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### The petrological expression of early Mars volcanism

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[1] Crystallization products of liquids produced by partial melting of a possible Martian mantle for conditions covering the earliest Noachian era to the most recent Amazonian times have been modeled using the MELTS thermodynamic calculator. The results imply a transition from low-calcium pyroxene dominated assemblages in the Noachian to high-calcium pyroxene assemblages in the Hesperian and Amazonian, which is remarkably consistent with observations made by orbiting visible and near-infrared spectrometers. This transition is interpreted as the consequence of the thermal evolution of the mantle, with no need for exotic conditions, such as higher water content or nonchondritic Ca/Al ratio of the mantle source, to produce low-calcium pyroxene rich lithologies. Our results are compatible with numerical models of the thermal evolution of Mars that predict high production rates of crust on early Mars, implying that Noachian rocks exposed at the surface may be petrological expressions of this volcanism rather than being associated with mantle overturn following the crystallization of a magma ocean.

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### 1. Introduction

[2] The composition of magmas produced by partial melting of planetary interiors has the potential to preserve a record of the pressure-temperature conditions of melting, an approach recently applied to Mars using surface chemistry data obtained by the gamma-ray spectrometer onboard Mars Odyssey [El Maarry et al., 2009; Baratoux et al., 2011]. However, this method can only be applied to spatially extensive regions that show clear morphological evidence for volcanism, restricting its application in the case of Mars to the more recent Hesperian and Amazonian terrains (age <3.7 Ga). On the other hand, orbital spectroscopy provides complementary constraints on the mineralogy of magmatic rocks of all ages [Bibring et al., 2006]. Such work shows that igneous rocks at the surface of Mars have a mineralogy broadly similar to that of basaltic rocks on Earth, dominated by plagioclase [Rogers and Christensen, 2007] and pyroxene [Mustard et al., 2005; Baratoux et al., 2007; Poulet et al., 2009] with or without olivine [Koeppen and Hamilton, 2008]. Of these minerals, pyroxene is particularly amenable to study, thanks to strong absorption features in the nearinfrared, which allow low-calcium pyroxenes (LCP) to be distinguished from high-calcium pyroxenes (HCP) [Cloutis

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and Gaffey, 1991]. The OMEGA and CRISM visible and near-infrared imaging spectrometers provide evidence for a significantly higher proportion of LCP in the Noachian Highlands (age >3.7 Ga) relative to Hesperian terrains such as Syrtis Major [Mustard et al., 2005; Baratoux et al., 2007; Poulet et al., 2009]. A systematic evolution of igneous mineralogy with geological time has been confirmed by subsequent studies. For example, LCP-rich outcrops have been identified in the Noachian walls of Valles Marineris [Flahaut et al., 2011], while high HCP/LCP ratios have been found associated with Hesperian volcanic deposits of the Circum-Hellas Volcanic province [Williams et al., 2008] and in excavated Hesperian rocks at Chryse and Acidalia Planitia in the Northern plains [Salvatore et al., 2010]. Characterization of the youngest volcanic regions (e.g., Tharsis dome, and Elysium and Amazonis Planitia) is complicated by extensive dust coverage, but a continued decrease in the proportion of LCP would appear to extend to the Amazonian, where localities such as Amazonis Planitia [Stockstill-Cahill et al., 2008], Noctis Labirynthus, Echus Chasma [Mangold et al., 2010], and volcanic domes in the northern plains [Farrand et al., 2011] all show assemblages strongly dominated by HCP, with associated plagioclase. These young areas would appear to be rich in olivine, as exemplified by the effusive volcanism in Amazonis Planitia, where one of the highest concentrations of olivine at the Martian surface has been described (up to 60% when oxides are removed) [Stockstill-Cahill et al., 2008].

[3] Overall, there is thus a clear transition in the nature of the pyroxenes observed in magmatic rocks at the surface of Mars as a function of geological time, and a possible increase in olivine. This transition in pyroxene composition has been shown to be particularly prominent near the Noachian/Hesperian boundary where the LCP/(HCP+LCP) ratio decreases from 0.4 at the Noachian to 0.2 at the

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Hesperian [*Mustard et al.*, 2005; *Baratoux et al.*, 2007; *Poulet et al.*, 2009]. Furthermore, the fact that a sharp contrast in LCP/(HCP+LCP) is observed where Hesperian volcanic material is in direct contact with the Noachian crust, (e.g., Syrtis Major [*Mustard et al.*, 2005; *Baratoux et al.*, 2007]) has prompted the view that construction of the Noachian crust may have taken place under conditions distinct from those of later periods [*Poulet et al.*, 2009; *Bibring et al.*, 2006]. For example, it has been proposed that LCP-rich outcrops may be associated with higher degrees of partial melting or may trace the crystallization of a H<sub>2</sub>O-bearing magma, followed by a drier and HCP-rich volcanism in the Hesperian [*Poulet et al.*, 2009].

#### 2. The Early Thermal Evolution of Mars

### 2.1. A Peak in Volcanic Activity at the Noachian/ Hesperian Boundary ?

[4] Changes in igneous mineralogy would appear to take place at approximately the same time as the transition from hydrated to sulfur dominated alteration products [Bibring et al., 2006]. This observation has led to the idea that a peak in volcanic activity may have occurred in the late Noachian, resulting in a massive release of sulfur, causing a transition from non-acidic to acidic surface conditions [Bibring et al., 2006]. The simultaneous formation of volcanic plains in both hemispheres during the Hesperian period [Salvatore et al., 2010] may be taken as evidence in favor of the existence of a peak in volcanism. In this scenario, the Noachian era would have been a period of subdued or non-existent volcanic activity, in which case Noachian igneous rocks may be remnants of a primary crust that formed during the solid-state overturn of a crystallized magma ocean, within 50 Ma of accretion [Elkins-Tanton et al., 2005]. If true, Noachian terrains would have the potential to provide insights into the details of magma ocean crystallization (i.e., allowing to distinguish deep versus shallow magma ocean models [Elkins-Tanton et al., 2005]).

# **2.2.** Scenarios for the Thermal Evolution of Mars in the Noachian

[5] On the other hand, a peak in volcanic activity at the Noachian/Hesperian boundary would appear in contradiction with the crust production rates predicted by numerical models of thermal evolution including mantle partial melting [Breuer and Moore, 2007]. Furthermore, low elastic thicknesses derived for the Noachian period also imply high heat fluxes at that time, arguing in favor of continuous cooling and growth of the lithosphere [Grott and Breuer, 2008]. An independent line of evidence to constrain the thermal evolution of the Martian mantle during the Hesperian/ Amazonian has been proposed based upon analysis of the chemistry of volcanic provinces [Baratoux et al., 2011]. This approach has been used to infer a drop in mantle temperature of 80K associated with a thickening of the lithosphere of 50 km during this period. These values imply a Urey number (ratio of heat production over heat losses) of approximately 0.7, as expected for the mature evolution of a stagnant-lid planet [Breuer and Moore, 2007]. Nevertheless, numerical extrapolation of the thermal evolution back in time is not a simple matter because of insufficient knowledge of the viscosity of the Martian mantle [Breuer and Spohn,

2006]. Numerical models suggest a wide range of possible values for the Urey number during the earliest periods of Martian history (typically from 0.3 to more than 1.5) [*Breuer and Moore*, 2007; *Morschhauser et al.*, 2011]. Most paleo-heat flows derived from lithospheric strengths [*Grott and Breuer*, 2008] imply that the Urey number was below 1, but values close to or slightly above unity for the Noachian have also been suggested [*Ruiz et al.*, 2011]. We will therefore consider that plausible evolutions of the thermal state of the mantle in the Noachian are bounded by two extreme scenarios. Both scenarios end with a Urey number of 0.7 at 3.7 Ga, the first having an initial Urey number of 0.3. An intermediate scenario assuming a constant Urey number of 0.7 is also considered.

[6] For the scenarios with a Urey number equal to or lower than 0.7, the Noachian lithosphere would be thinner, and partial melting would occur at lower pressures, a situation that necessarily leads to higher degrees of partial melting. For the situation beginning at higher Urey number, magmas equilibrate at a higher pressure in the Noachian than in the Hesperian, but an increase of the degree of partial melting is nevertheless induced by a hotter mantle.

# 3. Modeling the Mineralogy of Martian Igneous Rocks

#### 3.1. Thermodynamic Model

[7] The composition of primary melts and their crystallization sequence at the surface were calculated for conditions of partial melting covering the entire thermal evolution from Noachian to upper Amazonian. The time-dependent conditions of partial melting are defined by the potential mantle temperature T (the temperature that an unmolten mantle would have had if taken adiabatically to a pressure of 1 bar) and by the pressure P at the base of the lithosphere, assuming batch melting at those conditions. The thermal evolution of the mantle and the associated changes in the conditions of partial melting at mantle plumes may be represented by a single curve in this P-T space. The P-T paths associated with the different scenarios (Figure 1) considered for ages older than 3.7 Ga are calculated in three steps. First, surface heat flows are determined from the abundance of radiogenic elements given in Dreibus and Wänke [1985] and the assumed evolution of the Urey number (increasing to 1, constant, or decreasing to 0.3 at 4.3 Ga). The pressure at the base of the lithosphere is inversely proportional to surface heat flow and is extrapolated back in time from the value at 3.7 Ga multiplied by the ratio of heat flows at different ages. The change in mantle potential temperature before 3.7 Ga is then calculated by integrating between 3.7 Ga and an older age the difference between heat losses and heat production divided by the heat capacity of the planet.

[8] In order to cover possible thermal evolutions from the Noachian to the upper Amazonian, the compositions of liquids in equilibrium with the mantle at the base of the lithosphere are calculated for a wide range of potential temperatures and pressures spanning values from  $1350^{\circ}$ C to  $1500^{\circ}$ C (in steps of  $10^{\circ}$ C) and from 10 to 17 kbar (in steps of 0.5 kbar). These thermodynamic calculations were performed with pMelts [*Ghiorso et al.*, 2002] and corrected for the iron-rich composition of the primitive mantle of



Figure 1. Pyroxene composition, represented by the ratio LCP/(HCP+LCP), in the crystallized primary melts formed at various conditions defined from the potential temperature of the mantle and the pressure at the base of the lithosphere. Gray lines indicate the degree of partial melting. Three thermal scenarios anchored on the Amazonian/Hesperian periods are represented. The solid line corresponds to a constant Urey number of 0.7, the dotted line corresponds to an Urey number decreasing from 0.7 to 0.3, and the dash-dotted line corresponds to an Urey number increasing from 0.7 to 1.0. Abundances of heat-producing elements in the Martian mantle are constrained from chondritic and Shergottite-Nakhlite-Chassignite meteorites (Dreibus and Wänke, 1985). The thick black line indicates the complete elimination of the clinopyroxene in the mantle residue. White circles represent the conditions of partial melting for the three cases for which the equilibrium crystallization sequences are represented in Figure 2.

Mars [*Dreibus and Wänke*, 1985]. These corrections consist in a set of offsets derived for each oxide component to bring calculated values into the closest possible agreement with experimental values given by [*Bertka and Holloway*, 1994] following *El Maarry et al.* [2009]. Offset values are: SiO<sub>2</sub> -3 wt %, FeO -3 wt %, Al<sub>2</sub>O<sub>3</sub> +1 wt %, CaO + 1 wt %, and MgO -2 wt %. Then, for each partial melt composition, equilibrium crystallization sequences at 1 bar and for oxygen fugacity two log-units below the Quartz-Fayalite-Magnetite buffer have been calculated with the low-pressure Melts algorithm [*Ghiorso and Sack*, 1995; *Asimow and Ghiorso*, 1998].

## 3.2. Results—Crystallization Sequences and Pyroxene Compositions

[9] Values of LCP/(HCP+LCP) vary from 0 (clinopyroxene only) to 1 (orthopyroxene only), for the range of partial melting conditions considered (Figure 1). To illustrate the overall igneous mineralogy, equilibrium crystallization sequences at surface conditions of primary melts formed at the Amazonian/Hesperian and Hesperian/Noachian boundaries have been calculated and are shown in Figure 2a (corresponding to formation conditions of P=16 kbar,  $T=1380^{\circ}$ C) and Figure 2b



**Figure 2.** Equilibrium crystallization sequences for three thermal states defined from the mantle potential temperature (*T*) and the pressure at the base of the lithosphere (*P*) where batch melting occurs. (a) The first case represents the Amazonian/Hesperian boundary (P=16 kbar,  $T=1380^{\circ}$ C, see Figure 1), (b) the second case represents the Hesperian/Noachian boundary (P=14 kbar,  $T=1410^{\circ}$ C, see Figure 1) according to the path proposed by (*Baratoux et al.*, 2011). (c) The last case would represent a plausible scenario for the Noachian period with a hotter mantle and a thinner lithosphere (P=13 kbar,  $T=1440^{\circ}$ C, constant Urey number of 0.7). The positions of the three cases are represented in the *P*-*T* space on Figure 1.

(corresponding to formation conditions of P=14 kbar,  $T=1410^{\circ}$ C). A third case (c) represents the crystallization of a Noachian primary melt with conditions of partial melting extrapolated back in time assuming a constant Urey ratio of 0.7 (Figure 2c, corresponding to the intermediate scenario in Figure 1, P=13 kbar,  $T=1440^{\circ}$ C).

[10] Assuming that primitive magmas are a dominant component of the Martian crust [McSween et al., 2006; Baratoux et al., 2011], olivine-rich young volcanism (Figure 2a), and the evolution of the LCP/(HCP+LCP) ratio (Figure 1) observed at the Hesperian/Noachian transition would appear to be a natural consequence of the evolution of primary melt compositions over time. Higher values of LCP/(HCP+LCP) during the Noachian occur for all reasonable variations in Urev number, as illustrated in Figure 3. Moreover, we note that the transition from HCPdominated to LCP-dominated assemblages occurs over a restricted range of temperature. Indeed, the observed decrease of LCP/(HCP+LCP) from 0.4 to 0.2 corresponds to a temperature difference of less than 10K and may be easily reproduced in less than 300 Ma, especially if the Urey number remains well below 1 (Figure 3). This sharp transition can be related to complete elimination of the clinopyroxene from the residue, which occurs at conditions close to the Noachian/Hesperian boundary. For higher degrees of partial melting, a fundamentally different cotectic reaction is at work, for which melting of orthopyroxene contributes significantly to the liquid, as already observed in experimental studies [Bertka and Hollowav, 1994]. In addition, melting occurs at shallower depths in the Noachian, such that melting of olivine is inhibited, leading to the formation of Si-rich liquids in comparison with those of the Hesperian/Amazonian periods. This formation of melts richer in silica at low pressure as a consequence of progressive changes in melting reactions with pressure is well known in the case of the terrestrial mantle



**Figure 3.** Evolution of the LCP/(HCP+LCP) ratio around the Noachian/Hesperian boundary for three possible scenarios of thermal evolution of the Martian mantle defining the conditions of partial melting of the primitive mantle of Mars as a function of time. The solid line corresponds to a constant Urey number of 0.7, the dotted line corresponds to an Urey number decreasing from 0.7 at 3.7 Ga to 0.3 at 4.3 Ga, and the dash-dotted line corresponds to an Urey number increasing from 0.7 at 3.7 Ga to 1.0 at 4.3 Ga.

[*Kushiro*, 2001]. Both factors favor the crystallization of LCP-rich assemblages from Noachian melts.

[11] Examination of typical Noachian/Hesperian crystallization sequences (Figures 2b and 2c) indicates that LCP systematically saturates before HCP. An alternative explanation for the higher values of LCP/(HCP+LCP) in the Noachian could thus be that the surface rocks contain a higher fraction of cumulate rocks dominated by early saturating phases. Such a scenario would be consistent with Noachian erosion rates thought to be 3 to 6 orders of magnitude higher than in the Hesperian [Craddock et al., 1997], which would have acted to remove volcanic edifices and expose deeper rocks. Nevertheless, the recent finding of numerous Early Noachian (>4.0 Gy) volcanoes in the southern highlands [Xiao et al., 2011] confirms that morphological evidence for Early Noachian volcanism may be partially preserved, in agreement with the scenario that volcanic rocks are present on exposed sections of the Noachian crust.

### 4. Discussion

[12] The Shergottite-Nakhlite-Chassignite class of meteorites, generally accepted to be of Martian origin, are an additional potential source of information. In terms of the mineralogy, the Nakhlites are olivine-bearing clinopyroxene cumulates, and their age is well defined at 1.3 Ga [Bouvier et al., 2009]. This is perfectly consistent with the olivine and HCP-rich assemblages predicted to crystallize from Amazonian primary melts (Figure 2a). At the other extreme, one of the oldest Martian meteorites (ALH84001; with a crystallization age from Lu-Hf of  $4.091 \pm 0.030$  Ga [Larpen et al., 2010]) is an orthopyroxenite, consistent with our scenario of genesis from liquids produced by high degrees of partial melting. Unfortunately, the controversy surrounding the age of the Shergottites [Nyquist et al., 2001; Bouvier et al., 2009; Shafer et al., 2010] and in particular the possible shock-induced resetting of several radiometric systems [El Goresy et al., 2013] restrict their use in constraining magmatic evolution over time, but as they contain a mixture of both HCP and LCP, a case could be made that they are intermediate in age between ALH84001 and the Nakhlites. Considering the chemistry of these meteorites, rare-earth-element abundances and isotopic data suggest a heterogeneous source region for the Shergottites [Peslier et al., 2010; Shafer et al., 2010]. Depletion of the mantle source may be associated with the existence of a magma ocean isolating that reservoir for long periods of time [McSween, 2002]. Characteristics of the Shergottites are not readily reconcilable with melting of a primitive mantle source, despite the fact that the latter can explain the principal characteristics of the surface chemistry and mineralogy such as Si and Fe concentrations [Baratoux et al., 2011] and pyroxene compositions, available from in situ and remote sensing observations for the Noachian and Hesperian periods. Further work is required to understand this discrepancy, but we note that these various geochemical reservoirs have often been defined by trace elements and isotopes that are highly sensitive to even modest degrees of melting or contamination, whereas the major elements are much less sensitive in this respect.

[13] Based upon our analysis, we conclude that the Early Noachian was a time of widespread volcanic activity associated with planetary cooling and that most of the Noachian rocks exposed at the surface should be related to this period of intense volcanism. If a magma ocean on early Mars occurred, we contend that the volcanic products of mantle overturn are thus likely to have been buried by the subsequent Noachian magmatism. Within this framework, the igneous mineralogy of surface rocks does not require a peak in volcanic activity around the Noachian/Hesperian boundary. However, a global change in surface conditions from those producing clay-bearing rocks (alkaline conditions) to those producing sulfate-bearing rocks (acidic conditions) would also appear to have occurred at approximately that time [Bibring et al., 2006], requiring some explanation. In this respect, it has been shown that volcanic gas composition strongly depends on the atmospheric pressure [Gaillard and Scaillet, 2009], sulfur-dioxide rich volcanic gases being produced under the current low-pressure conditions. A decrease of atmospheric pressure at the Noachian/Hesperian boundary would therefore reconcile the idea that Hesperian volcanic activity is responsible for the formation of massive sulfate deposits [Bibring et al., 2006], whereas the Noachian crust was formed in the context of widespread volcanic activity under a denser atmosphere, with no need to invoke a peak in the amount of volcanism. On the other hand, further doubts were recently raised on the need for a global acidic event to produce the sulfate-bearing assemblages [Dehouck et al., 2012]. Indeed, this latter study emphasizes the role of the weathering of sulfide-rich basalts, pointing again to an intense period of volcanism in the Noachian.

### 5. Conclusion

[14] This study demonstrates that the principal characteristics of the igneous mineralogy of Mars may be explained by continuous magmatic activity since the Early Noachian in the context of thermal evolution of the interior of the planet. In particular, the apparent sharp transition in the LCP/(HCP+ LCP) ratio at the Noachian/Hesperian boundary may be due to a slightly higher degree of partial melting resulting from a warmer mantle and/or melting at lower pressure in the Noachian. The increasing number of remote sensing observations of ancient igneous rock exposures may reveal in this case a progressive change in pyroxene composition, reflecting continuous volcanic activity at the planetary scale in both the Hesperian and Noachian eras. An early start of volcanism related to mantle plumes is in perfect agreement with high crust production rates predicted by numerical models of the thermal evolution of Mars for the first 500 My of its history [Morschhauser et al., 2011].

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