that became the Burns formation. The Grasberg formation contains widespread gypsum veins, particularly in the lower unit (Figs. 3g and 13b; Mittlefehldt et al., 2018). If the friable, fine-grained precursor materials that are inferred to have eroded into the Burns sediments contained similar gypsum veins, crystals from these veins may have been incorporated into the sands that became the Burns formation. Subsequent dissolution of the gypsum crystals during diagenesis would then leave behind the tabular-shaped voids, which have shapes that closely resemble gypsum crystals.



The chemical compositions of the Burns rocks may provide some support for this possibility. While there is no evidence for significant net addition of Ca to the Burns formation as a whole, the abundances of CaO in a subset of the Burns rocks display a possible correlation with SO_3 that could be consistent with dissolution and local reprecipitation of Ca-sulfate minerals (Fig. 13c). Dissolution and reprecipitation of Ca-sulfate minerals could thus explain both the tabular shaped voids and the scatter of CaO data around the expected trend for diagenetic addition of MgO and SO_3 (Fig. 13c). Further study is required to determine whether the chemical conditions needed to facilitate this mobilization of CaO could be compatible with other diagenetic features.

The proposed scenario might also provide new insights into the ongoing enigma of the origin of the hematite spherules that are characteristic of the Burns rocks. Over the years, a number of different hypotheses and analogs have been proposed to explain the origin of the spherules (e.g., Catling et al., 2003; Morris et al., 2005; Glotch et al., 2006a; Golden et al., 2008; Sefton-Nash and Catling, 2008; Bowen et al., 2008; Madden et al., 2010; Potter et al., 2011; Sexton et al., 2017). To date, however, there is no consensus over how the spherules formed and it remains a matter of considerable debate. The absence of hematite spherules in the Grasberg rocks despite having nearly the same initial chemical composition as the Burns rocks and exposure to similar diagenetic conditions should provide new constraints on the conditions that promoted spherule formation. For instance, the absence of spherules from the Grasberg formation might indicate that the greater pore space present in the Burns sandstones was critical for their formation. The chemical and mineralogical changes induced by the fluids that enriched the rocks in MgO and SO₃ might also have played a role in creating the environment for spherule formation.

The proposed scenario might also help resolve the conundrum regarding the magnitude of S inputs required to explain the sulfur-bearing deposits on Meridiani Planum. The Burns and Grasberg formations represent the uppermost strata of a section of layered etched terrains that is several hundred meters thick and covers an area >4 ×10⁵ km² (Hynek and Phillips, 2008; Hynek and Di Achille, 2017). Spectral analyses indicate that kieserite and other hydrated sulfates are present in many of the underlying units, indicating a widespread enrichment in SO₃ (e.g., Hynek and Phillips, 2008; Wiseman et al., 2015; Flauhaut et al., 2015). As discussed by Hynek et al. (2019), all currently proposed mechanisms for transport of SO₃ into the deposits at Meridiani have great difficulty in accounting for the enormous amount of SO₃ that would need to be added to the deposits in order to attain levels similar to that of the Burns formation ([?]5 x10¹⁶ kg SO₃ in total).

Two aspects of the proposed scenario may be particularly relevant to this issue. First, in the scenario proposed here, a substantial fraction of SO_3 in the Burns rocks was already present in the airfall deposits when they were emplaced at Meridiani. If this pertains to the deeper deposits as well, it would significantly reduce the amount of SO_3 that would need to be imported by fluid transport or other means. Second, in the proposed scenario, it may only be the upper layers of the deposits (i.e., the Burns sandstones) that are further enriched in SO_3 during diagenesis, requiring addition of only modest amounts of SO_3 . If the bulk of the thick layered deposits at Meridiani Planum have SO_3 contents similar to the Grasberg while only some intervals reach the higher levels observed in the Burns rocks, the amount of sulfur that would need to be transported into Meridiani would be substantially reduced. At present, it is uncertain whether the lower amounts of SO_3 present in the Grasberg (average ~9.2 wt%) is sufficient to account for the hydrated sulfate deposits detected by remote observations, but this possibility may be worth additional study.

6.3. Relationship to previously proposed sedimentary-evaporite scenario

The scenario proposed here for the origin of the Burns sandstones has many components in common with the previously proposed sedimentary-evaporite scenario (Squyres et al., 2004, 2005; Grotzinger et al., 2005; McLennan et al., 2005). However, it also has many distinctly different features, and these would have distinctly different implications for the geologic history of the Meridiani region and for martian sedimentary rocks in general. For the sake of clarity, this section provides a brief overview of the principal similarities and differences between these two scenarios (Table 1).

One set of key differences relates to the nature and origin of the sediments that comprise the Burns rocks.

Both scenarios invoke erosion of preexisting materials into sulfate-cemented siliciclastic sand-grains as the source of the original sediments for the Burns sandstones. In the sedimentary-evaporite scenario, however, these sand grains formed by erosion of evaporites on the margins play lakes (Grotzinger et al., 2005; McLennan et al., 2005), whereas in the scenario proposed here the sands formed through erosion of a Grasberg-like precursor that had already been deposited on Meridiani Planum. The siliciclastic component in the sedimentary-evaporite scenario is thought to be derived from a chemically basaltic precursor depleted by 55% in Σ (Fe+Mg+Ca) and containing little or no S (Fig. 8; Squyres et al., 2006). The siliciclastic component in the proposed diagenetic scenario is an airfall deposit that is also ultimately derived from a basaltic precursor, but already contained a substantial amount of S and was possibly depleted in Mg by the time it arrived at Meridiani (Fig. 11). The sedimentary-evaporite scenario presumes that the entire sulfate component contained in the Burns sediments was added to the siliciclastic component on the margins of playa lakes prior to erosion into sand-sized grains and redeposition, with a possible subsequent loss of MgO and SO_3 from the sediments at depth during diagenesis (Squyres et al., 2004, 2006; Clark et al., 2005). In contrast, in the scenario proposed here, more than half of the current SO_3 contents of the rocks is only added during diagenesis of the sands following deposition, along with MgO. Furthermore, while long-lived playa lakes and standing surface water are a major component of the sedimentary-evaporite scenario, the diagenetic scenario proposed here invokes little involvement surface water and far less contribution of water overall.

Another key difference is that the proposed diagenetic scenario closely links the depositional and early diagenetic histories of the Burns and Grasberg formations, and accounts for both the nearly identical chemical compositions of these units and their spatial relationship. The Grasberg rocks were not encountered by Opportunity until long after the sedimentary-evaporite scenario was initially proposed, and the close similarity in chemical composition between the two units was only recently recognized. Consequently, as of yet, there has been no discussion in the literature of any possible relationship between the Burns and Grasberg formations by advocates of the sedimentary-evaporite scenario. However, it would appear to be very difficult to account for any connection between these units in the context of the sedimentary-evaporite scenario. That is, the chemical composition of the Grasberg rocks would be problematic to reproduce by the proposed playa lake evaporite model (Figs. 8 and 9), and the Grasberg rocks lack the bedding structures and other sedimentary features that have always been a critical component of the sedimentary-evaporite scenario (e.g., Grotzinger et al., 2005, 2006). Thus, it is hard to imagine how the playa lake evaporite hypothesis could simultaneously account for the characteristics of both units or explain their closely similar chemical compositions. Instead, one would have to imagine that the Grasberg is an unrelated unit formed by a completely different process that coincidentally has a similar composition, which would seem to be a much less parsimonious explanation than inferring a genetic relationship between the Burns and Grasberg formations.

Table 1. Summary of key differences and similarities in the diagenetic scenario proposed here and the previously proposed sedimentary-evaporite scenario.

Feature/process	Sedimentary-evaporite scenario (Squyres et al., 2004, 2006; Grotzinger et al., 2005; McLennan et al., 2005; Clark et al., 2005)	Diagenetic scenario (this study)
Source and composition of Burns sands	Sulfate-cemented siliciclastic sand-sized grains eroded from margin of playa lake	Sulfate-cemented siliciclastic sand-sized grains eroded from Grasberg-like precursor
Origin of initial siliciclastic component	Unspecified	Airfall deposit

Feature/process	Sedimentary-evaporite scenario (Squyres et al., 2004, 2006; Grotzinger et al., 2005; McLennan et al., 2005; Clark et al., 2005)	Diagenetic scenario (this study)
Chemical composition of initial siliciclastic component	Basalt-derived material with up to 55% of total (Fe + Mg + Ca) removed and containing little or no S	Similar to Grasberg and to Irvine-class basalts; enriched in several wt% SO ₃ and possibly depleted in MgO by acid-sulfate alteration prior to transport to Meridiani
Sulfur source	Evaporation of sulfate-bearing groundwater in playa lake environments	Part initial sediments, part in situ evaporation of sulfate-bearing groundwater
Timing of sulfur addition	All sulfur added prior to sand formation and deposition at current site	Partly at site of initial siliciclastic origin, partly during diagenesis
Cation transport into Burns deposits	Mg, Fe, and Ca added by evaporating groundwater prior to sand formation; Mg lost from deeper samples during diagenesis	Mg added to entire Burns formation during diagenesis; others unchanged or only redistributed locally
Sediment transport/deposition Major diagenetic processes	Mostly aeolian, some alluvial Recrystallization, hematite spherule formation, dissolution of minerals, development of secondary porosity, cementation, loss of MgO and SO ₃ with depth	Mostly aeolian, some alluvial Recrystallization, hematite spherule formation, dissolution of minerals, development of secondary porosity, cementation, gain of MgO and SO ₃ , localized redistribution of cations
Relationship to Grasberg formation	Not defined	Both units share closely related sediment sources and similar early diagenetic histories
Implications for surface environmental conditions	Long-term clement conditions at surface allowing prolonged presence of playa lakes	No requirement for long-term standing water at surface

6.4. Some consideration of broader implications

Further study will be required to fully appreciate the potential implications that the proposed diagenetic scenario would have for the geologic history of the Meridiani region and for sulfate-bearing sedimentary deposits across Mars. However, some initial thoughts on these topics are worth mentioning briefly here. First, the proposed diagenetic scenario may suggest a more prominent role for diagenesis in the origin of the sulfate-rich layered deposits that are widespread on the surface of Mars. Remote sensing studies have detected layered deposits containing sulfate minerals at numerous locations across the planet (Gendrin et al., 2005; Murchie et al., 2009a; Ehlmann and Edwards, 2014). Many of these deposits appear to contain the Mg-sulfate mineral kieserite, which in some instances is associated with grey hematite (e.g., Chojnacki and Hynek, 2008; Murchie et al., 2009b; Bishop et al., 2009; Wiseman et al., 2010; Flahaut et al., 2010; Weitz et al., 2012). The proposed diagenetic scenario suggests that enrichment of preexisting sedimentary deposits in Mg and sulfate during diagenesis could have contributed to many of these occurrences, and should be considered as a potential alternative to other sulfate sources that include surface evaporite deposits and acid-sulfate alteration of sedimentary materials or their precursors. Indeed, if the diagenetic scenario is valid, it

may indicate that surficial evaporites contribute far less to the sulfate-rich bedrock exposures than previously thought, since the presumed playa lake origin of the Burns formation sediments was a major motivation for many such interpretations. The possible contribution of diagenesis to Mg and sulfate enrichments may have immediate relevance as the Curiosity rover approaches the transition from clay-rich deposits to the kieserite-bearing layers of Mount Sharp in Gale crater (Milliken et al., 2010; Sheppard et al., 2020).

Second, if the sediments that became the Burns formation were initially emplaced on Meridiani as airfall deposits as suggested by the diagenetic scenario, then it would reinforce other geologic evidence that pyroclastic ash deposits are widespread on the surface of Mars and may be responsible for many large-scale layered units (e.g., Scott and Tanaka, 1982; Hynek et al., 2002, 2003; Le Deit et al., 2010; Kerber et al., 2011, 2012; Michalski and Bleacher, 2013; Ojha and Lewis, 2018). Moreover, the diagenetic scenario may illustrate one pathway by which materials originally deposited by airfall became transformed and sulfate-enriched, which could aid in the interpretation of other sulfate-bearing layered deposits that might have had a similar origin (e.g., Chojnacki and Hynek, 2008; Le Deit et al., 2010; Fueten et al., 2011; Weitz et al., 2011, 2012). As proposed for the Burns formation, reworking and diagenetic alteration could transform pyroclastic deposits in ways that might obscure the original nature of the source materials.

Lastly, the proposed diagenetic scenario would have very different implications for environmental conditions on the surface during emplacement of the Burns formation than the sedimentary-evaporite scenario. The sedimentary-evaporite scenario invokes formation of the Burns precursor sands by evaporating fluids on the margins of playa lakes, as well as the presence of surficial fluids and shallow groundwater water during deposition of the sands (e.g., Squyres et al., 2004, 2006; Grotzinger et al., 2005, 2006). These processes imply long-term stability of liquid water on the surface of Meridiani Planum, which in turn implies clement conditions that would allow the liquid water to persist for prolonged periods at the surface. Furthermore, these surficial aqueous environments would potentially be conducive to the existence of martian life and preservation of biosignatures (Knoll et al., 2005).

Conversely, the alternative scenario proposed here invokes a much more limited role for water during formation of the Burns sandstones and requires no more than occasional intervals of liquid water at the surface in order to explain the major features of the rocks. This scenario is consistent with a lack of fluvial features within the thick sequence of layered sulfate-bearing materials, but substantial large valley network systems buried by the margins of these deposits (e.g., Hynek and Phillips, 2008; Hynek and Di Achille, 2017). The proposed diagenetic scenario would allow for surface conditions that were substantially drier and cooler overall than those implied by the sedimentary-evaporite scenario. Needless to say, the diagenetic scenario would also suggest environmental conditions that were far less favorable for life, at least at the surface.

7. Conclusions

Quantitative mass-balance models demonstrate that the chemical composition of the Burns formation sandstones can be closely replicated by addition of MgO and SO_3 to Grasberg-like fine-grained sediments. This finding, combined with their stratigraphic relationship, strongly indicates that the Burns and Grasberg formations come from closely linked sediment sources and have similar initial depositional histories. As a consequence, any scenario for the origin of the Burns sandstones must be able to explain its relationship to the Grasberg rocks.

Motivated by the model results, a new scenario is proposed for the origin of the Burns rocks. In this new scenario, the Burns sediments are initially emplaced on Meridiani as a find-grained airfall deposit derived from a source closely related to that of the Grasberg (or maybe even the same source). Following moderate induration (possibly involving recrystallization of sulfate salts), the precursor materials are eroded into sand size particles, transported by wind and water, and redeposited at their present location. Infiltration by groundwater then diagenetically alters and cements the sands. Evaporation of groundwater at some stage of diagenesis leaves behind MgO and SO₃ in the Burns sediments, resulting in the current composition of the rocks.

This newly proposed scenario provides a plausible explanation for all of the most salient features of the Burns

rocks, including their overall chemical composition, the variation in chemical composition with depth, the bedding features that are ubiquitous in the deposits, and diagenetic alteration. In addition, the proposed scenario provides an explanation for the nearly identical composition and stratigraphic relationship of the Burns formation to the Grasberg rocks. Moreover, the newly proposed scenario invokes only a known and well-characterized source for the sands (i.e., erosion of Grasberg-like rocks) as well as depositional and diagenetic processes that have been widely documented to occur in other martian settings. Collectively, the new scenario provides a simpler pathway that requires fewer assumptions than other scenarios previously proposed to account for the same features in the Burns rocks, and warrants further consideration and study.

Data Availability statement

All data used in this study are available from the Planetary Data System website (https://pds.nasa.gov/) or in the cited references. The data are compiled in the spreadsheet provided as Supplemental Dataset1 which also includes all diagrams and models presented in this report.

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Key Points:

- The chemical compositions of Burns formation rocks are closely reproduced by adding Mg and SO_4 to a Grasberg-like precursor.
- The results imply that the Burns and Grasberg units have linked sediment sources, and share depositional and early diagenetic histories.
- A new origin is proposed for the Burns formation that involves reworking of airfall deposits and addition of Mg and SO_4 during diagenesis.

Abstract

The sulfate-rich sandstones of the Burns formation investigated by the Opportunity rover on Meridiani Planum, Mars, are directly underlain by the fine-grained sedimentary rocks of the Grasberg formation. It was recently shown that, except for differing amounts of MgO and SO₃, the Burns and Grasberg rocks have nearly identical chemical compositions, suggesting both units are genetically related. Here, quantitative models demonstrate that the chemical composition of the Burns formation can be accurately reproduced by addition of MgO and SO₃ to a Grasberg-like precursor, along with small amounts of Ni. Based on this result, a new scenario is proposed for the origin of the Burns formation: (1) deposition of fine-grained airfall deposits with composition similar to the Grasberg rocks; (2) inducation of the deposits, resulting in materials that closely resemble the current Grasberg formation in composition and texture; (3) erosion into sand-sized particles, which are then reworked by eolian and fluvial processes to form the bedding features observed in the Burns rocks; (4) infiltration of the deposits by one or more generations of groundwater, resulting in diagenetic alteration that included local element redistribution, dissolution/recrystallization of minerals, cementation, and formation of hematite spherules; (5) evaporation of groundwater at some point during diagenesis enriched the Burns sediments in MgO and SO₃, with greater amounts accumulated closer to the surface. This scenario fully accounts for the chemical composition of the Burns sandstones as well as their sedimentary and diagenetic features, while invoking only a known sediment source and sedimentary/diagenetic processes widely observed on Mars.

Plain language summary

The Mars Exploration Rover Opportunity spent several years exploring the sulfate-rich Burns sandstones with their distinctive hematite "blueberries" and prominent bedding features. Here, we propose a new scenario for the origin of the sandstones. A recent study showed that, except for differing amounts of Mg and sulfate, the chemical compositions of the Burns sandstones are nearly identical to the Grasberg formation, a thin unit of fine-grained sedimentary rocks that immediately underlies the Burns rocks. This result implies that the sediment sources for both units are closely related. Motivated by this finding, we propose a new scenario for the origin of the Burns rocks whereby the sediments that now compose the sandstones were first emplaced as an airfall deposit, with a fine-grained texture and chemical composition similar to the Grasberg rocks and derived from a related source. Following induration, the materials were eroded into sand-sized particles, reworked by wind and water, and redeposited to become the Burns sandstones. During diagenesis, evaporation of groundwater enriched the sediments in Mg and sulfate, accounting for the current chemical composition of the Burns rocks. This new scenario implies very different sediment sources, depositional history, and diagenetic processes for the Burns sandstones than previously proposed scenarios.

1. Introduction

The Burns formation on Meridiani Planum consists of sulfate- and hematite-rich sandstones with prominent bedding features indicative of deposition by eolian and fluvial processes. As one of the few places on Mars that have been examined in detail by rovers, the Burns sandstones are a keystone for interpretations of sediment sources and depositional mechanisms on Mars, for understanding of diagenetic alteration of martian sediment deposits, and for the evolution of environmental conditions at the surface of the planet. Investigation of the Burns rocks also offers potential insights into the origin of the layered sulfate-rich deposits that are widespread geologic features across Mars (e.g., Gaillard et al., 2013; Ehlmann and Edwards, 2014). Unraveling the processes involved in the formation of the Burns sandstones is therefore a critical component to understanding the early geologic history of Mars.

Given the limited amount of mineralogic information available for the Burns rocks, their chemical composition provides what is perhaps the most fundamental set of data that can be used to interpret the source of the sediments and their subsequent diagenesis. It was recognized very early in the Opportunity rover mission that the rocks currently have a chemical composition which closely resembles martian basalts with the addition of a sulfur component (e.g., Squyres et al., 2004, 2006; Clark et al., 2005; McCollom and Hynek, 2005). Accordingly, scenarios that have been proposed to explain the origin of the sandstones have largely focused on environments and processes that allow sulfur-bearing and basalt-derived components to be combined at some stage during formation of the rocks.

Over the years, a number of different models have been proposed to account for the chemical composition of the Burns rocks. Most of these models, however, can be categorized into two general types, as illustrated in Figure 1. One type of model (Fig. 1a) proposes the Burns rocks represent mixtures of two end-members consisting of (a) Mg-, Fe-, and Ca-sulfate salts and (b) chemically altered basalt depleted in Mg, Fe, and Ca (referred to hereafter as the "sulfurplus-cations" model; Squyres et al., 2006; Hurowitz and Fischer, 2014). This chemical model is generally portrayed in the context of a broader overall scenario for the origin of the Burns sandstones, which will be referred to here as the "sedimentary-evaporite" scenario. In this scenario, the sulfate and altered basalt components are combined through evaporation of groundwater on the margins of playa lakes, and these materials then eroded into sulfate-cemented siliciclastic sand-sized grains that were transported by wind and water to be deposited at their present location (Squyres et al., 2004, 2006; McLennan et al., 2005; Grotzinger et al., 2005, 2006; and others). Following deposition, it is thought that the sands were diagenetically modified during multiple episodes of groundwater infiltration (McLennan et al., 2005), ultimately resulting in the sandstones observed by Opportunity.

The second type of proposed chemical model ("sulfur-only"; Fig. 1b) infers that the composition of the rocks is accounted for by addition of a sulfur component to pristine martian basalt, likely as sulfuric acid derived from an atmospheric or volcanic source (McCollom and Hynek, 2005; Tréguir et al., 2008; Berger et al., 2009; Niles and Michalski, 2009; McCollom, 2018). In these models, the sulfur component is added to the basalt component without any accompanying cations or input of elements other than S and O (thus, "sulfur-only"). Geochemical mass-balance calculations indicate that either of these two types of models can potentially account for the observed chemical compositions of the Burns rocks (McCollom, 2018). However, of these two types, the sulfur-only model is found to provide a much simpler and more straightforward pathway to explain the current chemical composition of the Burns rocks.



a new alternative chemical model is proposed for the Burns sandstones that involves diagenetic addition of MgO and SO_3 to materials having an initial elemental composition similar to that of the underlying Grasberg formation (Fig. 1c). Motivation for this model largely derives from a recent study which showed that, except for differences in the abundances of MgO and SO_3 , the Burns and Grasberg rocks have nearly identical chemical compositions (McCollom and Hynek, 2021). This similarity in chemical compositions implies that the original sediments for the two formations likely came from closely related sources, or maybe even the same source.

Using analyses of compositional trends and a quantitative geochemical model, we show that the chemistry of the Burns rocks can be closely reproduced by addition of MgO and SO₃ to sediments having an initial composition similar to that of the Grasberg formation. This finding leads us to further propose a novel scenario for the origin of the Burns formation sandstones that involves erosion, reworking, and diagenetic alteration of materials that initially had a chemical composition and morphology similar to (or identical to) the existing Grasberg rocks. This new scenario implies a distinctly different depositional and diagenetic history for the Burns formation than previously favored scenarios, with very different implications for sediment sources, diagenetic processes, and environmental conditions on the surface of early Mars.

This communication begins with a brief overview of the Burns and Grasberg formations. We then present an analysis of the evidence for diagenetic mobility of chemical elements in these formations, followed by description of the proposed model for diagenetic addition of MgO and SO_3 to the Burns sediments. Finally,

we outline our proposed scenario for the origin of the Burns sandstones, which we refer to here as the "diagenetic scenario" to differentiate it from other proposed scenarios.

2. Overview of the Burns and Grasberg formations

The Burns formation consists of sandstones whose framework is thought to be composed of sulfate-cemented siliciclastic sand grains (Fig. 2) (Squyres et al., 2004, 2006; Grotzinger et al., 2005). The ubiquitous presence of sedimentary structures that includes cross-bedding, planar laminations, and festoon crosslaminations indicates the sands were deposited at their current location by a combination of eolian and aqueous processes (Grotzinger et al., 2005, 2006). Following deposition, the sediments underwent diagenetic alteration that included precipitation of isopachous cements, formation of hematite spherules, and dissolution of some minerals leaving behind tabular-shaped voids (Fig. 2a inset; McLennan et al., 2005). Multiple episodes of groundwater infiltration may have been involved in producing the observed diagenetic features (McLennan et al., 2005). The hematite-bearing Burns sandstones are a regional unit that covers a large area ($\sim 4 \times 10^5$ km²) and may have been even larger in the past (Hynek and Di Achille, 2017).



Burns formation rocks are highly enriched in sulfate, containing between 17 and 28.6 wt% SO₃ (Clark et al., 2005). The remaining chemical elements have a composition that closely resembles typical martian basalt (Squyres et al., 2004, 2006; McCollom and Hynek, 2005, 2006; McCollom, 2018). The Burns rocks displayed very little variation in their chemical composition across the rover traverse of more than 16 km (Fig. 1). One exception, however, is that a subset of nine Burns rocks have anomalously low abundances of MgO and SO₃, which has been widely attributed to partial loss of Mg-sulfate minerals during diagenesis

(e.g., Clark et al., 2005; Hurowitz and Fischer, 2014; McCollom, 2018).

Opportunity was not equipped with instrumentation to directly determine the mineralogy of the Burns rocks. However, their mineral composition can be constrained to some extent from other observations (with considerable uncertainty). Based on the bulk chemical compositions and data from the miniature thermal emission (mini-TES) and Mössbauer spectrometers onboard the rover, model mineral compositions include ~30-40% siliciclastic components (possibly including plagioclase, pyroxenes, and nontronite or other phyllosilicates), 15-25% amorphous silica and/or glass, 5-10% hematite plus other Feoxides/oxyhydroxides, and ~30-40% Mg-, Fe-, and Ca-bearing sulfate minerals including natrojarosite, together with minor chloride and phosphate components (Clark et al., 2005; McLennan et al., 2005; Glotch et al., 2006b; Glotch and Bandfield, 2006; Morris et al., 2006).

The Burns formation is directly underlain by the Grasberg formation, first encountered when the rover arrived at the rim of Endeavour crater (Fig. 3; Crumpler et al., 2015; Mittlefehldt et al., 2018). On the Endeavour rim, the Grasberg formation is a thin (~2 m) unit that consists of fine-grained sedimentary rocks, which appear in outcrop as light-toned, flat-lying polygonal blocks (Fig. 3d,f). Outcrops of the Grasberg formation form a distinctive bench which surrounds promontories such as Cape York on the crater rim (Fig. 3a,b). Although Opportunity only investigated exposures of the Grasberg on the western rim of Endeavour, outcrops of similar appearance are present around the crater (Grant et al., 2016) suggesting that the unit is regional in extent. The Grasberg formation has been divided into upper and lower units, with much of the lower unit covered by unconsolidated dark-toned materials that made observations of the underlying bedrock difficult (Fig. 3g).

Bedrocks of the Grasberg formation have a homogenous morphology and lack distinct bedding or other sedimentary structures like those that are ubiquitous in the Burns formation, including the Burns rocks that lie immediately above the Grasberg contact (Fig. 3e,f,g). Individual grains in the Grasberg bedrocks were too small to be resolved by the microscopic imager on Opportunity (<100 m) and are thus much finer-grained than the sands that compose the Burns formation rocks (0.1-1 mm diameter). The fine-grained textures and lack of bedding features suggests that the Grasberg sediments were originally emplaced as an airfall deposit derived from an impact or volcanic source (Crumpler et al., 2015; Mittlefehldt et al., 2018).

Geochemically, the rocks from the Grasberg formation have moderately high sulfur contents (SO₃ = 6.3 to 13.1 wt.%), albeit they are substantially less enriched in S than the Burns formation (17-28.6 wt.% SO₃). Compared to the Burns formation, the measured compositions of the Grasberg rocks have lower MgO, MnO, and Ni contents and higher SiO₂, K₂O, FeO, TiO₂, and Zn (Crumpler et al., 2015; Mittlefehldt et al., 2018). However, when normalized to the same MgO, SO₃ and MnO contents, the remaining elements have essentially identical abundances in both the Grasberg and Burns formations (McCollom

and Hynek, 2021). This close similarity in chemical compositions suggests that the sediments comprising the two units may have come from closely related sources, or maybe even the same source, with subsequent mobilization of MgO, $\rm SO_3$, and MnO accounting for the observed differences in their present compositions.

Little information is available on the mineralogical composition of the Grasberg rocks, in part because the mini-TES and Mössbauer spectrometers were no longer operating when the rover reached Endeavour. The relatively high SO₃ contents of Grasberg rocks indicates that sulfate minerals are likely to be present, but the identity of these minerals is undetermined. Centimeter-scale gypsum veins are widespread in the lower unit (Fig. 3g), but it is unclear whether gypsum is present in the surrounding bedrocks. Visible-near infrared (VNIR) spectra indicate that the Grasberg rocks contain higher amounts of red hematite than the Burns formation, but the gray hematite spherules that are ubiquitous in the Burns formation are absent from the Grasberg (Farrand et al., 2014).



3. Data sources

Chemical compositions of rocks from the Burns and Grasberg formations used for this study were downloaded from the Planetary Data System (PDS) website in October, 2014, and August, 2018, with one additional Grasberg sample (Ogallala) taken from Mittlefehldt et al. (2021). The chemical compositions of rocks were obtained using the Alpha Particle X-ray Spectrometer (APXS) mounted on the arm of the Opportunity rover (Rieder et al., 2003, 2004; Gellert et al., 2006), and processed using the method, fit program, and calibration parameters described in Gellert et al. (2006). Chemical compositions for other rocks that are included in the figures for context were either downloaded from PDS or derived from literature sources as described in the Supplemental Materials. All data used in the study as well as diagrams based on those data are included as a supplemental spreadsheet (Supplemental Dataset1). To avoid confusion, the names assigned to APXS targets in the PDS database are used in this communication, even though different names have been used for some of the same targets in other published studies.

To avoid contributions from surface deposits and alteration, only those Burns samples that were abraded with the rock-abrasion tool (RAT; Gorevan et al., 2003) are used in the analysis, with the exceptions of Callitris and CapeFairweather1. The latter two samples were either only brushed with the RAT (Callitris) or analyzed untreated (CapeFairweather1), but are included in the data compilation because they represent Burns samples that are adjacent to the contact with the underlying Grasberg formation. Despite not being abraded with the RAT, the compositions of these two targets are similar to the abraded Burns samples, and images of the targets show little evidence for contamination from surface debris or alteration of the bedrock (McCollom and Hynek, 2021). Because only a relatively small number of targets from the Grasberg formation were analyzed by Opportunity, the analysis includes both RAT abraded and brushed Grasberg samples. However, these samples form a coherent group with similar composition and appear to be a reasonable representation of the composition of the bedrock without any significant surface contribution (see McCollom and Hynek, 2021). Furthermore, images of the brushed Grasberg targets show very little surface debris and no obvious evidence of alteration (McCollom and Hynek, 2021).

4. Investigating diagenetic mobilization of MgO and SO_3 in the Burns formation

4.1. Geochemical trends in the Burns and Grasberg formations

The major element compositions of the Burns formation rocks analyzed by Opportunity were nearly uniform in composition across the rover's entire traverse from Eagle crater to Endeavour crater (Fig. 1; McCollom, 2018). One notable exception, however, is that a subset of nine rocks have significantly lowerthan-average MgO and SO₃ abundances. These rocks were first encountered in Endurance crater, where rocks exposed deep within the crater's interior were found to have anomalously low abundances of MgO and SO₃ (Fig. 4; Clark et al., 2005). Subsequently, rocks with similarly low MgO and SO_3 contents were identified for Burns rocks in the interior of Victoria crater (Squyres et al., 2006) and just above the contact with the underlying Grasberg formation (McCollom and Hynek, 2021). Heretofore, the trend of decreasing MgO and SO_3 at depth within Endurance and Victoria craters has generally been attributed to partial removal of Mg sulfate minerals from the deeper deposits during diagenesis (Clark et al., 2005; Niles and Michalski, 2009; Hurowitz and Fischer, 2014; McCollom, 2018; McCollom and Hynek, 2021). However, loss of MgO and SO₃ does not appear to be a unique interpretation, and alternative explanations have been



proposed (e.g., Amundson et al., 2008; Amundson, 2018).

The samples at depth within Endurance crater also exhibit relatively high abundances of several elements, including Si, Al, Na, and K (Fig. 4). However, mass balance calculations indicate that the higher abundances for this group of elements can be explained by passive enrichment in their relative abundances owing to the lower amounts of MgO and SO_3 without any need to invoke mobilization or differences in sediment composition (McCollom, 2018; Amundson, 2018). The abundances of Ca and Fe exhibit variable abundances with no discernible trend as a function of depth in Endurance (Fig. 4), which is potentially attributable to localized redistribution during diagenesis with no net transfer into or out of the formation (McCollom, 2018).

Because Ti is essentially immobile in a broad range of geologic environments, element:TiO₂ ratios provide a useful tool for assessing the extent of mobilization by aqueous fluids. Element:TiO₂ ratios have been used to assess mobilization of elements by fluids in a variety of martian settings, with anomalously higher ratios indicating enrichment in a particular element and lower ratios indicating loss of the element (e.g., Ming et al., 2008; Ruff et al., 2014; Zolotov and Mironenko, 2016; Yen et al., 2017a; Hausrath et al., 2018; McCollom, 2018; Amundson, 2018). Element:TiO₂ ratios can be effected by processes other than element mobilization, but there is no indication that these other factors have contributed to variations in element:TiO₂ ratios in the Burns or Grasberg formations (McCollom, 2018; McCollom and Hynek, 2021). For instance, heavier Ti-bearing minerals can be physically sorted and separated from silicate minerals during eolian or fluvial transport, resulting in variations in element:TiO₂ ratios within sedimentary deposits (e.g., Fedo et al., 2015). However, Ti abun-

dances in the Burns rocks exhibit strong positive linear correlations that converge on the origin for both Si and Al, and the Grasberg rocks plot on the same trend (Supplemental Fig. S1). These trends are inconsistent with the negative correlations that would be expected if sorting during transport had separated Ti-bearing minerals from siliciclastic components. Variations in element:TiO₂ ratios can also arise from variability in TiO₂ abundance of the sediments as they are deposited (e.g., Sheldon and Tabor, 2009; Sharma et al., 2013). But, when adjusted for differing amounts of MgO and SO_3 , the abundance of TiO₂ is constant within analytical error for all Burns and Grasberg samples (McCollom and Hynek, 2021). Furthermore, element: TiO₂ ratios for many elements are nearly uniform across the Burns formation, including Si, Al, Na, K, Mn, P, and Cr (McCollom, 2018). Consequently, there is no indication that there were significant variations in TiO₂ abundance of the sediments when they were initially deposited. Thus, it appears that element: TiO_2 ratios are an accurate indicator of the relative mobility of individual elements in the Burns and Grasberg formations.

Measured element: TiO₂ ratios in the Burns and Grasberg rocks are displayed in Figure 5 as a function of relative depth. To allow for better interpretation of general trends, the compositions of Burns rocks in this and other diagrams have been separated into four categories: (1) rocks encountered along the rover's traverse along the surface, rocks exposed within the walls of (2) Endurance and (3) Victoria craters, and (4) rocks located just above the contact with the underlying Grasberg contact (i.e., Callitris and CapeFairweather1). Also, to facilitate comparison, the relative depths of rocks exposed within Victoria crater are plotted next to those from within Endurance crater based on similarities in depth below the crater rim and physical appearance; however, the actual stratigraphic relationship of these materials is uncertain. Some studies have hypothesized that Victoria crater lies stratigraphically above Endurance crater (e.g., Squyres et al., 2009; Hayes et al., 2011) and that Opportunity traversed downward through a stratigraphic section more than 100 m deep as it drove towards Endeavour crater (Edgar et al., 2014). However, the available geologic evidence for this is equivocal since there are no continuous exposures of bedding over long distances between the craters or any other features (e.g., marker beds) that would allow stratigraphic relationships to be established along the rover's traverse. Therefore, it is equally plausible that the entire Burns formation consists of a relatively thin (<20 m) unit uniformly draped on top of existing topography. In the latter case, rocks exposed within Victoria and Endurance would be at an approximately equivalent stratigraphic depth. In any event, the Burns rocks found just above the Grasberg contact along the rim of Endeavour crater presumably lie at an even greater depth in the formation than those exposed within Endurance and Victoria craters, although how much deeper is unclear.

As seen in Fig. 5, both MgO:TiO₂ and SO₃:TiO₂ decrease with depth in Endurance crater, which is especially evident in the samples exposed in the deepest part of the crater below the Wellington contact (Fig. 1b). In addition, the deep

est samples that have the lowest MgO and SO₃ levels also have relatively low Ni:TiO₂ ratios, suggesting that mobilization of Ni may have been coupled to that of Mg. Coupled mobilization of Ni and Mg would be consistent with the inferred Ni enrichment of Mg-sulfate minerals on Mars (vanBommel et al., 2016; Yen et al., 2017b). As observed in Endurance, the deepest samples in Victoria crater also exhibit low MgO:TiO₂, SO₃:TiO₂, and Ni:TiO₂ ratios. Moreover, the Burns rocks closest to the Grasberg contact also exhibit low ratios for these same elements (Figs. 5a, 5b, and 5k).

Nearly all samples from within Endurance and Victoria craters have FeO:TiO₂ and CaO:TiO₂ ratios that are lower than the average for samples measured along the surface traverse (Figs. 5g & 5h). However, there is no clearly discernible trend in the FeO:TiO₂ and CaO:TiO₂ data as a function of depth like that observed for MgO and SO₃. Consequently, these variations may reflect small-scale heterogeneities or localized redistribution of Fe and Ca on the scale of centimeters rather than significant net transport into or out of the formation, consistent with other evidence for localized mobilization of these elements during diagenesis (e.g., formation of hematite spherules; McCollom, 2018).



Chlorine abundances in Burns formation rocks have a bimodal distribution, with one group of samples having abundances around 0.6 wt.% and a second group with ~1.6 wt.% Cl (Clark et al., 2005; McCollom, 2018). These values translate to Cl:TiO₂ ratios of ~0.4 and ~2.0, respectively (Fig. 5m). Notably, nearly all of the Burns samples with higher Cl abundances are found at depth within Endurance and Victoria craters, with a transition in Endurance crater that occurs near the Whatanga contact (Fig. 5m).

The remaining elements, including Si, Al, Na, K, Cr, Mn and P, all exhibit

element: TiO₂ ratios that are nearly constant throughout the formation with no discernible difference between the samples at depth and those at the surface. The constant ratios suggest that this group of elements was essentially immobile throughout diagenesis (McCollom, 2018). Constant ratios could also arise if the same amount of an element was added to or removed from all samples, but this seems to be a much less likely possibility.

The Grasberg rocks that immediately underly the Burns formation on the rim of Endeavour crater have even lower MgO:TiO₂ and SO₃:TiO₂ ratios than the Burns rocks, as well as lower Ni:TiO₂ ratios than all Burns rocks except for Callitris and CapeFairweather1 (Figs. 5a, 5b, and 5k). Most Grasberg rocks also have lower MnO:TiO₂ and P_2O_5 :TiO₂ ratios than the Burns rocks, although the two Burns samples immediately above the contact have similarly low MnO:TiO₂ ratios (Fig. 5j) and a couple of Grasberg samples have P_2O_5 :TiO₂ ratios similar to the Burns rocks (Fig. 5l). With few exceptions, element:TiO₂ ratios for all other major elements in the Grasberg rocks are within the range of the Burns samples, reflecting the close similarity in chemical composition between the two formations (McCollom and Hynek, 2021).

The Grasberg rocks exhibit a range of Cl:TiO_2 ratios that is similar to the Burns formation, but too few samples are available to determine if this range is representative of the formation as a whole. It is worth noting, however, that the two Grasberg analyses with the highest Cl:TiO_2 ratios ("Grasberg1 brush RAT brush" and "Grasberg3 brush RAT offset") were obtained on targets immediately adjacent to one another on the same outcrop, and the Cl levels in these adjacent samples were substantially higher than any other analyzed Grasberg rocks (including those samples that were not treated in any way by the RAT prior to analysis which were not included in this study; McCollom and Hynek, 2021). In addition, the two targets with elevated Cl have higher Na than any other Grasberg samples. Consequently, it is possible that the elevated Cl and Na in these two Grasberg targets may represent a local enrichment in Cl-bearing salts, with most of the formation having substantially lower amounts of these elements.

4.2. Interpretation of element mobility during diagenesis of the Burns and Grasberg formations

The chemical trends shown in Figure 5 allow several inferences to be made concerning element mobility in the sedimentary rocks on Meridiani Planum. First, the systematic variations in MgO and SO_3 with depth in the Burns rocks strongly suggests that these elements were mobilized during diagenesis (Figs. 5a and 5b; Clark et al., 2005; Niles and Michalski, 2009; Hurowitz and Fischer, 2014; McCollom, 2018; McCollom and Hynek, 2021). If, as the data suggest, the initial sediments that form both the Grasberg and Burns formations came from a related source with similar chemistry (McCollom and Hynek, 2021), then the even lower MgO and SO_3 levels in the Grasberg rocks can be viewed as continuation of the same trend as that observed for the Burns rocks (Figs. 5a

and 5b).

The lower abundances of MgO and SO_3 at depth within Endurance and Victoria craters has conventionally been attributed to partial loss of these components from the deeper deposits during diagenesis (Clark et al., 2005; Niles and Michalski, 2009; Hurowitz and Fischer, 2014; McCollom, 2018; McCollom and Hynek, 2021). Here, we propose an alternative model whereby the Burns sediments initially had much lower abundances of MgO and SO_3 that were similar to those of the Grasberg formation, and were subsequently enriched in these components during diagenesis. The mechanism for this enrichment would presumably involve evaporation of Mg- and sulfate-bearing groundwater. Nickel would be transported along with Mg and precipitate as a component of Mg-sulfate minerals during evaporation, accounting for the similar trends for Ni and MgO in the rocks (Figs. 5a and 5k). Alternatively, the precipitation of Mg- and Ni-bearing sulfate salts could have resulted from freezing of upwelling groundwater in the shallow subsurface (e.g., Marion et al., 2008) followed by gradual sublimation of the residual water ice.

In this proposed model, the lower MgO, SO_3 , and Ni abundances observed for the Grasberg rocks would represent the pristine composition of both formations, with all Burns rocks becoming significantly enriched in these components during diagenesis. Precipitation of greater amounts evaporite minerals closer to the surface would then account for the variation of MgO, SO_3 , and Ni with depth in Endurance and Victoria craters (Figs. 5a, 5b, and 5k), rather than transport of these components out of the deeper deposits. Thus, this model would simultaneously account for both the differences in composition between the Burns and Grasberg formations and for the increasing abundances of MgO, SO_3 , and Ni in the shallower samples.

If the original sediments that formed the two units initially had similar compositions, then the lower $MnO:TiO_2$ and $P_2O_5:TiO_2$ ratios in the Grasberg rocks relative to the Burns must also be accounted for (Figs. 5j and 5l). Potentially, the generally higher abundances of Mn and P in the Burns rocks relative to the Grasberg could be accounted for either by diagenetic enrichment of the Burns rocks in Mn and P or by depletion of these elements in the Grasberg rocks. Of course, it's also possible that the original sediment sources for the Burns and Grasberg formations initially had different abundances of Mn and P; however, this appears to be a much less likely explanation given the close similarity in abundances of the other elements (McCollom and Hynek, 2021). That is, it seems unlikely that that the Mn and P abundances would be radically different in the sediment sources for the two units when nearly all other elements are almost identical.

In the case of Mn, Ming et al. (2015) noted that the Grasberg rocks have FeO:MnO ratios that are substantially higher than is typical for martian crust (Fig. 6), and they proposed that the elevated ratios are attributable to partial removal of Mn by aqueous fluids during diagenesis. Removal of Mn would also account for the lower MnO:TiO₂ ratios in the Grasberg rocks (Figs. 5) and

6). If this explanation is valid, the higher $MnO:TiO_2$ ratios observed for most Burns rocks may represent the original composition of the sediments, and the Grasberg deposits would presumably have had similar ratios prior to the loss of Mn during diagenesis.



the lower MnO:TiO₂ ratios of the Grasberg formation may represent the pristine composition, which would then require that the entire Burns formation was enriched in Mn during diagenesis in order to explain the higher ratios in that unit. This possibility would also require that the original sediment source for both units had substantially higher FeO:MnO and lower MnO:TiO₂ ratios than is observed for most martian basalts or estimated for the average martian crust (Fig. 6b). However, this does not appear to be an unreasonable requirement given that many of the sedimentary rocks of the Murray formation in Gale crater examined by the Curiosity rover have FeO:MnO and MnO:TiO₂ values similar to those of the Grasberg (Fig. 6b). Unless there has been widescale transport of Mn out of the Murray rocks (for which there appears to be little evidence), their relatively high FeO:MnO and low MnO:TiO₂ ratios must reflect a sediment source that is depleted in Mn relative to most martian basalts and to the average martian crust.

On balance, it appears that the simpler explanation for the data is that the Grasberg sediments initially had Mn levels similar to that of most Burns rocks, but some of this Mn was lost from the Grasberg rocks during diagenesis as proposed by Ming et al. (2015). This explanation would be consistent with the similarity of the FeO:MnO and MnO:TiO₂ ratios in the Burns rocks to those of martian basalts and to average martian crust (Fig. 6b). It would also be consistent with the nearly uniform MnO:TiO₂ ratios throughout the Burns formation (excepting the two rocks adjacent to the Grasberg contact; Fig. 5j). If substantial amounts of Mn had been added to the Burns deposits during

diagenesis as required by the alternative explanation, it is difficult to imagine that all of the deposits were enriched by the same amount of Mn as would be required to explain the uniform $MnO:TiO_2$ ratios in the Burns rocks. Whether or not the inferred loss of Mn might be related to the process that enriched the Burns rocks in MgO and SO₃ is unclear and requires further study.

On this topic, it is worth noting that the two Burns rocks immediately above the Grasberg contact, Callitris and CapeFairweatther1, have FeO:MnO and $MnO:TiO_2$ ratios that are lower than the rest of the Burns samples, but similar to those of the underlying Grasberg rocks (Figs. 5j and 6a). This would imply that any diagenetic loss of Mn that occurred in the Grasberg rocks extended into the base of the Burns formation, at least in the region of the Endeavour crater rim explored by Opportunity. Furthermore, it would imply that the Mn loss took place after the Burns sediments were already emplaced (McCollom and Hynek, 2021).

Previously, McCollom et al. (2018) argued that P was immobile throughout deposition and diagenesis of the Burns formation. This inference was based on: (1) the limited variability in both the abundance of P and the P:Ti ratios in the Burns rocks (Fig. 5l), and (2) the close similarity of the P levels and P:Ti ratios in the Burns rocks to those of most martian basalts. If the original sediments for both the Burns and Grasberg formations had similar compositions and P was immobile during diagenesis of the Burns, then the lower P_2O_5 :TiO₂ ratios observed for most Grasberg rocks (Fig. 5l) would have to be attributed to partial removal of P or to variation in source sediment composition. Alternatively, the higher P_2O_5 :TiO₂ ratios in the Burns formation could be explained by mass transfer of P into the Burns sediments during diagenesis, enriching the amount of P in the sediments from an initial composition that was similar to the Grasberg rocks. However, as for Mn, this would require that P was added in almost uniform amounts to the Burns deposits to account for the limited variability in P_2O_5 :TiO₂, which seems less likely.

Lastly, the bimodal distribution of Cl indicates that it was likely mobilized to some extent during diagenesis. Of course, this is not surprising given the high solubility of Cl-bearing minerals and evidence for mobilization of Cl elsewhere on Mars. However, the extent of mobilization of Cl into the deposits, as well as its possible relationship with the inferred enrichment in MgO and SO_3 , is not immediately evident.

All but two of the Burns samples with high abundances of Cl are found at depth within Endurance and Victoria craters (Fig. 5m). One of the exceptions is LemonRind, where the analyzed target has the appearance of alteration rind or coating of a fracture surface (Supplemental Fig. S2). LemonRind has a much higher Cl content than the immediately adjacent target (Fruitbasket_Strawberry) where abrasion by the RAT appeared to penetrate the materials analyzed at LemonRind. Thus, the high Cl contents of LemonRind appear to represent a localized enrichment, perhaps caused by fluid flowing within a fracture. The other exception is the target BlackShoulder_Abraded, encountered on the plains north of Murray Ridge on the rim of Endeavour crater. Images of this target are less clear (Supplemental Fig. S2), but it could also represent a rind or fracture coating.

Notably, the transition from lower to higher Cl contents in the samples within Endurance crater appears to coincide with the Whatanga contact (Figs. 1a and 5m). The shift from lower to higher Cl coincides with a transition from lighter to darker tone in the exposures of bedrocks in the crater walls (Supplemental Fig. S3). The rocks below the contact have rougher surfaces with more cavities, and the darker tone is largely attributable to the accumulation of dark surface materials within these cavities rather than a darker color of the underlying bedrock itself. The contact has been interpreted as possibly representing the capillary fringe of a groundwater table, with recrystallization of cements in the saturated materials below the contact leading to the difference in morphology and surface texture (Grotzinger et al., 2005). In Victoria crater, the transition from lower to higher Cl contents with depth also appears to coincide with a transition from lighter- to darker-toned bedrock exposures (Supplemental Fig. S3).

These observations suggest that the elevated Cl contents for the bedrocks exposed at depth within Endurance and Victoria craters could be attributable to precipitation of Cl-bearing minerals as the groundwater table lowered and the capillary fringe retreated into the subsurface. Whether or not this inferred Cl enrichment is associated with enrichments in MgO and SO₃ is unclear at this time. It is worth noting, however, that the transition from lower to higher Cl appears to occur at a shallower depth (near the Whatanga contact; Fig. 5) than the transition from higher to lower MgO and SO₃ (near the Wellington contact). One possible explanation to explain these trends that might be worth exploring in future studies is that the MgO and SO₃ enrichments were caused by evaporation of fluids in a rising water table and wicking towards the surface, while the more soluble Cl-salts precipitated as the groundwater retreated back into the subsurface.

4.3. Geochemical model for enrichment of the Burns formation in Mg, SO_3 , and Ni

To test whether the inferred diagenetic enrichment of the Burns formation in MgO, SO_3 , and Ni can account for the chemical compositions of the rock samples analyzed by Opportunity, a quantitative mass-balance model was constructed to simulate addition of these components to a Grasberg-like precursor (Fig. 7). The model calculations involved addition of MgO, SO_3 , and Ni in increments to materials that were assumed to have an initial composition equivalent to the average of the Grasberg formation samples. Following the addition of each increment, the abundances of all elements were renormalized to total 100 wt%. The resulting model predicts trends of increasing abundances for MgO, SO_3 , and Ni, while the relative abundances of all other (immobile) elements progressively decrease owing to passive dilution by the addition of increasing amounts of MgO, SO_3 , and Ni (Fig. 7). The model calculations are included in the

accompanying spreadsheet (Supplemental Dataset1), where interested readers can vary the input parameters to examine how different input parameters effect model predictions.

It was assumed for this initial model that Mn and P were not transported into the Burns sediments along with MgO, SO₃, and Ni, but were instead partially removed from the Grasberg by a separate diagenetic process not explicitly incorporated into the model. To account for the presumed higher Mn concentrations in the original sediments relative to their current abundance in the Grasberg rocks, it was assumed that both units originally had an $MnO:TiO_2$ ratio similar to that currently observed in the Burns rocks. This assumption leads to an estimated MnO abundance of 0.43 wt% in the original sediments. Additionally, it was assumed that the two RAT-abraded Grasberg samples that have the highest P_2O_5 :TiO₂ ratios approximates the pristine composition of the sediments prior to the inferred loss of P. For simplicity, mobilization of Cl was not considered in this initial model. Although mobilization of Cl may well be linked to the inferred enrichment in MgO and SO_3 , exploring this possibility would require much more elaborate modeling strategies than employed here, and therefore must await subsequent studies. Again, readers can modify the model calculations in the accompanying spreadsheet to explore alternatives to these assumptions.



During development of the model, it was observed that addition of the MgO and SO_3 in a 1:1 molar ratio did not result in compositional trajectories that passed through the Burns MgO data. Therefore, the MgO:SO₃ ratio was varied in the model, and a ratio equal to 0.65 was found to provide the closest approximation to the Burns data overall based on visual inspection. Since Mg-sulfate minerals generally have a MgO:SO₃ equal to one, this result would imply that the evaporating diagenetic fluids precipitated greater amounts of SO₃ than could be accounted for by precipitation of Mg-sulfate minerals alone. The excess of SO₃ could be explained if additional cations were extracted from the sediments as

they reacted with the evaporating groundwater and were subsequently incorporated into precipitation of sulfate minerals. For instance, reaction of pyroxene in the sediments with SO_4 -bearing groundwater could result in precipitation of sulfate minerals together with amorphous silica (e.g., McCollom et al., 2013), as illustrated by the generalized reaction:

where the exact stoichiometry would depend on the composition of the dissolving pyroxene. The result of such reactions would be incorporation of sulfate from the fluid without additional enrichment of the sediments in Mg or other cations. The model results shown in Figure 7 also assume Ni is added at a Ni:SO₃ ratio of 0.00233.

Results of the mass-balance model are displayed in Figure 7, with the red arrows representing model predictions for how the abundances of individual elements should evolve with increasing addition of MgO, SO₃, and Ni. As seen in the figure, this simple model provides a very close fit to the observed Burns formation data for most elements, especially for the group of elements whose relatively constant element:TiO₂ ratios indicate that they have been immobile during diagenesis (i.e., Si, Al, Na, K, Ti, and Cr, see Fig. 5; McCollom, 2018). The model also captures the general trend of the P_2O_5 data for the Burns rocks, albeit the trend is offset to somewhat lower P_2O_5 abundances (Fig. 7l). Furthermore, the model accurately reproduces the MnO data for most Burns samples (Fig. 7k), provided the assumed higher Mn abundance is representative of the original sediments. The two Burns samples adjacent to the Grasberg contact lie well below the predicted MnO trend, but this could potentially be explained by loss of Mn from these samples during diagenesis similar to that inferred for the Grasberg.

The model also reproduces the general trends of higher MgO and lower FeO and CaO for the Burns rocks compared to the Grasberg (Figs. 7g, 7h, and 7i). However, the abundances of these elements in the Burns rocks are highly variable among samples and do not exhibit consistent trends as a function of SO_3 like that observed for most other elements (Fig. 7). A likely explanation for the scatter of Mg, Fe, and Ca around the predicted model trends is that they were affected by additional processes during diagenesis, which probably involved localized redistribution (~scale of centimeters) of these elements during mineral dissolution and reprecipitation (McCollom, 2018). The inferred localized redistribution of Mg, Fe, and Ca would be consistent with the abundant evidence for formation of hematite spherules and late-stage sulfate cements (Squyres et al., 2004, 2006; McLennan et al., 2005; Grotzinger et al., 2005).

It is also worth noting that, for most elements, the compositional trajectories predicted by the diagenetic model correspond very closely to linear regression lines fit to the Burns data as a function of SO_3 (Supplemental Fig. S4). The close agreement between the model predictions and the independently calculated

regression lines provides further support for the argument that the diagenetic model accurately replicates the observed chemical compositions of the Burns rocks. For Fe, Ca and Mn, the regressions provide a poor fit to the data and the predicted model trajectories do not correspond particularly well to the calculated regression lines (Supplemental Fig. S4). However, given the evidence that additional diagenetic process had a large effect on the distribution of these elements, neither a close correlation with SO₃ nor a close match between model predictions and the regressions would necessarily be expected.

4.5. Comparison with previously proposed geochemical models

Any proposition of a new model naturally raises questions about how it compares with other models proposed to explain the same data. Accordingly, in this section we compare our new diagenetic model with others that have been proposed to account for the chemical composition of the Burns formation, including the sulfur-plus-cations and sulfur-only chemical models (Fig. 1). We also briefly address a sulfide mineral oxidation model for the Burns formation that has been proposed by some authors (Zolotov and Shock, 2005; Dehouck et al., 2012).

Advocates of sulfur-plus-cations models have so far provided only rudimentary details of their chemical model, which to date consist only of demonstrating that the measured compositions of the Burns rocks lie on mixing lines between two endmembers projected onto element-ratio diagrams (Fig. 8; Squyres et al., 2006; Hurowitz and Fischer, 2014). Squyres et al. (2006) proposed that the chemical composition of the Burns rocks could be accounted for by a mixture of two endmembers composed of: (1) chemically altered martian basalt depleted by about 55% in Σ (Fe + Mg + Ca), and (2) a mix of Mg-, Fe- and Ca-sulfate minerals deposited by evaporating fluids. As shown in Figure 8a (modified after Figure 3 in Squyres et al., 2006), the Burns rocks fall close to a mixing line between the specified endmembers (black line) when plotted in the dimensions of $Al_2O_3/(FeO+MgO+CaO)$ versus SO_3 . The comparison shown in this diagram is the only criteria used by Squyres et al. (2006) to support their chemical model. Neither the proportions of cations removed from the basalt precursor nor those added in as sulfate precipitates are specified, and no compositional information on the endmembers is provided beyond the constraint that they possess element ratios consistent with the mixing line.



portrayed in Figure 8a by the red arrow is the calculated trajectory of rock compositions for diagenetic addition of MgO and SO₃ to a Grasberg-like precursor as proposed here, projected onto the same parameter space as the Squyres et al. (2006) diagram. As seen in the figure, the diagenetic model provides a comparably good match to the observed Burns data as the Squyres et al. (2006) model. The sample that deviates the most from the predicted diagenetic trajectory is MacKenzie_Campbell, which has the highest wt.% Al₂O₃ of any Burns sample and accounts for its position above the predicted trajectory. The anomalously high Al₂O₃ of this sample suggests a localized enrichment in Al-bearing minerals, either in the original materials or during diagenesis.

Hurowitz and Fischer (2014) proposed a similar two-endmember mixing model for the Burns rocks, but with somewhat different element ratios used to constrain the endmembers (Fig. 8b). Hurowitz and Fischer (2014) defined the endmembers in terms of two element ratios, $Al_2O_3/(FeO+MgO+CaO+Na_2O+K_2O)$ and SiO_2/SO_3 , and estimated endmember compositions by fitting mixing models to the measured ratios of the Burns rocks. Hurowitz and Fischer (2014) considered two separate fits that

either: (a) included the subset of Burns samples with the lowest MgO and SO_3 abundances, or (b) excluded them on the presumption that these components were partially removed during diagenesis.

As seen in Figure 8b, the fits of Hurowitz and Fischer (2014) accurately reproduce the chemical compositions of the Burns rocks when portrayed in this parameter space. Their preferred mixing model that excludes the low MgO and SO₃ samples constrains the groundwater-derived component to have high SO₃ together with little or no SiO₂ or Al₂O₃, while the siliciclastic component has an Al₂O₃/(FeO+MgO+CaO+Na₂O+K₂O) ratio between 0.15 and 0.18 and contains no more than a few wt% SO₃ (Fig. 1b). These authors noted that, on the siliciclastic component end, the inferred mixing lines extend through compositional fields for cation-conservative alteration of Adirondack class basalts by sulfur-bearing fluids and for soils analyzed by the Opportunity and Spirit rovers, which could potentially provide some insight into the source of the siliciclastic component (Fig. 8b).

For the dimensions portrayed in Figure 8b, the diagenetic model proposed here closely parallels the mixing model of Hurowitz and Fischer (2014). This is not totally unexpected, however, since the proposed diagenetic model is essentially a two-component mixing model with Grasberg-like materials and MgO-SO₃ precipitates as endmembers. The endmembers of the diagenetic model proposed here are consistent with the constraints derived by Hurowitz and Fischer (2014), and the compositions of the Grasberg rocks lie close to the extension of their mixing line to the inferred composition of the siliciclastic component. Again, the sample that deviates the greatest amount from the trends defined by both models is MacKenzie_Campbell, whose anomalously high Al₂O₃ abundance causes it to fall above the predicted lines in this parameter space.

Thus, the proposed diagenetic model appears to be generally consistent with the mixing model calculated by Hurowitz and Fischer (2014), although those authors interpret the mixing to take place in an entirely different context than proposed here. Hurowitz and Fischer (2014) interpret the mixing as occurring on the margins of a playa lake, where evaporating fluids precipitate multi-cation sulfates and mix with siliciclastic materials to account for the measured compositions of the Burns rocks. Conversely, the diagenetic model here involves addition of only a single cation, and invokes addition of the evaporite component during diagenesis rather than before deposition. Nevertheless, the convergence between the proposed diagenetic model (with compositions predicted independent of the measured compositions of the Burns samples) and the mixing model of Hurowitz and Fischer (which is derived through a fit to the measured compositions of the Burns rocks) provides additional confirmation that the diagenetic model accurately reproduces the Burns data.

Another perspective comparing these two types of models is provided in Figure 9, which shows the somewhat curious observation that total cation concentrations are nearly uniform across all Burns samples independent of their SO_3 abundance. This invariance is illustrated by linear regressions of the Burns

data, which are essentially horizontal lines (Fig. 9). If substantial amounts



cations were transported into the Burns precursor materials along with the sulfur component as suggested in the model proposed by Squyres et al. (2006), the Burns data should display a positive correlation between Σ (FeO + MgO + CaO) and SO_3 , which is not observed in the data (dashed blue arrows in Fig. 9). The only way that the observed trend in the Burns data could possibly be reconciled with the cation-plus-sulfur model is if there were substantial losses of cations and SO_3 from some samples during diagenesis along with gains in others, producing a trend that deviates from the expected positive correlation (see McCollom, 2018). In addition, it can be seen Figure 9 that Grasberg data fall even farther from the expected trajectory for the cations-plus-sulfur model. Consequently, the cation-plus-sulfur model cannot account for the close chemical similarity of the Grasberg and Burns formations unless there was an even more extensive loss of cations from the Grasberg during diagenesis. Although possible, this reconciliation of cations-plus-sulfur models with the observed data would require much more extensive mobilization of cations during diagenesis than required by sulfur-only models (McCollom, 2018) or the model proposed here. On the other hand, the proposed diagenetic model readily accounts for the observed trends in total cations in the Burns rocks as well as their similarity to the Grasberg rocks (Fig. 9).

With respect to the sulfur-plus-cations models, it is also worth emphasizing that although these models reasonably reproduce the Burns data when portrayed in the parameter spaces depicted in Figure 8, they have much greater difficulty in reproducing the data when examined from more comprehensive perspectives. Indeed, a major strength of the diagenetic model proposed here is that it is capable of accounting for the full suite of elemental compositions, and not just a couple of element ratios (e.g., Figs. 7, 8, and 9). As described in detail by McCollom (2018), sulfur-plus-cation models can only be reconciled with trends in the abundances of elements in the Burns rocks relative to SO_3 and TiO_2 if there was extensive mobilization and internal redistribution of Fe, Ca, and Mg during diagenesis at a scale far greater than that required in other types of models (e.g., Fig 9; see McCollom, 2018, for additional examples). This diagenetic remobilization would be in addition to the alteration of precursor basalt-derived materials required to make these models compatible with the measured compositions of the Burns rocks (e.g., Figs. 1a and 8). While plausible, these constraints result in cation-plus-sulfur models that are far more complex than other models proposed to explain the same data (McCollom, 2018), including the one proposed here.

Furthermore, siliciclastic components that might seem to be compatible with two end-member mixing models when examined only from the perspective of element-ratio plots can be seen to be incompatible when investigated in greater detail. For example, martian soils and altered Adirondack class basalts might appear to be plausible endmembers when portrayed in simple element-ratio diagrams like those shown in Figure 8 (Squyres et al., 2006; Hurowitz and Fischer, 2014). Yet, they are clearly eliminated as possible endmembers when examined in a broader context. Addition of a sulfur-rich component to martian soils or to altered Adirondack basalt cannot feasibly account for the measured amounts of Si, K, Ti, and P in the Burns sediments because the abundances of this suite of elements are far too low in these proposed precursors (Supplemental Fig. S5; McCollom, 2018). When the full suite of elements is considered, the only martian materials identified to date that actually have a close chemical affinity to the Burns sediments are the Irvine class basalts in Gusev crater (McCollom and Hynek, 2021).

The other category of previously proposed chemical models ("sulfur-only") invokes addition of only an oxidized sulfur component (i.e., sulfuric acid, sulfate, or sulfite) to pristine basalt to account for the composition of the Burns rocks (Fig. 10; McCollom and Hynek, 2005; Tréguir et al., 2008; Berger et al., 2009; Niles and Michalski, 2009). Depending on the model, the sulfur component is proposed to come from either an atmospheric or volcanic source. For elements other than MgO, predicted compositional trajectories for addition of sulfur to pristine basalt are very similar to those of the diagenetic model; however, the trajectories for sulfur-only models extend from a pristine basalt composition with little or no SO₃ rather than from the Grasberg (Fig. 10; see McCollom, 2018). Note that the elemental trajectories for the sulfur-only model pass close to the Grasberg samples, so this type of model could potentially explain the composition of that unit as well (McCollom and Hynek, 2021).



MgO, sulfur-only models require that the pristine basalt initially had a substantially higher abundance of MgO than either the Burns or Grasberg formations, and that some of this MgO was subsequently removed from a subset of samples during diagenesis (McCollom, 2018). Consequently, the primary differences between the sulfur-only models and the diagenetic model proposed here are assumptions concerning the MgO content of the initial sediments and whether some of this MgO was gained or lost during diagenesis (along with SO_3). If the Grasberg rocks formed through sulfur-only addition to the same basaltic precursor as the Burns, even greater diagenetic loss of MgO and SO_3 would be required to account for their current composition (i.e., they fall even further from the sulfur-only trajectory in Fig. 10g; McCollom and Hynek, 2021).

While both the sulfur-only model and the one proposed here make somewhat similar predictions for most elements, the diagenetic model appears to more accurately reproduce the slope of the trends in elemental compositions of the Burns rocks as a function of SO_3 than the sulfur-only model (Fig. 10). The predicted trajectories for the diagenetic model are slightly steeper than those

of the sulfur-only model because the addition of MgO along with SO_3 leads to greater dilution of the remaining elements, and the resulting trajectories more closely reproduce the linear trends observed in the Burns data for many elements including Si, Al, K, Na, Ti and Cr. We would argue, therefore, that the diagenetic model provides a somewhat better explanation for the chemical data.

As an additional note, advocates of the sulfur-plus-cations models have asserted that the addition of a sulfur component alone to pristine basalt cannot possibly explain the chemistry of the Burns rocks because this would produce chemical compositions that conform to horizontal trends when portrayed on diagrams like those shown in Figure 8 (Squyres et al., 2006; Hurowitz and Fischer, 2014). However, McCollom (2018) demonstrated that this assertion is incorrect because it fails to take into account mobilization of Mg, Fe, and Ca during diagenesis. When diagenetic mobility of these cations is accounted for, nearly all of the variation along the vertical axes in Figure 8 is eliminated and it becomes evident that the sulfur-only models can readily explain the data (McCollom, 2018). Furthermore, since the diagenetic model proposed here is also consistent with the data when plotted in the parameter space of Figure 8, it is evident that these types of element-ratio diagrams on their own are not suitable to discriminate among the alternative models.

Another alternative type of chemical model proposes that the sulfates present in the Burns sandstones are formed through oxidation of pyrite or other sulfides (Zolotov and Shock, 2005; Dehouck et al., 2012). It appears doubtful, however, that this type of model is compatible with the chemical composition of the Burns rocks. In order to explain the high sulfate contents of the Burns formation, the precursor would need contain $>\sim12$ wt% pyrite or other sulfide minerals (Dehouck et al., 2012), which in turn would require a substantial enrichment in Fe or other metallic elements to account for the sulfides (~8 wt% or more). The Burns rocks do not appear to have any significant enrichment in metallic elements compared to typical martian basalts, so a sulfide mineral-rich precursor does not appear to be tenable. Nevertheless, oxidation of sulfide minerals may well have contributed to other sulfate-rich deposits on Mars.

5. Proposed scenario for formation of the Burns sandstones

The success of the diagenetic model in accounting for the chemical composition of the Burns rocks leads us to propose a new overall scenario for the origin of the Burns formation sandstones. In this section, we first provide a brief overview of the scenario, followed by more detailed discussion of several of the components involved. We propose the following scenario to explain the origin of the sandstones:

1) Deposition of fine-grained airfall materials with a chemical composition similar to the Grasberg rocks and derived from a closely related source (or possibly the same source).

2) Moderate inducation of the fine-grained sediments then forms

friable mudrocks similar in texture and composition to the current Grasberg rocks.

3) The inducated sediments then eroded into sand-sized particles, followed by local transport, reworking, and deposition of the sand at its present location. Transport was primarily by eolian processes, but with fluvial transport driven by emerging groundwater active for brief intervals in isolated locations. These processes were responsible for the bedding structures currently observed in the rocks.

4) Infiltration of the sand deposits by one or more generations of groundwater, leading to diagenetic effects that include dissolution and recrystallization of minerals, formation of hematite spherules, localized element mobilization and redistribution, and cementation.

5) At some point during sediment deposition and groundwater infiltration, evaporation of groundwater enriched in dissolved Mg and $\mathrm{SO_4}^{2^-}$ results in precipitation of sulfate minerals and increased abundances of MgO and $\mathrm{SO_3}$ in the sediment deposits, with higher amounts precipitated closer to the ground surface.

6) Late-stage diagenetic processes remove Mn and P from the Grasberg as well as Mn from the bottom of the Burns formation, accounting for the lower levels of MnO and P_2O_5 in those deposits.

5.1. Original source and deposition of sediments

The proposed scenario assumes that the sediments which eventually became the Burns formation were initially deposited as fine-grain airfall deposits derived from an impact or explosive volcanic eruption. Deposition as volcanic ash would be consistent with the geologic context of the Meridiani region (Hynek et al., 2002, 2003). Hynek and Phillips (2008) noted that the depositional processes for the broader Meridiani region led to coherent bedding traceable over hundreds of km that conform to the regional slope. Hynek et al. (2003) used rudimentary particle fallout plus global circulation models to show that airfall from the Tharsis region could easily be carried to Meridiani Planum, and would be one possible source for airfall deposits. More recently, large craters in Arabia Terra (north of Meridiani) have been classified as volcanic calderas that could have potentially supply substantial amounts of ash to Meridiani and even Gale crater (Michalski and Bleacher, 2013). A large impact could also supply the fine-grained materials, although it is not clear that it could supply sufficient volume of homogenous materials to account for the entire regional extent of the Burns formation (Hynek and Phillips, 2008).

Presumably, the initial fine-grained sediments had a basaltic provenance, although the materials may have been altered to some extent at their source locale prior to being transported to Meridiani Planum. When normalized to similar S contents, the Grasberg and Burns rocks have chemical compositions that are very similar to the Irvine class basalts in Gusev crater (McCollom and Hynek, 2021). This is demonstrated, for instance, by hierarchical cluster analysis based on chemical composition where the Irvine basalt from Gusev is found to cluster together with the Grasberg and Burns samples in a coherent group that is distinctly separate from other martian basaltic rocks. Therefore, Irvine may serve as a proxy of the basaltic precursor to the sediments that became the Grasberg and Burns formations.

The proposed scenario assumes that the original fine-grained sediments were already enriched to some degree in S before being deposited on Meridiani. The RAT abraded and brushed Grasberg samples have an average SO_3 content of 9.2 wt%. Some of this SO_3 could have been added during diagenesis, and it is also possible that more recent alteration of the exposed bedrock surface added some SO_3 . However, it seems likely that these sources were minor contributors and that the initial sediments contained at least several wt% SO_3 . Many other martian basalts and sedimentary rocks measured in situ by rovers have comparable SO_3 levels. For instance, the sedimentary rocks of the Murray formation in Gale crater have an average SO_3 content of 6.2 wt%, and the basalts in Gusev crater have an average SO_3 content of 5.3 wt% (these averages exclude Murray samples associated with gypsum veins and Gusev samples that are extensively altered with highly elevated S abundances; see Supplemental Dataset1).

The source of the elevated S contents in the original sediments is unclear at this time. One possibility is that it is indigenous to the basaltic precursor through crystallization from a sulfur-rich magma. Many of the martian basalts analyzed in situ by rovers contain several percent SO_3 (see Supplemental Dataset1), although it is currently unclear to what extent this represents the original rocks rather than secondary alteration. Another possibility is that the basaltic precursor initially had much lower S contents, but was subsequently enriched in S through acid-sulfate alteration through reaction with sulfuric acid derived from an atmospheric or volcanic source. This alteration might have occurred, for instance, through fumarolic activity on the flanks of a volcano (e.g., McCollom et al., 2013) or by melting of ice deposited on top of volcanic ash or cinders (e.g., Niles and Michalski, 2009; Kite et al., 2013; Niles et al., 2017). Low water:rock ratios during this process could account for the addition of SO_3 without significant loss of cations from the basaltic precursor. Nevertheless, it is conceivable that the high solubility of Mg-sulfate salts resulted in the removal of some Mg from the basaltic materials during this process, resulting in the relatively low MgO contents of the Grasberg sediments compared to most martian basalts. These sulfur-enriched basaltic materials would then have been transported to Meridiani Planum by repeated explosive eruptions.

The results of a preliminary two-stage geochemical model that includes alteration of a basaltic precursor prior to deposition of the source materials at Meridiani Planum are shown in Figure 11 (see Supplemental Dataset1 for calculations). In this model, the basalt initially has a composition very similar to the basaltic Irvine target in Gusev crater (Supplemental Table S1). Alteration of the basalt, most likely under water-limited acid-sulfate conditions, adds SO₃ while removing MgO. All other elements remain largely unchanged during this initial stage. Magnesium is highly mobile under acid-sulfate conditions, and is typically the first major cation to be removed as acid-sulfate alteration progresses (e.g., Mc-Collom et al., 2013). This initial stage of alteration results in materials that have a Grasberg-like chemical composition, which were then transported to Meridiani. Following deposition, addition of MgO and SO₃ to the Burns sediments during diagenesis then accounts for their current composition. More detailed geochemical modeling will be needed to test the feasibility of this model and possible alternatives, but these preliminary calculations outline a complete and plausible pathway to attain the chemical composition of the Burns formation.

Although we favor an airfall source for the initial sediments, an alternative possibility is that the fine-grained materials first accumulated as wind-blown dust trapped within ice deposits and then were left behind when the ice sublimated (Niles and Michalski, 2009; Kite et al., 2013). Sulfuric acid present in the ice, derived from an atmospheric source, could have altered to materials to some degree and enriched them in SO_3 (Niles et al., 2017). Meltwater from overlying snow deposits could also have promoted recrystallization of sulfate salts within the deposits as they accumulated, cementing them to the point where they could later erode into sand-sized particles.



5.2. Inducation and erosion into sand-sized particles

Following deposition, the proposed scenario presumes that the fine-grained sediments became moderately indurated and were then eroded into sand-sized grains. This would require that the indurated materials were sufficiently coherent to form sand-sized grains when eroded, yet friable enough that they would erode. The materials that eroded may have been less-well lithified than the current Grasberg formation, but otherwise would have had similar texture and composition. Sand-size aggregates of clays and other minerals ("pebbles") form in arid terrestrial environments and maintain their structure through transport and re-deposition (Bowler, 1973; Magee, 1991; Müller et al., 2004; Wright and Marriott, 2007). In some cases, sulfate- and chloride-rich salts or carbonates hold these aggregates together. Some terrestrial deposits composed of mud aggregates have textures that appear similar to that of the Burns sandstones (e.g., Supplemental Fig. S6).

If the fine-grained source materials had undergone acid-sulfate alteration prior

to deposition at Meridiani, recrystallization of sulfate- and chloride-bearing minerals may have facilitated cohesion of the siliciclastic components and enabled the formation and transport of sand-sized aggregates. Recrystallization of sulfates and chlorides could have been promoted by water percolating into the fine-grained airfall deposits, either from a rising groundwater table or through melting of overlying snow and ice deposits (e.g., Kite et al., 2013).

5.3. Transport and deposition

A number of studies have examined the prominent cross-bedding and other sedimentary structures in the Burns formation sandstones (e.g., Grotzinger et al., 2005, 2006; Edgar et al., 2012). These studies document that the sands were deposited primarily by eolian processes, with evidence for fluvial transport in a few isolated locations. In the scenario proposed here, sulfate-cemented siliciclastic sand grains derived from erosion of a Grasberg-like precursor are inferred to have been reworked by mostly eolian processes and redeposited at their current location, resulting in the cross-bedding and laminations documented in previous studies. In some isolated locations, emerging groundwater facilitated the transport of some sand deposits and formation of fluvial bedforms, as proposed by Grotzinger et al. (2005, 2006).

5.4. Diagenesis and MgO-SO₃ enrichment

There is extensive evidence for diagenesis of the Burns sandstones as documented in detail by McLennan et al. (2005) and other studies. Among the more prominent diagenetic features observed in the rocks are the formation of hematite spherules, dissolution of minerals leaving behind tabular-shaped voids, and development of isopachous cements (Fig. 1). The Whatanga contact in Endurance crater (Fig. 1) has also been interpreted as marking the upper extent of recrystallization of minerals by diagenetic fluids (Grotzinger et al., 2005). The gradation in MgO and SO₃ abundances with depth in Endurance and Victoria craters has generally been inferred to be a diagenetic process as well, although it has hitherto been attributed to removal of Mg-sulfates at depth (Clark et al., 2005; Niles and Michalski, 2009; Hurowitz and Fischer, 2014; McCollom, 2018; McCollom and Hynek, 2021) or to deep weathering of the sediments by meteoritic water (Amundson et al., 2008; Amundson, 2018). There has been considerably less study of diagenetic impacts on the Grasberg formation; however, the unit contains numerous post-depositional gypsum veins (Mittlefehldt et al., 2018) and there is geochemical evidence for diagenetic mobilization of Mn (Ming et al., 2015; McCollom and Hynek, 2021).

It has been proposed that the diagenetic features found in the Burns sandstones may be attributable to two or more generations of groundwater infiltration (McLennan et al., 2005). Hydrologic models suggest that Meridiani Planum was a locus for groundwater upwelling from large-scale crustal aquifers on Mars (Andrews-Hanna et al., 2007, 2010; Andrews-Hanna and Lewis, 2011), and Meridiani is also proposed to have been an area that received high amounts of snowmelt on early Mars (Kite et al., 2013). Consequently, fluids could have infiltrated the Burns sediments from both above and below at various times during its early history.

The scenario proposed here does not appear to be incompatible with any of the diagenetic features or processes inferred by previous studies. The main difference in diagenetic processes proposed here is that MgO and SO_3 are inferred to be added to the Burns sediments during diagenesis. Presumably, this would have involved evaporation of fluid during one of the episodes of groundwater infiltration, leaving behind MgO and SO_3 . Alternatively, freezing of Mg-rich groundwater could also lead to precipitation of Mg-sulfates and other minerals (e.g., Marion et al., 2008).

Given the high solubility of Mg-sulfate minerals, sulfate-bearing fluids migrating through martian aquifers can be expected to accumulate relatively high concentrations of Mg. While it is possible that the fluids also transported and deposited some small amounts of Fe and Ca into the Burns rocks along with Mg, the geochemical data do not allow for significant net addition or removal of these elements from the formation as a whole (Figs. 5 and 7; McCollom, 2018). Furthermore, the data strongly indicate that many elements, including Si, Al, Na, K, and Cr were not mobilized to any discernible degree during diagenesis, and therefore were not added to the sediments during the inferred enrichment in Mg. More detailed geochemical modeling may allow further constraints to be placed on the composition of the evaporating fluid and its source.

One thing that can perhaps be inferred at this time about the fluid that added the MgO and SO₃ to the Burns deposits is that it was more likely to come from upwelling groundwater rather than from precipitation at the ground surface. Fluids infiltrating the sand deposits from above (for example, through melting of snow deposits; Kite et al., 2013) would be expected to initially contain very little or no Mg, and would leach Mg from the rocks as they percolated downwards until they became saturated with respect to Mg-sulfate minerals. This would produce a trend where the deposits had lower MgO abundance towards the top and increasing MgO with depth, opposite to the trend observed in the Burns rocks (Fig. 5a). Still, this possibility may warrant further study since the Mg-depleted deposits produced by downward-percolating fluids could have been removed from the top of the unit since erososion of at least a meter of the Burns formation is indicated by the lag deposits of hematite accumulated at the surface (Squyres et al., 2004).

It is possible to make an estimate of the minimal amount of evaporating fluid that would be required to account for the inferred diagenetic enrichment in Mg. At near freezing temperatures, the stable form of Mg-sulfate would be epsomite (MgSO₄ • 7H₂O), which has a solubility product (K_{sp}) at low temperatures (0-25°C) equal to ~3 (Steiger et al., 2011). Assuming an activity of water equal to 0.9 and neglecting activity coefficients for dissolved Mg and sulfate, the K_{sp} can be approximated as:

$$K_{\rm sp} \approx \left[{\rm Mg}^{2+} \right] \left[{
m SO}_4^{2-} \right] \left({0.9} \right)^7 \approx 3 \left({{
m mole}\over {
m kg}} \right)^2.$$
 (2)

If we further assume that Mg and SO_4 were present in the solution in the same proportions as they precipitate in the diagenetic model, then $[SO_4^{2^-}] = 1.55[Mg^{2^+}]$ and Eq. 2 reduces to $[Mg^{2^+}]^2 - 4.04 \text{ (mole/kg)}^2$ or $[Mg^{2^+}] - 2.0 \text{ M}$. Addition of approximately 32-72 g Mg per kg rock would be needed to account for enrichment of the Burns rocks relative to the Grasberg, corresponding to 0.8-1.8 moles Mg (see Supplemental Dataset1).

Thus, evaporation of less than 1 kg of groundwater saturated with respect to epsomite could account for the required enrichment of Mg in each kg of Burns rocks. If the Burns formation was originally 20 m thick and has a density of 2,500 kg/m³, this would correspond to evaporation of an equivalent water column of <50 m. This figure is much smaller than the amount of groundwater upwelling at Meridiani predicted by hydrologic models (2.5-17 km; Andrews-Hanna et al., 2007). Groundwater flow models that include geochemical and mineralogical constraints have called into question the feasibility of the large fluid fluxes predicted by the hydrologic models (Kite and Melwani Daswani, 2019), but could perhaps be compatible with the much smaller fluxes required to support the diagenetic model proposed here.

It has been noted many times that the presence of natrojarosite in the Burns rocks inferred from Mössbauer spectroscopy requires acidic conditions (e.g., Klingelhöfer et al., 2004; Elwood Madden et al., 2004; note that this mineral is typically referred to in the literature as "jarosite," which strictly speaking refers only to the K-rich endmember, but in actuality the mineral at Meridiani is probably an Al-bearing natrojarosite; Morris et al., 2006; McCollom et al., 2014). Groundwater migrating through martian crust is not expected to be acidic, since any source of acidity in the fluid would be rapidly buffered by fluid-rock interactions in the aquifer. However, the near-surface fluids could have become acidified through oxidation of ferrous Fe-bearing components as proposed by Hurowitz et al. (2010). Alternatively, if the original airfall materials had undergone acid-sulfate alteration at the source location, natrojarosite could have already been present when the fine-grained sediments were initially deposited at Meridiani Planum and then survived through subsequent diagenesis. The rapid decomposition of minerals from the alunite-jarosite group in laboratory experiments has led to suggestions that the natrojarosite in the Burns rocks would have rapidly decomposed if exposed to aqueous fluids for any substantial period of time after their formation (e.g., Elwood Madden et al., 2004, 2009). However, the persistence of minerals from this group in porous sandstones for millions of years suggests that they may be much more stable in natural settings than generally thought (e.g., Potter-McIntyre and McCollom, 2018).

More study will be required to evaluate the timing of the proposed MgO and SO_3 enrichment relative to other diagenetic processes. Sedimentary features in the Burns formation indicate that the sediments may have been saturated with water during some intervals while they were being deposited, at least in the lower parts of the formation (Grotzinger et al., 2005, 2006). Evaporation of fluids during these intervals could have added MgO and SO_3 at an early stage.
Alternatively, the enrichment may not have occurred until a much later stage, more-or-less simultaneous with other diagenetic features such as precipitation of isopachous cements and creation of the tabular-shaped voids. One intriguing possibility is the that the isopachous cements, whose precipitation evidently post-dated the formation of the hematite spherules (McLennan et al., 2005), might represent Mg-sulfate minerals precipitated from late-stage evaporation or freezing of infiltrating groundwater.

6. Discussion

6.1. Origin of the Burns formation

The recent recognition that the chemical compositions of the Burns and Grasberg formations are nearly identical is a strong indication that the origins of the two formations are closely linked (McCollom and Hynek, 2021). The alternative possibility that these two formations had entirely independent sediment sources which just happened to have the same chemical composition and yet were deposited immediately adjacent to one another would be a rather remarkable coincidence, and stretches credibility. Therefore, any proposed scenario for the origin of the Burns formation must now account for its relationship to the Grasberg formation.

The new scenario proposed here for the origin of the Burns sandstones accounts for all of the most salient features of the rocks while invoking only a known sediment source and processes that are recognized to be widespread across Mars. Moreover, it offers an explanation for the close similarity of its chemical composition to the Grasberg formation, which would be problematic to explain in the context of other proposed scenarios for the Burns rocks. The new scenario offers a simpler pathway to explain the principal observations of the Burns rocks and requires fewer assumptions than other proposed scenarios, and we argue that it warrants further investigation and testing against other proposed alternatives. If valid, the proposed diagenetic scenario would have substantial implications for the origin of sedimentary rocks on Meridiani Planum and across Mars, for interpretations of the widespread sulfate-rich deposits on the planet, and for surface environmental conditions on early Mars. The scenario would also provide new insights into diagenetic processes in martian sediments that may be particularly relevant as the Curiosity rover approaches rocks on Mount Sharp that are enriched in the Mg-sulfate mineral kieserite (Milliken et al., 2010; Sheppard et al., 2020; Rapin et al., 2021).

While our description of the proposed scenario refers to "Grasberg-like" materials as a precursor to the Burns formation, it is possible that the Grasberg formation itself may be the last vestiges of the materials that eroded to become the Burns formation. If this is the case, then the origins and geologic histories of the two units would be even more closely linked, which would directly contradict previous proposals that the two formations are separate units with distinctly different origins (Crumpler et al., 2015; Mittlefelhdt et al., 2018; Bouchard and Jolliff, 2018). Moreover, although Mittlefelhdt et al. (2021) suggests that the stratigraphic status of the Grasberg formation is uncertain, the scenario proposed here would connect the two units stratigraphically and temporally, with the Grasberg being emplaced immediately below and preceding deposition of the Burns sands. In this respect, the proposed scenario is consistent with the stratigraphic relationships inferred by Crumpler et al. (2015; Fig. 3).

The diagenetic scenario also implies that the original source of sediments for both units were airfall deposits, likely volcanic ash. If, so, these deposits could be related to other ashfall deposits identified across the equatorial regions of Mars as first proposed by Hynek et al. (2003). That work showed that the voluminous Medusae Fossae Formation on the opposite side of the planet from Meridiani Planum was likely derived from volcanic airfall from Tharsis. Similar layered deposits west of Meridiani thicken as they approach the Tharsis complex, implying a possible similar origin. Alternatively, Michalski and Bleacher (2013) argued for past regional supervolcano eruptions as a possible source for the widespread layered materials stretching from Meridiani Planum to Gale crater.

Fracture-filling deposits in the rocks that immediately underly the Grasberg and Burns formations may provide some supporting evidence for the inferred diagenetic alteration. During inspection of rocks from the Shoemaker formation (which lies directly beneath the Grasberg rocks on the rim of Endeavour crater; Fig. 3), Opportunity's wheels fortuitously uncovered two rocks, named Pinnacle Island and Stuart Island, which have white- and red-toned mineral deposits coating fracture surfaces (Fig. 12). These deposits were subsequently found to be enriched in Mg, Ni, SO₃, Mn, and P (Arvidson et al., 2016), the very same set of elements that are inferred to have been mobilized during diagenesis of the Burns and Grasberg formations. Consequently, these two rocks may record the groundwaters that led to diagenesis of the overlying rocks, and provide further support for the inferred mobilization of this suite of elements.



One question that naturally arises from the proposed scenario is why the Burns rocks became enriched in MgO and SO_3 while the Grasberg rocks did not. A likely explanation for this is that the finer-grained Grasberg rocks would have had much lower porosity and permeability than the sands that compose the Burns formation. This would provide much less opportunity for evaporating fluids to precipitate MgO and SO₃. Of course, this would not preclude localized

enrichments along fracture surfaces in the Grasberg formation similar to those observed in the Pinnacle Island and Stuart Islands samples (Fig. 12), but these would have been very difficult for the rover to detect.

6.2. Implications for other diagenetic processes and sulfur inputs

The scenario proposed here may also provide some new insights into the origin of other enigmatic diagenetic features of the Burns rocks. For instance, many of the Burns rocks were observed to contain tabular-shaped voids (e.g., Fig. 13a). The shape of the voids suggests dissolution of preexisting minerals during diagenesis (McClennan et al., 2005), but the identity of the dissolved minerals and timing of their dissolution remain uncertain. One possible explanation for these voids that would be consistent with the scenario proposed here is that they represent dissolution of gypsum crystals incorporated into the sands that became the Burns formation. The Grasberg formation contains widespread gypsum veins, particularly in the lower unit (Figs. 3g and 13b; Mittlefehldt et al., 2018). If the friable, fine-grained precursor materials that are inferred to have eroded into the Burns sediments contained similar gypsum veins, crystals from these veins may have been incorporated into the sands that became the Burns formation. Subsequent dissolution of the gypsum crystals during diagenesis would then leave behind the tabular-shaped voids, which have shapes that closely resemble gypsum crystals.



The chemical compositions of

the Burns rocks may provide some support for this possibility. While there is no evidence for significant net addition of Ca to the Burns formation as a whole, the abundances of CaO in a subset of the Burns rocks display a possible correlation with SO_3 that could be consistent with dissolution and local reprecipitation of Ca-sulfate minerals (Fig. 13c). Dissolution and reprecipitation of Ca-sulfate minerals could thus explain both the tabular shaped voids and the scatter of CaO data around the expected trend for diagenetic addition of MgO and SO_3

(Fig. 13c). Further study is required to determine whether the chemical conditions needed to facilitate this mobilization of CaO could be compatible with other diagenetic features.

The proposed scenario might also provide new insights into the ongoing enigma of the origin of the hematite spherules that are characteristic of the Burns rocks. Over the years, a number of different hypotheses and analogs have been proposed to explain the origin of the spherules (e.g., Catling et al., 2003; Morris et al., 2005; Glotch et al., 2006a; Golden et al., 2008; Sefton-Nash and Catling, 2008; Bowen et al., 2008; Madden et al., 2010; Potter et al., 2011; Sexton et al., 2017). To date, however, there is no consensus over how the spherules formed and it remains a matter of considerable debate. The absence of hematite spherules in the Grasberg rocks despite having nearly the same initial chemical composition as the Burns rocks and exposure to similar diagenetic conditions should provide new constraints on the conditions that promoted spherule formation. For instance, the absence of spherules from the Grasberg formation might indicate that the greater pore space present in the Burns sandstones was critical for their formation. The chemical and mineralogical changes induced by the fluids that enriched the rocks in MgO and SO_3 might also have played a role in creating the environment for spherule formation.

The proposed scenario might also help resolve the conundrum regarding the magnitude of S inputs required to explain the sulfur-bearing deposits on Meridiani Planum. The Burns and Grasberg formations represent the uppermost strata of a section of layered etched terrains that is several hundred meters thick and covers an area >4 ×10⁵ km² (Hynek and Phillips, 2008; Hynek and Di Achille, 2017). Spectral analyses indicate that kieserite and other hydrated sulfates are present in many of the underlying units, indicating a widespread enrichment in SO₃ (e.g., Hynek and Phillips, 2008; Wiseman et al., 2015; Flauhaut et al., 2015). As discussed by Hynek et al. (2019), all currently proposed mechanisms for transport of SO₃ into the deposits at Meridiani have great difficulty in accounting for the enormous amount of SO₃ that would need to be added to the deposits in order to attain levels similar to that of the Burns formation (5×10^{16} kg SO₃ in total).

Two aspects of the proposed scenario may be particularly relevant to this issue. First, in the scenario proposed here, a substantial fraction of SO_3 in the Burns rocks was already present in the airfall deposits when they were emplaced at Meridiani. If this pertains to the deeper deposits as well, it would significantly reduce the amount of SO_3 that would need to be imported by fluid transport or other means. Second, in the proposed scenario, it may only be the upper layers of the deposits (i.e., the Burns sandstones) that are further enriched in SO_3 during diagenesis, requiring addition of only modest amounts of SO_3 . If the bulk of the thick layered deposits at Meridiani Planum have SO_3 contents similar to the Grasberg while only some intervals reach the higher levels observed in the Burns rocks, the amount of sulfur that would need to be transported into Meridiani would be substantially reduced. At present, it is uncertain whether the lower

amounts of SO₃ present in the Grasberg (average ~9.2 wt%) is sufficient to account for the hydrated sulfate deposits detected by remote observations, but this possibility may be worth additional study.

6.3. Relationship to previously proposed sedimentary-evaporite scenario

The scenario proposed here for the origin of the Burns sandstones has many components in common with the previously proposed sedimentary-evaporite scenario (Squyres et al., 2004, 2005; Grotzinger et al., 2005; McLennan et al., 2005). However, it also has many distinctly different features, and these would have distinctly different implications for the geologic history of the Meridiani region and for martian sedimentary rocks in general. For the sake of clarity, this section provides a brief overview of the principal similarities and differences between these two scenarios (Table 1).

One set of key differences relates to the nature and origin of the sediments that comprise the Burns rocks. Both scenarios invoke erosion of preexisting materials into sulfate-cemented siliciclastic sand-grains as the source of the original sediments for the Burns sandstones. In the sedimentary-evaporite scenario, however, these sand grains formed by erosion of evaporites on the margins play lakes (Grotzinger et al., 2005; McLennan et al., 2005), whereas in the scenario proposed here the sands formed through erosion of a Grasberg-like precursor that had already been deposited on Meridiani Planum. The siliciclastic component in the sedimentary-evaporite scenario is thought to be derived from a chemically basaltic precursor depleted by ~55% in Σ (Fe+Mg+Ca) and containing little or no S (Fig. 8; Squyres et al., 2006). The siliciclastic component in the proposed diagenetic scenario is an airfall deposit that is also ultimately derived from a basaltic precursor, but already contained a substantial amount of S and was possibly depleted in Mg by the time it arrived at Meridiani (Fig. 11). The sedimentary-evaporite scenario presumes that the entire sulfate component contained in the Burns sediments was added to the siliciclastic component on the margins of playa lakes prior to erosion into sand-sized grains and redeposition, with a possible subsequent loss of MgO and SO_3 from the sediments at depth during diagenesis (Squyres et al., 2004, 2006; Clark et al., 2005). In contrast, in the scenario proposed here, more than half of the current SO_3 contents of the rocks is only added during diagenesis of the sands following deposition, along with MgO. Furthermore, while long-lived playa lakes and standing surface water are a major component of the sedimentary-evaporite scenario, the diagenetic scenario proposed here invokes little involvement surface water and far less contribution of water overall.

Another key difference is that the proposed diagenetic scenario closely links the depositional and early diagenetic histories of the Burns and Grasberg formations, and accounts for both the nearly identical chemical compositions of these units and their spatial relationship. The Grasberg rocks were not encountered by Opportunity until long after the sedimentary-evaporite scenario was initially proposed, and the close similarity in chemical composition between the two units was only recently recognized. Consequently, as of yet, there has been

no discussion in the literature of any possible relationship between the Burns and Grasberg formations by advocates of the sedimentary-evaporite scenario. However, it would appear to be very difficult to account for any connection between these units in the context of the sedimentary-evaporite scenario. That is, the chemical composition of the Grasberg rocks would be problematic to reproduce by the proposed playa lake evaporite model (Figs. 8 and 9), and the Grasberg rocks lack the bedding structures and other sedimentary features that have always been a critical component of the sedimentary-evaporite scenario (e.g., Grotzinger et al., 2005, 2006). Thus, it is hard to imagine how the playa lake evaporite hypothesis could simultaneously account for the characteristics of both units or explain their closely similar chemical compositions. Instead, one would have to imagine that the Grasberg is an unrelated unit formed by a completely different process that coincidentally has a similar composition, which would seem to be a much less parsimonious explanation than inferring a genetic relationship between the Burns and Grasberg formations.

Feature/process	Sedimentary-evaporite scenario (Squyres et al., 2004, 2006; Grotzinger et al., 2005; McLennan et al., 2005; Clark et al., 2005)	Diagenetic scenario (this study)
Source and composition of Burns sands Origin of initial	Sulfate-cemented siliciclastic sand-sized grains eroded from margin of playa lake Unspecified	Sulfate-cemented siliciclastic sand-sized grains eroded from Grasberg-like precursor Airfall deposit
siliciclastic component Chemical composition of initial siliciclastic component	Basalt-derived material with up to 55% of total (Fe + Mg + Ca) removed and containing little or no S	Similar to Grasberg and to Irvine-class basalts; enriched in several wt% SO_3 and possibly depleted in MgO by acid-sulfate alteration prior to transport to Meridiani
Sulfur source	Evaporation of sulfate-bearing groundwater in playa lake environments	Part initial sediments, part in situ evaporation of sulfate-bearing groundwater

Table 1. Summary of key differences and similarities in the diagenetic scenario proposed here and the previously proposed sedimentary-evaporite scenario.

Feature/process	Sedimentary-evaporite scenario (Squyres et al., 2004, 2006; Grotzinger et al., 2005; McLennan et al., 2005; Clark et al., 2005)	Diagenetic scenario (this study)
Timing of sulfur addition	All sulfur added prior to sand formation and deposition at current site	Partly at site of initial siliciclastic origin, partly during diagenesis
Cation transport into Burns deposits	Mg, Fe, and Ca added by evaporating groundwater prior to sand formation; Mg lost from deeper samples during diagenesis	Mg added to entire Burns formation during diagenesis; others unchanged or only redistributed locally
Sediment transport/deposition Major diagenetic processes	Mostly aeolian, some alluvial Recrystallization, hematite spherule formation, dissolution of minerals, development of secondary porosity, cementation, loss of MgO and SO_3 with depth	Mostly aeolian, some alluvial Recrystallization, hematite spherule formation, dissolution of minerals, development of secondary porosity, cementation, gain of MgO and SO ₃ , localized redistribution of cations
Relationship to Grasberg formation	Not defined	Both units share closely related sediment sources and similar early diagenetic histories
Implications for surface environmental conditions	Long-term clement conditions at surface allowing prolonged presence of playa lakes	No requirement for long-term standing water at surface

6.4. Some consideration of broader implications

Further study will be required to fully appreciate the potential implications that the proposed diagenetic scenario would have for the geologic history of the Meridiani region and for sulfate-bearing sedimentary deposits across Mars. However, some initial thoughts on these topics are worth mentioning briefly here. First, the proposed diagenetic scenario may suggest a more prominent role for diagenesis in the origin of the sulfate-rich layered deposits that are widespread on the surface of Mars. Remote sensing studies have detected layered deposits containing sulfate minerals at numerous locations across the planet (Gendrin et al., 2005; Murchie et al., 2009a; Ehlmann and Edwards, 2014). Many of these deposits appear to contain the Mg-sulfate mineral kieserite, which in some instances is associated with grey hematite (e.g., Chojnacki and Hynek, 2008; Murchie et al., 2009b; Bishop et al., 2009; Wiseman et al., 2010; Flahaut et al., 2010; Weitz et al., 2012). The proposed diagenetic scenario suggests that enrichment of preexisting sedimentary deposits in Mg and sulfate during diagenesis could have contributed to many of these occurrences, and should be considered as a potential alternative to other sulfate sources that include surface evaporite deposits and acid-sulfate alteration of sedimentary materials or their precursors. Indeed, if the diagenetic scenario is valid, it may indicate that surficial evaporities contribute far less to the sulfate-rich bedrock exposures than previously thought, since the presumed playa lake origin of the Burns formation sediments was a major motivation for many such interpretations. The possible contribution of diagenesis to Mg and sulfate enrichments may have immediate relevance as the Curiosity rover approaches the transition from clay-rich deposits to the kieserite-bearing layers of Mount Sharp in Gale crater (Milliken et al., 2010; Sheppard et al., 2020).

Second, if the sediments that became the Burns formation were initially emplaced on Meridiani as airfall deposits as suggested by the diagenetic scenario, then it would reinforce other geologic evidence that pyroclastic ash deposits are widespread on the surface of Mars and may be responsible for many large-scale layered units (e.g., Scott and Tanaka, 1982; Hynek et al., 2002, 2003; Le Deit et al., 2010; Kerber et al., 2011, 2012; Michalski and Bleacher, 2013; Ojha and Lewis, 2018). Moreover, the diagenetic scenario may illustrate one pathway by which materials originally deposited by airfall became transformed and sulfate-enriched, which could aid in the interpretation of other sulfate-bearing layered deposits that might have had a similar origin (e.g., Chojnacki and Hynek, 2008; Le Deit et al., 2010; Fueten et al., 2011; Weitz et al., 2011, 2012). As proposed for the Burns formation, reworking and diagenetic alteration could transform pyroclastic deposits in ways that might obscure the original nature of the source materials.

Lastly, the proposed diagenetic scenario would have very different implications for environmental conditions on the surface during emplacement of the Burns formation than the sedimentary-evaporite scenario. The sedimentary-evaporite scenario invokes formation of the Burns precursor sands by evaporating fluids on the margins of playa lakes, as well as the presence of surficial fluids and shallow groundwater water during deposition of the sands (e.g., Squyres et al., 2004, 2006; Grotzinger et al., 2005, 2006). These processes imply long-term stability of liquid water on the surface of Meridiani Planum, which in turn implies clement conditions that would allow the liquid water to persist for prolonged periods at the surface. Furthermore, these surficial aqueous environments would potentially be conducive to the existence of martian life and preservation of biosignatures (Knoll et al., 2005). Conversely, the alternative scenario proposed here invokes a much more limited role for water during formation of the Burns sandstones and requires no more than occasional intervals of liquid water at the surface in order to explain the major features of the rocks. This scenario is consistent with a lack of fluvial features within the thick sequence of layered sulfate-bearing materials, but substantial large valley network systems buried by the margins of these deposits (e.g., Hynek and Phillips, 2008; Hynek and Di Achille, 2017). The proposed diagenetic scenario would allow for surface conditions that were substantially drier and cooler overall than those implied by the sedimentary-evaporite scenario. Needless to say, the diagenetic scenario would also suggest environmental conditions that were far less favorable for life, at least at the surface.

7. Conclusions

Quantitative mass-balance models demonstrate that the chemical composition of the Burns formation sandstones can be closely replicated by addition of MgO and SO₃ to Grasberg-like fine-grained sediments. This finding, combined with their stratigraphic relationship, strongly indicates that the Burns and Grasberg formations come from closely linked sediment sources and have similar initial depositional histories. As a consequence, any scenario for the origin of the Burns sandstones must be able to explain its relationship to the Grasberg rocks.

Motivated by the model results, a new scenario is proposed for the origin of the Burns rocks. In this new scenario, the Burns sediments are initially emplaced on Meridiani as a find-grained airfall deposit derived from a source closely related to that of the Grasberg (or maybe even the same source). Following moderate induration (possibly involving recrystallization of sulfate salts), the precursor materials are eroded into sand size particles, transported by wind and water, and redeposited at their present location. Infiltration by groundwater then diagenetically alters and cements the sands. Evaporation of groundwater at some stage of diagenesis leaves behind MgO and SO₃ in the Burns sediments, resulting in the current composition of the rocks.

This newly proposed scenario provides a plausible explanation for all of the most salient features of the Burns rocks, including their overall chemical composition, the variation in chemical composition with depth, the bedding features that are ubiquitous in the deposits, and diagenetic alteration. In addition, the proposed scenario provides an explanation for the nearly identical composition and stratigraphic relationship of the Burns formation to the Grasberg rocks. Moreover, the newly proposed scenario invokes only a known and well-characterized source for the sands (i.e., erosion of Grasberg-like rocks) as well as depositional and diagenetic processes that have been widely documented to occur in other martian settings. Collectively, the new scenario provides a simpler pathway that requires fewer assumptions than other scenarios previously proposed to account for the same features in the Burns rocks, and warrants further consideration and study.

Data Availability statement

All data used in this study are available from the Planetary Data System website (https://pds.nasa.gov/) or in the cited references. The data are compiled in the spreadsheet provided as Supplemental Dataset1 which also includes all diagrams and models presented in this report.

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