

## **Spectroscopic studies on the Puga Hot Spring Deposits, Ladakh: a possible astrobiological Martian analog site in India**

S. Sarkar<sup>1, 2</sup>, H. Moitra<sup>3</sup>, S. Bhattacharya<sup>1, 3</sup>, A. Dagar<sup>1</sup>, D. Ray<sup>4</sup>, S. Gupta<sup>3</sup>, A. Chavan<sup>2</sup>, A. D. Shukla<sup>4</sup>, S. Bhandari<sup>2</sup>

<sup>1</sup>Space Applications Centre, Indian Space Research Organization, Ahmedabad-380015, Gujarat, India

<sup>2</sup>Department of Earth and Environment Science, Krantiguru Shyamji Krishna Verma Kachchh University, Bhuj- 370001, Gujarat, India

<sup>3</sup>Department of Geology and Geophysics, Indian Institute of Technology Kharagpur, Kharagpur- 721302, India

<sup>4</sup>Physical Research Laboratory, Ahmedabad 380 009, Gujarat, India

### **Key Points:**

- Continental hot springs with vital ingredients and alternate wet-dry cycles favoring RNA stability, are suitable sites for origin of life
- We characterize an analog martian hot spring locality hosting hydrous sulfates in association with Na-borates from Puga valley, Ladakh
- This mineral assemblage may be used to detect prospective fossilized hydrothermal sites on Mars that may have astrobiological significance

Corresponding author: S. Bhattacharya, [satadru@sac.isro.gov.in](mailto:satadru@sac.isro.gov.in)

### **Abstract**

Hot spring localities on continents may represent the most probable locales for the formation of early life constituents on Earth. Apart from liquid water and carbohydrates, these components also include elements like boron that are crucial for stabilization of the complex organic molecules that constitute life. Many of these life sustaining ingredients are commonly found in the vicinity of terrestrial hot springs. Analogously, similar existing or extinct hot spring localities on other planets may constitute prospective astrobiological sites. In the present study, we have characterized the complete mineralogical assemblage of the Puga hot spring deposit, Ladakh, India, using detailed spectroscopic and X-ray diffraction studies. The spectroscopic characterization was done using field based visible/near-infrared (VNIR; 400-2500 nm) and lab measured mid-infrared (MIR, 4000-400  $\text{cm}^{-1}$ ) hyperspectral data. The identified mineral phases include Na-borates, such as, borax and tincalconite, and hydrous sulfates such as jarosite, alunite, copiapite, tamarugite and gypsum, in conjunction with native sulfur, halite and opaline silica. Borate minerals have been identified from the valley-fill material along with halite and opaline silica, whereas sulfates occur alongside crystalline sulfur deposits. We have compared mineral assemblages found in Puga with other hot spring/hydrothermal deposits on Earth identified as martian analog sites, and also with mineral assemblages identified *in*

*situ* on Mars. We argue that the spectral characterization of hydrated borates in natural association with hydrous sulfates can be used for identification of fossilized martian hydrothermal settings that are prospective in the search for extinct/extant extra-terrestrial life.

### **Plain Language Summary**

Hot springs are supposed to be cradles for the origin of life on Earth. They provide essential ingredients to form carbohydrates, and also elements like boron, that are critical for stabilizing RNA. Detection of certain minerals, such as chlorite and opaline silica on Mars suggest the existence of ancient martian hot springs, while hydrous sulfate minerals prove past water activity on the martian surface. Compounds like borates that are present in some hot spring localities are known to stabilize RNA. To facilitate the identification of extraterrestrial hot springs, we have analyzed the complete mineralogical suite associated with the Puga hot spring deposit, Ladakh, India using VNIR, FTIR and XRD techniques. Sodium borate minerals like borax and tincalconite, and hydrous sulfates such as alunite, jarosite, copiapite, tamarugite and gypsum were identified along with halite and opaline silica. This mineralogical assemblage can help us identify localities on Mars that might have hosted life in the geologic past. Thus, we propose the Puga hot spring area as a prospective martian analog site with potentially exciting astrobiological implications.

### **Introduction**

The habitability of any planetary body is governed by its ability to sustain conditions favourable to life on parts of its surface or in its interior on geological timescales (Cockell, 2016). Habitability (as defined by Cockell et al., 2016) is contingent on a number of factors, such as the presence of surficial or subterranean liquid water, existence of a redox energy source and the presence of a number of critical elements essential to life (Drake and Sobel, 1992; Stoker et al., 2010; Domagal-Goldman et al., 2016). In the search for extra-terrestrial life, there has been a significant revival of scientific interest on Mars over the past two decades (e.g. MEPAG Special Regions – Science Analysis Group, 2006; Léveillé, 2010; Kral et al., 2011, 2014, 2016; Mickol and Kral, 2017; Jones et al., 2018; Arvidson and Catalano, 2018). Mars is presently located at a suitable distance from the sun which is conducive for the existence of liquid water on its surface, yet its present-day surface is largely dry. However, geomorphological and mineralogical analyses of data from lander-, rover- and orbiter-based instruments on board several recent missions have provided evidence for the prevalence of surficial water on this planet in its geological past (e.g. Hynek et al., 2010; Mangold et al., 2012; Phillips et al., 2001). Spectroscopic analyses of remotely sensed data have identified many hydrated minerals, including hydrous sulfates such as jarosite, alunite, gypsum, copiapite etc., on the martian surface, (e.g. Christensen et al., 2004; Gendrin et al., 2005; Murchie et al., 2009a, 2009b; Farrand et al., 2009; Milliken et al., 2008; Weitz et al., 2011; Tholot et al., 2012; Ehlmann and Mustard, 2012; Farrand et al., 2014; Vaniman et al., 2014; Léveillé et al., 2015; Ehlmann et al., 2016). Jarosite, having a restricted stabil-

ity field, can only be formed in a sulfur-bearing system by precipitation from highly acidic ( $\text{pH} < 3$ ), oxidizing aqueous fluids (e.g., Baron and Palmer, 1996; Bigham et al., 1996). Alunite also indicates similar acidic geochemical conditions during its formation, stabilizing in the presence of low pH, sulfurous fluids (Ehlmann et al., 2016). Thus, the presence of these minerals suggests that in the geological past, oxidising conditions and surficial water must once have existed on the Mars, although a subsequent major global-scale phenomenon led to the drying of the planet’s surface (Bibring et al., 2006). Recent studies suggest that such a transition might have taken place during the Hesperian ( $\sim 3.0$  Ga) and would be effectively capable of rendering the surface of Mars uninhabitable for common lifeforms (e.g. Andrews-Hanna and Lewis, 2011).

While water and oxygen are essential for the sustenance of most forms of life, the sulfur-rich environments of hydrothermal vents are often considered to have been the cradle for the origin of life on Earth much before the present-day oxidising atmosphere was formed, at around 2.5 Ga (Wächtershäuser, 1998; Martin et al., 2008; Martin and Russell, 2007; Farmer, 2000). Recent studies suggest that terrestrial, rather than marine, volcanic vents may have provided more favourable locales for the formation of early life components on Earth (e.g. Pearce et al., 2017; Djokic et al., 2017), and thus, study of hydrothermal activity related to hot springs on continents becomes particularly important in this context. Apart from the essential elements that are required to form carbohydrates, a variety of rarer elements in mineral form, such as borates, molybdates, germanates and vanadates, can also play a crucial role in stabilizing various organic molecules, such as ribose and other five-carbon sugars (Benner et al., 2010). Boron, in particular, is considered as one of the key elements needed for the origin of life, for it can control the reactivity of various prebiotic organic compounds (such as, tetroses, heptoses, pentoses etc.) and help in the stabilization of carbohydrates and ribose (Decker et al., 1982; Shapiro 1988; Larralde et al., 1995; Kim et al., 2011). On Earth, both boron and sulfur are commonly associated with hydrothermal vents or hot springs. Even though borates are yet to be detected on the martian surface, presence of substantial amounts of boron (166 ppm) has been confirmed in the martian meteorite MIL090030 (Stephenson et al., 2013) and in calcium sulfate-filled fractures in Gale Crater (Gasda et al., 2017). Stephenson et al. (2013) have also speculated about the presence of borate minerals on Mars, considering the oxidizing conditions of martian clay. If life had to originate and persist on Mars, locations bearing sulfate and borate deposits would be among the most favourable locales. Therefore, any search for extra-terrestrial life on the Red Planet should be focussed near the localities that are suspected to represent ancient hot spring- or hydrothermal vent-like environments, and additionally, contain sulfate and/or borate deposits.

In this study, we report the rare association of borates like borax and tincalconite with hydrous sulfate minerals such as alunite, jarosite, copiapite and tamarugite around the hot spring deposits in the Puga geothermal field in the Union Territory of Ladakh, India. In addition to this, we have conducted a detailed spectroscopic characterization of all these minerals. On the basis of

which we propose that the mineralogical association reported in this study can be used as an analog to the martian mineral assemblages. The spectral characterisation of such analog associations will help in the detection of these minerals in extra-terrestrial settings. Identification of such assemblages will further help in the detection of hydrothermal vents or hot spring deposits on surfaces of other planets and thus facilitate the search for life beyond earth.

## 1. Geological Setting

The study area is located in the Puga geothermal field (average altitude ~4400 m) which is situated about 180 km south-east of Leh town, Union Territory of Ladakh, India. The Puga geothermal field occupies an area of about 5 sq. km and forms the eastern part of the east-west trending Puga valley. The village of Sumdo and Pologonka La road-pass demarcate the eastern and western extremities of the Puga valley, respectively. This 15 km long valley, with a maximum width of ~1 km, is a part of the upper Indus valley (Harinarayana et al., 2004, 2006; Jha and Puppala, 2018). A small tributary stream of Indus, termed as Puga nala, flows from west to east through the Puga valley. A geological map of this region, modified after the Geothermal Atlas of India (1991), is shown in Figure 1.

The region can be divided into three major NW-SE trending belts that are separated from each other by distinct tectonic features. The Mahe and Zildat faults mark the northern and southern extremities of the central belt, and separate it from the northern and southern tectonic belts respectively (Geothermal Atlas of India, 1991). The northern tectonic belt is composed of shallow marine to fluvial sediments of Cenomanian to Miocene age, and lie nonconformably over the Mesozoic Ladakh Granite. The central belt demarcates the boundary along which the Indian and Eurasian plates collided during the Himalayan orogeny and thus is termed as the ‘Indus Suture Zone’ (ISZ) (Virdi et al., 1977). This belt consists of an ophiolite suite of rocks obducted during the Himalayan orogeny, and Middle Cretaceous to Upper Tertiary sedimentary rocks belonging to the Sumdo group. Paragneisses, schists, quartzites and associated phyllites and eclogites of Proterozoic age are the main constituents of the southern belt (Geothermal Atlas of India, 1991). Intrusions of granite, garnet-amphibolite, serpentine and tourmaline-quartz veins in this belt suggest multiple phases of igneous activity. The southern belt acts as the basement to the fossil-bearing Tethyan sediments which are exposed further to the south (Geothermal Atlas of India, 1991). The rocks of the southern belt are highly deformed and metamorphosed (under medium to high grade metamorphic conditions) compared to those of the northern and central belt, which indicates gradual increase in the intensity of deformation and metamorphism from north to south (Harinarayana et al., 2004, 2006). The Puga geothermal field is located in the southern tectonic belt which is bound by the NW-SE trending Zildat fault and NE-SW trending Kaigar Tso fault to the east and west, respectively. This area is covered with glacial moraine deposits, aeolian sand and scree. The hot spring deposits (mainly sulfur and borax) are formed *in situ* by the interaction of hydrothermal

fluid with the exposed rocks and are found as valley-fill material (Figure 2a) or encrustations (Figure 2b) extending up to 15 to 65 m depth. The basement of the Puga geothermal field comprises of paragneisses and schists of Paleozoic age (Harinarayana et al., 2004, 2006). This basement is termed as the Puga formation and is demarcated by the Sumdo formation in the east and intruded by Polokongka La granite in the west (Harinarayana et al., 2004, 2006).

## 1. Sampling Locations

Field samples of Na-borates and hydrous sulfates along with native sulfur have been collected in and around the Puga hot spring area. Among them, representative samples from three different localities have been investigated in this study to highlight the unique association of hydrous sulfates with Na-borates. A number of geothermal sinters were encountered in this area, having continuous flow of neutral to slightly alkaline hydrothermal water with temperatures ranging from 70 – 80 °C. Biological manifestations in the form of algal mats can be seen on these sinters. Molecular fossils of diatoms, photosynthetic proteobacteria and green sulfur bacteria (chlorobi, which oxidise sulfur) and non-sulfur bacteria (chloroflexi, which is a variety of photosynthetic bacteria and does not oxidise or reduce sulfur) have also been reported from these sinters (Ghosh et al., 2012).

White valley-fill materials comprising borax and tincalconite were collected near the Puga nala and this location is marked as PUG-18-06 (Figure 2a, 2b). A variety of sulfate minerals were identified from a mound to the south of the Sumdo-Pologongka La road and on road-cut sections to the north of the same road, about 2 km apart. The location of the small mound beside the road is henceforth referred to as PUG-18-05 (Figure 2a, 2c) and the road-cut section is named PUG-18-08 (Figure 2a, 2d). Location PUG-18-08 is situated on the northern boundary of the Puga valley.

Presence of native sulfur and sulfate deposits in this region have been reported by earlier workers in the area (Shankar et al., 1976; Shukla et al., 2017). Samples from PUG-18-05 are mainly comprise of alunite and jarosite with minor amounts of gypsum and opaline silica while the samples from the road cut section (PUG-18-08) show signatures of hydrous sulfates like alunite, jarosite, copiapite and tamarugite along with native sulfur. Alunogen and anhydrite are also present in a single sample collected from the location PUG-18-08.

## 1. Analytical Techniques

### (a) Visible and Near-Infrared Spectroscopy

For VNIR spectroscopy, a FieldSpec® 4 spectroradiometer (Analytical Spectral Devices, Boulder, CO, USA) was used to measure the spectral reflectance in the range of 400 - 2500 nm *in situ* and in the lab. This instrument has a spectral resolution of 3 nm at 700 nm and 10 nm at 1400/2100 nm, at the sampling interval of 1.4 nm for 400 - 1000 nm and 2 nm for 1000 - 2500 nm spectral range. A contact probe associated with the FieldSpec® 4 Hi-Res instrument

comprising of a 100W halogen reflector lamp and a conduit (making an angle of  $30^\circ$  with the halogen lamp) for the fibre-optic, was used to collect the spectra in the field so as to make the measurements independent of the ambient illumination conditions. As the contact probe is kept in physical contact with the sample while collecting the spectra, the effect of stray light, atmospheric gases and other noise inducing factors is minimized and the signal-to-noise ratios are improved compared to traditional laboratory techniques (McArthur et al., 2007). The measured spectra from all the samples have been standardized using a Spectralon panel (Labsphere, North Sutton, NH, USA) which has a very high reflectance ( $\sim 97-99\%$ ) in the entire spectral range of the FieldSpec® instrument. The in situ spectra of borate and sulfate samples from Puga geothermal area have been compared with the reference mineral spectra from the United States Geological Survey (USGS) Spectral Library (Kokaly et al., 2017)

### 1. Mid-Infrared Spectroscopy

The mid-infrared spectra of samples were obtained in the spectral range of  $4000-400\text{ cm}^{-1}$  at the resolution of  $4\text{ cm}^{-1}$  at the Central Research Facility (CRF) of Indian Institute of Technology, Kharagpur, India using NICOLET 6700 (THERMO FISHER SCIENTIFIC INSTRUMENTS, USA) FTIR spectrometer. The samples were powdered to a grain size range of  $\sim 180-250\text{ }\mu\text{m}$  and mixed with dehydrated KBr powder in the ratio of 1:300 by weight. The mixtures were then pressed into pellets and the sample spectra were obtained in transmittance mode using these pellets.

### 1. X-Ray Diffraction

Bruker D2 Phaser Table top XRD system at Physical Research Laboratory, Ahmedabad, India was used for the XRD analyses of the borate and sulfate samples. This XRD system uses a Cu-K excitation and Ni filter, with the current and power rating of 10 mA and 30 kV, respectively. The samples were prepared by grinding and homogenising using an agate mortar and pestle. The samples were then scanned for  $2\theta$  angle range of  $10 - 70^\circ$  (except for one sample for which  $2\theta$  was  $5 - 65^\circ$ ) at a scanning speed of  $0.02^\circ 2\theta/\text{s}$ . The accuracy of XRD analyses was examined with respect to the corundum-disc standard and always evaluated to be better than  $\pm 0.03^\circ 2\theta$ . The peaks of the XRD results were compared with the ICDD-PDF2 database using Bruker's phase identification software DIFFRAC.EVA provided with the instrument (Gates-Rector and Blanton, 2020).

## 1. Results

### 4.1 Visible and Near-Infrared Spectroscopy

Most of the minerals (primary as well as secondary) found on Earth show characteristic absorption features in the VNIR region as a function of wavelength and composition owing to the electronic and/or vibrational processes inside the crystal lattices of the minerals that eventually helps in their detection in remotely sensed data of planetary surfaces including Earth. The following section primar-

ily discusses about the minerals that have been detected at the Puga hot spring deposits based on *in situ* and lab-based VNIR spectroscopic measurements.

As already mentioned in section 2, borax and tincalconite are the major borate minerals from location PUG-18-06 (Figure 3), whereas, PUG-18-05 chiefly comprises of alunite and jarosite (Figures 4a and b). The samples collected from the third location i.e., PUG-18-08, mostly show spectral characteristics of native sulfur, alunite, copiapite, jarosite and tamarugite (Figures 5a, b, 6a and b). Hydrous sulfate minerals alunite, jarosite and copiapite along with pure sulfur, gypsum and opaline silica have been characterized and identified *in situ* from the Puga geothermal area. We have subdivided this section in different subsections. Firstly, the VNIR spectroscopic characterizations of major borate and sulfate minerals have been discussed based on the knowledge obtained through the works of previous researchers followed by detailed spectral characterizations of the samples collected from the Puga Geothermal Field.

#### 4.1.1 Borax

The absorption features related to B–O fundamental stretching vibrations appear in the 7000–14000 nm region whereas those for B–O fundamental bending occur in the 12500–22000 nm region (Ross, 1974). In the VNIR range (400-2500 nm), the spectral signatures comprise of various combinations and overtones of the B–O and fundamental water absorptions. Hunt et al. (1972) were the first to conduct a systematic VNIR spectral characterization of different borates. They assigned the 1000, 1170, 1450, 1930, and 2300 nm absorption features in their borax spectra to various combinations and overtones of water fundamentals. Only one single band in the VNIR region, i.e. near 2150 nm has been assigned to a B–O related feature by them - as a combination of the second overtone of the degenerate B–O stretches located near 7700 and 11800 nm (Table 1). Crowley (1991) characterized the VNIR reflectance spectra of commercial borax and identified prominent absorption features at 976, 1172, 1428, 1476, 1774, 1926, 2140 and 2264 nm (Figure 3, Table 1).

#### 4.1.2 Tincalconite

The VNIR reflectance spectra of tincalconite was acquired and characterized by Crowley (1991) for the first time. He listed the prominent band positions of the tincalconite spectra at 972, 1156, 1420, 1470, 1924 and 2148 nm (Figure 3, Table 1). In a recent study, Cloutis et al. (2016) have identified various water related features at 985, 1121, 1430, and 1495 nm along with a doublet near 1980/2030 nm in tincalconite spectra. They have also assigned two weak bands near 1580 and 1790 nm to higher order combinations of the various B–O stretches along with two prominent features near 2190 and 2280 nm (Table 1). We have used the ticalconite spectra of Crowley (1991) from the USGS spectral library as the reference for comparing the tincalconite spectra obtained from the Puga hot spring.

#### 4.1.3 Alunite

VNIR spectra of alunite shows four characteristic absorption features in the 1400 nm region, attributed to OH stretching overtones, among which two strong bands are located at 1425 and 1467 nm and two weaker bands are at 1450 and 1460 nm (Cloutis et al., 2006). The assignment of the 1775-nm absorption band to a combination of the OH fundamental stretch with the first overtone of the Al–OH bend is debated by Clark et al. (1990) due to its absence in other Al–OH bearing minerals (Cloutis et al., 2006). Bishop and Murad (2005) have also attributed this band to the combination of various OH fundamentals. Combinations and overtones of vibrations in H<sub>2</sub>O produce the 1940-nm absorption band in alunite spectra (Bishop and Murad, 2005). Bishop and Murad (2005) have assigned the bands from 2170 to 2220 nm to the S–O overtones and combination bands of sulfate or OH species. The assignment of 2330-nm absorption band is debated, as Hunt et al. (1971) have attributed this feature to a combination of the fundamental Al–O–H bend and the lowest frequency OH stretching fundamental while recent workers (Bishop and Murad, 2005 and Cloutis et al., 2006) have assigned this band to the combination of O–H stretch vibration, denoted by  $\nu_{OH}$ , and H–O–H out of plane bend vibration, denoted by  $\delta_{OH}$ .

#### 4.1.4 *Jarosite*

VNIR reflectance spectra of jarosite can be characterized by a sharp narrow absorption band at ~433 nm and a strong broad feature near 930 nm attributable to the spin forbidden transition of Fe<sup>2+</sup> present in jarosite (Hunt and Ashley, 1979). In the 1400-nm region, Cloutis et al. (2006) have assigned two absorption bands to first-order overtones of  $\nu_{OH}$  at 1465–1468 nm and 1510–1520 nm. Overtone and combination bands due to sulfate or OH species occur from 2260 to 2270 nm in jarosite reflectance spectra (Bishop and Murad, 2005).

#### 4.1.5 *Native Sulfur*

Reflectance spectra of pure sulfur shows a single diagnostic absorption feature centered at ~400 nm arising due to the band gap between the conduction band and valance band (Clark, 1999).

#### 4.1.6 *Copiapite*

Fe<sup>3+</sup> transitions can be ascribed to the absorption band positions at 430, 550 and 855–866 nm in the reflectance spectra of copiapite (Cloutis et al. 2006). Among these, the position of the 860-nm absorption feature is diagnostic to different Fe<sup>3+</sup>-bearing sulfate spectra (Cloutis et al. 2006). Two weak bands associated with H<sub>2</sub>O coordinated Fe<sup>2+</sup> can be found at 900 and 1170 nm (Cloutis et al. 2006). In the 1400 nm region, an OH stretching overtone occurs at 1360 nm whereas bands associated with H<sub>2</sub>O combinations/overtone can be found at 1452 and 1480 nm (Cloutis et al. 2006). OH- or H<sub>2</sub>O bending, stretching, and rotational fundamentals or S–O bending overtones can be attributed for a weak band near 1780 nm (Cloutis et al. 2006). An H<sub>2</sub>O related band occurs at 1940 nm with a weak band at 2000 nm in copiapite reflectance spectra (Cloutis et al., 2006). Two weak bands near 2420 and 2470 nm can be found on the shoulder of an intense band centered at 2530 nm of which the first one is attributed to



the third overtone of the asymmetric S-O stretch ‘ $\nu_3$ ’ and the remaining bands to O-H stretch ( $\nu_{OH}$ ) and H-O-H in and out of plane bending vibrations ( $\nu_{H-O-H}$  and  $\nu_{H-O-H}$ , respectively) (Cloutis et al. 2006).

#### 4.1.7 Gypsum

VNIR spectra of gypsum shows a characteristic vibrational triplet feature near 1500 nm, a prominent absorption feature at 1750 nm and a doublet near 2200 nm (Cloutis et al., 2006). Hunt et al. (1971) have assigned the 1750-nm feature in gypsum spectra to the OH/H<sub>2</sub>O librations, bends, and stretches and the 2200-nm doublet to combinations of stretching and rotational/translational H<sub>2</sub>O fundamentals and overtones. However, Cloutis et al. (2006) have assigned these features to S-O bending overtones.

#### 4.1.8 Opaline Silica

Opaline silica can be characterized by a OH-H<sub>2</sub>O related absorption feature near 1400 nm, one H<sub>2</sub>O related feature near 1900 nm and a doublet in the 2210 to 2260 nm region in the VNIR spectra. The 1400-nm absorption band, which arises due to the combination of overtones of the first fundamental of OH stretch and structural H<sub>2</sub>O, occurs near 1400–1410 nm in case of opaline silica (Langer and Flörke, 1974; Stolper, 1982). If the mineral is devoid of structural water, implying that this band position is purely dependent on the overtone of the OH stretch with some influence of the Si-OH bond, the 1400-nm absorption feature can shift towards shorter wavelengths up to 1380 nm (Anderson and Wickersheim, 1964; Swayze et al., 2007; Milliken et al., 2008). The bands at 1910 nm are formed due to the combinations of the H-O-H bend with the OH stretch. The 2200-nm region of the opal spectra exhibits a doublet feature due to the combination tones of Si-OH (Ehlmann et al., 2009). The shorter absorption band occurs at 2210–2220 nm due to isolated Si-OH and the longer band at 2260 nm due to H-bound Si-OH (Anderson and Wickersheim, 1964; Stolper, 1982; Goryniuk et al., 2004). The 2260-nm band can be weakened, and finally can reduce the 2200-nm feature, if the mineral is lacking water. Amorphous variety of opal (opal-A) and more crystalline variety like opal-CT can be distinguished based on the relative positions of 1400, 1900 and 2200 nm absorption features. For amorphous varieties the deeper absorption bands appear towards 1410, 1910 and 2260 nm regions but in case of crystalline silica, those absorption features occur more towards 1460, 1960 and 2210 nm (Sun and Milliken, 2018).

#### 4.1.9 PUG-18-06

Two samples of the white colored loose valley-fill material have been collected and labeled as PUG-18-06-A and PUG-18-06-B, respectively. The *in situ* spectra of the sample PUG-18-06-A shows prominent absorption bands at 982, 1172, 1432, 1481 and 1927 nm, which can be attributed to H<sub>2</sub>O related features. These H<sub>2</sub>O related features are situated at 972, 1161, 1424, 1476 and 1929 nm in reflectance spectra of the sample PUG-18-6-B (Figure 3, Table 1). The absorption features related to various overtones and combinations of different B-O fundamental stretching and bending (Cloutis et al., 2016) as discussed in section 4.1.1

and 4.1.2 have resulted in absorption bands at 1781, 2142 and 2261 nm for PUG-18-06-A and at 1556, 1801, 2156 and 2267 nm for PUG-18-06-B (Figure 3, Table 1). In Figure 3, both VNIR spectra of PUG-18-06-A and PUG-18-06-B have been compared with that of borax from Crowley, 1991 and tincalconite from USGS spectral library (Kokaly et al., 2017).

#### 4.1.10 PUG-18-05 (Alunite and Jarosite)

Four representative VNIR reflectance spectra of hydrous sulfates (namely, PUG-18-05-A, -D, -H and -G) among the samples collected from location number PUG-18-05 are shown in Figures 4a and b, and compared with the USGS spectral library alunite and jarosite spectra (Alunite HS295.3B and Jarosite GDS99) (Kokaly et al., 2017). Although, all these spectra exhibit the narrow absorption feature at 430 nm region associated with  $\text{Fe}^{2+}$  spin forbidden transition, spectra of samples D, G and H have the 500- and 900-nm  $\text{Fe}^{3+}$  crystal field transition characteristic of jarosite along with all the characteristics absorption bands present in alunite (Table 2). Only the spectrum of sample G shows the 650-nm feature, found in jarosite (Table 2). VNIR spectra of the four samples show a doublet feature with band absorption minima centered at 1430 and 1475 nm followed by a single absorption near 1765 nm, typically found in alunite. The 1900-nm  $\text{H}_2\text{O}$  related feature is found at 1904, 1935, 1917 and 1937 nm for the samples A, D, G and H, respectively (Table 3). A doublet feature is found in the 2170 to 2220 nm region in all these VNIR spectra which is attributed to the various overtones and combination bands of sulfate or OH species in alunite (Bishop and Murad, 2005), as mentioned above in section 4.1.3. In case of jarosite, a diagnostic absorption band attributable to various overtones and combination bands of sulfate or OH species occurs between 2260 to 2270 nm region (Bishop and Murad, 2005) (section 4.1.4) and it is detected only in the PUG-18-05- G sample as a narrow band centered at 2264 nm, thus confirming the presence of jarosite in the sample (Table 4). The band which arises due to the combination of  $\nu_{\text{OH}}$  stretch and  $\nu_{\text{OH}}$  out-of-plane bend at 2330 nm in alunite (Bishop and Murad, 2005; Cloutis et al., 2006) is clearly identified in all these spectra. The presence of strong absorption bands in 500, 650 and 900 nm regions, attributable to  $\text{Fe}^{3+}$  transitions, and the 2264 nm absorption, arising due to the various overtones and combinations of sulfate or OH vibrations, in the spectrum of sample PUG-18-05-G (Figure 4b) shows the closest match with that of jarosite (Table 2 & 4). Hence, this spectrum is shown in a separate panel in Figure 4 for clear representation and comparison.

#### 4.1.11 PUG-18-08

From location PUG-18-08, five representative VNIR spectra are discussed here. The major mineral phases identified from this location using VNIR spectroscopy and further confirmed through FTIR spectroscopy and XRD analysis, are native sulfur, alunite, jarosite, copiapite and tamarugite.

##### 4.1.11.1 Alunite and Native Sulfur

Samples numbered PUG-18-08-A and B have the 400-nm conduction band, char-

acteristic of sulfur, present at 419 and 433 nm, respectively. Sulfur produces more or less featureless spectrum in VNIR domain (400 to 2500 nm) except for the 400-nm conduction band (section 4.1.5). Apart from VNIR result, XRD and FTIR measurements have also confirmed that these samples contain native sulfur as a major constituent. Along with sulfur, in samples PUG-18-08-A and B, the characteristic absorption bands of alunite as described in section 4.1.3 are also clearly identified. The 1400-nm doublet feature arises at 1427 and 1477 nm for the spectra of sample A, and the same for sample B are found at 1430 and 1477 nm (Table 3). The characteristic absorption feature for alunite near 1750 nm is identified at 1767 and 1768 nm, respectively, for the VNIR spectra of sample A and B (Table 4). A water related feature is typically found at 1940 nm in alunite spectra, whereas this feature is found to be shifted towards shorter wavelengths- 1903 and 1935 nm for A and B, respectively (Table 3). The typical doublet at 2170 to 2220 nm and the strong OH combination band at 2330 nm (Bishop and Murad, 2005 and Cloutis et al., 2006) which are usually present in alunite spectra, are found at 2179, 2212 and 2322 nm for sample A, and at 2178, 2209 and 2323 nm for sample B (Table 4). The  $\text{Fe}^{3+}$  transition band occurring near 900 nm is found at 938 nm in the spectra of the sample number PUG-18-8-A, indicating presence of  $\text{Fe}^{3+}$ -bearing sulfate (probably jarosite) in the sample along with alunite (Table 2) in minor quantity. These two spectra, along with the USGS spectral library alunite and elemental sulfur (Alunite HS295.3B and Sulfur GDS94) (Kokaly et al., 2017) reflectance spectra, are presented in Figure 5a.

#### 4.1.11.2 Jarosite and Copiapite

Two other samples from this location (viz. PUG-18-8-C and E) are identified as copiapite and jarosite, respectively, based on their spectral match with the USGS spectral library reflectance spectra of copiapite and jarosite (Copiapite GDS21 and Jarosite GDS99) (Kokaly et al., 2017) (Figure 5b). The common VNIR spectral features of jarosite and copiapite are described in section 4.1.4 and 4.1.6 respectively. The  $\text{Fe}^{3+}$  transition related absorptions are found at 467, 675 and 874 nm in the VNIR spectrum of sample C (Table 2). The OH stretching overtones and  $\text{H}_2\text{O}$  overtones or combination absorption at 1400 nm (Cloutis et al. 2006) are identified at 1353 and 1462 nm in this spectrum (Table 3). A broad absorption band, attributable to OH- or  $\text{H}_2\text{O}$  bending, stretching, and rotational fundamentals or S-O bending overtones (Cloutis et al. 2006) is situated at 1793 nm (Table 4). The absorption feature at 1940 nm is due to combinations of water fundamentals. Although no absorption band could be identified in the 2400 nm region, the spectra of PUG-18-08-C shows remarkable match with the USGS spectral library copiapite (Copiapite GDS21) except for the 1400, 1800 and 1950 nm features where the spectra are much smoother and absorption bands are much more broad as compared to the library spectrum (Figure 5b). These differences in spectral shape might have been caused due to the presence of other impurities, especially anhydrite which has been detected in XRD but have a relatively smooth VNIR spectral signature with a moderate 1950-nm feature, or tamarugite which have been found at this location (sample number

PUG-18-08-F, described in detail in the following section). VNIR spectra of PUG-18-08-E exhibit a narrow absorption feature at 433 nm, followed by a broad band at 922 nm, typical of ferric sulfates (Table 2). In the 1400 nm region of this spectrum, a doublet is found with absorption positions at 1408 and 1465 nm, which can be attributed to OH stretching overtones in spectra of ferric sulfates (Table 3). The H<sub>2</sub>O combination absorption has its band minima at 1953 nm and the 2210-2260 nm doublet absorption, diagnostic of jarosite, are observed at 2219 and 2263 nm in the VNIR spectra (Table 4), thus confirming the presence of jarosite in this sample (Figure 5b).

#### 4.1.11.3 *Tamarugite*

The VNIR reflectance spectrum of the fifth sample from this location, namely, PUG-18-08-F, shows signatures of the mineral tamarugite (a Na-Al sulfate having formula NaAl(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O). However, VNIR spectrum of tamarugite is not available in any commonly used library (such as USGS, RELAB). The PUG-18-08-F spectrum is matched with published VNIR spectrum from Mougénot (1991) where the tamarugite sample was mixed with natroalunite (Figure 6a). The absorption band positions of sample -F endorsing a good match with the spectra of Mougénot (1991) are identified at about 432, 1481, 1763, 1958, 2175 and 2216 nm. Although, proper causal attribution of these band positions are yet to be done, they can be attributed to various transitional and vibrational processes related to hydrous sulfate minerals in general. The 432 nm absorption can be found due to Fe<sup>3+</sup> related transitions (Table 2); the OH-stretching overtone and H<sub>2</sub>O combinations can be identified at 1481 and 1958 nm, respectively (Table 3). The S-OH related absorption features are found at 1763 nm and as a weak doublet around 2175 and 2216 nm (Table 4).

#### 4.1.12 *Gypsum of Puga*

Colorless chunks of gypsum, associated with native sulfur, were collected from the northern section of the road. Based on the band assignment given in section 4.1.7, representative VNIR spectrum of gypsum (PUG-15-Gypsum) is identified from puga valley fill material and the VNIR spectrum is represented in Figure 6b, along with the USGS spectral library gypsum reflectance spectrum (Gypsum HS333.3B). The 1500 nm OH related vibrational absorption feature for both the gypsum samples are found to be situated at the same wavelength positions at, 1448, 1490 and 1532 nm (Table 3). An additional absorption feature located on the shoulder of a more intense absorption band in this region occurs approximately at 1390 nm for gypsum (Cloutis et al. 2006). For PUG-15-Gypsum, this feature is identified at 1428 nm (Table 3). The 1750 nm feature has been identified at 1754 and 1748 nm in PUG-15-Gypsum (Table 4). The 2200 nm doublet have been identified at 2222 and 2264 nm (Table 4).

#### 4.1.13 *Opaline Silica of Puga*

Opaline silica sample was found associated with hydrous sulfates (majorly alunite as confirmed by XRD) from the small mound at the southern side of the road (i.e. location number PUG-18-05). Sample number PUG-18-05-E is identi-

fied as opaline silica as it shows all the diagnostic features associated with opal spectra as listed in section 4.1.8. The combination of overtone of OH stretch and structural water occurs at 1408 nm and combination modes for H<sub>2</sub>O with stronger H-bonding occurs at 1462 nm (Cariati et al., 1981, 1983a, 1983b; Bishop et al. 1994). The combination band of H-O-H bend and OH stretch occurs at 1903 nm. In case of both the 1400 nm and 1900 nm features the shorter wavelength is more prominent. The 2200 nm doublet is identified as absorptions at 2217 and 2258 nm with the higher wavelength feature being more prominent. Affinity of 1400 nm and 1900 nm features to occur towards shorter wavelength and 2200 nm feature towards longer wavelength suggests that the opaline silica of our sample is more of the amorphous variety, i.e. Opal-A (Sun and Milliken, 2018). The *in situ* VNIR spectrum of sample PUG-18-05-E along with that of USGS spectral library reflectance spectrum of opal (Opal TM8896) is shown in Figure 6b.

### 1. Mid-Infrared Spectroscopy

The Mid-IR spectroscopic study of the samples further helps in the identification of the minerals (especially those that may not have strong VNIR absorptions) present in them. The FTIR spectra of the samples have been compared to published mid-IR spectra of different minerals and peak assignments have been done accordingly. The fundamental vibration ranges of most minerals lie between 400 and 1500 cm<sup>-1</sup>. In this range, the sulfates exhibit absorptions related to their fundamental asymmetric and symmetric S-O stretch and bend vibrations. In hydrous sulfates, such as jarosite, alunite and tamarugite, the sulfate ion is at a site with C3v symmetry. The C3v symmetry refers to the presence of a vertical 3-fold rotation axis with two symmetry operations, namely, rotations by 120° and 240°, along with three vertical reflection operations with the mirror planes passing through the 3-fold axis. So, there are total six S-O fundamental vibrations, out of which four asymmetric vibrations (two  $\nu_3$  and two  $\nu_4$ ) are strongly IR active and the remaining two ( $\nu_1$  and  $\nu_2$ ) are mostly IR inactive (Bhattacharya et al., 2016; Cloutis et al., 2006; Farmer, 1974). The borates also show their B-O symmetric and asymmetric stretch vibrations and, in- and out-of-plane B-O-H bend vibrations in this fundamental vibration range. Hydrous tetraborates like borax and tincalconite contain two boron atoms in 4-fold tetrahedral coordination and two boron atoms in 3-fold trigonal coordination. Each of the two types of boron shows their respective B-O stretch and B-O-H bend vibrations in this range. Below 700 cm<sup>-1</sup>, the B-O bending vibrations of the two types of boron occur along with the symmetric pulse vibrations ( $\nu_p$ ) of the tetraborate ion [(B(4)(OH)4)<sup>-</sup>]. {B(3)-O} refers to the B(3)-O bending vibrations whereas {B(4)-O} refers to B(4)-O bending vibrations (Kipcak et al., 2014; Jun et al., 1995; Weir, 1966).

The mid-IR spectra of the samples are shown in Figures 7-10. Figures 7a, 8a, 9a and 10a are dedicated to the fundamental vibration range of the suspected mineral groups, i.e., borates and sulfates, while figures 7b, 8b, 9b and 10b represent the range for absorptions related to O-H stretch and bend vibrations

and combinations and overtones of the fundamental S-O vibrations. While the spectra of samples PUG-18-06-A and -B show presence of hydrous tetraborates like borax and tincalconite, the spectra of samples PUG-18-08-A, -B, -E and -F and PUG-18-05-A, -D, -H are dominated by hydrous sulfates like alunite and jarosite. Silica also manifests its presence in the spectra of these sulfate bearing samples. The presence of tamarugite has been suspected in samples PUG-18-08-B and -F based on the analysis of VNIR spectra. The assignments of the vibrations are given in Tables 5-8.

The absorbance patterns of the spectra in Figures 7a and 7b are characteristic of hydrous tetraborates and suggest that the samples PUG-18-06-A and PUG-18-06-B are dominated by those minerals. The mid-IR spectra of sample PUG-18-06-A almost exactly matches with that of borax. The complete peak assignments for samples PUG-18-06-A and -B are given in Table 5. For sample PUG-18-06-B, the spectrum shows a good match with that of tincalconite. In a KBr disk (used during FTIR analysis), borax may dehydrate to tincalconite and hence show the spectra for tincalconite (Farmer, 1974). One of the major differences between the mid-IR spectra of tincalconite and borax is the presence of three absorption peaks between  $1200\text{ cm}^{-1}$  and  $1300\text{ cm}^{-1}$  in borax which is not present in tincalconite (Farmer, 1974). As these absorptions can be clearly seen in the spectra for samples PUG-18-06-A and B, we can be certain that borax in these samples have not dehydrated to tincalconite during the FTIR analysis. In sample PUG-18-06-B, the presence of these band indicates that some amount of borax is also present in the sample. Along with that, the additional peaks (other than those already assigned to tincalconite) can also be attributed to the presence of borax in this sample. However, not all the peaks of borax could be distinguished in the spectrum of this sample and hence, have not been assigned as most of the absorptions are almost at identical positions for borax and tincalconite, as shown by the overlapping lines in Figure 7a. For both of these spectra, the band near  $1680\text{ cm}^{-1}$  represents H-O-H bending vibrations ( $\nu_{\text{H-O-H}}$ ). While borax causes two distinct peaks in the band for sample PUG-18-06-A, the spectra for sample PUG-18-06-B shows a broader absorption. The dominance of borax in sample PUG-18-06-A and tincalconite in sample PUG-18-06-B is indicated by the pattern of the absorption bands between  $2850$  and  $3550\text{ cm}^{-1}$  in their respective spectra that have been assigned to the O-H stretch vibrations ( $\nu_{\text{OH}}$ ) in the respective borates. The pattern is typical of borax for sample PUG-18-06-A and of tincalconite for sample PUG-18-06-B.

In mid-IR spectra, hydrous sulfates show absorptions near  $3500\text{ cm}^{-1}$  for the (O-H) stretch, between  $2000$ - $2500\text{ cm}^{-1}$  for combinations and overtones of the fundamental S-O vibrations, between  $1000$ - $1300\text{ cm}^{-1}$  for the fundamental  $\nu_3$  S-O stretching vibrations, and between  $600$ - $700\text{ cm}^{-1}$  for the fundamental  $\nu_4$  S-O bend vibrations. Other than these, M-O (M= Mg or Fe) stretching bands occur between  $400$ - $700\text{ cm}^{-1}$  for  $\text{FeO}_6$  vibrations in jarosite and  $\text{AlO}_2(\text{OH})_4$  vibrations in alunite (Farmer, 1974; Cloutis et al., 2006). One of the very few differences between the spectra of alunite and jarosite lies in the position of the absorption for the out-of-plane M-O-H bend, given as  $\nu_{\text{MOH}}$  in Tables 6 and 7, where M is Fe

or Al. For jarosite, this absorption lies near  $580\text{ cm}^{-1}$ , whereas for alunite it lies near  $600\text{ cm}^{-1}$ . Also, in alunite, there is a single absorption for Al-O-H in-plane bend [ $\text{MOH}$ ] at around  $1028\text{ cm}^{-1}$ , whereas there are two such absorptions for Fe-O-H in jarosite at around  $1009$  and  $1024\text{ cm}^{-1}$  (Bhattacharya et al., 2016).

The spectra of samples PUG-18-05-A and PUG-18-05-H (Figure 8a and 8b) show a stark resemblance to that of alunite, showing its characteristic pattern and absorptions over the entire range  $400\text{--}4000\text{ cm}^{-1}$ . The peak assignment for alunite is given in Table 6. The assignment of the absorption at  $683\text{ cm}^{-1}$  is debatable as it could be due to both  ${}_4\text{ S-O}$  bend and Al-O-OH vibrations in alunite. The presence of silica in these samples is suggested by the absorptions near  $790\text{ cm}^{-1}$ , characteristic of silica, due to the symmetric Si-O-Si stretching vibrations. FTIR spectra of silica show two absorptions near  $790\text{ cm}^{-1}$  and  $780\text{ cm}^{-1}$  for these vibrations, and an adjacent absorption at around  $695\text{ cm}^{-1}$  for asymmetric Si-O bending (Farmer, 1974). The asymmetric Si-O-Si stretching vibrations cause absorptions between  $950$  and  $1200\text{ cm}^{-1}$ , peaking at around  $1080\text{ cm}^{-1}$ , which are possibly overshadowed in these spectra by absorptions due to the  ${}_3\text{ S-O}$  stretching vibrations of alunite in this region. A weak absorption detected near  $458\text{ cm}^{-1}$  has also been attributed to the asymmetric Si-O bending mode of silica (Saikia et al. 2008).

Sample PUG-18-05-D has a complex mid-IR spectrum, mostly resembling the spectral patterns of sulfates, possibly containing both alunite and jarosite. For this sample, Figures 8a and 8b show the absorptions attributed to alunite and quartz, whereas Figures 9a and 9b show the absorptions attributed to jarosite. There might be some other sulfates present in the sample, however, it could not be identified. The jarosite-like pattern of three strong absorptions in the  $1000\text{--}1300\text{ cm}^{-1}$  range can be seen, however, with additional strong absorptions that could not be assigned to either jarosite or alunite. Some of the absorptions at the higher wavenumber end of this range, near  $1250\text{ cm}^{-1}$ , have been assigned to alunite, owing to the broad structural similarity of the spectra with that of alunite. Other characteristic peaks of both alunite and jarosite have also been identified and assigned accordingly, as given in Tables 6 and 7. A very weak absorption is seen near  $785\text{ cm}^{-1}$ , which has been attributed to quartz.

In sample PUG-18-08-A, the presence of quartz is more pronounced, with a strong double peak absorption at around  $790\text{ cm}^{-1}$ , a strong absorption at  $463\text{ cm}^{-1}$ , and the detectable peak at  $1087\text{ cm}^{-1}$  that can be attributed to the asymmetric Si-O-Si stretching vibration (Figure 10a). However, there is an overall broadening of peaks that may be due to the adsorption of atmospheric moisture but the exact reasons are unknown to the authors at present. This broadening might have caused the lack of identifiable absorptions at around  $1160\text{ cm}^{-1}$ . The overall pattern of the spectra, in addition to the absorption at  $1218\text{ cm}^{-1}$ , suggests the presence of alunite. The peak assignment is given in Tables 6 and 8.

In sample PUG-18-08-B, alunite is identified on the basis of its characteristic absorptions and spectral pattern (Figure 10a and 10b). The peak assignments

are given in Table 6. However, the fundamental  $\nu_3$  S-O stretch vibration absorption near  $1200\text{ cm}^{-1}$  is found at a lower wavenumber. More importantly, the additional peaks at around  $914, 940, 974, 991, 1097$  and  $1187\text{ cm}^{-1}$  suggest the presence of one more sulfate mineral. In addition to this, the distinct shape of the absorption due to  $\nu_1$  (OH) stretch near  $2900\text{--}3500\text{ cm}^{-1}$  prompts the authors to suspect the presence of double sulfate hydrates, Na-alum or its dehydration product- tamarugite, in this sample (Figure 10b). At present, on the basis of FTIR spectra alone, it cannot be ascertained whether it is Na-alum or tamarugite. The VNIR spectrum of this sample indicates the presence of tamarugite, hence we are inclined to suggest that the double sulfate hydrate present here is tamarugite. As the complete band assignment for the mid-IR spectra of tamarugite is not available in the literature published to date, the authors have only partially assigned the peaks, on the basis of band assignments in double sulfate hydrates (Barashkov et al., 2004). The absorption near  $1680\text{ cm}^{-1}$  in this case can be attributed to the  $\nu_2$  (HOH) bend vibrations in tamarugite. The tamarugite FTIR spectra given in Chukanov (2013) and in the spectral library website [www.spectrabase.com](http://www.spectrabase.com) have been used for reference. The absorption peaks at  $2971$  and  $2496\text{ cm}^{-1}$  have been assigned to O-H stretch vibrations ( $\nu_1$  (OH)), while the peak at  $1184\text{ cm}^{-1}$  has been assigned to the fundamental  $\nu_3$  S-O stretching vibration. Minor amounts of quartz might also be present in this sample, as indicated by the weak absorptions near  $800\text{ cm}^{-1}$ .

The mid-IR spectral pattern of sample PUG-18-08-F is overall dominated by alunite, the characteristic absorptions of quartz are also present at around  $1088, 792, 779, 521$  and  $458\text{ cm}^{-1}$  (Figure 10a). The additional peaks at  $1103, 1093, 1182, 916, 943, 957$  and  $990\text{ cm}^{-1}$  again suggest the presence of one more sulfate mineral. This is further reinforced by the unique shape of the absorption near  $2400\text{--}3500\text{ cm}^{-1}$  due to  $\nu_1$  OH stretch (Figure 10). As in the case of sample PUG-18-08-B, this mineral is suspected to be tamarugite. The peak assignments are given in Tables 5, 6 and 8. Similar to the case of sample PUG-18-08-B, the absorption near  $1680\text{ cm}^{-1}$  can be attributed to the H-O-H bend vibrations ( $\nu_2$  HOH) in tamarugite. Additionally, for both these samples, absorption peaks around  $930\text{ cm}^{-1}$  might represent  $\text{H}_2\text{O}$  libration vibrations in tamarugite.

The mid-IR spectra of sample PUG-18-08-E may represent a mixture of jarosite and quartz (Figures 8a and 8b). The typical absorptions for jarosite at  $1013$  and  $579\text{ cm}^{-1}$ , with the overall similarity in the spectral pattern helps in confirming the presence of jarosite in this sample. Presence of adsorbed atmospheric moisture might have led to the broadened peak for the  $\nu_1$  (O-H) stretch. Presence of quartz is ascertained by the familiar peaks at  $786, 763$  and  $693\text{ cm}^{-1}$ , along with its other major absorptions at  $1080, 523$  and  $460\text{ cm}^{-1}$ . The peak assignments are given in Tables 7 and 8. A single peak near  $1380\text{ cm}^{-1}$  is present in some of the spectra that might be attributed to a potassium nitrate admixture.

## 1. X-Ray Diffraction

Spectroscopic analysis of the samples collected from the valley fill material of Puga geothermal area and the nearby road-cut section have confirmed the pres-



ence of hydrous sulfate minerals along with sodium borates. Borax and tinalconite are the main borate phases identified in the valley fill material, and alunite is the most dominant hydrous sulfate mineral. The presence of jarosite, copiapite, tamarugite, gypsum and native sulfur has also been substantiated using spectroscopic analysis. X-ray diffraction was used as a confirmatory tool to establish the mineralogical identification suggested by spectroscopic studies. The XRD spectrum of sample PUG-18-06-A is dominated by peaks associated with borax along with some characteristic tinalconite peaks, and for sample B the strongest peak is of halite, indicating the presence of halite in the sample along with a major proportion of tinalconite and some borax (Figure 11a and b). Borax has been identified in PUG-18-06-A and B by comparing the d values of 2.83, 2.56, 4.84, 5.68, 3.93, 2.92, 5.18, 1.99, 7.14 and 5.95 Å with the previously assigned values by Levy and Lisensky, 1978. The characteristic diffraction peaks of tinalconite occur at 2.93, 4.39, 3.45, 8.78 and 4.70 Å (Luck and Wang G, 2002), and by comparing these values we have confirmed the presence of tinalconite (2.91, 4.35, 3.43, 8.63 and 40.66 Å) in both the samples collected from the valley fill material (PUG-18-06-A and B). Presence of alunite has been established in samples PUG-18-05-A and D by matching the characteristic d values of 2.97, 4.92, 2.28 and 3.47 Å with that of published diffraction data of alunite (Zema et al., 2012) (Figure 11c and d). X-ray diffraction spectra of jarosite shows characteristic peaks at 3.07, 3.10, 5.08, 1.82, 2.28, 1.97 and 5.93 Å (Mills et al., 2013) which are matched with the d values (3.04, 3.23, 5.01, 1.81 and 5.62 Å) of the diffraction spectra of samples PUG-18-05-D and PUG-18-08-E to confirm the presence of jarosite in these samples (Figures 11d and 12a). X-ray diffraction spectra of the sample PUG-18-08-C shows major peak positions at 3.49, 4.46, 2.84, 2.32, 2.20, 8.99, 1.75, 1.87, 2.18, 8.19, 2.47, 1.65, 3.07 and 2.08 Å. Among these, 3.49, 2.84, 2.32, 2.20, 1.75 and 1.87 Å peaks are attributable to anhydrite (Bezou et al., 1995) (Figure 12b). Peaks at 4.46 and 13.22 Å match with those of alunogen (Fang and Robinson, 1976). All the remaining peaks match with ICDD-PDF2 (2016) crystallographic database copiapite (sample ID 00-035-0583). Peaks of sulfur are found at 3.87, 3.09 and 2.88 Å in the XRD spectra of PUG-18-08-E and matched with published diffraction data of sulfur (Crichton et al., 2001) (Figure 12a). XRD spectra of sample number PUG-18-08-A shows prominent peak positions at 7.52, 5.68, 4.92, 4.03, 3.89, 3.83, 3.42, 3.31, 3.20, 2.98, 2.84, 2.28 and 1.90 Å (Figure 12c). Among these, peaks at 4.92, 2.98 and 2.28 Å are attributed to alunite after comparing them with published diffraction data of alunite (Zema et al., 2012). All the remaining peaks are characteristic of native sulfur as described by Crichton et al. (2001) (Figure 12c). Presence of tamarugite has been confirmed using the powder diffraction technique in sample number PUG-18-08-F. This mineral shows characteristic X-ray diffraction peaks at 4.23, 3.97, 3.66, 4.24, 3.64 and 4.93 Å (Mereiter, 2013). Major peak positions identified for the sample PUG-18-08-F are at 4.94, 4.22, 3.96, 3.64, 3.49, 3.34, 3.17 and 2.98 Å. Comparing these peak positions with published literature data by Zema et al. (2012) and Mereiter (2013) confirms the presence of alunite and tamarugite in sample PUG-18-08-F (Figure 12d). Thus, in concurrence with the spectroscopic studies, the pres-

ence of hydrous sulfates is also established using X-ray diffraction in this unique evaporite setting associated with a boratic hot spring.

## 1. Discussion

### (a) Summary of results from spectroscopy and XRD Analyses

Naturally occurring tincalconite, a dehydrated Na-borate mineral, has been identified from the valley fill material of the Puga geothermal area along with borax by *in-situ* VNIR characterization. Although the overall VNIR spectral characteristics show good match with library tincalconite spectra, broadening and shifting of absorption features suggests the presence of an admixture of other evaporates with borax in sample PUG-18-06-B (Figure 3). This was confirmed by FTIR and XRD analysis of this sample. Garret (1998) reported the borate mineral kernite in the lower part of the valley fill material, which gets converted to borax by water absorption during the rainy season, and subsequently changes to tincalconite by dehydration, thus minute occurrences of borax in the sample are expected. FTIR data confirm the presence of borax in the sample, whereas XRD data also show a prominent halite signature along with borax and tincalconite. We have not found kernite in our samples as we have mainly sampled the upper portion of the loose valley fill material. VNIR spectra of halite are more or less featureless, except for two absorptions at about 1400 and 1900 nm (Kokaly et al., 2017), and therefore, in this case, the spectral signature of halite is masked by the strong absorption bands at 1400 and 1900 nm found in the reflectance spectra of tincalconite. On the other hand, the powder X-ray diffraction technique proves to be helpful in the identification of halite as the mineral shows better developed crystal faces than Na-borates.

The major sulfate minerals identified from the mound and road cut sections are alunite, jarosite, gypsum, copiapite and tamarugite, along with native sulfur. VNIR spectra of the samples PUG-18-05-A, -D, -G and -H show absorption features related to alunite, as shown in Figures 4a and b (see Tables 3 and 4). However, these samples also contain variable amounts of jarosite as manifested by absorptions near 430, 500 and 1000 nm due to the electronic transitions of  $\text{Fe}^{3+}$  in the crystal lattice of the mineral. Sample PUG-18-05-D shows a complex FTIR spectrum (Figure 8a and b) which may possibly be related to the presence of more than one type of sulfate species in the sample. This behaviour is not apparent in the VNIR spectrum of that particular sample, and most likely caused by the difference in sample preparation methods before data collection. VNIR data are collected in the field using a contact probe (basically, a very small field of view spectrometer with an artificial light source) which can detect spectral signatures of minerals residing on the outer surface of the analysed rock specimen, particularly at a localized position on the outer surface. On the other hand, FTIR and XRD data are obtained from powders of samples that are ground and, therefore, effectively homogenized and are therefore likely to record signatures of all the constituent minerals in the sample, and not just those from the outer surface. Also, the FTIR spectrometer is not a point spectrometer

and collect transmitted spectral signatures from the sample in the Mid-Infrared domain. Similarly, for XRD data collection, the entire  $2\theta$  range is scanned.

Sample VNIR spectra of tamarugite are not available in any VNIR spectral library so far, and therefore, the published spectrum of tamarugite by Mougénot (1991) was used to correlate the band absorption positions of the spectrum of sample PUG-18-08-F (Figure 6a). However, the spectrum published by Mougénot (1991) is from a sample which is a mixture of tamarugite and natroalunite. XRD analysis further confirmed the presence of a major amount of tamarugite in sample PUG-18-08-B along with minor amounts of alunite and quartz. FTIR results suggest the presence of tamarugite in sample PUG-18-08-B as well as PUG-18-08-F, while the VNIR results point to the presence of native sulfur in that sample along with a minor amount of alunite.

In this study, we also report the first positive identification of copiapite from Ladakh. VNIR spectra of sample PUG-18-08-C shows perfect resemblance with library spectra of copiapite (Figure 5a). However, XRD analysis of the same sample also shows prominent diffraction peaks of anhydrite and alunogen, which can be attributed to the differences in sample preparation methods (grinding and homogenization for XRD). This can also be explained by the fact that anhydrite and alunogen have typically featureless VNIR spectra, unlike copiapite.

A summary of the different borate and sulfate minerals detected in the samples used in this study, along with the specific techniques used for their identification, has been provided in Table 9.

## 1. Implications

### 5.2.1 The Puga valley as a martian analog locality – climate perspective

Primarily on account of its diverse and extreme environment, the region of Ladakh has recently become a focus of planetary science research in India, as a terrestrial analog from the viewpoint of both geological and astrobiological investigations (Shukla et al., 2017; Das et al., 2017; Sinha et al., 2018; Pandey et al., 2019). The debris-flow landforms preserved in the gullies and alluvial fans of the Ladakh Himalaya have already been suggested as geomorphological analogs to the deposits preserved over the equator-facing slopes of the Domoni and Maricourt Craters on Mars (Sinha et al., 2018). The present arid and cold climate of this region in a terrestrial oxidising setting has been speculated to be similar to the climatic conditions that existed on Mars for more than 100 million years, around the Noachian-Hesperian boundary (Wordsworth et al., 2021; Hurowitz et al., 2010, 2017; Lanza et al., 2016). Quay et al. (2020) combined topographic analyses with standard hydrological balances from some valley network-fed paleolakes on early Mars to calculate time-integrated precipitation during a given run-off episode for each basin. The computed Aridity Index, a measure of the aridity of a climate given by the ratio of precipitation to potential evapo-transpiration, suggests that some regions on Mars may once have been at least as humid as some present-day semi-arid terrestrial environments (Quay et al., 2020). The oxidation state of the present terrestrial

surface is not comparable with that of Mars, which at present has a thin, CO<sub>2</sub>-dominated (~6 mbar) atmosphere. However, redox fluctuations in the martian atmosphere may have led to periodic changes; the estimated oxidation state of the martian surface at the Noachian-Hesperian transition may have been as high as 0.05 bars, which is lower than that in the present-day terrestrial atmosphere (0.21 bar), nevertheless, capable of explaining the formation of hematite and manganese oxide deposits (Wordsworth et al., 2021). Thus, the climatic setting of present-day Ladakh may be considered comparable, though obviously not identical, to the martian surface at specific times in the geological history of the Red Planet, when more humid and oxidizing conditions than at present, might once have prevailed.

### *5.2.2 The Puga valley as a martian hot spring analog locality*

The results of this study demonstrate that the Puga geothermal area preserves an ensemble of hot springs associated with assemblages of hydrous sulfates, native sulfur and Na-borates along with algal mats, on a basement of granitic gneiss (the Puga gneiss). The hydrous sulfates at these locations include alunite, jarosite, copiapite, tamarugite and gypsum along with opaline silica; with the exception of tamarugite, all the other sulfate species have also been detected on the surface of Mars (e.g. Christensen et al., 2004; Gendrin et al., 2005; Murchie et al., 2009a, 2009b; Farrand et al., 2009; Milliken et al., 2008; Weitz et al., 2011; Thollot et al., 2012; Ehlmann and Mustard, 2012; Farrand et al., 2014; Vaniman et al., 2014; L  veill   et al., 2015; Ehlmann et al., 2016). The conditions required for the formation of jarosite include oxidizing, acidic environments and water scarcity (Elwood Madden et al., 2004). The water of the hot springs and the Puga nala show neutral to slightly alkaline pH values at present but the presence of sulfate species (namely, gypsum) and native sulfur in the region suggest a wide range of Eh-pH stability fields (Shukla et al., 2017; Elwood Madden et al., 2004). The identification of alunite, jarosite and copiapite indicate the presence of acidic water (low pH) in this region for at least some length of time in the geological past (Nordstrom and Alpers, 1999; Elwood Madden et al. 2004 and Elhman et al. 2016). Also, isotopic studies suggest a more inorganic than organic source for this sulfur (Shukla et al., 2017). The most probable source of the sulfur may have been the shallow subsurface melt reservoirs that have been suspected to exist below this part of the NW Himalaya (e.g. Hazarika et al., 2014). Specifically, below the Puga geothermal region, Harinarayana et al. (2004, 2006) identified a low resistivity layer using magneto-telluric (MT) studies that extended from the surface to a depth of 400 m; this was separated from another deeper (> 1.5 km) conductive zone by an intermediate resistive horizon. The shallow reservoir was expected to host the geothermal water while the deeper reservoir was suggested to correspond to shallow magma chambers. The presence of such shallow subsurface magmatic bodies is supported by the chemistry of the geothermal water and sediments, which reportedly contain chlorine, fluorine, boron, SiO<sub>2</sub>, sodium and total dissolved solids, with low concentration of magnesium coupled with high enrichment of Li, Rb and Cs (Chowdhury et al., 1974). The abundance of sulfur in the area was also considered to be consistent

with a magmatic source for the geothermal water (Harinarayana et al., 2006). This would suggest that the ultimate heat source of the Puga geothermal water are shallow partial melt pockets in the subsurface. It may thus be argued that apart from helping in constraining past water-rock interaction and the detection of fossilized hot springs on Mars, the Puga geothermal area may also indicate a comparable setting for the origin of sulfates, particularly jarosite and alunite, associated with suspected hot spring localities on the martian surface.

In addition to the hydrous sulfates, the Puga valley contains two other mineral groups that are of importance in the martian context – halites and opaline silica. In this study, the presence of halite in the valley-fill material of the Puga hot spring deposits was confirmed from XRD data, as VNIR and FTIR spectra of halite are relatively featureless compared to other associated minerals. On Mars, chloride salts have been identified with the help of Mars Odyssey’s Thermal Emission Imaging System (THEMIS) and Mars Global Surveyor’s (MGS) Thermal Emission Spectrometer (TES) instruments, and their presence has been explained by either evaporation of hydrothermal fluids or ponding (Osterloo et al., 2008, 2010; Hynke et al., 2015; Leask and Ehlmann, 2021). Presence of halite not only indicates an evaporitic set-up, but also provides evidence for multiple cycles of hydration and dehydration, which can help stabilize RNA-like polymers from 5'-phosphate mononucleotides (Rajamani et al., 2008; Da Silva et al., 2015). Opaline silica is also detected in the VNIR spectra of Puga samples, providing additional evidence for a hydrothermal signature. On Mars, remote detection of opaline silica in the Valles Marineris region has been made by Milliken et al. (2008) using the Mars Reconnaissance Orbiter (MRO) Compact Reconnaissance Imaging Spectrometer for Mars (CRISM). This is also consistent with the findings of the Spirit rover in Meridiani Planum (Glotch et al., 2006) and near the ‘Home Plate’ area in the inner basin of the Columbia Hills of Gusev crater (Squyres et al., 2008; Ruff et al., 2011, 2020; Ruff & Farmer, 2016). In the latter case, the silica appears as nodular masses and is thought to be the product of past volcanic hydrothermal activity (Squyres et al., 2008). Using the CRISM data, hydrated silica outcrops have been identified at Mawrth Vallis (Bishop et al., 2008; Mustard et al., 2008), near Nili Fossae (Ehlmann et al. 2009), at lower Mount Sharp within Gale crater (Fraeman et al., 2016), in the Nili Patera caldera on the Syrtis Major volcanic complex (Skok et al., 2010), and also near Antoniyadi Crater (Smith & Bandfield, 2012). The presence of hydrated silica has also been reported in various settings from Gale crater by the Curiosity Rover (Morris et al., 2016; Yen et al., 2017 and Ruff & Farmer, 2016). Sun and Milliken (2018, 2020) characterized the opaline silica-rich localities on Mars in order to facilitate identification of hot spring environments on the Red planet with high bio-signature preservation potential. They have shown that presence of the crystalline variety of opaline silica (opal-CT) points to hot spring environments while only the amorphous variety (opal-A) occurs in fumarolic settings. As in the case of many martian occurrences, the Puga area contains opal-A along with calcite or Fe/Mg clays indicating neutral to alkaline nature of the hot spring water. While not unambiguous, this association

may provide analogs for possible martian hot spring localities associated with possible biosignatures (Sun and Milliken, 2020).

Many different hot spring settings on Earth have been characterized and established as martian analogs, for example the Mammoth Hot Springs complex of Yellowstone National Park, the Taupo Volcanic Zone Jemez Springs, and the El Tatio in Chile. The major minerals associated with these hot spring deposits are mainly calcite, various hydrous sulfates, opaline silica and halite. A number of acidic and alkaline hot springs can be found in the Yellowstone National Park. The hot spring water dissolves the rhyolitic bedrock to form the opaline sinters (e.g., Walter and Des Marais, 1993; Cady and Farmer, 1996; Guidry and Chafetz, 2003). In the case of the Taupo hot spring, the country rock of dominantly rhyolitic composition interacts with the alkali-chloride and acid-sulfate water to form sinter precipitates (e.g., Wilson et al., 1995). The major minerals in these hydrothermal deposits are chlorite, calcite, pyrite, illite, detrital quartz, kaolinite, alunite, alunogen, hematite and jarosite (Herdianita et al., 2000a; Rodgers et al., 2002; Lynne and Campbell, 2003, 2004). The El Tatio hot spring, which most resembles the Puga hot spring locality in terms of its high elevation ( $\sim 4300$  m), low precipitation rate ( $<100$  mm per year), high mean annual evaporation rate (132 mm), common diurnal freeze-thaw and extremely high UV irradiance, has been characterized as a martian analog (Nicolaou et al., 2014; Cabrol et al. 2014). The dominant mineralogy here has been identified as halite and opaline silica.

The two apparently discrepant aspects with respect to Puga as a martian analog locality are: firstly, the hot springs at Puga are hosted within granitic bodies, unlike the dominantly basaltic crust on Mars, and secondly, the lack of any reporting of tamarugite as yet from the martian surface. Although felsic rocks have recently been identified on the surface of Mars (Schmidt et al., 2014; Santos et al., 2015; Cousin et al., 2017), the host granitic rocks in the Puga area do not necessarily render it an inappropriate analog locality, as the hot spring mineralogy is not considered to be a product of interaction with the host rock. On the other hand, the presence of tamarugite in the mineralogical association in the Puga geothermal field may simply indicate the possibility of this mineral being subsequently discovered along with other sulfates on the martian surface.

Thus, the mineralogical association documented in the Puga hot spring, with a hydrous sulfate mineral assemblage comprising alunite, jarosite and copiapite (along with tamarugite), halite and opaline silica, can also be considered as a potential mineralogical analog for ancient Mars. A similar, hydrous sulfate-bearing mineralogical analog has been previously reported from Kachchh in western India (Bhattacharya et al., 2016), but the sulfate occurrences at that locality were devoid of any hydrothermal connection. Hot springs provide an additional energy source – heat – that might have important astrobiological implications, providing a potential habitat for life to originate in seemingly hostile environments.

### *5.2.3 Significance of hot-spring associated borate occurrences*

The presence of borates in association with sulfates around the hot springs of the Puga valley adds an exciting astrobiological dimension to the potential of this analog locality. Recent studies suggest that earliest life may more likely have originated in ‘warm little ponds (WLP)’ on continents, rather than hydrothermal vents in the deep ocean (Pearce et al., 2017). ‘Wet-dry’ cycles, such as those that might prevail in hydrothermal continental environments, favour the synthesis of phosphodiester bonds by the chemical potential of fluctuating hydrous and anhydrous conditions (Rajamani et al., 2008; Da Silva et al., 2015). Interestingly, terrestrial evidence of the earliest life forms has been reported from fossilized hydrothermal localities in Archean terranes, such as the 3.48 Ga Dresser Formation in the Pilbara Craton (Djokic et al., 2017), and the 3.5-3.3 Ga cherts of the Onverwacht Group, South Africa (Westall et al., 2001).

The prebiotic origin of larger organic molecules such as ribose involves both compound synthesis and its stability. Gilbert (1986) conceived an RNA world on early Earth where RNA molecules were capable of catalysing their own synthesis, without involving proteins. Ribose and other sister pentoses are believed to have been initially produced under alkaline conditions from formaldehyde and glycolaldehyde, simple organic molecules known to exist in interstellar space (Hollis et al., 2001). However, several experimental studies have suggested that ribose would be unstable under these conditions even if synthesized, thus precluding the accumulation of pentoses (Larralde et al., 1995; Shapiro, 1988). Subsequently, Ricardo et al. (2004) demonstrated that the presence of borates facilitates stabilization of cyclic, less reactive forms of the pentoses, and are also compatible with their synthesis. The importance of borates in providing thermostability to ribose under acidic conditions, and glucose under basic conditions was confirmed by Scorei and Cimpoiu (2006), while Saladino et al. (2011) showed that formamide oligomerizes in the presence of borate minerals yielding nucleobases and biogenic carboxylic acids. Thus, the presence of boron as an element should be taken into consideration when searching for evidence of early life (Benner et al., 2010), as borates constitute important reagents that may have contributed to the origin of prebiotic structures (Boutlerow, 1861; Ricardo et al., 2004; Kim and Benner, 2010; Scorei, 2012; Neveu et al., 2013; Furukawa et al., 2015). The association of borates with hot springs, therefore, may have been instrumental in the evolution of life on Earth.

#### *5.2.4 Hot springs, borates and life on Mars*

As has been discussed above, hot springs may have great significance for exploration of extra-terrestrial life forms. Identification of ancient hot spring localities on other planets must necessarily be based on criteria used to detect present and past hot springs environments on Earth. The primary criterion is mineralogical: for instance, a key mineral that is common in almost all hot spring deposits on earth is opaline silica, although not all terrestrial opal is hydrothermal in origin (e.g. McLennan, 2003; Siever, 1962). Opaline silica associated with jarosite, alunite and kaolinite (Sun and Milliken, 2020) is commonly found in many fumarolic and some hot spring deposits and has also been identified around the

Puga hot springs. This association is also found in abundance on the martian surface (Squyres et al., 2008; Ruff and Farmer, 2016). An additional commonality of the Puga valley with the martian localities is the presence of chloride salts, which on the martian surface have been explained by either evaporation of hydrothermal fluid or ponding (Osterloo et al., 2008, 2010; Hynek et al., 2015). Thus, the coexistence of opaline silica, halite and hydrous sulfates in the Puga valley makes this region an appropriate analog site to Mars, particularly in our search for extraterrestrial life on that planet. The co-occurrence of microfossils of sulfogenic bacteria as well as other nanofossils and present-day algal mats in association with the borates, opaline silica, some sulfates and native sulfur around the hot springs in Puga further strengthens the possibility that such hydrothermal vents are favourable pockets for sustaining life in an environment that is eventually drying up, as was the case for ancient Mars (Ghosh et al., 2012; Wächtershäuser, 1998). All these minerals, except for borates, have been previously identified on the surface on Mars. Thus, this study will aid the detection of similar sites on Mars with high biosignature preservation potential.

Borates could also exist on the martian surface near hydrothermal vents. Although neither tinalconite nor borax have yet been identified on Mars, the recent detections of elemental boron in the martian meteorite MIL090030 (Stephenson et al., 2013), and in calcium sulfate-filled fractures in Gale Crater (Gasda et al., 2017) suggest that borates might also occur on Mars, and represent favourable locales for finding signatures of extant life forms. As seen in the case of the Puga hot springs, as well as many other hydrothermal vents, these environments are suitable for the growth of extremophiles, or even algal mats. Microfossils have also been detected around the Puga hot springs by Ghosh et al. (2012). In the spatial context, the borates are mostly found in recent valley fills around the hydrothermal vents in Puga, indicating that they are precipitated from the hot spring water itself. Steller et al. (2019) have used isotopic data to construe a multi-stage boron fractionation process, identifying the underlying granitic intrusions as the source of boron which, after interacting with hydrothermal fluid, got more fractionated.

We suggest that the systematic characterization and correlation of spectroscopic and mineralogical study on this Na-borate and hydrous sulfate-bearing hot spring deposit can help design sensors that can be deployed in future planetary missions, so that the specific absorption bands can be addressed and focused precisely. The major absorption bands occur in VNIR domain for Na-borate and hydrous sulfate are systematically described in section 4.1 and listed in tables 1 to 4. The major absorption features due to  $\text{Fe}^{3+}$  transition and various overtones and combination of B-O, S-O,  $\text{H}_2\text{O}$  and OH fundamentals occur in  $\sim 400$ ,  $\sim 500$ ,  $\sim 900$  to  $\sim 1000$ ,  $\sim 1400$ ,  $\sim 1700$ ,  $\sim 1900$  and  $\sim 2100$  to  $\sim 2500$  nm region (table 1 – 4). To identify the Na-borates and hydrous sulfate minerals, all these bands (or at least the majority of them) should be covered with highest possible resolution by the hyperspectral instrument to be deployed on board future orbiter missions. Future rover-based hyperspectral instruments will cover the complete spectral domain in the VNIR region. For example, the SuperCam instrument of



Mars 2020 rover, which have 400–900 nm and 1300–2600 nm spectral windows with more than 248 bands can easily be used to identify these minerals (Clegg et al., 2014; Maurice et al., 2015; Wiens et al., 2016). Thus, in future, more analogous minerals will need to be characterized from different terrestrial settings for the proper interpretation of the planetary spectroscopic data and subsequent identification of these minerals on Mars. This would help us to understand and compare the physical, chemical and biotic environments and related processes of the two neighbouring planets.

## Conclusions

The present study reports the occurrence and detailed spectral characterisation in the VNIR and Mid-IR range of the hydrous sulfates - jarosite, alunite, copiapite and tamarugite, and hydrated borates like borax and tincalconite, along with gypsum, native sulfur and opaline silica - in association with the hot springs of the Puga geothermal field area in the Union Territory of Ladakh, India. The assemblage reported here can be used as a mineralogical analog to the sulfate minerals detected on the martian surface. The study also indicates the possibility of detecting borates on Mars. Along with the borates and hydrated sulfates (which are found on Mars), we have detected tamarugite (a hydrous sulfate, yet to be found on Mars) for first time from Indian subcontinent. The scientific significance of such a mineralogical analog lies in its potential to help in the detection of ancient hot springs that might have acted as favourable locales for sustaining life forms on the martian surface, had any existed there. Subsequent studies on Mars focusing on astrobiological aspects should also explore the possibility of detecting borates on Mars, which may ultimately help in identifying signatures of early life on the Red Planet.

## Acknowledgements

We thank Shri Nilesh Desai, Director, Space Applications Centre (ISRO), Ahmedabad and Dr. I. M. Bahuguna, Deputy Director, Earth, Ocean, Atmosphere, Planetary Sciences and Application Area (EPSA), Space Applications Centre (ISRO), Ahmedabad for their constant support and encouragement. Dr. Bimal K. Bhattacharya, Group Director, Biological & Planetary Science and Applications Group and Dr A. S. Arya, Head, Planetary Science Division, Space Applications Centre (ISRO), Ahmedabad are duly acknowledged for their critical comments and suggestions on the manuscript. S. Sarkar thanks Department of Science and Technology, Government of India for funding his doctoral research through INSPIRE scheme (Fellowship Registration Number: IF170664). H. Moitra acknowledges the financial support provided by CSIR, India through the Shyama Prasad Mukherjee Fellowship scheme (Award letter no. SPM-06/081(0256)/2017-EMR-1). Authors would also like to thankfully acknowledge the financial support provided by SAC-ISRO, Department of Space, Government of India under Technology Development Program (TDP R&D, Project #A105). VNIR, FTIR as well as XRD data of samples used for this study can be accessed from Zenodo (Sarkar et al., 2020, 2022).

## References

- Anderson, J. H., Jr., & Wickersheim K. A. (1964). Near infrared characterization of water and hydroxyl groups on silica surfaces, *Surface Science*, 2, 252–260. 10.1016/0039-6028(64)90064-0.
- Andrews-Hanna, J. C., & Lewis, K. W. (2011). Early Mars hydrology: 2. Hydrological evolution in the Noachian and Hesperian epochs. *Journal of Geophysical Research: Planets*, 116(E2). 10.1029/2009JE003485.
- Arvidson, R. E., & Catalano, J. G. (2018). Martian Habitability as Inferred From Landed Mission Observations. In *From Habitability to Life on Mars* (pp. 77-126). Elsevier. 10.1016/B978-0-12-809935-3.00004-9
- Baron, D., & Palmer, C. D. (1996). Solubility of jarosite at 4–35 C. *Geochimica et Cosmochimica Acta*, 60(2), 185-195. [https://doi.org/10.1016/0016-7037\(95\)00392-4](https://doi.org/10.1016/0016-7037(95)00392-4)
- Benner, S. A., Kim, H. J., Kim, M. J., & Ricardo, A. (2010). Planetary organic chemistry and the origins of biomolecules. *Cold Spring Harbor perspectives in biology*, 2(7), a003467. 10.1101/cshperspect.a003467
- Bezou, C., Nonat, A., Mutin, J. C., Christensen, A. N., & Lehmann, M. S. (1995). Investigation of the crystal structure of  $\text{-CaSO}_4$ ,  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ , and  $\text{CaSO}_0 \cdot 0.6\text{H}_2\text{O}$  by powder diffraction methods. *Journal of Solid State Chemistry*, 117(1), 165-176. 10.1006/jssc.1995.1260
- Bhattacharya, S., Mitra, S., Gupta, S., Jain, N., Chauhan, P., & Parthasarathy, G. (2016). Jarosite occurrence in the Deccan Volcanic Province of Kachchh, western India: Spectroscopic studies on a Martian analog locality. *Journal of Geophysical Research: Planets*, 121(3), 402-431. 10.1002/2015JE004949
- Bibring, J. P., Langevin, Y., Mustard, J. F., Poulet, F., Arvidson, R., Gendrin, A., et. Al. (2006). Global mineralogical and aqueous Mars history derived from OMEGA/Mars Express data. *Science*, 312(5772), 400-404. 10.1126/science.1122659
- Bigham, J. M., Schwertmann, U., Traina, S. J., Winland, R. L., & Wolf, M. (1996). Schwertmannite and the chemical modeling of iron in acid sulfate waters. *Geochimica et Cosmochimica Acta*, 60(12), 2111-2121. 10.1016/0016-7037(96)00091-9
- Bio-Rad Laboratories, Inc. SpecraBase; <http://spectrabase.com/> (accessed Aug 25, 2019)
- Bishop, J. L., & Murad, E. (2005). The visible and infrared spectral properties of jarosite and alunite. *American Mineralogist*, 90, 1100–1107. 10.2138/am.2005.1700
- Bishop, J. L., Noe Dobrea, E. Z., McKeown, N. K., Parente, M., Ehlmann, B. L., Michalski, J. R. et al., (2008). Phyllosilicate Diversity and Past Aqueous Activity Revealed at Mawrth Vallis, Mars, *Science*, 321. doi: 10.1126/science.1159699

- Bishop, J. L., Pieters, C. M., & Edwards, J. O. (1994). Infrared spectroscopic analyses on the nature of water in montmorillonite, *Clays and Clay Minerals*, 42, 702–716. 10.1346/CCMN.1994.0420606.
- Boutlerow, M. A. (1861). Formation synthétique d’une substance sucrée. *CR Academy of Science*, 53, 145–147.
- Burns, R. G. (1987). Ferric sulfates on Mars. *Journal of Geophysical Research: Solid Earth*, 92(B4), E570-E574.
- Cariati, F., Erre, L., Micera, G., Piu, P., & Gessa, C. (1981). Water molecules and hydroxyl groups in montmorillonites as studied by near infrared spectroscopy. *Clays and Clay Minerals*, 29(2), 157-159.
- Cariati, F., Erre, L., Micera, G., Piu, P., & Gessa, C. (1983). Effects of layer charge on the near-infrared spectra of water molecules in smectites and vermiculites. *Clays and Clay Minerals*, 31(6), 447-449.
- Cariati, F., Erre, L., Micera, G., Piu, P., & Gessa, C. (1983). Polarization of water molecules in phyllosilicates in relation to exchange cations as studied by near infrared spectroscopy. *Clays and Clay Minerals*, 31(2), 155-157.
- Chowdhury, A. N., Handa, B. K., & Das A. K. (1974). High lithium, water rubidium and cesium contents of thermal spring sediments and borax deposits in Puga valley, Kashmir, India. *Geochemical Journal*, 8, 61 – 65.
- Christensen, P. R., Wyatt, M. B., Glotch, T. D., Rogers, A. D., Anwar, S., Arvidson, R. E., et al. (2004). Mineralogy at Meridiani Planum from the Mini-TES experiment on the Opportunity Rover. *Science*, 306(5702), 1733-1739. 10.1126/science.1104909.
- Chukanov, N. V. (2013). *Infrared spectra of mineral species: extended library*. Springer Science & Business Media. 10.1007/978-94-007-7128-4
- Clark, R. N. (1999). Spectroscopy of rocks and minerals, and principles of spectroscopy. *Manual of remote sensing*, 3(3-58), 2-2.
- Clark, R. N., King, T. V., Klejwa, M., Swayze, G. A., & Vergo, N. (1990). High spectral resolution reflectance spectroscopy of minerals. *Journal of Geophysical Research: Solid Earth*, 95(B8), 12653-12680. 10.1029/JB095iB08p12653
- Clegg, S. M., Wiens, R. C., Maurice, S., Gasnault, O., Forni, O., Sharma, S. K., et al. (2014). Remote geochemical and mineralogical analysis with SuperCam on the Mars 2020 Rover and on Earth. In American Geophysical Union, Fall Meeting. Abstract #P11A-3753
- Cloutis, E. A., Hawthorne, F. C., Mertzman, S. A., Krenn, K., Craig, S. A., Marcino, D. et al. (2006). Detection and discrimination of sulfate minerals using reflectance spectroscopy. *Icarus*, 184(1), 121–157. 10.1016/j.icarus.2006.04.003
- Cloutis, E., Berg, B., Mann, P., & Applin, D. (2016). Reflectance spectroscopy of low atomic weight and Na-rich minerals: Borates, hydroxides, nitrates, nitrites,

- and peroxides. *Icarus*, 264, 20–36. 10.1016/j.icarus.2015.08.026
- Cockell, Charles S., T. Bush, C. Bryce, S. Direito, M. Fox-Powell, J. P. Harrison, & H. Lammer., et al. (2016). "Habitability: a review." *Astrobiology*, 16(1), 89–117. 10.1089/ast.2015.1295
- Cousin, A., Sautter, V., Payré, V., Forni, O., Mangold, N., Gasnault, O. et al., (2017). Classification of igneous rocks analyzed by ChemCam at Gale crater, Mars, *Icarus*, 288, 265–283. <http://dx.doi.org/10.1016/j.icarus.2017.01.014>
- Crichton, W. A., Vaughan, G. B. M., & Mezouar, M. (2001). In situ structure solution of helical sulphur at 3GPa and 400°C. *Zeitschrift für Kristallographie-Crystalline Materials*, 216(8), 417–419. 10.1524/zkri.216.8.417.20360
- Crowley, J. K. (1991). Visible and near-infrared (0.4–2.5  $\mu\text{m}$ ) reflectance spectra of playa evaporite minerals. *Journal of Geophysical Research*, 96, 16231–16240.
- Cunningham, A., (1870) Ladak (a reprinting of earlier reports) (pp. 136–137, 140–141), New Delhi-I, India: Sagar Publications.
- Da Silva, L., Maurel, M. C., & Deamer, D. (2015). Salt-promoted synthesis of RNA-like molecules in simulated hydrothermal conditions. *Journal of molecular evolution*, 80(2), 86–97. 10.1007/s00239-014-9661-9
- Das, A., Singh, T., LokaBharathi, P. A., Dhakephalkar, P. K., Mallik, S., & Kshirsagar, P. R., et al. (2017). Astrobiological implications of dim light phototrophy in deep-sea red clays. *Life sciences in space research*, 12, 39–50. 10.1016/j.lssr.2017.01.002
- Decker, P., Schweer, H., & Pohlamnn, R. (1982). Bioids: X. Identification of formose sugars, presumable prebiotic metabolites, using capillary gas chromatography/gas chromatography—mas spectrometry of n-butoxime trifluoroacetates on OV-225. *Journal of Chromatography A*, 244(2), 281–291. 10.1016/S0021-9673(00)85692-7
- Djokic, T., Van Kranendonk, M. J., Campbell, K. A., Walter, M. R., & Ward, C. R. (2017). Earliest signs of life on land preserved in ca. 3.5 Ga hot spring deposits. *Nature communications*, 8(1), 1–9. 10.1038/ncomms15263
- Domagal-Goldman, S. D., Wright, K. E., Adamala, K., De La Rubia, L. A., Bond, J., Dartnell, L. R., et al. (2016). The astrobiology primer v2.0. *Astrobiology*, 16(8), 561. 10.1089/ast.2015.1460
- Drake, F. D., & Sobel, D. (1992). Is anyone out there. *Mercur*, 21, 120.
- Ehlmann, B. L., & Mustard, J. F. (2012). An in-situ record of major environmental transitions on early Mars at Northeast Syrtis Major. *Geophysical research letters*, 39(11). 10.1029/2012GL051594
- Ehlmann, B. L., Anderson, F. S., Andrews-Hanna, J., Catling, D. C., Christensen, P. R., Cohen, B. A., et al. (2016). The sustainability of habitability on terrestrial planets: Insights, questions, and needed measurements from Mars

- for understanding the evolution of Earth-like worlds. *Journal of Geophysical Research: Planets*, 121(10), 1927-1961. 10.1002/2016JE005134
- Ehlmann, B. L., Mustard, J. F., Swayze, G. A., Clark, R. N., Bishop, J. L., Poulet, F. et al. (2009). Identification of hydrated silicate minerals on Mars using MRO-CRISM: Geologic context near Nili Fossae and implications for aqueous alteration. *Journal of Geophysical Research*, 114, E00D08. 10.1029/2009JE003339, 2009
- Elwood Madden, M. E., R. J. Bodnar, & J. D. Rimstidt (2004). Jarosite as an indicator of water-limited chemical weathering on Mars, *Nature*, 431, 821–823, 10.1038/nature02971.
- Fang, J. H., & Robinson, P. D. (1976). Alunogen,  $\text{Al}_2(\text{H}_2\text{O})_{12}(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ ; its atomic arrangement and water content. *American Mineralogist*, 61(3-4), 311-317.
- Farmer, J. D. (2000). Hydrothermal systems: doorways to early biosphere evolution. *GSA Today*, 10(7), 1-9.
- Farmer, V. C. (1974). *Mineralogical society monograph 4: the infrared spectra of minerals*. The Mineralogical Society, London, 427.
- Farrand, W. H., Glotch, T. D., & Horgan, B. (2014). Detection of copiapite in the northern Mawrth Vallis region of Mars: Evidence of acid sulfate alteration. *Icarus*, 241, 346-357. 10.1016/j.icarus.
- Farrand, W. H., Glotch, T. D., Rice Jr, J. W., Hurowitz, J. A., & Swayze, G. A. (2009). Discovery of jarosite within the Mawrth Vallis region of Mars: Implications for the geologic history of the region. *Icarus*, 204(2), 478-488. 10.1016/j.icarus.2009.
- Fraeman, A. A., B. L. Ehlmann, R. E. Arvidson, C. S. Edwards, J. P. Grotzinger, R. E. Milliken, D. P. Quinn, and M. S. Rice (2016), The stratigraphy and evolution of lower Mount Sharp from spectral, morphological, and thermophysical orbital data sets, *Journal of Geophysical Research Planets*, 121, 1713–1736. doi:10.1002/2016JE005095.
- Furukawa, Y., Kim, H. J., Hutter, D., & Benner, S. A. (2015). Abiotic regioselective phosphorylation of adenosine with borate in formamide. *Astrobiology*, 15(4), 259-267. 10.1089/ast.2014.1209
- Garrett, D. E. (1998). *Borates: Handbook of Deposits, Processing, Properties, and Use*. San Diego, CA: Academic Press.
- Gasda, P. J., Haldeman, E. B., Wiens, R. C., Rapin, W., Bristow, T. F., Bridges, J. C., et al. (2017). In situ detection of boron by ChemCam on Mars. *Geophysical Research Letters*, 44(17), 8739-8748. 10.1002/2017GL074480
- Gates-Rector, S. D. and Blanton, T. N., (2020). “The Powder Diffraction File: A Quality Materials Characterization Database” *Powder Diffraction*. 34, 352-60.

- Gendrin, A., Mangold, N., Bibring, J. P., Langevin, Y., Gondet, B., Poulet, F., et al. (2005). Sulfates in Martian layered terrains: the OMEGA/Mars Express view. *Science*, 307(5715), 1587-1591. 10.1126/science.1109087
- Geological Survey of India. (1991), Geothermal Atlas of India, (Special Publication, 19, 110-113). Kolkata, India.
- Ghosh, W., Mallick, S., Haldar, P. K., Pal, B., Maikap, S. C., & Gupta, S. K. D. (2012). Molecular and cellular fossils of a Mat-like microbial community in geothermal boratic sinters. *Geomicrobiology Journal*, 29(10), 879-885. 10.1080/01490451.2011.635761
- Gilbert, W. (1986). Origin of life: The RNA world. *Nature*, 319(6055), 618-618.
- Glotch, T. D., Bandfield, J. L., Christensen, P. R., Calvin, W. M., McLennan, S. M., Clark, B. C., et al. (2006). Mineralogy of the light-toned outcrop at Meridiani Planum as seen by the Miniature Thermal Emission Spectrometer and implications for its formation. *Journal of Geophysical Research*, 111, E12S03. <https://doi.org/10.1029/2005JE002672>
- Goryniuk, M. C., Rivard, B. A. & Jones, B. (2004). The reflectance spectra of opal-A (0.5–25  $\mu\text{m}$ ) from the Taupo Volcanic Zone: Spectra that may identify hydrothermal systems on planetary surfaces. *Geophysical Research Letter*, 31, L24701. 10.1029/2004GL021481.
- Grabau, A. W. (1920). *Principles of Salt Deposition. In Geology of Non-Metallic Mineral Deposits (Vol. 1). Deposits Formed from Volcanic Waters.* New York: McGraw-Hill.
- Harinarayana, T., Abdul Azeez, K. K., Murthy, D. N., Veeraswamy, K., Eknath Rao S. P., Manoj, C., & Naganjaneyulu, K. (2006), Exploration of geothermal structure in Puga geothermal field, Ladakh Himalayas, India by magnetotelluric studies. *Journal of Applied Geophysics*, 58(4), 280–295. 10.1016/j.jappgeo.2005.05.005
- Harinarayana, T., Abdul Azeez, K. K., Naganjaneyulu, K., Manoj, C., Veeraswamy, K., Murthy, D. N., & Prabhakar Eknath Rao S. (2004), Magnetotelluric studies in Puga valley geothermal field, NW Himalaya, Jammu and Kashmir, India. *Journal of Volcanology and Geothermal Research*, 138(3-4), 405– 424. 10.1016/j.jvolgeores.2004.07.011
- Hazarika, D., Sen, K., & Kumar, N. (2014). Characterizing the intracrustal low velocity zone beneath northwest India–Asia collision zone. *Geophysical Journal International*, 199(3), 1338-1353. doi: 10.1093/gji/ggu328
- Hollis, J. M., Vogel, S. N., Snyder, L. E., Jewell, P. R. & Lovas, F. J. (2001). The spatial scale of glycolaldehyde in the galactic center. *The Astrophysical Journal*, 554 (1), L81–L85. <https://doi.org/10.1086/320930>
- Hunt, G. R., & Ashley, R. P. (1979). Spectra of altered rocks in the visible and near infrared. *Economic Geology*, 74, 1613–1629.

- Hunt, G. R., Salisbury, J. W., & Lenhoff, C. J. (1972). Visible and near-infrared spectra of minerals and rocks: V. Halides, phosphates, arsenates, vanadates and borates. *Modern Geology*, 3, 121–132.
- Hunt, G. R., Salisbury, J. W., Lenhoff, C. J., (1971). Visible and near-infrared spectra of minerals and rocks. VI. Sulfides and sulfates. *Modern Geology*, 3, 1–14.
- Hurowitz, J. A., Fischer, W. W., Tosca, N. J., & Milliken, R. E. (2010). Origin of acidic surface waters and the evolution of atmospheric chemistry on early Mars, *Nature Geoscience*, 3, 323 – 326. doi: 10.1038/NGEO831
- Hurowitz, J. A., Grotzinger, J. P., Fischer, W. W., McLennan, S. M., Milliken, R. E., Stein, N. et al., (2017). Redox stratification of an ancient lake in Gale crater, Mars, *Science*, 356. doi: 10.1126/science.aah6849
- Hynek, B. M., Beach, M., & Hoke, M. R. (2010). Updated global map of Martian valley networks and implications for climate and hydrologic processes. *Journal of Geophysical Research: Planets*, 115(E9). 10.1029/2009JE003548
- Hynek, B. M., Osterloo, M. K., & Kierein-Young, K. S. (2015). Late-stage formation of Martian chloride salts through ponding and evaporation. *Geology*, 43(9), 787-790. 10.1130/G36895.1
- Jha, S. & Puppala, H. (2018), Conceptual modeling and characterization of Puga geothermal reservoir. *Geothermics*. 72, 326–337. 10.1016/j.geothermics.2017.12.004.
- Jones, R. M., Goordial, J. M., & Orcutt, B. N. (2018). Low energy subsurface environments as extraterrestrial analogs. *Frontiers in microbiology*, 9, 1605. 10.3389/fmicb.2018.01605
- Jun, L., Shuping, X., & Shiyang, G. (1995). FT-IR and Raman spectroscopic study of hydrated borates. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 51(4), 519-532.
- Kim, H. J., & Benner, S. A. (2010). Comment on “The silicate-mediated formose reaction: Bottom-up synthesis of sugar silicates”. *Science*, 329(5994), 902-902. 10.1126/science.1188697
- Kim, H. J., Ricardo, A., Illangkoon, H. I., Kim, M. J., Carrigan, M. A., Frye, F., & Benner, S. A. (2011). Synthesis of carbohydrates in mineral-guided prebiotic cycles. *Journal of the American Chemical Society*, 133(24), 9457-9468. 10.1021/ja201769f
- Kipcak, A. S., Derun, E. M., & Piskin, S. (2014). Characterisation and determination of the neutron transmission properties of sodium–calcium and sodium borates from different regions in Turkey. *Journal of Radioanalytical and Nuclear Chemistry*, 301(1), 175-188. 7 10.1007/s10967-014-3161-7
- Klingelhöfer, G. R. D. S., Morris, R. V., Bernhardt, B., Schröder, C., Rodionov, D. S., De Souza, P. A., et al. (2004). Jarosite and hematite at Meridiani

- Planum from Opportunity's Mössbauer spectrometer. *Science*, 306(5702), 1740-1745. 10.1126/science.1104653
- Kokaly, R. F., Clark, R. N., Swayze, G. A., Livo, K. E., Hoefen, T. M., Pearson, N. C., et al. (2017). *USGS spectral library version 7* (No. 1035). US Geological Survey.
- Kral, T. A., Altheide, T. S., Lueders, A. E., & Schuerger, A. C. (2011). Low pressure and desiccation effects on methanogens: implications for life on Mars. *Planetary and Space Science*, 59(2-3), 264-270. 10.1016/j.pss.2010.07.012
- Kral, T. A., Birch, W., Lavender, L. E., & Virden, B. T. (2014). Potential use of highly insoluble carbonates as carbon sources by methanogens in the subsurface of Mars. *Planetary and Space Science*, 101, 181-185. 10.1016/j.pss.2014.07.008
- Kral, T. A., Goodhart, T. H., Harpool, J. D., Hearnberger, C. E., McCracken, G. L., & McSpadden, S. W. (2016). Sensitivity and adaptability of methanogens to perchlorates: Implications for life on Mars. *Planetary and Space Science*, 120, 87-95. 10.1016/j.pss.2015.11.014
- Langer, K., & Flörke, O. W. (1974). Near infrared absorption spectra (4000–9000  $\text{cm}^{-1}$ ) of opals and the role of “water” in these  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  minerals. *Fortschritte der Mineralogie*, 52(1), 17-51.
- Lanza, N. L., Wiens, R. C., Arvidson, R. E., Clark, B. C., Fischer, W. W., Gellert, R., et al. (2016). Oxidation of manganese in an ancient aquifer, Kimberley formation, Gale crater, Mars. *Geophysical Research Letters*, 43, 7398–7407. doi:10.1002/2016GL069109
- Larralde, R., Robertson, M. P., & Miller, S. L. (1995). Rates of decomposition of ribose and other sugars: implications for chemical evolution. *Proceedings of the National Academy of Sciences*, 92(18), 8158-8160. 10.1073/pnas.92.18.8158
- Leask, E. K., & Ehlmann, B. L. (2022). Evidence for Deposition of Chloride on Mars From Small-Volume Surface Water Events Into the Late Hesperian-Early Amazonian, *American Geophysical Union Advances*, 3(1), e2021AV000534.
- Léveillé, R. (2010). A half-century of terrestrial analog studies: from craters on the Moon to searching for life on Mars. *Planetary and Space Science*, 58(4), 631-638. 10.1016/j.pss.2009.04.001
- Léveillé, R. J., Oehler, D. Z., Fairen, A. G., Clark, B. C., Niles, P. B., & Blank, J. G. (2015). *Jarosite in Gale Crater, Mars: The Importance of Temporal and Spatial Variability and Implications for Habitability*. Paper presented in Astrobiology Science Conference.
- Levy, H. A., & Lisensky, G. C. (1978). Crystal structures of sodium sulfate decahydrate (Glauber's salt) and sodium tetraborate decahydrate (borax). Redetermination by neutron diffraction. *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry*, 34(12), 3502-3510.



- Luck, R. L., & Wang, G. (2002). On the nature of tinalconite. *American Mineralogist*, 87(2-3), 350-354. 10.2138/am-2002-2-319
- Mangold, N., Adeli, S., Conway, S., Ansan, V., & Langlais, B. (2012). A chronology of early Mars climatic evolution from impact crater degradation. *Journal of Geophysical Research: Planets*, 117(E4). 10.1029/2011JE004005
- Martin, W., & Russell, M. J. (2007). On the origin of biochemistry at an alkaline hydrothermal vent. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 362(1486), 1887-1926. 10.1098/rstb.2006.1881
- Martin, W., Baross, J., Kelley, D., & Russell, M. J. (2008). Hydrothermal vents and the origin of life. *Nature Reviews Microbiology*, 6(11), 805-814. 10.1038/nr-micro1991
- Maurice, S., Wiens, R. C., Anderson, R., Beyssac, O., Bonal, L., Clegg, S., et al. (2015). Science objectives of the SuperCam instrument for the Mars2020 rover. In *46th Lunar and Planetary Science Conference*, 2818.
- McArthur, A., McLellan, C., & Malthus, T. (2007). *The implications of non-uniformity in fields-of-view of commonly used field spectroradiometers*. In Proceedings of International Geoscience and Remote Sensing Symposium 2007, pp. 2890-2893, IEEE, Barcelona.
- McLennan, S. M. (2003). Sedimentary silica on Mars. *Geology*, 31(4), 315-318. 10.1130/0091-7613(2003)031<3C0315:SSOM>3E2.0.CO;2
- MEPAG Special Regions – Science Analysis Group (2006), Findings of the Mars Special Regions Science Analysis Group, *Astrobiology*, 6, 677 – 732.
- Mereiter, K. (2013). Redetermination of tamarugite, NaAl (SO<sub>4</sub>) 2 · 6H<sub>2</sub>O. *Acta Crystallographica Section E: Structure Reports Online*, 69(10), i63-i64. 10.1107/S1600536813025154
- Mickol, R. L., & Kral, T. A. (2017). Low pressure tolerance by methanogens in an aqueous environment: implications for subsurface life on Mars. *Origins of Life and Evolution of Biospheres*, 47(4), 511-532. 10.1007/s11084-016-9519-9
- Milliken, R. E., Swayze, G. A., Arvidson, R. E., Bishop, J. L., Clark, R. N., Ehlmann, B. L., et al. (2008). Opaline silica in young deposits on Mars. *Geology*, 36(11), 847-850. 10.1130/G24967A.1
- Mills, S. J., Nestola, F., Kahlenberg, V., Christy, A. G., Hejny, C., & Redhammer, G. J. (2013). What Lurks in the Martian Rocks and Soil? Investigations of Sulfates, Phosphates, and Perchlorates. Looking for jarosite on Mars: The low-temperature crystal structure of jarosite. *American Mineralogist*, 98(11-12), 1966-1971. 10.2138/am.2013.4587
- Morris, R. V., Ruff, S. W., Gellert, R., Ming, D. W., Arvidson, R. E., Clark, B. C et al., (2010). Identification of Carbonate-Rich Outcrops on Mars by the Spirit Rover, *Science*, 329(5990), 421-424. 10.1126/science.1189667

- Mougenot, B. (1991). *Caractéristiques spectrales de surfaces salées à chlorures et sulfates (Sénégal)*. Caractérisation et suivi des milieux terrestres en régions arides et tropicales', Colloques et Séminaires, Orstom, Paris, 49-70.
- Murchie, S. L., Mustard, J. F., Ehlmann, B. L., Milliken, R. E., Bishop, J. L., McKeown, N. K., et al. (2009b). A synthesis of Martian aqueous mineralogy after 1 Mars year of observations from the Mars Reconnaissance Orbiter. *Journal of Geophysical Research*. 114. 10.1029/2009JE003342
- Murchie, S., Roach, L., Seelos, F., Milliken, R., Mustard, J., Arvidson, R., et al. (2009a). Evidence for the origin of layered deposits in Candor Chasma, Mars, from mineral composition and hydrologic modeling. *Journal of Geophysical Research: Planets*, 114(E2).10.1029/2009JE003343
- Mustard, J. F., Murchie, S. L., Pelkey, S. M., Ehlmann, B. L., Milliken, R. E., Grant, J. A. et al., (2008). Hydrated silicate minerals on Mars observed by the Mars Reconnaissance Orbiter CRISM instrument, *Nature*, 305-309. doi:10.1038/nature07097
- Neveu, M., Kim, H. J., & Benner, S. A. (2013). The “strong” RNA world hypothesis: Fifty years old. *Astrobiology*, 13(4), 391-403. 10.1089/ast.2012.0868
- Nordstrom, D. K., & Alpers, C. N. (1999). Negative pH, efflorescent mineralogy, and consequences for environmental restoration at the Iron Mountain Superfund site, California. *Proceedings of the National Academy of Sciences*, 96(7), 3455-3462.
- Osterloo, M. M., Anderson, F. S., Hamilton, V. E., & Hynek, B. M. (2010). Geologic context of proposed chloride-bearing materials on Mars. *Journal of Geophysical Research: Planets*, 115(E10). 10.1029/2010JE003613
- Osterloo, M. M., Hamilton, V. E., Bandfield, J. L., Glotch, T. D., Baldrige, A. M., Christensen, P. R., et al. (2008). Chloride-bearing materials in the southern highlands of Mars. *Science*, 319(5870), 1651-1654. 10.1126/science.1150690
- Pandey, S., Clarke, J., Nema, P., Bonaccorsi, R., Som, S., & Sharma, M. (2019). Ladakh: Diverse, high-altitude extreme environments for off-earth analogue and astrobiology research. *International Journal of Astrobiology*, 19(1), 78-98. 10.1017/S1473550419000119
- Pearce, B. K., Pudritz, R. E., Semenov, D. A., & Henning, T. K. (2017). Origin of the RNA world: The fate of nucleobases in warm little ponds. *Proceedings of the National Academy of Sciences*, 114(43), 11327-11332. 10.1073/pnas.1710339114
- Phillips, R. J., Zuber, M. T., Solomon, S. C., Golombek, M. P., Jakosky, B. M., Banerdt, W. B., et al. (2001). Ancient geodynamics and global-scale hydrology on Mars. *Science*, 291(5513), 2587-2591. 10.1126/science.1058701
- Rajamani, S., Vlassov, A., Benner, S., Coombs, A., Olasagasti, F., & Deamer, D. (2008). Lipid-assisted synthesis of RNA-like polymers from

- mononucleotides. *Origins of Life and Evolution of Biospheres*, 38(1), 57-74. 10.1007/s11084-007-9113-2
- Ricardo, A., Carrigan, M. A., Olcott, A. N., & Benner, S. A. (2004). Borate minerals stabilize ribose. *Science*, 303(5655), 196-196. 10.1126/science.1092464
- Ross, S. D. (1974). Borates. In V. C. Farmer (Ed.), *The Infrared Spectra of Minerals* (pp. 205–226) London, UK: Mineralogical Society.
- Ruff, S. W., & Farmer, J. D. (2016). Silica deposits on Mars with features resembling hot spring biosignatures at El Tatio in Chile. *Nature communications*, 7(1), 1-10. 10.1038/ncomms13554
- Ruff, S. W., Campbell, K. A., Van Kranendonk, M. J., Rice, M. S., & Farmer, J. D. (2020). The Case for Ancient Hot Springs in Gusev Crater, Mars, *Astrobiology*, 20(4). doi:10.1089/ast.2019.2044
- Ruff, S. W., Farmer, J. D., Calvin, W. M., Herkenhoff, K. E., Johnson, J. R., Morris, R. V., et al., (2011). Characteristics, distribution, origin, and significance of opaline silica observed by the Spirit rover in Gusev crater, Mars, *Journal of Geophysical Research*, 116. E00F23, doi: 10.1029/2010JE003767.
- Saikia, B. J., Parthasarathy, G., & Sarmah, N. C. (2008). Fourier transform infrared spectroscopic estimation of crystallinity in SiO<sub>2</sub> based rocks. *Bulletin of Materials Science*, 31(5), 775-779. <https://doi.org/10.1007/s12034-008-0123-0>
- Saladino, R., Barontini, M., Cossetti, C., Di Mauro, E., & Crestini, C. (2011). The effects of borate minerals on the synthesis of nucleic acid bases, amino acids and biogenic carboxylic acids from formamide. *Origins of Life and Evolution of Biospheres*, 41(4), 317-330. 10.1007/s11084-011-9236-3
- Santos, A. R., Agee, C. B., McCubbin, F. M., Shearer, C. K., Burger, P. V., Tartèse, R., & Anand, M. (2015). Petrology of igneous clasts in Northwest Africa 7034: Implications for the petrologic diversity of the martian crust, *Geochimica et Cosmochimica Acta*, 157, 56–85. <http://dx.doi.org/10.1016/j.gca.2015.02.023>
- Sarkar, S., Moitra, H., Bhattacharya, S., Dagar, A., Ray, D., Gupta, S. et al. (2020). Spectroscopic and XRD data from PHS [Data set]. Zenodo. <http://doi.org/10.5281/zenodo.3992541>
- Sarkar, S., Moitra, H., Bhattacharya, S., Dagar, A., Ray, D., Gupta, S. et al. (2022). Spectroscopic data from PHS (lab characterization) [Data set]. Zenodo. <https://doi.org/10.5281/zenodo.6304000>
- Sautter, V., Fabre, C., Forni, O., Toplis, M. J., Cousin, A., Ollila, A. M. et al. (2014). Igneous mineralogy at Bradbury Rise: The first ChemCam campaign at Gale crater. *Journal of Geophysical Research: Planets*, 119(1). 10.1002/2013JE004472
- Sautter, V., Toplis, M. J., Beck, P., Mangold, N., Wiens, R., Pinet, P. et al. (2016). Magmatic complexity on early Mars as seen through a

- combination of orbital, in-situ and meteorite data. *Lithos*, 254, 36-52. 10.1016/j.lithos.2016.02.023
- Sautter, V., Toplis, M. J., Wiens, R. C., Cousin, A., Fabre, C., Gasnault, O. et al. (2015). In situ evidence for continental crust on early Mars. *Nature Geoscience*, 8(8), 605-609. 10.1038/NGEO2474
- Sautter, V., Toplis, M. J., Wiens, R. C., Cousin, A., Fabre, C., Gasnault, O. et al. (2015). In situ evidence for continental crust on early Mars. *Nature Geoscience*, 8(8), 605-609. 10.1038/NGEO2474
- Schmidt, M. E., Baker, M. B., Berger, J. A., Fisk, M. R., Gellert, R., McLennan, S. M., et al. (2014). Diverse, alkali-rich igneous and volcanoclastic rocks reflect a metasomatised mantle beneath Gale crater. In *American Geophysical Union Fall Meeting Abstracts*, P33E-06.
- Scorei R. (2012). Is boron a prebiotic element? A mini-review of the essentiality of boron for the appearance of life on earth. *Origins of life and evolution of the biosphere : the journal of the International Society for the Study of the Origin of Life*, 42(1), 3-17. <https://doi.org/10.1007/s11084-012-9269-2>
- Scorei, R., & Cimpoiușu, V. M. (2006). Boron enhances the thermostability of carbohydrates. *Origins of Life and Evolution of Biospheres*, 36(1), 1-11.
- Shankar, R., Padhi, R. N., Prakash, G., Thussu, J. L., & Wangdus, C. (1976). Recent geological studies in upper Indus valley and the plate tectonics. *Geological Survey of India*, 34, 41-56.
- Shapiro, R. (1988). Prebiotic ribose synthesis: a critical analysis. *Origins of Life and Evolution of the Biosphere*, 18(1-2), 71-85.
- Shukla, A. D., Ray, D., & Bhattacharya, S. (2017). Sulfate Mineral from Hot Springs in Cold Desert (Ladakh, India): Analogue to Martian Sulfate Deposit? In *48<sup>th</sup> Lunar and Planetary Science Conference*.
- Siever, R. (1962). Silica solubility, 0-200 C., and the diagenesis of siliceous sediments. *The Journal of Geology*, 70(2), 127-150. 10.1086/626804
- Sinha, N., Nepal, S., Kral, T., & Kumar, P. (2018). Effects of temperatures and high pressures on the growth and survivability of methanogens and stable carbon isotope fractionation: implications for deep subsurface life on Mars. *International Journal of Astrobiology*, 1-7. 10.1017/S1473550418000216
- Sinha, R. K., Vijayan, S., Shukla, A. D., Das, P., & Bhattacharya, F. (2019). Gullies and debris-flows in Ladakh Himalaya, India: a potential Martian analogue. *Geological Society, London, Special Publications*, 467(1), 315-342. 10.1144/SP467.9
- Skok, J. R., Mustard, J. F., Ehlmann, B. L., Milliken, R. E., & Murchie, S. L. (2010). Silica deposits in the Nili Patera caldera on the Syrtis Major volcanic complex on Mars, *Nature Geoscience*, 3, 838 – 841. doi: 10.1038/NGEO990

- Smith, M. R., & Bandfield, J. L. (2012). Geology of quartz and hydrated silica-bearing deposits near Antoniadi Crater, Mars. *Journal of Geophysical Research: Planets*, 117(E6). doi:10.1029/2011JE004038
- Squyres, S. W., Arvidson, R. E., Ruff, S., Gellert, R., Morris, R. V., Ming, D. W. et al., (2008). Detection of silica-rich deposits on Mars. *Science*, 320(5879), 1063-1067. doi:10.1126/science.1155429
- Steller, L. H., Nakamura, E., Ota, T., Sakaguchi, C., Sharma, M., & Van Kranendonk, M. J. (2019). Boron Isotopes in the Puga Geothermal System, India, and Their Implications for the Habitat of Early Life. *Astrobiology*, 10.1089/ast.2018.1966
- Stephenson, J. D., Hallis, L. J., Nagashima, K., & Freeland, S. J. (2013). Boron enrichment in martian clay. *PloS one*, 8(6), e64624. 10.1371/journal.pone.0064624
- Stoker, C. R., Zent, A., Catling, D. C., Douglas, S., Marshall, J. R., Archer Jr, D. et al. (2010). Habitability of the Phoenix landing site. *Journal of Geophysical Research: Planets*, 115(E6). 10.1029/2009JE003421, 2010
- Stolper, E. (1982), Water in silicate glasses: An infrared spectroscopic study. *Contributions to Mineralogy and Petrology*, 81(1), 1–17. 10.1007/BF00371154.
- Stolper, E. M., Baker, M. B., Newcombe, M. E., Schmidt, M. E., Treiman, A. H., Cousin, A., et al. (2013). The petrochemistry of Jake\_M: A Martian mugearite. *Science*, 341(6153).
- Stucky de Quay, G., Goudge, T. A., & Fassett, C. I. (2020). Precipitation and aridity constraints from paleolakes on early Mars. *Geology*, 48(12), 1189-1193. <https://doi.org/10.1130/G47886.1>
- Sun, V. Z., & Milliken, R. E. (2018). Distinct geologic settings of opal-A and more crystalline hydrated silica on Mars, *Geophysical Research Letters*, 45, 10,221–10,228. <https://doi.org/10.1029/2018GL078494>
- Sun, V. Z., & Milliken, R. E. (2020). Characterizing the Mineral Assemblages of Hot Spring Environments and Applications to Mars Orbital Data. *Astrobiology*, 20(4), 453-474. 10.1089/ast.2018.2003
- Swayze, G. A., Ehlmann, B. L., Milliken, R. E., Poulet, F., Wray, J. J., Rye, R. O., et al. (2008). Discovery of the acid-sulfate mineral alunite in Terra Sirenum, Mars, using MRO CRISM: Possible evidence for acid-saline lacustrine deposits?. Abstract (P44A-04) presented at American Geophysical Union Fall Meeting, San Francisco, CA.
- Swayze, G. A., Milliken, R. E., Clark, R. N., Bishop, J. L., Ehlmann, B. L., Pelkey, S. M., et al. (2007). *Spectral evidence for hydrated volcanic and/or impact glass on Mars with MRO CRISM*. In 7<sup>th</sup> International Conference on Mars (Vol. 1353, p. 3384), Pasadena CA

- Thollot, P., Mangold, N., Ansan, V., Le Mouélic, S., Milliken, R. E., Bishop, J. L., et al. (2012). Most Mars minerals in a nutshell: Various alteration phases formed in a single environment in Noctis Labyrinthus. *Journal of Geophysical Research: Planets*, 117(E11). 10.1029/2011JE004028.
- Thussu J. L. (2002). Geothermal Energy Resources of India. *Geological Survey of India Special Publication*, 69, 210 pp.
- Vaniman, D. T., Bish, D. L., Ming, D. W., Bristow, T. F., Morris, R. V., Blake, D. F., et al. (2014). Mineralogy of a mudstone at Yellowknife Bay, Gale crater, Mars. *Science*, 343(6169), 1243480. 10.1126/science.1243480
- Virdi, N. S., Thakur, V. C., Kumar, S. (1977), Blueschist facies metamorphism from the Indus suture zone of Ladakh and its significance. *Himalayan. Geology*, 7, 479–482.
- Von Schlagintweit, H. (1878). Borax in the Puga Valley, Ladak, India. *Munchen Academy sitzungsberichte*, 8, 518-522.
- Wächtershäuser, G. (1998). The case for a hyperthermophilic, chemolithoautotrophic origin of life in an iron–sulfur world. In WIEGEL J. and M.W.W. Adams (Eds.), *Thermophiles: the keys to molecular evolution and the origin of life* (pp. 47–57). London, UK: Taylor and Francis
- Weir, C. E. (1966). Infrared spectra of the hydrated borates. *Journal of Research of the National Bureau of Standards-A. Physics and Chemistry*, 70(2), 153-164.
- Weitz, C. M., Bishop, J. L., Thollot, P., Mangold, N., & Roach, L. H. (2011). Diverse mineralogies in two troughs of Noctis Labyrinthus, Mars. *Geology*, 39(10), 899-902. 10.1130/G32045.1
- Westall, F., de Wit, M. J., Dann, J., van der Gaast, S., de Ronde, C. E., & Gerneke, D. (2001). Early Archean fossil bacteria and biofilms in hydrothermally-influenced sediments from the Barberton greenstone belt, South Africa. *Precambrian Research*, 106(1-2), 93-116. 10.1016/S0301-9268(00)00127-3
- Wiens, R. C., Maurice, S., McCabe, K., Cais, P., Anderson, R. B., Beyssac, O., et al. (2016). The SuperCam remote sensing instrument suite for Mars 2020. In *47th Lunar and Planetary Science Conference*, 1322.
- Wordsworth, R., Knoll, A. H., Hurowitz, J., Baum, M., Ehlmann, B. L., Head, J. W., & Steakley, K., A. (2021). Coupled model of episodic warming, oxidation and geochemical transitions on early Mars, *Nature Geoscience*, 14, 127–132. <https://doi.org/10.1038/s41561-021-00701-8>
- Wray, J. J., Murchie, S. L., Squyres, S. W., Seelos, F. P., & Tornabene, L. L. (2009). Diverse aqueous environments on ancient Mars revealed in the southern highlands. *Geology*, 37(11), 1043-1046. 10.1130/G30331A.1
- Yen, A. S., Ming, D. W., Vaniman, D. T., Gellert, R., Blake, D. F., Morris, R. V. et al., (2017). Multiple stages of aqueous alteration along fractures in mud-

stone and sandstone strata in Gale Crater, Mars. *Earth and Planetary Science Letters*, 471, 186-198. <https://doi.org/10.1016/j.epsl.2017.04.033>

Zema, M., Callegari, A. M., Tarantino, S. C., Gasparini, E., & Ghigna, P. (2012). Thermal expansion of alunite up to dehydroxylation and collapse of the crystal structure. *Mineralogical Magazine*, 76(3), 613-623. 10.1180/min-mag.2012.076.3.12

**Figure 1.** Geological and structural map of the study area showing location of the site investigated (modified after Geothermal Atlas of India, 1991).

**Figure 2.** (a) Satellite image showing the field locations between Puga and Sumdo Village, taken from Google Earth images, (b) Collecting VNIR spectra of valley fill material at location PUG-18-08-06, (c) and (d) are field photographs of Location PUG-18-05 and PUG-18-08. (e), (f) and (g) are the images of the samples from location PUG-18-08-06, PUG-18-08-05 and PUG-18-08-08 respectively.

**Figure 3.** VNIR spectra of samples PUG-18-06-A and B (top) and USGS library spectra of tinalconite (GDS142) and VNIR spectra of borax from Crowley (1991) (bottom). Dotted lines at approximately 1430 (1), 1480 (2), 1800(3), 1920 (4), 2140 (5), and 2260 nm (6) are for visual guidance.

**Figure 4.** (a) VNIR spectra of samples PUG-18-05-A, D and H (top) and USGS library spectra of alunite (HS295.3B) and jarosite (GDS99) (bottom). Dotted lines at approximately 430 (1), 500 (2), 930(3), 1420 (4), 1460 (5), 1760 (6), 1940 (7), 2180 (8), 2210 (9) and 2320 nm (10) are for visual guidance. (b) VNIR spectra of sample PUG-18-05-G (top) and USGS library spectra of alunite (HS295.3B) and jarosite (GDS99) (bottom). Dotted lines at approximately 430 (1), 500 (2), 650 (3), 930(4), 1420 (5), 1460 (6), 1760 (7), 1940 (8), 2180 (9), 2210 (10), 2260 (11) and 2320 nm (12) are shown for visual guidance.

**Figure 5.** (a) VNIR spectra of sample PUG-18-08-A and B (top) and USGS library spectra of alunite (HS295.3B) and sulfur (GDS94) (bottom). Dotted lines at approximately 430 (1), 1420 (2), 1460 (3), 1760 (4), 1900 (5), 2180 (6), 2210 (7) and 2320 nm (8) are for visual guidance. (b) VNIR spectra of sample PUG-18-08-C and E (top) and USGS library spectra of jarosite (GDS99) and copiapite (GDS21) (bottom). Dotted lines at approximately 430 (1), 450 (2), 500 (3), 900 (4), 1460 (5), 1900 (6), 2210 (7) and 2260 nm (8) are for visual guidance.

**Figure 6.** (a) VNIR spectra of sample PUG-18-08-F (top) and spectra of tamarugite from Mougenot (1991) (bottom). Dotted lines at approximately 430 (1), 1430 (2), 1480 (3), 1760 (4), 1960 (5), 2175 (6) and 2210 nm (7) are for visual guidance. (b) VNIR spectra of sample PUG-15-Gypsum and PUG-18-05-E (top) and USGS library spectra of gypsum (HS333.3B) and opal (TM8896) (bottom). Dotted lines at approximately 1450 (1), 1500 (2), 1550 (3), 1750 (4), 1920 (5), 2200 (6) and 2260 nm (7) are for visual guidance. Dotted lines inside the circles are at approximately 1400, 1460 and 1900 nm.

**Figure 7.** (a) FTIR transmission mode (absorbance) spectra of samples PUG-18-06-A and -B in the range 2000-400  $\text{cm}^{-1}$  and (b) in the range 4000-2000  $\text{cm}^{-1}$ . (top) and Spectrabase library spectra of borax (HFt86gDWUJB) and tincalconite (Fu0WtyuEt0Y) (bottom). The dashed lines in red mark the wavenumbers of the absorptions due to borax in both the samples. The dashed lines in blue mark the positions of the absorptions due to tincalconite in sample PUG-18-06-B only. The labels on the dashed lines are numbered according to the absorptions mentioned in Table 7; i.e., the numbers correspond to the row number and the alphabet correspond to individual absorptions in that row for the respective samples. The dashed lines labelled as 4c for borax and as 4b for tincalconite show an overlap of borax and tincalconite absorption positions. In sample PUG-18-06-B, all the absorptions numbered from 5 to 11 show overlap of the absorption positions for borax and tincalconite.

**Figure 8.** (a) FTIR transmission mode (absorbance) spectra of samples PUG-18-05-D, -A and -H in the range 1600-400  $\text{cm}^{-1}$  and (b) in the range 4000-1600  $\text{cm}^{-1}$  (top) and spectra of alunite (Sample# S21) from Chukanov (2014) (bottom). The dashed lines in red and brown mark the wavenumbers of the absorptions due to alunite and quartz, respectively, in all the three samples. The labels on the dashed lines are numbered according to the absorptions mentioned in the tables; for alunite- Table 5; for quartz- Table 8; i.e., the numbers correspond to the row number and the alphabet correspond to individual absorptions in that row for the respective samples.

**Figure 9.** (a) FTIR transmission mode (absorbance) spectra of samples PUG-18-05-D and -E in the range 1600-400  $\text{cm}^{-1}$  and (b) in the range of 4000-1600  $\text{cm}^{-1}$  (top) and Spectrabase library spectra of jarosite (CNKP9gNFyuL) (bottom). The dashed lines in red and green mark the wavenumbers of the absorptions due to jarosite and quartz, respectively, in both the samples. The labels on the dashed lines are numbered according to the absorptions mentioned in the tables; for jarosite- Table 6; for quartz- Table 8, i.e., the digits correspond to the row number and the alphabet correspond to individual absorptions in that row for the respective samples.

**Figure 10.** (a) FTIR transmission mode (absorbance) spectra of samples PUG-18-05-A, -F and -B in the 1600-400  $\text{cm}^{-1}$  range and (b) in the range of 4000-1600  $\text{cm}^{-1}$  (top) and Spectrabase library spectra of tamarugite (DcifFvwXD2l) (bottom). The dashed lines in red and green mark the wavenumbers of the absorptions due to alunite and quartz, respectively, in all the three samples. The dashed lines in blue (labelled as T) mark the positions of the absorptions suspected to be due to presence of tamarugite in samples PUG-18-05-F and -B only. The labels on the dashed lines are numbered according to the absorptions mentioned in the tables; for alunite- Table 5; for tamarugite- Table 6; for quartz- Table 8; i.e., the numbers correspond to the row number and the alphabet correspond to individual absorptions in that row for the respective samples. The dashed line labelled 4a and 7b is an overlap of absorptions due to both alunite and quartz at the same wavenumber.



**Figure 11.** XRD results of samples PUG-18-06-A (**a**), PUG-19-06-B (**b**), PUG-18-05-A (**c**) and PUG-18-05-D (**d**). As in the VNIR spectra borax and tincalconite have been identified. Halite peaks are found in PUG-18-06-B and PUG-18-05-D.

**Figure 12.** XRD results of samples PUG-18-08-E (**a**), PUG-18-08-C (**b**), PUG-18-08-A (**c**) and PUG-18-08-F (**d**). As in the VNIR spectra alunite, tamarugite, jarosite and copiapite have been identified. Alunogen, metavoltine and anhydrite are found in PUG-18-08-C.

Sampler Number	Band Positions (nm)	Source of Data
<b>6A</b>	-	B
<b>6B</b>	B	B
<b>Borax</b>	-	-
<b>Borax</b>	-	-
<b>Tincalconite</b>	-	-
<b>BOR002 (Tincalconite)</b>	B	B /2030

Table: 1

*Absorption band (in nm) related to various combinations and overtones of B-O and water fundamentals, found in VNIR (350 to 2500 nm) region from this and previous studies.*

Note.

<sup>B</sup> Absorption bands likely attributable to various combinations and overtones of B-O fundamentals

Sample No.	Mineral	${}^6\text{A}_{1g} \rightarrow ({}^4\text{A}_{1g}, {}^4\text{E}_g)$	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$	Source
<b>5A</b>	Alunite	431	-	-	This S
<b>5D</b>	Alunite + Jarosite	433	500	984	This S
<b>5G</b>	Alunite + Jarosite	432	487, 654	938	This S
<b>5H</b>	Alunite + Jarosite	434	502	993	This S
<b>8A</b>	Sulfur + Alunite	-	-	-	This S
<b>8B</b>	Sulfur + Alunite	-	-	938	This S
<b>8C</b>	Copiapite	467	575	874	This S
<b>8E</b>	Qtz + Sulfur + Jarosite	433	-	922	This S
	Jarosite	430-436	500 <sup>a</sup> , 630 <sup>a</sup>	915-922	Clouti
	Copiapite	430	550	855-866	Clouti

Table 2

*Absorption band minima (in nm) of Fe3<sup>+</sup>-associated features for Fe3+-bearing sulfates from Puga hot spring area*

Note.

<sup>a</sup> Shoulder on a more intense absorption band, wavelength position approximate.

Nomenclature for crystal field states

**Superscripts 4 & 6:** refer to spin multiplicities

**States Symbols:**

**A:** non-degenerate mutlti-electron system; symmetric with respect to the principal axis of symmetry; no change of sign of the wave function when rotated through  $2/\pi$ .

**E:** two-fold degenerate mutlti-electron systems.

**T:** three-fold degenerate mutlti-electron systems.

**Subscripts:**

**g:** symmetric under the operation of inversion through the centre of symmetry; no change of sign of the wave function upon inversion.

**1:** refers to mirror planes parallel to a symmetry axis.

**2:** refers to diagonal mirror planes.

Table 3.

*Absorption band minima (in nm) of H<sub>2</sub>O- and OH-associated features in the 1400 and 1900 nm regions for hydrous sulfates from Puga hot spring area*

Vibrational Processes				
Sample No.	Mineral			
Overtones	<b>H<sub>2</sub>O</b>			
2 <sub>OH</sub> <sup>*</sup>	<b>Over- tones / Combi- nations</b>			
	<b>1400 nm Region</b>			
nm Region	<b>Source of Data</b>			
<b>5A</b>	Alunite	, 1477	-	This Study
<b>5D</b>	Alunite + Jarosite	, 1477	-	This Study
<b>5G</b>	Alunite + Jarosite	, 1478	-	This Study
<b>5H</b>	Alunite + Jarosite	, 1478	-	This Study

		<b>Vibrational Processes</b>			
<b>8A</b>	Sulfur + Alunite	, 1477	-		This Study
<b>8B</b>	Sulfur + Alunite	, 1477	-		This Study
<b>8C</b>	Copiapite				This Study
<b>8E</b>	Qtz + Sulfur + Jarosite	, 1465	-		This Study
<b>PUG-15-Gypsum</b>	Gypsum	-	<sup>a</sup> , 1448, 1490, 1532	, 1976	This Study
	Alunite	, 1460 <sup>a</sup> , 1467, 1500 <sup>a</sup>	-	-	Cloutis et al. (2006)
	Jarosite	-1468, 1510-1520	-	-	Cloutis et al. (2006)
	Copiapite		, 1480 <sup>a</sup>	, 2000 <sup>a</sup>	Cloutis et al. (2006)
	Gypsum	-	<sup>a</sup> , 1449, 1488, 1534	, 1970	Cloutis et al. (2006)

Note.

\* Second overtone of O-H stretch vibration.

<sup>a</sup> Shoulder on a more intense absorption band, wavelength position approximate.

		<b>Absorption Band Minima Position (nm)</b>	
<b>Sample No.</b>	<b>Mineral</b>	<b>1700–1800 nm Region</b>	<b>2000–2500 nm Region</b>
<b>5A</b>	Alunite	1767	2066 <sup>a</sup> , 2178 <sup>b</sup>
<b>5D</b>	Alunite + Jarosite	1767	2173 <sup>b</sup> , 2210 <sup>b</sup>
<b>5G</b>	Alunite + Jarosite	1764	2174 <sup>b</sup> , 2211 <sup>b</sup>
<b>5H</b>	Alunite + Jarosite	1764	2174 <sup>b</sup> , 2210 <sup>b</sup>
<b>8A</b>	Sulfur + Alunite	1767	2067 <sup>a</sup> , 2179 <sup>b</sup>
<b>8B</b>	Sulfur + Alunite	1768	2178 <sup>b</sup> , 2209 <sup>b</sup>
<b>8C</b>	Copiapite	1793	-
<b>8E</b>	Qtz + Sulfur + Jarosite	-	2219 <sup>b</sup> , 2263 <sup>b</sup>
<b>PUG-15-Gypsum</b>	Gypsum	1754, 1778 <sup>a</sup>	2222 <sup>c</sup> , 2264 <sup>c</sup>
	Alunite	1777	2070 <sup>a</sup> , 2160 <sup>a</sup>
	Jarosite	1840-1850	2080 <sup>c</sup> , 2210 <sup>c</sup>
	Copiapite	1780 <sup>a</sup>	2420 <sup>c</sup> , 2470 <sup>c</sup>
	Gypsum	1751, 1780	2170 <sup>c</sup> , 2220 <sup>c</sup>

Table 4.

*Absorption band minima (in nm) in the 1600–1900 nm and 2000–2500 nm regions that could be attributed to combinations of OH- or H<sub>2</sub>O-bending, stretching, and rotational fundamentals or S-O bending overtones for hydrous sulfates from Puga hot spring area*

Note.

<sup>a</sup> The 3000 nm region O-H stretch + 12000 nm region OH/H<sub>2</sub>O rotation.

<sup>b</sup> H-O-H in and out of plane bending vibrations

<sup>c</sup> third overtone of the asymmetric S-O stretch.

		Borax	Tincalconite	
		PUG-18-06-A	PUG-18-06-B	Weight
1	OH stretch	3585, 3504, 3446, 3359, 3197	-	3500
2.	HOH	1686, 1652	-	1620
3	B <sub>(3)</sub> -O asymmetric stretch ( <sub>as</sub> )	1456, 1423, 1355, 1279, 1254	1458, 1432, 1384, 1273, 1257	1450
4	B-O-H in plane bending	1218, 1156, 1130	1221, 1163, 1131	1155
5	B <sub>(4)</sub> -O asymmetric stretch ( <sub>as</sub> )	1077, 1031, 998	1080, 1029, 999	1070
6	B <sub>(3)</sub> -O symmetric stretch ( <sub>s</sub> )	946	944	935
7	B <sub>(4)</sub> -O symmetric stretch ( <sub>s</sub> )	824, 773	824, 769	800,
8	B-O-H out of plane bend	703	707	-
9	{B(3)-O}	668, 620	678, 619	665,
10	<sub>p</sub> {B <sub>(4)</sub> (OH) <sub>4</sub> } <sup>-</sup>	529	499	505
11	{B(4)-O}	461	462	420

Table 5.

*Band assignments in the Mid-IR spectral range for borax and tincalconite in samples PUG-18-06-A and -B.*

Note.

All Bands in cm<sup>-1</sup>

Table 6.

*Band assignments for vibrational features for alunite in samples PUG-18-05-A, -D, -H and PUG-18-08-A, -B and -F.*

	Alumina	PUG 18-05-A	PUG 18-05-D	PUG 18-05-H	PUG 18-08-A	PUG 18-08-B	PUG 18-08-F	Bishop and Mu-rad (2005)	Powell et al. (1975a)	Bhat et al. (2006)	Cloutier (1974)	Farmington et al. (1997)	Briet-Lagarde
1	OH stretching	3485, 3454	3484, 3457	3486, 3455	3488, 3393	3494, 3391	3487	3485	-	-	3472, 3412, 3246	-	-
2	$2_3(\text{SO}_4)^{2-}$ , $2_{\text{MOH}}$	2311, 2222, 2179, 2118	2215, 2169, 2106, 2058	2310, 2224, 2181, 2117	2331, 2239, 2041	2166, 2113, 2076	2227, 2181, 2116	2227, 2183, 2124	-	-	2293, 2222, 2173, 2114, 2079	-	-
3	$3(\text{SO}_4)^{2-}$	1091	1076	1079	1096, 1058	1090	1080	1083	1230 (I-II)	1097	1156, 1063	1086	-
4	MOH	1025	1024	1024	-	1026	1026	1028	-	1028	-	-	-
5	$4(\text{SO}_4)^{2-}$	627	624	623	622	620	621	622	680 (I)	631	613, 574	605	-
6	MOH	-	-	-	-	-	-	-	-	-	-	-	-
7	M-O(Al <sub>5</sub> Fe in $[\text{AlO}_4(\text{OH})_2]$ or $[\text{FeO}_6]$ )	528, 484, 443	528, 486, 443	520, 485, 432	444, 432	519, 487, 423	521, 480, 419	500	528, 486, 433	488	-	-	631, 602, 529, 432

Table 7.

Band assignments in the Mid-IR spectral range for jarosite and tamarugite in samples PUG-18-05-D PUG-18-08-E, -B and -F.

		Jarosite										Tamarugite	
		PUG-18-08-E	PUG-18-05-D	Cloutier et al. (2006)	Power et al. (1975)	Bhattacharya et al. (2016)	Bishop and Muir (2005)	Sasaki et al. (1998)	Farmers (1974)	PUG-18-08-B	PUG-18-08-F		
1	OH stretch	, 3444, 3411	, 3469	, 3412, 3333-3174	-		, 3405, 3365, 3383		-	, 2496	, 2538		
2	$2_3(\text{SO}_4)^{2-}$ , $2_{\text{MOH}}$	, 2035, 2007		, 2325, 2178, 2105, 2079, 2020, 1961	-	, 1992,	, 2101, 2076, 2016, 1961	-	-	-	-		
3	$3(\text{SO}_4)^{2-}$	, 1097, 1056	, 1098, 1061	, 1162, 1098, 1063	-	, 1230	, 1097.5, 1085	, 1088	, 1100				
4	MOH	, 1030(I)			-	, 1009.5				-	-		
5	$4(\text{SO}_4)^{2-}$	, 609	, 620, 607	, 680, 617, 606-602	-	, 680(II)	, 629	, 661	, 630	, 638		-	-
6	MOH				-					-	-		
7	M-O (Al/Fe in $[\text{AlO}_2(\text{OH})_4]$ or $[\text{FeO}_6]$ )	, 515, 475, 432	, 437		, 505, 469, 441	, 479	, 511,	, 478		-	-		

Note.

All Bands in  $\text{cm}^{-1}$

In some case, the previous authors have mentioned a range of wavenumber for a type of vibration. The proposed number of bands in the range is given in Roman numerals in parentheses.

‘ ’ refers to the frequency (wavenumber) of the fundamental vibrations in the SiO<sub>2</sub> structure

‘ ’- in-plane bending vibration

‘ ’- out-of-plane bending vibration

Table 8.

*Band assignments for vibrational features for quartz in samples PUG-18-05-A, -D, -H and PUG-18-08-A, -B, -E and -F.*

	Quartz	PUG-18-05-A	PUG-18-05-D	PUG-18-05-H	PUG-18-0
1	Asymmetric Si-O-Si stretch( <sub>3</sub> )	-	-	-	1087
2	Symmetric Si-O-Si stretch( <sub>1</sub> )	793, 782	785	794	795, 779
3	Asymmetric Si-O-Si bend( <sub>4</sub> )	-	-	-	685, 463
4	Symmetric Si-O-Si bend( <sub>2</sub> )	458			463

Note.

All Bands in cm<sup>-1</sup>

‘ ’ refers to the frequency (wavenumber) of the fundamental vibrations in the SiO<sub>2</sub> structure

Table 9.

*Borates and sulfate minerals identified in the samples used in this study along with the different techniques used for their identification*

	VNIR	FTIR	XRD
<b>Borax</b>	PUG-18-06-A	PUG-18-06-A and B	PUG-18-06-A and B
<b>Tincalconite</b>	PUG-18-06-B	PUG-18-06-B	PUG-18-06-A and B
<b>Alunite</b>	PUG-18-05-A, D, G and H PUG-18-08-A and B	PUG-18-05-A, D and H PUG-18-08-A, B and F	PUG-18-05-A and D PUG-18-08-A and F
<b>Jarosite</b>	PUG-18-05-D, G and H PUG-18-08-E	PUG-18-05-D PUG-18-08-A	PUG-18-05-D PUG-18-08-E
<b>Native Sulfur</b>	PUG-18-08-A and B	-	PUG-18-08-A and E

	<b>VNIR</b>	<b>FTIR</b>	<b>XRD</b>
<b>Copiapite</b>	PUG-18-08-C	-	PUG-18-08-C
<b>Tamarugite</b>	PUG-18-08-F	PUG-18-08-F	PUG-18-08-F