Dioctahedral phyllosilicates versus zeolites and carbonates versus zeolites competitions as constraints to understanding early Mars alteration conditions

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Jean-Christophe Viennet[a]*, Benjamin Bultel[a]*, Lucie Riu[b], Stephanie C. Werner[a]

[a] Centre for Earth Evolution and Dynamics, Department for Geosciences, University of Oslo, Postboks 1028 Blindern, 0316 Oslo, Norway

[b] Institut d'Astrophysique Spatiale, Université Paris-Sud, 91400 Orsay, France

* Authors to whom correspondence should be addressed:

Jean-Christophe Viennet

Email address: j.c.viennet@geo.uio.no

Benjamin Bultel

Email address: benjamin.bultel@geo.uio.no

Centre for Earth Evolution and Dynamics, Department for Geosciences, University of Oslo, Postboks 1028 Blindern, 0316 Oslo, Norway.

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Key points

- Experiments and geochemical modeling to investigate the effect of CO_2 content on mineral formation on ~~(~~early~~y)~~ Mars.

- Dioctahedral phyllosilicates versus ~~/~~zeolites and carbonates versus ~~/~~zeolites formation as a proxy to determining aqueous alteration history.

- Zeolite formation is inhibited in favor of carbonates by the presence of CO_2 in the aqueous solution.

Abstract

Widespread occurrence of Fe,Mg-phyllosilicates have been observed ~~by remote sensing instruments~~ on Noachian Martian terrains. Therefore, the study of Fe,Mg-phyllosilicates~~smectite~~ formation, in order to characterize early Martian environmental conditions, is of particular interest to the Martian community. Previous studies have shown that the investigation of Fe,Mg-smectite formation alone helps to describe early Mars environmental conditions, but there are still large uncertainties ~~(~~in terms of pH range, oxic/anoxic conditions, etc.~~)~~. Interestingly, carbonates and/or zeolites have also been observed on Noachian surfaces in association with the Fe,Mg-phyllosilicates.

~~Drawing on this~~Consequently, the present study focuses on the di/tri-octahedral phyllosilicate/carbonate/zeolite formation as a function of various CO_2 contents (100% N_2, 10% CO_2 / 90% N_2, 100% CO_2), from a combined approach including closed system laboratory experiments for 3 weeks at 120°C and geochemical simulations. The experimental results show that as the CO_2 content decreases, the amount of dioctahedral clay minerals decreases in favour of trioctahedral minerals. Carbonates and dioctahedral clay minerals are formed during the experiments with CO_2. ~~and carbonates are formed~~ ~~; while, w~~When Ca-zeolites are formed, no carbonates and dioctahedral minerals are observed. Geochemical simulation aided in establishing pH as a key parameter in determining mineral formation patterns. Indeed, under acidic conditions dioctahedral clay minerals and carbonate minerals are formed, while trioctahedral clay minerals are formed in basic conditions with a ~~the~~~~(~~neutral pH value of 5.98 at 120°C~~equal at)~~. Zeolites are favoured from pH >~7.2. The results obtained shed new light on the importance of dioctahedral clay minerals~~/~~ versus zeolites ~~versus~~and carbonates versus ~~/~~zeolites competitions, to better define the aqueous alteration processes throughout e~~(e~~arly~~)~~ Mars history.

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Keywords

Mars, clay minerals, carbonates, zeolites, experiments, geochemical modeling

1. Introduction

Among the various hydrated minerals detected by remote sensing instruments (such as: smectites (mainly Fe,Mg octahedral-rich), chlorites, kaolins, talc, serpentines and zeolites, in decreasing order of occurrence [*Carter et al*., 2013]), a particular interest has been devoted to the study of Fe,Mg-smectites. Indeed, their discovery on the Martian surface is a crucial observation because they could be an indicator for circum-neutral pH water activity, where a prebiotic chemistry could have been developed during the early Noachian [*Bibring et al.*, 2006].

Hence, laboratory experiments [*Dehouck et al.*, 2016; *Dehouck et al.*, 2014; *Peretyazhko et al.*, 2016] and/or geochemical simulation [*Catalano*, 2013; *Chevrier et al.*, 2007; *Fernández-Remolar et al.*, 2011; *Griffith and Shock*, 1995; *Liu and Catalano*, 2016] have been devoted to better understanding their formation. In particular, due to the Fe-rich Martian crust (compared to the Earth's) and the current oxidizing conditions, redox effects on the formation of Fe,Mg-smectites have been studied under conceivable early Martian environmental conditions. By using geochemical modeling, *Chevrier et al.* [2007] suggest that the presence of nontronite (Fe^{3+}-rich smectite) could be the result of highly oxidizing conditions; while, *Catalano* [2013] argues for a primary alteration period under reducing conditions followed by an oxidizing period, leading to Fe^{3+}-smectite formation. However, laboratory experiments [*Dehouck et al.*, 2016] have shown that if early Mars had a dense CO_2 atmosphere, highly oxidizing conditions would have strongly inhibited the formation of Fe,Mg-smectites and reducing conditions would have led to their formation. Moreover, a circum-neutral pH is sufficient to obtain Fe,Mg-phyllosilicates from volcanic rocks (especially basalt, *Gysi and Stefánsson* [2012a; 2012c]), but not necessarily. Indeed, *Peretyazhko et al.* [2016] have experimentally demonstrated that the weathering of a chemically representative Martian basaltic glass, with a water at pH 4 under oxic or anoxic N_2

atmosphere, leads to the formation of Fe,Mg-smectites. Finally, while our understanding of the early Martian atmosphere is dependent on our understanding of Fe,Mg-phyllosilicates ~~(especially Fe,Mg-smectites)~~, their formation conditions are too wide to provide enough constraints for a better understanding of the early history of Mars.

To a lesser extent, non-clay minerals associated with the Fe,Mg-phyllosilicates were observed on the Noachian Martian surface, such as carbonates [*Ehlmann et al.*, 2008; *Niles et al.*, 2013; *Wray et al.*, 2016] and zeolites (*Carter et al.* [2013], see also section 2 of this paper). The presence of carbonates could be linked to an early thicker CO_2-rich atmosphere [*Morse and Marion*, 1999], which allows for the presence of liquid water (e.g., *Pollack et al.* [1987]). *Brown et al.* [2010] propose that the formation of carbonates results from hydrothermal alteration of basaltic rocks. The limits of carbonate formation in basaltic rocks on Earth has been investigated in both experimental and modelling studies (e.g., CO2 sequestration, [*Gysi and Stefánsson*, 2011; 2012a; b; c; *Matter et al.*, 2016]), but in Martian environments this is yet to be fully explored. Indeed, geochemical simulation based on observations from altered Icelandic rocks ~~Icelandic observations~~ showed that hydrothermal alteration could be a source for carbonate formation and that at least ~~one bar~~ 1 bar of pCO_2 could have been stored in the subsurface [*Griffith and Shock*, 1995]. The geochemical simulation of *Chevrier et al.* [2007] concluded that 1 bar of partial pressure of CO_2 in oxidizing conditions could inhibit the formation of carbonates ~~(~~while Fe,Mg-smectites will be formed~~)~~. On the other hand, the experimental work of *Dehouck et al.* [2016] showed that the formation of carbonates is possibly enhanced by highly oxidizing conditions under a dense CO_2 atmosphere (from 0.8 up to 1.5 bars). Therefore, it is suggested that atmospheric conditions could have a strong influence on the formation of carbonates and/or Fe,Mg-phyllosilicates, and could be used as a probe to better understand the early Martian

environment. In addition to carbonates, zeolite formation and stability are strongly dependent on the geochemical conditions (such as alkaline pH solution, [*Dyer*, 2002]), and are therefore a good probe to investigate the Martian environmental conditions [*Ming and Gooding*, 1988]. Like clay minerals, zeolites are of prime importance, because they have a high potential for being major sinks of atmospheric gas [*Ming and Gooding*, 1988; *Mousis et al.*, 2016], Tthey can sorb and protect organic compounds and act as a catalyst for organic-based reactions [*Ming and Gooding*, 1988; *van Bekkum and Kouwenhoven*, 1989; *Venuto*, 1994]. Although, zeolite formation in Martian environments has not been widely studied, links between carbonation and clay formation (mainly smectite) from basaltic rocks has already been observed in hydrothermal (natural and laboratory simulated) systems on Earth [*Dyer*, 2002; *Gysi and Stefánsson*, 2012a; c; *Kralj et al.*, 2010; *Stefánsson and Gíslason*, 2001; *Utada*, 1988].

A review of zeolites detected on Noachian terrains is given in section 2, highlighting the associated minerals and probable geological processes. The aim of the present study is to investigate the formation of phyllosilicates/carbonates/zeolites by experimental work, in closed systems with various aqueous CO_2 levels (100% N_2, 10% CO_2 / 90% N_2, 100% CO_2). Note that due to the use of closed systems, the purpose of this study is not an attempt at determining pCO_2 level(s) of the Martian atmosphere. The cause and source of various aqueous CO_2 levels could be driven by either atmospheric and/or magmatic interaction [as explained in *Brown et al.*, 2010; *Bultel et al.*, 2015]. The various CO_2 % are chosen to reflect 1 order of magnitude of CO_2 content between each experiment. To better define this behaviour, we report on geochemical simulations constrained by the experimental results. Finally, the results obtained are used to evaluatebetter determine the environmental conditions during the early Noachian epoch. Compared to the sole investigation of clay minerals, shed new light on the importance of di/tri-

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~~phyllosilicate/carbonate/zeolite formation~~dioctahedral clay minerals versus zeolites and carbonates versus zeolites competitions is used ~~during the early Noachian epoch and~~ to highlight the pH conditions during the alteration~~will help to better determine the environmental conditions for such alteration products~~.

2. Martian Zeolites

2.1 Remote sensing detection of zeolites

In the near-infrared domain, ~~sampled by instruments in orbit around Mars,~~ zeolites have specific absorption bands near 1.20, 1.40, 1.90, 2.70-3.10 µm and one centered at 2.40-2.50 µm. The latter is attributed to the cation-OH liaison while the others are attributed to structural water or absorbed water on its surface ~~zeolites have specific absorption bands near 1.20, 1.40, 1.90, 2.70-3.10 µm, attributed to structural water or absorbed water on its surface, and at 2.40-2.50 µm, attributed to the cation-OH liaison~~ [*Cloutis et al., 2002*]. The detection of zeolites on the Martian surface is usually confirmed by a combination of absorptions near 1.40 and 1.90 µm due to hydration, and reduced reflectance from 2.30 µm due to a large absorption centered near 2.50 µm. Except for analcime identified by its specific NIR feature~~, a (~~ ~~band~~ near 1.79 µm~~)~~, ~~,~~ identification of other types of zeolites is challenging when mixed with hydrated minerals such as phyllosilicates. Indeed, the absorptions near 1.40 and 1.90 µm are common spectral bands among hydrated minerals. Therefore, no specific absorption can be attributed to zeolite if mixed with other hydrated minerals. However, the "zeolite background" spectrum is specific and, hence, zeolite detection is possible from the inflexion band after 2.30 µm. In addition to phyllosilicates, sulfates have a similar spectral shape with ~~(~~bands near 1.90 and 2.50 µm~~)~~. In this particular case, the geological context could be used as criteria to characterize the mineralogy. For example, the detection by proximity of monohydrated sulfates, kaolin, opal and nontronite suggest acidic environment, which is more favorable for sulfate than zeolite formation, as explained in *Pajola et al.* [2016].

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2.2 Absence and controversial detection of zeolites

Unlike the main alteration products~~-~~ observed on the Martian surface such as~~(i.e.~~ Fe,Mg clay minerals, carbonates~~, etc…)~~, zeolites have not been reported in Martian meteorites (*Gooding* [1992]; *Tomkinson et al.* [2013]). Nevertheless, Martian meteorites may not be representatives of the main Martian alteration features [*McSween*, 1994]; therefore, the zeolite formation process cannot be understood from meteorites. *Ruff* [2004] suggests that zeolite is a component of the dust on Mars from thermal infrared data. It could be an indication of a widespread zeolite presence on the Martian surface. Nevertheless, the zeolite presence in Martian dust is uncertain and disputed [*Bandfield et al.*, 2003]. Zeolites mixed with hydrated silica, opaline have also been suggested in the faulted region of Nili Fossae [*Ehlmann et al.*, 2009; *Viviano et al.*, 2013]~~)~~, and at the bottom of stratigraphic profiles in Terby crater and Eridania Basin, with a sequence ~~(~~from top to bottom~~:~~ of Al-phyllosilicates, Fe,Mg-phyllosilicates and possibly zeolite with hydrated silica (opaline)~~;~~ [*Ansan et al.* ~~[~~2011~~]~~; *Carter et al.* ~~[~~2015~~]~~; *Carter et al.* ~~[~~2010~~]~~; *Carter et al.* ~~[~~2013~~]~~; *Pajola et al.* ~~[~~2016]~~)~~. However, these detections remain uncertain because identification is based on the shape of spectra near 2.5 µm observed by the ~~CRISM (~~Compact Reconnaissance Infrared Spectrometer for Mars (CRISM)~~ spectra near 2.5 µm~~.

2.3 Reliable zeolite detections

Zeolites have been detected on crustal outcrops via CRISM ~~Compact Reconnaissance Imaging Spectrometer for Mars (CRISM)CRISM~~ data [*Ehlmann et al.*, 2011; *Sun and Milliken*, 2015; *Viviano-Beck et al.*, 2017; *Wray et al.*, 2009] together with Fe,Mg-rich phyllosilicates, hydrated silica or carbonates. We can now classify the different detections of zeolite by mineral associations. It is possible to distinguish three classes of zeolites based on their association with (i) Fe,Mg-phyllosilicates (Fe,Mg-smectites and/or chlorites) and hydrated silica; (ii) Fe,Mg-

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phyllosilicates~~(Fe,Mg-smectites and/or chlorites)~~ and carbonates; and (iii) only Fe,Mg-phyllosilicates ~~(Fe,Mg-smectites and/or chlorites)~~.

Near Nili Fossae, few craters excavated an association of ~~zeolite (~~analcime~~)~~, Fe,Mg-phyllosilicates (mainly chlorite and possible prehnite) and hydrated silica [*Ehlmann et al.*, 2011]. The association of zeolites with Fe,Mg-phyllosilicates and carbonates is found in Valles Marineris (see *Viviano-Beck et al.* [2017]). Zeolites in association with only Fe,Mg-smectites and/or chlorite are found in impact craters or in valleys formed by tectonic activity [*Viviano-Beck et al.*, 2017]. No particular stratigraphy is related to these detections. Moreover, detections are concentrated on ~~the~~ spurs (lateral ridge on the wall of a valley) or on the re-entrant (terrain between two spurs) of the canyon [*Ehlmann et al.*, 2009; *Loizeau et al.*, 2012; *Sun and Milliken*, 2015; *Viviano-Beck et al.*, 2017; *Viviano et al.*, 2013]. In at least three craters where zeolite is found with Fe,Mg-phyllosilicates, few authors suggest that a possible prehnite detection could be present [*Ehlmann et al.*, 2009; *Sun and Milliken*, 2015; *Viviano et al.*, 2013].

The detection of zeolites on Mars on crustal outcrops is therefore always associated with Fe,Mg-phyllosilicates ~~(smectite and/or chlorite)~~ and, in a few instances, with carbonates or hydrated silica. Note that, when analcime has been detected, no other zeolite types have been found nearby.

2.4 Possible process of formation

In cases of co-detection of zeolites, Fe,Mg-phyllosilicates and hydrated silica, the latter is found only on crater floors, while zeolites and phyllosilicates are found in both crater floors and the central structure. Their location could suggest post-impact hydrothermalism. Moreover, their detection in the ejecta layer, which would imply an alteration before the impact, is missing. In the case of zeolite detections exposed in the walls of Valles Marineris (assemblages ii and iii, see

section 2.4), they do not represent a particular stratigraphy [*Viviano-Beck et al.*, 2017]. The authors suggest hydrothermal alteration of layers in the subsurface prior to the opening of the canyon. The presence of zeolites in impact craters together with Fe,Mg-phyllosilicates (with or without carbonates), are attributed to either hydrothermalism before or after the impact, or diagenesis [*Viviano-Beck et al.*, 2017; *Ehlmann et al.*, 2009; *Sun and Milliken*, 2015]. However, the possibility of burial diagenesis seems unlikely since detection of the zeolite zonation (i.e. analcime to mordenite/clinoptilolite transformation) in the stratigraphy is lacking [*Hay and Sheppard*, 2001]. On the other hand, the zonation could also be below the resolution and the detectability of the instrument. Without a clear stratigraphic sequence unambiguously revealing zeolites, diagenesis, as well as surface weathering, are unlikely the source of zeolite formation on Mars. The most probable geological process resulting in the majority of zeolite detections could be hydrothermal systems, from ambient temperature to <200°C when prehnite is not present. This is in good agreement with the preferred alteration processes proposed for the alteration of the Noachian crust [*Carter et al*,. 2013].

Based on these surveys dedicated to zeolites and to the processes of formation of phyllosilicates and/or carbonates on Martian surfaces (see introduction), hydrothermal experiments have been set up to reproduce the main mineralogical assemblages described above (Fe,Mg-phyllosilicates/carbonates, Fe,Mg-phyllosilicates/zeolites). To do so, we set up closed system laboratory experiments for 3 weeks at 120°C with different percentages of CO_2 to study the aqueous alteration of basaltic glass.~~,~~ ~~and use g~~Geochemical simulations are used to decipher the pH conditions~~, especially water pH,~~ controlling the minerals formation~~ of minerals~~.~~.~~

3. Materials & Methods

3.1 Starting material and sample preparation

The raw material used for this study is a volcanic basaltic glass of tholeiitic composition from Iceland (Stapafell, Reykjanes Peninsula). The pristine rocks were manually crushed and the fraction between 0.5 to 1 mm was collected by using sieves. The 0.5-1 mm size fraction was cleaned by washing the particles with deionized water in an ultrasonic bath. Then, the particles were immersed in hydrochloric solution at pH 3 for 1 hour to remove any possible carbonates and washed three times in distilled water. The millimetric particles were manually crushed in a mortar to decrease the particle size to sizes between 100 and 500 µm. Finally, the particle size ~~(of less than 10 µm)~~ used for the experiments was obtained by crushing the 100-500 µm size fractions using a micro-mill to obtain particles < 10 µm. The total chemistry of the final product was obtained by fusion and XRF analysis (Actlabs, Canada, Table 1). The chemical composition of the basaltic glass is in the range of the chemical composition range of Noachian Martian meteorites [*Agee et al.*, 2013; *Lodders*, 1998], orbital [*Boynton et al.*, 2007] and in-situ analysis [*Gellert et al.*, 2006; *McSween et al.*, 2009; *McSween et al.*, 2006; *Ming et al.*, 2008] performed on the Martian surfaces.

3.2 Experimental set-up and procedure

The hydrothermal experiments were performed in closed systems at 120°C for a duration of 3 weeks in a 600 mL Parr Reactor ©. 4.0 g of the <10 µm size fraction was mixed with 80 ml of pure water and filled to the Parr reactor container leading to a gas head space of 520 ml at room temperature. The pure-water and head space were flushed for 10 minutes by injection of the desired gas into the reactors through two valves. Then the reactors were sealed and heated to 120°C. Three different high purity gases were used for the experiments: Nitrogen (100% N_2), Carbon Dioxide (100% CO_2) and a mixture of 10% CO_2 and 90% N_2, referred to as 10% CO_2 /

90% N_2 (with a CO_2 content uncertainty of less than ±1%). Note that, the experiments are referred to by the percentage of the initial content of CO_2 and/or N_2.

3.3 Solid phase analysis

3.3.1 X-Ray diffraction analysis

On the bulk and altered rocks, X-Ray diffraction (XRD) patterns were recorded with a D8 Advance Bruker (CuKα_{1+2} radiations) from 2 to 55°2θ using a step interval of 0.25°2θ and a counting time per step of 2.5 s. The size of the divergence slit, the two S~~s~~oller slits and the antiscatter slit were 0.25°, 2.5°, 2.5° and 0.5°, respectively. The bulk initial and final materials were analyzed on powder preparation. The clay minerals were analyzed by performing Ca- and K-saturation using four saturation cycles with 0.5 mol.L^{-1} of $CaCl_2$ and 1 mol.L^{-1} of KCl, respectively. Then the solutions were washed in distilled water and dried at 50°C. The XRD patterns for clay minerals were recorded from oriented samples, prepared by pipetting slurries of the particles dispersed in distilled water on glass slides and drying these at room temperature. The Ca- preparations were analyzed after air-dried preparation (the associated acronym is Ca-AD). Thereafter, the glass slides were exposed to ethylene-glycol vapor at 50°C overnight to obtain ethylene-glycol solvation; the subsequent XRD patterns recorded are referred to as Ca-EG. Heat treatments at 110°C, 330°C and 550°C were performed on the K-saturated glass slide preparations and the respective XRD patterns were recorded (referred to as K-110, K-330 and K-550, respectively). To obtain these XRD patterns for the different treatments, the slides were progressively heated over 4 hours stopping at each specific temperature to allow the slides to cool down to ambient temperature before XRD analysis was acquired.

3.3.2 Near Infra-red analysis

The near-infrared reflectance spectra were obtained with a PerkinElmer FTIR spectrometer. The wavelength range explored is from 1 to 4 µm with a spectral resolution of 1 cm^{-1} and a spectral sampling of 0.4 nm. On the bulk and altered rocks, the reflectance spectra were acquired on rock powder preparation under ambient temperature and pressure conditions. Additionally, a calibration was carried out prior to the analysis to derive the samples reflectance spectra, using an *Infragold* and a *Spectralon* 99% sample from Labsphere.

3.4 Geochemical simulation

The aim of the geochemical simulation exercise is to reproduce the mineralogical association obtained during the experiments as a function of the initial gas composition for the same rock composition, temperature and water/rock ratio. The thermodynamic simulations were performed by using the EQ3/6, software version 8.0 [*Wolery*, 1992a; b; *Wolery et al.*, 1990]. Backward reactions are authorized~~ (e.g.~~ which means that the dissolution of the product is authorized~~)~~. The thermoddem data base (http://thermoddem.brgm.fr/) was used to account for updated clay minerals and zeolite thermodynamic values compared to the *data0.cmp* database (see Table 2).~~(e.g., Fe-rich saponite (1 Fe atom in substitution of 1 Mg atom in the octahedral sheet), sudoite, sudoite(Fe), vermiculite, illite, phillipsite, clinoptilolite, heulandite, chabazite, mordenite and stellerite). Ideal solid-solutions were used during the geochemical exercise~~

The basaltic glass used during the experiments was also implemented in the database. The following structural formula of the basaltic glass $Si_1Al_{0.35}Fe_{0.23}Mg_{0.29}Ca_{0.26}K_{0.07}Na_{0.01}O_{3.345}$ was calculated from the total chemistry (Table 1) and it is ~~similar to~~ in accordance with previous studies using similar volcanic glass [*Aradóttir et al.*, 2012; *Gysi and Stefánsson*, 2011]. The

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estimation of the log(K) values for the dissolution of the basaltic glass were based on a theoretical approach [*Paul*, 1977], which considers the glass as oxide mixtures. Then, the solubility of the volcanic glass corresponds to the sum of the solubility products of the oxides weighted by the mole fractions. The values obtained (Table 1) are in good agreement with previous data on similar Icelandic volcanic glass [*Aradóttir et al.*, 2012].

To mimic the experimental procedure, we first saturate the water with the desired atmosphere. ~~Therefore, w~~We put in contact ~~80 grams (~~80 m~~l~~L~~)~~ of pure water with the desired gas at 25°C and at atmospheric pressure. ~~(~~The number of mol of gas was calculated by considering the volume of the head space in the reactor~~)~~. Then, the aqueous solution and the atmosphere are heated in a closed system model until the experiment's nominal temperature (120°C) is reached. ~~Therefore~~Hence, ~~,~~ the total content of C ~~(for the experiments involving $CO_{2(g)}$)~~ in the system is constant and similar to the experimental value. The last step of the geochemical simulation consists of mixing ~~the~~ 4 grams of basalt with the gas/water components and then letting the simulation reach equilibrium as a function of the mol of basalt destroyed (% of dissolution).

The numerical setup is slightly different compared with the experimental procedure. The original basalt is put in contact with the aqueous solution at 120°C during the simulation while ~~For the exper~~during the experiments the original basalt is mixed with pure water at 25°C and then heated to~~at~~ 120°C. However, this difference does not alter the simulated results compare to the experimental ones~~s~~. ~~t~~The slow reaction of basalt ~~at this temperature,~~ compared with the 1hour heating time ~~(less than 1 hour)~~ required to reach 120°C during the experiments, likely prevents alteration and mineral~~s~~ formation ~~formation and no stable thermodynamical state can be reached~~ during this period. The geochemical simulations take in account all ~~the~~ minerals present in the data base even if they are not in equilibrium in such pressure and temperature conditions. Hence,

~~In comparison,~~ preliminary ~~during the~~ geochemical ~~simulations~~ simulations were performed. Then, ~~minerals which~~ minerals, which are not assumed to form in such ~~systems/environments~~ conditions, are suppressed (see table 2). The final geochemical simulation~~s~~ corresponds to mineral~~s~~ formation possible in such temperature and pressure range.~~. Thus, although given in the database, minerals are suppressed if formed in much higher temperature and/or pressure ranges (e.g., prehnite, olivine, magnetite, biotite, graphite, wollastonite, amphibole and epidote) and in metamorphosed sediments (e.g., akermanite, monticellite and merwinite), as well as in lower temperature ranges (e.g., chabazite [*Blanc*, 2009]). In addition, the minerals which are already taken into account in the solid solution products are also suppressed, such as, dolomite, dolomite-ordered and disordered (carbonates solid solution from calcite, magnesite and siderite) and nesquehonite (calcite-nesquehonite solid solution). Finally, these phases have been considered because they actually form during simulation.~~

4. Results

4.1 Experimental results

The figure 1.I and 1.II presents the XRD powder patterns and the NIR spectra obtained on the unreacted sample (a) and after the experiments as a function of the gas composition (b, c and d under 100% CO_2, 10% CO_2 / 90% N_2 and 100% N_2, respectively). The large and intense bump between 5 and 2.33 Å, centered at 3.23 Å of the unreacted sample (Figure 1.I.a and 1.II.b) defines ~~is~~ ~~composed mainly of~~ ~~a~~the volcanic glass. The triangles at 5.12, 3.89, 3.50, 2.78, 2.52, 2.47, 2.36, 2.27, 2.56, 2.17 and 1.75 Å ~~(Figure 1.I.a, large and intense bump between 5 and 2.33 Å, centered at 3.23 Å) with a~~ correspond to a small proportion of forsterite (Figure 1.I.a, ~~triangles at 5.12, 3.89, 3.50, 2.78, 2.52, 2.47, 2.36, 2.27, 2.56, 2.17 and 1.75 Å~~), the stars at 4.26 and 3.33 Å correspond to quartz (Figure 1.I.a, ~~stars at 4.26 and 3.33 Å~~) and the diamonds at 3.20 and 2.99 Å correspond to a minor amount of pyroxene (Figure 1.I.a, ~~diamonds at 3.20 and 2.99 Å~~). The volcanic glass and quartz minerals have no specific absorption bands in this NIR range, which lead to a high intensity band corresponding to olivine and low-calcium pyroxene ~~(LCP)~~ (Figure 1.II.a, at 1.07 and 1.85 µm, respectively) [*Hunt and Salisbury*, 1970]. The large spectral band at around 2.90 µm corresponds to H_2O molecules present in the sample probably adsorbed on the edges of the basaltic particles (Figure 1.II.a). All XRD patterns obtained on the reacted materials show a decrease in the broad peak intensity (Figure 1.I.b, c and d) corresponding to the volcanic glass (Figures 1.I.a). These intensity decreases indicate that the initial glass was dissolved and that minerals were formed during the experiments (Figure 1.I). ~~(corresponding to the appearance of XRD peaks indexed by their position in Å on the XRD patterns, figure 1.I, and the indexed spectral band in µm, figure 1.II).~~ To assess the ~~rate of~~ dissolution % of the volcanic glass, the full pattern fitting method [*Chipera and Bish*, 2013] was applied. This method consists of determining the difference in area between the XRD peaks corresponding to both the original

glass and the weathered sample. The results obtained show that 19, 23 and 25% of volcanic glass (±2%, uncertainty on laboratory mixture between basaltic glass and zinc) was dissolved during the experiments under 100% N_2, 10% CO_2 / 90% N_2 and 100% CO_2 initial gas mixtures, respectively. The intensities of the XRD peaks corresponding to forsterite, pyroxene and quartz do not display ~~any~~ differences between the unreacted basalt and all the weathered products. This means that they have not been ~~weathered~~ dissolved ~~completely~~ ~~completely~~ during the experiments.

For non-clay minerals, the XRD peaks at 3.02, 2.48 and 1.87 Å (Figure 1.I.b) indicate the presence of Ca-Mg-Fe carbonate for the 100% CO_2 experiment while for the 10% CO_2 / 90% N_2 experiment, the XRD peaks at 3.85, 3.04, 2.49, 2.09, 1.93, 1.91 and 1.88 Å (Figure 1.I.c) correspond to calcite. The NIR spectra confirm the presence of carbonates, due to the spectral band at 3.85 and 3.98 µm corresponding to the C-O liaison (Figure 1.II.b and c, [*Gaffey*, 1985 and *Hunt*, 1977]). Note that, during the 100% N_2 experiment no carbonate mineral was formed. The XRD peaks at 7.13, 4.94, 4.14, 4.06, 3.25, 3.13 and 2.67 Å correspond to the formation of garronite zeolite for the experiment under 100% N_2 (Figure 1.I.d), while no zeolite is formed in experiments involving CO_2 gas (Figure 1.I.b and c). There is no evidence of a characteristic zeolite band from the NIR analysis. This could either be due to low proportions relative to the trioctahedral phyllosilicates, and/or due to overlapping of the characteristic spectral bands for phyllosilicates and zeolites. Indeed, the bands near 1.41 µm and at 1.91 µm correspond to the bending and stretching overtone of bound water, and between 2.19 - 2.5 µm to cation-OH liaison (Figures 1.II.b, c and d). The combination of bands at 2.76, 2.90 and 3.07 µm (Figures 1.II.b, c and d) corresponds to OH fundamental stretching and H_2O stretching in di/tri-octahedral

phyllosilicates, such as, smectites and/or chlorites [*Bishop et al.*, 1994; *Clark et al.*, 1990; *Hunt and Salisbury*, 1970].

The presence of clay minerals can be confirmed by the bulk XRD patterns due to the presence of 00*l* reflections at 15.09 and 2.57 Å (F~~f~~igures 1.I.d c and b), at 7.35 and 2.39Å under 10% CO_2 / 90% N_2 and 100% CO_2 experiments (F~~f~~igures 1.I.b and c, respectively); as well as 020 reflections at 4.57 Å (Figures 1.I.b, c and d). No evidence of rational series of 00*l* reflections (*l*×00*l* is constant for all the reflections) was seen; therefore, clay minerals present in the samples are mainly mixed layer minerals (MLM). More detailed identification of clay minerals present in the samples after the experiments, was performed using conventional XRD treatments (s~~S~~ee section 3.3.1 and ~~F~~figures 2.I and II) and by removing the continuum of the spectral data to highlight the absorption band intensities (Figure 2.III). The determination of the di/tri-octahedral character~~s~~ of the minerals formed are based on the NIR analysis and not on the XRD patterns dedicated to the d(060) peaks (see supplementary Figure S1). Indeed, the XRD patterns dedicated to the measurement of the d(060) (Figure S1) exhibit only slight differences in peak position between the three experiments. Conversely, the NIR analysis (Figure 2.II) exhibits more variation on the di/tri-octahedral character of the minerals formed. Different reasons can be evoked, as explained below. The NIR analysis is a direct probe to investigate the metal-OH bond in the octahedral sheet of clay minerals (see *Petit and Madejova*, [2013] and references therein). Therefore, NIR analysis is less affected by the difference in poorly compared to ~~/~~well crystalline clay minerals formed than XRD analysis.~~,~~ ~~and~~ In addition NIR spectroscopy has already been largely used in the identification of di/tri-octahedral clay minerals on the Martian surface (s~~S~~ee *Carter et al.*, [2015] and references therein). ~~Moreover, t~~The investigation of the di/tri-octahedral clay minerals via the d(060) position could be more difficult than explained by *Brindley and*

Brown, [1985]. In fact, the d(060) peak position is also dependent on the amount of Fe^{3+}/Al^{3+} substitution in the octahedral and/or tetrahedral sheets [*Baron et al.*, 2017; *Iriartre et al.*,2005; *Petit and Decarreau*, 1990*; Petit et al.*, 2015]. Depending on the Fe^{3+}/Al^{3+} content ~~(~~both octahedral and/or tetrahedral~~)~~, the d(060) could reflect the position of trioctahedral clay minerals (~1.54 Å, *Brindley and Brown*, [1985]), while only dioctahedral clay minerals are present [*Petit et al.*, 2015]. ~~NIR analysis is also less affected by the difference in crystallinity of the clay minerals formed than XRD analysis.~~ Additionally, non-clay minerals calcite, forsterite and quartz present XRD peaks in the range of the 060 peaks analysis, complicating interpretation.

For the 100% N_2 experiment (Figure 2.I.c, 2.II.c), the reflection at 14.82 Å in the Ca-AD state shifts to 16.69 Å, and its 002 reflection at 8.35 Å appears in the Ca-EG state. Moreover, the reflection shifts to 11.55 Å in the K-110 state and then to 10.41 Å after heating at 330 and 550°C. This XRD behavior is attributed to smectite layers. NIR confirmed this analysis with V-shaped bands at 1.91 and 2.31 µm (Figure 2.III.c), which correspond to H_2O stretching and bending bands, and $(Fe,Mg)_3$-OH stretching and bending bands of trioctahedral smectite, respectively. The absorption band at 2.35 µm could correspond to $(Fe,Mg)_3$-OH liaisons of Fe-rich trioctahedral chlorite (Figures 2.III.a, b and c) [*Bishop et al.*, 2008; *King and Clark.*, 1989]. The band near 2.43 µm (Figures 2.III.b and c) could be due to the presence of Fe^{2+} and/or Mg^{2+} in the octahedral sheet of TOT phyllosilicates and its intensity is related to the relative amount of Fe and Mg [*Mustard*, 1992]. The position and the strength of this band would indicate a high Fe content in the smectite layers for the 100% N_2 experiment. The slight band at 2.25 µm (Figures 2.III.a and b) corresponds to Al^{3+},Fe^{3+}-OH bending and stretching overtone in dioctahedral chlorite and/or smectite. Therefore, from the XRD behavior and NIR analysis, this sample

~~constitutes~~ is composed of a trioctahedral-rich smectite and to ~~in~~ a lesser extent of ~~a minor proportion of~~ a dioctahedral smectite or ~~/~~chlorite ~~mixed-layer mineral (~~MLM~~)~~.

With CO_2 % increase (Figures 2.I.b, 2.I.a, 2.II.b, 2.II.a, 2.III.b, 2.III.a), the XRD behavior of smectite layers corresponding to a ~~(~~shift of the XRD peaks between Ca-AD and Ca-EG state to lower angles~~)~~ becomes less pronounced and spectral band intensities of the smectite layers decreases. The ~~(~~ absorption of the hydration band near 1.9 µm~~,~~, the absorption band of $(Fe,Mg)_3$-OH liaison at 2.31 µm decrease and the band at 2.43 µm ~~disappearance~~ disappears ~~of the band at 2.43 µm~~, (Figures 2.III.a and b). While this phenomenon could be partly attributed to a decrease in the coherent scattering domain size of the clay minerals, it mainly indicates a decrease in trioctahedral smectite layers content with the CO_2 % increase. Inversely, the XRD peak intensities at 7.35 Å in the Ca-AD state increase with the CO_2 % (Figures 2.I.a, b). This XRD peaks shifts slightly to 7.60 Å in the Ca-EG state and hence shows the presence of smectite layers (Figures 2.I.a and b). Moreover, this XRD peak does not shift between 110 - 330°C and disappears after 550°C (Figures 2.II.a and b). This XRD behavior is suggestive of kaolinite layers and/or of the 002 reflection of Fe-rich chlorite layers (dehydration of the octahedral sheet of 2:1 layer of Fe(II) rich chlorite below 550°C; *Barnishel and Bertsch*, [1989]). However, the infra-red spectra do not exhibit the characteristic bands of kaolinite (at 2.16 and 2.2µm, *Bishop et al.*, [2008])~~;~~. In addition, ~~therefore, no kaolinite layers are present in these samples. T~~the absorption bands at 2.35 µm are more pronounced with the CO_2 % increase and disappear after heating at 550°C (s~~S~~ee supplementary Figure S2). This band could be linked to $(Fe,Mg)_3$-OH liaisons of Fe-rich trioctahedral chlorite [*King and Clark.*, 1989]. Note that, this XRD and NIR behavior could not be attributed to serpentine (while the XRD peak position could correspond to serpentine) because its dehydration temperature is at 600°C [*Dlugogorski. and Balucan*, 2014].

Therefore, from the XRD behavior and the ~~2.35 µm~~ NIR ~~band~~analysis, this clay mineral ~~constitutes~~ is ~~mainly~~ a Fe-rich dioctahedral MLM with a much lower amount of smectite layers. Finally, in order a Fe-rich trioctahedral chlorite/smectite MLM with increasing the CO_2 %. The relative amount of such MLM, compared to the trioctahedral smectite, ~~content for the 100% N_2 experiment,~~ increases with the CO_2%. In addition with the CO_2% increase, the dioctahedral character of the clay minerals is increasingly pronounced and can be assessed by the NIR analysis. The ~~due to the intensity~~ intensities ~~increase~~ of the 2.19 and 2.25 µm spectral band (Figures 2.III.a, b and c), which are related to Al_2-OH and (Al,Fe)$_2$-OH liaison, increase with the CO_2 %. These bands correspond to dioctahedral smectite/chlorite MLM. The presence of this MLM is confirmed by XRD due to the shift of the peak positions at 14.82 and 16.69 Å in the Ca-AD and CA-EG state, respectively (Figures 2.I.a, b and c).

Table 3~~2~~ presents the summary of minerals formed during the experiments. The results obtained show that zeolite~~s~~ formed without carbonate formation for the 100% N_2 experiment, while carbonates without zeolites are formed under experiments involving CO_2. Moreover, with the increase in CO_2 levels, the trioctahedral smectite/chlorite MLM content decreases, while the dioctahedral MLM increases. In addition with the increasing CO_2 levels, the relative content of trioctahedral smectite layers decreases ~~relative to~~in favor of the Fe-rich trioctahedral chlorite~~,~~ ~~with increasing CO_2 levels~~. Note that, zeolite mineral formation during the 100% N_2 experiment cannot be observed by NIR analysis, but XRD analyses confirms its presence.

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4.2 Geochemical model results

To better understand the mechanism leading to mineral formation as a function of gas composition, geochemical modeling was performed and constrained by the experimental results (for more details see section 3.4, materials and methods).

At first~~In a first time~~, the geochemical simulations are run until the given dissolution basaltic glass % estimated by XRD is reached. This solution has been chosen rather than a

kinetics method in order to avoid any limitation due to clay minerals, carbonates and zeolites formation, which lead to a decrease of the dissolution rate of the basaltic glass (s~~S~~ee for example, *Stockmann et al.* [2008]). Then, ~~T~~the ~~results obtained from the~~ geochemical modeling ~~are presented at the corresponding percentage of glass dissolution determined by XRD for each experiment (see section 4.1)~~results ~~and~~ are compared to the mineral identification ~~results~~ (Table 3~~2~~). ~~The aim is to compare mineral formation between the experimental results and the geochemical simulation,~~ in order to confirm that the ~~results obtained by the~~ geochemical simulations are coherent with the experiments. The clay mineral~~s~~ identification has shown that their crystal structure constitutes s~~a s~~tacking of layers with different nature~~s~~ (mixed-layer-minerals). Nevertheless, the geochemical simulation does not take into account the formation of these MLMs. Indeed, even if solid-solution products (~~(~~same layer nature but different interlayer cations)~~)~~ are authorized, it does not simulate mixed~~-~~-layer minerals. Therefore, clay mineral identification (Table 2 and 3~~2~~) is split into two families, the di- and tri-octahedral phyllosilicates. The dioctahedral phyllosilicates formed during the simulations consist of the sum of montmorillonite ~~(mainly $(Mg,Ca)_{0.165}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$)~~, nontronite ~~(mainly $(Mg,Ca)_{0.165}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$)~~, dioctahedral chlorite ~~$(Fe,Mg)_2Al_4Si_3O_{10}(OH)_8$~~ and kaolinite ~~$(Al_2Si_2O_5(OH)_4)$~~. The trioctahedral phyllosilicates formed during the simulations correspond to the sum of saponite ~~(mainly $(Mg,Ca)_{0.165}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$)~~, trioctahedral chlorite ~~$(Fe,Mg)_5Al_2Si_3O_{10}(OH)_8$~~ and talc ~~$(Fe_3Si_4O_{10}(OH)2)$~~. Due to the lack of garronite in the geochemical database, the zeolites considered and that appear during the geochemical simulation are mainly gismondine ~~$(Ca_2Al_4Si_4O_{16}\cdot 9H_2O)$~~ and, to a lesser extent, phillipsite ~~$((Na,Ca_{0.5})_4AlSi_3O_8\cdot 3H_2O)$~~. Gismondine, phillipsite and garronite belong to the group of zeolites with chains of edge-sharing four-membered rings [*Dyer*, 2002]. In particular the gismondine, which is the zeolite mainly formed during the geochemical simulation, has the same subgroup structure type as the garronite: the GIS group. Moreover, the structural formula of garronite

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($Ca_{2.5}NaAl_6Si_{10}O_{32}$:$13H_2O$) is similar to that of gismondine and phillipsite zeolites (in terms of cation content). In addition, the Si/Al ratio of garronite is comprised between the Si/Al ratio for gismondine and phillipsite zeolites (1 for gismondine, 3 for phillipsite and ~1.7 for garronite). Therefore, even if the garronite zeolite is not thermodynamically documented, the choice of simulating its formation with gismondine and phillipsite is coherent.

The geochemical simulation results show that the same minerals formed during the experiments were simulated during the geochemical exercise (Table 23). The characterization of the carbonates formed is the same (e.g., calcite under 10% CO_2 / 90% N_2 and solid-solution of Ca/Mg/Fe carbonate under 100% CO_2). Note that at the end of the experiment, the final pCO_2 obtained by the geochemical simulation in the experiments with initial gas mixture of 100% CO_2 and 10% CO_2 / 90% N_2 (calculated from the geochemical modeling results) are equal to 0.79 and 0, for initial gas mixture of 100% CO_2 and 10% CO_2 / 90% N_2 respectively. Zeolite is formed for the 100% N_2 experiment in both the geochemical simulation and the experiments. ; while fFor the 10% CO_2 / 90% N_2 experiment, a minor amount is estimated during the geochemical simulation while, no zeolite is observed during the experimentthis is not the case for the experimental part. Nevertheless, the amount estimated is low relative to the other minerals (1%). If zeolite was formed during the experiment, it could explain why it had not been detected by XRD and NIR. The geochemical simulation could have estimated zeolite formation and long experiment time will have led to their formation. Concerning geochemical simulation of the clay minerals, as for the experimental results mainly trioctahedral clay minerals are predicted (as for the experimental results) for the 100% N_2 experiment while mainly dioctahedral phyllosilicates are predicted and observed in the experiments during the experiments involving CO_2. More generally, the same overall trends are obtained between the experiments and the geochemical simulation. Indeed, with the CO_2 % increase, the amount of trioctahedral phyllosilicates decreases and the inverse trend is observed for the dioctahedral minerals. In the same manner, the

CO_2 % increase leads to a decrease in zeolite content and an increase in carbonate~~s~~ formation. The pH values at the end of the experiments obtained by geochemical simulation are 6.3, 7.8 and 10.1 for the 100% CO_2, 10%CO_2 / 90% N_2 and 100% N_2 experiments, respectively. The final pH values decrease with the increase of initial CO_2 %. To conclude, while there are noticeable differences between the geochemical simulation and the experimental results, the same general trends are observed with CO_2 % increase, which confirms the constraints, used and validates the geochemical simulation.

5. Discussion

5.1 pH, a key to understanding mineral formation competition

The hydrothermal alteration of the tholeiitic volcanic glass, performed in this work, produced ~~phyllosilicates~~clay minerals~~ (di- and/or tri-octahedral, depending on the experimental conditions)~~, carbonates (with CO_2) and zeolites (initially CO_2-free). The minerals formed are in line with previous experiments performed on tholeiitic basalt. Reaction products obtained from experiments with various pCO_2 (from 1 to 35 bars) at various temperatures (from ambient to 250°C) on volcanic glass, contain trioctahedral smectites, chlorites, talc, carbonates and zeolites [*Declercq et al.*, 2009; *Gysi and Stefánsson*, 2011; 2012a; b; c; *Hellevang et al.*, 2013; *Stefánsson and Gíslason*, 2001]. The experimental conditions have been chosen to better understand the key parameters driving zeolite and/or carbonate formation with trioctahedral minerals as observed on Mars (*Viviano-Beck et al.* [2017]; *Wray et al.* [2016] and section 2 of this study). The initial experimental conditions have a strong influence on whether such minerals form and the relative amounts produced (Table ~~2~~3). In order to grasp the factors involved in these mechanisms of formation, geochemical modeling has been applied in this work.

Figure 3 presents the results of the geochemical modeling. The~~,~~ predicted mineral formed ~~(~~in mol~~)~~ by the simulation (mineral in equilibrium with the aqueous solution during the dissolution of the basaltic glass) and the percentage of dissolution (mol of basaltic glass dissolved divided by the initial mol of basaltic glass) are plotted as a function of pH. We consider ~~As.,~~pH ~~which is a~~ key parameter to understand the formation of these minerals from the weathering of tholeiitic volcanic rock [*Gysi and Stefánsson*, 2012a; *Stefánsson and Gíslason*, 2001]. ~~Figure 3 represents the evolution of the minerals formed (solid lines) as a function of pH for closed systems (atmosphere and aqueous solution are not renewed during the simulation).~~ The mineral predicted and dissolution~~se~~ evolutions vary between the experiments. This is driven by ~~and the % of dissolution (dashed grey lines) due to~~ the decrease of ~~the~~ CO_2 content in the available head-space gases~~-~~ (carbonation) and ~~due to~~ the release of the chemical elements from the dissolution of the basaltic glass. The presence of CO_2 in the aqueous solution and in the head space controls the pH of the aqueous solution, due to the dissociation of aqueous CO_2 into $HCO_3^- + H^+$. Therefore, the increase of the initial CO_2 % leads to a decrease of the initial pH (Figure 3), with pH ~~(~~6, 4.8, 4.3 for the 100% N_2, 10% CO_2 / 90% N_2 and 100% CO_2 simulations, respectively~~)~~. During the basaltic glass dissolution (represented by the % of dissolution, dotted grey lines, Figure 3), the CO_2 present in the aqueous solution and in the head space are consumed by the carbonation as a consequence the aqueous pH increase. The ~~(~~ final pCO_2 calculated from the geochemical modelling results are equal at 0.32 and 0 for the 100% CO_2 and 10% CO_2 / 90% N_2, respectively~~;~~ ~~the pCO_2 were calculated from the geochemical modelling results)~~.

During carbonation (Fig.3.I and II), di- and tri-octahedral phyllosilicates are formed with a pH <~7.2, while when pH >~7.2 (after 12% of dissolution for 10% CO_2 / 90% N_2 and 100% N_2 simulation Figures 3.II and 3.III, respectively) the minerals formed are trioctahedral

phyllosilicates and zeolites. Therefore, the CO_2 % content has a strong influence on the mechanism leading to the dioctahedral clay minerals, carbonate or zeolite formation. As seen by the models dedicated to the 10% CO_2 / 90% N_2 experiments (Fig 3.II), the dioctahedral phyllosilicate~~s~~ content increases until pH ~7.2 and then decreases in favor of zeolite content. The increase of zeolite content is also accompanied by a decrease in the formation of carbonates. These minerals are competing and the formation of one inhibits the formation of the other, such as: dioctahedral clay minerals versus zeolites and carbonates versus zeolites (see figure 3.II).

~~Indeed, t~~The increase in zeolite formation is due to both the availability of Ca^{2+} and due to the decrease in formation of carbonates, which is accompanied by a pH increase (due to carbonation) until pH ~7.2. That pH dependency has already been suggested as a key factor to understand zeolite formation. In fact, *Burriesci et al.* [1984] argue that pH is a more important factor than time and temperature. Moreover, as observed on soil on Earth, zeolite minerals are generally described in neutral to basic soils [*Ming and Boettinger*, 2001; *Ming and Mumpton*, 1989]. Reciprocally, zeolites can be dissolved from soil samples by using acid treatments [*Ming and Boettinger*, 2001]. Moreover, it is also described during the weathering process of basaltic glass by geochemical modeling: a pH above 6.5 at 45°C leads to the formation of zeolite [*Gysi and Stefánsson*, 2012a]. Indeed, the pH increase leads to the deprotonation of $H_4SiO_{4(aq)}$ into $H_4SiO_3^-$ and $H_4SiO_2^{2-}$ and to high cation/H^+ ratios that are needed for the formation of zeolite minerals [*Chipera and Apps*, 2001; *Ming and Boettinger*, 2001; *Mora-Fonz et al.*, 2007]. Conversely, dioctahedral phyllosilicates are formed with pH <~7.2 in disfavor of zeolites (Figure 3, Table ~~2~~3). This pH dependency could be a consequence of the incorporation of aluminum and silica to build the framework of dioctahedral phyllosilicates and zeolites. The similarity between zeolites and dioctahedral minerals are their structural formulae, notably regarding the

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predominance of Si and Al. Even if no further explanation can be drawn from our study, it seems that the silica and aluminum in solution plays a key role in mineral formation: pH <~7.2 lead to dioctahedral phyllosilicates, while pH >~7.2 conditions lead to zeolites.

~~Moreover, t~~The formation of trioctahedral ~~smectite~~ clay minerals ~~dedicated to Martian environments~~ does not appear to have strong pH dependency.~~;~~ They can be formed~~it is possible to form these~~ from both acidic and basic conditions (pH 4 in~~,~~ *Peretyazhko et al.* [2016], basic~~)~~ ~~and basic conditions [~~, *Tosca et al.*, [2008], both *Gysi and Stefánsson* [2012a]). Nevertheless, for the same temperature and alteration time, the content of Fe-rich trioctahedral chlorite increases relative to the content of trioctahedral smectite with the increase of CO_2 % and ~~/~~or acidity ~~(source of acidity could come from other aqueous species in the solution).~~ . The source of acidity could either come from atmospheric gases or aqueous solution. Finally, the ratio between di- to tri-octahedral minerals decreases with the pH increase and is therefore a good indicator of alteration conditions.

The intrinsic parameter, which seems to govern the competition of formation between dioctahedral phyllosilicates~~/~~ versus zeolites and carbonates~~/~~ versus zeolites, is pH. When the pH is <~7.2, dioctahedral clay minerals are favored; while, when the pH is above 7.2, zeolites are formed in disfavor of dioctahedral clay minerals. The competition between di- and tri-octahedral phyllosilicates/carbonates/zeolites ~~competition~~ formation is a probe of the pH evolution of the weathered solution. The association of dioctahedral phyllosilicates with carbonates will be an indicator of acidic conditions, while the association of trioctahedral phyllosilicates with carbonates will be an indicator of a fluid that could be acidic to < ~7.2. The indicator of basic conditions is the association between trioctahedral phyllosilicates and zeolites. As consequence,

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the association with trioctahedral phyllosilicates, carbonates and zeolites will indicate that the weathering fluid has passed through pH =~7.2.

5.2 Martian implications

The results of this study are likely more relevant to understanding alteration by hydrothermal fluids with different CO_2 % content rather than the impact of total atmospheric CO_2 levels. In closed system experiments, the CO_2 in the gas~~-~~head space is consumed during the experiment. ~~and t~~Hence, the CO2 levels ~~herefore~~ do ~~es~~ not necessarily represent a CO_2 partial pressure change, as suggested for the early Mars atmosphere evolution, because the real atmosphere would buffer this level. ~~Nevertheless, c~~Co-occurrence of carbonates and/or zeolites with trioctahedral phyllosilicates has been observed on Martian Noachian crust (*Viviano-Beck et al.* [2017]; *J. J. Wray et al.* [2016] and section 2). The geological formation process for such mineral assemblages has putatively been assigned to hydrothermalism [*Brown et al.*, 2010; *Ehlmann et al.*, 2011; *Niles et al.*, 2013; *Viviano et al.*, 2013]. The hydrothermal experimental results obtained during this study are in line with previously discussed Martian observations (Figure 1 and 2 and Table ~~2~~3). Indeed, these two mineralogical assemblages have been formed during the experiments under 100% N_2 and 10% CO_2 / 90% N_2.

The source of CO_2 levels in the hydrothermal fluids cannot be determined from this study, but it could come from either the Martian atmosphere or magma [*Brown et al.*, 2010*; Bultel et al.*, 2015]. The hydrothermal experiments and their geochemical modeling show the strong link between the formation of carbonates and zeolites during hydrothermal alteration in the presence of CO_2. Due to the occurrence of trioctahedral phyllosilicates/carbonates and trioctahedral phyllosilicates/zeolites at different conditions, a counter relationship between these two assemblages (Al-phyllosilicates/zeolites and carbonates/zeolites) could certainly have existed

during early Mars. Thus, these reaction products can be used as an indicator for environmental conditions due to the constraint given by their formation limits. Therefore, the observation of trioctahedral phyllosilicates and zeolites on the Martian crust [*Ehlmann et al.*, 2009; *Viviano-Beck et al.*, 2017] is an indicator of an alteration with an aqueous solution from a pH > ~7.2, while the occurrence of trioctahedral clay minerals and carbonates is an indicator of slightly acidic to ~7.2. Trioctahedral phyllosilicates associated with carbonates and zeolites were observed in Valles Marineris [*Viviano-Beck et al.*, 2017] and impact craters [i.e.: *Sun and Milliken*, 2015]. This mineralogical association is an indicator that the aqueous solution has passed through a pH value of ~7.2 during the alteration process and perhaps in a closed hydrothermal system.

The formation of trioctahedral phyllosilicates characterizes the major part of the Martian weathered surface/outcrops formed in the Noachian~~ by~~ [*Bibring et al.* ~~(~~2006]. However, here we demonstrated that, with the wide range of aqueous CO_2 levels present during the experiments and used in the geochemical simulations, trioctahedral phyllosilicates have never been formed alone. Different studies without CO_2 involved have been able to produce trioctahedral minerals by~~from the~~ hydrothermal alteration~~ism~~ of a volcanic glass and have pointed out that specific acidic conditions (experiments using rock of basaltic composition, constant pH equal to ~4, *Peretyazhko et al.* [2016]) are needed to form only trioctahedral minerals. Therefore, the widespread presence of trioctahedral phyllosilicates (mainly smectitic) on Martian crust could imply acidic conditions instead of a circum-neutral pH [*Bibring et al.*, 2006; *Peretyazhko et al.*, 2016]. Nevertheless, the identification of zeolite when mixed with trioctahedral phyllosilicates (see section 2 of this study), is difficult by NIR analysis. Therefore, the confirmation of the presence/absence of zeolites (notably by lander/rover equipped with XRD, such as that on board the MSL mission)

with the widespread presence of trioctahedral phyllosilicates [*Bibring et al.*, 2006] is of prime interest. It could imply drastically different environmental conditions during early Mars: acidic and/or basic conditions. In addition, pH appears to be one of the most important parameters as a driver of mineralogical competitions (in addition to silica activity for the formation of zeolites). More experimental and geochemical modeling studies are required to investigate the clay minerals/carbonates/zeolites competition. Indeed, other gases such as SO_2, which is considered one of the important gases released during Martian volcanism [Cradock and Greeley, 2009], will significantly modify the competitive behavior.

Interestingly, when the percentage of aqueous CO_2 increases and consequently the pH decreases, the content of trioctahedral chlorite increases in disfavor of the trioctahedral smectite content (Figure 1 and 2). The observation on the relative content of chlorite compared to smectite as a function of depth (*Bultel et al.* [2015]; *Carter et al.* [2013]; *Loizeau et al.* [2012]; *Sun and Milliken* [2015]) could not only be related to burial diagenesis on Mars [*Sun and Milliken*, 2015], but also to fluid composition during hydrothermal alteration. Further experiments dedicated to this transformation using infrared and XRD characterization of the smectite/chlorite relative amounts in MLM will bring more constraints to the processes which led to this specific observation.

Conclusion and remarks

~~In the present study, we have investigated the di/tri-octahedral clay minerals/carbonates/zeolites relationship to better understand the early aqueous alteration in Martian history. Indeed~~On Mars, widespread occurrence of Fe,Mg-phyllosilicates have been observed by remote sensing instruments on Noachian terrains. Experimental investigations had shown that their conditions formations could be widespread in terms of pH range, oxic/anoxic

conditions, etc... Thus, the present study is dedicated to better constraint the formation conditions of clay minerals by using other minerals found in association with them on the Martian surface. While Fe,Mg clay minerals are the main minerals observed, c~~C~~arbonates and zeolites were also detected always associated with Fe/Mg phyllosilicates~~are~~. Here, we report on the dioctahedral versus zeolites and carbonates versus zeolites formation to better define the early Mars alteration history. ~~always associated with Fe/Mg phyllosilicates or can occur with both zeolites and Fe/Mg phyllosilicates. Hydrothermal~~ Hydrothermal experiments on a tholeiitic volcanic glass were performed~~, in this study,~~ in a closed system with a water-rock ratio of 20 and a head space of 520 ml. Three different initial gas mixtures with various CO_2 contents were used in the experiments: 100% CO_2, 10% CO_2 / 90 % N_2 and 100 % N_2. The minerals formed during the experiments were characterized by XRD and NIR analyses. Complementary geochemical modeling was done to reproduce the different experiments to establish the parameter driving the mineralogical formation. The experimental results show that ~~W~~with the decrease of CO_2 percentage, the content of dioctahedral clay minerals decreases in favor of trioctahedral minerals and zeolites. Carbonates are formed during the experiments containing CO_2 while zeolite is formed with a CO2-free fluid. The geochemical simulation provides insight into the aqueous alteration environment as a function of the mineral association. Three mineralogical associations could be used to follow the pH conditions during the alteration. ~~Indeed, d~~Dioctahedral clay minerals and carbonate minerals are formed under pH <~7.2 (at 120°C)~~acidic conditions.~~ ~~and trioctahedral~~ Trioctahedral minerals are formed with carbonates from pH >6 (at 120°C)~~neutral pH aqueous solutions~~. ~~Moreover,~~Finally, trioctahedral clay minerals and zeolites are formed with a pH >~7.2.

~~Moreover,~~In addition, ~~–~~the results obtained here show that the relative content of trioctahedral chlorite compares to trioctahedral ~~/~~smectite increase with ~~de~~ decrease of acidity.

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Hence, the relative content of chlorite and smectite could not only have been related to burial diagenesis, but may also be a result of differing acidic fluids. More experiments and geochemical modeling using different fluids or ~~/~~atmosphere compositions (rich in SO_2, for example) will help to better define the mineral competition behavior and, therefore, to grasp the aqueous and alteration processes of early Mars.

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Figure caption

Figure 1: Bulk XRD patterns between 2-55 °2θ and NIR spectra of the unreacted basalt (I.a and II.a, respectively)~~, bulk XRD patterns and NIR spectra~~ and of the weathered basalt under 100% CO_2 (I.b and II.b, respectively), under 10% CO_2 / 90% N_2 (I.c and II.c, respectively) and under 100% N_2 (I.d and II.d, respectively). T~~he t~~riangles, ~~the~~diamonds and~~-~~, ~~the~~ stars represent the XRD peaks of forsterite, pyroxene and quartz respectively. From low to high angles, the peak position corresponding to: the triangles are at 5.12, 3.89, 3.50, 2.78, 2.52, 2.47, 2.36, 2.27, 2.56, 2.17 and 1.75 Å; to the stars are at 4.26 and 3.33 Å; and to the diamonds are at 3.20 and 2.99 Å

Figure 2: Comparison of the XRD patterns recorded on oriented preparation obtained in Ca-AD (black line) and Ca-EG (grey line) states for the weathered basalt under 100% N_2 (I.c), under 10% CO_2/90% N_2 (I.b) and under 100% CO_2 (I.a). Comparison of the XRD patterns recorded on oriented preparations obtained in Ca-AD (black line), K-110 (grey line), K-330 (blue line) and K-550 (red line) states for the weathered basalt under 100% N_2 (II.c), under 10% CO_2/90% N_2 (II.b) and under 100% CO_2 (II.a). Comparison of the NIR spectra continuum removed for the weathered basalt under 100% N_2 (III.c), under 10% CO_2/90% N_2 (III.b) and under 100% CO_2 (III.a).

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Figure 3: Geochemical results obtained from the dissolution of the basaltic glass for the 100% N_2 (I), 10% CO_2 / 90% N_2 (II) and 100% CO_2 (III) simulation as a function of pH.

Tables

Table 1: Total chemistry in oxides, the related calculated structural formulae and the Log(K) values of the original basalt used in the present study.

Oxides	SiO_2	Al_2O_3	Fe_2O_3(T)	MgO	NaO	K_2O	CaO	
%	48.2	14.2	12.0	9.4	1.9	0.3	11.7	
Elements	Si	Al	Fe	Mg	Na	K	Ca	O
mol	1	0.35	0.23	0.29	0.01	0.07	0.26	3.345
Temperature (°C)	0	25	60	100	150	200	250	300
Log(K)	18.10	16.30	13.86	11.59	9.28	7.37	5.71	4.21

~~**Table 2:** List of minerals and solid-solution added during the geochemical simulation to account of the lack of the original at the data0.cmp data base (from EQ3/6 software).~~ **Table 2:** List of minerals, ~~and~~ solid-solution added and suppressed during the geochemical simulation to account of the lack of the original at the data0.cmp data base (from EQ3/6 software).

Minerals / Solid-solutions	Structural formulae
Trioctahedral clay minerals:	
Saponite	$(Ca,Mg,Na_2,K_2)_{0.17}(Mg_3)(Al_{0.34}Si_{3.66})O_{10}(OH)_2$
Fe-rich saponite	$(Ca,Mg,Na_2,K_2)_{0.17}(Fe,Mg_2)(Al_{0.34}Si_{3.66})O_{10}(OH)_2$
Tri-chlorite	$(Fe,Mg)_5Al_2Si_3O_{10}(OH)_8$
Talcs	$(Mg,Fe)_3Si_4O_{10}(OH)_2$
Dioctahedral clay minerals:	
~~Montmorrillonite~~Montmorrillonites	$(Mg,Ca, Na_2,K_2)_{0.165}(Mg_{0.33}Al_{1.67})Si_4O_{10}(OH)_2)$
Nontronites	$(Mg,Ca, Na_2,K_2)_{0.165}(Fe_2)(Al_{0.33}Si_{3.67})O_{10}(OH)_2)$
Beidellites	$(Mg,Ca, Na_2,K_2)_{0.17}Al_{2.34}Si_{3.66}O_{10}(OH)_2$
Kaolinite	$Al_2Si_2O_5(OH)_4$
Di-chlorites~~Fe-sudoite~~	$(Fe,Mg)_2Al_4Si_3O_{10}(OH)_8$
~~Vermiculite~~Vermiculites	$(Ca,Mg, Na_2,K_2)_{0.43}(Mg_3)(Al_{0.43},Si_{3.14})O_{10}OH_2$
~~Illite~~Illites	$K_{0.85}(Mg,Fe)_{0.25}Al_{2.35}Si_{3.4}O_{10}(OH)_2$
Zeolites~~Phillipsite~~	
Phillipsites	$(Ca,N_2,K_2)_{0.5}AlSi_3O_8:3H_2O$
Gismondine	$Ca_2Al_4Si_4O_{16}:9H_2O$
Clinoptilolites	$(Ca, Na_2,K_2)_{0.55}(Si_{4.9}Al_{1.1})O_{12}:3.9H_2O$
Heulandites	$(Ca,Na_2)_1Al_2Si_7O_{18}:5H_2O$
Mordenite	$Ca_{0.2895}Na_{0.361}Al_{0.94}Si_{5.06}O_{12}:3.468H_2O$
Stellerite	$Ca_2Al_4Si_{14}O_{36}:14H_2O$

Natrolites	$(Ca,Na_2)Al_2Si_3O_{10}{\cdot}3H_2O$
Carbonates	$(Ca,Mg,Fe)CO_3$
Suppressed minerals	Reason why
prehnite, olivine, magnetite, biotite, graphite, wollastonite, amphibole and epidote	Formed in higher/pressure ranges
akermanite, monticellite and merwinite	Formed in metamorphosed sediments
Serpentines	Formed from olivine dissolution

Table ~~2~~3: Summary of the experimental results and mol of minerals predicted by the geochemical modeling at the same rate of dissolution as a function of the gas composition.

[a] The percentage of dissolution of the basaltic glass has been estimated by XRD with an uncertainty of ±2 % (for more details see section 4.1)

[b] The trioctahedral minerals correspond to the sum of trioctahedral smectite, trioctahedral chlorite and talc.

[c] The dioctahedral minerals correspond to the sum of dioctahedral smectite, kaolinite and illite.

[d] The carbonates are expressed as a solid solution between the proportion of calcite (Ca), magnesite (Mg) and siderite (Fe).

[e] The zeolites correspond to garronite for the experiments and to the sum of gismondine and phillipsite for the geochemical modeling (for more details see section 4.1 and 4.2).

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-, +, ++, +++ represent the relative abundance of the minerals (based on peak intensities) between the different atmospheres from non-present to the highest relative proportion.

Experiments / Simulation names	Dissolution %[a] (±2 %)	Minerals Experiments / Geochemical modeling ($.10^{-4}$ mol) Trioctahedral[b]		Dioctahedral[c]		Carbonates (Ca/Mg/Fe) %[d]		Zeolites[e]		pH (simulated)
100% N_2	19	+++	9.9	-	0.2	-	-	+	4.5	10.1
10% CO_2 / 90% N_2	23	++	6.6	+	9.4	+	16.6 (97/2/1)	-	2.8	7.8
100% CO_2	25	+	5.6	++	20.1	+	35.9 (68/20/12)	-	-	6.3

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