Icarus 243 (2014) 440–453

Contents lists available at ScienceDirect

Icarus

journal homepage: www.elsevier.com/locate/icarus

Use of miniaturized Raman spectrometer for detection of sulfates of different hydration states – Significance for Mars studies

Adam Culka, Filip Košek, Petr Drahota, Jan Jehlička *

Charles University in Prague, Institute of Geochemistry, Mineralogy and Mineral Resources, Albertov 6, 12843 Prague, Czech Republic

ARTICLE INFO

Article history:
Received 5 March 2014
Revised 31 July 2014
Accepted 12 August 2014
Available online 23 August 2014

Keywords:
Mars
Mineralogy
Spectroscopy

ABSTRACT

The presence of sulfates of different hydration states, specifically magnesium sulfates, has been firmly established on Mars from data acquired by both orbital and *in-situ* measurements. A lander mission typically involves a variety of instruments capable of performing a wide range of experiments from mineralogical tasks to the search for traces of life. It is clear from ongoing research that Raman spectroscopy can cover all of these tasks, and it has already been decided that future mission to Mars will employ a miniature Raman spectrometer. In this paper we report and discuss the Raman spectra of various sulfate minerals, with an emphasis on the magnesium sulfates. These were acquired by a hand-held Raman instrument, using the presently uncommon 532 nm excitation, the wavelength that is planned for the ESA lander mission. A sufficient quality of spectra were obtained with reasonably low spectral acquisition times, and the characteristic shift of the sulfate ν_1 band in the $MgSO_4 \cdot n(H_2O)$ minerals was confirmed. This was used for the unambiguous identification of magnesium sulfates of different hydration states. The present testing has confirmed the good performance of the handheld instrumentation for discrimination of structurally similar sulfates of relevance for Mars studies. This step has been proposed as the basis for subsequent testing of this instrumentation under Earth-based but Mars-analogous conditions, even using currently existing miniaturized Raman prototypes.

1. Introduction

1.1. Scientific background

The chemical and mineralogical properties of the surface and subsurface of Mars have a major significance in any understanding of the processes of rock formation throughout the course of its geologic history. Sedimentary sequences can tell us about the sedimentation environments, origins of these sedimentary materials, as well as about the potential presence and role of liquid water. The surface of Mars is mostly covered by aeolic layers of dust originating from different rocks. However, what are presumed to be non-aeolic sediments of different types have also been discovered on the martian surface (Squyres et al., 2004b); including clay rich layers (Poulet et al., 2005; Bibring et al., 2006) as well as zones of evaporites (Rieder et al., 2004), environments which are frequently thought to be formed through accumulation/precipitation in water basins.

In a few places, along with sulfates, the presence of zeolites and clay minerals (such as illite and montmorillonite) have also been indicated (Ruff, 2004; Clark et al., 2007; Ehlmann et al., 2009), which will be summarized further in the text. Areas where these minerals and rocks occur are of major interest for deciphering of the paleoalteration processes, as well as for astrobiology. A detailed knowledge of the local mineralogy will permit a reconstruction of the geochemical as well as (potentially) of the biogeochemical processes in the past. This would include redox conditions, evolution over time, as well as basic climatic estimates. The detection and estimates of minerals containing OH and water molecules in the framework of the sedimentary sequences can be considered as the primary task, along with the potential detection of water in all of its different physical states.

Several orbital remote-sensing techniques for mineral detection have been applied to obtain rough estimates of the surface distributions of minerals (Christensen et al., 2001; Bibring et al., 2004; Murchie et al., 2007). Further analytical tools were included in the rovers operating on the martian surface, or have been proposed for future missions (e.g. Squyres et al., 2003, 2004a). In 1976, the Viking landers discovered sulfur on the martian surface (Clark and Baird, 1977). Other minerals have been identified solely upon the basis of data obtained by the Mars Express (MEX) mission, specifically by its OMEGA instrument (Langevin et al., 2005; Bibring et al., 2006). Additionally, the presence of jarosite was directly

---

* Corresponding author.
E-mail address: jehlicka@natur.cuni.cz (J. Jehlička).

http://dx.doi.org/10.1016/j.icarus.2014.08.017
0019-1035/© 2014 Elsevier Inc. All rights reserved.

discovered in the Meridiani Planum on Mars using the Mössbauer spectroscopy onboard the Mars Exploration Rover (MER) *Opportunity* (Klingelhöfer et al., 2004).

To date, a Raman spectrometer has never been included as an instrument on a martian rover. It has now been adopted by the European Space Agency/Russian Federal Space Agency consortium as part of the Pasteur suite for the ExoMars-C mission, due for launch as early as 2018, and specifically designed to detect signatures of life on the surface and in the subsurface of Mars. The simplest life signatures are biomarkers, trace chemicals, and the presence of any remnants of biota from the past. There is a rather extensive discussion about the biomarkers of importance for martian studies. Parnell et al. (2007) suggested suitable target biomarkers for the ExoMars mission, however, compounds such as pigments, nucleobases, amino acids, terpenoids, will most likely occur in tiny amounts, and be dispersed or accumulated into the structure of minerals, either as inclusions or in the porous spaces within minerals. For this reason, a combined investigation of selected rock assemblages would be preferable to study those minerals present, and to eventually discover which biomarkers are potentially conserved and incorporated within the mineral masses (Villar and Edwards, 2006). The hydration states of these mineral phases is of great importance in these studies. The potential use of common miniature Raman spectrometers for detection of sulfates, including the identification of their anhydrous phases as well as those displaying different degrees of hydration, will be presented in this study.

The presence of sulfates, specifically magnesium sulfates of different hydration states, have been firmly established on Mars by data acquired from both orbital and *in-situ* measurements. A lander mission typically involves a variety of instruments capable of performing a wide range of experiments from mineralogical tasks to the search for traces of life. From ongoing research, it is clear that Raman spectroscopy can cover all of these tasks; and it has been decided that future mission to Mars will employ this methodology (Rull et al., 2011a). The majority of astrobiology-related research has been conducted with the use of full-fledged laboratory Raman instruments, but there arguably is the potential to utilize also portable or hand-held Raman instruments (Jehlička et al., 2011; Jehlička and Oren, 2013; Culka et al., 2012) serving as approximation to the instrument on ExoMars' rover.

Terrestrial analogue studies represent another possible approach to learn about the processes that are presently occurring or are suspected to have occurred in past martian environments (e.g. comparisons of sedimentary structures and properties). Some feasible sites from an astrobiological point-of-view have been suggested to learn about possible habitable environments, extreme environments, the life-style of extremophiles and/or potential biomarker conservation within rocks (Nisbet and Sleep, 2001; Edwards et al., 2005; Fernández-Remolar et al., 2011). An important iron-rich environment has been systematically investigated at Río Tinto (Spain) (Fernández-Remolar et al., 2005, 2008).

The different sedimentary structures are testimonies to the movements of liquid water on the surface (or within the subsurface) of Mars sometime in the past. The precise geochemical nature of these ancient bodies of water is still not well understood (Squyres et al., 2004b). Many of the research findings have suggested highly acidic and saline martian hydrochemistry. For example, at Melas Chasma, the past existence of a lake has been hypothesized (Metz et al., 2009). Brines and the occurrence of rocks having been formed by the evaporation of such solutions in the past are well known on Earth in sedimentary units of different ages. Halite as well as sulfates are the most characteristic minerals of these rocks. Recent as well as past processes of formation of evaporites can be followed in dry and temperate areas. On Mars, seasonal flows of brines have been proposed on the basis of detailed sedimentological investigations of the surface (McEwen et al., 2011).

1.2. Sulfates on Mars

Sulfates from the classes 07. A–D of the mineralogical system by Strunz and Nickel (2001) represent varied phases containing the sulfate anion in different molecular surroundings, bound to one or more cations. Some sulfate minerals do not contain water or the OH group, while others are hydrated. On Earth, sulfates can typically be found in sediments and sedimentary rocks being formed by water evaporation from salt lakes, for instance. Other modes of formation of crystalline or massive accumulations of sulfates include crystallization from hydrothermal solutions, such as veins associated with magmatic activity.

Sulfates on Mars play an important role in the reconstruction of martian geological history, in relationship to the past presence of liquid water. Magnesium, calcium, and iron sulfates were repeatedly identified on Mars during both the Mars Express mission and Mars Reconnaissance Orbiter project (Arvidson et al., 2005; Bibring et al., 2005; Lichtenberg et al., 2007; Milliken et al., 2007; Roach et al., 2007; Wiseman et al., 2008). Other sulfates (mainly iron-containing) were identified in the course of the Mars Exploration Rovers missions, with their rather heterogeneous distribution along the route of Spirit's rover (Haskin et al., 2005; Gellert et al., 2006; Ming et al., 2006; Wang et al., 2008). At Gusev crater different sulfates were identified, some of them being hydrous, as seen by MiniTES (Ruff et al., 2006). The iron sulfates ferricopiapite, hydronium jarosite, fibroferrite, rhomboclase, and paracoquimbite were suggested as the major sulfate minerals, based on a Pancam spectral analysis (Johnson et al., 2007), after comparing the data with laboratory spectra (Lane et al., 2008). Wang et al. (2006b) suggested, based on mineral mode analysis that Mg- and Ca-sulfates coexist with ferric sulfates. Hydrated sulfates have also been detected in dune areas in the northern polar regions, and within the Valles Marineris and Aram Chaos (Gendrin et al., 2005). Meridiani-like groundwater systems seem to have been representative of an extensive acid-sulfate aqueous system (Bibring et al., 2007). Others have proposed different means of sulfate formation in the Meridiani bedrock, suggesting reactions of sulfur dioxide with water-bearing vapors in volcanic ash accumulations (McCollom and Hynek, 2005). Acid sulfate vapors also seem to have been significant alteration agents in the vicinity of Home Plate, such as for the hydrated Fe-sulfate soils of Tyrone (Yen et al., 2008).

At the Gusev crater, the sulfate-rich minerals were possibly formed by the weathering of ferromagnesian and Ca-silicate substrates (Wang et al., 2006b; Hurowitz and McLennan, 2007). During the Hesperian period of Mars, these sulfates precipitated in acidic environments, and the subsurface water–rock interaction also played a major role in their formation (McLennan et al., 2005). At Meridiani, the precipitation of acidic sulfates is presumed to be the main geochemical process; at Gusev the production of kaolinite and the formation of other secondary minerals can be related to hydrothermal acidic leaching (Yen et al., 2008; McCubbin et al., 2009), meteoric weathering of basalts (Zolotov and Mironenko, 2007), or sulfide oxidation (Zolotov and Shock, 2005). The CRISM instrument onboard the Mars Reconnaissance Orbiter revealed the presence of H_2O- and SiOH-bearing phases, as well as hydrated Fe-sulfates related to the late Hesperian to Amazonian deposits at Valles Marineris (Milliken et al., 2008). The OMEGA instrument on the Mars Express and the CRISM instrument on the Mars Reconnaissance Orbiter (MRO) yielded evidence for the extensive presence of magnesium and calcium sulfates on the martian surface (Arvidson et al., 2005; Bibring et al., 2005; Gendrin et al., 2005; Langevin et al., 2005; Lichtenberg et al., 2007; Murchie et al., 2009); however, they showed a less obvious and less extensive