Earth and Planetary Science Letters 359–360 (2012) 117–123

Contents lists available at SciVerse ScienceDirect

Earth and Planetary Science Letters

journal homepage: www.elsevier.com/locate/epsl

The nakhlite hydrothermal brine on Mars

J.C. Bridges [a,*], S.P. Schwenzer [b]

[a] Space Research Centre, Department of Physics and Astronomy, University of Leicester, LE1 7RH, UK
[b] CEPSAR, Open University, Milton Keynes MK7 6AA, UK

ARTICLE INFO

Article history:
Received 10 July 2012
Received in revised form
24 September 2012
Accepted 27 September 2012
Editor: T. Spohn
Available online 8 November 2012

Keywords:
Mars
nakhlite
hydrothermal
brine
phyllosilicate
carbonate

ABSTRACT

Water is the basis of habitability; and formation conditions of hydrous alteration minerals are key to temperature and chemical conditions of that water. Using new, detailed observations on nakhlite martian meteorite alteration, composition, temperature and redox conditions of the water that formed the observed hydrous alteration can be determined through thermochemical modelling. We show that the nakhlite parent rocks on Mars encountered a CO_2-rich hydrothermal fluid at $150 \leq T \leq 200$ °C, pH 6–8 with a water:rock ratio (W/R) ≤ 300. Under these conditions, Fe-rich carbonate was precipitated within brittle fractures. As the fluid cooled to 50 °C, at pH 9 and W/R of 6, Fe-rich phyllosilicate precipitated, followed in turn by rapid precipitation of an amorphous gel. It was enriched in the most soluble species (e.g. K, Na), of alkaline pH, and similar to terrestrial, i.e. not seawater-influenced, dilute brines in basaltic terrains on Earth. Our results show that environments associated with this type of fluid were habitable, unlike those associated with acid-sulphate fluids. Considering the timing of the nakhlite alteration, the most likely cause is impact-generated hydrothermal alteration of the nakhlite pile at the margins of an impact crater. The martian subsurface fluid forming phyllosilicates provided habitable temperatures and many of the nutrients required for life.

1. Introduction

Mars research focuses on searching for signs of past liquid water, with firm evidence from lander missions (Grotzinger et al, 2005; Squyres et al., 2012; Tosca et al., 2008), orbiter near IR spectral measurements (Bibring et al., 2005; Mustard et al., 2008), photographic imagery and the SNC meteorites (Harvey and McSween Jr., 1996; Bridges et al., 2001; Treiman, 2005; Changela and Bridges, 2010; Hallis and Taylor, 2011). In order to assess the past habitability of Mars for microbial life it is necessary to have an accurate knowledge of the temperature, pH, composition and duration of water-related processes in the martian crust (Brack et al., 2010; Cockell et al., 2012). The nakhlite martian meteorites are our best source of information on alteration mineralogy, because assemblages and successions of phases can be studied in Earth-based laboratories. With this and a thermochemical model of the secondary mineralogy in the nakhlite SNCs this work presents an accurate characterisation of a fluid that is representative of the neutral to alkaline fluid type associated with large impact structures across Mars.

2. Starting point: the nakhlite hydrothermal mineral assemblage

The nakhlites are olivine-clinopyroxenite cumulates, formed from basaltic magma at ~1.3 Ga in a near surface intrusion or lava flow and were ejected from Mars 11 Myr ago (Nyquist et al., 2001). All of the nakhlites are similar enough, including their martian alteration mineralogy, to be recognisably from the same, or very close, sources on Mars. Their crystallisation age, when compared to crater count chronologies for Mars, suggest that the nakhlites formed on the large volcanic plains of the Northern Plains, or Tharsis, or Syrtis Major (Treiman, 2005). After accumulation of their augite and olivine crystals, they were affected, to varying degrees, by interstitial crystallisation of the magma, and chemical equilibration. The nakhlite group of 8 meteorites consists of 1 documented fall, Nakhla (Prior, 1911), with the remainder being either Antarctic finds (Y000593, MIL03346 and pairs), North West African finds (NWA998, NWA817, NWA5790), or in the case of Lafayette and Governador Valadares finds of uncertain provenance (Treiman, 2005). A pair of the Y000593 nakhlite (Y000749) shows the clearest terrestrial weathering overprint, in particular containing the sulphate jarosite which cross cuts that meteorite's fusion crust (Changela and Bridges, 2010). Terrestrial calcite is present in NWA998. However, each of the nakhlites contains traces of the martian alteration, which can be distinguished from any terrestrial overprints.

* Corresponding author.
E-mail address: j.bridges@le.ac.uk (J.C. Bridges).

0012-821X/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.epsl.2012.09.044

Pyroxene comprises 66–85% of the nakhlites, olivine 5–20%, with feldspathic mesostasis, magnetite and silica comprising most of the remainder (Mikouchi et al., 2003, 2012). The pyroxene is Fe-rich augite ($En_{0.37-0.62}$ $Wo_{0.37-0.43}$ $Fs_{0.24-0.41}$) with lesser amounts of pigeonite ($En_{0.48-0.54}$ $Wo_{0.06-0.13}$ $Fs_{0.35-0.39}$) (Bridges and Warren, 2006). The most abundant hydrothermal assemblage is present in Lafayette ~1% (Changela and Bridges, 2010). The olivine, which crystallised after the augite grains, has a compositional range across all the nakhlites of Fo_{6-44}, through some meteorites e.g. Lafayette, NWA998 have a narrow range Fo_{29-33}, Fo_{34-44} (Treiman, 2005; Mikouchi et al., 2012; Bridges and Warren, 2006). Varying mineral equilibration is one of the criteria, along with volume of mesostasis and plagioclase grain size, used to reconstruct the stratigraphy of the nakhlites (Harvey and McSween, 1992) and refined by Mikouchi et al. (2003, 2012) who proposed that nakhlites formed from the top to the bottom of the cumulate pile in the order NWA817, MIL033346, Y00593, Nakhla/Governador Valadares, Lafayette and NWA998. The uppermost meteorites were derived from within a few metres of the surface, with Lafayette and NWA998 derived from >30 m depth (Mikouchi et al., 2003, 2012). Although Mikouchi et al. (2003, 2012) were unsure whether NWA5790 was derived from the same igneous body as the other nakhlites, because of its relatively Fe-rich mineral compositions, our analyses of alteration phases suggest that it was part of the same igneous body (Changela and Bridges, 2010).

The distinctive brown colour of the Nakhla olivine and presence of brown inclusions was first noticed by Prior (1911). More modern studies (Ashworth and Hutchison, 1975) suggested that the brown colour was associated with preterrestrial alteration. The preterrestrial, and thus martian, origin of the veining was firmly established by Gooding et al. (1991) through the identification of veins truncated by fusion crust. Similar, truncated veins have been identified in Lafayette by Treiman et al. (1993).

The hydrothermal fluid is recorded in two ways within the nakhlite meteorites. The clearest traces are seen in the secondary minerals deposited along veins in the olivine and mesostasis. Secondly, trails of dark, relict fluid inclusions are trapped along fractures within the augite grains (Bridges et al., 2000). The absence of cross cutting veins suggests that the nakhlites experienced one fluid event rather than multiple events. The hydrothermal assemblage in Lafayette has been dated by K–Ar within the time range ≤ 670 Ma (Swindle et al., 2000) and so this constrains the timing of the hydrothermal alteration to a relatively recent time in Mars' history during the Amazonian period. The presence of Fe-rich carbonate in some of the nakhlites and the variation in the secondary mineralogy between the different nakhlites was first shown by Bridges et al. (2001) and Bridges and Grady (2000). Lafayette Fe-rich ankerite has the range of compositions (mol%) $CaCO_3$ 21.6–36.8, $MnCO_3$ 4.2–35.3, $MgCO_3$ 0.1–1.6, $FeCO_3$ 27.4–67.0; Governador Valadares siderite is $CaCO_3$ 3.6–11.1, $MnCO_3$ 1.1–2.1, $MgCO_3$ 9.0–29.2, $FeCO_3$ 64.3–77.8; Nakhla siderite is $CaCO_3$ 0.1–5.7, $MnCO_3$ 1.0–39.9, $MgCO_3$ 2.0–40.9, and $FeCO_3$ 23.2–87.0 (Bridges and Grady, 2000). Carbonate data available on request to the first author. Lafayette, upon which much of the mineralogical evidence for our modelling is based, contains smectite (saponite) with d-spacings of ~1 nm, within veins in the olivine. However, within the mesostasis, much of the phyllosilicate is a serpentine with d spacings of 0.7 nm (Changela and Bridges, 2010; Hicks et al., 2012). The sequence of hydrothermal mineral growth–most clearly shown in Lafayette–is: Fe-rich ankerite then partially replaced by phyllosilicate, then a fine inner rim of Fe oxide, followed by amorphous gel in the centre of the veins. This gel has the same composition as the smectite (saponite) but high resolution TEM shows that it lacks crystallographic structure, indicating the rapid cooling of this assemblage. This gel is the most common alteration phase in the nakhlites, and has been identified in all of them, with the exception of NWA998 within which discrete gel fillings to veins have not yet been found (Changela and Bridges, 2010). The gel composition shows a compositional fractionation, with decreasing Mg# from Lafayette (0.37) to Governador Valadares (0.32), Nakhla (0.24), and Y-000593 (0.15) (Changela and Bridges, 2010).

A more problematic part of the alteration assemblage is in the soluble phases: Governador Valadares has gypsum and anhydrite in interstitial areas, and Nakhla has gypsum-bearing veins in olivine and anhydrite and halite in interstitial areas (Bridges and Grady, 2000). The association with the main veins and siderite supports a martian provenance, although the nature of such phases means that recrystallisation in situ during their terrestrial residence may well have changed the textures.

The veins within brittle fractures, and the requirement for a rapidly cooled heat source, suggest an origin for the secondary minerals at the margin of an impact (Changela and Bridges, 2010). Hydrothermal systems are associated with craters ≥ 7 km on Mars (Abramov and Kring, 2005; Schwenzer and Kring, 2009) and so this may have been the size of the impact crater. The relatively low peak shock stage of the nakhlites 20 GPa (Nyquist et al., 2001) is consistent with being at the margins of an impact rather than being in the central part of the crater. Impact-generated formation of the observed alteration assemblages results in the need of two shock events, the first one causing the hydrothermal alteration, the second one launching the nakhlites off Mars. This is consistent with the helium loss being higher than expected from the shock pressure measured in the nakhlites (Schwenzer et al., 2008). The fractionation of the gel compositions (e.g. decreasing Mg# with fluid migration) is consistent with the fluid source being close to Lafayette, with the hydrothermal brine then migrating upwards towards Nakhla and the other parent rocks. Final precipitation of the gel and the soluble salts marked the end of the hydrothermal alteration.

The great majority of fluid inclusions have decrepitated at some stage in their history, probably during a shock event associated with ejection from Mars, and these empty inclusions appear dark in thin section. Other fluid inclusions have only partially decrepitated and show dark rims between the fluid and their outer margin. Attempts to determine trapped fluid compositions from thin section (Bridges et al., 2000) have not to date proved successful due to issues of sample contamination by mounting resin and polishing fluids.

An accurate fluid characterisation from the nakhlite martian meteorites is now possible using the above described new and detailed knowledge of the secondary mineralogy to build on thermochemical modelling of such systems on Mars (Griffith and Shock, 1995, 1997; Chevrier et al., 2007; Zolotov and Mironenko, 2007; Schwenzer and Kring, 2009).

3. Fluid modelling method

We calculate the alteration mineral assemblage and corresponding fluid using CHILLER (Reed and Spycher, 2006), which is a Fortran code to compute mineral-fluid equilibria; see also (Palandri and Reed, 2004) for method details but also its limitations. CHILLER's capability to assess alteration minerals in basalt-hosted hydrothermal systems has been demonstrated in terrestrial mid ocean ridge systems (Palandri and Reed, 2004) and on martian nontronite formation (Schwenzer and Kring, 2009) including protolith variation (Schwenzer and Kring, in preparation). For this study a diluted starting fluid was derived by using Ca-concentrations as found in waters that vent at the Deccan Trap units (Minissale et al., 2000). Fe and Mg were adjusted to the ratios in the Lafayette meteorite,