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Key Points:

- Subsurface brines can deposit significant potassium in volcanic rocks while preserving original textures.
- Spectral signatures of K-metasomatism include K-feldspar and illite.
- Felsic compositions on Mars might occur because of low-temperate alteration by subsurface brines.

Supporting Information:
Supporting Information may be found in the online version of this article.

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Infrared Spectral Evidence for K-Metasomatism of Volcanic Rocks on Mars

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Abstract

Potassium metasomatism is a common geologic process occurring in a range of environments on Earth. K-metasomatism can dramatically change the chemistry of large volumes of crust resulting in formation of abundant K-rich feldspar while preserving original rock textures. Remote sensing of Mars has revealed the presence of rare but striking felspar-rich terrains as well as K-rich phyllosilicates such as illite or muscovite. Furthermore, the Curiosity Rover has detected evidence for K-enrichment in rocks at Gale Crater. In this study, we use spectroscopic and remote sensing analyses of K-metasomatized rocks on Earth as a comparison to K-rich and/or possible granitic rocks on Mars. The results suggest that evidence for K-feldspar rich, quartz-bearing, and illite-bearing rocks on Mars is consistent with K-metasomatism. K-rich rocks in Gale Crater have themselves likely not been metasomatized, but the abundant feldspar within them might have been derived from metasomatized crust.

Plain Language Summary

Mars is a volcanic planet with a surface dominated by basalt and sedimentary rocks derived from basalt, similar to oceanic crust on Earth (though Mars’ crust is thicker). For decades, Mars has been considered a “one plate planet” where plate tectonics never occurred and where continental type rocks never formed. Recent observations have, however, revealed enticing evidence that felsic “continental type” rocks containing K-feldspar and quartz are present. Such rock units were recognized in Gale Crater based on their high potassium abundances. Granite-type rocks detected from orbit using infrared data would also presumably be rich in potassium. However, rocks of the same composition can be made through aqueous alteration rather than from magma in the crust. This study shows a striking example of potassium enrichment and mineralogical changes in basaltic rocks on Earth caused entirely by low-temperature hydrothermal brine in the crust. We use analogous remote sensing measurements to study these potassic rocks on Earth and compare the results to Mars. It appears that at least some of the felsic rock compositions on Mars were caused by metasomatism.

1. Introduction

Potassium is an incompatible lithophile element that is mobilized and concentrated by aqueous processes under a range of conditions. Its concentration and distribution on Mars therefore contain valuable information about past igneous and alteration processes that have affected the crust. Gamma Ray Spectroscopy (GRS) measurements of Mars from orbit indicate that the crust is generally potassium-poor, with atomic K concentrations of ~0.2–0.6 (Boynton et al., 2007). But variations in K-concentration and K/Th ratios speak to possible igneous evolution or limited aqueous alteration at the broad spatial scales of the Mars Odyssey GRS measurements (Karunatillake et al., 2009; Taylor et al., 2007).

Orbital infrared remote sensing data provide additional perspective on the idea of igneous evolution and K-enrichment at higher spatial resolution than is possible with GRS data (Christensen et al., 2005; Rogers et al., 2007). Thermal infrared emission data from the 2001 Mars Odyssey Thermal Emission Imaging System (THEMIS) have revealed rock compositions similar to granite exhumed from the subsurface in some ancient terrains (Figure 1; Bandfield, 2006). THEMIS data combined with Mars Global Surveyor (MGS) Thermal Emission Spectrometer (TES) data suggest that the rocks are composed of K-feldspar and quartz, along with other phases (Bandfield et al., 2004). These detections are categorically related to, but distinct from, anorthosite-bearing rocks detected with the Mars Reconnaissance Orbiter (MRO) Compact Reconnaissance Imaging Spectrometer for Mars (CRISM; Carter & Poulet, 2013; Wray et al., 2013). The units...
identified by CRISM have been shown to be inconsistent with highly felsic rocks, although anorthosite compositions are permissible (Rogers & Nekvasil, 2015). Some key differences between the detections made using THEMIS and TES thermal infrared data versus CRISM near infrared data is that the thermal IR data suggest the presence of K-feldspar and quartz, and the CRISM data suggest Ca/Fe-rich plagioclase (and the near infrared is not sensitive to quartz or K-feldspar).

A complication arises, however, in considering the effects of alteration on igneous interpretations of infrared data. CRISM-based near infrared observations of the THEMIS granitoid-type rocks show that they contain a suite of alteration phases such as amorphous silica and Al-rich clay minerals (Smith & Bandfield, 2012). These observations differ from the infrared signature of weathered, natural surfaces of granitic rocks on Earth (Michalski et al., 2004) and are instead suggestive of hydrothermal or diagenetic processes. The Martian granitoid-type rocks are also layered, which suggests they might be altered ash deposits. These rock compositions might indicate K-enrichment in the form of secondary feldspar and Al-clays such as illite or muscovite.

In the same ancient terrain where the granitoid-type compositions occur, CRISM data have revealed the presence of K-rich phyllosilicates such as illite or muscovite (the two are not readily distinguishable with CRISM data) in rocks exhumed from the subsurface by impact craters (Ehlmann et al., 2009). The mineralogy and geologic context of these rocks points to the origin of K-rich rocks in some cases by diagenetic and hydrothermal processes (Ehlmann et al., 2011). It bears noting here that the anorthite-rich rocks detected elsewhere on Mars using CRISM data also contain spectral absorptions near 2.2 μm indicating the likely presence of Al-phyllosilicates in many of those deposits (Carter & Poulet, 2013; Wray et al., 2013).

Surface operations by the Curiosity Rover have shown K-enrichments within multiple rock types in Gale Crater. Measurements by the Alpha Particle X-ray Spectrometer (APXS) and Chemistry Camera (ChemCam) and Mast Camera (Mastcam) show that some large boulders with plutonic textures (e.g., plagioclase laths) have elevated K-content (Figure 1d). These rocks have been interpreted as evidence for distal “continental” type crustal units near the northern rim of Gale Crater, to the north of the landing site (Sautter et al., 2015). Some sedimentary units Gale Crater represent the most K-rich rocks identified on Mars to date (Le Deit et al., 2016; Thompson et al., 2016). Chemical associations in the analyses published to date suggest that the K resides in detrital K-feldspar such as sanidine or orthoclase, rather than secondary minerals such as illite (Treiman et al., 2016).

Although the surface of Mars appears to be generally K-poor from a GRS perspective, regional and local remote sensing and rover results demonstrate that potassic sedimentary and igneous rocks are part of the Martian geological puzzle. One possible explanation is that igneous evolution has produced K-rich rocks through fractional crystallization of magmas from a mantle that is K-rich compared to that of Earth (Stolper et al., 2013). Another possibility is that local or regional-scale K-metasomatism has occurred on Mars, causing K-enrichment in igneous rocks by low-temperature brines at the surface or in the subsurface. This study explores the second hypothesis, K-metasomatism, through investigation of a case of brine alteration of mafic volcanic rocks that occurred in western Arizona, USA.
2. A Terrestrial Analog for K-Metasomatism of Basalt on Mars

During the Miocene, tectonically controlled, arid basins existed throughout the southwestern USA (Spencer et al., 1995). Saline lakes formed in arid tectonic basins. Downwelling and laterally migrating low-temperature hydrothermal brine in the subsurface produced widespread K-metasomatism of volcanic rocks throughout the region (Chapin & Lindley, 1985; Ennis et al., 2000). An unusual and interesting aspect of K-metasomatism is that it is only recognizable from chemical measurements, typically in a laboratory setting. Rock textures and color are often completely preserved, despite significant changes in geochemistry.

In the Buckskin Mountains in western Arizona, Miocene basalt, tuff and volcaniclastic breccias have been K-metasomatized. Previous work focused on the mineralogy and geochemistry of these rocks in the Swansea area of western Arizona with regard to geologic history and economic geology (Michalski et al., 2007). Those results show that the metasomatized basalts have K$_2$O abundances 5.4–11.8% and K/Na ratios of 104–526. The altered pyroclastics have K$_2$O values of 8.8–9.4% and K/Na ratios of 31–44. XRD results show that the original mineralogy of the volcanic rocks has been completely changed to a simple assemblage of K-feldspar, illite and minor hematite and quartz (Michalski et al., 2007). An atypical aspect of the alteration at Swansea is that the early phase of K-metasomatism was followed by a subsequent phase of carbonation, which unlike the K-metasomatism, did disrupt the volcanic textures. Though the carbonate replacements at Swansea have no direct link to K-enrichment, this character of the rocks is also of interest for better understanding carbonated rocks exhumed from Martian subsurface (Michalski & Niles, 2010; Wray et al., 2016). This study applies new remote sensing and spectroscopic data of K-metasomatized rocks from Swansea in order to better understand remote sensing of K-feldspar and illite-bearing terrains on Mars, and K-enrichments detected geochemically within Gale Crater.

3. Laboratory Spectroscopy of Metasomatized Volcanic Rocks

Micro-infrared spectroscopic mapping was carried out in the Planetary Spectroscopy and Mineralogy Laboratory (PSML) at the University of Hong Kong. Reflectance spectra were collected from 650 to 4,000 cm$^{-1}$ on a Nicolet Continuum Infrared microscope with 8 cm$^{-1}$ spectral sampling, using a gold reference standard. Using a 30 μm step size (spatial sampling) and 8 scan integration, hyperspectral maps of $\sim 8 \times 8$ mm areas of polished thin sections were collected over $\sim 20$ h with a nitrogen-cooled mercury cadmium telluride detector. Figure 2a shows a field photo of the outcrop of altered basalt in the Swansea area (34.16°N, 113.87°W), and micro-infrared reflectance images of basalt and pyroclastic materials.

Blue areas in Figure 2b correspond to carbonate replacements that are younger than the K-metasomatism. The orange-yellow silicate pattern in Figure 2b reflects the original volcanic texture of the rock. Here, the original 100–300 μm-long plagioclase laths (yellow) are observed within an orange groundmass of what was previously glass, amphibole and pyroxene. However, extracted infrared spectra from each of these phases shows that the plagioclase has been entirely converted to K-feldspar and the ferromagesian phases have been entirely replaced by illite. Later carbonate replacements are nearly pure calcite with accessory hematite.

The brecciated pyroclastic unit shows similar, but not identical patterns. Fragments of basaltic ash have been replaced by K-feldspar and illite (Figures 2d and 2e). The altered basalt is physically mixed with fragmented quartz and carbonate. Note that hematite has no spectral features in this part of the thermal infra-red spectral range and cannot be detected or mapped uniquely.

Visible/near-infrared reflectance spectra of rock powders and chips were acquired at the PSML from 550 to 2,500 nm using a Spectralon reflectance standard by integrating 60 scans over a period of $\sim 1$ min from a spot size of $\sim 3$ mm$^2$ in a Praying Mantis diffuse reflectance chamber attached to a Nicolet iS50 interferometer. Figure 3 shows reflectance spectra of a natural surface of altered basalt as well as the same unit powdered to $<2$ μm. Note that the rock chip shows a strong blue-slope, but also exhibits OH and HOH absorptions at $\sim 1,410$ and $\sim 1,910$ nm, respectively. These features and an Al-OH absorption at 2,214 nm trace the occurrence of illite clay. However, typical illite (shown in green in Figure 3a) is relatively Fe-poor and the illite in the altered basalt from Swansea contains 4–5 times more Fe (Michalski et al., 2007). A strong,
Figure 2. A field photo of altered basalt in the Swansea, Arizona area is shown in (a). Micro-infrared reflectance maps of thin sections are shown for metasomatized basalt (b) and metasomatized ash (c). The corresponding emittance spectra of each image are shown below, (d) shows emittance spectra (1-reflectance) of spectra from the metasomatized basalt and (e) shows emittance spectra from the metasomatized ash. The spot size of each spectrum is approximately 30 micrometers across. Colors of spectra in (c and e) correspond to colors observed in the corresponding images above each plot. Emittance spectra are measured reflectance converted using Kirchoff’s Law (1-reflectance) top emissivity.
broad absorption between 1,000 and 2,000 nm in Swansea illite indicates that Fe$^{2+}$ occurs in 6-coordinated octahedral sites (Chemtob et al., 2015).

Thermal infrared emission spectra were collected from 200 to 2,000 cm$^{-1}$ at the Arizona State University Mars Space Flight Facility using procedures described previously (Ruff et al., 1997). Both basalt whole-rock samples and 1 cm-diameter pellets composed of the <2 μm (clay-size) fraction were measured (Figure 3b). The whole rock samples contain spectral absorptions at ∼1,160, 1,060, 640, and 460 cm$^{-1}$ indicative of K-feldspar and absorptions at 460, 540, and 1,065 cm$^{-1}$ indicative of illite. Note that the Si-O-metal absorption in illite is shifted to longer wavenumber in this illite compared to the IMt-1 standard because of the substitution of larger Fe$^{2+}$ for Al$^{3+}$ in the octahedral sheet, creating longer bond distances and lower frequency vibrations (Michalski et al., 2006).


High spatial resolution multispectral remote sensing analysis was carried out using data from the Worldview-3 (WV3) satellite. WV3 provides panchromatic data at ∼30 cm/pixel spatial resolution, 8 spectral channels in the visible-near infrared (VNIR; ∼400–1,000 nm) range at ∼1.2 m/pixel, and 8 spectral channels in the short wave infrared (SWIR; ∼1,200–2,400 nm) at 3.7 m/pixel (see supplementary material for details). Data were obtained from the vendor (Satellite Imaging Corporation) in calibrated, geo-rectified format. No atmospheric corrections were applied to any of the wavelengths because such corrections are not necessary for the VNIR range and because only band ratios and relative spectral index measurements were used for the SWIR data (e.g., Mars, 2018).

VNIR data displayed in near true color show colorful sedimentary, volcanic, and plutonic rocks within a shallow SW-NE trending valley in the Swansea area (Figure 4a). In fact, the valley is a shallow synform bounded by similarly trending mylonitic crystalline rock to the north and south. All of the sedimentary, volcanic and plutonic rocks in the valley represent the upper plate of the Buckskin-Rawhide detachment fault (BRDF), which has significant extension in the Miocene.

A SWIR principal components analysis (PCA) image emphasizes compositional differences among units. Principle components 4, 3, and 2 are displayed as R, G, and B, respectively (Figure 4b). The geological units (defined by white dotted lines) shown in Figure 4b are based on mapping carried out by Spencer and Reynolds 1986 but simplified here for clarity. The most important units to note are units “MB,” which is the K-metasomatized basalt, “MBa,” which is alluvium derived from erosion of unit MB, and “MBb,” which is metasomatized basaltic breccia. Other units include: “mc” is mylonitic crystalline basement rock; “XTi” is Jurassic-Tertiary intrusive meta-granite, “MPs” corresponds to Mesozoic and Paleozoic metasediments, mostly dolostone-marble with some sandstone; “Tb” is the lower breccia unit; In panel “d,” the MBa unit derived from erosion of the metasomatized bedrock is marked by arrows.

A band ratio of WV3 SWIR data was used to delineate and map clay minerals according to the following formula: $(R_{2260}/R_{2205}) * (R_{2165}/R_{1730})$ where the subscript corresponds to the wavelength position in nm of WV3 bands 4, 5, 6, and 7 (Figure 4c). This spectral index measures the occurrence of the Al-OH absorption in the numerator and the presence of an Fe$^{2+}$-related spectral slope in the denominator, resulting in high values for surfaces that have both of those features. The spectral index map illustrates how illite is associated with the occurrence of unit MB (metasomatized basalt) and MBb (metasomatized basaltic breccia).
Furthermore, the sediments derived from these two units (MBa), which are transported toward the north and northeast, carry the spectral signature of the alteration as detected by remote sensing instruments.

Thermal infrared emissivity data from the Advanced Spaceborne Thermal Emission and Reflectance Radiometer (ASTER) show a different perspective on the K-metasomatized rocks. ASTER emissivity data were obtained as atmospherically corrected, calibrated emissivity. Figure 5 shows a false color (pan-sharpened) emissivity image of the Buckskin Mountains and the extracted emission spectrum of the metasomatized basalt unit. At multispectral resolution (5 bands, in the case of ASTER), the spectral shape of K-metasomatized basalt is strikingly similar to alkali granite measured in the laboratory (Guha & Vinod Kumar, 2016).

Figure 4. Worldview VNIR color data (bands 5,3,2 as RGB) of the Swansea, Arizona area (113.9 W, 34.2 N) are shown in (a). Worldview 3 SWIR PCA image where PCA bands 4,3,2 are displayed as RGB are shown in (b). The WV3 clay index (5 over 6 over 7) are shown in (c). Panchromatic WV data are shown in (d), illustrating the exposure of bedrock and sediments derived from the bedrock.
THEMIS emissivity extracted from granitoid-type compositions on Mars (Bandfield, 2006) are compared to the ASTER emissivity data of K-metasomatized basalt and lab spectra of igneous rocks in Figure 5. At multispectral resolution, K-feldspar-rich, illite-bearing K-metasomatized volcanic rocks are similar to granitoid-type compositions detected on Mars. Metasomatic alteration by low-temperature hydrothermal brines could be a viable mechanism to produce feldspar-rich, clay-bearing rocks detected on Mars by infrared techniques (Figure 5).

5. Summary and Conclusions for Mars

Swansea, Arizona contains a striking example of K-metasomatized volcanic rocks, but the processes that operated in that area are not geologically uncommon. Rift basins (Roddy et al., 1988), calderas (Nusbaum & Grant, 1987), seafloor sediments (Rouchon & Orberger, 2008) and paleosols (Novoselov & de Souza Filho, 2015) all display evidence for K-metasomatism. A similar process would likely have operated on Mars as well given that surface and shallow subsurface has at times likely contained abundant reactive, glassy rocks (Bandfield et al., 2013; Horgan & Bell, 2012) to liberate cations, concentrated, mobile brines to transport those cations (Knauth & Burt, 2002), and reactive rocks susceptible to metasomatism (see supporting information). Gradual extraction of cations from the fluid including Mg$^{2+}$, Ca$^{2+}$ during crystallization of sulfates or carbonates in the crust would further serve to concentrate K$^+$. But even if Na$^+$ is more abundant than K$^+$ in a hydrothermal fluid, K-feldspar can form because it is more stable in low-temperature hydrothermal conditions (Chapin & Lindley, 1985).

This study describes chemical, spectroscopic and remote sensing signatures of K-metasomatized rocks on Earth, providing insight into their potential signatures on Mars. Multispectral thermal infrared remote sensing shows that K-metasomatized basalts have similar spectral character to granite and alkali granite. The K-rich clay illite is generally common in K-metasomatism and Fe-bearing illite is a key component of the alteration assemblage at Swansea. The spectroscopic and remote sensing signatures of K-metasomatism demonstrated at Swansea are in many ways similar to infrared observations of Mars showing granitoid-like,

**Figure 5.** An ASTER pan-sharpened emissivity image is shown in (a). The extracted emissivity spectrum of the K-metasomatized basalt unit is shown in (b) (labeled “Swansea”). A THEMIS emissivity spectrum of the granitoid-type materials from Bandfield (2006) is shown in green. Note this spectrum corresponds to the material in Figures 1b and 1c. The remote sensing spectra are compared to laboratory spectra of granite (Michalski et al., 2004), alkali granite and basalt resampled to ASTER spectral resolution. A THEMIS spectrum of Martian basalt is shown for comparison (yellow).
Al-clay-bearing rocks in the Noachian Crust (Figure 1) or illite-bearing crust exhumed by meteor impact. Given that the granitoid-type compositions actually correspond to layered rocks (Figure 1b), we propose that these materials might represent mafic volcanic materials (e.g., pyroclastics) that have been metasomatized by crustal fluids.

K-enrichment detected chemically at Gale Crater is more complicated. The sedimentary rocks containing the K-rich clasts have likely not been metasomatized because those rocks contain abundant Ca, Na, and Mg, all of which are strongly depleted by K-metasomatism. But, the K-enrichment at Gale Crater likely reflects detrital K-feldspar in the rocks. It is therefore unknown if the K-feldspar was eroded from a felsic volcanic or granitic protolith, though in cases where sanidine is the carrier of K, primary volcanic processes should be expected. The occurrence of K-feldspars such as microcline and orthoclase, be they in igneous rocks or as detritus in sedimentary rocks could have ultimately formed in hydrothermal settings in mafic volcanic terrain on Mars and are not necessarily indicators of felsic crust.

Data Availability Statement

JMARS software used in this study is available through Arizona State University at https://jmars.asu.edu/. Mars remote sensing data are all available through the Planetary Data System. All data used in this study are available in the NASA Planetary Data System (pds.jpl.nasa.gov). Mars Odyssey Gamma Ray Spectrometer data are available at https://pds-geosciences.wustl.edu/missions/odyssey/grs.html. Mars Odyssey THEMIS data are available at: https://pds-geosciences.wustl.edu/missions/odyssey/themis.html. Mars Curiosity Rover Mastcam data are available at: https://pds-geosciences.wustl.edu/missions/msl/. Worldview 3 remote sensing data are available at: https://zenodo.org/record/4643735#.YGGlHeYRVp8. Micro-infrared data are available at: https://zenodo.org/record/4643764#.YGGlBuYRVp8. ASTER data are available at: https://search.earthdata.nasa.gov/search.

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