Particular H₂O dissolution mechanism in iron-rich melt: Application to martian basaltic melt genesis

Chloé Larre | Yann Morizet | Antoine Bézos | Christèle Guivel | Carole La | Nicolas Mangold

Laboratoire de Planétologie et Géodynamique (LPG), Université de Nantes, UMR-CNRS 6112, Nantes, France

Correspondence
Laboratoire de Planétologie et Géodynamique (LPG), Université de Nantes, UMR-CNRS 6112, Nantes, France.
Email: chloe.larre@univ-nantes.fr

Funding information
Agence Nationale de la Recherche (ANR), Grant/Award Number: ANR-16-CE31-0012; Programme National de Planétologie; Région Pays de la Loire; Centre National d'Etudes Spatiales (CNES)

Abstract
Martian basalts are different from Earth by their iron-rich abundance with 18 wt% FeO_{tot} in average for Mars upper crust. The H₂O dissolution mechanism in this atypical melt composition is not well understood. We have synthesized H₂O-bearing martian basaltic glass analogs (10 < FeO_{tot} < 16 wt%) under high pressures (0.5–1.5 GPa) and temperatures (>1500°C) conditions. We used Raman and Fourier transform infrared spectroscopies to investigate the effect of H₂O as well as the high FeO_{tot} content on the molecular structure of Fe-rich glasses. Increasing Fe content appears to inhibit the dissolution of H₂O in the melt. In fact, it appears that Free OH groups are formed at relatively low H₂O content in Fe-rich melts (1 wt%), whereas they only appeared at high H₂O content (~6.5 wt%) for Fe-poor glasses. We suggest that the Free OH are bonded to Fe²⁺ cations in the melt forming isolating clusters of Fe(OH)₂. Such configurations are suspected to induce an increase in the melt polymerization. The presence of free hydroxyls dissolved in the melt is likely to have a major impact on the genesis of aqueous fluid phase at the surface of Mars.

KEYWORDS
Fe-rich silicate glasses, Free hydroxyl, H₂O dissolution, Mars degassing

1 | INTRODUCTION

Many evidences of features related to liquid flows and aqueous phases at the surface of Mars led to the conclusion that water was present in its youth (e.g., these works¹⁻³). To stabilize liquid water at the surface of Mars, an atmosphere thicker and denser than the present one is needed.⁴⁻⁷ Several studies have demonstrated that such primitive atmosphere could be obtained by volatiles degassing from the interior of the planet through volcanism.⁸ Indeed, Mars went through an intense volcanic activity during the Noachian (>3.7 Ga), resulting in large provinces of igneous basaltic rocks covering the surface.⁹⁻¹³ Among the igneous rocks, sedimentary bedrocks have also been observed from both orbital and lander spatial missions. The presence of hydrated minerals inside these sedimentary rocks are another clue to the presence of water on Mars. The hydrated minerals detected were mostly phyllosilicates and hydrated sulfates.¹⁴ Then, numerous clues are available to postulate that water was available at the surface of Mars and may have contributed to the past dense atmosphere of Mars. However, the amount of H₂O degassed into the atmosphere, and the amount present at depth remains an open debate.

The quantification of the volatile fluxes from a planetary mantle to its atmosphere depends chiefly on the volatile content at the source and their respective solubility in the magmatic system. During volcanic eruptions, for instance, volatile species such as CO₂, H₂O, and SO₂ (for the most important) are degassed into the atmosphere.
The behavior of volatile species has been widely investigated for the different terrestrial melt compositions: (a) CO₂, H₂O, and SO₂ for basaltic melt compositions (e.g., these works[15–20] and many others); (b) CO₂ and H₂O for silica-poor melts (e.g., these works[21–24]). These studies have led to subsequent solubility models established on various silicate melts [e.g., these works[25–29]]. Although studies have focused their work on the volatile solubility in Earth magmatic systems, only few of them have focused on the solubility of volatile elements in martian magmas to constrain the volatile geochemical cycle of Mars. From geochemical modeling and meteorite analyses, estimations of the H₂O in a martian melt have been proposed although values are very scattered from thousands of ppm to 2 wt% H₂O.[30–32]

Martian interior can be characterized by a wide range of redox conditions: from iron Wüstite to above the quart–fayalite–magnetite buffer.[33–35] Experimental studies on martian melt were mainly focused on the C behavior under oxidizing and reducing conditions (e.g., these works[36–39]). Studies of the crystallization sequence for martian melt analogs in presence of H₂O have been proposed[40–42] and the water content determined. However, the H₂O quantification established in those studies cannot reflect the solubility of H₂O in an iron-rich melt. Up to now, there is no experimental study scrutinizing the H₂O dissolution mechanism in an iron-rich glass (>10 wt% FeOtot).

The Raman spectroscopy is a dedicated tool used to investigate qualitatively and quantitatively both crystallized and amorphous materials. Spectroscopic studies were achieved to establish calibrations from Raman spectra in crystallized materials (e.g., these works[43–45]). Many studies on amorphous materials based on the investigation of CO₂ and S behaviors in a silicate melt have led to subsequent calibrations (e.g., these works[46–48]). Calibrations to quantify the H₂O in melts by Raman spectroscopy have been proposed by these works.[49–52] Nonetheless, the behavior of volatile species dissolved in an iron-rich melt prevailing on Mars has been merely addressed by Raman spectroscopy.

In the present study, we investigated the dissolution behavior of H₂O in Fe-rich melt. We synthesized Fe-rich basalt glasses (10 < FeOtot < 16 wt%) under high-pressure conditions (0.5–1.5 GPa) in equilibrium with a H₂O fluid phase (up to 3 wt% starting H₂O content). The results obtained on Fe-rich glasses are compared with an Fe-poor terrestrial basalt analog (~6 wt% FeOtot). Experiments at high H₂O content (>6 wt% FeOtot) have also been performed on the terrestrial analog composition. The silicate structure of the obtained glasses has been characterized by Raman spectroscopy. Fe²⁺ and FeOtot (total iron) wet chemistry analyses have been realized in order to discuss the interplay of the Fe coordination state and the H₂O dissolution mechanism. The growth of Free OH molecular groups is observed at very low H₂O content in Fe-rich basaltic glasses, and the possible impact of these molecular clusters on element transportation within Mars interiors is discussed.

2 | METHODS

2.1 | Starting material

Investigated synthetic compositions were prepared in the SiO₂–Al₂O₃–FeO–MgO–CaO–Na₂O system from a mixture of oxides and carbonate (Na₂CO₃). The Fe-rich synthetic basaltic compositions were made according to basaltic rocks identified at the surface of Mars by the Spirit and Curiosity rovers at Gusev and Gale craters, respectively.[7–12] The two Fe-rich synthetic basaltic compositions were prepared with 15.5 and 23.5 wt% FeO and were referred as GC and CL, respectively. A natural popping rock (PR) 2πD43 glass (i.e., ~10 wt% FeOtot; Bézos and Humler[53]) has also been studied to investigate the H₂O behavior in a terrestrial analog. The theoretical glass chemical compositions are reported in Table S1.

The natural PR and the synthetic compositions were crushed in an agate mortar for homogenization. Some powders were decarbonated at 850°C for at least 4 hr in a 1-atm furnace (i.e., GCD and PR samples). The wet chemistry results of the starting materials showed that iron is mostly under Fe³⁺ state, Fe²⁺/∑Fe at 0.03 and 0.02 for GC and CL starting powders, respectively (see Table S1). Prior to the high pressure experiments, the Fe is almost fully oxidized.

The initial degree of polymerization representing the silicate network tetrahedral units interconnection and calculated according to Brooker et al.[22] is represented by the nonbridging oxygen per tetrahedron (NBO/T) parameter in the Table S1. For this calculation, Fe is considered as Fe³⁺ in the mixtures and therefore as a network former cation like Si⁴⁺ and Al³⁺. The studied compositions have comparable NBO/T with 0.38, 0.56, and 0.33, for PR, GC, and CL, respectively, which represent slightly depolymerized composition. In other words, there is a relatively strong interconnection between the tetrahedral units forming the silicate network.

2.2 | High-pressure experiments

Pure distilled H₂O was added with a microsyringe in several proportions (1.0 to 6.5 wt%) at the bottom of a 10-mm Pt capsule (2.5–2.9 mm in diameter) before loading the starting powder. The capsules were welded shut and
It should be stressed out that we did not find evidence for weight loss from the recovered capsules after the high-pressure experiments suggesting that (a) there is no elemental escape from the capsule and (b) there is no elemental gain in the capsule, which could be ascribed to elemental diffusion through the capsule walls.

The experiments were carried out using piston-cylinder apparatus in the pressure range of 0.5–1.5 GPa (equivalent to ~80–120 km in depth for Mars) and 1500–1600°C for temperature range. The isotropic hydraulic pressure is applied and transmitted through the assembly. A three-fourth inch talc-pyrex assembly was used. Previous work showed that using talc assemblies apply intrinsic \( fO_2 \) conditions close to quartz-fayalite–magnetite + 1 buffer. Temperature was controlled with a B-type thermocouple (PtRh6–PtRh30) with an accuracy of ±5°C. The accuracy on pressure was ±10%, and a 10% friction correction was applied during the experiment. The run duration varied between 1 and 6 hr. Quenching was achieved by cutting off the power, and the quench rate was measured and estimated to be above 80°C/s between 1600°C and 1000°C. We conducted an isobaric quench resulting in a glass free of bubbles. The excess fluid phase (if present) will be located at the top of the capsule in the case of isobaric quench. Several experimental charges did not produce a hiss at capsule opening indicating that these experiments were probably \( H_2O \) undersaturated.

### 2.3 Analytical methods

#### 2.3.1 Spectroscopic methods

The Fourier transform infrared (FTIR) spectroscopy was used for several samples. The spectra were acquired with an infrared microscope attached to a Nicolet FTIR 5700, with a X15 Cassegrain objective. The analysis conditions were a white light source, an InSb detector, and CaF\(_2\) beamsplitter. Acquisitions were performed in the near infrared area between 3,000 and 6,000 cm\(^{-1}\) with a spectral resolution of 4 cm\(^{-1}\). Each spectrum is an accumulation of 100 repetitive scans. Due to the size of the samples, no double polishing was performed. However, if the sample is measured properly, whatever the thickness is, the Beer–Lambert law can still be applied and theoretically reliable. The advantage of polishing is to get a planar surface. Here, our samples are homogenized and presented planned surfaces. Nonetheless, it is a less controlled method than the double polishing treatment. If we consider 10% error on the thickness measurement, the variation of \( H_2O \) content is of 0.2 wt%. Measurements of the thickness of each glass chips were realized with a digital indicator (with an accuracy of ±1 \( \mu \)m) to link the absorption to the \( H_2O \) content using the Beer–Lambert law.

We used a Jobin-Yvon Labram HR800 Raman spectrometer equipped with a 532-nm solid-state laser at the Laboratory of Planetology and Geodynamic (Nantes University, France). The output power was set at 50 mW to prevent sample damage. The laser power at the sample was measured at ~1.5 mW. This low power has prevented the degradation of the sample through oxidation, according to Di Genova et al. We used a grating of 1,200 grooves/mm corresponding to a spectral resolution of ~0.8 cm\(^{-1}\). The acquisition time was typically 30 s with six repetitive scans. Spectra were acquired in a nonconfocal mode with a slit aperture of 200 \( \mu \)m and a spot size estimated ~1 \( \mu \)m in diameter and 5 \( \mu \)m in depth. A X50 Olympus objective was used. At least five spectra were acquired on each sample to investigate the homogeneity of the recovered sample with respect to the dissolved \( H_2O \). The studied spectral range was between 200 and 1,250 cm\(^{-1}\) and between 2,600 and 4,000 cm\(^{-1}\), covering the area of the silicate network and the \( H_2O \) vibrations, respectively.

\( H_2O \) dissolved in silicate glasses exhibits Raman vibrations corresponding to the symmetric and antisymmetric stretch vibrations (\( \nu_1 \) and \( \nu_3 \)) of \( H_2O_{\text{mol}} \) and OH represented by an envelope with a peak maximum at ~3,550 cm\(^{-1}\). A shoulder at 3,660 cm\(^{-1}\) can be observed and is attributed to Free OH groups vibrations. We tested several calibrations to quantify \( H_2O \) in glasses using the ratio between the high-frequency (HF) area (i.e., high wavenumbers) band in the 800–1,200 cm\(^{-1}\), the \( H_2O \) band at 3,550 cm\(^{-1}\) and the intensity of the same band. Although, these calibrations were not fully tested to quantify \( H_2O \) in Fe-rich basaltic glasses, at a given composition, the \( H_2O \) content can be compared from one sample to another. Furthermore, we used the FTIR results to investigate the reliability of one Raman calibration or another.

#### 2.3.2 Secondary electron microscopy and electron probe microanalysis

We performed electron probe microanalysis (EPMA) and secondary electron microscopy (SEM) equipped with energy dispersive spectroscopy to determine the major elements compositions of our glasses. The SEM analyses were performed with a JEOL JSM 5800LV with a beam current at 5 nA and a voltage at 15 V, at Institut des Matériaux Jean Rouxel of Nantes (France).
The EPMA analyses were made using a Cameca SX 100 at IFREMER of Brest (France). A spot size of 10 μm and a beam current at 6 nA were chosen for the glass components. The acquisition time was 10 s on the sample and 5 s on the background. The standards chosen for our analysis were wollastonite (Si, Ca), corundum (Al), TiMn oxide, andradite (Fe), albite (Na), forsterite (Mg), apatite (P), and orthoclase (K). The associated error is on the order of 2% in relative to the measured value (see Table 1).

We can see in the Table 1, that the PR-3H-6h sample has experienced a strong Fe loss (2.7 wt% FeOtot) during the experiment considering that the FeOtot in the PR composition is ~10 wt%. This Fe loss has previously been observed,[60] and it is known from experimental study that the Fe can form an alloy with the Pt capsule. Even knowing the loss of Fe during experiments, the Fe enrichment of the capsules has not proven its efficiency either. Then, the Fe loss cannot be accurately controlled in high-pressure and high-temperature experiments. However, all the experiments have experienced depletion with respect to Fe. The following results are then considering the FeOtot after the experiments.

### 2.3.3 Colorimetric determination of the Fe$^{2+}$/∑Fe ratio

The Fe$^{2+}$/∑Fe ratios were measured using the colorimetric method of Wilson[61] recently modified by Schuessler et al.[62] About 3 mg of samples were weighted in 7-ml crystal polypropylene beakers, with a precision of 10$^{-3}$ mg, and dissolved for 3 days at room temperature in 1 ml of concentrated HF and 1 ml of 0.139 mol·L$^{-1}$ ammonium vanadate ($V^{5+}$). As the digestion progresses in such low pH solutions, the Fe$^{2+}$ released from the silicate matrix reacts immediately with the $V^{5+}$ to form Fe$^{3+}$ and V$^{4+}$. This reaction, which prevents any other accidental and irreversible oxidation of Fe$^{2+}$ into Fe$^{3+}$,[61] may be reversed if the pH of the solution is raised up to 5. Once the digestions were completed, 5 ml of beryllium sulfate solution (500 g·L$^{-1}$) was added to the beakers in order to neutralize the excess of HF and breakdown all insoluble fluorides. The final solutions for FeO colorimetric measurement were prepared in volumetric flasks filled with 10 ml of ammonium acetate buffer solution at 500 g·mol$^{-1}$ (to raise pH up to 5), 5 ml of 2.2'-dipyridyl solution as the ferrous colorimetric reagent, and ultrapure water filled up to 100 ml. The FeOtot analytical solutions were prepared by adding between 5 and 10 mg of hydroxyamine hydrochloride to an aliquot of the ferrous analytical solutions.[62] This strong reducing agent ensures the quantitative reduction of all remaining Fe$^{3+}$ into Fe$^{2+}$.

The colorimetric measurements were made with the ultraviolet/visible spectrophotometer Cary UV500 (Varian). The optical density measurements were done at 525 nm where the ferrous 2.2’-dipyridyl complex absorption is maximum.[61] The peak heights were measured relative to the baseline at 700 nm, and the Fe$^{2+}$/∑Fe ratios were determined by dividing the absorbance ratios corrected for the procedural blanks. The results of the Fe$^{2+}$/∑Fe measurements on the international reference material JB-2 (Fe$^{2+}$/∑Fe = 0.78 ± 0.005, N = 19) are in good agreement with the recommended values (i.e., 0.78, Govindaraju[63]).

### 3 RESULTS

#### 3.1 Raman spectra

The Raman spectra obtained on H$_2$O-bearing glasses synthesized at 1 GPa are represented in Figure 1a. The Raman spectra were treated with Labspec 6 software and a 5° polynomial fit, which goes through entrenched points (200–250 cm$^{-1}$, −600, −800, and >1,150 cm$^{-1}$) to subtract the baseline.[49] The spectra are arranged according to their FeOtot. We distinguish two spectral regions: the HF region 800–1200 cm$^{-1}$ and the low-frequency (LF) region 200–600 cm$^{-1}$. The 800–1,200 cm$^{-1}$ region represents the stretching of the silicate network ($v_1$). The region between 200 and 600 cm$^{-1}$ in amorphous material is still not well constrained owing to the complexity of the many vibrations occurring and overlapping together. Previous studies[49–51,64] have shown that the LF region is a complex combination of several vibrations: bending of tetrahedron from the silicate network (e.g., Al, Si, Ti, or Fe in tetrahedral coordination), and bending of tetrahedron in relation to cation network modifiers (e.g., Mg, Ca, Na, K, and Fe in octahedral coordination), and ring or rocking of tetrahedral structural units.

We observe that the LF region is more intense than the HF region for the PR-6Hb and PR-3H-6h, with 4.5 and 2.7 wt% FeOtot, respectively. On the contrary, the Fe-rich synthetic glasses (e.g., GC-3H-6h, GC-H$_2$O-4h, GCD-3H-6h, and CL-3H-6h) show the opposite behavior. The change of intensity between the LF and HF region has also been observed in the study of Giordano et al.[65] with a possible change in the polymerization degree. In the PR samples (PR-3H-6h and PR-6Hb), the HF region is asymmetric and exhibits three main features: 850, ~1,000, and 1,050 cm$^{-1}$. The most intense peak is localized around 1,000 cm$^{-1}$. In the GC samples (GC-H$_2$O-4h and GCD-3H-6h) peaks at 850 and 1050 cm$^{-1}$ are smooth but distinguishable. An intense peak around 950 cm$^{-1}$ is present...
<table>
<thead>
<tr>
<th>Sample</th>
<th>GC-H$_2$O-chiller</th>
<th>GC-H$_2$O-4h</th>
<th>GC-3H-6h</th>
<th>GC-1H-4h</th>
<th>GCD-3H-6h</th>
<th>GCD-3H-6h-1.5GPa</th>
<th>GCD-2H-0.5GPa$^a$</th>
<th>CL-3H-6h</th>
<th>PR-3H-6h</th>
<th>PR-6H-4h</th>
<th>PR-6H$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O$^{ini}$ (wt%)</td>
<td>2.6</td>
<td>2.6</td>
<td>2.4</td>
<td>0.9</td>
<td>2.7</td>
<td>3.0</td>
<td>1.9</td>
<td>2.9</td>
<td>2.9</td>
<td>5.7</td>
<td>6.5</td>
</tr>
<tr>
<td>CO$_2$ (wt%)</td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
<td></td>
<td></td>
<td></td>
<td>3.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P (GPa)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1.5</td>
<td>0.5</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>T (°C)</td>
<td>1600</td>
<td>1600</td>
<td>1600</td>
<td>1600</td>
<td>1600</td>
<td>1600</td>
<td>1600</td>
<td>1600</td>
<td>1600</td>
<td>1600</td>
<td>1500</td>
</tr>
<tr>
<td>t (h)</td>
<td></td>
<td>1</td>
<td>4</td>
<td>6</td>
<td></td>
<td>6</td>
<td></td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>48.6(8)</td>
<td>50.1(3)</td>
<td>50.9(3)</td>
<td>51.1(3)</td>
<td>48.5(2)</td>
<td>47.8(4)</td>
<td>49.4(2)</td>
<td>50.9(2)</td>
<td>52.7(3)</td>
<td>51.2(3)</td>
<td>51.1(2)</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.9 (1)</td>
<td>1.7 (1)</td>
<td>1.5 (1)</td>
<td></td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>11.5 (5)</td>
<td>10.7 (4)</td>
<td>10.8 (2)</td>
<td>10.6 (2)</td>
<td>10.2 (2)</td>
<td>10.4 (20)</td>
<td>10.9 (1)</td>
<td>8.7 (2)</td>
<td>15.2 (3)</td>
<td>14.5 (3)</td>
<td>14.5 (1)</td>
</tr>
<tr>
<td>FeO$_{tot}$</td>
<td>13.4 (4)</td>
<td>12.1 (3)</td>
<td>10.6 (3)</td>
<td>11.6 (3)</td>
<td>14.2 (3)</td>
<td>14.1 (3)</td>
<td>13.4 (1)</td>
<td>16.0 (4)</td>
<td>2.7 (1)</td>
<td>5.8 (2)</td>
<td>4.5 (1)</td>
</tr>
<tr>
<td>MnO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1 (0)</td>
<td>0.1 (0)</td>
<td>0.1 (0)</td>
</tr>
<tr>
<td>MgO</td>
<td>12.7 (1.0)</td>
<td>12.7 (4)</td>
<td>12.8 (3)</td>
<td>12.9 (3)</td>
<td>12.3 (3)</td>
<td>12.0 (3)</td>
<td>11.3 (1)</td>
<td>10.0 (1)</td>
<td>7.9 (2)</td>
<td>7.4 (2)</td>
<td>8.4 (2)</td>
</tr>
<tr>
<td>CaO</td>
<td>5.9 (1)</td>
<td>5.6 (3)</td>
<td>5.9 (2)</td>
<td>6.0 (1)</td>
<td>6.9 (3)</td>
<td>6.6 (2)</td>
<td>7.6 (1)</td>
<td>5.6 (2)</td>
<td>10.7 (2)</td>
<td>10.1 (3)</td>
<td>10.7 (2)</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>3.6 (3)</td>
<td>4.0 (6)</td>
<td>4.3 (2)</td>
<td>4.5 (1)</td>
<td>4.2 (3)</td>
<td>3.7 (3)</td>
<td>5.1 (1)</td>
<td>4.0 (2)</td>
<td>2.7 (1)</td>
<td>2.5 (1)</td>
<td>3.1 (1)</td>
</tr>
<tr>
<td>K$_2$O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.7 (0)</td>
<td>0.7 (0)</td>
<td>0.6 (0)</td>
<td></td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.3 (1)</td>
<td>0.3 (1)</td>
<td>0.3 (0)</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>95.6</td>
<td>95.2</td>
<td>95.3</td>
<td>96.8</td>
<td>96.4</td>
<td>94.7</td>
<td>97.8</td>
<td>95.3</td>
<td>94.8</td>
<td>92.8</td>
<td>93.6</td>
</tr>
<tr>
<td>H$<em>2$O$</em>{final}$ (wt%)</td>
<td>1.0 (4)</td>
<td>1.0 (4)</td>
<td>1.5 (4)</td>
<td>0.8 (4)</td>
<td>0.7 (4)</td>
<td>0.8 (4)</td>
<td>0.9 (4)</td>
<td>0.9 (4)</td>
<td>2.7 (4)</td>
<td>4.1 (4)</td>
<td>6.5 (4)</td>
</tr>
<tr>
<td>Free OH (%)</td>
<td>6.0</td>
<td>3.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6.6</td>
<td></td>
<td>17.1</td>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td>$F_{Fe^{2+}}$</td>
<td>0.47</td>
<td>0.49</td>
<td>0.53</td>
<td>0.57</td>
<td>0.37</td>
<td>0.46</td>
<td>0.44</td>
<td>0.58</td>
<td>0.83</td>
<td>0.70</td>
<td>0.82</td>
</tr>
<tr>
<td>$\sum_{Fe}^{Fe^{2+}}$</td>
<td>3.0</td>
<td>6.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>17.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NBO/T$^c$</td>
<td>0.51</td>
<td>0.48</td>
<td>0.52</td>
<td>0.52</td>
<td>0.50</td>
<td>0.46</td>
<td>0.49</td>
<td>1.08</td>
<td>0.53</td>
<td>063</td>
<td>0.68</td>
</tr>
</tbody>
</table>

**Note.** Chemical compositions of the samples determined by electron probe microanalysis and secondary electron microscopy analyses. Final content of H$_2$O and FeO$_{tot}$ are also reported, associated with wet chemistry results. The Free OH percentages are added for samples presenting the features at 3,660 cm$^{-1}$. The calculation of Free OH percentages is made on the deconvolution of the H$_2$O area. Detailed of deconvolutions are reported in the Table S3. Standards errors (1σ) are reported in brackets at 10$^{-3}$. The associated standard errors of wet chemistry measurements are 0.01.

$^a$Final chemical compositions determined by secondary electron microscopy only.

Abbreviation: NBO/T, nonbridging oxygen per tetrahedron.

$^b$Free OH percentages are calculated from wet chemistry analyses.

$^c$NBO/T calculated according to Brooker et al.$^{[14]}$ on an anhydrous basis.
for GC synthetic glasses. Finally, for CL-3H-6h, the HF region shape is almost symmetric with an intense peak centered at 950 cm\(^{-1}\). A Lorentzian-shape peak is observed between the LF and HF region a 670 cm\(^{-1}\) for the H\(_2\)O-bearing iron-rich sample CL-3H-6h and the popping rock PR-6Hb. The overall lineshape of our synthetic basaltic glasses is similar to the basaltic glasses investigated in the study of Di Genova et al.\[66\]

### 3.2 H\(_2\)O quantification by Raman spectroscopy

Raman spectra of glasses synthesized 1 GPa are shown in Figure 1b in the H\(_2\)O vibration region between 3,400 and 3,700 cm\(^{-1}\). Raman acquisitions were also performed between 4,000 and 4,300 cm\(^{-1}\) to investigate the possible presence of H\(_2\) at 4,135 cm\(^{-1}\),[67] but no signal was found. A main broad feature is observed at 3,550 cm\(^{-1}\). At 3,660 cm\(^{-1}\), we can observe a shoulder only present for the CL-3H-6h and PR-6Hb samples and is attributed to Free OH species.

The quantification of H\(_2\)O in our samples was performed using the calibration of Mercier et al.\[49\] and according to the following Equation (1):

\[
H_2O (wt\%) = \frac{I_{H_2O_{tot}}}{I_{HF}} \times \frac{1}{a}
\]

with \(I_{H_2O_{tot}}\) the maximum peak intensity at 3,550 cm\(^{-1}\), HF the intensity taken at 960 cm\(^{-1}\), and \(a\) the correlation coefficient chosen for a basaltic composition (i.e., 0.26). The basaltic coefficient taken from Mercier et al.\[49\] study best corresponds to all of our data according to the NBO/T calculated (see Table 1). This calibration also has to be performed on basaltic glasses containing up to 12 wt% FeO\(_{tot}\), which is close to the GC samples; although the CL sample is richer with respect to Fe, this calibration represents correctly most of our samples.

Quantifications have been done on at least five spectra collected at different location on the sample and on several glass chips. The estimated error on the quantification method is \(\pm 0.4\) wt% H\(_2\)O.\[49\] Therefore, the H\(_2\)O errors mentioned in Table S2 are a combination of (a) the error relative to the H\(_2\)O homogeneity in the glass if above the error calibration provided by Mercier et al.,\[49\] (b) the calibration error (0.4 wt%) if H\(_2\)O homogeneity is lower than this value.

In Figure 1b, spectra are normalized according to the concomitant HF peak intensity in Figure 1a. Hence, we can provide a direct comparison of the H\(_2\)O content from one sample to another. The PR glass with 4.5 wt% FeO\(_{tot}\) dissolves 6.5 wt% H\(_2\)O and shows the highest peak at 3,550 cm\(^{-1}\) (i.e., PR-6Hb). The peak intensity is decreasing towards higher FeO\(_{tot}\) contents: For the CL-3H-6h (with 16.0 wt% FeO\(_{tot}\)), 0.9 wt% H\(_2\)O is recovered. The
The derived H₂O contents are reported in Table 1. High water content experiments at 1 GPa have been measured for the PR composition with 4.1 and then 6.5 wt% H₂O dissolved in the melt with 5.7 and 6.5 wt% H₂O<sub>ini</sub>, respectively (i.e., PR-6H-4h and PR-6Hb). Experiment with 0.9 wt% H₂O<sub>ini</sub> at 1 GPa, has been tested for the GC composition (i.e., GC-1H-4h sample). Almost all the H₂O initially added is recovered in the melt: 0.8 wt% H₂O. Experiments with more than 3 wt% H₂O for the synthetic martian basalt compositions were performed at 1 GPa, but no quenched glass could be obtained. At 1.5 GPa, 0.8 wt% H₂O is determined in GCD-3H-6h-1.5GPa, with ~3 wt% H₂O<sub>ini</sub>. Finally, at low pressure, 0.9 wt% H₂O is dissolved in the same starting composition (i.e., GCD).

3.3 FTIR versus Raman for H₂O quantification

FTIR spectroscopy has been conducted on several glass samples in order to investigate the applicability of the Mercier et al.<sup>[49]</sup> calibration on Fe-rich basalts. Not all samples could be analyzed because of FTIR of (a) sample size (<1 mm) and (b) quenched crystals at the rim of the samples. Only pure glass chips with a size >2 mm have been analyzed: GC-3H-6h, GC-1H-4h, GCD-3H-6h, PR-3H-6h, PR-6H-4h, and PR-6Hb.

The determination of water content by FTIR follows the Beer–Lambert equation<sup>[16,18]</sup>:

\[
C_{H₂O} = \frac{100 \times MM \times A}{d \times \rho \times \varepsilon},
\]

(2)

where, C is the H₂O mol or OH<sup>-</sup> content in wt%, A the height of the band for OH (4,500 cm<sup>-1</sup>) or H₂O<sub>mol</sub> (5,200 cm<sup>-1</sup>), MM the H₂O molar mass in g/mol, d the thickness in cm, ρ the density in g/L, and ε the linear molar absorption coefficient in L/mol/cm.

Coupled to the H₂O signal between 4,500 and 5,200 cm<sup>-1</sup>, no H₂ was detected at 4,100 cm<sup>-1</sup><sup>[68,69]</sup> which is consistent with the absence of H₂ signal in Raman spectra. However, a small presence of H₂ will not change the H₂O quantification because the calibrations are not established at these wavenumbers for both Raman and FTIR spectroscopies. Although the recent study of Kirmizi et al.<sup>[70]</sup> as shown that protonic species may be present even with no strong Raman nor infrared signatures, it evokes the possibility presence of such species in our samples.

For PR samples, we used the extinction coefficients derived from Ohlhorst et al.,<sup>[71]</sup> 0.56 L/mol/cm for both peaks at 4,500 and 5,200 cm<sup>-1</sup>. For our Fe-rich, we used the extinction coefficient given by Stolper<sup>[72]</sup> considering that the studied basalts are closer in composition to ours. The molar absorptivity coefficients are 0.98 and 1.76 L/mol/cm for 4,500 and 5,200 cm<sup>-1</sup>, respectively.

Glass density measurements were not possible considering the size of our glass chips. It was calculated using the calibration of Schiavi et al.<sup>[51]</sup> which takes into account the chemical composition and is applicable to Fe-rich glass compositions. Results from subsequent measurements are shown in Figure 2a and in Table S2.

In Figure 2a, we observe that the H₂O quantified with Mercier et al.<sup>[49]</sup> provided better correspondence to the FTIR results. At low H₂O content (Figure 2b), for Fe-rich glasses, the H₂O quantification by Mercier et al.<sup>[49]</sup> is close to the 1:1 line. As an example, for the GC-3H-6h sample, 1.4 and 1.5 wt% H₂O are determined by FTIR and Raman, respectively. At higher H₂O content (>2 wt %; Figure 2a), the results are more scattered, but still in reasonable agreement with the FTIR results. For the
water-rich sample (PR-6HB), 6.9 wt% H₂O is determined by FTIR, where 6.5 is calculated by the method of Mercier et al. There is a strong discrepancy for PR-6H-4h with 4.1 wt% H₂O determined by Raman, whereas 6.1 wt% is determined by FTIR. However, this sample has the highest error bar due to possible heterogeneity in the H₂O distribution with the glass.

In Figure 2b, the calibration provided by Behrens et al. slightly overestimates the water content for Fe-rich glasses at low H₂O content. For GC-1H-4h, 1.1 wt% H₂O is quantified with Raman and 1.0 wt% by FTIR, although 0.9 wt% H₂O was initially added before the experiment. The discrepancy becomes more important at high H₂O content in PR-6Hb glass (see Figure 2a): 8.1 wt% H₂O by Raman with 6.5 wt% H₂O ini. However, it should be emphasized that the calibration is accurate to 4.7 wt% H₂O, and at higher content, the error in determining the amount of H₂O will be larger.

The calibration established by Schiavi et al. shows good results for low H₂O content in Figure 2b with 0.7 wt% for GC-1H-4h against 1.0 wt% H₂O by FTIR. However, with increasing H₂O content, there is an increasing deviation with the FTIR results. This difference can be ascribed by the high Fe content of basalts in Schiavi et al. (FeOtot > 7 wt%) compared with our Fe-poor basalts (<6 wt% FeOtot).

We also compared the FTIR results with the calibration established by Di Genova et al. for Fe-rich glasses. We can see that the calibration does not seem accurate for terrestrial basalt glasses as shown in Figure 2a, where the results are at least 2 wt% below the FTIR results (see Table S2). On the other hand, in Figure 2b, we can see that the calibration is better suited for Fe-rich glasses; however, the results are still less in accordance with the FTIR compared with Mercier et al.

The comparison provided in Figure 2 suggests that we can reasonably assess that the Raman calibration established by Mercier et al. is more appropriate to quantify H₂O in our Fe-rich and Fe-poor basaltic glasses. However, there is still a matter of discussion on whether one calibration is applicable to a given composition (i.e., Fe-rich glasses) or not. At low H₂O content (<2 wt%), as shown in Figure 2b, all calibrations are in reasonable agreement and can be used to determine the H₂O content in Fe-rich silicate glasses.

4 | DISCUSSION

4.1 | H₂O content in Fe-rich basalts

Differences between H₂O dissolved in the melt and H₂O ini can be observed for PR samples (Table 1). For 5.7 wt% H₂O added in PR-6H-4h experiment, less than 4 wt% H₂O is dissolved. For 6.5 wt%, ~6.5 wt% H₂O is recovered in the PR glass. Under these conditions (i.e., 1 GPa), H₂O solubility is close to 7 wt% [73]. The difference between initial and final amount of H₂O for PR glasses can be explained by the thermodynamic equilibrium of the H₂O species in the liquid and fluid phase [25]; by extension, there is a partitioning of H₂O between the fluid phase and the melt phase.

Some mixtures were not decarbonated, and CO₂ was present in the fluid phase during the experiments. However, after the experiments, no CO₃²⁻ signal at 1,080 cm⁻¹ was observed with Raman spectroscopy, implying that only hundreds ppm of CO₂ could be dissolved. It is consistent with previous studies that estimated the CO₂ solubility in these iron-rich melt at ~0.3 wt% under oxidized conditions [35,36].

The presented results in Figure 1b and Table 1 suggest that increasing Fe content will induce a substantial decrease in the H₂O dissolution. For instance, if we compare the PR-3H-6h and GCD-3H-6h samples with 2.9 and 2.7 wt% H₂O ini, the total H₂O dissolved in the melt is 2.8 and 0.7 wt% H₂O, respectively. For those two experiments made at identical intensive conditions and with no CO₂ present, there is a difference of ~2 wt% between the H₂O dissolved and the H₂O initially loaded in the sample charge. The most likely hypothesis to explain this difference is the change in the Fe content: ~13 wt% for GC samples and 5 wt% FeOtot for PR.

![FIGURE 3](wileyonlinelibrary.com)
We have presented the H₂O dissolved as a function of the FeO_{tot} for 1 GPa experiments in Figure 3. We observe a decrease of the H₂O content from 6.5 wt % H₂O at 5 wt % FeO_{tot} for PR-6Hb to less than 1 wt% at 16 wt% FeO_{tot} for CL-3H-6h (see Table 1). Hence, increasing the FeO_{tot} in the melt composition seems to hamper the H₂O dissolution. Even though the studied melt compositions of Hou et al.[74] are richer in Fe than ours, they investigated the immiscibility of a Fe-rich melt in presence of H₂O and observe a subsequent decrease of H₂O dissolution with increasing Fe content.

The calibration established by Raman spectroscopy to quantify H₂O can be user- and composition-dependent. However, we suggest that our values can be representative of the real H₂O dissolved in our glasses, especially at the lowest H₂O content. Indeed, Di Genova et al.[50] have shown that the presence of nanolite of Fe³⁺ in Fe-rich composition can provoke some differences in the H₂O quantification compared with nanolite-free samples. In this study, small quench crystals were observed in the rim of glasses for the following samples: CL-3H-6h, GCD-3H-6h, GC-H₂O-chiller, GC-3H-6h. From the Figure 2, we can see that the FTIR measurements are in good accordance with the method of Mercier et al.[49] to quantify H₂O. Then we can assume that quantifications established on the FTIR samples are correct. We performed FTIR on two samples presenting rims quenched crystals. We can see from Figure 2 that the results are still good and in accordance with the Raman spectroscopy calibration. Because there is currently no study attesting that the H₂O quantification can be underestimated for such glasses by FTIR, we can assume that our H₂O content is correct with this method. According to Di Genova et al.,[49] an underestimation of H₂O content can be expected due to the presence of nanolites. During our Raman acquisitions, we make sure to investigate only glass component. Coupled to SEM images, where the crystals are almost invisible, we obtained a homogenized chemical composition. Then, partitioning of H₂O between crystals and the melt seems unlikely. In addition, the small needle-shape size (nm) of the crystals make their identification impossible by Raman spectroscopy. This peculiar shape is a characteristic of quench phases that should not alter the glass composition. Then, we can postulate that the H₂O content obtained in the four samples (CL-3H-6h, GCD-3H-6h, GC-H₂O-chiller, and GC-3H-6h) are reliable although more investigation of the possible presence of nanocrystals is needed with different analytical tool (e.g., transmission electron microscopy).

Although we did not observe any variation in the mass of the Pt capsules after experiments, there is a possibility for additional H₂O to be formed from the diffusion of hydrogen through the capsule walls. In that case, the formation of H₂O during the experiment could be possible due to O₂ produced by reduction of Fe³⁺ to Fe²⁺ during the experiment. From wet chemistry measurements, we can see that part of the initial Fe³⁺ is converted into Fe²⁺. Hence, following the reaction below, O₂ will be formed in the fluid phase:

\[ \text{Fe}_2\text{O}_3^{\text{melt}} = 2\text{FeO}^{\text{melt}} + \frac{1}{2}\text{O}_2. \]  (3)

It is possible that H₂ diffuses into the Pt capsule, even though the pyrex of the talc–pyrex assembly is supposed to prevent it acting as a shield.[75] The H₂O formation with H₂ diffusion follow the reaction:

\[ \text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}^{\text{melt}}. \]  (4)

This H₂O could contribute to total H₂O dissolved in the glass. Therefore, the total available H₂O during the experiment would be higher. Such a case will reflect an even lower capability for Fe-rich glasses to dissolve within its structure. A simple calculation based on the change in Fe redox state leads to a possible increase in the H₂O content of less than 0.5 wt%; which is within the possible error in the H₂O determination.

### 4.2 | Peculiar H₂O dissolution mechanisms in Fe-rich basalt

Previous spectroscopic investigations[16,57,71,76] have shown that H₂O can dissolve in silicate glasses as two main species: (a) hydroxyl groups (i.e., OH) or (b) molecular H₂O (i.e., H₂O_{mol}). At low H₂O content, OH is the predominant species to be formed in silicate glasses owing to the water dissociation reaction:

\[ \text{H}_2\text{O}^{\text{melt}} + \text{O}^{2-\text{melt}} \rightarrow 2\text{OH}^{\text{melt}}. \]  (5)

For instance, this dissolution mechanism induces a depolymerization of the silicate network through the formation of silanol groups (SiOH):

\[ \text{Si} - \text{O} - \text{Si}^{\text{melt}} + \text{H}_2\text{O}^{\text{fl}} \rightarrow 2\text{SiOH}^{\text{melt}}. \]  (6)

At higher H₂O content, the H₂O dissolves as a molecular species (H₂O_{mol}) and becomes the predominant species (i.e., OH species remain almost constant) according to the following reaction:

\[ \text{H}_2\text{O}^{\text{fl}} = \text{H}_2\text{O}^{\text{melt}}. \]  (7)

An additional H₂O dissolution mechanism has been inferred in recent studies based on Raman and nuclear
magnetic resonance spectroscopic results\cite{58,74} and corresponds to the formation of Free OH groups. With opposition to the first mechanism, the formation of Free OH will induce a polymerization of the silicate melt structure as the network-modifying cation charges are consumed by the OH⁻ negative charges according to the following Equation (8):

\[
2Si - O^–M^{n+} + H_2O_{\text{fluid}} \rightarrow Si - O - Si + 2M^{n+}OH^n, \quad (8)
\]

with M for cations (i.e., Ca, Mg, and Fe) and n representing the charge of the cation. It has to be noted that the example of Si has been taken to simplify the changes occurring with H₂O dissolution mechanism. The Equation (8) could easily be rewritten using the other network former cations (i.e., Al³⁺, Fe³⁺). The dissociation of either Si, Al, or Fe tetrahedra with H₂O will have the same impact. According to the chemical composition in this study, Al is not very abundant compared with Si (0.2 mol% against 0.8). Then, the Fe³⁺ content is also less important in the sample (~12 mol%), according to wet chemistry measurements. Then it is likely that H₂O will favor the dissociation of Si tetrahedra because they are more abundant; however, it may not be the only tetrahedron to be dissociated with.

A shoulder at 3,660 cm⁻¹ corresponding to Free OH vibrations\cite{57–59} is observed for the Fe-rich glass (CL-3H-6h) and the water-rich terrestrial analog (PR-6Hb) in Figure 1b. Coupled with the shoulder at 3,660 cm⁻¹, a peculiar peak at 670 cm⁻¹ has been detected for those two spectra (Figure 1a) with a Lorentzian shape. The occurrence of the 3,660 and 670 cm⁻¹ peaks appear correlated, although the assignment of the 670-cm⁻¹ peak to a peculiar vibration remains to be determined. In the study of Di Genova et al.,\cite{50} Raman spectra acquired on Fe-rich basaltic glasses exhibit a specific peak at ~690 cm⁻¹ that is correlated with nanolite particles due to high Fe content. Furthermore, we have noticed that some other experiments showed the same peaks: GC-H₂O-chiller, GC-H₂O-4h, and GCD-3H-6h-1.5GPa.

To determine the proportion of the 3,660 cm⁻¹ peak, we carried out spectrum simulation using four peaks: three Gaussians and one Voigt (combination of a Gaussian and a Lorentzian component). Values of simulations are reported in Table S3. Typical simulations for PR-6Hb and CL-3H-6h are shown in Figure S1.

In Figure 4A, we have reported the proportions of Free OH as a function of the proportion of the 670-cm⁻¹ peak (i.e., 670* corresponding to the ratio between the 670-cm⁻¹ area and the total area of H₂O) for the samples: CL-3H-6h, PR-6Hb, GC-H₂O-chiller, GC-H₂O-4h, and GCD-3H-6h-1.5GPa. Here, we proposed a simple way to determine the proportion of Free OH based on the deconvolution of the 3,500 cm⁻¹ area, although more accurate method could be used. Each data reported in this graph corresponds to the proportion determined from the simulation of a given spectrum. In Figure 4a, we observe a correlation between the percentage of Free OH and the 670-cm⁻¹ peak. The increase of the 670 cm⁻¹ is correlated to an increase in Free OH. For PR-6Hb, we measure the 670* = 6% and Free OH = 2%. For CL-3H-6h, we obtain 670* ~60% and 20% of Free OH.

In Figure 4b, the Free OH percentages are represented against the FeOtot. The Free OH fraction appears also correlated to the FeOtot in the sample. The Fe-rich sample, CL-3H-6h with 16.0 wt% FeOtot, presents ~17% of Free OH. The GC and GCD samples exhibit values from 3% to 7% of Free OH, with ~12 and ~14 wt% FeOtot, respectively. On the other hand, PR-6Hb with 4.5 wt% FeOtot shows only 2% of Free OH.

**FIGURE 4** (a) Percentage of Free OH (i.e., A₃₆₆₀/A₃₅₀₀; with A the area from deconvolution of the 3,660 cm⁻¹ and the water band from 3,000 to 4,000 cm⁻¹) versus the percentage of the 670 cm⁻¹ peak (i.e., 670*) normalized by the total H₂O area (A₃₂₀₀); (b) Free OH percentages in function of the total iron content (FeOtot). GCD, greatest common divisor; PR, pooping rock [Colour figure can be viewed at wileyonlinelibrary.com]
Di Genova et al.\textsuperscript{[50]} demonstrate that the 690-cm\textsuperscript{-1} peak is attributed to magnetite nanolites. For instance, the Raman spectra of magnetite\textsuperscript{[77]} (Fe–OH component) and portlandite (Ca–OH) taken from the RRUFF database exhibit the same Raman signature at ~670 cm\textsuperscript{-1} as in our glass samples. In addition, it could also be enhanced with the presence of spinel or hematite nanocrystals.\textsuperscript{[78]} It seems that multiple parameters control the occurrence of these two correlated peaks (i.e., 670 and 3,660 cm\textsuperscript{-1}), such as the H\textsubscript{2}O and FeO content, but also the Fe redox state. Further investigation is needed to understand these atypical features developing at low H\textsubscript{2}O content in Fe-rich glasses.

Previous works have shown that the formation of Free OH is observed (a) when H\textsubscript{2}O is dissolved in a strongly depolymerized composition,\textsuperscript{[76]} (b) with high H\textsubscript{2}O concentrations,\textsuperscript{[58]} and (c) in aqueous solutions.\textsuperscript{[59]}

The presence of Free OH is rather surprising in Fe-rich glasses investigated here. This glass composition is not strongly depolymerized (i.e., NBO/T < 1), and the total H\textsubscript{2}O content does not exceed 1 wt%. One possible reason for the existence of Free OH groups in Fe-rich glasses could be ascribed to the structural role of iron within the glass. Recovered Fe-rich glasses (i.e., GC and CL) from high-pressure experiments have an Fe ratio between Fe\textsuperscript{2+}/\sum\text{Fe} = 0.4 and 0.6, respectively (see Table 1) suggesting that Fe plays a network-modifying role within the glass when under its Fe\textsuperscript{2+} state. Although additional work is clearly needed to better characterize the correlation between the Free OH groups and the Fe redox state, it is possible that Fe\textsuperscript{2+} has a high affinity to form isolated complexes with OH.

The observation of Free OH in Fe-rich melt at low H\textsubscript{2}O content (~1 wt%) has implications on the mineralogical composition at the Mars surface. The formation of Free OH molecular clusters could constitute a precursor for an immiscible Fe-rich phase; in a similar manner to the immiscibility observed between carbonatite and silicate melts owing to the formation of Free carbonates.\textsuperscript{[80]} Previous spatial missions identified multiple forms of Fe-oxides, mostly hematite and magnetite at the surface of Mars.\textsuperscript{[81–83]} The separation of Fe-(OH)\textsubscript{2} rich phase could favor the formation of Fe-oxides by weathering of the basalt at the surface.

4.3 Evolution of the silicate network signature as a function of the Fe redox state estimation

The presence of Free OH should induce a change on the overall silicate network considering that Fe\textsuperscript{2+} cations are scavenged by the OH species. Therefore, the deficit of positive charges from the network-modifying cations should induce an increase in the degree of polymerization according to the reaction (9):

\begin{equation}
2O^{NBO}_{melt} + Fe^{2+}_{melt} + H_2O^{melt} \\
= 10^{BO}_{melt} + Fe(OH)_2^{melt},
\end{equation}

where, O\textsuperscript{NBO} and O\textsuperscript{BO} are a NOB/T from a tetrahedral Q\textsuperscript{n} species, respectively. This reaction is equivalent to Equation 8 and shows that Q\textsuperscript{n} species proportions should decrease in proportion due to the formation of Free OH clusters that use an available NBO, and a more polymerized Q\textsuperscript{n+1} species is formed. For instance, Q\textsuperscript{3} species should merge to form Q\textsuperscript{4} species upon the dissolution of water as Free OH clusters. This change is likely to be observed by Raman spectroscopy.

The HF region is a composition of several Gaussians\textsuperscript{[84]} referred to a Q\textsuperscript{n} species with, n the number of bridging O varying from 0 to 4. Each Q\textsuperscript{n} species will represent a network former cation (Si, Al, Fe\textsuperscript{3+}) linked to an oxygen. We conducted spectrum deconvolution of the HF region that are exhibited in Figure 5. The results from the deconvolutions are reported in the Table S2. The deconvolutions of the Raman spectra for PR-6H-4h, GCD-3H-6h, and CL-3H-6h (i.e., synthetic martian basalts) are reported in Figure 5. Although the attribution of Q\textsuperscript{n} species can be debated, we assumed these positions according to Rossano and Mysen\textsuperscript{[85]} and references therein. Hence, we attributed Q\textsuperscript{4} at 1,080 cm\textsuperscript{-1}, Q\textsuperscript{3–O–Si at ~1,020 cm\textsuperscript{-1}, Q\textsuperscript{2} at ~950 cm\textsuperscript{-1}, and Q\textsuperscript{1} at ~880 cm\textsuperscript{-1}. The Q\textsuperscript{3–O–Si} corresponds to the vibration of the interconnected oxygen between two tetrahedral Q\textsuperscript{n} units as stated in previous studies,\textsuperscript{[86,87]} although Trcera et al.\textsuperscript{[88]} assigned it to Q\textsuperscript{3} species. Considering the work of Micoulaut et al.\textsuperscript{[89]} and Mysen,\textsuperscript{[90]} and the low NBO/T of our glasses (i.e., <1), Q\textsuperscript{3} species cannot be present. Indeed, all the Q\textsuperscript{n} species that can be present are following the equilibrium\textsuperscript{[86]}:

\begin{equation}
2Q^{n} = Q^{n+1} + Q^{n-1}.
\end{equation}

Hence, with the calculated NBO/T and H\textsubscript{2}O present in our basaltic glasses (both Fe-rich and Fe-poor), Q\textsuperscript{3} species cannot be attributed in the deconvolution shown in Figure 5.

For the PR-6H-4h sample, the deconvolution shows that the Q\textsuperscript{4} (~1,080 cm\textsuperscript{-1}) is the most intense peak compared with the same Q\textsuperscript{n} species for GCD and CL samples. On the opposite, Q\textsuperscript{2} species is more intense for GCD and CL. Di Genova et al.\textsuperscript{[91]} have experimented Fe-rich glasses obtained at 1 atm. In the Raman spectra analyses of these glasses, they stated that the 950-cm\textsuperscript{-1} peak is attributed to the occurrence of Fe\textsuperscript{3+} in the melt. Our Fe-
rich glasses exhibit ~50% of Fe³⁺. Then, it is possible that the 950 cm⁻¹ peak is the vibration of Fe³⁺ tetrahedron.

The presence of high Fe²⁺ content should enhance the depolymerization on the structure considering Fe²⁺ cation as a network modifier. It is confirmed with the deconvolution of the GCD glass in Figure 5. We can see that the iron-rich composition (CL sample) is richer in Fe²⁺ species (9.8 wt%) in comparison with the PR sample at ~4.2 wt% Fe²⁺. The decrease of Q⁴ intensity with respect to Q²⁺ species when increasing Fe²⁺ is observed from PR to GC and CL. Hence, a depolymerization is observed with the deconvolutions for the Fe-rich composition (Figure 5).

When looking at the calculated NBO/T (anhydrous basis), and whether Fe²⁺ or Fe³⁺ is the major component (according to wet chemistry) exhibited in Figure 5, there are some differences. PR-6H-4h is the most reduced compared with GCD and CL (the NBO/T considers Fe³⁺ as the main specie of Fe); hence, the NBO/T = 0.6. For the GCD sample, Fe³⁺ is predominant and NBO/T = 0.5. Finally, CL-3H-6h is more reduced than GCD with Fe²⁺/∑Fe = 0.6; thus, NBO/T = 1.1. It is rather surprising that the CL sample has the most depolymerized structure according to the NBO/T (more depolymerized than GCD) compared with the opposite observation on deconvolution in Figure 5. Indeed, there seems to have a decrease in Q² intensity with the increase of Q³ and Q⁻Si–O–Si, even though the latter cannot traduce the polymerization degree of the melt. The polymerization observed could be ascribed to the formation of Free OH clusters in this sample.

From Figure 6, we wish to discriminate the possible effect of Free OH and in relation with Fe²⁺ local environment on the degree of polymerization. We expected a measurable effect of the Free OH on the polymerization degree: Increasing the Free OH will increase the degree of polymerization according to Equation (9). As observed in Figure 6, the presence of Free OH species seems to have a limited effect on the degree of polymerization. The data points in Figure 6a for Free OH-bearing sample are aligned to the general trend of the effect of Fe²⁺ on the degree of polymerization. For instance, for GCD-3H-6h without Free OH and GCD-3H-1.5G with Free OH, we observe a Q⁴ proportion of 0.18 and 0.19, respectively. The same applies for the Q³ proportion in Figure 6b. Simulations of Q³ and Q⁻Si–O–Si over the Fe²⁺ content are exhibited in Figure S2.

Several aspects could explain the absence of effect shown in Figure 6: (a) The abundance of Free OH is too low for an effect to be seen on the degree of polymerization, and (b) it is also possible that the Free OH species are not exclusively linked to Fe²⁺ and other cations such as Mg²⁺ and Ca²⁺ form Free OH clusters.
CONCLUSION

In the present work, we have shown that Fe concentration in glass has a nonnegligible effect on the H2O dissolution within the melt structure. Increasing the Fe content appears to induce a decrease in the H2O dissolution. This result has major implications for Mars, notably for the transport of H2O in Fe-rich melt from the mantle to the surface that will be less efficient than on Earth. We inferred the formation of Free OH in Fe-rich glasses (i.e., martian basalt analogs) at relatively low H2O content (~1 wt%), whereas such molecular groups appear at very high H2O content for terrestrial basaltic glasses (>6 wt%). The presence of Free OH molecular clusters seems to be dependent on the Fe content with increasing the FeOtotal. In detail, Free OH species are likely to be correlated to the Fe2+ in Fe-rich composition. Free OH are supposed to induce a polymerization effect on the silicate network, although further work is currently needed to investigate the exact molecular configuration in the surrounding of cations forming Free OH groups. The possibility for Free OH in the vicinity of Fe2+ cations represents a precursor for producing Fe-rich mineral phases through weathering of the erupted Fe-rich basalts, which will be consistent with Fe-oxides found at Mars surface.

ACKNOWLEDGEMENTS

The author is thankful for the Centre National d’Etudes Spatiales (CNES), the Région Pays de la Loire, and the Programme National de Planétologie for funding the present work. We also want to acknowledge the Laboratoire de Planétologie et Géodynamique, the IFREMER of Brest and the Institut des Matériaux Jean Rouxel of Nantes to allow us to perform our experiments and analyses. Part of this research was carried out with funding from the Agence Nationale de la Recherche (ANR) under the program ANR-16-CE31-0012 entitled “Mars-Prime”.

ORCID

Chloé Larre https://orcid.org/0000-0002-5791-8176

REFERENCES


SUPPORTING INFORMATION
Additional supporting information may be found online in the Supporting Information section at the end of the article.

How to cite this article: Larre C, Morizet Y, Bézos A, Guivel C, La C, Mangold N. Particular H2O dissolution mechanism in iron-rich melt: Application to martian basaltic melt genesis. J Raman Spectrosc. 2020;51:493–507. https://doi.org/10.1002/jrs.5787