

USING MINERAL CHEMISTRY IN GALE CRATER SEDIMENTARY ROCKS TO CONSTRAIN ANCIENT IGNEOUS PROCESSES ON MARS. V. Payré¹, K. L. Siebach¹, R. Dasgupta¹ and E. B. Rampe²

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Introduction: Over the last decade, various datasets have shown evidence for unexpected Noachian felsic materials at the surface of Mars. The Martian meteorite NWA 7034, also well-known as *Black Beauty*, has been identified as a regolith breccia containing mafic clasts along with remarkable felsic igneous clasts dated at 4.43 Gyr and classified as monzonitic [1-2]. In addition, the Curiosity rover has been analyzing felsic materials within Gale crater since its landing in 2012 [3-4]. The X-ray diffractometer (XRD) in the CheMin instrument and the laser induced breakdown spectrometer (LIBS) ChemCam onboard Curiosity identified plagioclase and K-spar along with augite and pigeonite [3-5]. In sedimentary rocks, those minerals are detrital, coming from a magmatic source of Noachian age that was sufficiently evolved to form K-spar [1,6]. Several igneous materials analyzed by ChemCam have been classified as part of the alkaline trend including Harrison, a trachy-andesite [7].

All these findings in Gale provide evidence for the occurrence of a Si and alkali-rich melt in Noachian time [6]. The objective here is to constrain how this melt could have formed. However, no instrument onboard the rover is able to measure a bulk composition as terrestrial studies would. In addition, Curiosity mainly encountered sedimentary rocks, which contain random mixtures of igneous minerals. Therefore, we use the crystal chemistry of the igneous minerals identified in soils and ancient igneous and sedimentary rocks to constrain the magmatic processes that could have formed them to form the Noachian-age igneous source rocks for the Gale crater sedimentary fill.

Igneous minerals from ChemCam: The ChemCam LIBS instrument enables analysis of oxide compositions of targets 100s of μm in scale, which may provide uncontaminated mineral analyses when minerals are $>500 \mu\text{m}$ [8-9]. We consider here the targets analyzed within the fluvio-deltaic sediments observed in the first 750 sols, during which ~ 5500 points were analyzed by LIBS. These points include primary minerals, secondary authigenic or diagenetic minerals, and mixtures of minerals and with amorphous materials. To focus on pure igneous minerals as feldspar, pyroxene and olivine, stoichiometric and compositional filtering was performed on all LIBS points. Based on this filtering, a total of 118 feldspars and 9 pyroxenes were analyzed by LIBS (Fig. 1a-b). No pure olivine has been sampled, meaning that either the grains were

too small to be solely analyzed i.e., $< \sim 500 \mu\text{m}$, or none exist in the analyzed spots.

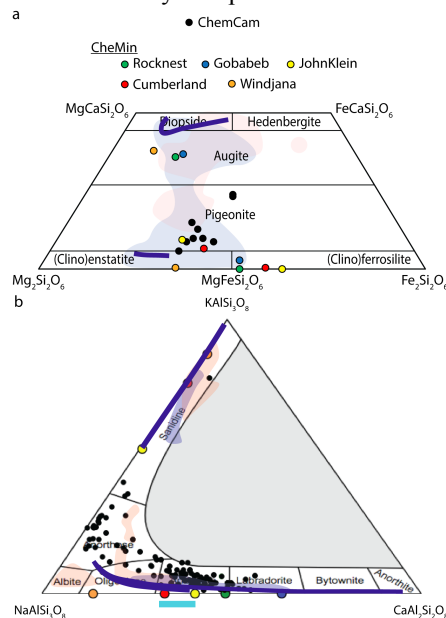


Fig. 1. Ternary diagrams of (a) pyroxenes and (b) feldspars from ChemCam and CheMin analysis [10]. Rocknest and Gobabeb are loose sediment, other CheMin samples are rocks. Black dots are minerals identified by ChemCam analyses. For reference, the blue and red patches show pyroxenes (a) and feldspars (b) of the mafic and felsic clasts from NWA 7034 respectively. The light blue line shows the An component suggested from APXS data [11]. The dark blue lines are MELTS model results showing the minerals produced by a fractional crystallization path of a melt (14 wt.% partial melt at 15 kbars from a model Martian mantle [12]) at 1 kbar, FMQ +1 with 1% H_2O .

Pyroxenes are mainly Mg-pigeonites, and feldspars range from labradorites to alkali-rich feldspars.

Igneous minerals from CheMin: Five CheMin XRD samples were included in this study: two Sheepbed mudstone samples, one fluvial sandstone, and an inactive sand shadow and an active eolian dune, which likely have distinct sources than the three other rocks. All of them contain pyroxenes and feldspars as shown in Fig. 1. Interestingly, pigeonites and feldspar compositions are similar between CheMin and ChemCam analysis. However, CheMin analyzed orthopyroxenes and augites that ChemCam did not. These minerals may have been too small to be measured by ChemCam, or the low angular resolution of CheMin may adversely affect the identification of specific pyroxene

compositions [10]. In addition to these igneous minerals, olivine has been detected by CheMin. Rocknest and Gobabeb are two soils, containing 21 and 26 wt% olivine respectively, with Mg# 0.57 and 0.54 [10]. All of the sedimentary rocks contain less than 8 wt% olivine with Mg# between 0.57 and 0.68.

Discussion: Thermodynamical pMELTS and rhyolite-MELTS modeling was performed to match the compositions of the set of minerals observed by CheMin and ChemCam. Udry et al. [14] showed that low pressure fractional crystallization of a basaltic Martian magma composition can produce evolved melts with compositions similar to igneous rocks' analyzed by ChemCam. Starting simulations from Martian basalt compositions and melts resulting from 5 to 20% of partial melting of a primitive mantle composition, fractional crystallization has been performed at pressures from 1 kbar to 7 kbars, with an oxygen fugacity varying from FMQ-1 to FMQ+2. Interestingly, one of the more challenging mineral compositions to replicate under these conditions was plagioclase feldspar with An₄₅₋₅₅. Most of these tests formed feldspars beginning from plagioclases with too high Ab component, i.e., An < 45%. These tests are inconsistent with the occurrence of An₄₅₋₅₅ plagioclase, which represent 13% of feldspars reported here (Fig.1b). Moreover, if the measured plagioclases in Gale are a little weathered, they would have lost some Ca, meaning that initial An content must have been slightly higher than 50%. A set of models have been performed to understand the igneous conditions under which plagioclase with higher An component can form. The successful models unexpectedly form higher An feldspars at late stage when feldspar solvus is reached, which may be consistent with several ChemCam observations[7]. Fig. 2 shows the conditions enabling crystallization of high An feldspars within the entire range proposed for Gale.

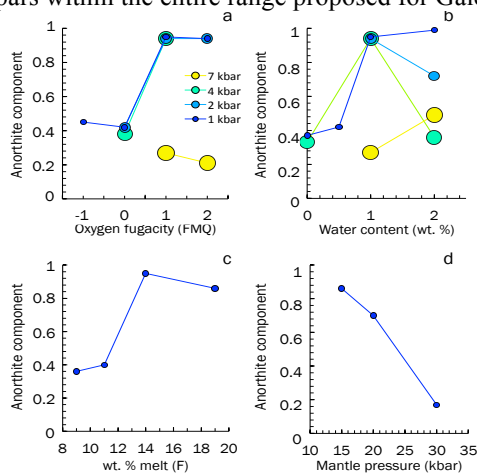


Fig.2. An content of feldspars crystallizing from fractional crystallization of a melt resulting from 14 wt.% partial melt from a

model Martian mantle at 15 kbars with 1% H₂O in (a) and various H₂O contents at FMQ +1 in (b). (c-d) shows the highest An component in a melt that has undergone fractional crystallization at 1kbar FQM+1 and 1%H₂O, resulting from (c) isobaric partial melting of a primitive mantle composition at 15 kbars and (d) 19-17% of partial melting of a primitive mantle composition at 15, 20 and 30 kbars.

As shown in Fig. 2, An > 45% is formed only at pressures <4 kbars for melts with >1 wt.% H₂O in the melt (e.g., Fig. 1). High oxygen fugacities (FMQ > +1) favor their formation. Melts resulting from low-degree partial melting of a primitive mantle composition during an isobaric or adiabatic ascent do not form these Ca-plagioclases: > 14% of partial melting is likely a reasonable threshold according to these models. We note that fractional crystallization of melts coming from partial melting of a primitive mantle composition at high pressure (30 kbars) is not likely since the stability of garnet would deplete too much Al from the melt, preventing the crystallization of the full range of feldspars observed in Gale.

In the model conditions that most successfully replicate the observed feldspars, low and high Ca- magnesian pyroxenes crystallize, but the whole range of observed iron-rich pyroxenes is not formed (Fig. 1a). This discrepancy could be due to the weathering of pyroxene, which releases first calcium and then magnesium. Similarly, olivine Mg# is predicted to be mostly higher than observed CheMin data (Mg#>0.7), but the weathering of olivine preferentially releases magnesium first, lowering its Mg#. Another explanation could be that some oxide contents in the models are shifted, as previously observed in some studies, since MELTS software is not well calibrated for Fe-rich melts as found on Mars (e.g., [15]). The liquid line of descent paths of such processes still overlap well with felsic igneous compositions from Gale crater and from the Martian breccia.

Experiments need to be pursued to ensure that these models are valid. If these models are valid, they indicate that a crustal melt with 1% H₂O at relatively high oxidation state would have been formed during the first Gyr after the formation of the solar system, and undergone fractional crystallization at shallow depths on Mars.

Reference: [1] Humayun M. et al. (2013) Nat. 503(7477), 513-516; [2] Agee C. B. et al. (2013) Science, 339(6121), 780-785; [3] Sautter V. et al. (2015) Nat. Geosc., 8(8), 605-609; [4] Treiman A. H. et al. (2016) JGR, 121(1), 75-106; [5] Meslin P.-Y. et al. (2013) Science, 341(6153), 1238670; [6] Sautter V. et al. (2016) Lithos, 254, 36-52; [7] Cousin A. et al. (2017) Icarus, 288, 265-283; [8] Maurice S. et al. (2012) SSR, 170, 95-166; [9] Wiens R. C. et al. (2012) SSR, 170, 167-227; [10] Morrison S. M. et al. (2018) Am. Min., 103(6), 857-871; [11] Siebach K. L. et al. (2017) JGR, 122(2), 295-328; [12] Dreibus & Wanke (1985) Met. 20, 367-381; [13] Payré V. et al. (2018) LPSC#2071; [14] Udry A. et al. (2018) JGR; [15] Collinet M. et al. (2015) EPSL, 427, 83-94.