

## Carbon sequestration on Mars

Martin R. Lee<sup>1</sup>, Tim Tomkinson<sup>1,2</sup>, Darren F. Mark<sup>2</sup>, and Caroline L. Smith<sup>3</sup>

<sup>1</sup>University of Glasgow, Geographical and Earth Sciences, Glasgow G12 8QQ, UK

<sup>2</sup>Scottish Universities Environmental Research Centre, East Kilbride G75 0QF, UK

<sup>3</sup>Natural History Museum, Earth Science, London SW7 5BD, UK

Using data acquired from the Nili Fossae region of Mars by orbital remote sensing, Edwards and Ehlmann (2015) have demonstrated that CO<sub>2</sub> was removed from the planet's late Noachian–early Hesperian atmosphere by replacement (carbonation) of olivine-enriched basalts. Given the relatively low volumes (~20% at most) of carbonate present in the study area, and the apparent absence of carbonate-rich terranes of similar size elsewhere on Mars, they questioned whether carbonation alone could account for the loss of a putative thick CO<sub>2</sub>-rich atmosphere. The work of Edwards and Ehlmann is therefore a highly significant contribution to the long-running debate about the nature and evolution of the climate of early Mars. The authors noted that Martian meteorites contain carbonates, and suggested that further evaluation of these rocks could improve our understanding of the planet's carbon cycle. Here we review published results from Martian meteorites, in particular the nakhlite group, which have already provided important insights into the mechanisms and time scales of mineralization and storage of CO<sub>2</sub> in Mars' crust. This evidence can help to discriminate between the various models for sequestration of Martian carbon that were discussed by Edwards and Ehlmann.

The nakhlites were impact-ejected from Mars, probably from one location and in a single event. They are clinopyroxenites, and most contain olivine. The majority of these igneous rocks have been partially aqueously altered to produce a very fine-grained intergrowth of minerals including Fe-rich carbonates (up to ~1 vol%) and hydrous silicates (Gooding et al., 1991; Treiman et al., 1993; Changela and Bridges, 2011; Lee et al., 2013). These alteration products are collectively called 'iddingsite.' Water-rock interaction took place at some time between crystallization of the melt (ca. 1300 Ma) and impact-ejection (ca. 11 Ma; Eugster et al., 1997); the best current estimate is ca. 633 Ma (Borg and Drake, 2005). The high deuterium/hydrogen ratio of the iddingsite demonstrates that its parent aqueous fluids had equilibrated with Mars' atmosphere (Hallis et al., 2012).

Mineralogical and crystal-chemical records of atmosphere-water-rock interactions that are contained within the nakhlites support some of the conclusions of Edwards and Ehlmann, but also emphasize the importance of incorporating the meteorite record in any comprehensive model. For example, microstructural evidence demonstrates that the carbonates were formed by replacement of olivine and a plagioclase feldspar-rich mesostasis, whereas the volumetrically dominant augite has remained unaltered (Tomkinson et al., 2013). The differential susceptibility of silicates in these meteorites to carbonation helps to account for distinct contrasts between Nili Fossae rock units in their relative abundances of olivine and carbonate. The occurrence of carbonates within veins in the nakhlites (Tomkinson et al., 2013) is also consistent with the suggestion by Edwards and Ehlmann that fracturing had facilitated the movement of aqueous solutions through the Nili Fossae basalts. However, the partial replacement of nakhlite carbonates by phyllosilicates and Fe-oxyhydroxides (Tomkinson et al., 2013) demonstrates that this crustal store of carbon was not necessarily permanent.

The age of the nakhlite carbonates shows that atmospheric CO<sub>2</sub> was being mineralized and stored in the late Amazonian. Scarce 3900-m.y.-

old carbonates also occur in the Martian orthopyroxenite Allan Hills (ALH)84001 (Borg et al., 1999). The meteorite record therefore supports the 'deep-diffuse sequestration' model that was invoked by Edwards and Ehlmann to account for the carbonate that is 'missing' from the Martian crust on the assumption that its early atmosphere was thinned mainly by mineral sequestration. The deep-diffuse model proposes that low volumes of finely disseminated carbonate formed within the crust throughout much of Mars' history, and as Edwards and Ehlmann note, these carbonates would be "undetectable by remote sensing." Products of aqueous alteration are essentially absent from the shergottite meteorites, which sample younger than ca.600 Ma basalts from several different locations, thus indicating that the drivers of crustal sequestration had effectively ceased within the past few hundred million years.

The record of reactions between the Martian atmosphere, hydrosphere, and lithosphere in our meteorite collections is manifestly very patchy as regards age spectrum and rock types (i.e., it is highly biased toward igneous rocks from younger terranes). Additionally, stresses accompanying impact ejection of these rocks, their interplanetary transfer and fall to Earth may militate against the sampling of heavily carbonated lithologies that are likely to be brittle and fractured. Nonetheless, information on the presence/absence and petrographic context of carbonate minerals in Martian meteorites provides very valuable information on the magnitude of CO<sub>2</sub> sequestration, petrologic and microstructural controls on the carbonation reaction, and its temporal and geographical range. This record indicates to us that the deep-diffuse model remains viable, and it can be tested further as new meteorites from regions of Mars that have not been previously sampled become available for study.

### REFERENCES CITED

- Borg, L., and Drake, M.J., 2005, A review of meteorite evidence for the timing of magmatism and of surface or near-surface liquid water on Mars: *Journal of Geophysical Research*, v. 110, p. E12S03, doi:10.1029/2005JE002402.
- Borg, L.E., Connelly, J.N., Nyquist, L.E., Shih, C.Y., Wiesmann, H., and Reese, Y., 1999, The age of the carbonates in martian meteorite ALH84001: *Science*, v. 286, p. 90–94, doi:10.1126/science.286.5437.90.
- Changela, H.G., and Bridges, J.C., 2011, Alteration assemblages in the nakhlites: Variation with depth on Mars: *Meteoritics & Planetary Science*, v. 45, p. 1847–1867, doi:10.1111/j.1945-5100.2010.01123.x.
- Edwards, C.S., and Ehlmann, B.L., 2015, Carbon sequestration on Mars: *Geology*, v. 43, p. 863–866, doi:10.1130/G36983.1.
- Eugster, O., Weigel, A., and Polnau, E., 1997, Ejection times of martian meteorites: *Geochimica et Cosmochimica Acta*, v. 61, p. 2749–2757, doi:10.1016/S0016-7037(97)00115-4.
- Gooding, J.L., Wentworth, S.J., and Zolensky, M.E., 1991, Aqueous alteration of the Nakhla meteorite: *Meteoritics*, v. 26, p. 135–143, doi:10.1111/j.1945-5100.1991.tb01029.x.
- Hallis, L.J., Taylor, G.J., Nagashima, K., Huss, G.R., Needham, A.W., Grady, M.M., and Franchi, I.A., 2012, Hydrogen isotope analyses of alteration phases in the Nakhlite Martian meteorites: *Geochimica et Cosmochimica Acta*, v. 97, p. 105–119, doi:10.1016/j.gca.2012.08.017.
- Lee, M.R., Tomkinson, T., Mark, D.F., Smith, C.L., and Stuart, F.M., 2013, Evidence for silicate dissolution on Mars from the Nakhla meteorite: *Meteoritics & Planetary Science*, v. 48, p. 224–240, doi:10.1111/maps.12053.
- Tomkinson, T., Lee, M.R., Mark, D.F., and Smith, C.L., 2013, Sequestration of Martian CO<sub>2</sub> by mineral carbonation: *Nature Communications*, v. 4, p. 2662, doi:10.1038/ncomms3662.
- Treiman, A.H., Barrett, R.A., and Gooding, J.L., 1993, Preterrestrial aqueous alteration of the Lafayette (SNC) meteorite: *Meteoritics*, v. 28, p. 86–97, doi:10.1111/j.1945-5100.1993.tb00251.x.