

Crust-atmosphere coupling and carbon sequestration on palaeo-Mars

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Introduction:

The modern surface of Mars displays evidence for past liquid water flows (Figure 1), with mounds and polygons in the Chryse-Acidalia region possibly indicating large bodies of ancient standing liquid (Oehler and Allen, 2012). For liquid water to be stable at the planet's surface, temperatures of $>273.2\text{K}$ and a saturation water vapour pressure of $>6.1\text{ mbar}$ are required (Martínez and Renno, 2013). To achieve such conditions, atmospheric pressures $>1\text{ bar CO}_2$ have been hypothesised during the late Noachian/early Hesperian period (i.e. $\sim 1.4\text{-}3.0\text{ Ga}$ e.g. Fernández-Remolar *et al.* 2011). Mars' currently thin (6 mbar) atmosphere poses the question of the fate of the hypothesised multi-bar CO_2 atmosphere. Estimates for $\sim 270\text{ mbar}$ lost to space (Niles and Michalski, 2011), with $\sim 5\text{ mbar}$ at the poles (Phillips *et al.* 2011), leaves a minimum 750 mbar unaccounted for.

The nakhlite martian meteorites display

clear evidence of low water to rock (W/R) ratio isochemical silicate mineral carbonation (Tomkinson *et al.* 2013). Such carbonation processes can also be observed in basic to ultra-basic terrestrial rock exposures, such as the Samail peridotite (Oman; Kelemen *et al.* 2011) and Del Puerto ophiolites (Californian; Blank *et al.* 2009). The present research project aims to compare martian meteorite petrology and geochemistry with basic to ultra-basic carbonated terrestrial ophiolite analogues, conduct carbonation experiments on terrestrial Mars analogue samples and construct a crust-atmosphere coupling model. By analysing carbon sequestration processes at differing scales and environments, carbonation rates and total silicate carbonation volumes under palaeo-martian atmospheric and mineralogical conditions can be estimated.

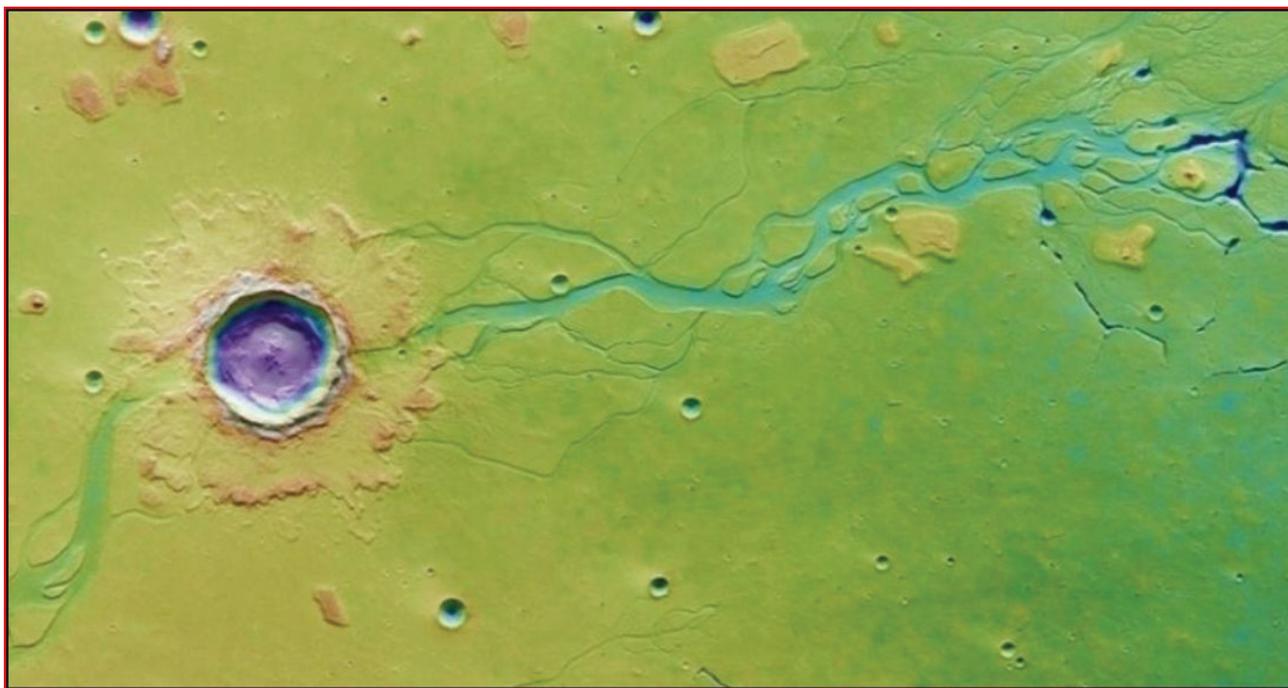


Figure 1. Impact crater in the Hephaestus Fossae with morphological evidence for liquid flow. Image courtesy of the European Space Agency (ESA) from their Mars Express Orbiter.

Background:

Hydration and carbonation of silicate rocks is an important negative feedback process in the terrestrial carbon cycle. Significant atmospheric CO₂ removal via silicate weathering partly balances the volcanic CO₂ output. Peridotite contains >40% olivine, which can hydrate to form quartz, magnesite and serpentine via reactions 1 to 3 of table 1. These reactions may be followed by carbon sequestration via reactions 4 to 7 of table 1.

Basic to ultra-basic rocks also contain abundant pyroxenes which can hydrate and carbonate via reaction 8 of table 1, usually in two discreet steps through reactions 9 and 10 of table 1. These reactions form highly alkaline travertine springs (pH>11), which have been observed in terrestrial ophiolites worldwide.

Carbonation is exothermic, with the total fully carbonated solid products possessing 44% greater mass than the reactants (Kelemen *et al.* 2011). This causes cracking (Kelemen and Hirth, 2012), exposing fresh reactant surfaces, although this can be offset by expansion causing reduced porosity (Alt and Teagle, 1999). The raised temperatures increase reaction rates, and a positive feedback mechanism of sustained carbonation can develop.

The crust of Mars is composed of similarly basic to ultra-basic minerals, mostly basalt on the surface (Taylor *et al.* 2010). By investigating carbonated terrestrial analogues a deeper understanding of Martian crust-atmosphere dynamics can be achieved, possibly resolving currently unexplained martian anomalies, as well as accounting for the loss of an early >1bar CO₂ atmosphere. For example, the recent crater wall slumps observed by the Mars Global Surveyor (Figure 2) could potentially be explained as alkaline spring extrusions from subsurface carbonation processes.

Table 1. Hydration and carbonation reactions for olivine and pyroxene. Based on Kelemen *et al.* (2011).

Olivine hydration reactions

- 1.) $4\text{Mg}_2\text{SiO}_4(\text{Mg-olivine}) + 4\text{H}_2\text{O} + 2\text{CO}_2 = 2\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4(\text{serpentine}) + 2\text{MgCO}_3(\text{magnesite})$
- 2.) $4\text{Mg}_2\text{SiO}_4 + \text{H}_2\text{O} + 5\text{CO}_2 = \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2(\text{talca}) + 5\text{MgCO}_3$
- 3.) $4\text{Mg}_2\text{SiO}_4 + 8\text{CO}_2 = 4\text{SiO}_2(\text{quartz}) + 8\text{MgCO}_3$

Olivine carbonation reactions

- 4.) $4\text{Mg}_2\text{SiO}_4 + 6\text{H}_2\text{O} = 2\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{Mg}(\text{OH})_2(\text{brucite}),$
- 5.) Products of 4.) + $2\text{CO}_2 = 2\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{MgCO}_3 + 2\text{H}_2\text{O}$
- 6.) Products of 5.) + $3\text{CO}_2 = \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + 5\text{MgCO}_3 + 5\text{H}_2\text{O}$
- 7.) Products of 6.) + $3\text{CO}_2 = 4\text{SiO}_2 + 8\text{MgCO}_3 + 6\text{H}_2\text{O}$

Pyroxene (with olivine) hydration and carbonation reactions

- 8.) $4\text{Mg}_2\text{SiO}_4 + \text{CaMgSi}_2\text{O}_6 + 6\text{H}_2\text{O} + \text{CO}_2 = 3\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \text{CaCO}_3(\text{calcite})$
- 9.) $4\text{Mg}_2\text{SiO}_4 + \text{CaMgSi}_2\text{O}_6 + 7\text{H}_2\text{O} = 3\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Ca}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$ (subsurface reaction)
- 10.) $\text{Ca}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq}) + \text{CO}_2(\text{aq or gas}) = \text{CaCO}_3 + \text{H}_2\text{O}$ (surface reaction)

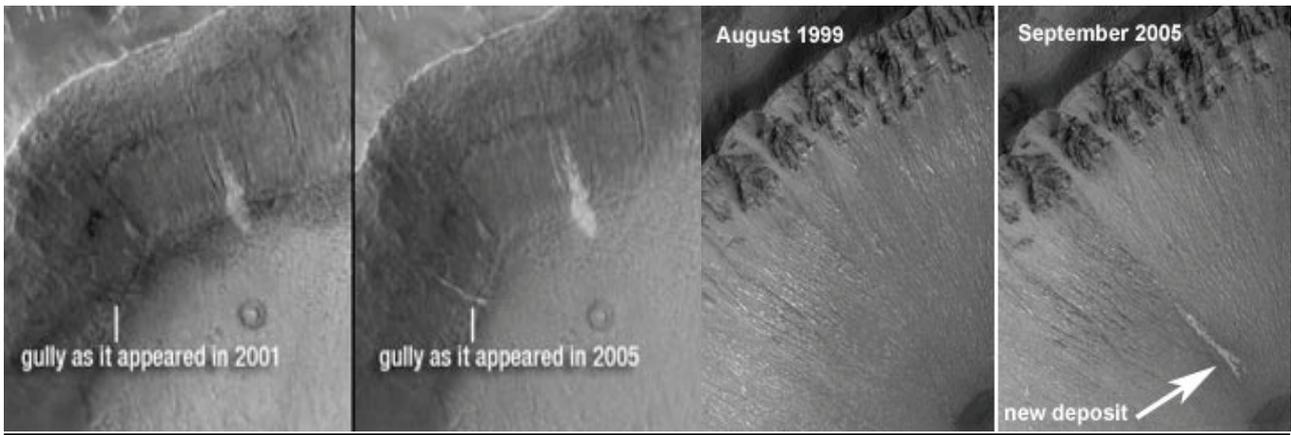


Figure 2. Gully morphology changes imaged by the Mars Global Surveyor. Far-centre left: Crater wall changes in the Centauri Montes. Far-centre right: Crater wall changes in the Terra Sirenum. (NASA, 2006).

Objectives of the present research:

- 1.) Conduct detailed petrographic observational analysis of terrestrial carbonation from collected samples of the Oman and Californian ophiolites, comparing the results with data available for Martian meteorites.
- 2.) Conduct chambered carbonation experiments on terrestrial ophiolite samples using a variety of mineralogical compositions under incrementally increased CO₂ pressures, repeating with increasing ratios of CO₂/SO₂ mixtures.

- 3.) The results of objectives 1 and 2 will be synthesised to create a quantitative Martian CO₂ model with variable parameters of atmospheric compositions, pressures and crustal compositions.
- 4.) Further mineralogical evidence to validate the model will be sought using the Curiosity Rover's Mars Science Laboratory, and collaborating with partners, new tools (rock polishing and deep drilling capabilities) will be designed, built and tested for planned use on future rovers (Figure 3).

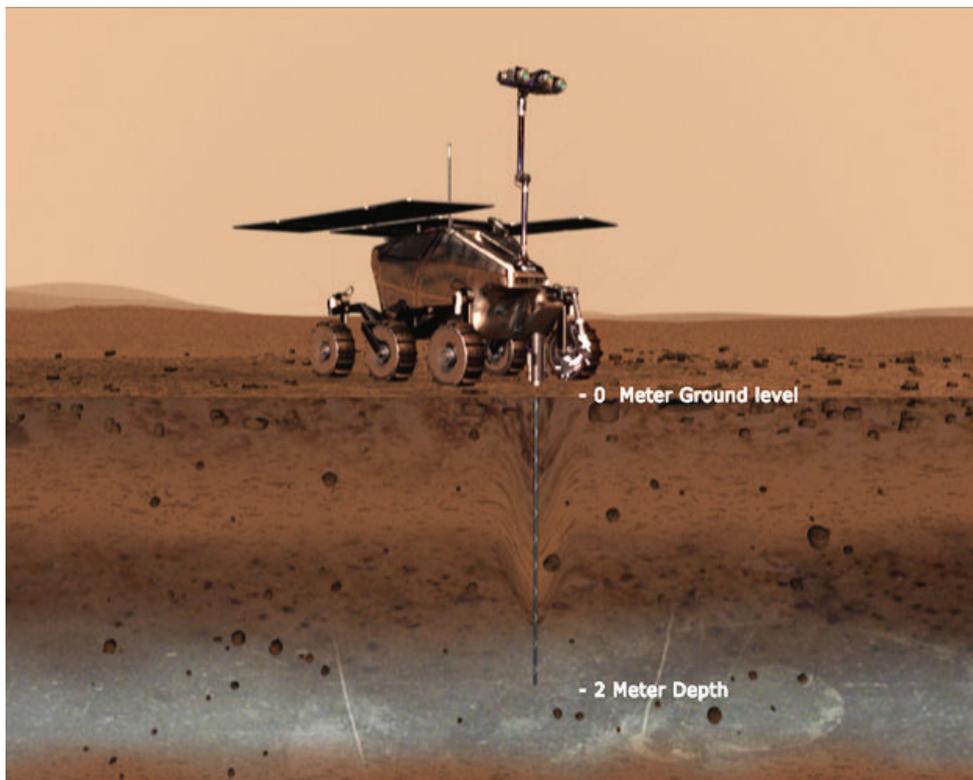


Figure 3. ExoMars drilling illustration. ESA, (2006).

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