

## LETTERS MARS

# Water alteration of rocks and soils on Mars at the Spirit rover site in Gusev crater

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Gusev crater was selected as the landing site for the Spirit rover because of the possibility that it once held a lake. Thus one of the rover's tasks was to search for evidence of lake sediments<sup>1</sup>. However, the plains at the landing site were found to be covered by a regolith composed of olivine-rich basaltic rock and wind-blown 'global' dust<sup>2</sup>. The analyses of three rock interiors exposed by the rock abrasion tool showed that they are similar to one another, consistent with having originated from a common lava flow<sup>3-8</sup>. Here we report the investigation of soils, rock coatings and rock interiors by the Spirit rover from sol (martian day) 1 to sol 156, from its landing site to the base of the Columbia hills. The physical and chemical characteristics of the materials analysed provide evidence for limited but unequivocal interaction between water and the volcanic rocks of the Gusev plains. This evidence includes the softness of rock interiors that contain anomalously high concentrations of sulphur, chlorine and bromine relative to terrestrial basalts and martian meteorites<sup>9</sup>; sulphur, chlorine and ferric iron enrichments in multilayer coatings on the light-toned rock Mazatzal; high bromine concentration in filled vugs and veins within the plains basalts; positive correlations between magnesium, sulphur and other salt components in trench soils; and decoupling of sulphur, chlorine and bromine concentrations in trench soils compared to Gusev surface soils, indicating chemical mobility and separation.

In addition to basaltic rocks and global dust, volcanic gases containing sulphur, chlorine, bromine and other volatiles were likely reactants for materials now covering the Gusev plains. Atmospheric oxidants are solar photoproducts<sup>10</sup> from the action of ultraviolet radiation on CO<sub>2</sub> and H<sub>2</sub>O, but volcanogenic SO<sub>3</sub> and HCl provide acidic molecules, which, with the help of liquid water, are capable of dissolving basaltic materials<sup>11</sup>. Acidic alteration of volcanic rocks in an aqueous environment would result in an increase of oxidation state and changes in concentrations of soluble cations (K, Na, Mg, Ca, Fe<sup>2+</sup>) relative to less-soluble cations (Ti, Si, Al, Cr, Fe<sup>3+</sup>). Sources of small quantities of water include precipitation and condensation from the atmosphere (for example, frost), and 'snow' or ice that might have covered the surface at Gusev<sup>12</sup>. Ice might have been

trapped at shallow depths during periods of high obliquity, then melted and risen (in response to warming of the surface) as transient water: at times when the atmospheric water-vapour pressure was high enough, liquid water could have been formed<sup>13</sup>.

The survival of basaltic minerals such as olivine, plagioclase and magnetite in the soils and rock coatings<sup>6</sup> suggests that chemical reactions took place with a low water/rock ratio. From sol 1 to sol 156, no examples of large-scale conversion of basaltic materials to alteration products were found. Physical processes (for example, impacts and aeolian weathering) are responsible for comminution of the basaltic component of the soil<sup>14</sup>. Volatile elements (S, Cl, Br), however, are found inside plains basalts in higher concentrations than in terrestrial basalts<sup>5,15</sup>. The specific grinding energy used for the hardest plains basalt, Humphrey, is only ~50% of the energy used for typical terrestrial basalts<sup>16</sup>.

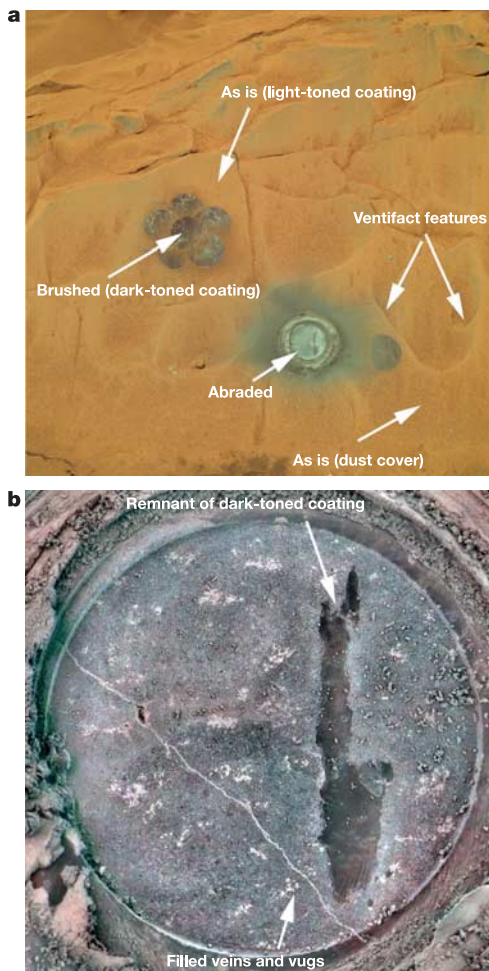
The coatings and interior features of the light-toned rock Mazatzal (Fig. 1; see Methods) indicate post-crystallization aqueous alteration. The inverse correlation of Fe<sup>3+</sup> in nanophase ferric oxides (Fe<sub>np-Ox</sub><sup>3+</sup>) with Fe<sup>2+</sup> in olivine (Fe<sub>olivine</sub><sup>2+</sup>) (Fig. 2) and a positive correlation with SO<sub>3</sub> (ref. 17) are qualitatively consistent with the hypothesis that the source of increased Fe<sup>3+</sup> was mainly oxidation of Fe<sub>olivine</sub><sup>2+</sup>. (Here Fe<sub>np-Ox</sub><sup>3+</sup> refers to a group of fine-grained (<10 nm) poorly crystalline phases considered as general alteration products of plains basalts. These include, for example, the superparamagnetic forms of Fe-oxides, oxyhydroxides, sulphates, and the Fe<sup>3+</sup> pigment in palagonitic tephra<sup>6,18</sup>.) Furthermore, the coatings on Mazatzal have 2–5 times higher S and Cl concentrations than the rock interior. These coatings also contain the only occurrence of crystalline haematite detected to date on the basaltic plains of Gusev<sup>6</sup>.

The coatings on Mazatzal are not pure evaporates, nor are they common soil, either local or the proposed global soil<sup>19</sup>. Their properties require alteration of the silicate component of adhering soil or of the rock itself (especially olivine), the oxidation of Fe<sup>2+</sup>, and the incorporation of S and Cl. Given their mode of occurrence<sup>20</sup>, light-toned rocks such as Mazatzal were probably buried in the soil (or dirty snow during the periods of high obliquity) when their coatings developed. Liquid water, even if present in small quantity as

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an 'acid fog', is needed to concentrate S-correlated elements from the surrounding soils and to transport resulting acidic brine into rocks along fractures or interconnected vugs. The brines reacted with the igneous minerals of the rock surface and any adhering soil to produce the different visible coatings (some are light-toned and some are dark), which are rich in S, Cl and haematite. Multilayer coatings covering ventifact grooves<sup>14</sup> indicate episodic burial and exhumation. Ground water might have been the source of liquid water, or alteration could have occurred during periods of high obliquity<sup>12</sup> from contact of the rock surface with transient surficial liquid water<sup>13</sup> from snow melt.

The interiors of all three samples of Gusev plain basalts contain partly filled vugs and veins (plates 9c, 12, 13 in ref. 14). On Earth, such features have distinct chemical compositions resulting from interaction with aqueous fluids during low-temperature or hydrothermal alteration, transport, and deposition of soluble salts and zeolites<sup>21</sup>. The interiors of both Humphrey and Mazatzal contain higher concentrations of Br than their exteriors, with the highest Br/Cl ratio found in abraded Mazatzal (Fig. 2). The Pancam visible-near-infrared spectra of fill materials in vugs and veins indicate that they are different from the rock surface dust or local soil<sup>3</sup>.

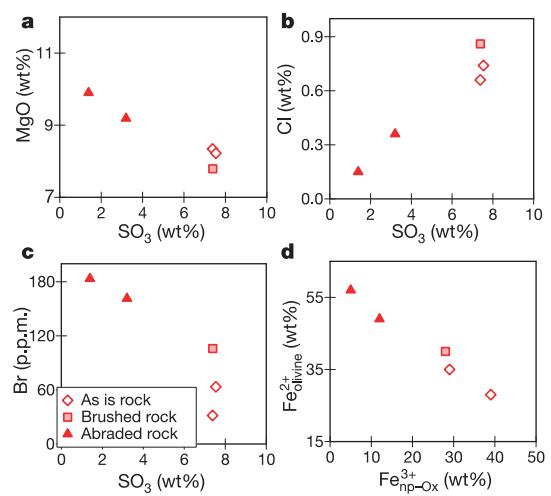


**Figure 1 | Rock Mazatzal and its coatings.** **a**, Pancam image (P2599 sequence; 480, 530, 600 nm filters) with a 'daisy' brush pattern and an abraded depression. A light-toned yellowish coating occurs beneath the reddish dust cover and atop ventifact grooves and scallops. **b**, Mosaic of four images taken by the Microscopic Imager (merged with Pancam colour data), ~45 mm across. A circular subsurface exposure was ground by the second abrasion. The dark strip (centre right, ~10% area) is a remnant of the dark-toned coating. The basaltic interior shows vugs and veins filled with light-toned materials.

Introduction from volcanic exhalations and the decoupling of Br from Cl owing to the higher solubility of Br in aqueous solution<sup>22</sup> are plausible mechanisms to produce the characteristics of alteration observed in these rocks. A network of veins and vugs occurs in the abraded surface of Humphrey (plate 12 in ref. 14). The high salinity (especially Cl) depresses the freezing points of brines<sup>22</sup>, which would permit penetration into rock interiors at low temperatures. Such brines may become more concentrated by loss of H<sub>2</sub>O during their diffusion into the veins and vugs, either by evaporation, addition of soluble compounds, or through chemical reaction with host rocks (especially olivine or glass) to produce hydrated salts, and possibly oxyhydroxides, or hydrated silicates<sup>23,24</sup>. Sulphates or chlorides would precipitate early, whereas Br-enriched brine would be the last to crystallize; bromides would thus be deposited at the deepest locations reached by the brine. In this mechanism, elevated Br concentrations and higher Br/Cl values in rock interiors would represent the last stages of brines. Compared with the ≤50 p.p.m. Br in typical Gusev soils, the 183 p.p.m. Br found in the interior of Mazatzal would correspond to >1,800 p.p.m. Br in veins and vugs, which constitute 5–10% of the area measured by the APXS (Alpha Particle X-ray Spectrometer).

Soil crusts present beneath the uppermost surface dust<sup>12</sup> suggest some cementing of soil materials by salts deposited from water after the soils were emplaced. Martian humidity and cold night-time temperatures can, in the right seasons and obliquities, produce saturation and even frost or aerosol H<sub>2</sub>O. Over geologic timescales, this water could plausibly explain the observed clodding. Evaporating liquid water would also preferentially transport S and Cl towards the surface, explaining the observation that the salts are bound to the soil as precipitates bridging particles, rather than merely mixed with them.

The Laguna trench was dug into the continuous ejecta deposit of Bonneville crater. Imaging and compositional data indicate that the trench site was filled with relatively young basaltic sand deposited by aeolian processes<sup>3,4,12</sup>. In contrast, the Big Hole and The Boroughs trenches were selected to represent intercrater plains, and were located in topographic lows, in areas with low thermal inertia, away from fresh impact craters and dust-filled hollows. The selection

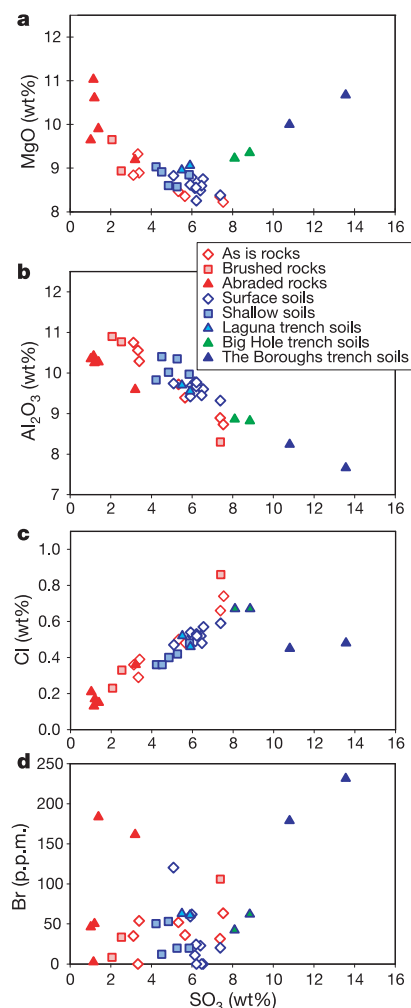


**Figure 2 | Chemistry and mineralogy of Mazatzal and coatings.** One 'as is' surface target was densely covered by dust and the other was less dusty (exposing the light-toned coating). The brushed surface was entirely covered by the dark-toned coating. The subsurface after the first abrasion was half covered by the dark coating, and the other, ~10% coated. Concentrations of Mg (**a**), Cl (**b**) and Br (**c**) vary with S and span over the range of variation seen in soils (Fig. 3). **d**, The wt% Fe in olivine (as Fe<sup>2+</sup>; Fe<sup>2+</sup><sub>olivine</sub>) varies inversely with Fe<sup>3+</sup> in nanophase ferric oxides (Fe<sup>3+</sup><sub>np-ox</sub>).

was done purposely to seek mature regolith, which may hold a record of more ancient aqueous interactions at Gusev than those expected under current martian surface conditions.

Ratios of four elements (S, Cl, Br and Mg) that are roughly constant in most Gusev soils<sup>25</sup> show extended ranges for the soils at both trenches (Fig. 3). The highest concentrations of Mg, S and Br among all Gusev soils occur in the upper-layer soils at The Boroughs trench, accompanied by the highest  $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$  value. These characteristics indicate coupling and decoupling of water-soluble compounds of these elements during chemical separations and perhaps transport. Some elemental correlations for the trench soils are strong, even though each trench has only three measurement points. At The Boroughs, a positive correlation exists for  $\text{SO}_3$  with MgO, Cl and Br ( $r \approx 0.996$ ,  $0.999$  and  $0.998$ ; statistically,  $r = 0.988$  is significant at the 90% level for three points); a negative correlation exists for  $\text{SO}_3$  with  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  ( $r \approx 0.999$  and  $r \approx 0.995$ ); and no obvious correlation exists for  $\text{SO}_3$  with CaO and  $\text{Fe}_2\text{O}_3(\text{total})$ . These characteristics suggest mutual transportation of Mg with the volatile elements (Fig. 3a), and a dilution of basaltic minerals by deposition of salts. These same trends were found in soils at the Viking sites<sup>26</sup>.

In the trench soils, the concentration of  $\text{Al}_2\text{O}_3$  decreases sharply and linearly with increasing  $\text{SO}_3$  along the same line as for basaltic rocks and their coatings, and the other soils (Fig. 3b). This inverse correlation suggests mixing with an evaporate component having a



**Figure 3 | Concentrations of Mg, Al, Cl and Br versus S in rocks and soils. a–d,** Diamond, as is; square, shallow subsurface; triangle, deeper subsurface; red, rocks, blue and green, soils.

high S content. Extrapolation along this trend to zero  $\text{Al}_2\text{O}_3$ , which appears unaffected by processes other than dilution, yields an  $\text{SO}_3$  concentration of  $\sim 45$  wt%. The extrapolated values for all elements are consistent with a mineral assemblage that includes Mg, Ca and Fe sulphates, silica, Ti- and  $\text{Fe}^{3+}$ -oxides, alkali halides, and phosphate. Moreover, the molar proportions of MgO plus CaO are roughly equal to that of  $\text{SO}_3$ , consistent with 5 parts  $\text{MgSO}_4$  and 1 part  $\text{CaSO}_4$ . Mixing-model calculations suggest  $\sim 7$ – $22$  wt% of sulphates (Mg-, Ca- and Fe-sulphate) in The Boroughs soils, and the potential  $\text{H}_2\text{O}$  in hydrated sulphates would constitute up to 4 wt% of the soil in the trench wall (which has the highest Mg and S content).

The  $\text{SO}_3$ –Cl and  $\text{SO}_3$ –Br correlations for The Boroughs trench soils have significantly different slopes (Fig. 3c, d) from the Big Hole trench soils and common Gusev soils, indicating a decoupling of the three soluble elements. Migration of brine upward, driven by the thermal gradient near the surface, could leave high salt concentrations there. The freezing-point depression of the brine would enable Cl to be carried farther and thus to become decoupled from S; elevated and highly variable Br concentrations argue for episodic migration and evaporation of brines. As an alternative to multiple episodes of brine migration, deposition of impact ejecta could play a role<sup>27</sup> in the formation of these compositionally variable soil deposits—highly concentrated salts and strongly altered basaltic regolith (with high  $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$ ) formed at some distant location(s) could have been brought by impact ejecta to become part of the mixture that is now The Boroughs subsurface regolith. In these highly altered basaltic materials, olivine might have been totally consumed and leaching of Ca from clinopyroxene and plagioclase might also have occurred. It is possible that these two mechanisms both contributed to the formation of the observed subsurface regolith at the two trench sites.

Taken together, the data indicate that the geochemical effects of aqueous alteration, though ubiquitous with respect to plains basalts, occurred at low water/rock ratios. Effects on rocks include multiple, oxidized coatings and filled vugs and veins. Effects of aqueous activity are also seen in subsurface soils, including deposition of salts and oxidation of  $\text{Fe}^{2+}$ . The pattern of alteration of igneous minerals and the deposition and transport of soluble materials implicates interaction with water, but not pools of surface or ground water, or hydrothermal conditions. Small quantities of transient, possibly acidic water could be produced by precipitation and condensation from the atmosphere or by melting of ground ice formed during episodes of high obliquity<sup>12</sup>. Water may be involved in the production of the global dust component of the soils, and even the tiny amounts currently present in the martian atmosphere might suffice over time to produce the oxidized material in the dust, with relatively high S and Cl concentrations. More water than at present available from the atmosphere seems to be required, however, to dissolve and mobilize the soluble S-rich components that contributed to the coatings and the salts in subsurface soils. Conditions wetter than at present (and at higher water vapour pressures) are thus implied.

## METHODS

**Rock and soil targets.** Data from three rocks and the soils in three trenches form the basis of discussion in this Letter. Rocks include Adirondack (sols 14–36), Humphrey (sols 54–60) and Mazatzal (sols 76–87). Trenches include Laguna (203 m from Bonneville rim on continuous ejecta deposit, 6–7 cm deep, sols 46–50), Big Hole (556 m from Bonneville,  $\sim 9$  cm deep, sols 113–115) and The Boroughs (1,698 m from Bonneville,  $\sim 11$  cm deep, sols 135–142).

**Method of investigation.** A full set of analyses<sup>1</sup> was obtained for rock and soil targets discussed in this Letter. These include Pancam multispectral images and Mini-TES spectra; brushing and grinding using the Rock Abrasion Tool (RAT)<sup>28</sup>; trenching using rover wheels; and microscopic imaging, Mössbauer spectra, and  $\alpha$ -particle X-ray spectra for surface analysis before and after the RAT and trench operations.

**Rocks and coatings.** All rocks investigated from sol 1 to sol 156 at the Spirit site are fine-grained, olivine-rich basalt<sup>4–8</sup>. Most rocks are angular blocks emplaced

as impact ejecta<sup>20</sup>. Dust cover and surface coatings cause variations in rock brightness in Pancam images<sup>3</sup> ranging from dark-toned (for example, Adirondack and Humphrey) to light-toned (for example, Mazatzal)<sup>9</sup>. Dark-toned rocks tend to lie on the surface or are perched, and light-toned rocks tend to be partially buried with low relief<sup>20</sup>.

Adirondack and Humphrey are relatively coherent and hard, as estimated from the specific grinding energy (SGE) of the RAT<sup>16</sup>, although they are softer than terrestrial basalt used for laboratory testing. Microscopic images of rock interiors show dark phenocrysts (interpreted as olivine<sup>8</sup>) within a fine-grained basaltic matrix<sup>4</sup>. Rock interiors contain vugs and veins filled with light-toned materials, distinct from the dust coverings as shown in their Pancam visible-near-infrared spectra<sup>3</sup>.

The light-toned rock Mazatzal has a similar SGE value to Adirondack<sup>16</sup>; both are softer than Humphrey. Mazatzal has a complex multilayer surface coating (Fig. 1). Materials encountered as brushing and abrasion proceeded were: (1) loose dust cover, (2) an outer light-toned soft coating (removed by brushing), (3) a dark-toned hard coating (partially removed by abrasion), (4) an inner light-toned coating, and (5) the basaltic interior matrix with filled vugs and veins. The Mazatzal surface is shaped by ventifact grooves<sup>14</sup>, indicating exposure to wind before application of the coatings. A vein cuts across all the coatings except the dust-cover layer.

The dust cover and the coatings on all three rocks have higher concentrations of S and Cl and higher Fe<sup>3+</sup>/Fe<sub>total</sub> than the interiors<sup>5,6</sup> (Figs 2 and 3). The interiors of three rocks have almost identical compositions (except volatiles) and Fe-mineralogy, that is, olivine, pyroxene (or basaltic glass), nanophase ferric oxides (Fe<sub>np-Ox</sub><sup>3+</sup>), and non-stoichiometric magnetite (ns-Mt), only Mazatzal has a higher Fe<sub>olivine</sub><sup>2+</sup> and a lower ns-Mt than others. Concentrations of S in rock interiors (>1 wt%) are higher than is common for basalt (<0.2 wt%)<sup>15,24</sup>. The dust cover and underlying light-toned and dark-toned coatings on Mazatzal contain crystalline haematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) and the highest Fe<sub>np-Ox</sub><sup>3+</sup>/Fe<sub>total</sub> (0.39) analysed by the Spirit Mössbauer spectrometer in rocks thus far<sup>5</sup> (Fig. 2d). The light-toned and dark-toned coatings of Mazatzal have 2–3 times more S than the surfaces of Adirondack and Humphrey, and the highest concentration of Cl among all rocks and soils examined (Fig. 3c). The interior of Mazatzal has a higher Br concentration than the coatings (Fig. 2c), and much lower Fe<sub>np-Ox</sub><sup>3+</sup>/Fe<sub>total</sub> (0.1) without haematite, indicating no residual surface dust from grinding or aeolian infiltration in vein or vug fills.

**Soils and trenches.** The bulk material of the surface soils is fine-grained, but poorly sorted sand, granules, pebbles and cobbles were observed in the sub-surface soils within some trenches. Slightly cohesive crust was observed beneath the surface dust throughout the Spirit site<sup>12</sup>.

Overall, the soils have higher concentrations of S, Cl, P, K and Ti than the interiors of the rocks, and lower Mg, Ca, Cr and Fe (ref. 25). Subsurface soils in rover wheel tracks have lower S and Cl and higher Al (Fig. 3c, b) than the surface dust. There is a site-wide, thin, oxidized upper soil layer ( $\leq 1$  mm thick)<sup>12,25</sup>, having a slightly higher Fe<sup>3+</sup>/Fe<sub>total</sub> value (0.29–0.40) than found in the disturbed soils (0.26–0.27) in the rover wheel tracks. The types of Fe-minerals found in the surface and subsurface soils are the same as those in the plains basalts—that is, olivine, pyroxene (or basaltic glass), Fe<sub>np-Ox</sub><sup>3+</sup>, and ns-Mt; no haematite was detected<sup>6</sup>.

The subsurface soils exposed by the Laguna trench have nearly identical compositions to the surface soils (Fig. 3), but are less oxidized (Fe<sup>3+</sup>/Fe<sub>total</sub> = 0.22 compared to 0.3). In contrast, the concentrations of S, Mg and Br, and the Fe<sup>3+</sup>/Fe<sub>total</sub> values (0.33–0.44) from the subsurface soils within the Big Hole and The Boroughs trenches are significantly higher than those at the surface (Fig. 3). The highest Fe<sup>3+</sup>/Fe<sub>total</sub> and S, Mg, Br concentrations among all Gusev soils were found on the wall of The Boroughs trench.

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