Carbon sequestration on Mars

Christopher S. Edwards* and Bethany L. Ehlmann
1Jet Propulsion Laboratory/California Institute of Technology, Pasadena, California 91109, USA
2California Institute of Technology, 1200 E. California Boulevard, MC 150-21, Pasadena, California 91125, USA

ABSTRACT

On Earth, carbon sequestration in geologic units plays an important role in the carbon cycle, scrubbing CO₂ from the atmosphere for long-term storage. While carbonate is identified in low abundances within the dust and soils of Mars, at <1 wt% in select meteorites, and in limited outcrops, no massive carbonate rock reservoir on Mars has been identified to date. Here, we investigate the largest exposed carbonate-bearing rock unit, the Nili Fossae plains, combining spectral, thermophysical, and morphological analyses to evaluate the timing and carbon sequestration potential of rocks on Mars. We find that the olivine-enriched (~20%–25%) basalts have been altered, by low-temperature in situ carbonation processes, to at most ~20% Fe-Mg carbonate, thus limiting carbon sequestration in the Nili Fossae region to ~0.25–12 mbar of CO₂ during the late Noachian–early Hesperian, before or concurrent with valley network formation. While this is large compared to modern-day CO₂ reservoirs, the lack of additional, comparably sized post–late Noachian carbonate-bearing deposits on Mars indicates ineffective carbon sequestration in rock units over the past ~3.7 b.y. This implies a thin atmosphere (<500 mbar) during valley network formation, extensive post-Noachian atmospheric loss to space, or diffuse, deep sequestration by a yet-to-be understood process. In stark contrast to Earth’s biologically mediated crust:atmosphere carbon reservoir ratio of ~10⁹ to ~10¹⁰, Mars’ ratio is a mere ~10⁴ to ~10⁵, even if buried pre-Noachian crust holds multiple bars.

INTRODUCTION

Martian carbonates have been observed telescopically from orbit (e.g., Bandfield et al., 2003; Ehlmann et al., 2008; Michalski and Niles, 2010), in situ (e.g., Boynton et al., 2009; Morris et al., 2010), and in Martian meteorites; however, a long-postulated geologic reservoir that accounts for proposed thinning of a multi-bar early Mars atmosphere by CO₂ sequestration (Booth and Kieffer, 1978; Pollack et al., 1987) has not yet been identified (Niles et al., 2013). One striking aspect of the Martian geologic record is the presence of valley networks and open-basin lakes last active around the Noachian-Hesperian boundary at ca. 3.5 Ga (Fassett and Head, 2008). If surface waters were supported by a thicker atmosphere (Hynek et al., 2010), hundreds of millibars of CO₂ would need to have been lost to space during the Hesperian–Amazonian, inconsistent with atmospheric loss models (e.g., Lammer et al., 2013). Was this late CO₂ sequestered in the Martian crust? We consider the role of diffuse and localized CO₂ sequestration and constrain the timing and implications for late Noachian atmospheric conditions via examination of the age and composition of the largest contiguous exposure of carbonate-bearing rock on Mars, the Nili Fossae carbonate plains (21.5°N, 78.5°E; Ehlmann et al., 2008). Morphological, spectral, and thermophysical data from the Thermal Emission Spectrometer (TES), Compact Reconnaissance Imaging Spectrometer for Mars (CRISM), Thermal Emission Imaging System (THEMIS), Context Imager (CTX), and High Resolution Imaging Science Experiment (HiRISE) are considered in the context of past atmospheric drawdown.

MINERAL MAPPING AND ABUNDANCES

At a scale of kilometers, we map two distinct TES spectral units using the carbonate decomposition product–carbonate index (Fig. 1; Table DR1 in the GSA Data Repository1; Glotch and Rogers, 2013). Basaltic terrains (TES C) have low carbonate (~10%), low olivine (~4%), and elevated feldspar/pyroxene abundances similar to those of Syrtis Major (Rogers and Christensen, 2007). In contrast, TESA&B spectra (TES² and TESP) have elevated Fe-Mg carbonate (~15%), ~20% olivine (~Fo₆₀₋₇₀; Hamilton and Christensen, 2005), and comparable pyroxene but substantially less feldspar. Carbonate is close to the detection limit for TES² and TES²², however, TESA%B spectral model fits (specifically the ~350 cm⁻¹ feature) are improved by the additional ~5% carbonate and are not well matched by increases in other mafic minerals with absorptions at these wavelengths.

Figure 1. A: Thermal Emission Spectrometer (TES) carbonate decomposition product–carbonate index (Glotch and Rogers, 2013) over a Context Imager (CTX) mosaic (6 m/pixel; 5° N, 78.5° E) highlights locations with carbonate. B: Thermal Emission Imaging System (THEMIS) thermal inertia (TI) data over a CTX mosaic, showing moderate TI units are correlated with olivine and carbonate-bearing bedrock units. C: TES spectral observations (OCK 3358) corresponding to locations in A. TES² is consistent with typical Syrtis Major compositions. TESA&B have increases in both olivine (~23%) and Fe-Mg carbonate (~15%) over TES². Abundances are detailed in Table DR1 and the end-member library in Table DR3 (see footnote 1).

*Current address: U.S. Geological Survey, Astrogeology Science Center, 2255 N. Gemini Road, Flagstaff, Arizona 86001, USA.
1GSA Data Repository item 2015291, detailed data processing methods, abundance tables, mineral libraries, and Figures DR1–DR3, is available online at www.geosociety.org/pubs/ft2015.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.
High-Si phases are elevated (~20%) in all TES spectra, likely evidence of the aqueous alteration prevalent in the region (Mangold et al., 2007, Rogers and Christensen, 2007). Carbonate content of ~5% is a minimum, as the TES footprints are a combination of carbonate- and non-carbonate-bearing materials observed at finer scales (CRISM, HiRISE; Figs. 2 and 3).

Five distinct CRISM spectral units are identified (Fig. 2), correlated with morphology (Fig. 3): (1) low-albedo, olivine-bearing basaltic bedrock; (2) olivine-enriched basaltic sands; (3) olivine-carbonate-bearing basaltic bedrock; (4) a basaltic capping unit; and (5) an Fe-Mg smectite-bearing Noachian basement (not investigated here; see Ehlmann et al., 2009; Mustard et al., 2009). Spectra from morphological units 1–3 have similar spectral shapes around ~1 µm (Fig. 2B), distinct from unit 4 and consistent with intermediate Fo and/or large-grain-size olivine.

Hapke modeling of single scattering albedo (SSA) spectra extracted from discrete ordinates radiative transfer–processed CRISM data (see the Data Repository) yields mineral abundances and grain sizes (Table DR2; Fig. 2). The carbonate-bearing unit (3) has ~15% (1 mm grain size) carbonate in an olivine-enriched (~25%, ~1 mm) basalt (~60%, ~1 mm), with minimal Fe-Mg smectite (<2%). Other olivine-bearing units (units 1–2) have ~20%–30% olivine and are coarse grained (~1 mm) with ~60% basalt and negligible carbonate. The basaltic cap unit (4) is distinct, composed mostly of a finer-grained (~400 µm) basaltic material with little olivine or smectite. A second modeling approach with scene-derived olivine bedrock SSA (unit 3) and lab-derived carbonate SSA indicates ~5% carbonate, using the observed depth of the 2.5 µm absorption (the most unique indicator of carbonate; Ehlmann et al., 2008) (Fig. DR1 in the Data Repository).

THEMIS band 7 band depth is correlated with the CRISM OLINDEX2 (olivine index). THEMIS ratio data show a downturn in bands 1/2 correlated with and coincident with locations where CRISM shows the strongest band depths at 2.3 and 2.5 µm (Fig. 4; Fig. DR2). Spectra of an olivine-carbonate mixture and of olivine are good matches for the ratio spectra extracted from spatially coherent THEMIS data (Fig. 4B).

MORPHOLOGY

Carbonate abundance is anti-correlated with the presence of the olivine-bearing sand cover (Fig. 2C). The carbonate-bearing unit is highly fractured and light toned with darker, fracture-filling materials (likely sand; Fig. 3B). The carbonate-poor olivine-bearing outcrops exhibit a rough and pitted texture and typically lie filling materials (likely sand; Fig. 3B). The carbonate-bearing unit is highly fractured and light toned with darker, fracture-filling materials (likely sand; Fig. 3B). The carbonate-poor olivine-bearing rock is morphologically distinct from the capping unit, which has a massive appearance (Fig. 3).

PHYSICAL PROPERTIES

Regional thermal inertia (TI) ranges from ~250 to 600 J m⁻² K⁻¹ s⁻¹/² (units hereafter SI), corresponding to grain sizes from fine regolith (~300 µm) to weakly consolidated and/or heavily altered bedrock (>1 mm), inconsistent with crystalline Martian volcanics (>1200 SI in THEMIS; Edwards et al., 2009). Surface materials (e.g., aeolian bedforms, dust) can reduce derived TI, but many clean exposures are observed at HiRISE scales.

The thermophysical and compositional characteristics show distinct groupings. The olivine- and carbonate-bearing materials typically have TI of ~400–500 SI (Fig. 2; Fig. DR3), and the...
that of THEMIS spectrum of carbonate-bearing rocks (Comanche and Algonquin classes, <550 SI) observed in the Columbia Hills (Fig. 1B; Ferguson et al., 2006b; Ruff et al., 2014) or highly fractured materials. The basaltic capping unit, while forming significant topographic highs, has the lowest TI (<300 SI). Its distinct composition, morphology, and thermophysical properties suggest that it may be an eroded ash deposit (e.g., Bandfield et al., 2013).

The olivine-enriched and olivine-carbonate-enriched units likely had the same original lithology, given their similar compositions (except for Mg-Fe carbonate), morphology, and TI. Their low TI suggests a clastic rock or pervasive fracturing at centimeter scale in a crystalline igneous rock. Given the fractures observed (advantageous for fluids to migrate more easily), mineral assemblages and abundances, we find that the likely scenario for the formation of the Nili Fossae carbonate plains is low-temperature, in situ carbonation (van Berk and Fu, 2011), akin to the Samal ophiolite in Oman (Kelemen and Matter, 2008), or in-place serpentinization reactions. Variability of fractures and/or pore space in the precursor rock or limited groundwater percolation may have produced the spatial variability of carbonate-bearing outcrops, leaving some regions largely unaltered.

Of critical importance is the timing of carbonation and atmospheric CO$_2$ sequestration in Nili Fossae and in other potential reservoirs. Sequestration in Nili Fossae must have occurred after emplacement of the olivine-rich precursor (syn- or post-Isidis formation, i.e., early/middle Noachian; Hamilton and Christensen, 2005; Mustard et al., 2009). The carbonate-bearing units are incised by valley networks and overlap by the Hesperian Syrtis Major unit, indicating carbonation prior to or contemporaneous with valley network formation. This important local timing constraint can be extended globally, as >50% of the Mars surface is composed of Noachian and Hesperian terrains of similar age to or younger than Isidis (Tanaka et al., 2014). The lack of additional late Noachian and younger carbonate-bearing units is not likely a sampling bias, as a host of other secondary minerals are observed (Ehlmann and Edwards, 2014).

CARBONATE ABUNDANCE, EXTENT, AND CO$_2$ SEQUESTRATION POTENTIAL

TES and CRISM locations with elevated carbonate spatially correlate, and quantitative modeling agrees on total carbonate (~5%–15%) and relative differences in carbonate abundance (~5%–15%). In the inverse model, the diagnostic 2.5 µm absorption is overmodeled (Fig. 2B), favoring the ~5% CRISM-derived carbonate abundance from forward modeling (Fig. DR1). Checkerboard mixing of olivine-basaltic sands at sub-CRISM pixel scales lowers the apparent carbonate abundance, though HiRISE 25 cm/pixel data suggest that >75% of the surface is clean. By coupling HiRISE to TES and/or CRISM abundances, our work indicates that ~20% carbonate is a likely maximum for Nili Fossae carbonate plains bedrock. The areal extent of the unit is constrained using only carbonate-bearing outcrop exposures (~6800 km$^2$) or the entire extent of the regional Nili Fossae olivine outcrops (300,000 km$^2$) that are variably buried by Syrtis lavas. Depth is constrained by (1) a 6-km-diameter impact crater excavating ~500 m below the carbonate (21.35°N, 78.80°E), (2) previous estimates for the thickness of the olivine-bearing unit (Mustard et al., 2009), and (3) the typical depth of in situ carbonate (<200 m; van Berk and Fu, 2011). Thus, the Nili Fossae carbonate plains unit likely sequestered ~0.25–12 mbars of atmospheric CO$_2$ (~4 x 10$^4$ mbar of CO$_2$ per km$^2$ of MgCO$_3$).

The CO$_2$ sequestered in the Nili Fossae is significant relative to the current ~6 mbar atmosphere and CO$_2$ within the south polar cap (5 mbar; Phillips et al., 2011) and that sequestered in the ubiquitous Martian dust (~1 mbar for ~5% abundance, ~1 m thick global layer of 40% porosity; Bandfield et al., 2003). However, it is small relative to the hundreds of millibars to bars of CO$_2$ suggested to sustain surface waters during late Noachian–early Hesperian valley network formation. If carbon sequestration occurred by carbonate mineralization and >500 mbar late Noachian atmosphere was removed, either post-Noachian carbonate formation is more volumetrically widespread but diffuse than has been observed in landed missions and meteorites, or >35 “hidden” Nili Fossae-scale post-Noachian carbonate-bearing rock deposits remain to be discovered.

While orbital remote sensing could miss small-scale deposits (e.g., Ruff et al., 2014), given the mineralogical discrimination and spatial coverage, it is unlikely that many significant reservoirs of Nili Fossae scale and age (or younger) have been overlooked. Remote sensing data cannot exclude pre- or early Noachian formation of carbonate-bearing rocks (e.g., Michalski and Niles, 2010; Niles et al., 2013, and references therein) as these are deeply buried, exposed over <10% of the surface (Tanaka et al., 2014), and tapped only infrequently by impact craters. However, if an pre- or early Noachian episode of carbon sequestration occurred, it pre-dates formation of Mars’ valley networks and hence cannot explain removal of a thick atmosphere that may have enabled precipitation at that time.
Destruction of carbonates by acid waters cannot resolve the paradox of the missing carbon reservoir because dissolution would release CO₂ back into the atmosphere, i.e., a recycling resulting in no net carbon sequestration. Post-Noachian deep-diffuse alteration could, however, be undetectable by remote sensing. For example, the nakhlites and meteorite ALH84001 contain trace carbonates. Martian missions investigating equatorial geologic units have found carbonates at <2% in rocks and soils (e.g., Leshin et al., 2013), and the Phoenix lander found soil carbonates at ~5% (Boynton et al., 2009). To sequester ~500 mbar of atmospheric CO₂, the crust would have to be altered at an average of 1 wt% to a depth of ~1 km. Sequestering carbon this deep in the crust is challenging: open hydrologic systems do not typically support alteration to great depths (hundreds of meters or less; van Boekel, 2012). Carbonate rocks exposed by meteor impact on Mars: Season of Geophysical Research, v. 114, E11001, doi:10.1029/2009JE003363.


Manuscript received 18 May 2015 Revised manuscript received 23 July 2015 Manuscript accepted 24 July 2015 Printed in USA

ACKNOWLEDGMENTS

We thank R.E. Arvidson for providing the CRISM DISORT processed image, A.D. Rogers for the Syrtis-type TES spectra, and S. Piqueux for helpful discussions. T.D. Glotch, P.D. Niles, and an anonymous reviewer provided helpful formal reviews. A Mars Exploration Program Future Landing Sites grant administered by the Jet Propulsion Laboratory provided partial support for Edwards and Ehlmann to conduct this analysis.
Carbon sequestration on Mars

Christopher S. Edwards and Bethany L. Ehlmann

*Geology* published online 21 August 2015; doi: 10.1130/G36983.1