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Elemental Composition of the Martian Crust

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The composition of Mars' crust records the planet's integrated geologic history and provides clues to its differentiation. Spacecraft and meteorite data now provide a global view of the chemistry of the igneous crust that can be used to assess this history. Surface rocks on Mars are dominantly tholeiitic basalts formed by extensive partial melting and are not highly weathered. Siliceous or calc-alkaline rocks produced by melting and/or fractional crystallization of hydrated, recycled mantle sources, and silica-poor rocks produced by limited melting of alkali-rich mantle sources, are uncommon or absent. Spacecraft data suggest that martian meteorites are not representative of older, more voluminous crust and prompt questions about their use in defining diagnostic geochemical characteristics and in constraining mantle compositional models for Mars.

Over the past decade, instruments on orbiting spacecraft, landers, and rovers have measured the abundances of elements present in martian rocks and soils. Some analyses are incomplete, and the scales of analyzed areas range from centimeters to hundreds of kilometers in diameter, complicating comparisons. Martian meteorites [shergottite, nakhlite, and chassignite (SNC)] constitute another important source of geochemical data. Although the meteorites come from as-yet undetermined locations on Mars, laboratory analyses permit complete chemical characterizations that cannot be obtained by remote sensing techniques.

Based on these data, Mars has been viewed as a basalt-covered world (*1*). Although basalts are ubiquitous on rocky planets, the apparent lack of other rock compositions suggests that the geologic evolution of Mars has been distinct from Earth. Rocks at the Mars Pathfinder landing site previously identified as andesite (*2*) may be coated with alteration rinds, and martian spectral signatures formerly interpreted as andesitic (*3*) are now attributed to the effects of chemical weathering (*4*, *5*). Only a few occurrences of evolved siliceous rocks have been discovered in global spectral surveys (*6*), supporting the view that magmatic differentiation has been very limited. Although much of the surface is covered by sediments, these materials largely retain the chemical compositions of their basaltic precursors.

Sufficient geochemical data now exist to better characterize the crust and the igneous processes that produced it. Here, we compare and critically evaluate geochemical data from all these sources to constrain the composition of the crust and consider how martian magmatism may have differed from that on Earth.

Geochemical Data Sets

The Gamma-Ray Spectrometer (GRS) on the Mars Odyssey orbiter has provided elemental abundance data and global distribution maps for H, Si, Ca, K, Cl, Fe, and Th (*7*). A global map will be available for Al, but at present we use only the global Al mean value. We used data collected from June 2002 to January 2006. Reduced elemental concentrations were originally binned at 0.5° by 0.5° and smoothed using mean filters over radii of 5° (K), 10° (H, Fe, and Th), or 15° (Si and Ca). For our analysis, we rebinned data to 5° by 5° grid points, resulting in large spatial resolution. We used only points in regions where H contents are low enough not

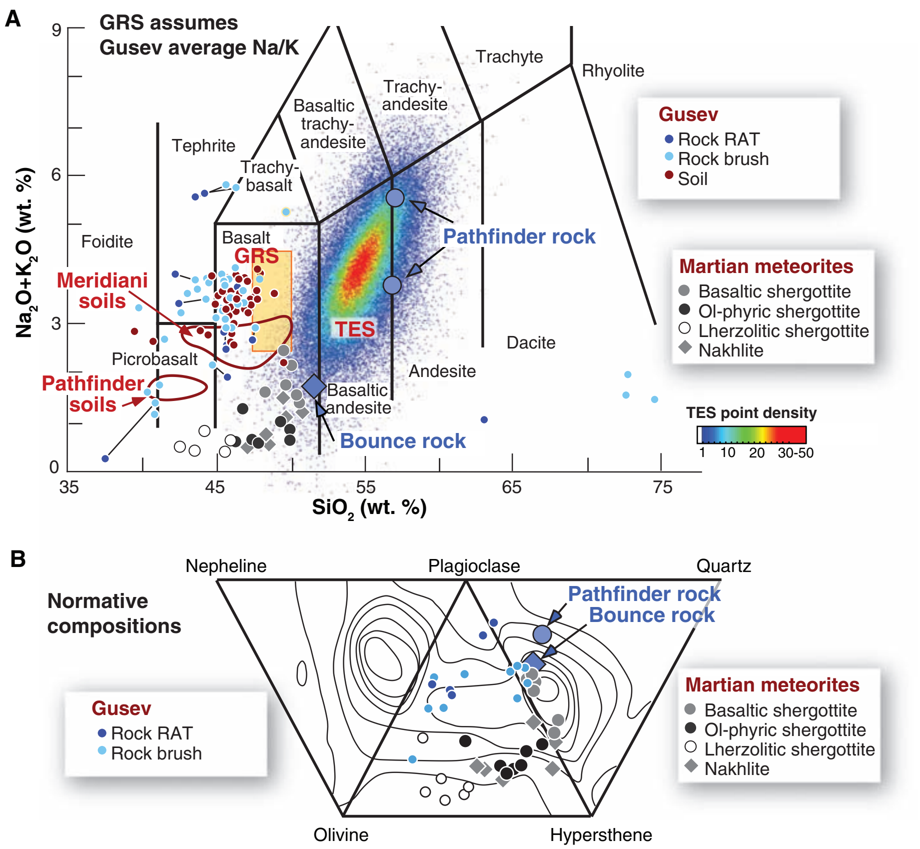

Fig. 1. (**A**) Total alkalis-silica diagram used for classification of volcanic rocks. Gusev RAT-ground and RAT-brushed compositions for the same rocks are connected by tie-lines. Analyses of Gusev rocks and soils, martian meteorites, and global GRS data (calculated on a volatile-free basis) indicate a crust dominated by basalts. TES-derived data and possibly the Mars Pathfinder rock composition may reflect alteration. Data sources in this and other figures are discussed in the text. (**B**) Calculated normative minerals in the martian crust. The three triangles correspond (from left to right) to alkaline basalts, olivine tholeiites, and quartz tholeiites. The critical plane of silica undersaturation separates alkaline basalts and olivine tholeiites; fractionating liquids to the left of this plane form silica-deficient compositions, whereas those to the right evolve to silica-enriched compositions. Contours indicate the relative abundances of terrestrial basaltic rocks (*37*). Martian meteorites and Gusev rocks plot mostly in the fields of olivine tholeiites and quartz tholeiites; nepheline-normative rocks have not been encountered.

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to interfere in the determination of Si, Fe, and Ca concentrations. Hydrogen has a high cross-section for capturing thermal neutrons, substantially affecting the neutron flux in the upper ~30 cm of the martian surface. We corrected the data for this effect (*7*) by a process that uses measured fluxes of γ-rays from H, Fe, Si, and Ca, and the fluxes calculated from a neutron transport γ-ray production model. This approach produces reasonable values at equatorial latitudes but uncertain values at higher polar latitudes where H dominates elemental signatures. Accordingly, we constrained our results using a mask based on H concentration, corresponding to roughly ±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. To compare igneous rock compositions, we further adjusted the data to a volatile-free basis by removing H_2O, Cl, and SO_2, the quantities of which were calculated from the S/Cl ratio of ~5 found at rover landing sites. We represent GRS element abundances as boxes defined by global averages and standard deviations (1σ).

Measurements of the Thermal Emission Spectrometer (TES) onboard the Mars Global Surveyor orbiter are sensitive to the chemistry and structure of silicates (*8*). Complex mixtures can be deconvolved into mineral abundances using a spectral library of known minerals (*9*). The major oxide concentrations can be estimated from TES data to within ±5 weight percent (wt %) using known mineral chemistries and deconvolved mineral abundances from thermal emission studies (*10*, *11*). We modeled the spectra (*12*) over 233 to 508 cm^{-1} and 825 to 1301 cm^{-1} using an end-member set consisting of primary (e.g., plagioclase, pyroxene, and olivine) and secondary (e.g., phyllosilicates, sulfates, and oxides) phases with known chemistries. Finally, we calculated major oxide concentrations on a H_2O-free and CO_2-free basis. The data clouds in our graphs represent derived chemical compositions from global TES data binned at 4 pixels per degree.

In comparing GRS analyses and TES-derived compositions, it is necessary to realize that γ-rays can penetrate to depths of 20 to 30 cm and thus analyze a much greater volume of material, relative to thermal emission spectra that sample only the outermost 10 to 100 μm. Thus, surface alteration processes may have a profound effect on geochemical classifications based on TES data.

Sediments potentially sample broad areas of the crust, although fractionation of heavy minerals is likely during their transport. X-Ray Fluorescence (XRF) instruments on the Viking landers obtained six soil analyses from two landing sites (*13*). Another five soils were analyzed by the Alpha-Proton-X-ray Spectrometer (APXS) on the Mars Pathfinder rover. APXS (*14*) on the Mars Exploration Rovers (MER), Spirit and Opportunity, analyzed nearly 100 soils at two different sites (*15*, *16*). We plot Gusev crater soil

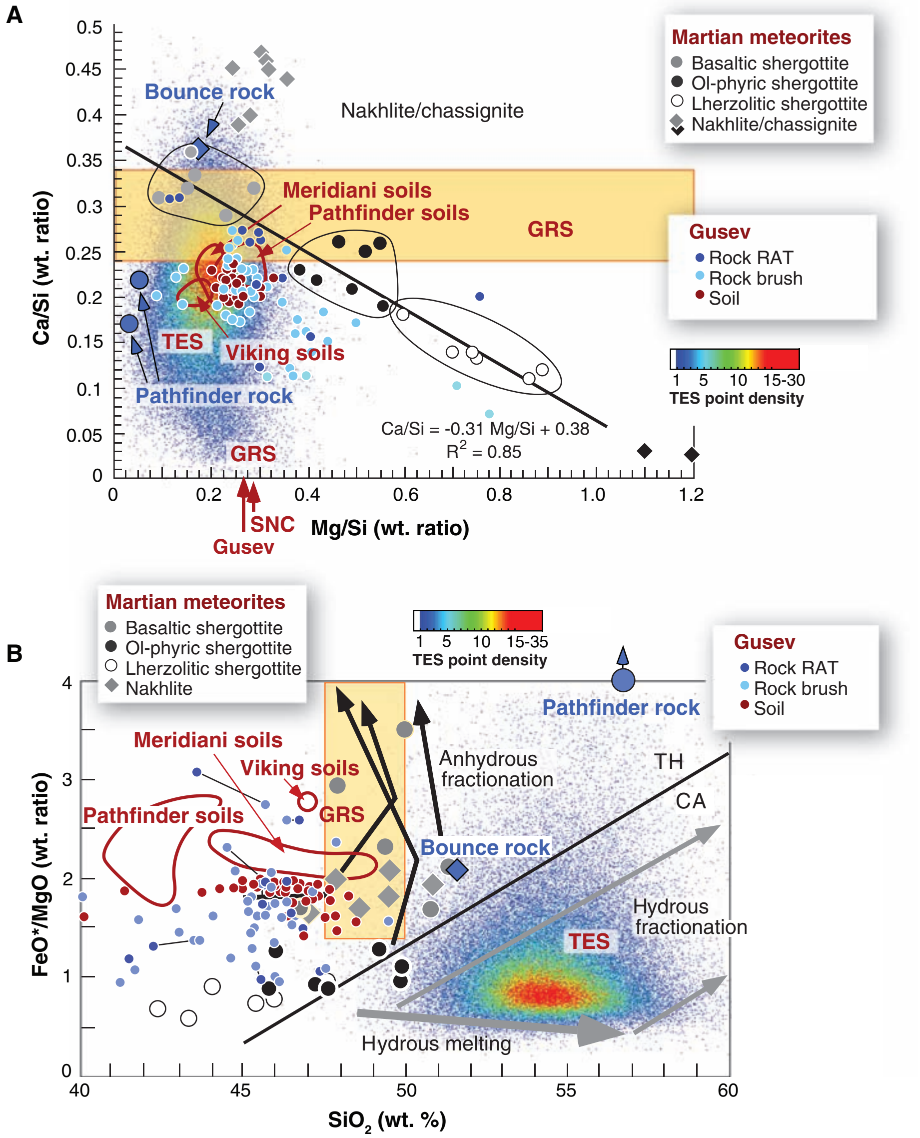

Fig. 2. (**A**) Ca/Si-Mg/Si diagram used for classification of martian meteorites. The GRS-measured Ca/Si ratio and standard deviation is represented by a horizontal band. Global Mg/Si can be estimated from the intersection of that band with the regression line for shergottites or from the average Mg/Si value for Gusev rocks and soils (red arrows). (**B**) FeO*/MgO-silica diagram used for distinguishing dry tholeiitic (TH) and wet calc-alkaline (CA) rocks. All martian samples are tholeiitic. TES-derived compositions result from alteration. Arrows represent melting and fractionation trends in terrestrial magmas.

compositions measured by Spirit, but Viking, Pathfinder, and Opportunity soils are illustrated by ovoids enclosing the data, to minimize complexity in our diagrams.

Two different calibrations of five rock analyses by the Mars Pathfinder APXS have been published (*17*, *18*). The true compositions of the Pathfinder rocks are unknown, because the APXS analyzed only the outermost few micrometers. The dust-free rock composition has been estimated by plotting abundances of various oxides versus sulfur and extrapolating trends to zero sulfur, in effect removing the sulfur-rich dust coatings. There remains, however, a concern that alteration rinds might have been present on these rocks.

The MER have performed analyses of more than 250 rocks with their APXS (*15*, *16*). Rock Abrasion Tools (RAT) brushed away surface dust and ground into rock interiors. Detailed observations of RAT holes and comparison of brushed and abraded rock compositions reveal that rocks at both sites commonly have alteration rinds (*19*). In compiling MER rock analyses, we used only data from RAT-ground or RAT-brushed rocks. Rocks at the Opportunity landing site in Meridiani Planum are altered basaltic sandstones cemented by salts (*20*). Meridiani has a distinctive TES spectrum (*21*) produced by lag deposits of hematite concretions; this spectrum is not representative of the martian surface. Consequently, these evaporitic sediments are not likely to be a major crustal component. However, one sample from Meridiani, Bounce Rock (*22*), has a chemical and mineralogical composition similar to martian meteorites (shergottites) and was included in our compilation. Unlike Meridiani, Spirit's Gusev landing site spectrally resembles most of the martian surface, and thus its igneous rocks are more likely to represent other parts of the crust. Here, we focus especially on Gusev samples, estimated to have formed at ~3.7 billion years ago (*23*).

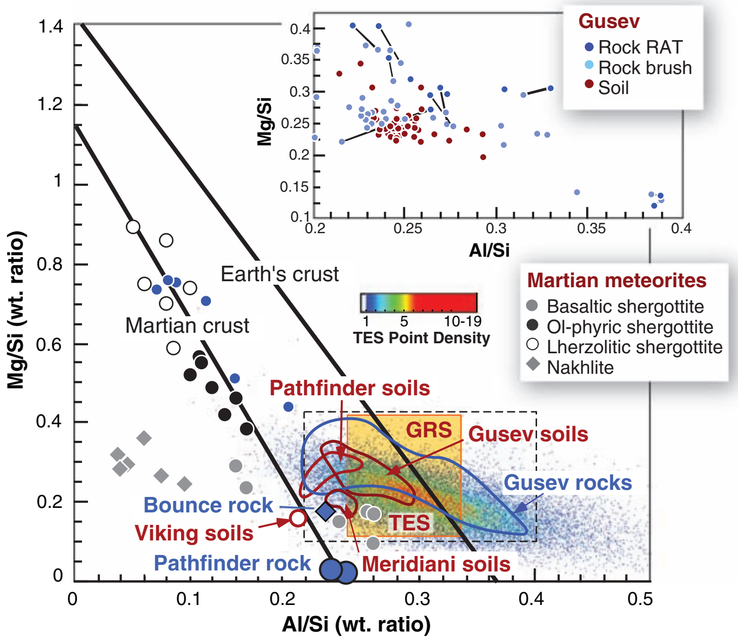

Fig. 3. Mg/Si-Al/Si diagram previously thought to discriminate between Mars and Earth rocks. Gusev and GRS data do not show the Al depletion seen in martian meteorites. GRS Al data represent the global mean ± 1 SD analytical uncertainty.

Martian meteorites (*24*) include three types of shergottites (basaltic, olivine-phyric, and lherzolitic), nakhlites, chassignites, and ALH84001—all igneous rocks. We focus on shergottites and nakhlites, because they are the most abundant and well characterized. Moreover, their petrographic characteristics are consistent with near-surface rocks. With the exception of ALH84001, the radiometric ages of all these meteorites indicate that they crystallized since ~1.4 billion years ago (*25*). Thus, they are considerably younger than Gusev rocks. The times of ejection of these meteorites from Mars, estimated from cosmogenic nuclide measurements (*26*), define four clusters with several outliers, each containing a single meteorite type and likely representing a distinct launch site. Although crystallization ages suggest that these meteorites constitute a chronologically biased sampling of the martian crust, they represent more sampling locations than those visited so far by landers and rovers. Bulk-rock geochemical data for shergottites and nakhlites from various sources were compiled by (*27*). Here, we consider major and minor elemental abundances that can be compared with remote sensing data.

Geochemical Classification of Crustal Rocks

The total alkalis-silica diagram (Fig. 1A) is commonly used for geochemical classification of volcanic rocks. Martian meteorites plot within the basalt field, as does compositionally similar Bounce Rock. Gusev rocks also are concentrated within the basalt field, but they have higher Na_2O+K_2O values. Their compositions are scattered (some are tephrites or picrobasalts), possibly resulting from fractional crystallization at varying depths (*28*). Gusev rocks are clearly more alkali-rich than other martian compositions. The Mars Pathfinder dust-free rock composition is andesite, although this composition may reflect surficial silica enrichment during weathering.

Gusev soils plot in the basalt field, superimposed on compositions of the local basaltic rocks. Meridiani soils are basaltic, but with slightly lower alkalis than Gusev soils. Pathfinder soils have lower silica and alkalis and are distinct from the composition of the local rocks. Viking soils are not plotted because Na was not analyzed.

The globally averaged GRS-measured silica abundance (Fig. 1A) corresponds to basalt, and the standard deviation indicates that few analyses lie outside the basalt range. The GRS analyzed K but not Na, so the average Na_2O/K_2O weight ratio for Gusev rocks and soils (8.9) was assumed in constructing the GRS box. Martian meteorites have very low K_2O abundances and thus a high average Na_2O/K_2O ratio (12.5); using this ratio gives unreasonable results when combined with GRS measurements of K.

TES-derived compositions are clearly distinct from other data sets (Fig. 1A). We interpret this difference to result from surface chemical weathering. Global variations in silica abundances are modest, and, at the course scale of GRS data, no areas dominated by siliceous rocks are apparent in a GRS silica distribution map (*7*).

Additional information about basaltic compositions is revealed by calculated norms (Fig. 1B), which recast bulk chemistry into minerals. The normative mineral abundances for martian meteorites, Bounce Rock, the Mars Pathfinder dust-free rock, and the least altered Gusev rocks (*29*) plot within the field of olivine tholeiites or in the quartz tholeiite field close to the plagioclase-hypersthene join. The absence of nepheline-normative rocks suggests that melts from alkali-rich mantle sources are uncommon, despite GRS observations and models that suggest Mars is enriched in alkalis relative to Earth (*30*, *31*). Terrestrial alkaline magmas typically form by melting altered mantle sources, and their absence on Mars points to limited fluid-assisted metasomatism at depth.

We use the Ca/Si-Mg/Si diagram for geochemical classification of martian meteorites (Fig. 2A). Our version uses weight ratios, although the original diagram (*32*) used molar ratios. Basaltic, olivine-phyric, and lherzolitic shergottites are enclosed by ovals, and increasing Mg/Si reflects increasing proportions of olivine. Nakhlites have higher Ca/Si ratios, reflecting abundant augite. Gusev rocks and soils have lower Ca/Si, and Gusev, Meridiani, Pathfinder, and Viking soils all nearly overlap.

The GRS-measured average Ca/Si value and standard deviation are indicated by a horizontal bar (Fig. 2A). The GRS cannot measure Mg, but we estimated a global Mg/Si value of 0.29 (range 0.11 to 0.42) from the intersection of the average GRS Ca/Si value with the Ca/Si-Mg/Si regression line for shergottites (Fig. 2A). The value agrees closely with the average Mg/Si ratio for Gusev rocks and soils (0.27 ± 0.10), so it is immaterial whether we derive this value from martian meteorites or Gusev analyses. The Mg/Si ratio corresponds to ~11.0 wt % MgO, which will be used as the global GRS value in other diagrams. TES-derived Mg/Si and Ca/Si ratios partly overlap with those of Gusev samples.

Tholeiitic or Calc-Alkaline Magmas?

Magmatic trends are markers for plate tectonics on Earth, reflecting melting of dry or wet mantle sources at spreading centers or subduction zones, respectively. The compositions of martian meteorites, Bounce Rock, Gusev rocks, and the soils from all sites are tholeiitic (Fig. 2B). The GRS average FeO*/MgO ratio (FeO* is total Fe, expressed as FeO; MgO was estimated from Fig. 2A) is likewise tholeiitic. However, TES-derived compositions plot in the calc-alkaline field.

Tholeiitic magmas, which are relatively dry, show Fe enrichment during fractionation, as illustrated by the nearly vertical black arrows. Different degrees of hydrous partial melting produce magmas distributed along the thick gray arrow at the bottom of the figure, and fractionation of those hydrous magmas produces silica-enriched (calc-alkaline) liquids that follow the smaller diagonal gray arrows. It has been speculated (*1*) that the ancient Mars mantle was wet, accounting for the TES-derived compositions of older geologic units. In this model, early melting events dehydrated the mantle, so that magmas derived by later melting (martian meteorites having young radiometric ages) were tholeiitic. However, this model must be incorrect, because chemically weathered surface compositions, as measured by TES spectra, cannot be interpreted in terms of igneous processes. Instead, TES-derived calc-alkaline compositions are artifacts of alteration, and they provide no evidence for crustal recycling.

Mars Geochemical Discriminants

Several distinctive geochemical characteristics of martian meteorites are commonly assumed to be fingerprints of Mars, although it has been noted that some unusual terrestrial rocks (ferropicrites) share their compositions (*33*). Martian meteorites are depleted in Al relative to terrestrial rocks (*30*) (Fig. 3). This distinguishing characteristic might result from depletion of Al during early melting of mantle source regions (*34*) and, indeed, ancient Gusev rocks are not as depleted in Al as are the younger meteorites. The GRS global average data also support the higher Al/Si ratios for Gusev rocks. This brings into question the validity of Al depletion as a geochemical discriminant for all Mars samples. The Gusev RAT-ground rock compositions have consistently higher Mg/Si ratios than RAT-brushed compositions (inset in Fig. 3). This difference can be explained by preferential leaching of olivine in alteration rinds during acidic weathering (*35*).

The Fe/Mn ratio is another geochemical characteristic thought to be diagnostic for Mars. Fe/Mn ratios of pyroxene and olivine in martian meteorites are distinct from those of lunar and terrestrial minerals (*36*), and the average bulk Fe/Mn in meteorites was used to constrain the martian mantle composition (*31*). The Fe/Mn weight ratio in the martian mantle, based on martian meteorites, is ~41, lower than that of Earth's mantle (~62). However, Fe/Mn ratios for Gusev rocks and soils are significantly different (Fig. 4A). It is unclear which ratio provides a more accurate assessment of the Mars mantle composition.

Ni/Mg ratios are distinctive for martian meteorites (Fig. 4B) and have been used to estimate a Ni abundance for Mars that is considerably lower than for Earth (*31*). However, RAT-ground Gusev basalts plot along the terrestrial trend, clearly distinct from the meteorites (Fig. 4B). RAT-brushed rocks and soils generally fall to the Mg-poor side of this trend. This diagram suggests that Ni/Mg may not be a valid discriminant for Earth and Mars rocks. The global Mg abundance estimated for GRS data is shown by a vertical bar, but Ni data are unavailable.

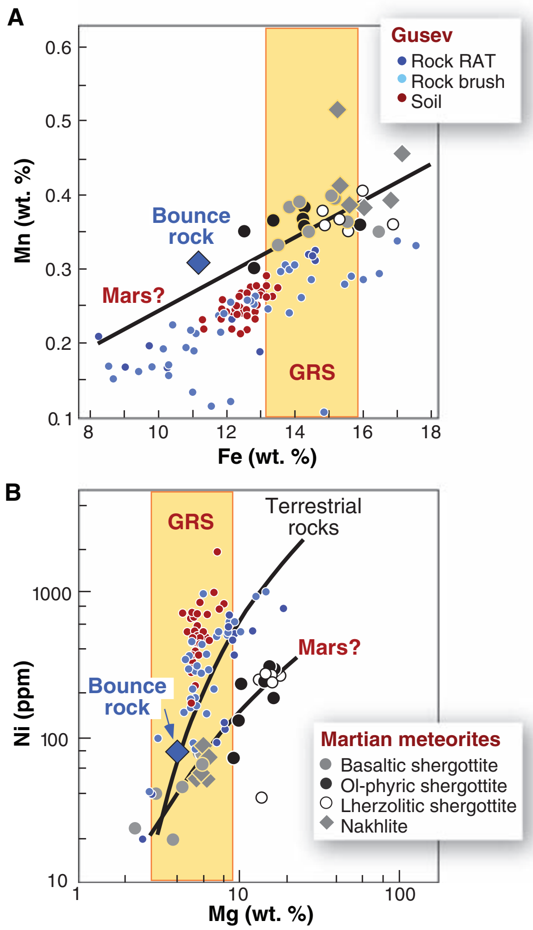

Fig. 4. (**A**) Mn-Fe diagram suggests that the commonly accepted Fe/Mn ratio for the martian mantle, based on martian meteorites, may not apply to all mantle sources, such as that for Gusev rocks. (**B**) Ni-Mg diagram thought to distinguish Mars and Earth samples. Gusev rocks and soils plot along a trend defined by terrestrial basalts rather than martian meteorites.

Conclusions

A critical review of element abundance data for Mars from available sources supports the conclusion that the crust is basaltic, with very limited siliceous rocks and no rocks critically undersaturated in silica. The basalts are tholeiites, and a previous hypothesis that older crustal rocks are calc-alkaline is incorrect. Thus, important roles for crustal differentiation or melting of recycled, hydrous, or alkali-rich mantle sources are not supported by the data, pointing to distinct magmatic processes in producing the crusts of Mars and Earth. The abundance of basalts indicates that chemical weathering has been limited over much of the planet's history. The spacecraft data also suggest that young martian basaltic meteorites are not representative of the older crust and cast doubt on the validity of geochemical fingerprints for Mars that are based on martian meteorite data alone. Although martian meteorites remain a critically important data set, element abundances in the crust derived from spacecraft measurements suggest that magma source regions are heterogeneous and constraints on mantle compositional models from the meteorites may not apply to the entire mantle.

References and Notes

1. H. Y. McSween, T. L. Grove, M. B. Wyatt, *J. Geophys. Res.* **108**, (E12), 5135 10.1029/2003JE002175 (2003).
2. H. Y. McSween *et al.*, *J. Geophys. Res.* **104**, 8679 (1999).
3. J. L. Bandfield, V. E. Hamilton, P. R. Christensen, *Science* **287**, 1626 (2000).
4. M. B. Wyatt, H. Y. McSween, K. L. Tanaka, J. Head, *Geology* **32**, 645 (2004).
5. J. R. Michalski *et al.*, *Icarus* **174**, 161 (2005).
6. P. R. Christensen *et al.*, *Nature* **436**, 504 (2005).
7. W. V. Boynton *et al.*, *J. Geophys. Res.* **112**, E12S99 10.1029/2007JE002887 (2007).
8. P. R. Christensen *et al.*, *J. Geophys. Res.* **97** (E5), 7719 (1992).
9. M. S. Ramsey, P. R. Christensen, *J. Geophys. Res.* **103**, 577 (1998).
10. M. B. Wyatt *et al.*, *J. Geophys. Res.* **106**, 14711 (2001).
11. V. E. Hamilton *et al.*, *J. Geophys. Res.* **106**, 14733 (2001).
12. TES spectra are limited from the mapping orbit data set up to 5317 and are constrained by surface temperatures >250 K, lambert albedo <0.15, dust extinctions of <0.18 (1075 cm^{-1} opacity of ~0.3), water ice extinctions of <0.1 (800 cm^{-1} opacity of ~0.15), and emission angles of <30°.
13. B. C. Clark *et al.*, *J. Geophys. Res.* **87**, 10059 (1982).
14. The APXS on Mars Pathfinder was an Alpha Proton X-ray Spectrometer; the same abbreviation on MER stands for Alpha Particle X-ray Spectrometer.
15. R. Gellert *et al.*, *J. Geophys. Res.* **111**, E02S05 10.1029/2005JE002555 (2006).
16. D. W. Ming *et al.*, *J. Geophys. Res.* **113**, E12S39 10.1029/2008JE003195 (2008).
17. H. Wanke, J. Bruckner, G. Dreibus, R. Rieder, I. Ryabchikov, *Space Sci. Rev.* **96**, 317 (2001).
18. C. N. Foley, T. E. Economou, R. N. Clayton, *J. Geophys. Res.* **108** (E12), ROV 37-1 (2003).
19. L. A. Haskin *et al.*, *Nature* **436**, 66 (2005).
20. S. W. Squyres, A. H. Knoll, *Earth Planet. Sci. Lett.* **240**, 1 (2005).
21. P. R. Christensen *et al.*, *J. Geophys. Res.* **106**, 23873 (2001).
22. J. Zipfel *et al.*, *Meteorit. Planet. Sci.* **39** (Suppl.), A118 (2004).
23. R. Greeley *et al.*, *J. Geophys. Res.* **110**, E05008 (2005).
24. H. Y. McSween, A. H. Treiman, *Rev. Mineral.* **36**, 6-1 (1998).
25. L. E. Nyquist *et al.*, *Space Sci. Rev.* **96**, 105 (2001).
26. R. Christen, O. Eugster, H. Busemann, *Antarc. Met. Res.* **18**, 117 (2005).
27. C. Meyer Jr., The Mars Meteorite Compendium (JSC #27672 Revision, NASA Johnson Space Center, Houston, TX); http://curator.jsc.nasa.gov/antmet/mmc/index.cfm (2006).
28. H. Y. McSween *et al.*, *J. Geophys. Res.* **111**, E09S91 10.1029/2006JE002698 (2006).
29. H. McSween *et al.*, *J. Geophys. Res.* **113**, E06S03 10.1029/2007JE002970 (2008).
30. H. Wanke, G. Dreibus, *Philos. Trans. R. Soc. Lond. Ser. A* **325**, 545 (1988).
31. A. N. Halliday, H. Wanke, J.-L. Birck, R. N. Clayton, *Space Sci. Rev.* **96**, 197 (2001).
32. Y. Ouri, N. Shirari, M. Ebihara, *Antarc. Met. Res.* **16**, 80 (2003).
33. J. Filiberto, *Icarus* **197**, 52 (2008).
34. J. Longhi, *Proc. Lunar Planet. Sci. Conf.* **21**, 695 (1991).
35. J. Hurowitz *et al.*, *J. Geophys. Res.* **111**, E02S19 10.1029/2005JE002515 (2006).
36. J. J. Papike, *Rev. Mineral.* **36**, 7-1 (1998).
37. A. R. McBirney, *Igneous Petrology, 3rd ed.* (Jones & Bartlett, Sudbury, MA, 2007).

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