An integrated view of the chemistry and mineralogy of martian soils

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The mineralogical and elemental compositions of the martian soil are indicators of chemical and physical weathering processes. Using data from the Mars Exploration Rovers, we show that bright dust deposits on opposite sides of the planet are part of a global unit and not dominated by the composition of local rocks. Dark soil deposits at both sites have similar basaltic mineralogies, and could reflect either a global component or the general similarity in the compositions of the rocks from which they were derived. Increased levels of bromine are consistent with mobilization of soluble salts by thin films of liquid water, but the presence of olivine in analysed soil samples indicates that the extent of aqueous alteration of soils has been limited. Nickel abundances are enhanced at the immediate surface and indicate that the upper few millimetres of soil could contain up to one per cent meteoritic material.

The 1976 Viking landers[1,2] provided the first elemental analyses[3] of martian surface materials. These results, using X-ray fluorescence spectrometers, indicate a mafic composition of the soils and a level of sulphur two orders of magnitude higher than the average crust of Earth[4]. Two decades after the Viking missions, Mars Pathfinder[5] arrived with an Alpha Proton X-ray Spectrometer (APXS)[6] capable of identifying elements below the detection limit of the Viking X-ray fluorescence spectrometer. More importantly, the Pathfinder APXS was mounted on a mobile platform, enabling analyses of rock surfaces as well as soils. Compositional averages showed that soils were significantly enhanced in Fe and Mg relative to the rocks, suggesting that soil compositions are not dominated by the physical weathering products of local rocks[7–9]. The Viking and Pathfinder landers were also equipped with multispectral imagers[10,11], which confirmed orbital and Earth-based observations of ferric iron absorptions, indicative of oxidized surface materials.

In January 2004, the Mars Exploration Rovers (MERs) Spirit and Opportunity landed in Gusev crater[12] and on the haematite-rich plains of Meridiani Planum[13], respectively. The science payload of each rover consists of the Panoramic camera (Pancam)[14], the Miniature Thermal Emission Spectrometer (Mini-TES)[15], the Microscopic Imager[16], the Mössbauer spectrometer[17], the APXS[18], the Rock Abrasion Tool[19], and a suite of magnets[20]. The use of identical sets of complementary instruments at the two landing sites enables a thorough investigation of martian soils.

Primarily on the basis of morphology evident in Microscopic Imager images, the soils at Gusev crater can be categorized into four components (Table 1 and Fig. 1). A thin, ~1-mm-thick layer of easily compacted, fine-grained, 'bright dust' is found at the immediate surface. Beneath this layer is a 'dark soil' with a grain size of up to 100 μm, just at the limit of the Microscopic Imager resolution. Imprints produced by the Mössbauer spectrometer upon contact with these dark soils indicate that they also contain a significant population of smaller grains[21]. Aeolian (wind-deposited) 'bedform armour' consists of millimetre-sized grains, and larger 'lithic fragments' are embedded in the soil.

Four components of the soil are also present at Meridiani Planum (Table 1 and Fig. 1). Haematite-rich 'spherules' and their fragments are present throughout this landing site[22] in amounts that can be detected from orbit[23]. 'Clasts' of variable angularity and vesiculation are interspersed among the spherules[24]. Excluding spherules and other clasts, the fine-grained deposits at the surface are dominated by a 'dark soil' with a maximum grain size of approximately 100 μm. 'Bright dust' is present in small patches at the surface as well as in subsurface deposits exposed by the rover wheels.

Bright dust

The elemental composition of the bright surface dust at Gusev crater is remarkably uniform[25]. Undisturbed soils that do not include pebbles or other rock fragments (Table 1) have variations in major and minor elements that are less than 15% of the average value. The combination of Mössbauer and APXS data establishes that the nanophase iron oxide[26] component of soils is closely associated with the occurrence of sulphur (Fig. 2a). Furthermore, the negative

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correlation between sulphur and olivine indicates that this ferrous iron component decreases as the amount of sulphur increases (Fig. 2b), firmly refuting suggestions of abundant ferrous sulphate in martian soils[27]. These results are consistent with the expectation that the sulphur component of the soil (a proxy for alteration) is associated with the most weathered and oxidized mineral phases.

At Meridiani, the majority of surface soils consists of clasts, spherules and/or dark soil, but there have been two measurements of bright surface dust (Table 1). Compositions of these targets are within 15% of the average of bright dust at Gusev crater for all major and minor elements, with the exception of Na (22%) and Cr (28%). The variability in Na might result from differences in the low energy threshold of the two APXS instruments, and the Cr variation could be attributable to the small sample set and the low count rates for an oxide present at ~0.3 weight per cent. Subsurface soils at Meridiani exposed by the rover wheels also provide an excellent match to the bright surface dust deposits. Major- and minor-element abundances of Big Dig/Hema Trench 1 (Table 1) are within 15% of the average bright surface dust composition. PhotoTIDD/Nougat is also similar but the relatively volatile elements S and Cl are 20% and 27% lower, respectively, than the average bright surface dust. These subsurface soils probably represent an earlier episode of dust deposition that has since been covered by the influx of the dark soil.

The elemental chemistry of the soils measured at the five landing sites on Mars are plotted in Fig. 3. The bright dust at Gusev crater and the Meridiani plains plot in relatively tight clusters with respect to each other and are distinct from the rock compositions. Systematic offsets in Viking Mg, Al, and Ti could represent actual variability in the soil chemistry or the absolute accuracy of the instruments. Nonetheless, the observed chemistry of the surface soil is remarkably similar given the separation of the landing sites and the differences in the instrument hardware.

Pancam spectra of bright dust deposits (Fig. 4) are similar at Gusev and Meridiani, and both are similar to bright dust spectra measured over the same wavelengths by Mars Pathfinder[28] and telescopic observations[29]. The spectra are consistent with a composition dominated by nanophase ferric oxides[30]. Differences in the absolute reflectivity of the bright soils at the MER landing sites could result from a smaller mean particle diameter at Meridiani relative to Gusev, to the presence of an additional spectrally neutral component in the Meridiani dust, and/or to differences in surface texture.

Bright, undisturbed soils at Gusev have a Mini-TES spectral signature similar to that of Mars Global Surveyor TES spectra of regions of Mars[31,32] with high albedo and low thermal inertia. A bright streak downwind of Eagle crater at the Meridiani site exhibits a spectral signature that also matches Mars Global Surveyor TES global dust (Fig. 5)[33]. This remarkable consistency indicates that local dust deposits have the same homogeneous composition as the global average Mars dust.

The bright dust deposits at Gusev and Meridiani have similar physical properties and the dust readily adheres to the contact plate in front of the Mössbauer spectrometer, resulting in extraction of clods (Fig. 1d and e). In addition, the magnetic properties investigation on both rovers indicates that all dust particles are magnetic and that they have a composition consistent with the bright dust[34,35]. These data, taken collectively, indicate that the thin layer of bright surface dust is a global soil unit with distinct compositional and physical properties.

Dark soil

The dark soils are low-sulphur endmembers. With the exception of haematite-rich soils at Meridiani, which have increased levels of iron[36] and the interiors of trenches, other soils at Gusev and Meridiani plot on a line between the dark soil and bright dust (Fig. 3). The dark soils at the two landing sites are reasonably consistent with each other, and ratios of dark soil (Table 1) to bright surface dust exhibit similar profiles (Fig. 6). The large discrepancy in Br results from the location of the soil units at the two MER sites. At Meridiani, the plotted samples of dark soil and bright dust are found at the immediate surface, and Br is at the instrument detection limit, so the ratio is that of small numbers. At Gusev, the dark soil is found beneath the immediate surface, where Br is enriched (see discussion below).

A direct comparison of Mössbauer spectra shows that the dark soil targets at the two sites are essentially identical in iron mineralogy and dominated by olivine and pyroxene (Supplementary Fig. A). The mean percentages of iron in olivine, pyroxene, nanophase iron oxide, and magnetite are 38%, 38%, 15% and 9%, respectively[22], for the dark soil targets listed in Table 1. The standard deviations of the four iron minerals across these five samples are 1.6%, 2.8%, 1.9% and 4.3%. The variability in magnetite results from the presence of grains of magnetite-rich bedform armour (Table 1) in the Bear Paw/Panda New target. All other variations are near the ±2% absolute accuracy of the fits to the Mössbauer data and are small relative to the overall variability in the soils[22,26].

Pancam spectra of dark soil deposits are also similar at Gusev and Meridiani (Fig. 4). The dark soil spectra at both MER sites are similar to Pathfinder and telescopic data of dark soils and low-albedo regions[28,29] in that they exhibit a weak ferric absorption edge

Table 1 | Endmember components of martian soils

Site	Soil component	Description	Figure	Representative APXS/Mössbauer Targets*	Sol(s)
Gusev crater	Bright dust	Global unit	1a	Gusev/First Soil	14
				Sugar Loaf Flats/Soil 1	65
				Deserts/Gobi 1	68–71
				Truckin Flats/Accelerator	126
	Dark soil	Similar to dark soil at Meridiani	1b	Bear Paw/Panda New	73–74
				Santa Anita/Seattle Slew	135
				Shredded/Dark 4	158
	Bedform armour	Abundant magnetite	1c	Arena/Crest	41
				Angel Flats/Halo 01	45
	Lithic fragments	Abundant magnetite	1d	Ramp Flats/Soil 1	44
				Wrinkle/Ridge 1 (Mössbauer only)	54
Meridiani Planum	Bright dust	Global unit	1e	Mont Blanc/Les Hauches (surface)	59–60
				Hilltop/McDonnell (surface)	123
				Big Dig/Hema Trench 1 (subsurface)	24–25
				PhotoTIDD/Nougat (subsurface)	89–90
	Dark soil	Similar to dark soil at Gusev	1f	Millstone/Dahlia	165–167
				Auk/Auk RAT	237–238
	Spherules	Haematite concretions	1g	Dog Park/Jack Russell	80
				PhotoTIDD/Fred Ripple	91
	Clasts (mostly angular/vesiculated)	Possibly basaltic	1h	Not yet analysed	–

*MER APXS data used in analyses are tabulated in Supplementary Tables A, B and C.

indicative of the presence of altered iron-bearing minerals. However, in the near-infrared the MER dark soil data are different from average Pathfinder or telescopic data. Specifically, MER dark soils exhibit a shallow and broad absorption band centred near 900 nm that is probably due to the presence of ferrous-iron bearing silicates (for example, pyroxene)[37]. A similar band at the same position is observed in Pancam spectra of dust-poor rock surfaces at Gusev[38]. Thus, the dark soils at both MER sites appear to contain a significant component of less-altered mafic material, consistent with the Mössbauer results.

The variability observed in the Mini-TES spectra of dark soils at Gusev is dominated by contributions of the ubiquitous dust. Linear deconvolution of dark soil spectra from a rover track, normalized to remove the dust component, indicates a suite of basaltic minerals: ~45% pyroxene, ~35% plagioclase feldspar, ~15% olivine, 5% glass, and less than 5% sulphates or oxides. These compositions are the same as previously reported results[32] with the exception of glass, which was not included as an endmember in the earlier analyses. Dark soils at Meridiani are spectrally similar to those at Gusev (Fig. 5). A representative target called Auk in Endurance crater has a basaltic composition consisting of ~35% pyroxene, ~40% plagioclase feldspar, ~10% olivine, ~15% glass, and less than 5% sulphates and oxides, a result similar to previously analysed haematite-poor dark soil in Eagle crater[33]. The accuracy of Mini-TES mineral retrievals are ±5–10% (ref. 32), which is of the order of the variation in mineral abundances between the two landing sites. Dark soils at both MER sites are well matched by Mars Global Surveyor TES data of low-albedo, globally common, basaltic surfaces on Mars[39–41].

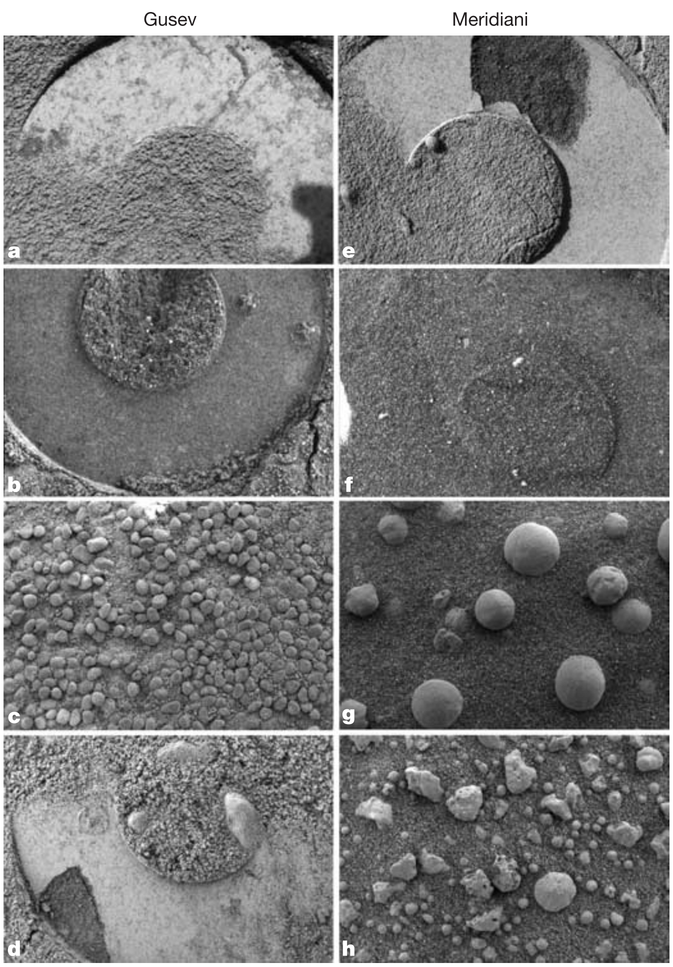

Figure 1 | Microscopic Imager images, each 3 cm across. a–d, Gusev crater images: **a**, Bright dust (sol 65); **b**, dark soil (sol 158); **c**, millimetre-sized bedform armour (sol 41); **d**, rounded pebbles in a matrix of surface dust (sol 54). Meridiani Planum images: **e**, Bright dust (sol 123); **f**, dark soil (sol 167); **g**, haematitic spherules on a bed of dark soil (sol 14); **h**, sub-angular, vesicular clasts on dark soil (sol 53). All images except **g** and **h** show an imprint of the annular Mössbauer contact plate. In **d** and **e**, small patches of soil adhered to the Mössbauer contact plate, revealing underlying dark soil.

Other soil components

The surfaces of aeolian bedforms on the Gusev plains are armoured with rounded, well-sorted, millimetre-sized grains (Fig. 1c). Mössbauer spectra of these targets are significantly enhanced in magnetite, by over a factor of two in certain cases, relative to bright dust and dark soil. Subrounded pebbles (Fig. 1d) also exhibit magnetite enrichments and probably have a similar origin. The elemental composition of the bedform armour indicates that the grains are sorted fragments of Gusev plains basalts. Relative to the average composition of the surface dust, these grains are enhanced in Fe, Ca and Cr and depleted in Ti, Ni, Zn, S, Cl and K, as is expected for a mixture of Gusev basalts with global dust. That is, the abundance of these elements in the bedform armour is between that of the dust and the Gusev basalts[42]. Mg and Br, however, do not conform to this interpretation. The Mg abundance in the bedform armour is comparable to that in the dust, but the amount of Mg in rocks is ~20% higher. This apparent loss of Mg in the bedform armour could be explained by the preferential retention of heavy minerals such as magnetite relative to the olivine phases in the original rocks[43]. This possibility is consistent with the increase in the magnetite to olivine ratio in the Mössbauer measurements of bedform armour as compared to the same ratio in plains basalts. Concentrations of Br in the bedform armour can be more than twice as high as in typical surface soils. An explanation for this enrichment is discussed below.

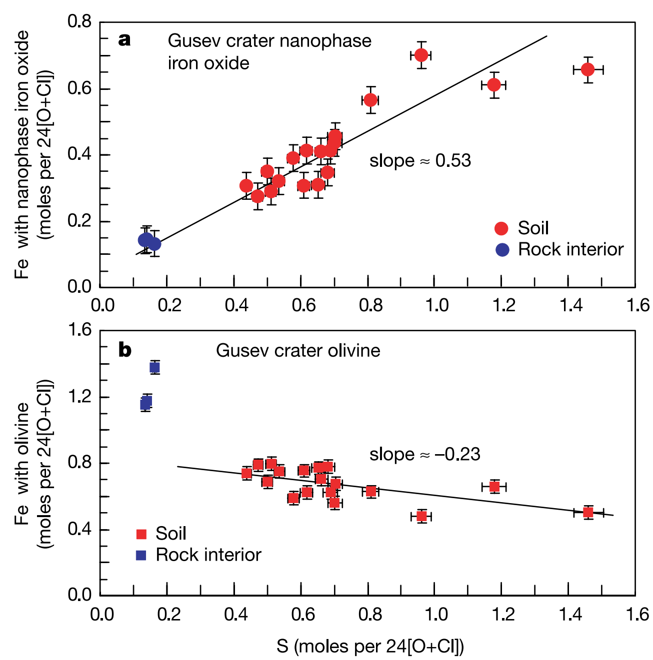

Figure 2 | Correlations between APXS elemental chemistry and iron mineral phases measured by Mössbauer[26] in Gusev soils. Molar concentrations with respect to the number of anions are shown. **a**, Positive correlation indicates that nanophase iron oxide is a carrier of S. The low Fe:S ratio (~1:2) suggests that S is also present in phases which do not contain iron. **b**, Negative correlation between iron in olivine and the S concentration is consistent with olivine being an unweathered mineral and S associating with altered phases. Error bars represent 2-sigma statistical errors in the APXS data and fitting uncertainties in Mössbauer data.

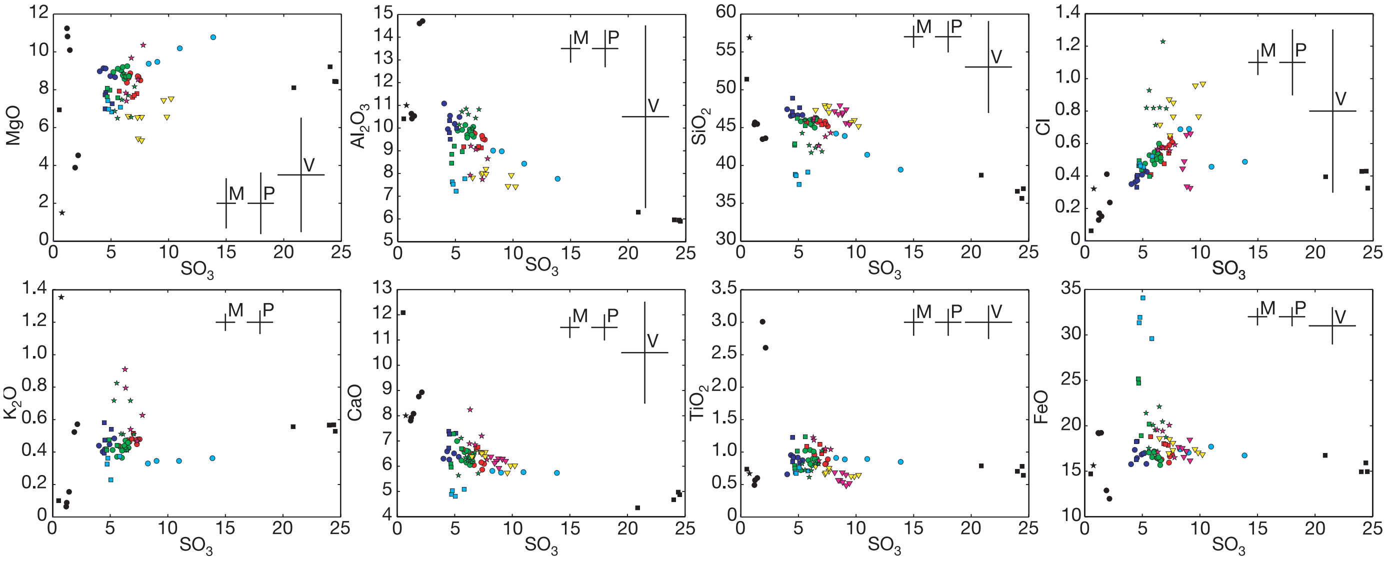

Figure 3 | Composition of martian surface materials. Circles, squares, stars and triangles represent Spirit, Opportunity, Pathfinder[7,8] and Viking[3] data, respectively. MER data: black (rocks), red (bright dust), blue (dark soil), cyan (haematitic soils at Meridiani, high-sulphur trench interiors at Gusev), green (other soils). Pathfinder data in magenta[7] and green[8] represent independent fits of the same data; black is the sulphur-free rock composition[7]. Viking 1 and 2 data are plotted in yellow and magenta, respectively. Renormalization uses iron as FeO and average Gusev values for elements not measured. Approximate error bars representing the uncertainty shown for MER ('M'), Pathfinder ('P'), and Viking ('V') data.

The spherules in rocks and soils at Meridiani Planum are clearly enriched in haematite[22]. Ratios of APXS data on the spherules relative to a spherule-free background show the expected increase in iron content as well as a decrease in most other elements resulting from dilution (for example, more haematite means less silicates in the field of view). In spherule-rich targets, the abundance of Ni correlates with Fe, indicating that these cations exhibit similar chemical responses during the formation of the spherules.

Origin of the soils

At Gusev crater, the bright dust and dark soil have substantially greater concentrations of S, Cl, K, Ti, Ni and Zn relative to the analysed rocks[42] in the plains (Supplementary Fig. B). The increases in S, Cl and Zn could be attributed to precipitates of volcanic outgassing[44], but variations in other elements are difficult to explain without a significant contribution of material with compositions different from that of the plains basalts.

At Meridiani, the bright dust and dark soil components have sulphur levels comparable to that of bright dust and dark soil at Gusev, yet the local rock outcrops have sulphur concentrations a factor of 4 or 5 larger. From the Mössbauer data, jarosite is not detected in Meridiani soils, and a maximum of only 1% olivine is detected in abraded outcrop rocks[22]. Therefore, the bright surface dust and the dark soil have been transported to Meridiani Planum by wind-related processes. A similar situation probably applies at Gusev.

There are clearly basaltic fragments at Gusev and haematitic spherules in Meridiani soils that originated from the local rocks. However, the available compositional data indicate that outcrop rocks at Meridiani and plains basalts at Gusev do not contribute significantly to the surrounding bright surface dust and dark soil. This interpretation is further supported by Fig. 3, which shows that soil compositions at five landing sites on Mars are more similar to each other than to the analysed rocks.

The extent of aqueous alteration of the soil at both MER sites has been rather limited. In contrast to Meridiani outcrop rocks that have ferric to total iron ratios in excess of 0.84 (ref. 22), soils that do not include spherules have ferric to total iron ratios of less than 0.42. The one exception is the floor of Big Dig/Hema Trench 1, which has $Fe^{3+}/Fe_{total} = 0.52$. The bottoms of the Gusev and Meridiani trenches, exhibiting the highly oxidized, sulphur-rich soils, still have 19% to 26% of the iron in olivine. This presence of olivine indicates that the soils at depth are either only partially weathered or result from mixing with olivine-rich soils.

Bromine concentrations at Meridiani and Gusev soils are typically less than ~50 p.p.m. at the surface and elevated (factors of 2 to 30 higher) in bedform armour, low-lying rocks, and subsurface soils. Compounds that contain Br are among the most soluble mineral phases, and thus its presence is a probable indicator of liquid water activity. Given the association with high-thermal-inertia materials and subsurface cold traps, the observed behaviour of Br is consistent

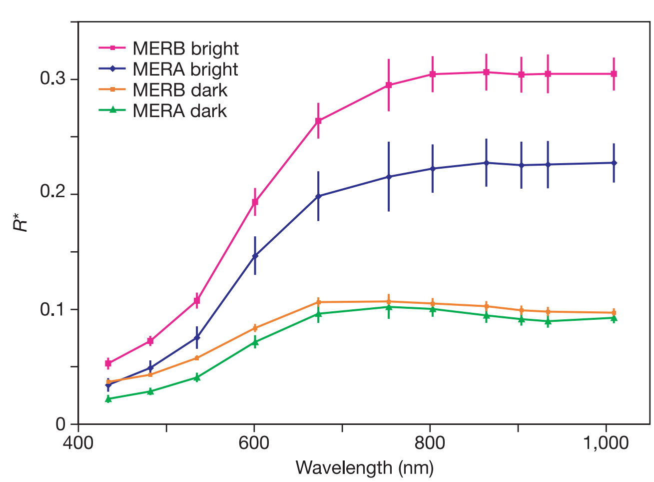

Figure 4 | Average Pancam 11-colour spectra of bright surface dust and dark soil at the Gusev and Meridiani sites. The parameter R^* is the brightness of the surface divided by the brightness of the Pancam radiometric calibration target scaled to its equivalent Lambert reflectance. Error bars represent the variance of all the spectra used to generate the average value plotted.

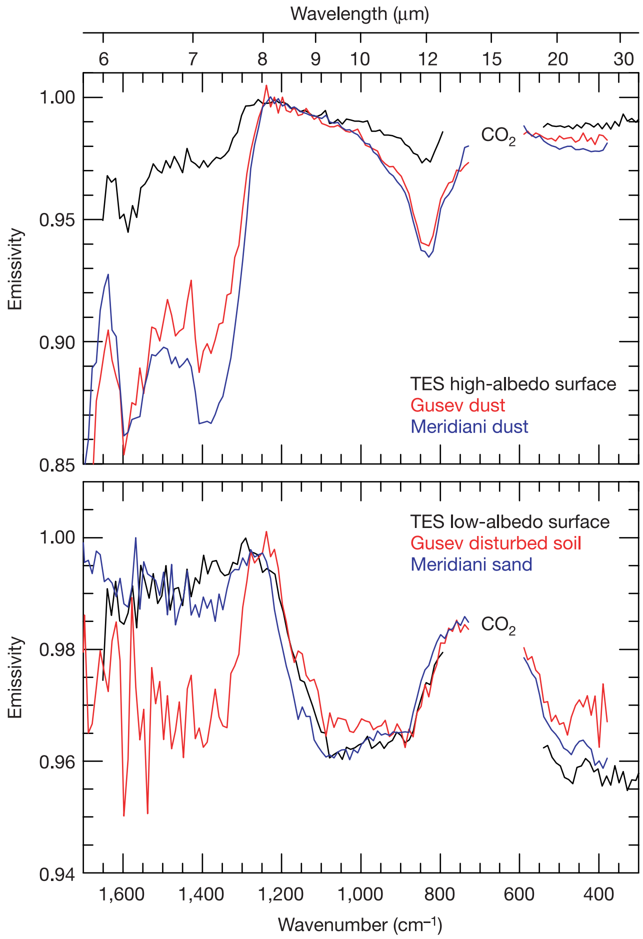

Figure 5 | Comparison of orbital (TES) and surface (Mini-TES) thermal infrared spectra. Bright dust (top): Gusev ('Serpent', sol 70); Meridiani ('CoolWhip', sol 57). Due to averaging over multiple incidence angles, the TES signature has lower spectral contrast[31]. Dark soil (bottom): Gusev ('Skid', sol 89); Meridiani ('Auk', sol 197). A contribution from bright dust[32] is present in the Gusev dark soil spectrum, producing differences in the 6–8-μm region and the negative slope between 8 and 12 μm. The broader absorption in the 8–12-μm region of the Meridiani dark soil is attributable to additional sulphate components[33].

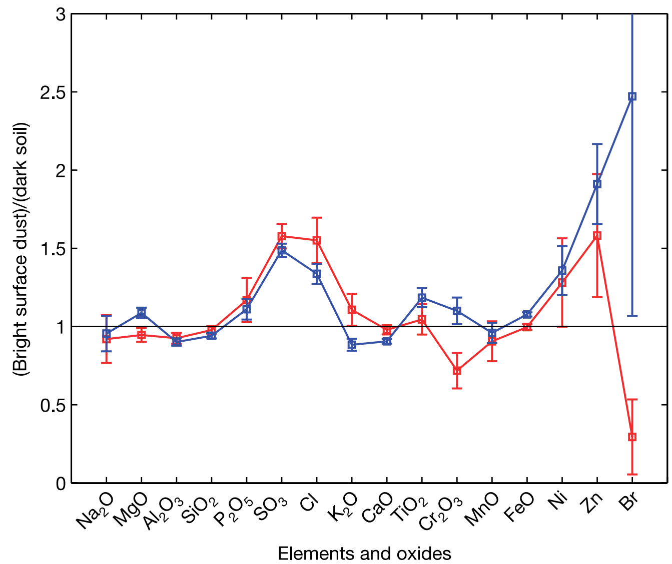

Figure 6 | Ratios of bright surface dust to dark soil exhibit similar trends for Gusev (red) and Meridiani (blue). Error bars represent 2-sigma statistical errors in the data.

with mobilization under climatic conditions similar to present-day Mars or during periods in the obliquity cycle where the mixing ratio of atmospheric water vapour is enhanced.

In this proposed scenario, frost deposited at night rapidly sublimes in the morning and condenses in cold traps. Condensation in excess of a single molecular monolayer allows the H_2O molecules to behave as a liquid and mobilize ions in salts. Diurnal, or perhaps seasonal, cycling of these thin films of water over geologic timescales may be sufficient to concentrate Br to the observed levels.

The concentrations of Ni at Gusev are approximately 200 p.p.m. in the interiors of rocks, 550 p.p.m. in the dark soil, and 650 p.p.m. in the bright surface dust. Nickel is present in chondritic (CI) meteorites at an average level of 1.1% (ref. 45), and the difference between the Ni abundance in rocks and dust can be accounted for by adding 3.4% chondritic material to the rock composition. This approach, however, produces significant mismatches in other elements (Supplementary Fig. C). Thus, the surface dust at Gusev is not simply a product of meteoritic additions to a local rock composition. The 100 p.p.m. enhancement of Ni in bright surface dust relative to the dark soil does not necessarily result from, but is compatible with, a 1.2% addition of CI material (Supplementary Fig. C). This value is consistent with predictions of a meteoritic component in martian soils[46,47] and is comparable to the estimated admixture of 1.9% chondritic material in lunar soils[48].

Overview

The bright dust at the immediate surface of Mars is a globally distributed unit. The dark soils at Gusev and Meridiani are similar in composition and may also represent a distinct global unit, or given the apparent uniformity of basaltic terrains mapped from orbit, the connection between these dark soils may be a result of the general similarity in the rocks from which they originated. The fine-grained soil components at the MER sites are not derived from the local rocks and are products of wind redistribution. Oxidative weathering of the soil has not been extensive, suggesting rather limited interactions with liquid water. The action of thin films of water, possibly under current climatic conditions, is indicated by the distribution of bromine.

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