In-situ evidence for continental crust on Early Mars.

V. Sautter[1], M.J. Toplis[2], R.C. Wiens[3], A. Cousin[2], C. Fabre[4], O. Gasnault[2], S. Maurice[2], O. Forni[2], E.M. Stolper[5], J. Lasue[2], A. Ollila[6], M. Fisk[7], N. Mangold[8], P.-Y. Meslin[2], P. Beck[9], P. Pinet[2], L Le Deit[8], W. Rapin[2], J.C. Bridges[10], D. Dyar[11], J.J. Wray[12], D. Vaniman[13], S. Le Mouélic[8], H. Newson[15], S. Clegg[3] and N. Lanza[3].

[1]IMPMC, Muséum d'Histoire Naturelle, Paris, France, [2]IRAP, Toulouse, France, [3]Los Alamos National Laboratory, Los Alamos, NM, U.S.A. [4]GeoRessources-Université de Lorraine, Nancy, France, [5]Caltech, Pasadena, CA, USA, [6]Chevron Energy Technology Company, Houston, TX, U.S.A., [7]College of Earth, Ocean, and Atmospheric Sciences, OR, USA, [8]LPG, Nantes, France, [9]Institut de Planétologie et d'Astrophysique, Grenoble, France, [10]Space Research Centre, Dept. of Physics and Astronomy, University of Leicester, UK, [11]Mount Holyoke College, South Hadley, MA, USA, [12]Georgia Institute of Technology, Atlanta, GA, USA, [13]Planetary Science Institute, Tucson, AZ, USA, [15]Institute of Meteoritics, Albuquerque, NM, USA.

Understanding of the geological evolution of Mars has increased dramatically thanks to new orbital[1-3], *in-situ*[4-5], and meteorite[6-8] data, but insight into the earliest epochs of magmatism (the Noachian, 4.1 to 3.7 Ga) remains scarce[9]. The landing site of the Curiosity rover, an early Hesperian age crater (~3.61 Ga[10]) formed within Noachian terrain[11], provides an unprecedented opportunity to understand Mars' earliest igneous history. Along its traverse, Curiosity has discovered light-toned rocks that contrast with samples found in regions of younger age[12]. Here we show that these are feldspar-rich magmatic rocks belonging to two distinct geochemical series. The first is an alkaline suite including both porphyritic (low Si) and aphyric (high Si) members reaching up to 67wt% SiO_2 and 14wt% total alkalis. The second is plutonic and close to quartz-diorite and granodiorite in composition. These samples reveal unexpected magmatic diversity and the ubiquitous presence of silica- and feldspar-rich lithologies. Given orbital identifications of feldspar-rich rocks elsewhere in the southern hemisphere[9, 13-14] and in light of the low average density of the highlands crust[15], we conclude that silica-rich magmatic rocks may constitute a significant fraction of the Noachian crust, providing evidence for an ancient and widespread 'continental crust' on Mars.

Current understanding of the Martian crust is largely based upon orbital spectroscopy[1-4] and meteorite analysis[6-8], which both indicate the predominance of basalts, thought to have formed through partial melting of the mantle and transport of magmatic liquids towards the surface. Indeed, the composition of younger Hesperian and Amazonian volcanic terrains is consistent with production of liquids from a mantle that was cooling over time[3]. However, in contrast to the Earth, evidence for significant volumes of deep-seated silica-rich 'continental-crust' is lacking on Mars. Localized outcrops of feldspar-rich and silica-rich material have been identified using thermal emission spectroscopy[1,9] and some nearly pure feldspar lithologies have been observed by visible and near-infrared spectroscopy (VNIR)[13-14], although there are inherent challenges in characterizing silicic rocks using these methods. Understanding the petrogenesis of these rocks requires information on their texture, composition and mineral chemistry, which can only be obtained with *in situ* measurements.

The Mars Science Laboratory (MSL) rover Curiosity landed in Gale Crater at the northern edge of the highly cratered Noachian ancient highlands. Curiosity's drive began at the Bradbury landing site, subsequently crossing a distal portion ofPeace Vallis, a fluvial channel cutting through the northern rim of Gale crater (SOM Fig. S1a-b). Gale crater contains highly alkaline rocks[16,-17], a feldspar-rich soil component[18], and evidence for feldspar-dominated rocks[19]. Here we focus on leucocratic rocks encountered by Curiosity, concentrating on results from the ChemCam instrument, a laser-induced breakdown spectrometer (LIBS) that provides chemical analyses at a submillimeter scale and detailed images with the Remote Micro Imager (RMI)[20-21]. Twenty two light-toned igneous targets have been selected along the traverse (Table S1 in SOM). They are floats within the Hummocky unit (Fig S1b) closely associated with discontinuous conglomerate outcrops (e.g. Fig. 1d) of the Peace Vallis system. These rocks have been transported by, and are thus older than, the fluvial system, making them Noachian in age[11]. Their ultimate provenance is a subsurface crustal sequence ,several km thick, sampled through the northern wall of the crater.

These light-toned rocks have been grouped into three classes based upon crystal textures observed with onboard cameras (Fig. 1).

Group 1 rocks are coarse grained (>5 mm), dominated by leucocratic minerals (~80% of the rock volume: SOM, Fig. S2b). Rock surfaces vary from flat (Fig. 1a-c) to a knobby appearance (Fig. 1b). Pearly coarse crystals (>5 mm) are locally intergrown with finer (1 mm) rectangular translucent grey grains in a graphic texture (white arrow in Fig.1a). Anhedral dark grey material forms 20% of the rock (red arrow). Grain sizes and shapes suggest igneous intrusives.

Group 2 samples are vesiculated with conchoidal fractures and shiny scoriaceous surfaces (Fig. 1f). They are largely aphyric at the RMI resolution of 100 microns and they appear to be effusive volcanics.

Group 3 rocks are porphyritic with euhedral, leucocratic phenocrysts up to 2 cm long and 2 mm wide constituting ~50% of rock volume (SOM, Fig. S2a), And embedded in a dark matrix (Fig. 1d-e). These rocks have textures typical of effusive rocks and occur both as float rocks and as clasts (~10 cm in size) in polymict conglomerates (Fig. 1d-e).

Of the 22 samples studied, 11 were selected for their pristine appearance (SOM[jcb361]). Ninety LIBS measurements on these rocks have been analysed using Independent Component Analysis (Method Section, MS). When plotted in an Al vs. Si diagram (Fig. 2) with the 4 silicate-based ChemCam Calibration Targets onboard Curiosity (three synthetic basaltic glasses and a natural ‘macusanite’ rhyolite[22] with 72% SiO_2 and 16% Al_2O_3) analyses from leucocratic rocks (groups 1 and 2) plot in the Al-Si-rich felsic range. Group 3 rocks plot in the mafic range with the basaltic calibration targets. Some overlap occurs between groups 1 and 3, as both contain a mixture of mafic and felsic materials. Felsic groups 1 and 2 are not as siliceous as the rhyolite calibration target, and Al/Si in the coarse intrusive rocks of group 1 is high. Independent classification using a hierarchical clustering method (SOM, Fig. S3) leads to 3 chemical clusters for these 90 points. The first is Ca-Al-Si-Sr rich pointing to analyses dominated by plagioclase. The second cluster is rich in K, Al, Si, Ba (Table S4) showing a K-feldspar component. The third cluster is rich in mafic components and may be subdivided into a Si-bearing, Mg- Ca–rich cluster and a Ti and Fe-rich one (Fig.S3) consistent with mixtures dominated by clinopyroxene and Ti-rich oxides. Details of the relative proportions of individual phases can be found in the MS.

Analyses have also been quantified using an univariate technique[22] (MS). In a molar Al/Si vs. (Fe+Mg)/Si diagram (Fig. 3, Table S4), LIBS analyses plot along three distinct trends: (i) analyses of felsic intrusives (group 1) define a trend along the *y*-axis from andesine (An ~30-45: molar Al/Si of 0.48-0.55) extending towards quartz (Al/Si <0.1 and (Fe+Mg)/Si < 0.2); (ii) analyses of felsic effusives (group 2) also plot along the y-axis, extending from an Al/Si close to that of alkali-feldspar (with Al/Si=0.33), decreasing to an Al/Si of ~0.15; (iii) In contrast, LIBS points from porphyritic rocks (group 3) form a clear trend joining oligoclase (An ~10-30 with Al/Si 0.37-0.48) and a mafic component with a (Fe+Mg)/Si ratio on the *x*-axis of ~0.5, consistent with an augite-dominated mesostasis.

Whole-rock compositions for each rock type have been estimated (MS, table S5). All rocks of group 2, with grain size smaller than the laser beam diameter, have SiO_2 >64 wt% and Na_2O+K_2O >10 wt% consistent with a trachytic composition in total alkali vs. silica (TAS) diagram (Fig. 4). For coarser grained group 1 rocks, only samples with multi-point rasters were selected to estimate whole-rock composition. The calculated average composition (Table S5) has ~64 wt% SiO_2, and (Na_2O+K_2O) ~4.5 wt%). These rocks are poor in mafic oxides (e.g., FeO+MgO+TiO_2 <12 wt%) and they have an evolved Mg# of ≈ 0.20-0.30. Normative calculations (Table S5) indicate 11-25% quartz, 40-62% plagioclase (An_{40-49}), 5-16% orthoclase, 15-21% pyroxene and a calculated density of ~2.8 g/cm^3, corresponding to quartz monzodiorite/quartz diorite and granodiorite. The whole-rock compositions of porphyritic group 3 rocks were constrained through a combination of modal proportions (Fig. S2b) and compositions of the constituent phases (see SOM Fig. S4, Table S5 and MS for details). Calculated compositions calculated plot in the trachyandesite field (Fig. 4) and normative calculations indicate 56% plagioclase ($An_{34}Ab_{65}$), 20% orthoclase, 17% diopside, 6% hypersthene, and 0.5% ilmenite. Rocks from groups 2 and 3 define a geochemical trend, from porphyritic trachyandesite rocks to evolved trachytes (Fig. 4).

The bulk composition of igneous rocks observed at Gale, with SiO_2 reaching 67 wt% and Na_2O+K_2O reaching 14 wt%, greatly extends the magmatic diversity observed by lander missions (Fig. 4). While the Mars Exploration Rover *Spirit* found alkali-rich compositions during its examination of the Noachian terrain in Columbia Hills (Na_2O+K_2O up to 5.5 wt %), those rocks are basaltic with bulk SiO_2 content <52 wt%. They did not exhibit visible feldspar phenocrysts and were interpreted as volcaniclastic tuff [23]. On the other hand, the Martian meteorites NWA 7533[7] and NWA 7034[8] are Noachian breccias that include mm-sized lithic clasts containing andesine, anorthoclase, and K-feldspar[7-8] providing independent evidence for early alkali-rich magmatism on Mars, but they are quartz-free.

The generation of alkali-rich parent basalts may be related to low-degree partial melting of the mantle. For example, the compositional trend of groups 2 and 3 is consistent with the 1 bar liquid line of descent for a primary basalt produced by 6% melting at 1 GPa (Fig. 4). Near-surface crystallization of such primary liquids should be associated with low proportions of olivine and high proportions of plagioclase, contrasting with later Hesperian volcanism[12, 24], but compatible with terrains of Noachian age[25]. If such alkaline magmatism is indeed a widespread feature of the Noachian, this would challenge the idea of continuous cooling of the martian mantle over geological time[3], pointing to more complex global or local variations in mantle temperature, for example, associated with the onset or waning of plume-related magmatism.

Our most intriguing finding is the quartz-normative rocks of group 1 (red symbol in Fig. 4). Texturally, these rocks are intrusive (quartz-diorite/quartz-monzonite/granodiorite composition) thus differ from andesite (Mars Pathfinder dust-free rock composition[26] in Fig. 4). They clearly originated from a deep-seated unit. This unit could be a pluton, formed through the fractional crystallization of a low-alkali parent. However, we note that quartzo-feldspathic material has also been detected in distinct locations: ancient uplifted material near the central peaks of craters in the north of Syrtis Major[25]; near the rim of Antoniadi Crater[9]. Furthermore, spectra of the CRISM instrument have shown sporadic feldspar-rich deposits, interpreted as either anorthosite[13] or granite[14], in other regions. Because orbital VNIR spectroscopy is only capable of identifying feldspar if the rock is more or less devoid of mafic minerals, these kilometer apart detections may represent end members of widespread Si-rich intrusions and it is possible that rocks such as group 1 samples occur throughout the crust in the martian highlands.

Further evidence in favour of this idea is provided by consideration of average crustal density[27]. The density calculated from *in-situ* data, SNC meteorites and gamma-ray measurements (>3100kg/m^3) is considerably higher than the density of the highlands crust constrained by geophysical data[15]. This density paradox could be solved by a buried 'light' component in the southern hemisphere[28]. Our observations thus provide the first *in-situ* evidence for such a buried crust.

Class 1 samples are petrologically reminiscent of Archean trondhjemites, tonalites, and granodiorites (TTG) some of the Earth's oldest preserved crust[29] and consistent with the interpretation of high silica material detected from orbit[25]. In detail, we note that the lower Mg# of the martian mantle and its higher potassium content relative to the Earth may explain the lower Mg# of our group 1 samples and the absence of Tonalite compared to terrestrial samples.

Pursuing this analogy, we propose that generation of granodiorite (or rocks slightly poorer in silica such as quartz (monzo-)diorite could occur through partial melting of pre-existing basaltic crust at relatively low pressure. On early Mars it is possible that dense primitive crust sank into a hot and soft lithosphere leading to partial melting although further work is required to explore the details of the geodynamical context and the nature of the volatiles required for remelting of a primitive mafic crust. An alternative scenario may involve formation of a martian equivalent of icelandites[30], recently proposed for the generation of the earliest continental crust on Earth, as these rocks too have bulk compositions similar to our group 1 rocks. Note that such an hypothesis has also been proposed to explain Pathfinder dust-free, silica-rich compositions[26]. Independently of the process leading to their formation, our data point to the possibility of generating 'continental' crust on Mars, making the early geological history of Mars much more similar to that of the Earth than currently acknowledged. 2055 words

REFERENCES

1. Christensen, P.R. et al. Evidence for magmatic evolution and diversity on Mars from Infrared observations. *Nature* **436**, 504-509 (2005).
2. Mustard, J.F. et al. Olivine and pyroxene diversity in the crust of Mars. *Science* **307**, 1594-1597 (2005).
3. Baratoux, D. et al. Thermal history of Mars inferred from Orbital geochemistry of volcanic provinces. *Nature* **472**, 338-341 (2011).

4. McSween H. Y. et al. Elemental composition of the Martian crust. *Science* **324,** 736, doi:10.1126/Science/1165871 (2009)**.**
5. Ming D.W. et al. Geochemical properties of rocks and soils in Gusev Crater, Mars: Results of the Alpha Particle X-Ray Spectrometer from Cumberland Ridge to Home plate, *J. Geophys. Res. Planets*. **113**, (E12), E12S39, doi:10.1029/2008JE003195 (2008).
6. Aouddjehane, H.C. et al. Tissint Martian meteorite: a fresh look at the interior, surface, and atmosphere of Mars. *Science* **338**, 785-788 (2012).
7. Humayun, M. et al. Origin and age of the earliest Martian crust from meteorite NWA753, *Nature,* doi :10.1038/nature, (2013).
8. Agee C. B. et al. Unique meteorite from early Amazonian Mars: water-rich basaltic breccia Northwest Africa 7034, *Science* **339**, 780-785 (2013)
9. Bandfield J.L. Extended surface exposures of granitoid composition in Syrtis Major Mars. G.R.L. **33**, L06203, doi:10.1029/2005GL025559 (2006).
10. Le Deit et al. Sequence of infilling events in Gale crater, Mars: Results from morphology, stratigraphy, and mineralogy**.** *J. Geophys. Res.,* **118**, 1-35, doi:10.1002/2012JE004322 (2013).
11. Farley et al. In Situ radiometric and exposure age dating of the Martian surface, *Science* (2013).
12. McSween H.Y. et al., Characterization and petrologic interpretation of olivine-rich basalts at Gusev Crater, Mars. *J. Geophys.Res.*111 (E10), E02S10, doi:10.1029/2005JE002477 (2006).
13. Carter J. and F. Poulet. Ancient plutonic processes on Mars inferred from the detection of possible anorthosite terrains. *Nature Geosci*. **6**,1008-1012 (2013).

14. Wray J et al. Prolonged magmatic activity on Mars inferred from the detection of felsic rocks. *Nature Geosci*. ***6**, 1013-1018*. (2013).
15. Wieczorek, M.A. and M.T. Zuber. The thickness of the martian crust; Improved constraints from geoid to topography ratios, *J. Geophys. Res*, **109**, E01009, doi:10.1029/2003JE002153, 2004 (2004).
16. Stolper, E.M. et al. The petrochemistry of Jake_M: a Martian mugearite. *Science* **341**, 1239463 (2013).
17. Schmidt M.E. et al. Geochemical diversity in first rocks examined by the Curiosity rover in Gale crater: Evidence for and significance of an alkali and volatile-rich igneous source. *J. Geophys. Res. Planets,* **119**, 648, doi: 10.1002/2013JE004481
18. Meslin P.Y. et al. Soil diversity and hydration as observed by ChemCam at Gale crater, Mars, *Science*, **341**, doi:10.112670. (2013).
19. Sautter V. et al. Igneous mineralogy at Bradbury Rise: The first ChemCam campaign at Gale crater**.** *J. Geophys. Res. Plan,* **119**, doi :10.1002/2013JE004472
20. Wiens R.C. et al. The ChemCam instruments in the Mars Science Laboratory (MSL) Rover: Body unit and combined system performance, *Space Sci. Rev*. **170**, 167-227,doi: 10.1007/s11214, doi:10.1007/S11214-012-9902-4 (2012)
21. Maurice S. et al. The ChemCam instruments on Mars Science Laboratory (MSL) Rover: Science objectives and Mast unit, Space Sci. Rev., **170**, 95-166, doi: 10.1007/s11214-012-9912-2 (2012).
22. Fabre C. et al. In situ calibration using univariate analyses based on the onboard ChemCam targets: first prediction of Martian rock and soil compositions. *Spectrochim. Acta B* , **99** , 34-51, doi: 10.1016/j.sab.2014.03.014 (2014).

23. Arvidson et al. Overview of the Spirit Mars Exploration Rover Mission to Gusev Crater: Landing site to Backstay Rock in the Columbia Hills. *J. Geophys. Res. Planets*, **111**, E02S01, doi: 10.1029/2005JE002499 (2006).
24. Ody A. et al. Global investigation of olivine on Mars: Insights into crust and mantle compositions. *J. Geosphys. Res. Planets*, **118**, 234-262, doi:10.1029/2012JE004149 (2013)
25. Bandfield J.L. et al. Identification of quartzofelspathic materials on Mars. *J. Geophys. Res. Planets,* **109**, E10009, doi:10.1029/2004JE002290. (2004)
26. McSween H.Y. et al. Chemical, multispectral, and textural constraints on the composition and origin of rocks the Marth Pathfinder landing site. *J. Geophys.Res*., **104**, 8679-8715.
27. Belleguic V. Lognonné P. and Wieczorek M.A *J. Geophys. Res. Planets*, **110**, E11005, doi: 10.1029/2005JE002437 (2005).
28. Baratoux D. et al. Petrological constraints on the density of the Martian crust. *J. Geophys. Res. Planets.* Doi: 10.1002/2014JE004642 (2014).
29. Moyen J.F. and Martin H. Forty years of TTG research. *Lithos,* **148**, 312-336 (2012)
30. Reimink J. et al. Earth's earliest continent formed like Iceland *Nature Geosci.***7**, 529-532 (2014).

ACKNOWLEDGMENTS : The MSL team is gratefully acknowledged. We would like also to thank David Baratoux for helpful comments on the manuscript. This research was carried out with funding from NASA's Mars Exploration Program in the US and in France with the Centre National d'Etudes Spatiales (CNES). The two anonymous reviewers are gratefully acknowledged for their helpful comments.

FIGURE LEGENDS

Figure 1. Diversity of rock textures. (a) MaHLI image of Clinton (0512MH0001630000200884R00), showing 5 mm-crystals intergrown with greyish translucent 1mm-crystals forming graphic texture (white arrow). Coarse broken feldspars show fractures filled by darker material (red arrow). (b) Mastcam image of Little Wind River (0358MR1458000000E1), similar to Bird River, showing the knobby surface of a buried bedrock. (c) RMI image of Sparkle (0514MR022000000) displaying anhedral coarse light-toned crystals. (d) Mastcam100 image of a polylithic conglomerate including Harrison (center). (e) RMI merged with Mastcam showing the igneous clast Harrison, with elongated light-toned crystals embedded in a dark matrix. (f) Mastcam image of the vesiculated light-toned float rock Becraft (0421MR1726000000E1)

Figure 2. ICA diagram in Al vs. Si compositional space of the 103 spectra on 11 targets from this study, and Jake-M. X- and Y-axes represent the co-variance between each of the spectra and the independent component. Red symbols are Group 1 (coarse intrusives, Fig. 1a-b-c), brown symbols are Group 2 (felsic aphanitic rocks, Fig.1f) and green symbols are Group 3 (porphyritic rocks; Table S1). The purple diamond is the rhyolitic macusanite calibration target (37% quartz, 38% albite, and 23% orthoclase), and the other purple symbols are the mafic basaltic calibration targets.

Figure 3 Element ratio diagrams Al/Si versus (Fe + Mg)/Si

The diagram includes 90 observation points on the 11 selected targets of this study and 2 of the onboard calibration targets (macusanite and shergottite glass). Error bars represent the accuracy of the quantification. The compositions plotted in these diagrams are consistent with the presence of plagioclase, alkali-feldspar, a silica-rich phase which all plot on the *y-axis*, and augite that plots on the *x-axis*. The three different rock groups are indicated using the symbols of Figure 2 and each group is shown in a separate panel.

Figure 4 . Total alkali versus silica diagram summarizing the findings of this study. The black curve indicates the alkaline-subalkaline boundary from Irving and Baragar (1971)[SOM31]: Group1 Ca-felsic intrusive targets (red symbols) plot within the sub-alkaline field (below the black curve) and are Si-rich relative to Surface 2 and Pathfinder composition[26]. Group 2 (brown symbols) and 3 (green symbols) are on the alkali field along a common trend starting from trachy-basalt (dark-green symbols; Table S5 in the SOM). The dashed black line is a calculated 1 bar fractional crystallization trend of a primary liquid (details in the MS). The Jake-M APXS analyses (Stolper et al. 2013[17], light grey squares) are shown for comparison.