

LETTER

Meridianiite: A new mineral species observed on Earth and predicted to exist on Mars

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ABSTRACT

Meridianiite, $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$, was recently discovered on the surface of a frozen pond in central British Columbia, Canada. Meridianiite is stable below 2 °C. Above 2 °C, it melts incongruently to a slurry of epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and water. Magnesium sulfate minerals are thought to exist in the soils at Gusev crater and elsewhere on the Martian surface. These minerals can form by precipitation from a saturated solution or through evaporation of a brine solution at or below the surface. Meridianiite, instead of epsomite, is the expected magnesium sulfate phase in equilibrium with saturated brines below 2 °C on or below the Martian surface. It is expected to be the magnesium sulfate mineral in equilibrium with ice in the Martian polar ice caps. Meridianiite, if exposed to low humidity conditions in equatorial regions of Mars, would ultimately dehydrate to a fine dust of kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) that could be dispersed by wind across the Martian surface. The name, meridianiite, was chosen to reflect the locality on Mars where the MER rover Opportunity observed crystal molds in sedimentary rock that are thought to be caused by minerals that have since dehydrated or dissolved.

Keywords: Mars, epsomite, new mineral, sulfate, hydrated magnesium sulfate, meridianiite, kieserite

INTRODUCTION

Hydrated magnesium sulfates in various forms likely exist throughout the solar system on planets, moons and asteroids. Carbonaceous (C1) chondrites contain up to 20% by weight of soluble salts of various degrees of hydration (Kargel 1991; Fortes 2005). $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$ may exist on and below the surface of the Jovian moons Europa and Ganymede. It has been suggested that features observed on their surfaces are a result of hypersaline brine volcanism and plate tectonics (Gregg and Lopes 2004) that are driven by the density differences and melting points of various minerals in the Mg-Na-K-SO₄-Cl-H₂O system. These minerals could include meridianiite ($\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$), epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), water ice, frozen CO₂, mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), and natron ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$).

DATA, IMAGES, AND ANALYSIS

The Mars Exploration Rovers (MER) Spirit and Opportunity have been returning spectroscopic and photographic data of the regolith at Gusev Crater and Meridiani Planum, respectively. Observations obtained by using the rover wheels to dig trenches into the Martian soil indicate that magnesium sulfate minerals, with minor calcium sulfates and possibly iron sulfates have been deposited in the subsurface regolith at Gusev crater (Wang et al. 2006). Based on spectroscopic measurements (Arvidson et al. 2005), the magnesium sulfate is thought to exist as kieserite

($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) as well as starkeyite ($\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$), hexahydrate ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$), and epsomite. The most probable model for the formation of these sulfates involves saturated sulfate solutions as either a periodic fluid infiltration and precipitation or as an open hydrologic system where sulfates precipitate through ion transport in a fluid and precipitation resulting from evaporation and the resulting super saturation of the fluid. Evidence from sedimentary textures support the presence of solutions on the surface of Mars in the past (Hynek 2004; Squyres et al. 2004). The temperature of the Martian surface varies widely with latitude and season. In the polar regions, the temperatures may be as low as -140 °C in winter and in equatorial regions in summer as high as 25 °C. Across wide regions of Mars the temperature is below 0 °C and the magnesium sulfate phase in equilibrium with a saturated brine solution or ice at these temperatures is meridianiite ($\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$).

Images of euhedral molds in rock, obtained by the MER Opportunity, are interpreted as being the result of dissolution of soluble crystals (Squyres et al. 2004; Herkenhoff et al. 2004). The substance that left these molds in the rock after dissolving has been suggested to be gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or ice (Wdowiak 2007). These molds may also have formed through the dissolution of meridianiite, based on the observed magnesium-rich chemical composition of the soils (Wang et al. 2006) and the similar shape of the molds to the crystal forms exhibited by synthetic $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$ (Peterson and Wang 2006). Furthermore, MgSO_4 saturated solutions may persist in the polar regions of Mars in equilibrium with ice and provide ideal conditions for

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the existence of meridianiite.

$\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$ was originally described (Fritzsche 1837) as $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$ and became known as Fritzsche's salt. The original synthesis was done out of doors in 1837 and the number of water molecules was determined by weight loss on dehydration. More recently, the crystal structure of $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$, was solved indicating 11 waters of hydration and triclinic symmetry (Peterson and Wang 2006).

There are places on the surface of the Earth where meridianiite could occur. Figure 1 presents the phase diagram for the $\text{MgSO}_4\text{-H}_2\text{O}$ system at 1 atm pressure as a function of temperature. For meridianiite to form, the solutions must be saturated with respect to magnesium sulfate and at a temperature below 2 °C. Chipera et al. (2007) show that meridianiite forms quite readily from simple freezing of Mg-sulfate brine solution to form a mixture of meridianiite and ice. Meridianiite also exists in brine inclusions in the Antarctic ice cap (Ohno et al. 2005; F.C. Genceli, pers. comm.). Once formed, meridianiite is stable with ice. There are numerous evaporite settings on the surface of the Earth where epsomite is observed to form. Epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) forms in limestone caves, in salt lakes and playas with mirabilite and as an efflorescence on dolomitic or calcareous rocks. If the temperature of formation is below 2 °C meridianiite will form instead of epsomite. Near Ashcroft, British Columbia, Canada (N50° 36.039/W121° 21.530), a series of small ponds were mined for 600 tonnes of MgSO_4 between 1919 and 1972. These ponds, known as the Basque claims, occur in a small valley in the Thompson region of central British Columbia. The climate is hot and dry in summer and is cold in winter with little precipitation. The ponds have been studied as an analog of Martian conditions on Earth (Hyde et al. 2007). The average January temperature is -4 °C with a relative humidity of 77% (Statistics Canada over the period 1961 to 1990). In January of 2007, the ponds were frozen with a 20 cm thick layer of ice. The solution under the ice was -2 °C, dark brown in color, and smelled strongly of sulfur. It was hoped that the pond had frozen

sufficiently to concentrate the remaining solution, under the ice, to the point where $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$ would precipitate, according to the phase diagram for the $\text{MgSO}_4\text{-H}_2\text{O}$ system (Fig. 1). A solution temperature of -4 °C would indicate a binary eutectic condition with ice, meridianiite, and solution in equilibrium. The composition of the solution and the observed temperature of -2 °C indicated that $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$ would not be in equilibrium with the pond solution. However, protruding through the ice was a tree trunk that was inclined from vertical (Fig. 2). On the underside was a deposit of white precipitate that adhered to the bark and wood. Around the base of the trunk where it entered the ice was an area where solution had existed even though a layer of ice had formed on the pond. This aureole of solution around the trunk provided a channel for solution from the pond to migrate up the surface of the trunk through capillary action where it evaporated and deposited meridianiite. The freezing point of -4 °C, or lower due to the presence of additional dissolved salts, allowed evaporation and crystallization to continue at temperatures well below the freezing point of water. The white granular material was collected at -2 °C and placed in an insulated cooler containing dry ice for transport back to the laboratory for analysis.

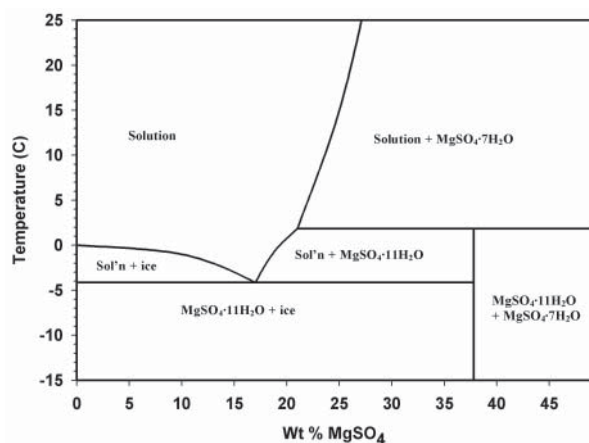


FIGURE 1. Phase diagram for the $\text{MgSO}_4\text{-H}_2\text{O}$ system (Peterson and Wang 2006). $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$ melts incongruently to epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and a saturated solution at 2 °C (275 K) in this binary system. Below 2 °C meridianiite is in equilibrium with a saturated magnesium sulfate solution or ice.



FIGURE 2. Meridianiite on the underside of a post in a frozen pond in central British Columbia, Canada. The white material on the upper side of the post is snow. Meridianiite is the material that formed by crystallization from a solution that was drawn up from the pond through capillary action in the bark on the post. A mixture of meridianiite and bark can be seen on the underside of the post. The temperature at the time of collection was -1.5 °C and a relative humidity of 50%.

The samples were stored in sealed containers in a chest freezer at $-15\text{ }^{\circ}\text{C}$. Samples were prepared for the X-ray diffraction experiment by grinding in a mortar and pestle in a cold environment at $-12\text{ }^{\circ}\text{C}$ and placing the powder on a zero-background silicon plate in an Anton Parr environmental cell, which was also at $-12\text{ }^{\circ}\text{C}$. The environmental cell was placed into a cooler with dry ice and taken into the X-ray diffraction laboratory. The cell was quickly placed onto a Panalytical X'pert Pro diffractometer and a powder diffraction measurement was made using $\text{CoK}\alpha$ (Fe filtered) radiation. The Anton Parr chamber is sufficiently massive that the temperature inside, at the sample holder, rises quite slowly even if the chamber is surrounded by the $20\text{ }^{\circ}\text{C}$ atmosphere of the diffractometer hutch. A thermocouple at the sample indicated that during the experiment the temperature eventually rose to $-1\text{ }^{\circ}\text{C}$. Figure 3 shows a portion of the diffraction data. A broad peak at $8\text{ }^{\circ}2\theta$ indicates an amorphous component in this material and also in addition to meridianiite, the original sample contained epsomite. The powder diffraction data collected below $-1\text{ }^{\circ}\text{C}$ were refined by the Rietveld method and the cell dimensions obtained are close to those obtained for synthetic $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$ (Table 1). A second diffraction experiment was made after the sample had warmed above $2\text{ }^{\circ}\text{C}$ and the sample had incongruently melted to a mixture of epsomite and solution.

Some material contained single crystals and these were im-

TABLE 1. Chemical analysis of pond water and dissolved solid (mg/L)

	Natural, X-ray, 267 K, Present study	Synthetic, X-ray, 200 K, Peterson and Wang (2006)	Synthetic, neutron, 250 K, Fortes et al. in review
a (Å)	6.7459	6.7322(6)	6.75097(5)
b (Å)	6.8173	6.7915(7)	6.81440(6)
c (Å)	17.280	17.293(2)	17.2923(2)
α (°)	88.137	88.220(2)	88.122(1)
β (°)	89.481	89.494(2)	89.483(1)
γ (°)	62.719	62.664(2)	62.694(1)

Note: "solid" was obtained by dissolving 6 g of solid in 200 mL of de-ionized water.

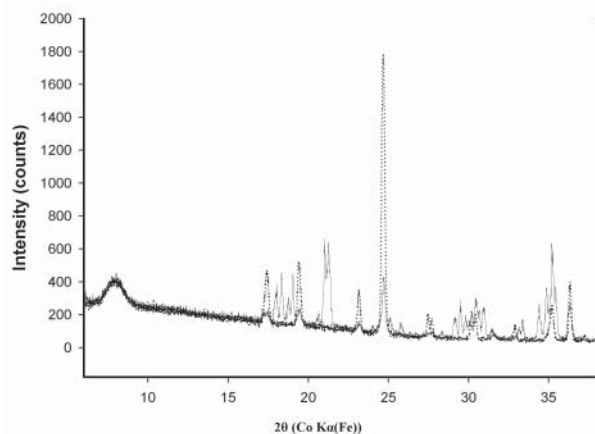


FIGURE 3. The X-ray powder diffraction patterns (Fe filtered $\text{CoK}\alpha$) of the sample collected below $-1.0\text{ }^{\circ}\text{C}$ (solid line) and above $5\text{ }^{\circ}\text{C}$ (dashed). Below $-1.0\text{ }^{\circ}\text{C}$, the sample consists of meridianiite, some epsomite, and an amorphous phase that creates a broad peak at $8\text{ }^{\circ}2\theta$. Above $5\text{ }^{\circ}\text{C}$, the sample has melted incongruently to epsomite and solution.

mersed in refractive index oil. The refractive indices, measured at $-6\text{ }^{\circ}\text{C}$ using the Becke line technique, were observed to fall between 1.418 and 1.448. The refractive indices of the oils were determined using an Abbe refractometer at the same temperature. Meridianiite has been approved as a valid mineral species by the Commission on New Mineral Names and Mineral Nomenclature of the International Mineralogical Association (2007-11, Peterson and Genceli). The full submission to the IMA commission including powder diffraction data, chemical analysis and physical properties has been deposited. The holotype material is deposited in the Canadian Museum of Nature. A complete description of the atomic structure of meridianiite was completed in 2006 (Peterson and Wang 2006).

The chemical composition of the water obtained from the pond and the composition of a fluid obtained by dissolving the solid in de-ionized water are presented in Table 2. There is significant Na in both the pond solution and the dissolved solid solution. The Na measured in the solid is a result of an amorphous sodium sulfate mixed with meridianiite. This material likely formed originally as mirabilite, which subsequently dehydrated to an amorphous phase in the dry cold mountain environment. X-ray diffraction data show peaks due to thenardite (Na_2SO_4) in a few samples. Some samples exhibit a green yellow fluorescence under long wavelength ultraviolet light that is characteristic of thenardite. The epsomite and thenardite are the phases that result if a sample of the bulk natural material melts incongruently above $2\text{ }^{\circ}\text{C}$ and then evaporates and crystallizes at $20\text{ }^{\circ}\text{C}$. The lack of mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) with meridianiite at the Basque pond suggests it is stable only at a higher relative humidity and has dehydrated to amorphous sodium sulfate. Work is in progress to study the relative humidity and temperatures where meridianiite and mirabilite are stable.

Infrared transmission spectra of $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$ were recorded below and above the transition temperature ($+2\text{ }^{\circ}\text{C}$). Two sampling methods were used. One consisted of suspending powdered sample material between two 25 mm diameter CsI windows. The second involved mulling the powdered sample with mineral oil and suspending the mull between the CsI windows. All apparatus was pre-cooled before sample preparation commenced. The cold sample material was finely ground in a cooled agate mortar. The prepared sample was maintained at a low temperature using a glass cell equipped with external CsI windows and an inner cold finger containing cold snow. The sample windows were held in a copper block at the end of the cold finger. The cold finger was inserted into the outer part of the cell and the cell evacuated. Infrared spectra were recorded using a Nicolet Avatar 320 spectrometer. The resolution was 4 cm^{-1} and 32 scans were collected for each spectrum. The mulling technique proved to be the better of the two sampling methods (Fig. 4). In the spectrum of $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$ (trace A of Fig. 4b), fine structure is observed on the sulfate band centered near 1100 cm^{-1} .

TABLE 2. Comparison of unit-cell dimensions of $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$

Sample	water	solid
Ca	354	172
K	269	84.3
Mg	14400	23400
Na	4390	7620
S	20900	37000
Sr	8.8	3.7

Three components are observed: two sharp peaks at 1148 and 1079 cm^{-1} and a shoulder at 1102 cm^{-1} . This may be attributed to "crystal splitting." The band in

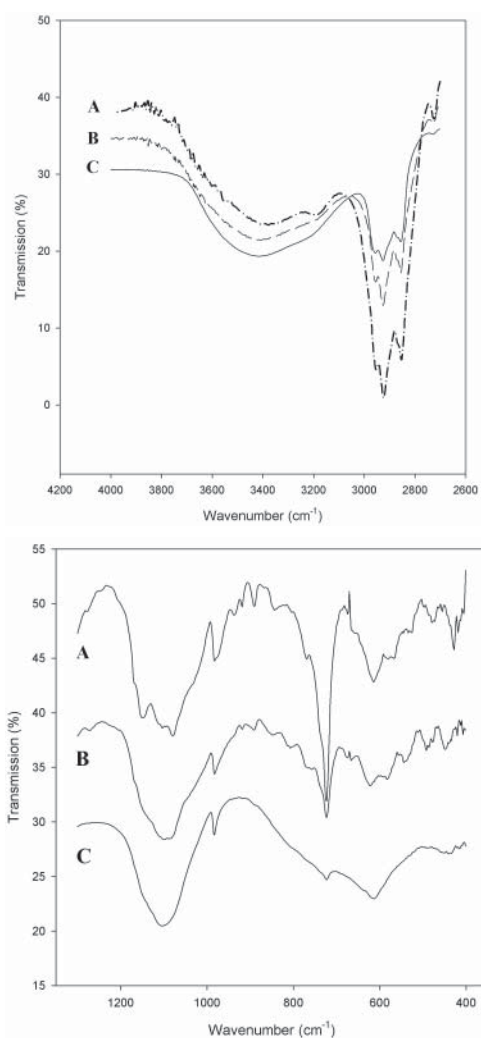


FIGURE 4. Infrared absorption of meridianiite. Trace A was obtained below 0 °C, trace B was recorded after the sample was warmed and had incongruently melted to epsomite and solution, and trace C was recorded from a mixture containing epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) with paraffin oil and a small amount of water prepared to simulate the product of the transition from $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$ to $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} + 4\text{H}_2\text{O}$. As the sample was warmed, changes were observed in both the water band centered near 3400 cm^{-1} , and the sulfate band centered at 1100 cm^{-1} . In both regions, the new bands of trace B resemble those observed in the spectrum of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ with a small amount of water added (trace C).

question is due to the degenerate (antisymmetric) SO_4^{2-} stretching vibration. The degeneracy is removed by the lower symmetry experienced by the SO_4^{2-} ion in the crystalline structure. This gives rise to a splitting of the band. Additional splitting can result from interaction between more than one sulfate ion in the unit cell. When the temperature is raised, meridianiite decomposes to give a slurry of epsomite and water and the sulfate band loses its fine structure (trace B of Fig. 4b).

CONCLUDING REMARKS

Meridianiite is a valid mineral species on the surface of the Earth and is found where, at temperatures below 2 °C, solutions

rich in magnesium sulfate evaporate and form supersaturated solutions or where magnesium sulfate-rich solutions freeze to a solid. Meridianiite is a likely sulfate mineral species on the surface of Mars in mid to high latitude regions in equilibrium with ice. Meridianiite would dehydrate if exposed to the current low humidity conditions of the equatorial regions of Mars. The resulting kieserite would be fine grained and could be easily dispersed by wind across the Martian surface.

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