

EVIDENCE FOR A WET, REDUCED MARTIAN INTERIOR. M.D. Dyar¹, S.J. Mackwell², S.J. Seaman³, and G.J. Marchand¹ ¹Dept. of Astronomy, Mount Holyoke College, 50 College St., South Hadley, MA 01075 USA. mdyar@mtholyoke.edu; ² Lunar and Planetary Institute, 3600 Bay Area Blvd, Houston, TX 77058, USA; and Dept. of Geosciences, University of Massachusetts, Amherst, MA 01003 USA.

Introduction: Knowledge of the oxygen fugacity and hydrogen content of the source regions of martian meteorites is of paramount importance in constraining phase equilibria, crystallization sequences, and geodynamic processes of the martian interior, as well as models of the planet's evolution. To date, these interpretations have been hindered by the paucity in SNC meteorites of Fe-Ti oxides used in conventional oxybarometry, and by the presence of secondary alteration products that make it impossible to quantify primary hydrogen abundances in SNC minerals and melts based on whole rock samples.

We present here the first transmission FTIR spectra of individual mineral grains from SNC meteorites, and interpret those results along with Mössbauer data on mineral separates from the same meteorites. Our goal is to quantify the amount of water and the oxygen fugacity present in the source regions for the rocks comprising the meteorites.

Background: In the Earth, and potentially in other terrestrial planetary interiors, the majority of H is contained within the crystal structures of nominally anhydrous minerals. Even ppm concentrations of H dramatically affect rheological behaviors and solidus temperatures of rocks that contain them. However, interpretation of direct measurements of H contents is complicated by the mobility of the H atom. In the Fe-bearing minerals that constitute the majority of mantle phases on terrestrial bodies, dehydrogenation can occur via the reaction $H^+_{\text{mineral}} + Fe^{2+}_{\text{mineral}} = \frac{1}{2}[H_2]_{\text{gas}} + Fe^{3+}_{\text{mineral}}$. The kinetics of this mechanism are well-constrained for cpx, opx, and olivine [e.g. 1]. Based upon these data, it is likely that dehydrogenation occurs in SNC meteorites as a result of the high pressures and temperatures experienced during impact and removal from the martian surface. Thus, understanding the H and Fe³⁺ contents of SNC source regions requires that both H and Fe³⁺ be constrained in the same samples.

Methods: Mineral phases constituting >10% of the mineral mode were hand-picked from martian SNC meteorites for analysis by FTIR reflectance and transmission spectroscopy for H contents and Mössbauer spectroscopy for Fe³⁺/Fe²⁺. Sample masses ranged from 1.5-34 mg. Room temperature Mössbauer spectral acquisition, data reduction, and interpretation are discussed in [2]. Reflectance spectra were collected by Taki Hiroi at the RELAB facility at Brown University and are reported in [3]. FTIR spectra were also col-

lected on individual pyroxene and olivine grains using beamline U10a at the National Synchrotron Light Source using infrared radiation generated by the UV-IR synchrotron. H contents were estimated using the calibrations of [4]. Samples analyzed were doubly-polished, 40-50 μm -thick individual mineral grains supported on the edges only by Crystal Bond adhesive. Preparation of transmission FTIR samples was greatly complicated by diffusion of Crystal Bond along fracture surfaces within single crystals; only spectra with no organic bands could be quantified.

Table 1. Mössbauer Fe³⁺ and Derived H₂O Contents

Meteorite and mineral	%Fe ³⁺	Wt% H ₂ O
Chassigny ol	0.0	0.000
ALHA 77005 ol	0.4	0.016
Nakhla ol	1.8	0.011
EETA 79001,B ol*	7.9	0.240
ALHA 84001 opx	0.0	0.000
LEW 88516 px	1.8	0.031
LA px	1.9	0.070
Nakhla px	2.3	0.040
QUE 94201 px	2.3	0.017
Shergotty px	1.7	0.040
Zagami px	1.4	0.028

*This sample is probably a xenocryst.

Mössbauer Results: Mössbauer data on Fe³⁺ contents of SNC mineral separates are given in Table 1. Proper interpretation of these data depends on understanding the relationship between Fe³⁺ contents and f_{O_2} for the minerals of interest., which is complicated by steric constraints on the accommodation of Fe³⁺ in each mineral's crystal structure. The best data on this relationship come from mantle xenoliths, in which coexisting phases allow f_{O_2} to be calculated. Based upon those samples, it is known that olivines containing measurable Fe³⁺ (by Mössbauer) are only found in metasomatized samples.

The oxidized olivines are always in equilibrium with highly oxidized (40% Fe³⁺) clinopyroxene with f_{O_2} 's > IW+5 (QFM+2) at ~1100-1200 °C [5]. At that temperature range, unmetasomatized clinopyroxenes typically contain ~30% Fe³⁺ at IW+4 [6]. Similar conclusions on the relationship between f_{O_2} and Fe³⁺ in clinopyroxene have been reached based on experimental studies by [7]. Near QFM, Fe³⁺ contents of high Ca cpx decrease rapidly, and range from 16% Fe³⁺ down to 0% Fe³⁺ over the range of IW+3 to IW [7]. Both low-Ca pyroxene and orthopyroxene have severe steric

constraints on Fe^{3+} accommodation, and their Fe^{3+} contents rarely exceed 10% of the total Fe even in highly oxidized samples.

Viewed relative to these known relationships, the Mössbauer data on SNC meteorites might at first appear puzzling. It is clear that Fe^{3+} -bearing olivines cannot be in equilibrium with clinopyroxenes with such low Fe^{3+} contents. The lack of equilibrium suggests to us that the observed Fe^{3+} in SNC meteorites instead represents charge left from dehydrogenation. If the measured Fe^{3+} is recalculated as H, then the values of wt% H_2O in SNC's could range from 0-0.016 in olivine and 0-0.07 in pyroxene, below the measured solubilities of H in olivine (0.03 wt% H_2O) and pyroxene (0.3 wt% H_2O)[8]. Thus, the excess charge on Fe^{3+} represents an amount of H that could easily be stored in pyroxene in the structure under upper mantle or lower crustal conditions.

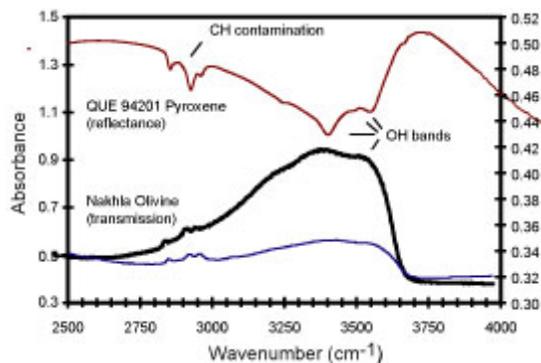


Fig. 1. Reflectance and transmission FTIR spectra of mineral separates and grains (respectively) from SNC meteorites.

FTIR Results: While the Mössbauer data constrain the amount of H that may once have been present, FTIR results address the issue of how much H remains. As shown in Fig. 1, reflectance spectra of the SNC pyroxenes display the characteristic water bands at 3100-3600 cm^{-1} . Quantitative analyses of reflectance data are routinely obscured by contamination of adsorbed water and C-H, but it is clear that sharp bands typical of structural water are present in at least the spectrum of QUE 94201. Transmission FTIR spectra show more clearly the presence of H bands. Although it is possible that in some cases these bands may represent humite or other alteration products (of terrestrial or martian origin) or melt inclusions, their ubiquitous presence suggests some incorporation into olivine and pyroxene. In other words, some olivine and pyroxene grains in the SNC meteorites are not completely dehydrogenated. Rather, the H_2O contents in Tables 1 and 2 may express lower limits for H contents of these phases. TEM work is planned to search

for the presence of alteration products and/or melt inclusions.

Table 2. Transmission FTIR Results for H

Meteorite /mineral	H concentration (ppm)
Chassigny ol	1792
ALHA 77005 ol	1196
Nakhla ol	457-6175
EETA 79001,B ol*	318
ALHA 84001 opx	327
LEW 88516 px	122
LA px	577
Nakhla px	0
QUE 94201 px	179
Shergotty px	676-915
Zagami px	108-1532

Discussion and Conclusions: The best explanation for the observed % Fe^{3+} contents of SNC olivine and pyroxene is that both phases were originally *completely reduced but H-rich*, and both were dehydrogenated by the impact that excavated them from the Martian surface. Such a reduced source region is consistent with results from Eu and Fe-Ti oxide barometry from SNC meteorites [9]. A hydrous source region has also been suggested previously based on indirect evidence [10], and D/H ratios have been measured on magmatic minerals from martian meteorites [11].

Both olivine and pyroxene in SNC's contain H in amounts comparable to what is observed in terrestrial mantle samples. Thus, hydrogen stored in nominally anhydrous minerals may constitute the largest reservoir of hydrogen in the martian interior, and thus control its water budget and mechanical properties. The gradual release of this water into the martian crust from intrusions could feed into subsurface water and ice deposits, and episodic release of hydrogen via volcanic eruptions would have dramatic effects on atmospheric evolution.

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