

Geology

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Geology 2010;38;183-186
doi: 10.1130/G30470.1

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Notes

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ABSTRACT

Using multivariate cluster analysis, we identify six distinct geochemical provinces on Mars from the concentrations of K, Th, Fe, Si, Ca, Cl, and H₂O determined by the Mars Odyssey gamma ray spectrometer. The results show that the Martian surface is dominated by basaltic rocks that vary in their abundance of incompatible (K, Th) and major elements (Fe, Si, and Ca). These chemically distinct geochemical provinces are in large, contiguous regions comprising a mixture of geologic units. The K/Th ratios are uniform among the geochemical provinces. To prevent measurable fractionation of K from Th, aqueous events must have been brief and/or the total throughput of water small. The muted weathering effects led to deposition of younger sedimentary deposits with the same compositions as older igneous units, explaining why a geochemical province may contain mapped units with the same composition but a range of ages.

INTRODUCTION

The Mars Odyssey gamma ray spectrometer (GRS) has acquired a nearly global data set for the concentrations of seven elements (K, Th, Si, Fe, Ca, Cl, and H) on the surface of Mars. Initial results (e.g., Boynton et al., 2007, 2008) show that concentrations vary across the surface, but except for a few cases, most notably K and Th, elements are not strongly correlated with one another. Individual element maps are informative, but the lack of viable element-element correlations and spatial uncertainties due to spatial autocorrelation make it difficult to infer overall compositional variations. Thus we have turned to statistical techniques (Gasnault et al., 2009; Karunatillake et al., 2009). Here we report the results of cluster analysis with which we produced a map of geochemically distinct provinces on Mars.

GRS DATA

The GRS determines elemental concentrations from the intensities of gamma rays produced by neutron capture and/or scattering reactions (Si, Fe, Ca, Cl, H) or by radioactive decay (K, Th). For details on data acquisition and reduction, see Boynton et al. (2007, 2008) and the GSA Data Repository¹. For this paper, the most important features of the data set are spatial resolution, depth of sampling, and extent of coverage.

Spatial Resolution

The GRS footprint, defined as the nadir-centered region within which ~50% of the sig-

nal originates, is ~3.7° arc radius (~220 km), although this varies somewhat with the gamma ray energy. The data were binned initially at 0.5° × 0.5°, smoothed using a boxcar filter over a much larger radius, and then rebinned to 5° × 5° grid points. The radius of the smoothing filter varies with element: 5° for K, 10° for Cl, H, Fe, and Th, and 15° for Si and Ca. Smoothing is necessary to improve signal to noise, but results in interdependency of neighboring data points, an effect called autocorrelation (discussed further herein).

Depth of Sampling

The measured gamma rays are produced in the upper few tens of centimeters of the Martian surface, much deeper than sensed by visible to thermal infrared spectral instruments (10–100 μm).

Extent of Coverage

We used only points in regions where H contents are low enough not to interfere in the determination of Si, Fe, and Ca concentrations. Hydrogen has a high cross section for capturing thermal neutrons, significantly affecting the neutron flux in the upper ~30 cm of the Martian surface. The GRS data are corrected for this effect, but the correction is uncertain at polar latitudes where H dominates elemental signatures. Accordingly, we constrained our results using a mask based on H concentration, corresponding to ~±45° of latitude from the equator. (The concentration of H does not affect K and Th data because their γ rays result from radioactive decay.)

The aqueous history of Mars is of great interest and is recorded in part in the concentrations and distribution of Cl and H, as discussed in Gasnault et al. (2009) and Karunatillake et al. (2009). In this paper we wish to assess the geochemical nature of the igneous rocks making up

the surface of Mars: thus we further adjusted the data to be on a volatile-free basis to emphasize igneous rock compositions. This was accomplished by removing H₂O, Cl, and SO₃, with SO₃ calculated from the mean SO₃/Cl ratio of 8.9 for soils at the Mars Exploration Rover landing sites (Brückner et al., 2008), and increasing the concentrations of the remaining elements on the basis of the sum of the volatile species. That is, we increased Si, Fe, Ca, K, and Th in each grid point by factors given by $100/(100 - [Cl] - [H_2O] - [SO_3])$, where the values in brackets are concentrations and $[SO_3]$ equals $8.9 \times [Cl]$.

STATISTICAL METHODOLOGY

We used a cluster analysis on the GRS grid points to discern global trends in this multivariate data set. We use the K-means clustering algorithm implemented in ENVI (Environment for Visualizing Images), which optimizes the Euclidian distances between the cluster centers. We standardized the element concentrations by subtracting the arithmetic mean of the global data set from each point, and dividing by the global standard deviation, yielding standardized values, or z-scores. The normalization weights by relative variability of elements and provides information about the statistical significance of the mean composition of each calculated cluster. K and Th correlate strongly (mutually contributing 65% of variability in bivariate space and 25% in multivariate space), so to avoid redundancy in the cluster analysis, we use only K, which is known more precisely. To determine the optimum number of clusters, we used a silhouette parameter (Rousseeuw, 1987) that defines a silhouette width, involving the average difference between a given bin and all other bins within a cluster, compared to the average difference of that bin from all other clusters. The results suggest that the optimum number of clusters is 4–6: we use 6 clusters in the data reported here. (For more information about the cluster analysis technique, see footnote 1.)

RESULTS

The geochemical clusters map into contiguous areas (Fig. 1A) far larger than the GRS spatial resolution size (5°–15° in radius, including smoothing). This is important because spatial autocorrelation effects (Haining, 2003) cause spatially proximate grid points to contain redundant information. Therefore, regions with only a

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¹GSA Data Repository item 2010036, details of gamma-ray data acquisition and data reduction, and description of statistical methods (including Figure DR1), is available online at www.geosociety.org/pubs/ft2010.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

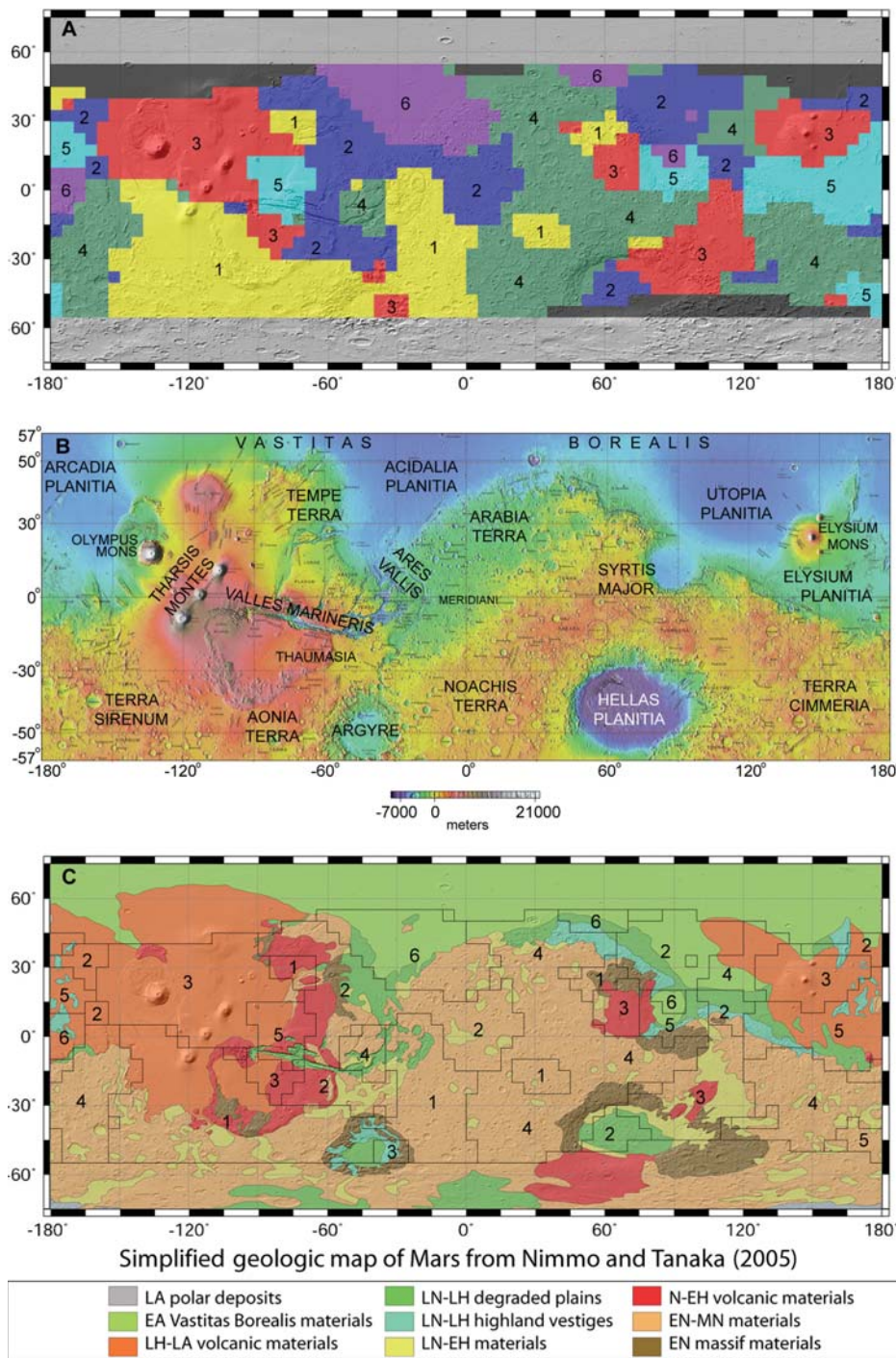


Figure 1. Results of K-means cluster analysis obtained from $5^\circ \times 5^\circ$ smoothed gamma ray spectrometer data (Fe, Si, Ca, K). **A:** Six geochemical provinces (clusters; described in text) superimposed onto Mars Global Surveyor Mars Orbiter laser altimeter shaded relief map. Data are truncated at -45° north and south for analytical reasons (Boynton et al., 2007). **B:** Topographic map showing locations of key features discussed in text. **C:** Simplified geologic map of Mars (Nimmo and Tanaka, 2005), with geochemical provinces in A outlined. E—early; L—late; M—middle; A—Amazonian; H—Hesperian; N—Noachian.

few GRS grid points in them are not significant. The most conservative approach is to ignore areas smaller than the largest smoothing radius, 15° . (The different smoothing radii do not affect the outcome of the cluster analysis significantly; see footnote 1.)

The clusters, which we call geochemical provinces, have unique mean element abundance patterns (Fig. 2). For five of the six provinces the mean of at least one element is close to one standard deviation larger or smaller than the global mean, demonstrating that the clas-

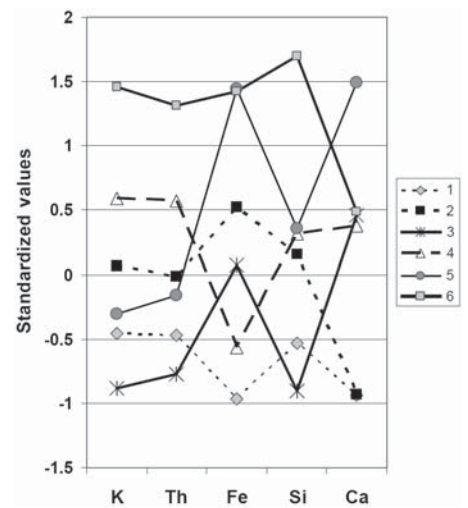


Figure 2. Compositions of six geochemical provinces described in text, using standardized values (class means divided by standard deviation of global mean). Mean values converted to weight percent oxides are given in Table 1.

sification is significant. Province 6 is the most distinct, with four of the five elements enriched significantly (Fig. 2). Province 4 does not have enrichments or depletions at the one-standard deviation level, but is nonetheless different in its element abundance pattern.

The differences in the standardized values are reflected in the mean concentrations of elements (converted to oxides, except for Th) for each province (Table 1). We report Th data in Table 1 even though they were not used in calculating the clusters (provinces). The reduction in the effective number of data due to spatial autocorrelation causes the typical calculation of the standard error of the mean to be an underestimate. Therefore, we conservatively report the root mean square of the individual uncertainties of grid points in each class for each element in Table 1. A brief discussion of each geochemical province (Fig. 1A) follows. Geographic areas mentioned below are identified in Figure 1B. In Figure 1C we compare the provinces with the simplified geologic map of Nimmo and Tanaka (2005). This map combines many units to give a broad picture of Mars, so it is more suitable for comparison with the spatial resolution of the GRS data, and is based on the geologic map of Mars (Scott and Tanaka, 1986; Greeley and Guest, 1987).

Province 1 is relatively low in all five elements, although only Fe is low at the 1σ level. The largest region of it encompasses the southern highlands from Terra Sirenum through Aonia Terra to western Noachis Terra on the east side of Argyre basin, then extends north to Meridiani, ending at Ares Vallis. This region includes diverse geological units with a range of ages. It is dominated by early to middle Noachian materials and includes

TABLE 1. MEAN COMPOSITIONS AND UNCERTAINTIES OF GEOCHEMICAL PROVINCES ON MARS

	Province 1	Province 2	Province 3	Province 4	Province 5	Province 6
K ₂ O	0.39 ± 0.02	0.43 ± 0.03	0.37 ± 0.02	0.47 ± 0.02	0.40 ± 0.03	0.53 ± 0.03
FeO	18.3 ± 1.1	21.4 ± 1.5	20.5 ± 1.3	19.2 ± 1.3	23.3 ± 1.6	23.3 ± 1.8
SiO ₂	47.1 ± 0.7	48.0 ± 1.0	46.7 ± 0.8	48.1 ± 0.9	48.2 ± 0.9	49.8 ± 1.1
CaO	7.5 ± 1.2	7.5 ± 1.5	9.7 ± 1.3	9.6 ± 1.4	11.4 ± 1.6	9.8 ± 1.9
Th	0.64 ± 0.05	0.70 ± 0.06	0.60 ± 0.06	0.78 ± 0.06	0.68 ± 0.06	0.88 ± 0.07
K/Th	5100 ± 460	5090 ± 560	5040 ± 560	4960 ± 430	4930 ± 560	4970 ± 490

Note: Values in weight percent, except Th (parts per million). Uncertainties (σ , root mean square uncertainty) for elements are calculated from mean measurement uncertainties for the grid points composing a geochemical province. Uncertainty in K/Th ratio calculated from $(K/Th)[(\sigma_K/K)^2 + (\sigma_{Th}/Th)^2]^{1/2}$, where K and Th are mean concentrations of K and Th.

massifs in Thaumasia and surrounding Argyre. A significant percentage encompasses Noachian to early Hesperian and Amazonian volcanics on and near Tharsis. The latter includes an intriguing overlap between radar stealth and compositional anomalies, as discussed in Karunatillake et al. (2009).

Province 2 has a composition close to average Mars, except for distinctively low Ca. It occurs in two main regions. One is adjacent to province 1 northwest of Argyre and extends northward across Valles Marineris to Tempe Terra. The other main region is in Utopia Planitia in the northern lowlands. A much smaller region encompasses most of the floor of Hellas. This geochemical province is composed of a mixture of geological units, from Noachian units in Arabia Terra to Amazonian materials in Utopia.

Province 3 is low in K, Th, and Si, and roughly average in Fe and Ca. It is associated with volcanic constructs in northern Tharsis (Olympus Mons and the Tharsis Montes), Syrtis Major, and Elysium, and with late Noachian and early Hesperian plains and in the area east of Hellas.

Province 4 has an average composition that is not much different from the global mean; it is average Mars. It is the largest of our geochemically defined provinces, occupying 25% of the mapped area. It is confined almost entirely to early to middle Noachian highlands, including Arabia Terra, eastern Noachis Terra, Terra Cimmeria, and western Terra Sirenum. Some Hesperian plateau units also occur, particularly in Sirenum.

Province 5 has distinctively high average Fe and Ca concentrations. The largest occurrence is west of Tharsis in southern Elysium and northernmost Terra Cimmeria. This region is a mixture of late Noachian to late Hesperian highlands and plains, and late Hesperian to late Amazonian volcanic deposits. The other main occurrence is in eastern Tharsis, straddling Valles Marineris and including Noachian to Amazonian volcanics.

Province 6 is the most distinct compositional province. It is enriched in K, Th, Fe, and Si both on average and consistently in some subregions (Karunatillake et al., 2009). The province is located mostly in Acidalia Planitia and adjacent

highlands in Arabia Terra. The major geological units are early Amazonian Vastitas Borealis materials and much older early to middle Noachian materials in northern Arabia Terra. The distribution of this chemically distinctive unit in the northern lowlands is similar to the distribution of the original TES (thermal emission spectrometer) surface type 2 defined by Bandfield et al. (2000).

DISCUSSION

We have identified six statistically meaningful geochemical provinces on Mars. The compositions of all provinces are in the range of basaltic rocks (Table 1). No large units at the 500 km scale of the GRS measurements have compositions more silicic (>52.5 wt%) than the basaltic range (also see McSween et al., 2009). It appears that the Martian surface is dominated by several distinct compositions of basalt that vary in their abundances of K and Th (and almost certainly in other incompatible lithophile elements), and FeO and CaO (Table 1). McSween et al. (2009) pointed out that the abundances of alkalis in Martian rocks at landing sites and in the GRS data set are consistent with tholeiitic magmas.

It is important that identifiable geochemical provinces exist on Mars, considering the numerous processes that affected surface composition over billions of years. These processes include weathering, sediment transport and deposition by wind and water, glaciation, reworking by impacts, and volcanism. In addition, a global dust component tends to blunt chemical variations (e.g., Newsom et al., 2006). Tharsis and the large region to its west up to Elysium (mainly our provinces 3 and 5) have significant amounts of reworked mantling dust (Putzig et al., 2005; Newsom et al., 2006). Thus, the compositions of some dusty regions may not reflect local igneous rocks (e.g., Karunatillake et al., 2009). On the other hand, less mantled regions, such as southeastern province 1 and most of 4 (cf. Putzig et al., 2005), more closely reflect the composition of the underlying geologic units.

Geochemical provinces do not overlap compellingly with age or mapped geologic units

(Fig. 1C). The imperfect correlation may be caused by eolian deposits diminishing the original contrast in surface compositions, decoupling of surficial processes from the underlying bedrock, by the large footprint of the GRS measurements averaging smaller features, or a combination thereof. Of course, the blending of geologic units within each geochemical province may simply reflect that on average magmas with similar composition erupted over time as the crust was constructed. In addition, weathering on Mars might not have been intense enough to cause significant chemical fractionation during erosion, transport, and deposition of sediments (see following). If so, then young sedimentary deposits have the same compositions as older igneous units, thereby blurring the variation of surface composition with mapped geologic units.

The northern plains and their borders with the highlands compose the most distinct geochemical province (province 6). This was first observed by Bandfield et al. (2000) from TES data, and reinforced by Rogers et al. (2007). Bandfield et al. (2000) identified two dominant surface compositional types, surface type 1 (mostly in the southern highlands) and surface type 2 (mostly in the northern plains). Karunatillake et al. (2006) show that areas corresponding to TES surface type 2 are distinctly enriched in K and Th compared to surface type 1, in accord with our identification of province 6. The composition of province 6 (Table 1) is consistent with a basaltic composition (SiO₂ content of 49.8 wt%), not basaltic andesite or andesite, as originally argued by Bandfield et al. (2000), a point also made by others (e.g., Wyatt and McSween, 2002; Karunatillake et al., 2006). On the other hand, it does have the highest average SiO₂ concentration of any of the provinces, allowing for the presence of somewhat more silicic rocks as suggested by TES data. Thus, province 6 must contain a significant contribution from distinctive igneous rocks. The Vastitas Borealis Formation, composing most of province 6, appears to be composed of a thin layer of sediment overlying volcanic plains (Head et al., 2002). The sediments almost certainly came from the highlands, namely provinces 2 and 4, but the large difference in chemical composition between them and province 6 suggests that the highlands were not the only source for the sediments making up the veneer on the northern plains. One explanation is that there was considerable mixing of detrital materials with underlying lava flows during sediment emplacement. If so, the volcanic rocks in the substrate have a distinctive chemical composition compared to those in the southern highlands and in the province 3 volcanic regions.

Dohm et al. (2007) marshaled evidence from diverse sources to conclude that Arabia Terra

represents an ancient impact basin, uplifted after its formation. Its interior layered deposits are likely sediments derived from the surrounding highlands. The hypothesized basin has substantially more H₂O than other regions of the highlands, ~7 wt% versus 3 wt% elsewhere (Boyn-ton et al. 2007; Dohm et al., 2007). Our analysis shows that Arabia is dominated by province 4, with a contribution from province 2. This is consistent with derivation of the sediments in Ara-bia from surrounding highlands.

The basaltic nature and striking lack of varia-tion of K/Th among the geochemical provinces (Table 1) suggest that the erosion and transport of sediments into the ancient Arabia basin, from the southern highlands to the northern plains, or within provinces 1 and 4 did not cause sub-stantial chemical fractionation. As summarized in Taylor et al. (2006), K and Th fractionate readily under typical terrestrial conditions of roughly neutral pH and high water/rock ratios, conditions that might have prevailed during the Noachian or somewhat later. The presence of clay minerals (mostly smectites; Bibring et al., 2005) in the Noachian highlands is consis-tent with clement, terrestrial-like conditions. However, weathering, transport, and deposi-tion during this early putative wet period do not appear to have involved sufficient water to pro-duce the extensive alteration we see on Earth, in spite of the production of clay minerals in some places. To prevent measurable fraction-ation of K from Th, aqueous events must have been brief or the total throughput of water small. Perhaps clay minerals formed in locations with inefficient drainage, allowing more water to be present for longer times. For the subsequent ~3.5 Ga, Martian weathering occurred under conditions of low pH and low water/rock ratios (e.g., Hurowitz and McLennan, 2007). Th and K might not fractionate at low pH because of enhanced Th solubility, but this depends on the total water/rock ratio and duration of weather-ing events (Taylor et al., 2006). Thus, the water/rock ratio must have been low enough to pre-vent K-Th fractionation, arguing for very dry conditions for the past 3.5 Ga. The uniform K/Th on Mars indicates aqueous alteration at low water/rock throughout discernible Martian his-tory, consistent with the widespread presence of olivine, which weathers rapidly (e.g., Tosca et al., 2004; Stopar et al., 2006).

The use of cluster analysis to identify distinct geochemical provinces on Mars is promising. The provinces identified here show clearly that the Martian surface materials vary significantly, in spite of a pervasive global dust component, and that large regions of chemically similar materials are identifiable. We plan detailed geo-logic and remote sensing studies of each of the identified provinces to understand their geologic

and geochemical histories and their relation to underlying geologic units (as shown in Karuna-tillake et al., 2009).

ACKNOWLEDGMENTS

We thank the Mars Odyssey project and the Na-tional Aeronautics and Space Administration (grant NNX07AV40G) for financial support, GRS (gamma ray spectrometer) team members for their expertise, and Nick Tosca, Ross Taylor, and three anonymous reviewers for valuable reviews.

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Manuscript received 17 June 2009

Revised manuscript received 9 September 2009

Manuscript accepted 10 September 2009

Printed in USA