富含橄榄石的玄武岩模拟风化:对火星早期环境的启示

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摘要:在有水的环境中,橄榄石会风化形成次生矿物。而火星的表面探测到大量的橄榄石,这使得过去的火星表面是否有水成为一个争议的问题。根据模拟实验结果我们曾在国际太阳系研究学报《ICARUS》上提出:火星的表面可能存在过有机物的海洋。本文以富含橄榄石的玄武岩为原料,在温度为80~160 ℃的甲醇体系中研究了富含橄榄石的玄武岩风化规律,并对风化后的样品进行了表征。XRD分析结果表明,风化实验中没有新的次生矿物形成。SEM结果表明,经过风化实验后的样品表面出现了物理风化的痕迹。该结果支持了我们先前提出的假设,也说明在大规模的橄榄石形成后,火星表面不再有大量的水出现。

关键词:橄榄石;风化;火星;大气;进化
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Laboratory-simulated Weathering of Olivine-rich Basalt in Methanol-thermal System: Implication for Early Martian Climate

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Abstract: The detection of abundant olivine on Mars has led to hot debate over the history of water since olivine readily evolves to other minerals in the presence of water. Based on the experimental results, the hypothesis that early Mars may have had a methanol ocean has been published in Icarus. Olivine-rich basaltic materials are weathered in the laboratory under methanol-thermal conditions at temperatures of 80~160 ℃ and the alteration products are characterized. No additional secondary mineral phases are formed after methanol treatment, SEM images show physical weathering features. The experiment results presented here support the hypothesis that early Mars may have had a methanol ocean, suggesting that there has no substantial amount of liquid water on Mars since the formation of a large olivine deposits.

Key words: olivine; weathering; Mars; atmosphere; evolution

The occurrence of abundant olivine on Mars has been identified by the thermal emission spectrometer (TES) carried by the Mars Global Surveyor (MGS) spacecraft and is now confirmed by the instruments of

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the Mars Exploration Rover and the Mars Express spacecraft[1-4]. Olivine, a greenish magnesium/iron orthosilicate common in many volcanic regions, is susceptible to chemical weathering and readily alters to other minerals such as iddingsite, goethite, serpentine, chlorite, smectite, maghemite and hematite in the presence of water[5]. The detection of specific olivine-rich areas on the Martian surface has led to several interpretations on the history of water on Mars. The fact that massive quantities of olivine on the surface of Mars would imply that chemical weathering by water is low on Mars and that Mars has been dry for a sufficiently long period of time since the formation of olivine[1,2]. On the contrary, Tosca et al.[6] have proposed that use of olivine-bearing materials as reliable indicators for dry surface conditions on Mars relies heavily on the kinetics of weathering. The presence of unaltered olivine deposits associated with outcrops enriched in phyllosilicates detected by OMEGA spectra provides strong evidence for major alteration processes during the early history of Mars[7].

Methane on Mars has been detected by the Planetary Fourier Spectrometer (PFS) on Mars Express and the ground-based observations[8,9]. Methane could be abundant in the early Martian atmosphere[10,11]. But the present Martian atmosphere is highly oxidized, which can be evidenced by the presence of 95% carbon dioxide in the Martian atmosphere[12]. It is, therefore, reasonable to suggest that methane was oxidized to oxygenated organic species such as methanol and formaldehyde during some period of time in Martian history, and finally to CO_2, forming present Martian atmosphere. We have previously shown experimentally that the crystalline gray hematite with layered structure and sulfates can form in methanol-thermal system and concluded that early Mars may have had a methanol ocean[13]. The possibility of existence of methanol ocean at some time during Martian history is supported by the observation that lakes of liquid methane and ethane are present on Saturn′s moon Titan[14]. We in this report focus on the experimental results concerning laboratory-simulated weathering of olivine-rich basalt at temperatures of 80~160 ℃ after runs of 5 d in methanol-thermal system, and discuss the implications for interpreting Martian surface alteration as well as for illuminating the possible evolution of Martian atmosphere.

1 Experimental

Weathering reactions in natural environments are usually slow processes, often taking many years to show measurable results. In order to increase kinetics of weathering processes to achieve measurable results in a relatively short period of time, the weathering experiments approximating closed systems were performed at elevated temperatures. Samples of slightly altered olivine-rich basalt obtained from Dabieshan Mountains, China were used as starting materials for the weathering experiments. 0.506 0 g slightly altered olivine-rich basalt and 40 mL of analytical grade methanol were put in a 50 mL stainless steel autoclave at temperatures of 80~160 ℃ for 5 d, and then cooled to room temperature naturally.

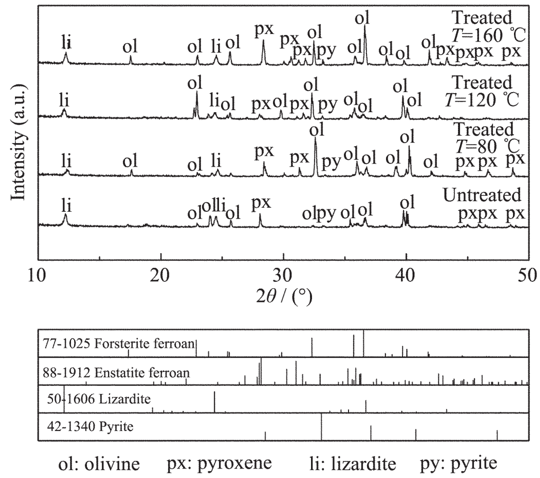
The mineralogical composition of the starting material and experimental run products was investigated by X-ray powder Diffraction (XRD). The samples were recorded at a scanning rate of $0.05°\cdot s^{-1}$ over $10°\sim50°\ 2\theta$ using a Philips X′pert 18 kW X-ray diffractometer with germanium monochromatized Cu $K\alpha$ radiation (λ = 0.154 056 nm). Scanning Electron Microscope (SEM) imaging and chemical analyses were performed by a XT30 environmental scanning electron microscopy (ESEM-TMP) at an accelerating voltage of 5 kV.

The preparation of olivine was carried out to further investigate the stability of olivine in methanol system at elevated temperatures. In a typical procedure, 0.030 g of amorphous silica formed from dissolution of olivine-rich basaltic sand, 0.034 6 g as-prepared anhydrous iron(Ⅱ) oxalate derived from vacuum-annealed iron (Ⅱ) oxalate, 0.070 g magnesium carbonate and 16 mL of analytical grade methanol were put in a 20 mL stainless steel autoclave at temperatures of 300~350 ℃ for 2 d and then cooled to room temperature naturally. The resulting precipitates were rinsed with absolute ethanol and then dried under vacuum at 40 ℃ for 4 h. Afterwards the products were immediately characterized by

XRD analysis over the range of 20° to 50° 2θ.

2 Results and discussion

Weathering: The minerals in the untreated sample identified by XRD analysis include olivine, pyroxene, along with alteration products lizardite and a trace of pyrite (Fig.1). No additional secondary mineral phases are formed after 5 d methanol treatment at different temperatures. However, peak positions are slightly shifted compared to those of the starting materials, and the intensities of some reflections have changed significantly. The olivine-rich basalt sample is complex mixture, with four phases present in each sample. A slight shift in the peak positions and variation of the peak intensity are probably due to compositional variabilities from sample to sample. In addition, the variation of relative intensity suggests development of structural defects. The detailed conditions and the XRD analysis results for methanol weathering experiments are shown in Table 1.



The untreated sample consists mostly of olivine and pyroxene, along with alteration products lizardite and a trace of pyrite

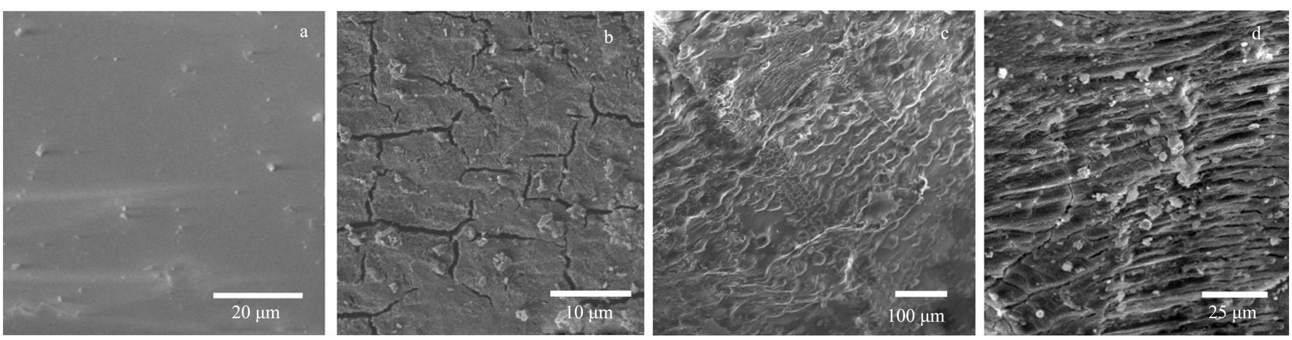
Fig.1 XRD patterns of untreated and methanol treated olivine-rich basalt at temperatures of 80~160 ℃

Table 1 Detailed conditions and the XRD analysis results for methanol weathering experiments at temperatures of 80~160 ℃

Temperature / ℃	Pressure / kPa	XRD analysis: Immediately after the completion of the experiment
80	181.1	olivine, pyroxene, lizardite, pyrite
120	641.9	olivine, pyroxene, lizardite, pyrite
160	1765	olivine, pyroxene, lizardite, pyrite

Fig.2 shows the surface features of the samples prior to and after the weathering experiment. In general the surface of the untreated samples shown in Fig.2a is relatively smooth, whereas the irregular crack of the samples at local scales is related to prior terrestrial weathering process (Fig.2b). The ratio of smooth surface area to crack surface area is 4:1. At 160 ℃ after 5 days of methanol treatment, the surface texture consists of wave textures (Fig.2c) or cracks parallel to the surface (Fig.2d), no smooth areas are observed. Grains samples from olivine-rich basalt are not ground before methanol treatment, suggesting that these features are not formed during the grinding procedure. Various dissolution features indicate that the physical weathering has taken place.

Synthesis: The XRD analysis shows that sample at



(a) Most surface of staring materials is smooth; (b) Irregular crack indicates that physical weathering process has taken place in the starting material; (c) Wave-like structures have formed on the surface of olivine-rich basalt; (d) Fracture parallel to the surface has formed on the surface of olivine-rich basalt

Fig.2 SEM images of untreated and methanol treated olivine-rich basalt sample at 160 ℃ for 5 d

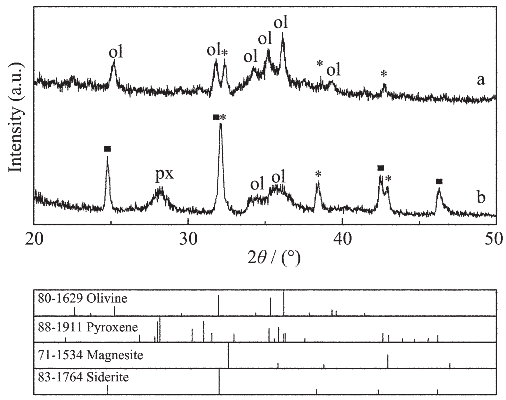
300 ℃ consist mostly of olivine, along with unreacted peaks for carbonates and amorphous silica (see Fig.3a). Apart from the existence of unreacted reagent, the sample at 350 ℃ gives a two-phase mixture of poorly crystalline olivine and pyroxene (see Fig.3b). The XRD patterns of the product show a very broad peak at 20°~30° (2θ), indicating the presence of unreacted amorphous silica. The reaction equations can be described as below:

$$FeC_2O_4 \rightarrow FeCO_3 + CO \quad (1)$$

$$FeCO_3 + MgCO_3 + SiO_2 \rightarrow (Fe, Mg)_2SiO_4 + 2CO_2 \quad (2)$$

$$FeCO_3 + MgCO_3 + 2SiO_2 \rightarrow (Fe, Mg)_2Si_2O_6 + 2CO_2 \quad (3)$$

Experimental conditions and phases that formed during the synthesis are listed in Table 2.



ol: olivine; px: pyroxene; * : unreacted magnesite; ■: unreacted siderite

Fig.3　XRD patterns of the samples between 300 ℃ (a) and 350 ℃ (b) for 2 d

Table 2　Experimental conditions and phases that formed during the synthesis

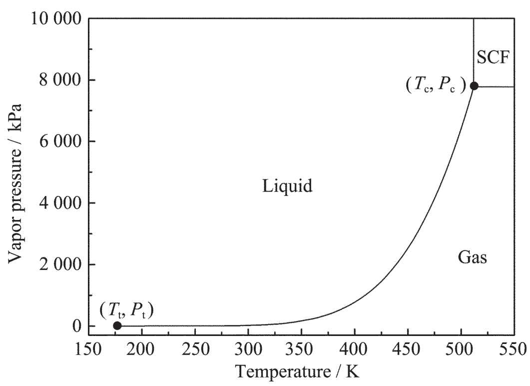
Temperature / ℃	Pressure / MPa	XRD analysis: Immediately after the completion of the experiment
300	38	olivine, magnesite, amorphous silica
350	42	olivine, pyroxene, magnesite, siderite, amorphous silica

Olivine is a significant component of several Martian meteorites and has been identified on the surface of Mars using thermal infrared remote sensing techniques[1~4]. The formation mechanism of the elevated concentrations of olivine observed remains controversial. However, there is general agreement that the olivine on Mars is the igneous rocks of volcanic origin based on the geomorphology, mineralogy, petrology, and geochemistry of olivine-bearing deposits on Mars, as well as comparisons with terrestrial analogs[1,15,16].

Olivine exposed to a warm and wet environment will alter to secondary minerals. For this reason the existence of extensive olivine on Mars has been the subject of considerable debates on the nature of olivine weathering. The fact that so much olivine is exposed at the surface indicates that there has been little or no weathering due to water, thus no liquid water-mineral chemical reactions [1,2]. However, Tosca et al. [6] have argued that the distinction between weathered and unweathered olivine on Mars may be difficult because olivine dissolved stoichiometrically over a wide range of fluid compositions. Therefore, the use of olivine as a mineralogical marker for the presence of water on Mars depends largely on the kinetics of weathering. Recently, the detection of unaltered olivine in association with diverse phyllosilicates favors the alteration hypothesis[7]. Field weathering rates of basalt in a Mars-analog environment suggest that chemical weathering is a relatively minor process and physical weathering plays a larger role[17].

There is extensive study of the olivine weathering in laboratory and natural settings [18~23]. Although field and laboratory weathering rates on Earth differ significantly, by up to 5 orders of magnitude[24], several workers have suggested that reactivity trends and mechanisms prove to be the same in both cases [18~20]. Therefore, laboratory-simulated weathering of olivine-rich basalt may also provide information on the duration of weathering on Mars, which in turn will help to illuminate the climate history of Mars. On the basis of our experiments, physical weathering has dominated over chemical weathering during the time that olivine-rich basalt has been exposed to the methanol-thermal system, and chemical weathering may have been a relatively minor process. Olivine and orthopyroxene are thermodynamically stable at high temperatures and pressures present deep within the Earth(or within Mars), whereas they are thermodynamically unstable at lower temperatures in the near-surface environments[25]. This may explain the synthesis of olivine and pyroxene at elevated temperatures and physical weathering of olivine and pyroxene at low temperatures.

The fate of water on Mars is a hotly debated topic. Catastrophic outflow channels and dendritic networks of valleys triggered the proposal that the water must have flowed at the surface in order to form these features[26,27]. The discovery of the gray crystalline hematite exposures may provide the evidence that a lake or ocean environment has emerged in the Martian history[28]. In the previous work we have shown experimentally for the formation of crystalline gray hematite with layered structure and sulfates in methanol-thermal system and suggested that early Mars may have had a methanol ocean[13]. Definitive evidence obtained during the Cassini Radar flyby of Saturn′s haze-shrouded moon Titan for the presence of methane and ethane lakes on the surface of Titan due to Titan´s low temperature and atmospheric pressure[14]. Similarly, the extreme cold conditions at Mars, with surface average temperature around 220 K globally and a total atmospheric pressure averaging about 6 mbar, allow for methanol to be existed in liquid form on the surface of early Mars. Fig.4 presents vapor pressure data available in the literature versus temperature, which covers the temperature range from the triple point to the critical point[29,30]. The potential for liquid methanol to be existed in the past is



T_t: the temperature of the triple point; P_t: the vapor pressure of the triple point; T_c: the temperature of the critical point; P_c: the vapor pressure of the critical point

Fig.4 Pressure-temperature phase diagram of methanol in the temperature range between the triple point and the critical point

strongly governed by the stability of liquid methanol even if the Martian atmosphere may have been thicker and the climate warmer in the past[31]. On the basis of SEM analysis, olivine-rich basalt shows weathering features after methanol treatment at temperatures of 80~160 ℃. Actual weathering rate of olivine on Mars is slower due to the great difference in temperature between laboratory and Mars, which might account for the presence of extensive olivine on Mars. In the following sections we describe hypotheses regarding formation of organic chemicals′ ocean and assess the plausibility of the model.

The evolution of the chemistry of the Martian atmosphere is of fundamental importance in understanding how the climate of Mars has changed. There is substantial evidence that the Martian volatile inventory and climate have changed markedly throughout the planet′s history[31]. The Sun′s luminosity was about 30% lower 4 Gyr ago compared with that of today, which requires a very thick greenhouse atmosphere to generate enough greenhouse warming to maintain a warm climate at that time[32,33]. Ammonia was the suggested greenhouse gas at that time[34]. However, ammonia rapidly photodissociates to form nitrogen and hydrogen[35] unless it is protected by some sort of UV shield[36]. As on Earth and Venus, a dense CO_2 atmosphere has been believed to play a central role in controlling Martian surface temperature[33,37,38], whereas subsequent work as discussed by Kasting indicated that the condensation of CO_2 would reduce the atmospheric temperature lapse rate and severely limit the magnitude of the greenhouse effect[39]. The reason why methane may play an important role in early Martian climate is that methane may be an important greenhouse gas on early Earth[11,40,41]. In fact, the European Space Agency′s Mars Express orbiter and the ground-based observations have detected methane in the present Martian atmosphere[8,9].

When the atmosphere is an oxidizing environment, methane is subject to photolysis by the solar ultraviolet rays in the upper atmosphere and oxidation by OH radicals and ozone, whereby methane is gradually degraded toward its oxidative products such as methanol, formaldehyde, other oxygenated organic chemicals, and finally endpoints carbon dioxide through a sequence of radical and nonradical intermediates. Photochemical models as illustrated by Wong et al.[42,43] support this loss mechanism of methane on Mars. In addition, a laboratory study of Tyndall et al.[44] has essentially confirmed the hypothesis. It seems rational to assume that organic solvent systems such as methanol are present in the distant Martian past for several reasons. First, compared with results of a point model with CH_2O measurements carried out in the terrestrial upper troposphere, Jaegle et al.[45] suggested that the conversion of CH_3OH to CH_2O on aerosols could be another CH_2O source in addition to standard CH_4 chemistry in the upper troposphere. Second, the existence of oxygenated organic chemicals is further supported by the detection of the methane and formaldehyde in the Martian atmosphere [46]. As discussed previously, methane and formaldehyde lost to photolysis must be continually replenished, which is consistent with a surviving remnant of oxygenated organic chemicals′ ocean. Additional evidence in favor of such methane photochemistry and methane oxidation processes comes from the predominant presence of carbon dioxide in the present Martian atmosphere[12].

3 Conclusions

Experiments have been performed to investigate the stability of olivine-rich basalt in methanol-thermal system. The present observations imply that chemical weathering of olivine is minimal, and physical weathering plays a more important role. Thus, the existence of large quantities of olivine on the surface of Martian suggests that there has no substantial amount of liquid water on Mars since the formation of large olivine deposits. Although the experimental results presented here are used to support the hypothesis that early Mars may have a methanol ocean, any conclusions drawn here can only be firmly validated by more in-depth mineralogical and geochemical characterization of rock and soil from different climate regions, from different locations within each region, and from different depths beneath the surface of Mars.

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