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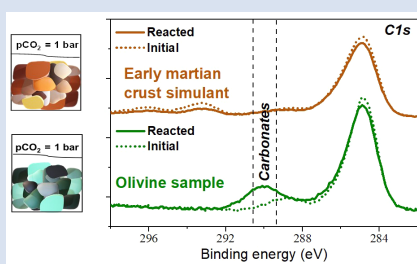
# The key role of bedrock composition in the formation of carbonates on Mars

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## Abstract



Martian carbonates are fundamental minerals for understanding the geochemical and climatic evolution of the planet and the search for potential life, representing one of the key objectives for the Perseverance rover at Jezero Crater. However, the scarcity of carbonate reservoirs on the surface compared to the extent of terrestrial carbonates questions whether these carbonates are indicators of past surface conditions or products from deeper processes unrelated to martian climate. We investigate the formation of carbonates by surface weathering under a CO<sub>2</sub> atmosphere in a suite of individual minerals and martian simulants based on the early Mars crust composition. We identify the formation of magnesium carbonates in olivine-bearing samples, but not in the early martian crust simulants. These findings are consistent with the association of carbonates with olivine-rich substrate detected on Mars and highlight the role of the substratum composition in the distribution of carbonates formed by surface processes. Hence, we conclude that the limited surface reservoirs of carbonate are reconcilable with the existence of a CO<sub>2</sub>-rich atmosphere on early Mars.

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## Introduction

Carbonates on Mars are reported from orbital, *in situ*, and martian meteorite studies. Apart from minor carbonates (<5 wt. %) identified within more recent polar terrains (Boynton *et al.*, 2009) and the carbonate compounds identified in three nakhlite meteorites (Bridges *et al.*, 2019), these carbonates are inferred to have formed during the Noachian epoch (*i.e.* >3.6 Ga). Indeed, the largest known carbonate-bearing unit, at Nili Fossae, is inferred to be pre-Hesperian in age (~3.8 Ga; Mandon *et al.*, 2020). Hypotheses for the formation of the Nili Fossae carbonates include both local hydrothermalism (Mangold *et al.*, 2007; Ehlmann *et al.*, 2009), and regional weathering (Ehlmann *et al.*, 2009), which is consistent with the persistence of fluvial activity in the region (Mangold *et al.*, 2007) and the inferred lacustrine precipitation of carbonates in the Jezero Crater (Horgan *et al.*, 2020). Similarly, the carbonate concretions in the ALH84001 meteorite, which formed at ~3.9 Ga, originated from cool water (18 ± 4 °C) that had interacted with atmospheric CO<sub>2</sub> (Halevy *et al.*, 2011). These observations indicate that carbonate minerals likely formed at, or near, Mars' surface during its early history, coinciding with the development of fluvial valleys and deep weathering profiles. These findings suggest that Mars experienced a warmer and wetter climate in its early history, likely

sustained by a thicker CO<sub>2</sub> atmosphere. Indeed, the MAVEN's observations show a significant loss of Mars' atmosphere (<0.8 bar CO<sub>2</sub>) in its early history (Jakosky *et al.*, 2018). Therefore, the observational evidence from both the surface and the upper atmosphere points toward extensive interactions between the early Martian crust, an active hydrosphere, and a thicker CO<sub>2</sub> atmosphere.

Climatic conditions in this early Mars could have induced abundant carbonate precipitation in near surface environments. However, orbiting near-infrared spectrometers primarily detect phyllosilicates and sulphates among alteration minerals, whereas carbonate minerals are relatively rare (Carter *et al.*, 2023). Keep in mind that the identification of minerals by remote sensing spectra can be obscured by dust. The scarcity of large carbonate reservoirs could be explained by an acidic period in the Hesperian age that prevented their formation and dissolved those previously formed. However, the extension and age of Nili Fossae carbonates contradict such a hypothesis.

The overall composition of Mars' bedrock is commonly inferred to be basaltic and olivine-rich (olivine > 20 wt. %) (*e.g.*, McSween *et al.*, 2006). However, recent analyses of igneous rocks from the ancient bedrock surrounding Gale Crater (Mangold *et al.*, 2016) and of ancient Martian meteorites (Hewins *et al.*, 2017) suggest that felsic and alkali-rich rocks

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**Table 1** Summary of the samples analysed in this study. The bulk chemical composition of martian simulants samples was estimated according to the proportion of the minerals used (Baron *et al.*, 2019).

Individual minerals	Structural formula			
Mg-olivine (Fo <sub>92</sub> )	Al <sub>0.01</sub> Mg <sub>1.78</sub> Fe <sub>0.16</sub> Si <sub>1.05</sub> O <sub>4</sub>			
Ferroan olivine (Fo <sub>65</sub> )	Mg <sub>1.30</sub> Fe <sub>0.70</sub> Si <sub>1.00</sub> O <sub>4</sub>			
clinopyroxene (augite)	Na <sub>0.09</sub> Ca <sub>0.58</sub> Al <sub>0.19</sub> Mg <sub>0.92</sub> Fe <sub>0.21</sub> Si <sub>1.92</sub> Al <sub>0.08</sub> O <sub>6</sub>			
plagioclase (An <sub>60</sub> )	K <sub>0.01</sub> Na <sub>0.39</sub> Ca <sub>0.60</sub> Al <sub>1.53</sub> Mg <sub>0.01</sub> Fe <sub>0.01</sub> Si <sub>2.44</sub> O <sub>8</sub>			
K-feldspar (Or <sub>85</sub> )	K <sub>0.85</sub> Na <sub>0.15</sub> Al <sub>0.97</sub> Mg <sub>0.01</sub> Fe <sub>0.01</sub> Si <sub>3.01</sub> O <sub>8</sub>			
Martian crust simulants	Minerals (wt. %)		Chemical Compositions (wt. %)	
Martian crust simulant-O (Sim-O)	Ferroan olivine (Mg <sub>1.30</sub> Fe <sub>0.70</sub> Si <sub>1.00</sub> O <sub>4</sub> )	11.8	SiO <sub>2</sub>	52.5
	Orthopyroxene (Na <sub>0.03</sub> Ca <sub>0.04</sub> Al <sub>0.08</sub> Mg <sub>1.58</sub> Fe <sub>0.27</sub> Si <sub>2.01</sub> O <sub>6</sub> )	17.7	Al <sub>2</sub> O <sub>3</sub>	13.3
	Clinopyroxene (Na <sub>0.09</sub> Ca <sub>0.58</sub> Al <sub>0.19</sub> Mg <sub>0.92</sub> Fe <sub>0.21</sub> Si <sub>1.92</sub> Al <sub>0.08</sub> O <sub>6</sub> )	23.5	FeO	6.9
	Plagioclase (K <sub>0.01</sub> Na <sub>0.39</sub> Ca <sub>0.60</sub> Al <sub>1.53</sub> Mg <sub>0.01</sub> Fe <sub>0.01</sub> Si <sub>2.44</sub> O <sub>8</sub> )	32.4	MgO	13.2
	K-feldspar (K <sub>0.85</sub> Na <sub>0.15</sub> Al <sub>0.97</sub> Mg <sub>0.01</sub> Fe <sub>0.01</sub> Si <sub>3.01</sub> O <sub>8</sub> )	12.8	CaO	8.4
	Apatite (Ca <sub>4.67</sub> Na <sub>0.08</sub> Mg <sub>0.04</sub> (P <sub>2.85</sub> Si <sub>0.06</sub> O <sub>4</sub> ) <sub>3</sub> F <sub>1.21</sub> Cl <sub>0.06</sub> )	2	Na <sub>2</sub> O	2.0
			K <sub>2</sub> O	1.9
		P <sub>2</sub> O <sub>5</sub>	1.7	
Martian crust simulant-M (SIM-M)	Magnetite (Fe <sub>3</sub> O <sub>4</sub> )	10.9	SiO <sub>2</sub>	49.3
	Orthopyroxene (Na <sub>0.03</sub> Ca <sub>0.04</sub> Al <sub>0.08</sub> Mg <sub>1.58</sub> Fe <sub>0.27</sub> Si <sub>2.01</sub> O <sub>6</sub> )	17.8	Al <sub>2</sub> O <sub>3</sub>	13.7
	Clinopyroxene (Na <sub>0.09</sub> Ca <sub>0.58</sub> Al <sub>0.19</sub> Mg <sub>0.92</sub> Fe <sub>0.21</sub> Si <sub>1.92</sub> Al <sub>0.08</sub> O <sub>6</sub> )	23.7	FeO	12.9
	Plagioclase (K <sub>0.01</sub> Na <sub>0.39</sub> Ca <sub>0.60</sub> Al <sub>1.53</sub> Mg <sub>0.01</sub> Fe <sub>0.01</sub> Si <sub>2.44</sub> O <sub>8</sub> )	32.7	MgO	9.6
	K-feldspar (K <sub>0.85</sub> Na <sub>0.15</sub> Al <sub>0.97</sub> Mg <sub>0.01</sub> Fe <sub>0.01</sub> Si <sub>3.01</sub> O <sub>8</sub> )	12.9	CaO	8.6
	Apatite (Ca <sub>4.67</sub> Na <sub>0.08</sub> Mg <sub>0.04</sub> (P <sub>2.85</sub> Si <sub>0.06</sub> O <sub>4</sub> ) <sub>3</sub> F <sub>1.21</sub> Cl <sub>0.06</sub> )	2	Na <sub>2</sub> O	2.1
			K <sub>2</sub> O	2.0
		P <sub>2</sub> O <sub>5</sub>	1.8	

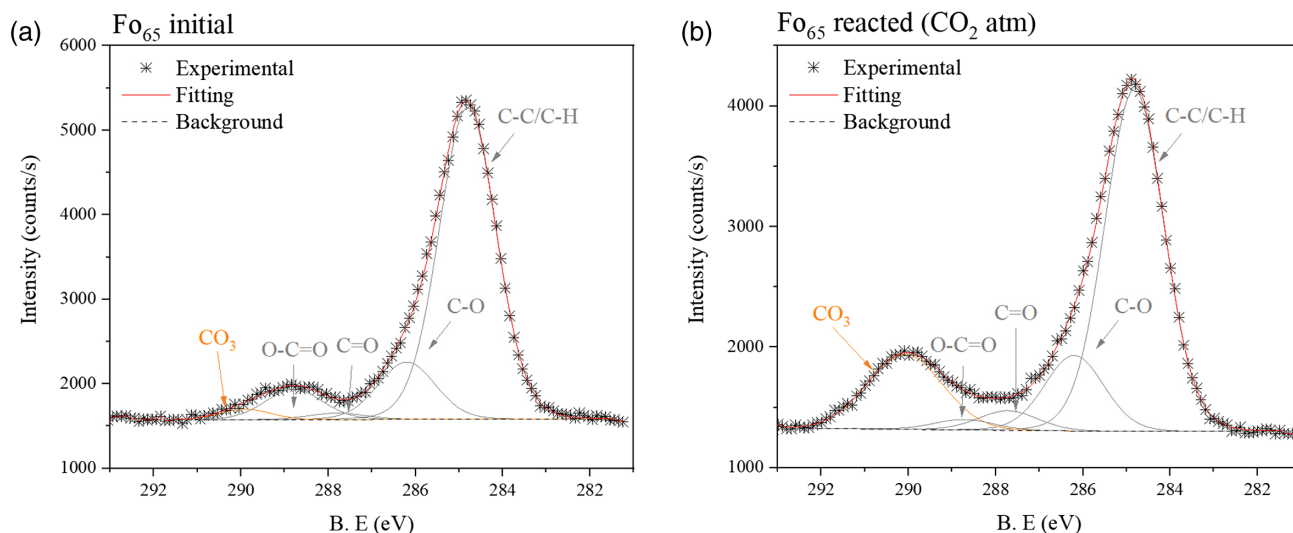
are more abundant in the Mars' ancient crust than initially presumed (Sautter *et al.*, 2016). Therefore, most carbonates >3.6 Ga old may have been formed from the alteration of this ancient crust, and not from the post-Noachian basaltic plains. In this study, we investigate the role of the bedrock compositions on the formation of carbonate by aqueous alteration. In prior experiments simulating early Mars conditions (pCO<sub>2</sub> = 1, T = 45 °C), moderate (Gaudin *et al.*, 2018) to minor magnesium carbonates (Dehouck *et al.*, 2014) were identified from forsteritic-olivine (Fo<sub>90</sub>) weathering. However, Fourier transform infrared spectroscopy (FTIR) showed no carbonate detection (>~0.8 wt. %) in less magnesian olivines under similar geochemical conditions (pCO<sub>2</sub> from 0.1 to 1 bar, T = 25 °C; Kissick *et al.*, 2021). These weathering experiments focused on olivine minerals alone. Here, we experimentally investigate the reactions of a range of potential crustal compositions (*e.g.*, from ultramafic to more felsic composition) on carbonate formation under a thick CO<sub>2</sub> atmosphere (1 bar). The initial materials cover various individual silicate minerals including two types of olivine (Fo<sub>92</sub> and Fo<sub>65</sub>) to assess differences between the Mg-rich forsterite with the more Fe-rich forsterite identified at Nili Fossae (Brown *et al.*, 2020), pyroxenes, and feldspars. We also analyse two synthetic ancient crust samples based on the chemical composition of the NWA 7533 and NWA 7034 martian regolith breccias (*e.g.*, Hewins *et al.*, 2017) and the more alkali-rich composition of the early Mars crust identified in conglomerates in Gale Crater (Mangold *et al.*, 2016) (Table 1). To explore the influence of olivine concentration, we added Fo<sub>65</sub> (~11.8 wt. %) to the crust simulant-O (Sim-O), whereas the simulant-M (Sim-M), contains magnetite but no olivine. The description of the experimental set up (Fig. S-1) and the chemical properties of the experimental solutions (Fig. S-7) have been reported by Baron *et al.* (2019). Here, we investigate the potential carbonate occurrences in the altered solids. Aiming to analyse the surface alteration of the samples, we used X-ray Photoelectron Spectroscopy (XPS) (sampling

depth between 3–10 nm) in addition to the more conventional FTIR.

## Results

We estimate the atomic percentages of the elements on the samples' surfaces by analysing XPS survey spectra (Fig. S-2). Then, we fit the binding energy of the core level C1s feature to identify the specific carbonate species (Fig. 1). In this energy range, all samples exhibit the usual contribution of ubiquitous adventitious carbon resulting from hydrocarbon physisorption onto surfaces. The primary peak of this adventitious carbon, denoted as C-H, occurs at 284.8 eV, while the carbonate peak (CO<sub>3</sub>) emerges around ~289.7 eV, depending on the ionic character of the metal-carbon bond (*e.g.*, MgCO<sub>3</sub> ~290 eV and CaCO<sub>3</sub>/FeCO<sub>3</sub> ~289.5 eV). All the unreacted samples (*i.e.* fresh material before reaction) except potassium feldspar (K-spar), show minor contribution from carbonate. However, only the reacted olivine-bearing samples (Fo<sub>92</sub> and Fo<sub>65</sub>) show a substantial increase of a well resolved carbonate peak around 290 eV, which represents Mg-CO<sub>3</sub> groups (Fig. 1, extended Fig. S-3 and Table S-1).

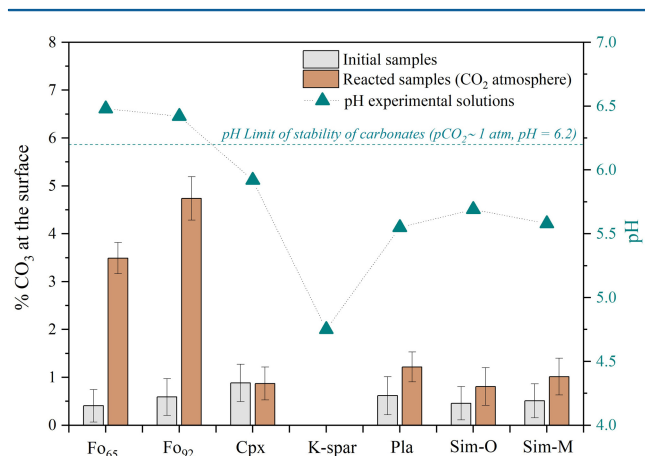
Figure 2 depicts the amount of carbonate at mineral surfaces before and after reactions together with the final pH values of the solutions. High pH values result from the weathering of mafic minerals (*i.e.* olivine and pyroxene), which neutralise the acidity derived from a CO<sub>2</sub>-rich atmosphere (pH<sub>0</sub> ~ 3.6); the solutions with lower pH values reflect the hydrolysis of felsic minerals (*i.e.* feldspars). Solutions from the martian simulants also have low pHs because they contain abundant feldspars. Only the olivine samples (Fo<sub>92</sub> and Fo<sub>65</sub>) formed substantial proportions of carbonates during reaction, and only their solutions had pH > 6.2, the threshold for carbonates formation under a pCO<sub>2</sub> = 1 bar atmosphere (Bullock and Moore, 2007). Mg-rich olivine (Fo<sub>92</sub>) produced higher carbonate formation than Fe-rich



**Figure 1** Fitting model of the  $C1s$  orbital for  $Fo_{65}$  sample, (a) initially, and (b) after reaction (under  $CO_2$  atmosphere) (see SI for spectra deconvolution).

olivine ( $Fo_{65}$ ). Conversely, potassium feldspar (K-spar) lacked carbonates and yielded the lowest pH solution (pH  $\sim 4.75$ ). Simulant samples (Sim-O and Sim-M) did not show either a significant increase in carbonate compounds, nor appreciable differences between them, despite the presence of olivine in Sim-O ( $Fo_{65} \sim 11.8$  wt. %) and their differences in the iron and magnesium content.

Figure 3 shows the magnesium high resolution XPS spectra ( $Mg2p$  orbital) of the olivine and Sim-O samples. When comparing initial and reacted samples, we only identified a change in the magnesium peak of olivine samples. This change manifests as a shift towards higher binding energies and an asymmetric broadening, a feature not observed in Sim-O. This change suggests the presence of  $MgCO_3$  ( $\sim 50.6$  eV), consistent with the carbonate peak position identified in their  $C1s$  spectra (*i.e.* 290 eV  $\sim MgCO_3$ ).



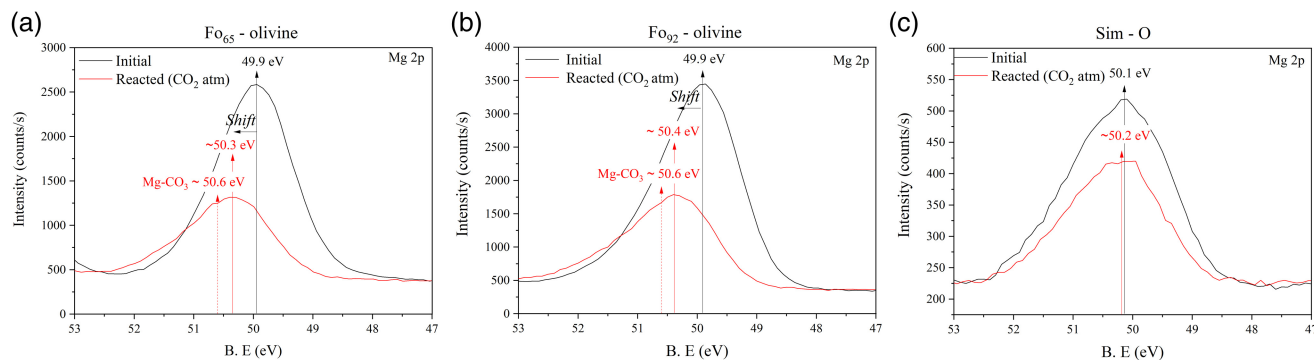
**Figure 2** Amount of carbonate in the samples (bars) and pH value (triangles) of the solutions at the end of the experiment (see SI for % calculations). The error bars show the uncertainty of the carbon estimation associated with the survey quantification (standard deviation in Fig. S-2). The  $pH_0 = 3.6$ , corresponding to the pure water equilibrated with the  $pCO_2 = 1$  bar. The dashed line marks the pH threshold of carbonates stability for  $pCO_2 = 1$  bar (Bullock and Moore, 2007).

We also examined FTIR spectra for signatures of carbonate minerals. The bulk samples (*i.e.* whole size fractions) showed no features assignable to carbonate minerals, because of their low degree of alteration. However, the finest size fractions ( $<1 \mu m$ ), did show absorptions from the strongest vibrational IR band for carbonates (*i.e.* the asymmetric stretching mode [ $\nu_3(CO_3)$ ]) in several samples (Fig. S-4). The intensity of this band in reacted olivine samples suggests that carbonate formed during reaction, in agreement with the XPS results (Fig. 2). FEG-SEM images also suggest the presence of small particles of carbonate minerals, inferred by their crystal shape, on olivine samples (Fig. S-5). Note, however, that we cannot directly use the carbonate IR band intensity as a measure of carbonate abundances because it is only apparent in the size fraction  $<1 \mu m$ . The spectra enlargement ( $2000\text{--}600\text{ cm}^{-1}$ ) of olivine samples shows that  $\nu_3(CO_3)$  feature is split into two barely resolved peaks, which match well with a hydrated magnesium carbonate (*e.g.*, hydromagnesite; Fig. S-6). The saturation indices of carbonates calculated from the chemistry of experimental solutions (Figs. S-7, S-8) (Baron *et al.*, 2019) are also consistent with the solid products identified in this study. However, the use of this variable to predict mineral formation should be employed with caution (see geochemical modelling and carbonates in SI).

## Discussion

Our weathering experiments under early Mars-like conditions show that, among potential materials of the early Mars crust, only olivine ( $Fo_{92}$  and  $Fo_{65}$ ) reacts to form significant proportions of carbonate minerals (Fig. 1). Carbonation resulting from ultramafic rock reaction has been extensively studied as a  $CO_{2(g)}$  capture strategy on Earth (*i.e.* high T and/or high P conditions) because it can neutralise the acidity imposed from  $CO_2$  dissolution (Snæbjörnsdóttir *et al.*, 2020). The pH values of our post-reaction solutions show that under early Mars-like conditions, this neutralisation is particularly effective in olivine samples (Fig. 2), where we identify the formation of Mg carbonates (Figs. 1, 3 and Figs. S-3, S-6). The formation of magnesite is usually linked to elevated temperatures ( $T > 50^\circ C$ ) due to the high hydration energy of  $Mg^{2+}$ . However, hydrated Mg carbonates can form in solutions with a high concentration of  $Mg^{2+}$  under near ambient temperatures (Gaudin *et al.*, 2018), as shown by our XPS and FTIR spectra (Figs. 1, 3 and Figs. S-3,





**Figure 3** *Mg 2p* high resolution XPS spectra before (black colour) and after reaction under a  $\text{CO}_2$  atmosphere (red colour) of (a)  $\text{Fo}_{65}$ -olivine, (b)  $\text{Fo}_{92}$ -olivine, and (c) simulant sample with  $\text{Fo}_{65}$  (Sim-O). The solid arrows (black colour) mark the position of the main peak of the unreacted samples whereas dashed arrows (red colour) mark the position of the  $\text{MgCO}_3$  peak.

S-6). Then, this hydrated precursor can turn into anhydrous magnesite as occurs in low temperature evaporitic environments on Earth (e.g., Scheller *et al.*, 2021). This geological scenario could explain the formation of carbonates identified (from orbit) along the margins of the Jezero (playa) lake (Horgan *et al.*, 2020), setting aside the specific interferences that the development of passivation layers may cause on olivine carbonation rates (Oelkers *et al.*, 2018 and references therein). Interestingly, we do not identify siderite, not even in the iron-rich forsterite ( $\text{Fo}_{65}$ ) in agreement with Baron *et al.* (2019), who showed that olivine reaction solutions were oxidising, hindering siderite formation. These results seem in disagreement with the iron-rich carbonate minerals observed in the nakhlite Martian meteorites (Nakhla, Lafayette, and Governador Valadares). However, they are inferred to have formed through high temperature hydrothermal subsurface processes induced by an impact event (Bridges and Schwenzer, 2012), contrasting with our experimental conditions (i.e. water equilibrated with a  $\text{pCO}_2 = 1$  bar atmosphere,  $T = 45^\circ\text{C}$ ). Moreover, the lower carbonation observed on the  $\text{Fo}_{65}$  compared to the  $\text{Fo}_{92}$  sample (Fig. 2) suggests that the Fe enrichment in martian olivine limits the quantity of carbonate but does not prevent its formation, in agreement with the results of Brown *et al.* (2020) who identify  $\text{Fo}_{40-66}$  in the olivine-carbonate lithology of Nili Fossae region. This effect could be due to the development of an Fe-rich silica layer on the olivine surface that limits the carbonation reaction (Oelkers *et al.*, 2018). Interestingly, in Kissick *et al.* (2021), no carbonates were detected from aqueous alteration of fayalite-forsterite mixtures, but this could be due to the FTIR detection limit. We do not identify either a carbonate signal when analysing the whole fraction of the sample with this technique.

An important question is why carbonates do not form in the crustal simulant samples. As noted by Baron *et al.* (2019), our experiments demonstrate that the mineralogy of the reactants significantly influences solution properties, particularly pH, subsequent reaction pathways, and the formation of secondary products. In a dense  $\text{CO}_2$  atmosphere on early Mars (i.e.  $\text{pCO}_2 = 1$  bar), carbonate minerals are not stable at  $\text{pH} < 6.2$  (Bullock and Moore, 2007) and the simulant samples yield solutions with pH values below this threshold (Fig. 2); the pH values of the simulant solutions are intermediate between those of pure olivine and pure feldspar samples. In our experiments, dissolution-precipitation reactions are likely coupled, and both martian simulants contain high percentages of feldspars that generally form Al-OH-rich secondary minerals (e.g., amorphous Al-OH precursors, gibbsite or kaolinite) as alteration products (Zhu and Lu, 2009). The insoluble nature of the  $\text{Al}^{3+}$  under weathering conditions favours precipitation of such phases and therefore

the production of  $\text{H}^+$  by the hydrolysis of this cation (e.g.,  $\text{Al}^{3+} + 3\text{H}_2\text{O} = \text{Al}(\text{OH})_{3(s)} + 3\text{H}^+$ ). As we do not identify  $\text{Al}^{3+}$  in simulant solutions (Fig. S-7), we hypothesise that the incorporation of OH in these secondary products helps to hold the pH at slightly acidic values. Comparing the fluid chemistry of forsterite and simulant solutions (Fig. S-7) is evident that forsterite solutions hold the highest  $\text{Mg}^{2+}$  concentration from the incongruent dissolution of forsterite, favouring the formation of Mg-carbonates.

These findings suggest that the formation of carbonates by surface weathering on early Mars depends on the host rock composition, as suggested by Kissick *et al.* (2021). Accordingly, surface carbonate deposits might only have formed from olivine-rich rock (i.e. olivine  $> 20$  wt. %), like in Nili Fossae region, but not from more felsic rocks. Regardless, this scenario does not preclude the formation of carbonates by migration of meteoric water and/or diffusion which would induce a pH increase with depth, groundwater circulation, or hydrothermal processes. Indeed, Thorpe *et al.* (2022) recently identified Fe-rich carbonate in Glen Torridon (Gale Crater) and inferred that it likely formed in a subsurface mixing zone between lacustrine water and deep groundwater.

Geochemical models for basalt dissolution under a  $\text{CO}_2$ -rich early Mars atmosphere generally predict more abundant carbonate formation than observed on the martian surface. However, these models usually assume olivine-rich basalts as starting protoliths (i.e. olivine  $> 20$  wt. %) and equilibrium conditions. Consequently, they do not address kinetic barrier effects (Kissick *et al.*, 2021; Scheller *et al.*, 2021), which may result in an overestimation of the carbonate abundance (see geochemical modelling and carbonates in SI).

Carbonate occurrences detected on Mars are commonly associated with olivine-bearing lithologies (olivine  $> 20$  % in volume) (Wray *et al.*, 2016), consistent with our experimental results. The Comanche outcrops in the Columbia Hills (Gusev Crater) contain a mineral assemblage of olivine and carbonates. These carbonates, of inferred Noachian age, are abundant (16 to 34 wt. %) and intimately associated with olivine ( $\text{Fo}_{68}$ ) and amorphous silicate (Morris *et al.*, 2010). Orbital reflectance spectra of the Capri Chasma region also show phyllosilicates, carbonates, and a host rock potentially rich in olivine (Jain and Chauhan, 2015), like the carbonate-olivine association observed at Nili Fossae (Ehlmann *et al.*, 2009). In Jezero Crater, carbonates detected from orbit are associated with olivine-bearing rocks and mapped as the same geological unit identified across Nili Fossae (Mandon *et al.*, 2020). These alteration units share similarities with the mineralogical associations described in the oldest

carbonates identified in ALH 84001, likely formed by a low temperature weathering fluid equilibrated with CO<sub>2</sub> atmosphere (Halevy *et al.*, 2011).

Recent results show that the ancient Mars crust was more alkali-rich and felsic than previously thought (Sautter *et al.*, 2016), as indicated by the abundance of felsic igneous rocks (trachytic, alkali feldspar-rich) found in Gale Crater as float and pebbles sourced from Noachian age crust around the crater (Mangold *et al.*, 2016). Likewise, the ancient meteorite breccia NWA 7034 (and pairs) is rich in feldspars and lacks primary olivine (Hewins *et al.*, 2017). Regarding the olivine distribution through Mars, olivine-rich regions such as Nili Fossae (*i.e.* olivine > 20 wt. %) are rare in Noachian highlands (*e.g.*, Ody *et al.*, 2013). Our results show that a more felsic and alkali-rich crustal composition does not produce carbonates by weathering under early Mars-like conditions, *i.e.*, pCO<sub>2</sub> = 1 bar, moderate temperature. Our results are likewise consistent with the limited occurrence of carbonates (<3.2 wt. %) detected by CheMin in the Glen Torridon area of Gale Crater (Thorpe *et al.*, 2022) and the absence of carbonates in other crater locations (Bristow *et al.*, 2017), despite significant diagenetic alteration in the mudstones (*i.e.* 20 to 30 wt. % of phyllosilicates). However, the sedimentary record in Gale reveals a rich spectrum of alteration stages, which may encompass processes such as the formation-dissolution of pre-existing carbonates and the later formation of clay minerals, as observed in Nakhilites. Our results also help to illustrate why martian carbonates did not form abundant surface deposits, thus, serving as a limited storage for atmospheric CO<sub>2</sub> (Edwards and Ehlmann, 2015). Considering that there have been no detections of substantial CO<sub>2</sub> reservoirs at Mars' surface, MAVEN observations propose that gas loss to space may have driven Martian climate change (Jakosky *et al.*, 2018).

The weathering experiments presented here suggest that (1) Fo<sub>65</sub> and Fo<sub>92</sub> samples induce the formation of Mg carbonate (no evidence of siderite is here detected), and (2) the inhibiting effect of a more felsic composition in the early Mars crust could have on carbonate formation. As a corollary, we suggest that the sparse distribution of surface carbonates under a warmer and thicker CO<sub>2</sub> atmosphere can be associated with the compositional diversity of the magmatic rocks in the ancient martian crust. Therefore, their scarcity does not have to be evidence of a cold and dried early Mars.

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## Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2403>.



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# The key role of bedrock composition in the formation of carbonates on Mars

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## Supplementary Information

The Supplementary Information includes:

- Materials and Methods
- Table S-1
- Figures S-1 to S-8
- Geochemical Modelling and Carbonates
- Supplementary Information References

## Materials and methods

**Starting materials and experimental set-up.** As starting minerals we chose a list of individual minerals, namely forsterite – magnesium and iron-rich-, clinopyroxene, plagioclase, and potassium feldspar, as well as two prepared martian crust simulants constrained by the early Mars crust composition inferred by the conglomerate analysed in the Gale crater (Mangold *et al.*, 2016) and the Martian regolith breccia NWA 7533 and NWA 7034 (Agee *et al.*, 2013; Humayun *et al.*, 2013; Hewins *et al.*, 2017) (Table 1). These martian crust simulants were built by a mixture of individual minerals. This procedure allowed us to increase the dissolution rate of silicate minerals under low temperature conditions. The bulk chemical composition of Mars simulants samples was estimated according to the proportion of the minerals (wt. % in Table 1). Both Mars crust simulants present a high proportion of K-feldspars to balance the low Na-content of plagioclase and fit the alkali-rich composition of martian regolith breccias. Specifically, in a total alkali-silica (TAS) diagram (Le Bas *et al.*, 1986) the chemical composition of simulant containing Fo<sub>65</sub>-olivine (Sim-O) is consistent with basaltic andesite, whereas the simulant containing magnetite but lacking olivine (Sim-M), with high Fe content fits better with a basaltic composition. Each mineral was crushed, sieved ( $\varnothing < 63 \mu\text{m}$ ) and settled in ethanol to remove the fine fraction ( $\varnothing < 2 \mu\text{m}$ ).

Aqueous alteration experiments reproducing martian weathering under a thick CO<sub>2</sub> atmosphere were performed under a controlled anoxic CO<sub>2</sub> atmosphere (*i.e.* Mbraun-LABstar glovebox with a constant pCO<sub>2</sub> = 1 bar, Air Liquide® Alphagaz CO<sub>2</sub>) for 6 months (Baron *et al.*, 2019) (Fig. S-1). The O<sub>2</sub> concentration was continuously monitored with an oxygen analyser (MB-OX-EC-PLC, over the 1- to 1000 ppm range) and kept below pO<sub>2</sub> < 0.5 ppm by a gas purification unit. The samples were placed into batch Savillex™ PFA reactors (90 mL– references 100-0090-01 for the reactor and 600-053-20 for the closure) (containing 1.8 g of starting material and 18 mL of ultrapure water, 18 MΩ cm) and allowed



to react in closed conditions at a relatively low water-to-rock ratio (W/R ~10 by weight). Milli-Q® ultrapure water (18 MΩ cm) was previously degassed three times under vacuum for 3 hours each time and then equilibrated under continuous stirring for 2 days with 1 atm of CO<sub>2</sub>. The batch reactors were kept under continuous stirring (50 rpm using an orbital agitator) and at 45 °C (thermostatic hot plate) to increase the reaction rate. Initial pH values of anoxic ultrapure water were measured after 2 days of stirring conditions inside the glovebox to ensure equilibrium with pCO<sub>2</sub> = 1 bar atmosphere (pH<sub>0</sub> = 3.6). The final pH values of each experimental solution were measured at the end of the experiments in contact with minerals at 25 °C. The pH values were then estimated at 45 °C for each experimental solution from thermodynamic calculations. The calculations were performed using the PHREEQC® software (Parkhurst and Apello, 2014) associated with the Thermoddem database (<http://thermoddem.brgm.fr/>), further details concerning the sample preparation and experimental design can be found in Baron *et al.* (2019).

After 6 months of reaction, the samples were filtered (< 0.2 μm) and dried inside the glovebox to separate the solid product from the solutions. The previous work of Baron *et al.* (2019) analysed the physicochemical parameters of the experimental solutions. Here, we analyse the carbonate in the solid products, but some information about fluid chemistry that helps us to discuss the results can be found in Figures S-7 and S-8.

**Analytical techniques.** The initial and altered samples were analysed with X-ray photoelectron spectroscopy (XPS), Fourier transforms infrared spectroscopy (FTIR), and Field Emission Gun Scanning Electron Microscope (FEG-SEM).

XPS analyses were performed using a Kratos Axis Nova spectrometer (Institut de Matériaux de Nantes, IMN, Nantes) equipped with a monochromatic Al-Kα (hν = 1486.6 eV) with a surface analysed of 700 μm x 300 μm. The base pressure of the system was below 10<sup>-9</sup> mbar. Survey spectra were acquired by using 160 eV pass energy, whereas a 40 eV pass energy was applied for the analysis of the core level spectra (C1s, Si 2p, O1s, Mg 2p, and Fe2p). With the pass energy 160 eV and 40 eV, the all-over instrument resolution on the Fermi edge is about 1.9 eV and 0.56 eV, respectively. All data were acquired using charge compensation to establish a steady-state surface potential.

Mid-Infrared spectra (MIR: 4000-400 cm<sup>-1</sup>) were collected using an FTIR-Nicolet 5700 spectrometer (LPG, Nantes), using a DTGS KBr detector, and a KBr beamsplitter at 4 cm<sup>-1</sup> resolution. All spectra correspond to an addition of 100 scans. The analyses were carried out on the bulk samples (*i.e.*, whole size fractions) and the finest fraction (particle size <1 μm) of the reacted samples. This fine fraction was extracted by the sedimentation method based on Stokes' law in ultrapure water (18 MΩ cm) inside the glovebox, subsequently filtered (< 0.2 μm), and allowed to dry under the controlled CO<sub>2</sub> atmosphere. Then, it was dispersed in a KBr matrix and measured under room conditions.

Field Emission Gun Scanning Electron Microscope (FEG-SEM) images were acquired using a JEOL JSM 7600F scanning electron microscope equipped with an Energy Dispersive Spectrometer (EDS) (IMN, Nantes).

**Processing XPS data.** XPS spectra were referenced to the C1s peak at 284.8 eV and analysed using CasaXPS software (version 2.3.24rev1.OR) (Fairley *et al.*, 2021). The XPS survey spectra provide information on the chemical composition of the samples (Fig. S-1), whereas C1s spectra provide the chemical composition of the carbon species. We focused on the C1s high-resolution spectra for carbonate species because the O1s orbitals are hard to deconvolve due to the presence of several oxygen-bearing species (*i.e.*, oxides, hydroxides, silicates, carbonates) and can occur within a narrow range of binding energies (Kloprogge and Wood, 2020). In the C1s spectra, all the samples present the usual contribution of ubiquitous adventitious carbon due to the physisorption of hydrocarbon layers from both the exposure to the atmosphere and the vacuum system of the instrument (Cánneva *et al.*, 2017; Kloprogge and Wood, 2020). We performed a curve fitting of the C1s high-resolution spectra to determine the amount of the carbonate component in the samples using reported literature values (Payne *et al.*, 2011; Kloprogge and Wood, 2020). The fit was performed with fixed components positions resulting in good FWHM homogeneity (Fig. 1, Fig. S-2, and Table S-1). Specifically, we used four components for the ubiquitous hydrocarbon species (Payne *et al.*, 2011): C-C/C-H (284.8 ± 0.1 eV); C-O (286.1 ± 0.1 eV); C=O (287.7 ± 0.1 eV) and O-C=O (288.7 ± 0.1 eV); whereas the carbonate component position was assigned with higher deviation (289.7 ± 0.4 eV) because it depends on the ionic character of the metal-carbon bond (*e.g.*, MgCO<sub>3</sub> ~ 290 eV and CaCO<sub>3</sub>/FeCO<sub>3</sub> ~ 289.5 eV) (Kloprogge and Wood, 2020). We used a Voigt line Lorentzian Asymmetric (LA) function for the line shape and a U 2 Tougaard function for the background. Individual peak parameters of the fitting

can be found in Table S-1. To obtain a comprehensive overview of the total amount of the surface carbonates formed (Fig. 2), we normalised the percentages of carbonate species from the high-resolution spectra (Table S-1) to the total carbon content on the surface estimated from the survey spectra (Fig. S-1). Then, we subtracted the contribution of hydrocarbon adventitious species and the oxygen component related to them using the calculator described by Payne *et al.* (2011) and recalculated the % of the carbonate component.



## Supplementary Tables

**Table S-1** Individual peak parameters identified in the fitting of the C1s high-resolution spectra for iron-rich olivine (Fo<sub>65</sub>-olivine), magnesium-rich olivine (Fo<sub>92</sub>-olivine), clinopyroxene (cpx), potassium-feldspar (k-spar), plagioclase (PLA), simulant with olivine (Sim-O) and simulant with magnetite (Sim-M) (Fig. 1 and extended Fig. S-2)

Fo<sub>65</sub>-olivine initial (residual STD=1.06)

Name	Position	FWHM	%Con.
C-C, C-H	284.8	1.5	75.2
C-O	286.2	1.5	13.8
C=O	287.8	1.5	1.5
O-C=O	288.8	1.5	7.3
CO <sub>3</sub>	289.9	1.4	2.2

Fo<sub>65</sub>-olivine reacted (CO<sub>2</sub> atm) (residual STD=0.80)

Name	Position	FWHM	%Con.
C-C, C-H	284.8	1.6	63.1
C-O	286.2	1.6	14.0
C=O	287.7	1.6	3.6
O-C=O	288.7	1.6	1.9
CO <sub>3</sub>	290.1	2.0	17.4

Fo<sub>92</sub>-olivine initial (residual STD= 1.15)

Name	Position	FWHM	%Con.
C-C, C-H	284.8	1.6	72.1
C-O	286.2	1.6	16.2
C=O	287.6	1.6	1.9
O-C=O	288.8	1.6	7.6
CO <sub>3</sub>	289.9	1.6	2.2

Fo<sub>92</sub>-olivine reacted (CO<sub>2</sub> atm) (residual STD=1.02)

Name	Position	FWHM	%Con.
C-C, C-H	284.8	1.6	64.9
C-O	286.3	1.6	15.3
C=O	287.6	1.6	3.7
O-C=O	288.6	1.6	1.7
CO <sub>3</sub>	290.1	2.1	14.5

Cpx initial (residual STD=0.95)

Cpx reacted (CO<sub>2</sub> atm) (residual STD=1.34)

Name	Position	FWHM	%Con.
C-C, C-H	284.8	1.6	66.3
C-O	286.1	1.6	21.0
C=O	287.6	1.6	4.6
O-C=O	288.8	1.6	3.5
CO <sub>3</sub>	289.7	2.0	4.6

Name	Position	FWHM	%Con.
C-C, C-H	284.8	1.6	75.4
C-O	286.2	1.6	14.6
C=O	287.6	1.6	2.1
O-C=O	288.8	1.6	5.1
CO <sub>3</sub>	289.4	1.4	2.8

K-spar initial (residual STD=0.94)

K-spar reacted (CO<sub>2</sub> atm) (residual STD=1.33)

Name	Position	FWHM	%Con.
C-C, C-H	284.8	1.5	91.0
C-O	286.1	1.5	8.7
C=O	287.6	1.5	0.3
O-C=O	288.8	1.5	0.0

Name	Position	FWHM	%Con.
C-C, C-H	284.8	1.6	83.4
C-O	286.1	1.6	15.2
C=O	287.6	1.6	1.4
O-C=O	288.7	1.6	0.0

Pla initial (residual STD=1.33)

Name	Position	FWHM	%Con.
C-C, C-H	284.8	1.6	73.9
C-O	286.1	1.6	18.5
C=O	287.6	1.6	2.6
O-C=O	288.8	1.6	2.3
CO <sub>3</sub>	289.5	1.8	2.7

Pla reacted (CO<sub>2</sub> atm) (residual STD=1.02)

Name	Position	FWHM	%Con.
C-C, C-H	284.8	1.5	74.3
C-O	286.1	1.5	15.8
C=O	287.6	1.5	3.2
O-C=O	288.8	1.5	2.1
CO <sub>3</sub>	289.5	1.7	4.6



## Sim-O initial (residual STD=1.55)

Name	Position	FWHM	%Con.
C-C, C-H	284.8	1.6	69.2
C-O	286.2	1.6	21.7
C=O	287.8	1.6	3.1
O-C=O	288.6	1.6	2.7
CO <sub>3</sub>	289.4	1.8	3.3

Sim-O reacted (CO<sub>2</sub> atm) (residual STD=1.71)

Name	Position	FWHM	%Con.
C-C, C-H	284.8	1.6	69.0
C-O	286.2	1.6	22.2
C=O	287.8	1.6	3.4
O-C=O	288.8	1.6	0.9
CO <sub>3</sub>	289.4	1.9	4.5

## Sim-M initial (residual STD=1.34)

Name	Position	FWHM	%Con.
C-C, C-H	284.8	1.6	72.6
C-O	286.2	1.6	20.1
C=O	287.8	1.6	3.0
O-C=O	288.8	1.6	1.3
CO <sub>3</sub>	289.4	1.8	3.1

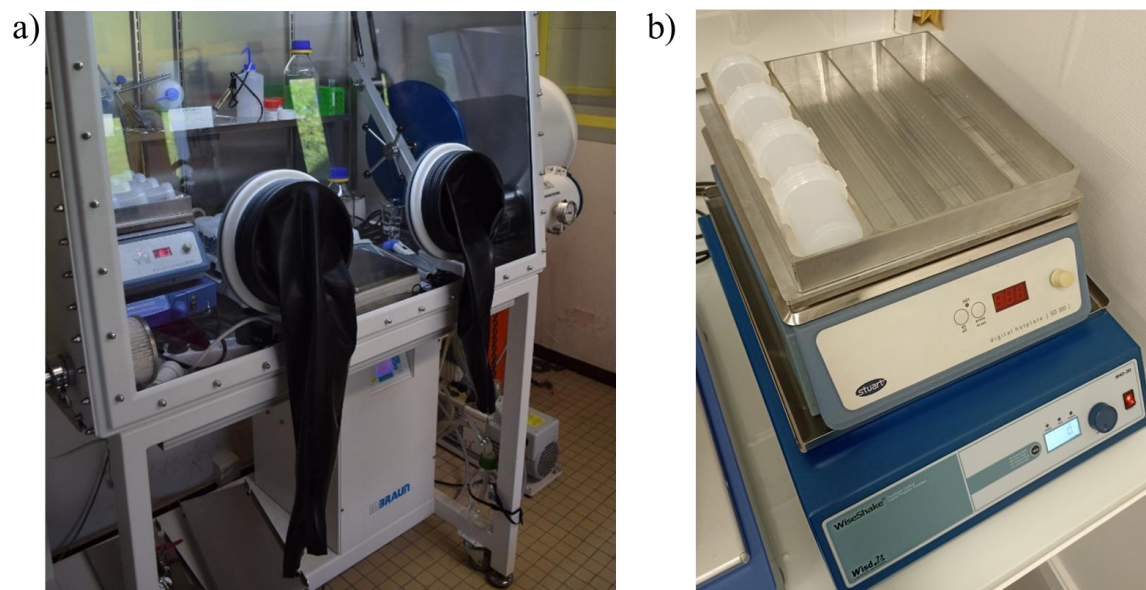
Sim-M reacted (CO<sub>2</sub> atm) (residual STD=2.44)

Name	Position	FWHM	%Con.
C-C, C-H	284.8	1.6	69.9
C-O	286.2	1.6	22.1
C=O	287.8	1.6	2.9
O-C=O	288.6	1.6	0.3
CO <sub>3</sub>	289.5	1.9	4.8

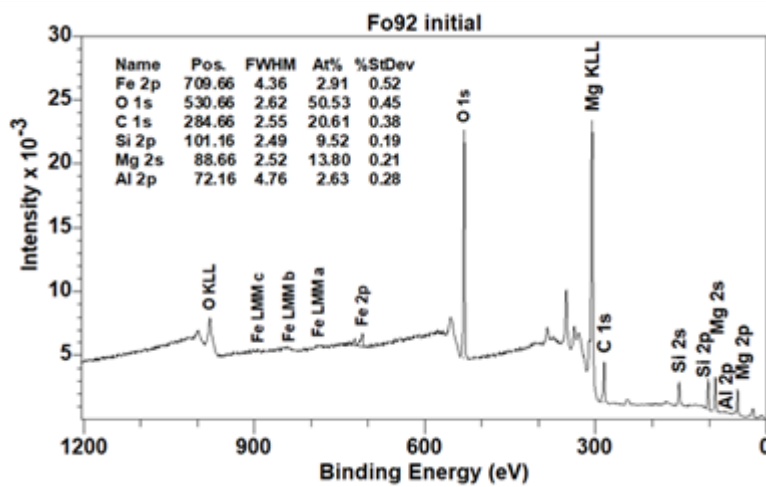
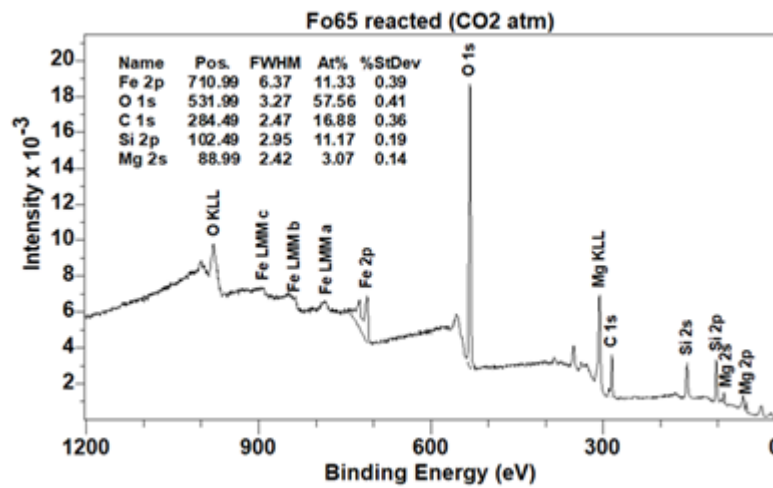
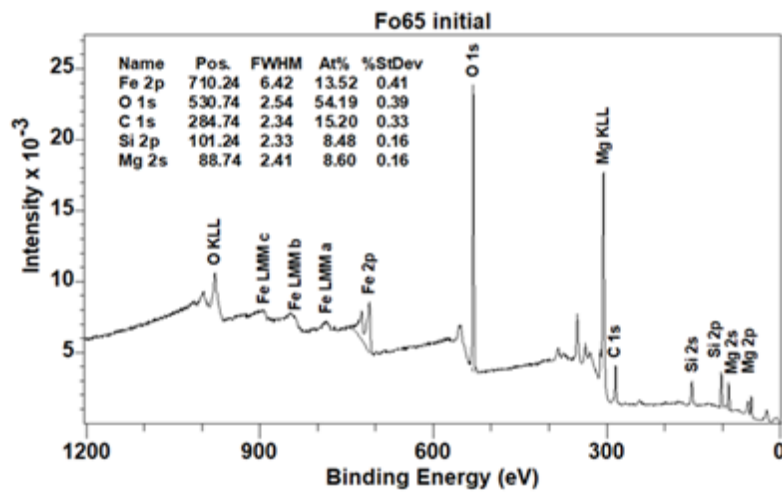


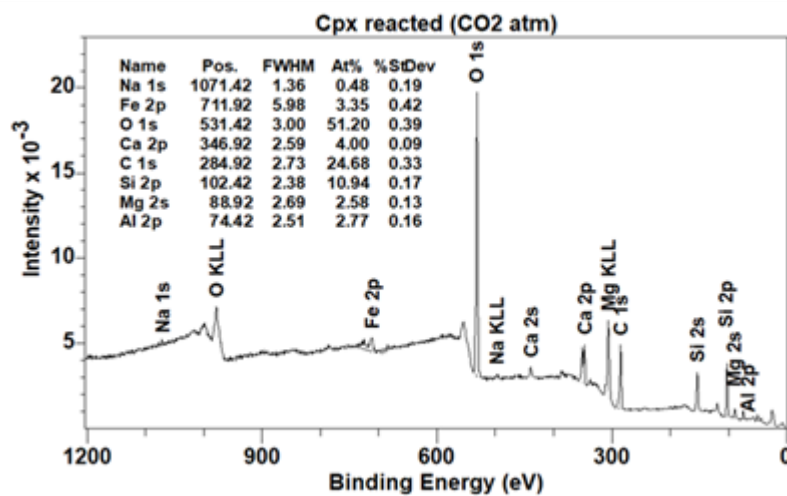
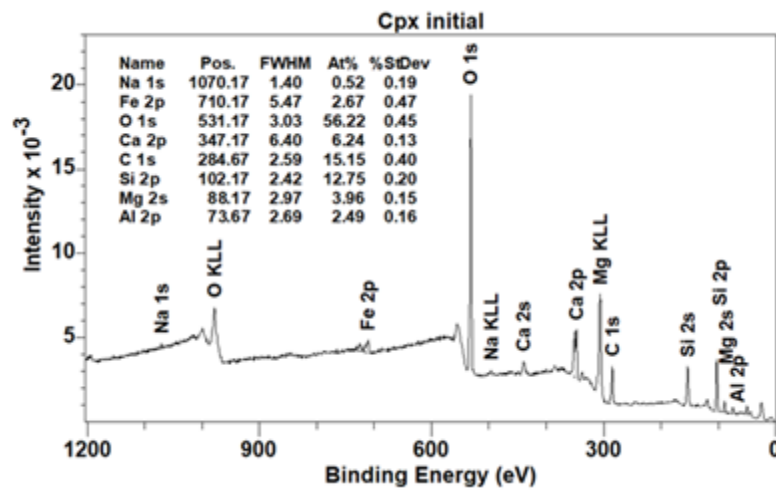
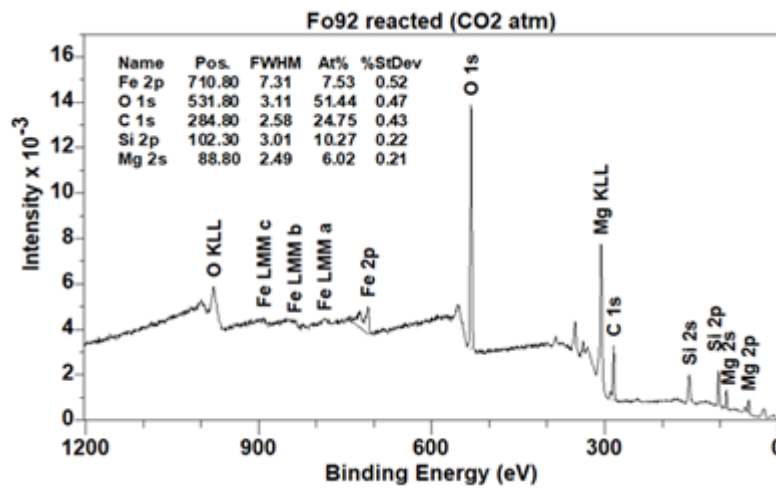


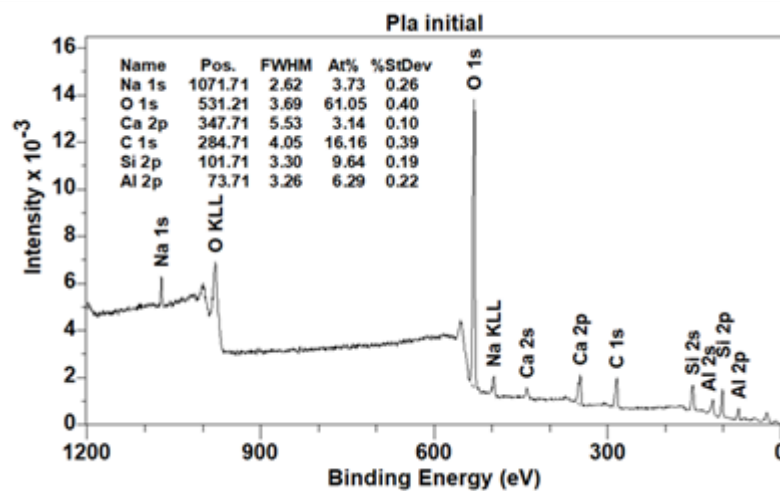
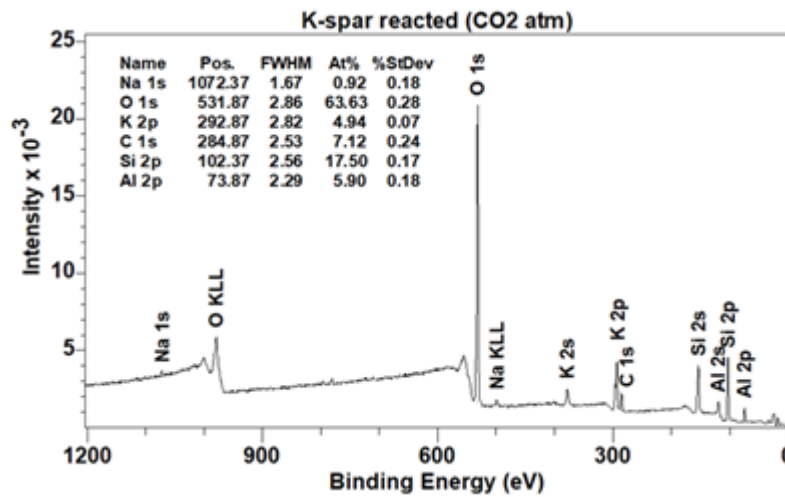
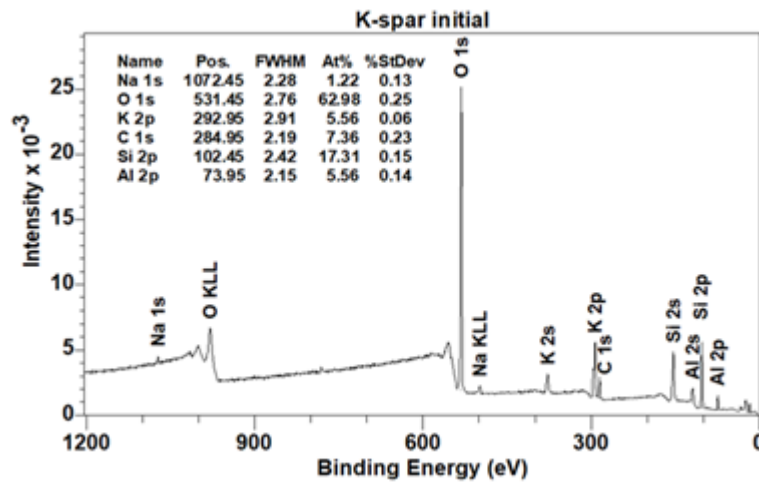
## Supplementary Figures



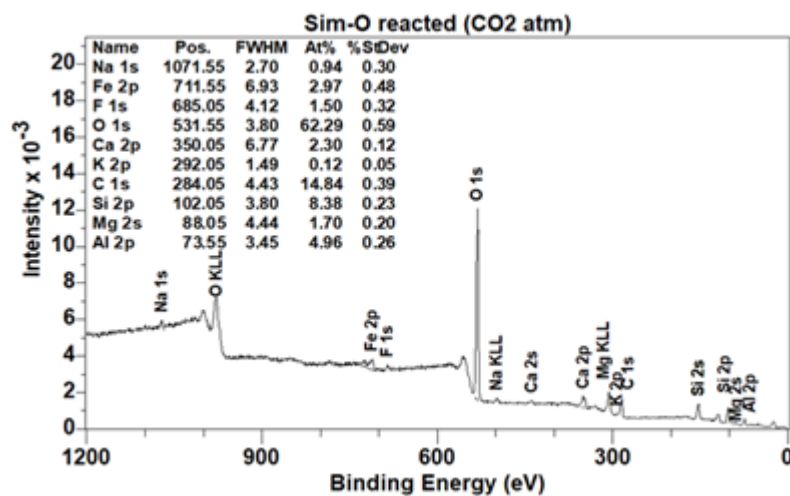
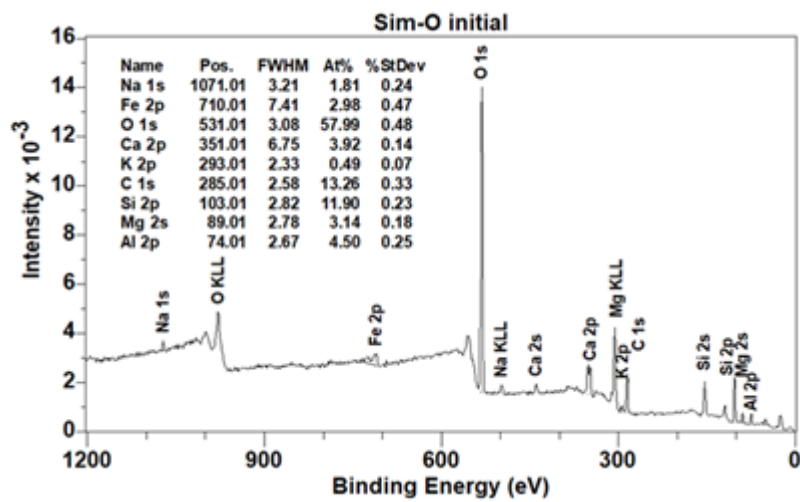
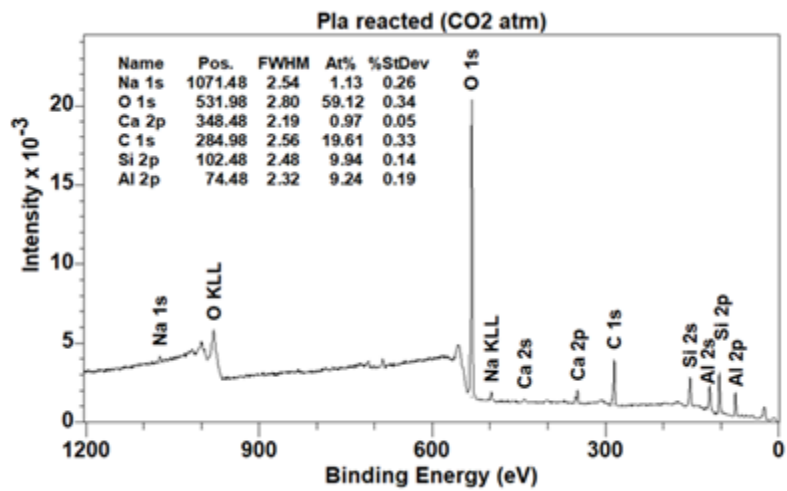
**Figure S-1** (a) Picture of the experiment running in the glovebox. (b) Picture of the reactors, showing from down to top: stirring plate, hot plate and, an aluminium sample holder for the heat conductivity.

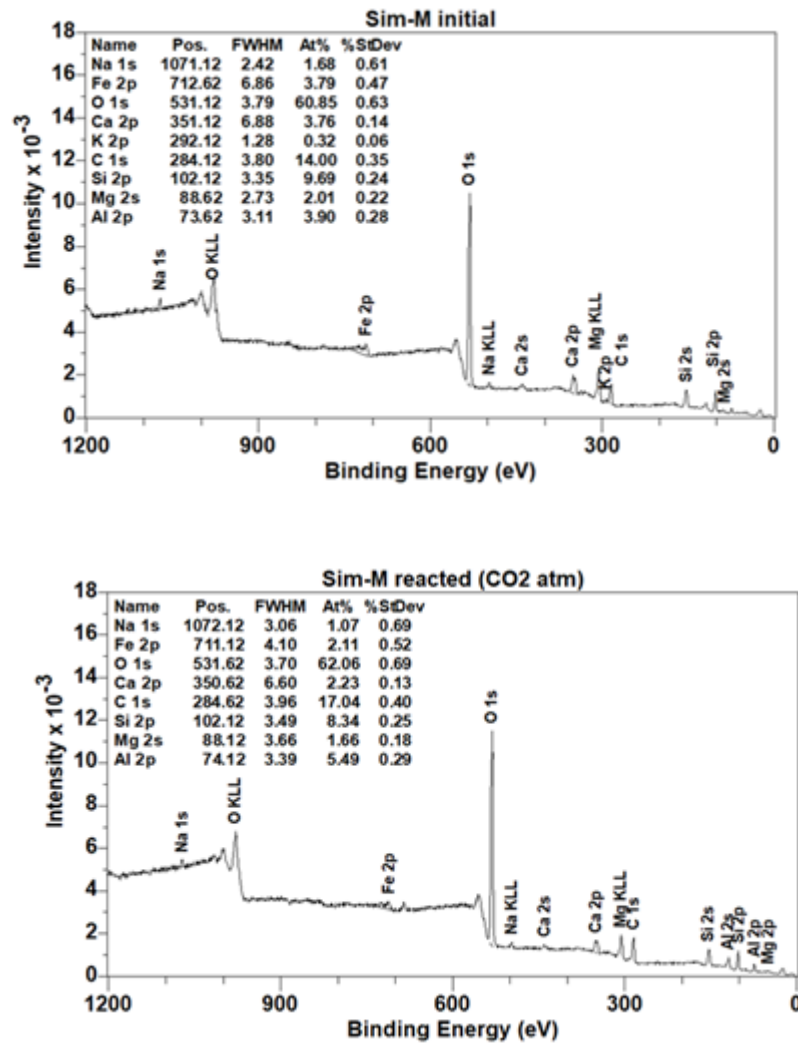




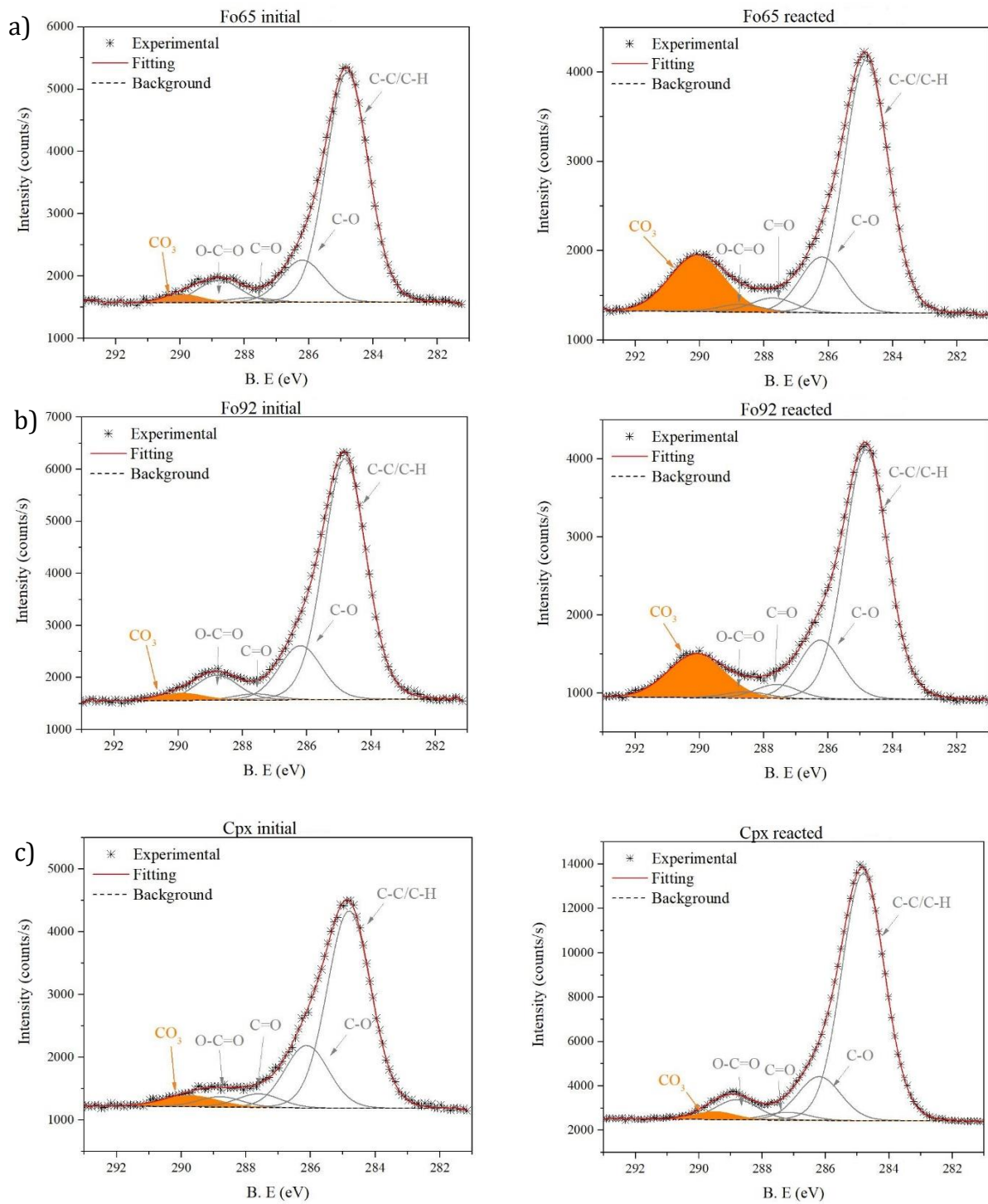


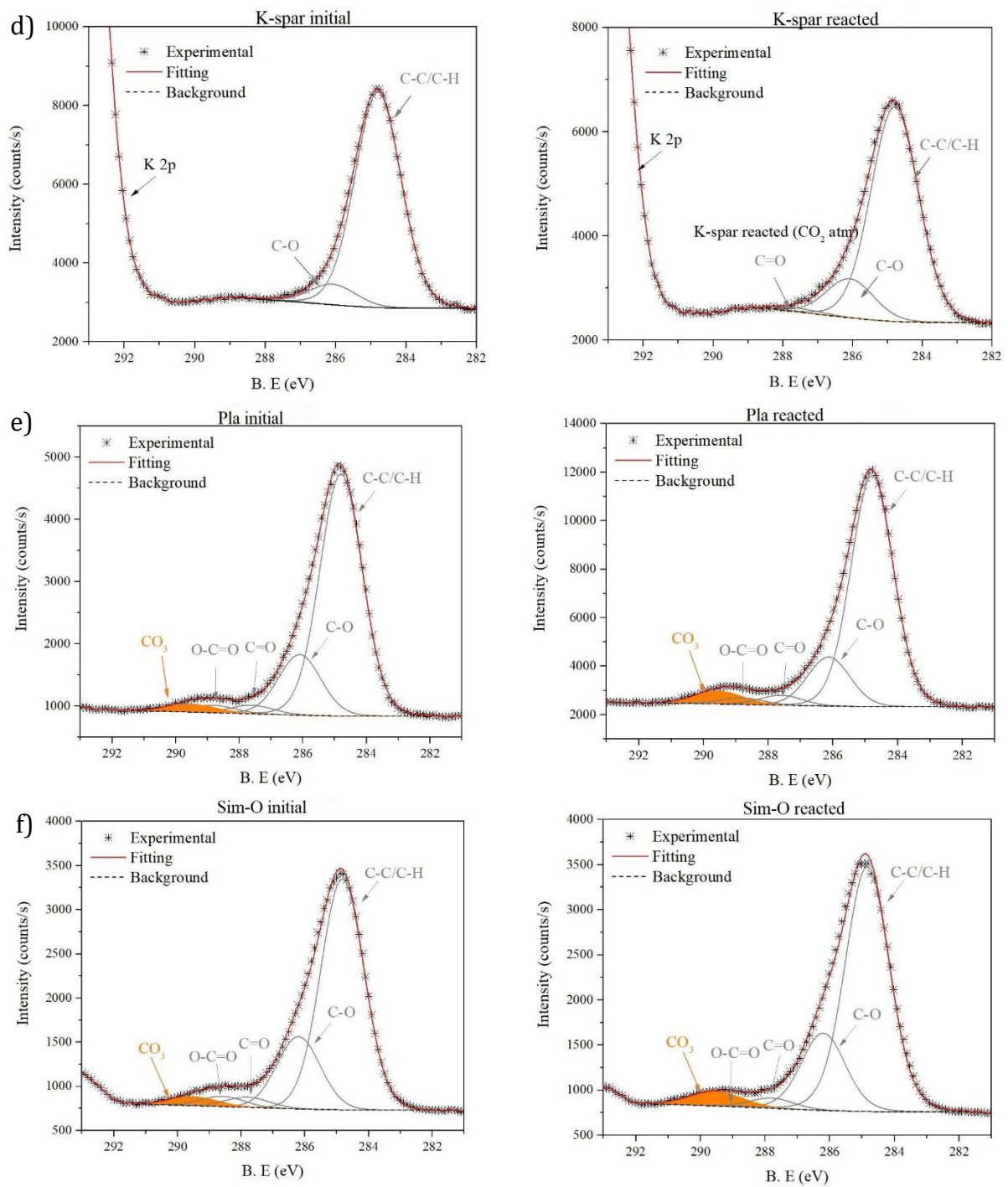




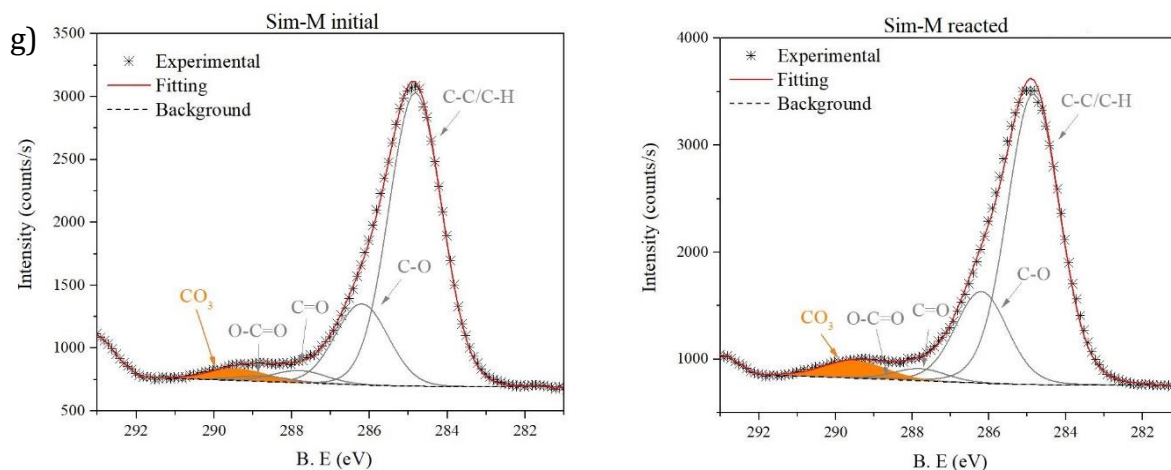


**Figure S-2** Quantification of XPS survey spectra from the samples analysed in this study. From the top to the bottom, initial (before reaction) and reacted (after aqueous alteration under pCO<sub>2</sub>): Fo<sub>65</sub>-olivine (Fo<sub>65</sub>); Fo<sub>92</sub>-olivine (Fo<sub>92</sub>); augite (Cpx); K-feldspar (K-spar); anorthite (Pla); simulant-O (Sim-O); simulant-M (Sim-M).

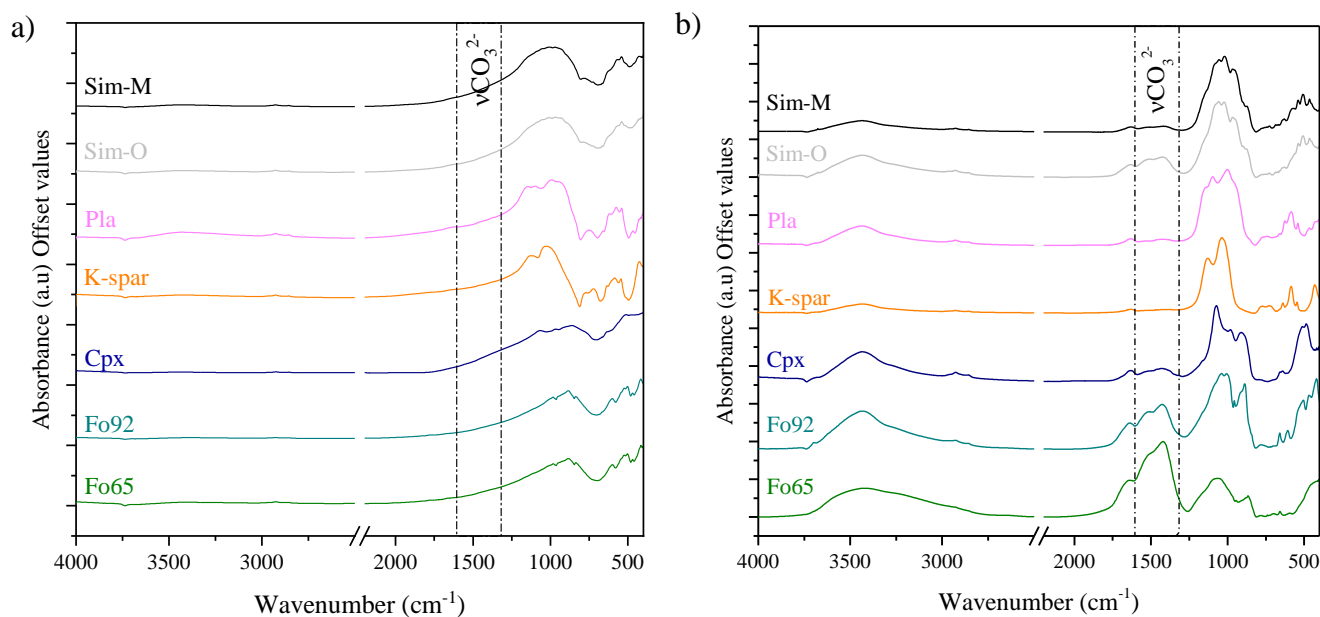






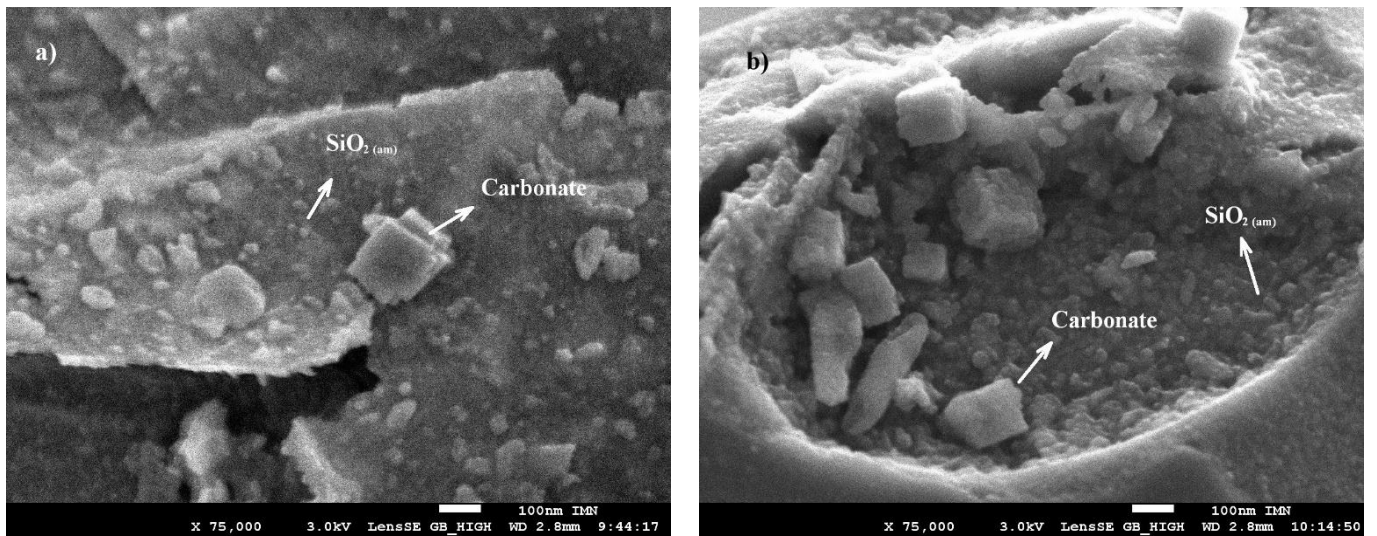


**Figure S-3** Fitting model of high-resolution C1s spectra to identify adventitious carbon (grey) and carbonate species (orange). Individual peak parameters are shown in Table S.1. The left column shows the initial samples and the right the reacted samples under a CO<sub>2</sub> atmosphere: **(a)** Fo<sub>65</sub>-olivine (Fo<sub>65</sub>), **(b)** Fo<sub>92</sub>-olivine (Fo<sub>92</sub>), **(c)** clinopyroxene (Cpx), **(d)** potassium feldspar (K-spar), **(e)** plagioclase (Pla), **(f)** Mars crust simulant-O (Sim-O) and, **(g)** Mars crust simulant-M (Sim-M).

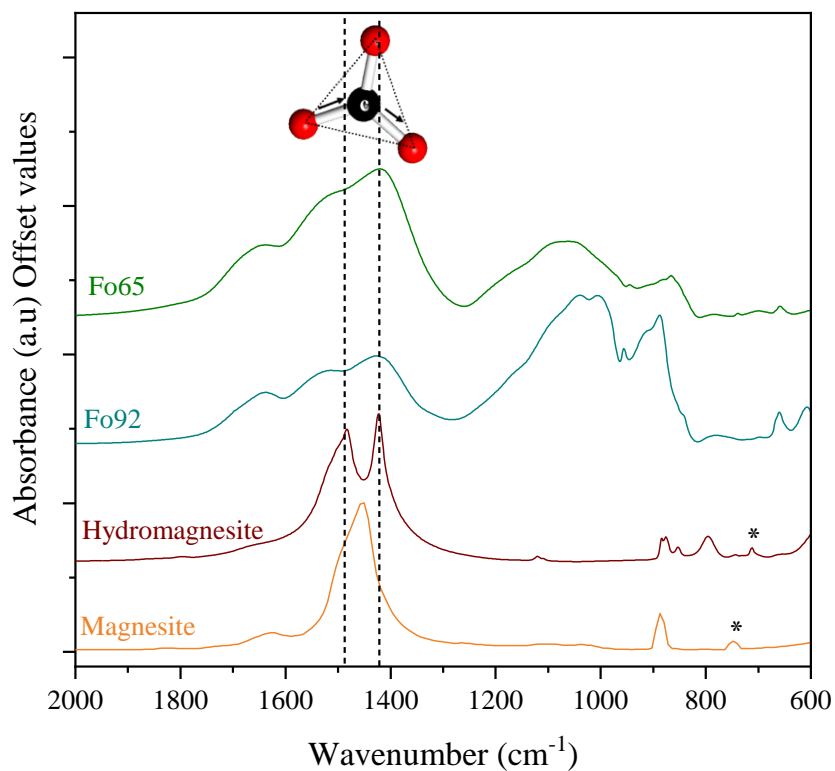


**Figure S-4** Mid-IR spectra of reacted samples: **(a)** bulk samples, **(b)** size fraction <1 μm. From the bottom to the top: Fo<sub>65</sub>-olivine (Fo<sub>65</sub>), Fo<sub>92</sub>-olivine (Fo<sub>92</sub>), clinopyroxene (Cpx), K-feldspar (K-spar), plagioclase (Pla), simulant-O (Sim-O), and simulant-M (Sim-M). Dashed lines mark the region of the asymmetric stretching vibration of the carbonates group ( $\nu_3(\text{CO}_3)^{2-}$ ) (Jones and Jackson, 1993).

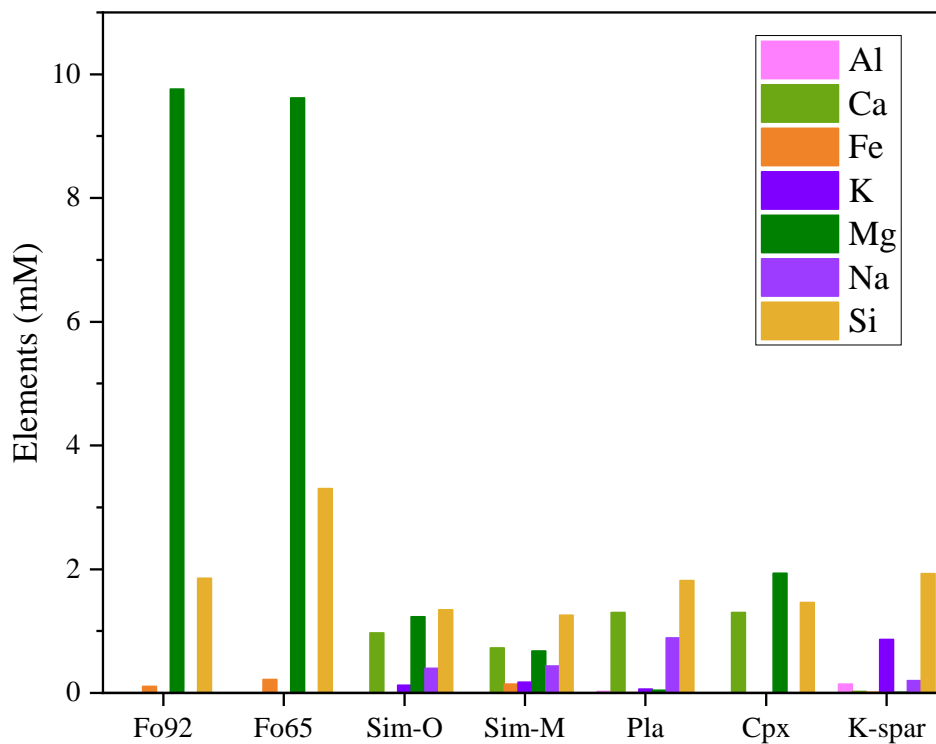




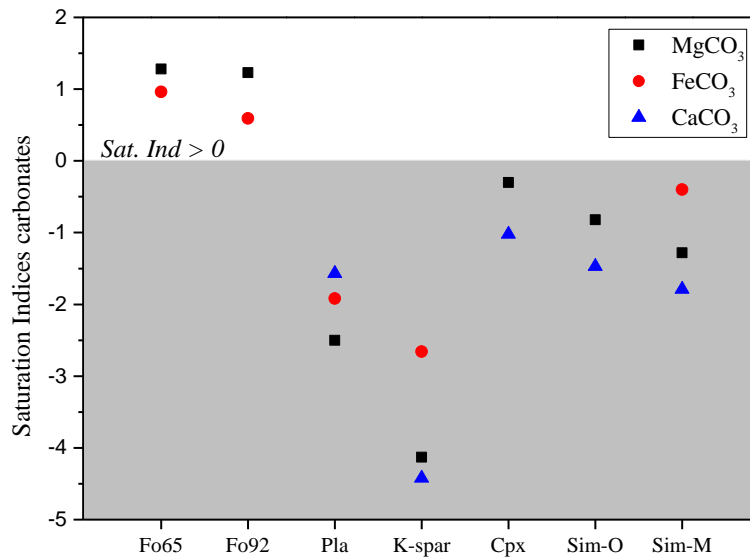
**Figure S-5** FG-SEM images of Fo<sub>65</sub>-olivine reacted sample.



**Figure S-6** IR-spectra in the 2000-600  $\text{cm}^{-1}$  region of the finest fraction (particle size  $< 1 \mu\text{m}$ ) of olivine-weathered samples (Fo<sub>65</sub> and Fo<sub>92</sub>) on the top and, hydromagnesite and magnesite spectra on the bottom for comparison (from HR inorganics Thermo Fisher database). The split band of asymmetric stretching bands of carbonates ( $\nu_3(\text{CO}_3)^{2-}$ ) matches better with hydromagnesite (dashed lines) than with the magnesite spectrum. The asterisks mark the symmetric band  $\nu_4(\text{CO}_3)^{2-}$ , which only appears in crystalline carbonate (Gago-Duport *et al.*, 2008).



**Figure S-7** The fluid chemistry of the samples: magnesium forsterite (Fo<sub>92</sub>); ferroan forsterite (Fo<sub>65</sub>), simulant with olivine (Sim-O); simulant with magnetite (Sim-M); plagioclase (Pla); clinopyroxene (Cpx); K-feldspar (K-spar). They were analysed by Baron *et al.* (2019) using inductively coupled plasma atomic emission spectroscopy (ICP-AES).



**Figure S-8** Mineral saturation indices of carbonates were calculated by Baron *et al.* (2019) with the Phreeqc software and the Thermoddem database. The Eh-pH predominance diagrams of iron solutions showed that olivine reacted samples yielded oxidising conditions that inhibit the formation of siderite.

## ➤ Geochemical Modelling and Carbonates

The geochemical models considering equilibrium conditions might lead to some uncertainties about the secondary products formed. In these models, a mineral phase can instantaneously precipitate or dissolve, depending on its saturation index (SI), Equation S-1:

$$SI = \log \left( \frac{IAP}{K_{sp}} \right) \quad \text{Eq. S-1}$$

Being IAP, the ionic activity product of the chemical species, and  $K_{sp}$  the solubility product of the mineral. Accordingly,  $SI > 0$  indicates mineral precipitation, and  $SI < 0$ , mineral dissolution.

However, equilibrium calculations are usually biased by the mineral assemblage chosen in the input file, having a significant impact on the model results (Dethlefsen *et al.*, 2012). Additionally, previous studies with batch reactor experiments have shown a strong coupling between mineral dissolution/precipitation kinetic reactions, and consequently, equilibrium conditions were not attained (Zhu and Lu, 2009; Lu *et al.*, 2013). In this regard, it is important to mention the role of metastable phases, usually not considered in equilibrium models, which are essential to determine the growth of carbonates (Montes-Hernandez and Renard, 2016). Another issue is the effect of secondary ions on the formation of carbonates, such as the well-known inhibition effect of the  $Mg^{2+}$  or  $SO_4^{2-}$  ions over calcite formation (*e.g.*, Nielsen *et al.*, 2016).

More challenging is to adapt the macroscopic rate laws (*i.e.* that are based upon the chemical affinity of bulk experiments) to incorporate surface microscopic processes (Teng *et al.*, 2000), including the dependence on the degree of supersaturation to overcome the nucleation processes and begin crystal growth (Jiang and Tosca, 2020; Kissick *et al.*, 2021).

For these reasons, geochemical models from basalt dissolution on early Mars might overestimate the carbonate formation. Thus, more laboratory experiments are necessary to refine geochemical models and adjust kinetic rates.



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