

WHAT LURKS IN THE MARTIAN ROCKS AND SOIL? INVESTIGATIONS OF SULFATES, PHOSPHATES, AND PERCHLORATES Gypsum in modern Kamchatka volcanic hot springs and the Lower Cambrian black shale: Applied to the microbial-mediated precipitation of sulfates on Mars†‡

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ABSTRACT

Gypsum is a mineral that commonly precipitates in hydrothermal environments. This study reports the electron microscopic analyses of gypsum morphologies and crystal sizes found in hot springs on the Kamchatka Peninsula, Russia, and compares these analyses with gypsum morphologies of hydrothermal genesis found in Lower Cambrian black shale. In sediments of the Kamchatka hot springs, we observed prismatic, prismatic pseudo-hexagonal, fibrous, tubular, lenticular and twinned gypsum crystals, with crystal sizes ranging from <200 nm to >200 μm. The coexistence of diverse crystal habits of gypsum implies a constant interaction between hot spring geochemistry and the metabolisms of the microbial community. The crystallization of Ca- and Ba-sulfates in the black shale of the Lower Cambrian, which shows similar but less varied morphology, was influenced by post-depositional hydrothermal fluids. The partial replacement of pyrite by sulfates in a situation coexisting with rich biomass deposits and animal fossils indicates limited modification of the sedimentary records by biological materials. If the gypsum precipitated on Mars underwent similar interactions between microbial communities and their geochemical environments, the resulting crystal habits could be preserved even better than those on Earth due to the weak geodynamics prevailing on Mars throughout its evolutionary history.

Keywords: Kamchatka, volcanic hot spring, Lower Cambrian, geothermal system, gypsum, Mars

INTRODUCTION

Gypsum shows very little variation in its chemical composition (Deer et al. 1992), but a lot of variation in its crystal habits (Jafarzadeh and Burnham 1992; Buck and Van Hoesen 2002). This mineral may precipitate with diverse morphologies in aqueous environments such as lakes, seawater, hot springs, or geothermal fluids with high concentrations of Ca²⁺ and SO₄²⁻. Micro-environmental factors such as pH, temperature, or the presence of microbial communities can influence the crystallization of gypsum and result in varied crystal habits (Cody and Cody 1988a; Thompson and Ferris 1990; Jafarzadeh and Burnham 1992; Allwood et al. 2013).

According to photographs obtained by orbital missions around Mars, a pre-Viking assessment was made on the potential for habitable conditions and organic life on the planet (Sagan and Lederberg 1976). Since the successful landing of Viking 1 on Mars in 1976, mankind began to search for life on the planet's surface. A series of instruments was placed on two Viking Mars Landers that provided preliminary data on the basic geochemical, mineralogical, and biological characteristics of Mars (Klein et al. 1976; Baird et al. 1976, 1977; Farmer et al. 1977; Toulmin et al. 1977; Klein 1978). More recently, this exploration has

turned to a search for mineral records of geochemical processes mediated by microorganisms (Wierzchos et al. 2011; Barbieri and Stivaletta 2012; Nixon et al. 2013; Arvidson et al. 2014). In 2004, the Mars Exploration Rover Spirit used a miniature thermal emission spectrometer (Mini-TES) to detect sulfates in the Gusev Crater on Mars (Squyres et al. 2004). In 2011, the Opportunity rover found a gypsum vein near the rim of the Endeavor Crater (Squyres et al. 2012). This vein forms a discontinuous ridge 1–1.5 cm wide and ~50 cm long, in which gypsum is the most abundant mineral (Squyres et al. 2012). As sulfate minerals can preserve co-deposited organic materials (e.g., amino acids) in geobiological environments, these minerals are considered prime targets in searching for organic compounds, or even endolithic life on Mars (Aubrey et al. 2006; Dong et al. 2007). Sulfates are also of particular interest for their roles as proxies for ancient environments on Mars (Parnell et al. 2004; Squyres et al. 2004; Borg and Drake 2005; Bibring et al. 2007; Morris et al. 2008; Murchie et al. 2009). Gypsum indicates the existence of water-rock interactions on Mars that might reveal a wet geochemical environment in its geological history (Borg and Drake 2005).

Various hypotheses have been suggested for the origin of the massive martian sulfate deposits. These hypotheses include evaporative deposition, hydrothermal alteration of volcanic rocks, sulfide oxidation in bedrock, or leaching of bedrock by volcanic vapors (Bibring et al. 2005; Langevin et al. 2005; Tanaka 2006; Fishbaugh et al. 2007; Squyres et al. 2007; Szyrkiewicz et al. 2010; Dehouck et al. 2012). As an important component in the biogeochemical sulfur cycle, gypsum can be the product

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of chemolithoautotrophic oxidization of reduced sulfur, or it may be reduced by sulfate-reducing bacteria through anaerobic respiration (Oschmann 2000). Understanding the genesis of gypsum in various terrestrial environments may provide essential modeling parameters for understanding similar mineral deposits that have been detected on Mars. Most geobiological investigations of terrestrial gypsum have focused on bulk depositions (e.g., Aubrey et al. 2006; Allwood et al. 2013), which provide suitable mineralogical and petrologic information for remote sensing techniques (Bibring et al. 2005; Langevin et al. 2005; Weitz et al. 2013). This approach, however, is insufficient when explorations for martian life turn to on-site inspections or sample-returns. The possibility of influence from microorganisms on the crystal habits of sulfates on Mars has not been investigated due to a lack of martian samples that could offer evidence for life.

Modern hot springs are considered similar to the environments in which life arose on Earth (Westall 2005). Gypsum is one of the most common minerals found in these hydrothermal springs. This mineral can precipitate with or without microbial mediation when metallic sulfide is oxidized along with the dissolution of calcium (Jones et al. 1998). As microbial mats in a hot spring may be suitable for the formation and aggregation of gypsum crystals (Bonny and Jones 2003), the various habits of gypsum crystal formation may be associated with distinct precipitation kinetics or micro-environment conditions. In such environments, microbial metabolisms can affect aquatic chemistry at the micro-scale, changing the pH levels, the concentrations of SO_4^{2-} and the amounts of organic matter, all of which can influence the morphology of gypsum crystals (Cody and Cody 1988a). Thus, under the influence of mixed biotic and abiotic factors, the deposition of gypsum preserves information on the ecophysiology of the microbial community. Opal, clay, and gypsum have been discussed as potential lines of evidence for detecting hydrothermal systems on Mars (Squyres et al. 2008; Ruff et al. 2011). The comparison between mineral records from ancient hydrothermal activity and modern hot springs that sustain microbial communities can provide a mineralogical database for high-resolution detection of life on Mars.

Sulfate is also one of the main components in ancient and modern seawater (Holland 1984; Brimblecombe 2003). Although oxygen in the atmosphere kept rising during the Lower Cambrian, which led to the further oxygenation of the ocean (Holland 2006), the large-scale degradation of organic matter could deplete oxygen and create anoxic environments in the upper sediments (Tourtelot 1979). Such environments favored the formation of black shale. The Lower Cambrian black shale of the Niutitang Formation in southwestern China formed in an organic-rich euxinic basin (Jiang et al. 2006, 2007) where sulfate was reduced by sulfate-reducing bacteria (Steiner et al. 2001; Meister et al. 2013). A hydrothermal model has been established through geochemical analysis (Jiang et al. 2006), which indicates that hydrothermal fluids induced gypsum precipitation during the diagenetic stage of the black shale.

In this study, we compared the crystal habits of gypsum in modern volcanic hot springs in Kamchatka, Russia, with those of gypsum crystals found in the Lower Cambrian black shale. We investigated the crystal habits of gypsum (e.g., size and morphology) formed in geothermal environments and the diverse

crystal habits of gypsum formed with microbial mediation. The findings may offer clues for understanding the mineral evidence of microbial life on Mars.

SAMPLES AND METHODS

Kamchatka hot springs

The Kamchatka Peninsula is located in the transition zone where the Eurasian plate, the North American plate, and the Pacific plate meet. This intersection of continental plates makes the Peninsula one of the most active volcanic and seismic regions in the world (Fig. 1a; Gorbатов et al. 1997). Kamchatka features about 31 active volcanoes and hundreds of monogenetic vents (Kozhurin et al. 2006). Hot springs and geothermal systems in the volcanic regions are sources of geothermal energy, sites for many kinds of metal resources, and habitats for diverse microorganisms (Zhao 2008; Kiryukhin et al. 2012). The Uzon Caldera (54°26'–54°31'N, 159°55'–160°07'E) is located in the central part of the East Kamchatka volcanic region. This caldera has highly active volcanoes that collectively contain hundreds of geothermal sites. Most of the sites are located along a main fault trending WNW and its subsidiary faults trending NNE (Karpov and Naboko 1990). The caldera formed during the collapse of Mount Uzon ~40000 years ago, and has a basement of Pliocene volcanic-sedimentary deposits (Kontorovich et al. 2011).

Five hot springs were chosen for this study (Fig. 1a), and their water chemistry records were compiled, as shown in Table 1. All of the five springs are characterized by high temperatures (42–87 °C), acidic to neutral pH (pH 4.4–7.0), and reduced electrochemical potential (Eh –240 to –90 mV) (Table 1). A mass of thermophilic anaerobes (e.g., sulfur-reducing bacteria such as *Thermoanaerobacter sulfurophilus*, sulfur-oxidizing bacteria such as *Sulfurihydrogenibium*, and sulfur-reducing archaea such as *Thermoproteus uzoniensis*) were isolated from the samples (Wagner and Wiegel 2008; Burgess 2009). The presence of these anaerobes indicated that the mineral deposits in these hot springs were built up in an environment influenced by both physicochemical and biological factors. The locations of the five hot springs and their basic physicochemical conditions are described as follows.

The Burlyashii Pool (54°29'58.79"N, 160°00'08.09"E) has a diameter of ~5 m, lies in a topographically low area of the basin, and has many vents. The pool's temperature varies from 51 to 87 °C, and the pH value of its fluids is around 6 (Goin and Cady 2009).

Thermophile Spring (54°29'55.18"N, 160°00'42.42"E) is ~1 m in diameter. The <74 °C vent pool drains into an outflow channel. The pH value changes from 4.4 in the center of the pool to 7 in the outflow channel (Goin and Cady 2009).

Zavarzin Pool (54°29'53"N, 160°00'52"E) is a 4.5 by 2.2 m pool located several hundred meters from Thermophile Spring. Numerous small vents feed the pool continuously with water at a temperature lower than 55 °C and a pH value of about 6.3 (Goin and Cady 2009). In the main pool, pH values range from 5.5 to 7.5 and the temperature varies from 54 to 74 °C.

Data on the Oil Pool's chemistry and location are lacking, but it is in the same area. Samples from Jen's Pool (54°30'2.01"N, 160°0'24.35"E) were collected from vents 1 and 2, which both discharge into Winding Stream, which then flows into Chloride Lake. The temperatures of both these vents are high (~80 °C), and they have acidic to neutral pH values (pH 5.3–6) (Kyle et al. 2007). Vent 1 is a sulfate-type spring, whereas vent 2 is a mixed sulfate-chloride-bicarbonate spring (Kyle 2005).

The Lower Cambrian black shale in the Niutitang Formation

We analyzed samples of black shale from the Niutitang Formation near Zunyi, Guizhou province, China (Fig. 1b). The Niutitang Formation black shale shows a SHRIMP U-Pb zircon age of 532.3 ± 0.7 Ma (Jiang et al. 2009). This shale deposit is composed of a few thin siliceous phosphorite layers that have a width of a few centimeters (Jiang et al. 2007), a polymetallic Ni-Mo-PGE-Au enriched layer (which varies from a few centimeters to 1–2 m in width) (Jiang et al. 2006), and some thick layers of black shale. The Niutitang Formation unconformably overlies the Dengying Group dolomite (551–542 Ma) (Condon et al. 2005; Chen et al. 2009). A wide diversity of fossils that mark the "Cambrian Explosion" are abundant in the black shale and its imbedded phosphorite layers (Steiner et al. 2007). Although the formation of the Ni-Mo-PGE-Au extremely enriched layer is still a matter of debate, mineralogical observations have identified an alteration of the black shale by geothermal fluids (Lott et al. 1999; Steiner et al. 2001; Mao et al. 2002; Coveney 2003; Lehmann et al. 2003; Jiang et al. 2006; Xu et al. 2013).

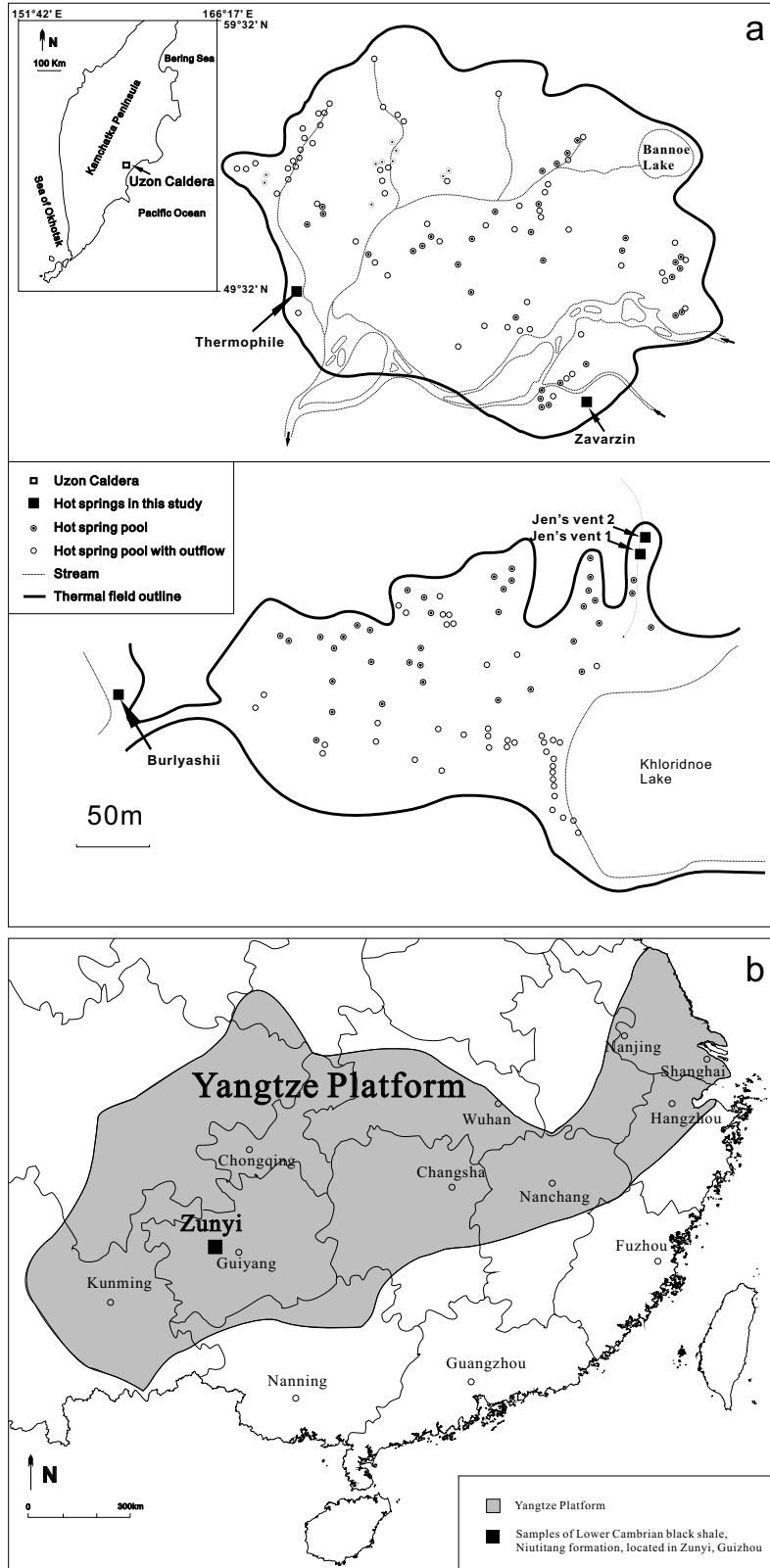


FIGURE 1. (a) Location of hot springs in Uzon Caldera, Kamchatka Peninsula (after Hollingsworth 2006; Zhao 2008). (b) Location of the Lower Cambrian black shale of the Niutitang Formation in Zunyi, Guizhou Province.

TABLE 1. Water chemistry of Kamchatka hot springs

	Burlyashii	Zavarzin	Thermophile	Jen's Vent 1	Jen's Vent 2
Temperature (°C)	51–87	54–74	42–70	83	85
Eh (mV)	–90	–96		–240	–240
pH	6–6.5	5.5–7.5	4.4–7	5.3–5.9	5.3–5.9
Alkalinity	1.18–1.23			2.2	0.16–0.18
Soluble Fe	3.75×10^{-3}			0.18×10^{-3}	0.54×10^{-3}
Ca	0.86	0.498	0.85	0.541	0.7
SO ₄ ²⁻	0.23–2.3	0.335–0.557	0.1–0.3	1.35–1.96	1.29–3.125
S ²⁻	$(6.3–43.8) \times 10^{-3}$		$(0.6–43.1) \times 10^{-3}$		
NO ₃		0.5		0.063	0.011
NO ₂	$(0.1–0.3) \times 10^{-3}$		$(0.2–0.6) \times 10^{-3}$	0.41×10^{-3}	0.54×10^{-3}
NH ₄ ⁺	1.1–1.5	0.84	0.2–4		
CH ₄	1.0	24×10^{-3}	0.18×10^{-3}		
H ₂	45×10^{-3}	6.47×10^{-3}	89×10^{-3}		
References	a	b	c	d	d

Notes: All concentration values are in mmol/L unless otherwise noted. Water chemistry data came from multiple references thus standard deviation values were not shown in the context. a: Goin and Cady (2009), Kochetkova et al. (2011), Zhao et al. (2011). b: Hollingsworth (2006), Burgess (2009), Goin and Cady (2009), Gumerov et al. (2011), Kochetkova et al. (2011). c: Hollingsworth (2006), Goin and Cady (2009), Zhao et al. (2011). d: Kyle (2005), Kyle et al. (2007).

Sampling and electron microscopic observations

As participants in the Kamchatka Microbial Observatory, researchers from the University of Georgia collected samples from the Kamchatka hot springs in sterilized bottles and stored them at 5 °C in the field (Zhao 2008). The samples were transported at low temperature with dry ice to the University of Hong Kong, and then stored at –20 °C until analysis. The samples were dried with ethanol and transferred onto silicon chips for direct electron microscopic observations. Specimens of black shale and the imbedded phosphorite layer samples from the Niutitang Formation were polished using a glass lapping plate, and then thin flakes were peeled off to get fresh surfaces for immediate observation. After about 20 s of gold sputtering treatment, the samples were observed using a Hitachi S4800 scanning electron microscope (SEM) in the Electron Microscope Unit of the University of Hong Kong. Micromorphology images of minerals were taken under secondary electron (SE) mode at 5 kV. The chemical compositions of samples were measured with energy-dispersive X-ray spectroscopy (EDS) at 20 kV.

RESULTS AND DISCUSSION

Considering the wide range of crystal sizes (<200 nm to >200 μm) and the high diversity of the crystal habits observed in our samples, it is insufficient to classify them according to size alone. Laboratory experiments (performed in environments that might lack the microbial communities existing in nature) have revealed that the nucleation and growth mechanisms involved in crystallization of gypsum are affected by variations in temperature, supersaturation, water salinity, pH, redox conditions, and the quantities or types of organic matter or organisms present (Cody and Cody 1988a, 1988b; Thompson and Ferris 1990; Ahmi and Gadri 2004; Vogel et al. 2010; Allwood et al. 2013). For example, lenticular gypsum crystals might form in the presence of organic materials (Cody 1979), and prismatic crystals might form in acid conditions (Edinger 1973). However, only a few crystal habits of gypsum were reported in previous experiments, which indicated limited influence from abiotic factors.

As shown in the water chemistry data summarized in Table 1, the water in the Zavarzin, Thermophile, and Burlyashii hot springs is a mixture of diluted alkali-chloride water and atmospheric precipitation. Jen's Pool represents acid springs (Kyle 2005), and the Thermophile hot spring has the lowest temperature of the five springs. The concentrations of SO₄²⁻ and Ca²⁺ in these springs are almost the same, except for Jen's hot spring, which has a concentration of SO₄²⁻ ten times higher than the others. The concentrations of Ca²⁺ in all of these hot springs are much lower than the concentrations found in the sea (McSween et al. 2003).

A microbial community can build up a micro-environment

that influences the deposition of gypsum in an indirect way. Microbial consortia are of high diversity, with redox-sensitive respirations from hydrogen-oxidizing bacteria or archaea, and sulfate-reducing bacteria that are important in regulating the biogeochemical cycles of nitrogen, sulfur and iron in Kamchatka hot springs (Zavarzina et al. 2000; Wagner and Wiegel 2008; Zhao 2008; Wagner et al. 2013). For example, the respiration by sulfate-reducing bacteria alters the concentration of SO₄²⁻ by taking sulfate as a terminal electron acceptor in the oxidation of organic matter (Hugenholtz et al. 1998). Also, the anaerobic reduction of NO₃ tends to acidify the environment (Amend and Shock 2001).

Gypsum in the Kamchatka hot springs

Prismatic gypsum crystal with well-developed faces l{111}, b{010}, and m{110} of about 200 μm long coexisted with diatoms, organic matter, and smaller prismatic gypsum crystals (<20 μm) attached to its surfaces (Fig. 2a). The large variations among prismatic gypsum crystals observed in this study (Figs. 2a and 2c) may reflect heterogeneous temperature fields within the hot springs, because these crystals may grow longer at low than at high temperatures (Cody and Cody 1988a). Low pH also facilitates the growth of prismatic gypsum (Cody 1979). Hemi-bipyramidal crystals (~10 μm, Fig. 2b) with well-developed b{010} faces that were aggregated with clay minerals indicated acidic conditions, or a pH lower than 6 (Edinger 1973). The edges separating the l{111} and e{103} faces were obscured. However, prismatic gypsum crystals were also observed in samples from the Burlyashii hot spring, in which pH values were higher than 6 (Fig. 2a, Table 1).

Prismatic pseudo-hexagonal crystals with prevailing developments of the m{110} and b{010} faces were commonly observed in these hot springs. Such crystals appeared as either radiating from a center in clusters (Figs. 2d, 2e, 2f, and 2h) or emerging randomly in large numbers (Fig. 2i). The crystals radiating from a center had clear or obscured edges and irregular terminations. They aggregated in different sizes, scaling from 200 nm to a few μm. Figure 2d shows gypsum crystals (longer than 5 μm) lying on top of many small gypsum clusters with crystal sizes <300 nm, and with a pyrite crystal in the vicinity. The gypsum crystal clusters varied in number from just a few prisms (Fig. 2h) to dozens of prisms (e.g., Fig. 2e, rosette arrangement).

Tubular crystals of ~50 μm in length, (with hollows of ~1

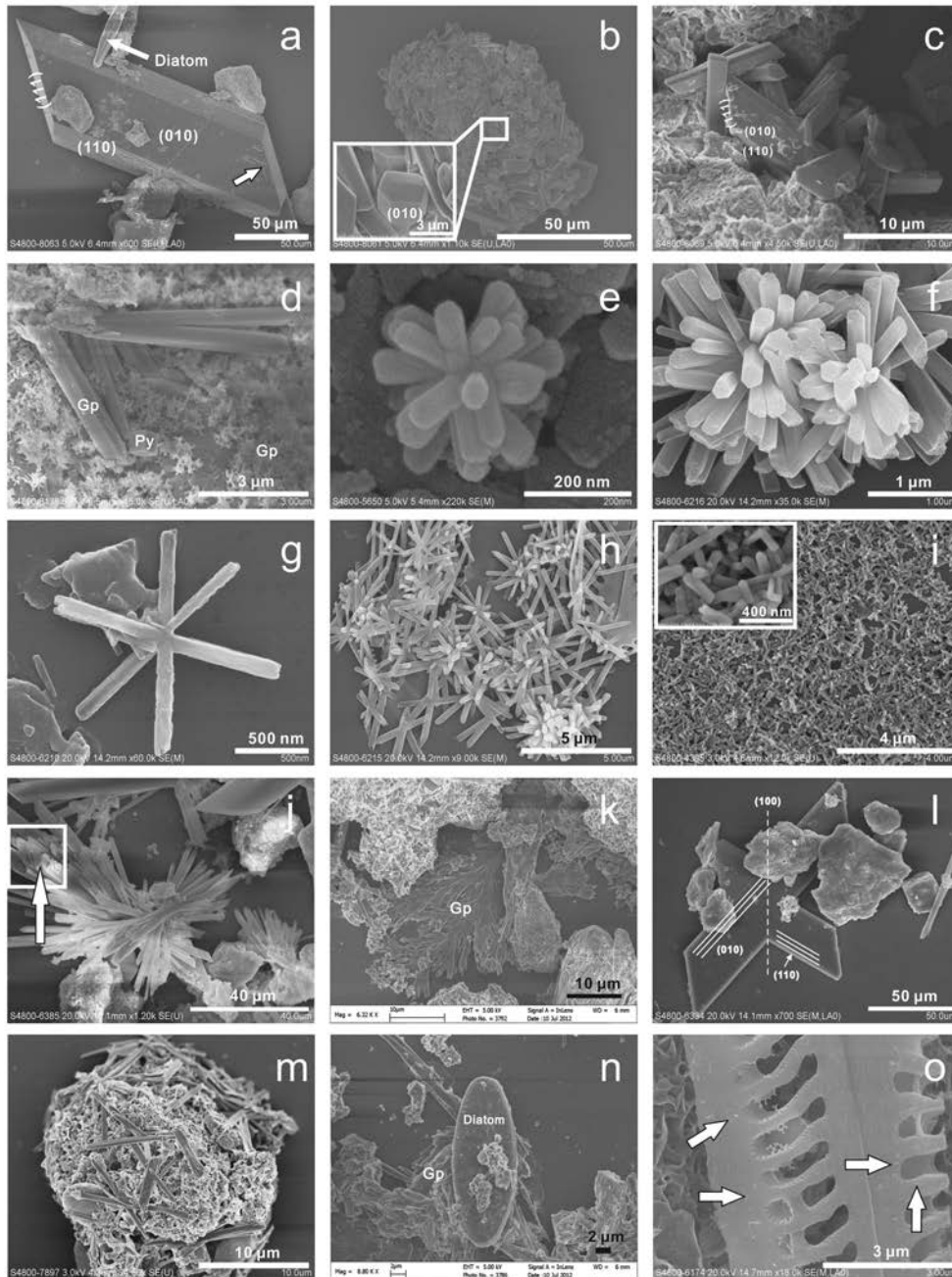


FIGURE 2. SEM images of gypsum crystals in Kamchatka hot springs. Prismatic (a–c), prismatic pseudo-hexagonal (d, e, f, and h), fibrous (g, j, k, m, n, and o), tubular (j), and twinned gypsum (l) are observed. White arrow in a points out smaller prismatic gypsum crystals. White arrow in j points out hollows at the end of some crystals. White parallel lines in l point out striations on gypsum crystal surfaces. White arrows in o point out small gypsum crystals (~nm) attached to the diatom surface. Gp = gypsum. Py = pyrite.

μm at the ends of some crystals) and fibrous pseudo-hexagonal crystals formed radiating aggregations (Fig. 2j). Fibrous crystals also appeared as seaweed-shaped aggregations (Fig. 2k), which might have formed under strain, or could have resulted from displacive crystallization (Jafarzadeh and Burnham 1992). Some crystals were stellar-shaped with six symmetrical rays (Fig. 2g). Other crystals were aggregated with organic compounds (Fig.

2m). A penetration twin on $\{100\}$, which was partly destroyed, had striations on face $\{010\}$ parallel to $m\{110\}$ (Fig. 2l). These striations were probably formed by a slow evaporation process (Jafarzadeh and Burnham 1992) in water with high concentrations of organic materials (Cody and Cody 1988b). Diatoms are often observed associated with gypsum crystals (Figs. 2a, 2n, and 2o).

Lenticular crystals were either rod-shaped like microorganisms

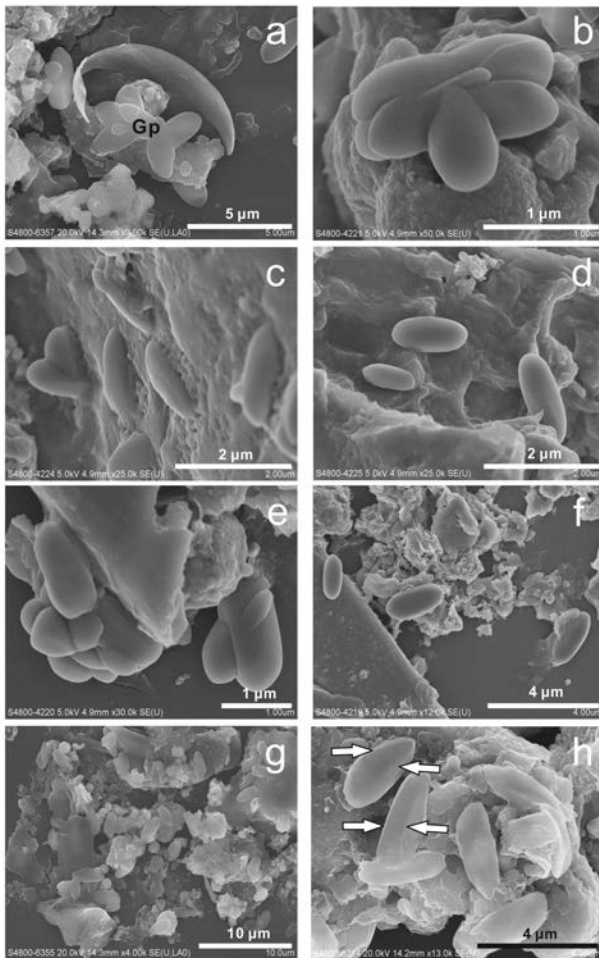


FIGURE 3. SEM images of rod-shaped lenticular gypsum crystals in Kamchatka hot springs. White arrows in (h) point out obscured edges rather than round edges of other rod-shaped lenticular gypsum crystals (a–g). Gp = gypsum.

(Fig. 3) or disk-shaped (Fig. 4). The $m\{110\}$ and $b\{010\}$ faces of lenticular gypsum crystals were missing due to predominant developments of the $l\{111\}$ and $e\{\bar{1}03\}$ faces. Some of the rod-shaped lenticular crystals were single crystals that coexisted with clay minerals (Figs. 3d, 3f, and 3g) and pyrite (covered by clay minerals in Figs. 3g and 3h). Other rod-shaped crystals were attached to quartz (Fig. 3a), diatoms (Figs. 3e and 3f), or other sedimentary surfaces (Fig. 3c). Some of these crystals had obscured edges (see arrows in Fig. 3h) rather than round edges (Figs. 3a–3g), which indicated a continuous development of the crystal habits. The individual petals of rosette aggregations appeared as rod-shaped crystals radiating from a center (Fig. 3b), or as crystals of varied sizes growing in different directions (Fig. 3a). The disk-shaped lenticular crystals were usually much smaller, and were observed attached either to the surfaces of other minerals (Figs. 4a–4g) or distributed loosely (Fig. 4h). These crystals were attached to different surfaces such as pyrite cubes (Fig. 4a), silica (Fig. 4b), unidentified minerals (Figs. 4c–4e), or bigger gypsum crystals (Fig. 4g). Some of them were single lenticular crystals with sinuous

seam lines along their lenticular edges, looking like the edge of clam shell (Fig. 4f). Other crystals penetrated each other (Fig. 4g). Prismatic gypsum crystals could transform to lenticular crystals if a high degree of adsorption of organic compounds on the $n\{\bar{1}11\}$ and $e\{\bar{1}03\}$ faces and high temperatures led to different rates of growth among the different faces (Barcelona and Atwood 1978; Cody and Cody 1988a; Aref 1998). The $l\{111\}$ face could dominate the crystal habits of gypsum at low temperatures, and low temperatures commonly led to the formation of prismatic habits (Fig. 2a). Lenticular crystals tended to form due to the preferred development of $e\{\bar{1}03\}$ (e.g., Fig. 4f) (Cody and Cody 1988a).

Gypsum in the Lower Cambrian black shale of the Niutitang Formation

Bundles of fibrous crystals (size ranging from 1 to 30 μm) were observed in the black shale samples (Figs. 5a and 5c). Fibrous pseudo-hexagonal gypsum crystals were also observed in the thin siliceous phosphorite beds (Fig. 5b). Crystal clusters displayed flower-like shapes of $\sim 40 \mu\text{m}$. Some of the crystals in clusters were transformed into lenticular crystals due to the preferred development of $e\{\bar{1}03\}$ (Fig. 5b). Gypsum veins were observed in phosphorite-rich layers (Figs. 5d and 5e). These veins were several millimeters long, about 50 μm wide and resembled fluid channels.

In black shale layers, prismatic, prismatic pseudo-hexagonal, and irregular gypsum crystals ranged from 1 to 10 μm in size (Fig. 6). Prismatic and pseudo-hexagonal crystals showed clear edges formed by their well-developed $l\{111\}$, $b\{010\}$, $m\{110\}$, $n\{\bar{1}11\}$, and $e\{\bar{1}03\}$ faces (Fig. 6f). Most of the prismatic pseudo-hexagonal and irregular crystals had rough surfaces with parallel cracks (Figs. 6c–6e). Gypsum crystals were commonly found growing in or on round-shaped fossils in black shale of the Niutitang Formation (Figs. 6b, 6h, and 6i). Gypsum crystals were also observed to have replaced framboidal pyrite crystals (the pyrite microcrystallites were $\sim 200\text{--}300 \text{ nm}$ in diameter), which was evidence of post-depositional hydrothermal fluid activity (Fig. 6g). Some of the crystals were covered by thin layers of organics with high carbon content (Figs. 6a, 6d, 6g, and 6h). The diversity of crystal sizes and morphologies of geothermal genesis in black shale was much less than that found in gypsum from the Kamchatka hot springs.

In black shale of the Niutitang Formation, the microfossils were commonly replaced by pyrite in the early diagenetic stage. Figure 9a shows that a microfossil surrounded by phosphate was first filled by biogenic pyrite, and later partly replaced by barite due to the influence of hydrothermal fluids. The compositional mapping structures shown in Figures 9b to 9h consistently showed that silica, calcium phosphate, iron, and sulfur in pyrite and clay minerals were syndepositional with the microfossils. The distribution of Ba revealed that only part of the pyrite was replaced by barite during the activity of thermal fluids.

Application to the preservation of gypsum in ancient sedimentary archives and on Mars

The authigenic gypsum samples represent various crystal habits in hot spring microbial environments on Earth, without alteration by geothermal fluids. For example, gypsum twinned crystals and rosettes have been observed either alone or inter-

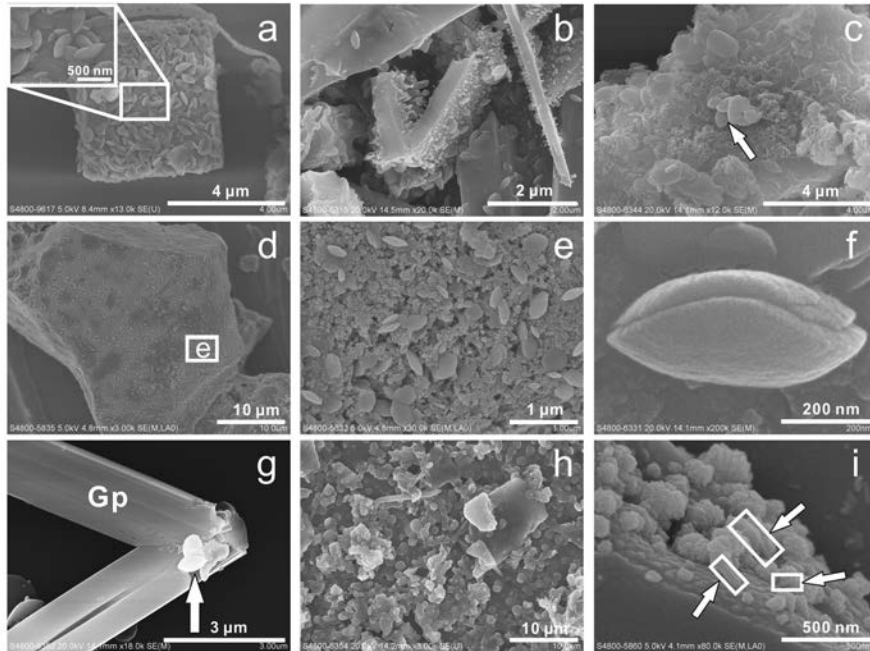


FIGURE 4. SEM images of gypsum crystals in Kamchatka hot springs. (a–h) Disk-shaped lenticular gypsum crystals. (i) Gypsum crystals attach to the surface of silica with organic compounds. Image (e) is a part of d. White arrows point out gypsum crystals. Gp = gypsum.

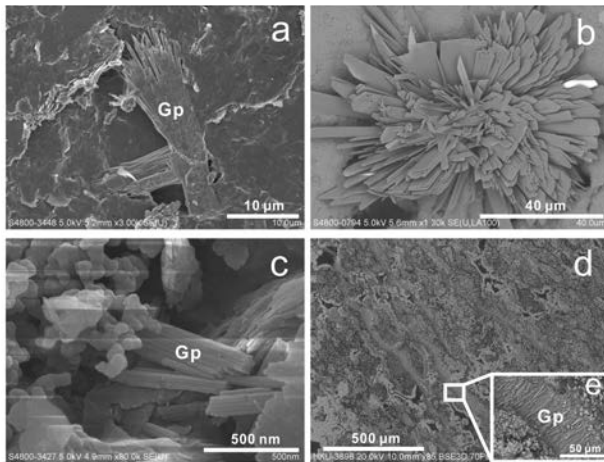


FIGURE 5. SEM images of gypsum crystals in phosphorite. Fibrous (a, c), fibrous pseudo-hexagonal gypsum crystals (b), and gypsum in vein (d–e) are observed in phosphorite. Gp = gypsum

grown with pyrite rods in deep sea sediments (Muza and Wise 1983). Although pseudo-hexagonal, fibrous, prismatic, and lenticular gypsum crystals may indicate dynamic soil environments in soils of southwestern Iran (Owliaie et al. 2006) or in the Las Vegas basin and southern New Mexico in the U.S.A. (Buck and Van Hoesen 2002; Buck et al. 2006), the variations of these crystal habits are still not comparable to those found in the hot springs of Kamchatka.

Surprisingly, gypsum crystals with a high variety of habits have been well preserved in Kamchatka's small volcanic hot springs for about 40000 years. The continuous supply of energy

and nutritional elements by the active hot springs and the microbial metabolisms combined to facilitate the continuous precipitation and development of gypsum crystals, so that changing crystallinities have coexisted for such a long time. The existence of authigenic kaolinite and opal-A in both the hot springs and the black shale (Figs. 7 and 8), and of barite in black shale (Fig. 9), all indicate the influence of hydrothermal fluids. However, gypsum in the Kamchatka hot springs has a much higher morphological diversity and a greater distribution of crystal sizes than gypsum in the Lower Cambrian black shale. Prismatic pseudo-hexagonal clusters of gypsum are very common in hot spring samples (e.g., Fig. 2f), but are not found in black shale. These crystals might have evolved into lenticular forms due to the high degrees of adsorption of organic compounds that resulted in varied growth speeds among different faces. The mineralization of lenticular crystals in hot springs might have been induced by microbial metabolism. Especially with the nucleation of gypsum inside of organic cells, crystals can inherit microbial morphology at an early stage (Fig. 3d), although the faces and edges of such crystals gradually become clearer and sharper with the increase of crystallinity (Fig. 3h). Gypsum crystals are commonly observed accompanied by materials with high-organic carbon content (e.g., Figs. 4i and 6a). In the Lower Cambrian black shale, hydrothermal fluids had altered the sulfide minerals into gypsum either after the burial of biomass or later during diagenetic processes (Figs. 6g and 9), so the development of morphology in the gypsum crystals had no influence on the microfossils. The replacement of pyrite crystals by gypsum (Fig. 6g) or barite (Fig. 9) crystals in the black shale samples indicates that the post-depositional hydrothermal fluids altered the original sedimentary mineralogy only to a limited extent. Tubular, lenticular, rosette, and compound twin gypsum crystals exist in samples from hot

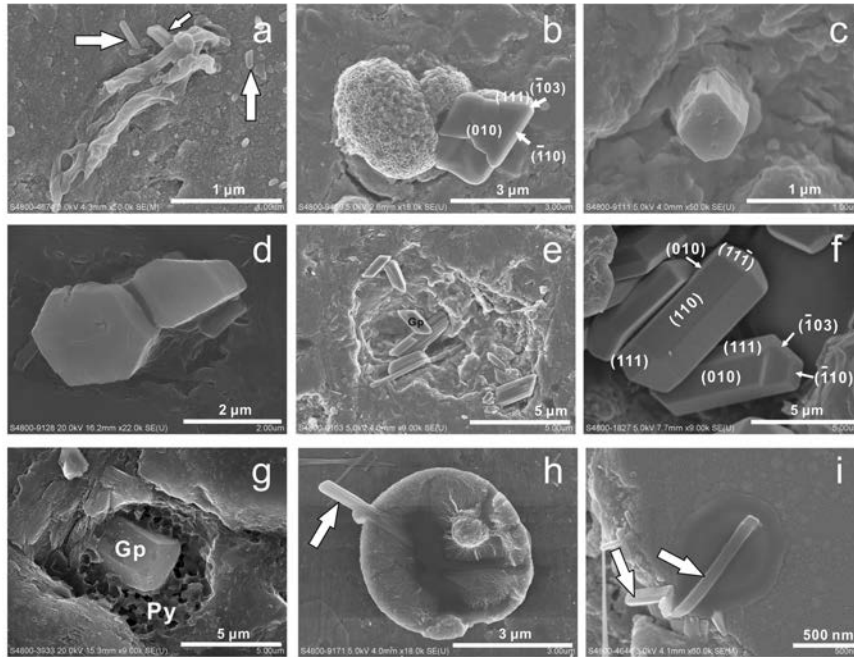


FIGURE 6. SEM images of gypsum crystals in the Lower Cambrian black shale. White arrows point out gypsum crystals. Gp = gypsum. Py = pyrite.

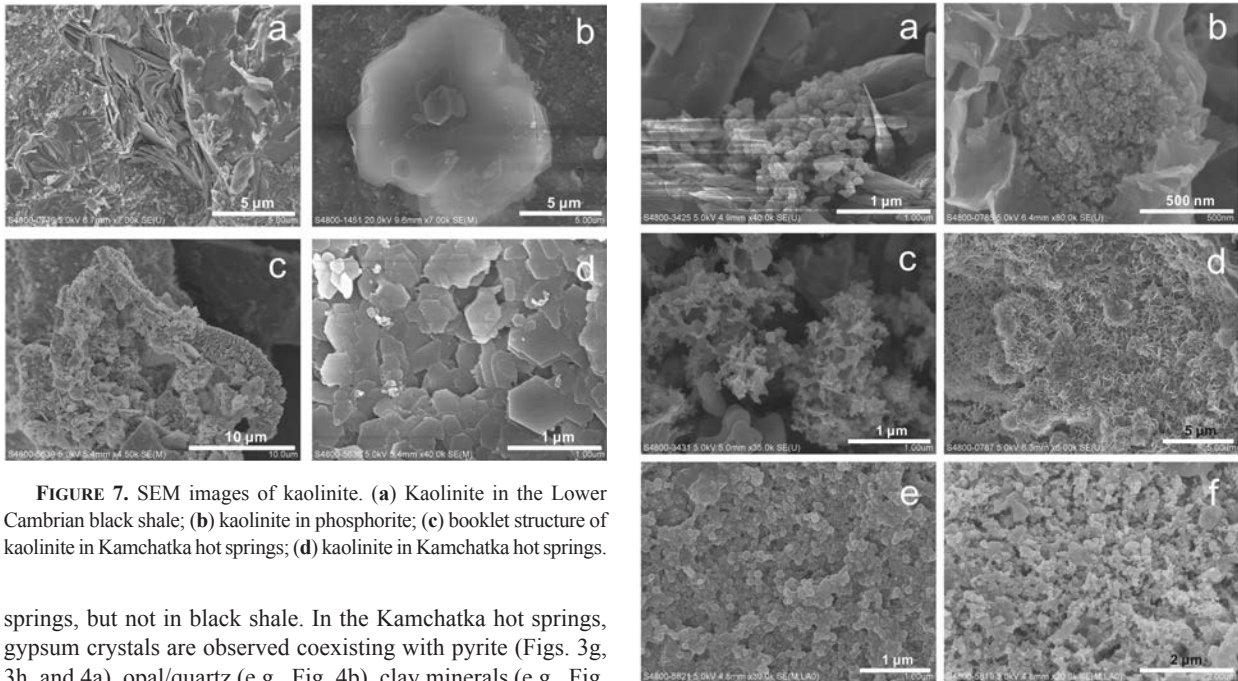


FIGURE 7. SEM images of kaolinite. (a) Kaolinite in the Lower Cambrian black shale; (b) kaolinite in phosphorite; (c) booklet structure of kaolinite in Kamchatka hot springs; (d) kaolinite in Kamchatka hot springs.

springs, but not in black shale. In the Kamchatka hot springs, gypsum crystals are observed coexisting with pyrite (Figs. 3g, 3h, and 4a), opal/quartz (e.g., Fig. 4b), clay minerals (e.g., Fig. 2b), organic compounds (e.g., Fig. 2m), and diatoms (e.g., Fig. 2o). This diversity reflects the physicochemical conditions of hydrothermal environments, which provide various surfaces for the nucleation of gypsum crystals (Lynne and Campbell 2003; Jones and Renaut 2004; Owen et al. 2008).

The coexistence of various morphologies of gypsum crystals in the Kamchatka hot springs could be considered a signature indicating a hydrothermal environment with possible microbial

FIGURE 8. SEM images of opal and lepisphere. (a–c) Opals in phosphorite; (d) lepisphere in phosphorite; (e–f) opals in Kamchatka hot springs.

activity, although microorganisms do not directly control the precipitation of those minerals or their crystal-forming habits. Similarly, the preservation of diverse gypsum crystallographic habits should be common in terrestrial hot springs, both now

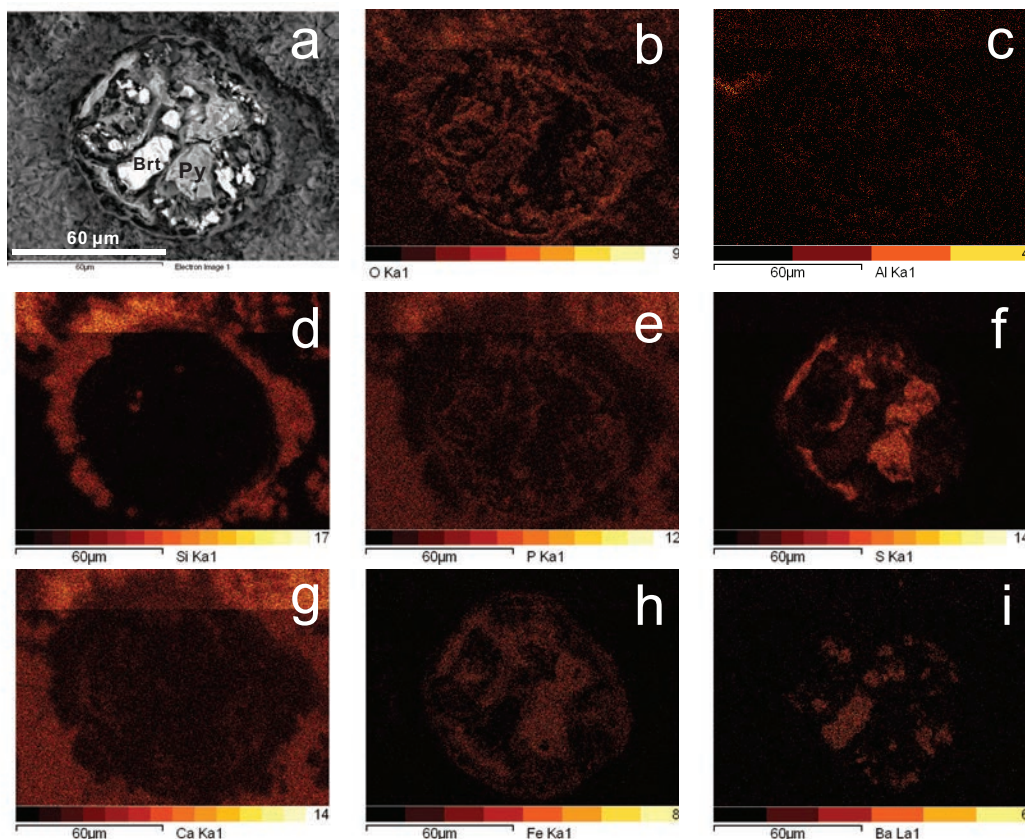


FIGURE 9. SEM image and EDS mapping images of phosphorite spherule in black shale. (a) Barite crystals are observed coexisting with pyrite (Py) crystals in a possible animal fossil; (b–i) EDS mapping data of elements in selected area of sample which demonstrate barite and pyrite by bright point aggregation in (f, h, and i). Brt = barite; Py = pyrite.

and in the geological past (e.g., Bonny and Jones 2003; Walker et al. 2005), as the microbial mediations and the geochemical conditions have remained similar over time.

Martian gypsum may have precipitated from chemical weathering, evaporation, hydrothermal activities, or possibly biotic factors in certain regions (Tanaka 2006; Chevrier and Mathé 2007; Dehouck et al. 2012). For comparison, several hot springs on Earth were chosen to provide mineralogical information relevant to searching for hydrothermal environments on Mars (Bishop et al. 2004, 2009; Allen and Oehler 2008; Rossi et al. 2008). Geochemical models were built to investigate whether hydrothermal fluids or groundwater could indicate suitable environments for supporting martian life (Varnes et al. 2003). Schulze-Makuch et al. (2007) suggested 34 candidate targets where hydrothermal activity probably still exists on Mars. Olympia Planitia and Noctis Labyrinthus are two of these candidate targets where gypsum has been identified (Langevin et al. 2005; Weitz et al. 2013). Sulfate, as a trace of acidic aqueous alterations, is considered to have formed from the late Noachian (4.5–3.7 Ga) to the Hesperian periods (3.7–3.2 Ga) in martian geological history (Bibring et al. 2006; Grotzinger et al. 2011; Arvidson et al. 2014). On Mars, the lack of springs representing environments with liquid water is the strongest constraint on the planet's habitability for microbial life (Farmer and Des Marais 1999). In the early history of Mars, microbial life might

have developed on the surface or in the subsurface (Michalski et al. 2013), where geomicrobiological processes similar to those in the Kamchatka hot springs might have prevailed. Mars is currently inactive due to rapid cooling (Harder and Christensen 1996; Pirajno and Van Kranendonk 2005; Grott et al. 2013), which is propitious for the preservation of biological and minerals records. The cool and dry martian surface and subsurface developed before the Amazonian period, soon after the disappearance of surface water (Barlow 2008). These conditions, together with weak geodynamic processes (Phillips et al. 2008), are the preferred conditions for preserving the mineral records of hydrothermal and possibly biological activities in the past (Arvidson et al. 2014). Remote sensing approaches such as the Microscopic Imager (MI) and the Alpha Particle X-Ray Spectrometer (APXS) have outlined the bulk deposition of gypsum vein structures on Mars (Squyres et al. 2012). However, the confirmation of microbial activity in the mineral records still requires high-resolution observation. With the prospect of a martian sample return mission around 2020 (Mustard et al. 2013), the high-resolution electron microscopic observations of the martian hot spring gypsum will provide an easy means of revealing the possible existence of microbial communities on Mars. Otherwise, a landing rover could be equipped with an onboard environmental electron microscope to allow in situ observation of martian sediments.

IMPLICATIONS

Terrestrial hot springs have unique microbial community structures because of their high temperatures and particular geochemical environments. The volcanic hot springs on the Kamchatka Peninsula of Russia are distinctive because of their isolated location and unusual tectonic environment. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is a common mineral in hot springs, which usually precipitates chemically upon the saturation of Ca^{2+} and SO_4^{2-} . However, electron microscopic observations reveal that these hot springs, although only a few square meters in size, are encyclopedias of gypsum crystal morphologies and sizes. We suggest that the long-term interactions between local microbial communities and the ever-changing geochemical environments have allowed these accumulations of gypsum deposits with a wide spectrum of crystallographic features and crystal sizes. Comparatively, we also find that abiotic geothermal fluids could not produce gypsum with such a high diversity in crystal habits. As the high-resolution examination of martian sediments (either in situ or in returned samples) becomes possible in the near future, the terrestrial hot spring gypsum, which carries information on specific geological environments that are influenced by microbial activities, can be used as mineral references for the detection of similar microbial life on Mars, if it ever existed.

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