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High-temperature chlorine-rich fluid in the martian crust: A precursor to habitability

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ABSTRACT

We report scapolite in a melt inclusion in olivine in Nakhla, which is the first occurrence of Cl-scapolite found in a martian meteorite. Using terrestrial metamorphic experiments and modeling we constrain its origin. Cl-rich scapolite in Nakhla is consistent with formation from either a late stage Cl-rich, water-poor magma or magmatic Cl-rich hydrothermal brine at a minimum temperature of 700 °C. The temperature of hydrothermal activity recorded by the Cl-scapolite is significantly higher than the temperatures recorded by alteration minerals in Nakhla, and the fluid was Cl-rich, not CO_2-rich. Our results demonstrate that high-temperature Cl-rich fluids were present within the martian crust, and any potential biologic activity would have to survive in these high temperatures and saline fluids. Halophiles can thrive in NaCl-rich systems but at significantly lower temperatures than those recorded by the scapolite. During cooling of the fluid, the system could have reached a habitable state for halophiles. Importantly, halophiles can survive the conditions of space if they are encased in salt crystals, and therefore chlorine-rich phases present an opportunity to investigate for extant life both on the surface of Mars and in martian meteorites.

1. Introduction

In order to evaluate the potential for habitability within the martian crust, it is vital to understand the temperature, duration, and composition of any martian fluids (Cockell et al., 2012). Orbiter and lander missions have revealed extensive evidence of hydrous minerals on the surface that precipitated in a range of conditions, from acidic to neutral pH and cold to warm temperatures (Poulet et al., 2005; Bibring et al., 2006; Hurowitz and Fischer, 2014). Mars Science Laboratory has already found evidence for near-neutral pH water in an ancient streambed and from hydrous minerals (Williams et al., 2013; Grotzinger et al., 2014; Vaniman et al., 2014). Alteration minerals in the nakhlites have also revealed evidence for martian CO_2-rich fluids at temperatures <150–200 °C (Bridges and Schwenzer, 2012). However, evidence for higher temperature hydrothermal fluids on the surface of Mars and in the martian meteorites has been enigmatic. Here we report the first occurrence of Cl-scapolite in a martian meteorite – in a melt inclusion in olivine in Nakhla – and use terrestrial metamorphic experiments and modeling to constrain its origin.

On Earth, scapolite is a hydrothermal, metamorphic, or metasomatic mineral that commonly forms by the reaction of plagioclase and a Cl- or CO_2-rich fluid (Goldsmith, 1976; Mora and Valley, 1989; Rebbert and Rice, 1997). It is less common as a primary igneous phase, but has been reported as megacrysts, phenocrysts, and oikocrysts in alkali-rich basaltic magmas (Vaggelli et al., 1992; Smith et al., 2008). Based on reflectance spectra, scapolite has also been suggested to exist on the surface of Mars as a possible alteration mineral (Clark et al., 1990). Scapolite has three main end member compositions: marialite ($Na_4Al_3Si_9O_{24}Cl$), meionite ($Ca_4Al_6Si_6O_{24}CO_3$), and mizzonite ($\sim NaCa_3Al_5Si_7O_{24}CO_3$) (Goldsmith, 1976). Unlike other chloride bearing minerals (such as apatites, amphiboles, and micas), scapolite contains little to no OH. The chemistry of scapolite can therefore be used as a tracer of the Cl and CO_2 contents of the fluid responsible for its formation, independent of fH_2O (Ellis, 1978; Mora and Valley, 1989; Rebbert and Rice, 1997).

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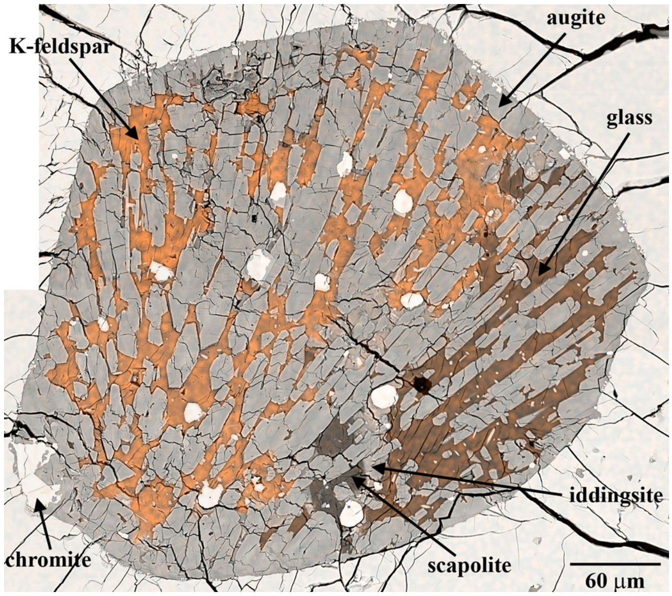

Fig. 1. Melt inclusion NK12A1 in Nakhla (Goodrich et al., 2013). Combined potassium X-ray map (orange) and backscatter electron image. Igneous and alteration phases labeled. (For interpretation of the reference to color in this figure legend, the reader is referred to the web version of this article.)

2. Sample and methods

During a study of melt inclusions in Nakhla (Goodrich et al., 2013), Cl-scapolite was found within a large melt inclusion in olivine. The melt inclusion was characterized petrographically with backscattered electron imaging (BEI) and energy-dispersive spectral (EDS) analysis, using the Zeiss EVO50 XVP scanning electron microscope (SEM) in the Department of Geosciences at the University of Massachusetts, Amherst (U. Mass). Following repolishing to remove beam damage caused by high-current X-ray mapping and grid analysis from Goodrich et al. (2013), the scapolite was analyzed using the Cameca SX-100 (U. Mass) and the following beam conditions: 15 keV and 10 nA beam current, counting times ranged from 5 to 20 s on peaks, with a nominally 2-µm-diameter beam (Goodrich et al., 2013). Na and K were always analyzed first, with shorter counting times than other elements. Na was analyzed using a PCO monochromator, which is optimized for light element analysis. Natural and synthetic minerals and glasses were used as standards; NaCl was used as a Cl standard.

3. Results

Scapolite was analyzed in an olivine-hosted melt inclusion in Nakhla (Fig. 1), melt inclusion NK12A1 from Goodrich et al. (2013). The olivine-hosted melt inclusion was the largest observed by Goodrich et al. (2013) and is approximately 430 µm across. The inclusion is roughly oval in shape and the olivine surrounding it is moderately free of cracks. It is dominated by high-Ca pyroxene, K-feldspar and K-rich glass, with minor chromite, Fe-sulfides, Fe–Ti oxides (Goodrich et al., 2013). One grain of scapolite, ∼100 µm long, was found in the inclusion. Texturally, the occurrence of the scapolite appears to be equivalent to the K-feldspar or the glass (i.e., interstitial to the pyroxenes), and may therefore be replacing, or contemporaneous with, one (or both) of these phases. It is adjacent to alteration materials (Fe-rich carbonates and phyllosilicates which are labeled as iddingsite in the figure) similar to those that have been reported in many of the nakhlite meteorites (Gooding et al., 1991; Treiman et al., 1993; Bridges and Grady, 1999; Treiman, 2005; Changela and Bridges, 2010; Hicks et al., 2014).

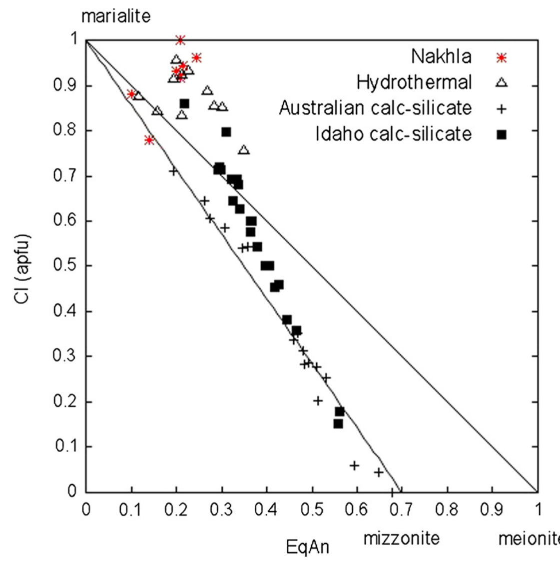

Fig. 2. Range of natural terrestrial scapolite compositions (black symbols) distinguished by mode of occurrence. Terrestrial data and figure modified from Rebbert and Rice (1997) and references therein. Martian scapolite from this study is in red. EqAn = equivalent anorthite content. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Average analyses of scapolite in melt inclusion NK12A1 in Nakhla.

	Average scapolite	2 sigma std. dev.
$n = 8$		
SiO_2	57.82	1.64
TiO_2	0.01	0.03
Al_2O_3	20.83	1.61
Cr_2O_3	0.01	0.01
FeO	1.61	2.57
MnO	0.00	0.00
MgO	0.40	0.54
CaO	4.90	0.94
Na_2O	9.35	1.23
K_2O	1.49	0.10
Cl	3.72	0.40
Total	100.15	

n = number of analyses.

The scapolite contains ∼3.9 wt.% Cl and has the formula $(Na_{2.8}Ca_{0.7}K_{0.3})_{3.9}(Si_{8.3}Al_{3.7})_{12}ClO_{24}$. It is almost pure end-member marialite with little meionite component (Fig. 2). Based on the chemical analyses and scapolite stoichiometry (Table 1), the scapolite contains enough Cl to preclude the presence of significant CO_3 or SO_4, although we did not analyze for C or S.

3.1. Martian vs terrestrial origin

Alteration materials found in the nakhlites are thought to be both martian and terrestrial in origin (Gooding et al., 1991; Bridges and Grady, 1999; Treiman, 2005; Changela and Bridges, 2010; Hicks et al., 2014). The scapolite is found within an olivine-hosted melt inclusion that shows minor to moderate evidence for fracturing. The scapolite occurs well within the melt inclusion and is not adjacent to any large fractures. It is adjacent to the alteration material (labeled “iddingsite”) which is thought to be martian in origin (Gooding et al., 1991; Treiman et al., 1993). Most importantly, Cl-scapolite forms at conditions >700 °C at 1 bar (see below for discussion, Ellis, 1978; Mora and Valley, 1989; Rebbert and Rice, 1997), while terrestrial alteration would occur at surface temperatures and pressures. Therefore, based on textural