II- Detectability of Martian silica

The presence of silica on Mars may provide clues to past conditions. In addition to being an excellent preservative of possible fossil traces or geochemical conditions of the formation environment (such as cherts; Maliva et al. 1989, 2005; Robert and Chaussidon 2006; Perry and Lefticariu 2014; or Wegel Tena's opals; Chapter Three), silica can make it possible to constrain the processes that took place on Mars (hydrothermally, meteoric alteration, pedogenesis or even biogenesis). The process of silica formation is often interpreted via the presence of minerals and morphologies associated with it. Sometimes associated with hydrothermal processes (as in Toro Crater or Nili Patera, Marzo et al. 2010; Skok et al. 2010; Smith et al. 2013) or groundwater alteration (as at Terra Sirenum or Marwth Vallis; McKeown et al. 2008, 2009, 2011; Wray et al. 2011; Smith et al. 2013), silica can also carry information about these conditions (as shown in Chapter Four). Indeed, in this work, criteria allowing the determination of the structure and the environment of genesis have been developed. The identification of pedogenetic processes (as observed in Ethiopia) would show that in the past, Mars experienced climatic conditions allowing the development of soil. Similarly, the presence of diagenetic silica sequences (opal-A, opal-CT and chalcedony) would suggest significant silica deposits, mainly observed on Earth during the presence of organisms allowing its precipitation in large quantities.

Even if the presence of Martian silica is demonstrated, are the data acquired by the various instruments sufficiently precise to make it possible to discriminate the nature of this silica, as well as their formation process?

1°)   Orbital detections

Most orbital silica detections on Mars rely on infrared signatures. The entire infrared range (near, medium and far, defined in Chapter II-III-2°-a) is used to identify silica. The orbital detection method uses Spectro-imagers. These instruments have the particularity of acquiring a spectrum for each pixel of an image of the planetary surface (all these data are called a cube). Two main types of Spectro imaging exist, multispectral (using wide-banded and non-contiguous spectral band sensors) and hyperspectral (using narrowband and contiguous sensors).

a)   Spectro-imagers

i)   *Infrared* process

The water bands embedded in silica (visible in the near infrared) were used in the first orbital silica detection (Milliken et al., 2008). This detection was made thanks to the hyperspectral Spectro-imager Compact Reconnaissance Imaging Spectrometer for Mars (CRISM), which acquires a spectrum between 0.4 and 4µm (between 25000 and 2500 cm^{-1}) per pixel of acquired image, embarked on the Mars Reconnaissance Orbiter (MRO). In this range, the spectral resolution is 6.5 nm, or between 400 and 5 cm^{-1} resolution depending on the spectral range *. This instrument makes it possible to make images with a spatial resolution of 18 m per pixel under the best conditions (Murchie et al., 2007).

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* Attention, the conversion of wavelength (µm or nm) to wavenumber $(cm\text{-}1)$ is not a linear relationship $(\upsilon(^{cm\text{-}1}) = 1/ \lambda_{(cm)})$. In fact, a spectral resolution in wavelength will not have the same equivalent in number of waves depending on the range studied.

Another spectro-imager uses near infrared: the Observatory for Mineralogy, Water, Ice and Activity (OMEGA). This instrument, on board the Mars Express probe, can acquire spectra between 0.38 and 5.1μm. In the range 0.93-2.73μm (10750 and 3660 cm-1) that interests us, the spectral resolution is 13 nm (which is equivalent to a resolution of $\approx$ 150 cm-1 in low wavelengths and $\approx$ 17 [cm-1] in high wavelengths). It makes it possible to make images with a spatial resolution of 350 m per pixel at best (Bibring et al., 2004).

ii)   Middle and far infrared

The mid-infrared and [far-infrared] range is also exploited thanks to the Thermal Emission Imaging System (THEMIS), a multispectral spectro-imager that has 10 measurement channels between 6.5 and 15μm (between $\approx$ 1540 and 660 cm-1; Christensen et al., 2004). Another instrument, the Thermal Emission Spectrometer (TES) aboard Mars Global Surveyor, samples this range (6 to 50μm; 1665 to 200 cm-1) with a spectral resolution of 5 and 10 [cm-1] (Christensen et al., 1992). However, although TES has a finer spectral resolution, its spatial resolution (several kilometers) is much wider than THEMIS ($\approx$ 100 m per pixel maximum).

The mid-and far-infrared range is used to distinguish between different silica phases (Lippincott et al., 1958; Michalski, 2003) and to quantify silica abundance on the surface (Lyon, 1965; Vincent and Thomson, 1972; Walter and Salisbury, 1989; Ramsey and Christensen, 1998). Only the TES instrument has the spectral ability to distinguish the different phases of silica. However, the spatial resolution of TES is too low (and most silica indices too narrow) to make this possible. In fact, mid-and far-infrared orbital on Mars is used primarily for quantifying$SiO2$ concentration over large areas (Smith et al., 2013).

b)   Instrumentation Limitation

Silica detections on Mars are subject to the same limitations and biases as the detection of all hydrated minerals. The spectral resolution of CRISM and OMEGA spectro-imagers is considered sufficient for the detection of the majority of hydrated minerals (Carter et al., 2013). Statistically, spatial resolution has been shown to be the limiting factor for detection. Indeed, Carter et al. (2013) showed that detection density (number of detections per unit area) increased with improved spatial resolution.

 Another limitation of detection via orbital spectro-imagers is attributed to the population covering the planet. This dust, composed mainly of   iron-rich anhydrous silicates, covers $\approx$ 88% of the planet's surface (Poulet et al., 2007; Ody et al., 2012; Carter et al., 2013). The composition of the surface becomes inaccessible by Spectro imaging as soon as a layer of several hundred micrometers covers this surface (Singer and Roush, 1983; Fischer and Pieters, 1993). The majority of hydrated mineral detections   are therefore made in areas less covered by dust (Carter et al., 2013).

The spectra acquired are corrected for the Martian atmosphere, mainly composed ofCO_2 (Owen et al., 1977). The presence of CO_2 implies 3 thin bands in the region around 2μm (1.955, 2.013 and 2.060μm; 5115, 4968 and 4855 [cm-1]; Martin and Barker 1932), thus close to the molecular water zone of silica. The correction of   these bands of atmospheric origin is mainly done using a technique called "volcano-scan". The principle (simplified) is to take a spectrum at the top of Olympus Mons (a volcano, highest point of Mars) and a spectrum devoid of dust and ice at the base of this volcano. An algorithm will calculate the difference between the two spectra (corresponding to the atmosphere) and correct the spectra (McGuire et al., 2009). This correction is widely used and induces slight approximations in this range.

c)   Spectral library

Mineral detection refers to spectra obtained after correction and spectral libraries listing a large quantity of minerals. The bookstores used are mainly those of the USGS (Clark et al., 2007) and RELAB (Pieters, 2010).   In the USGS library, only two opals are present (compared to 17 spectra available for olivines). The first (TM8896) is identified as a mixture of opal-A and –CT and the second (WS732) is an opal-CT rich in cristobalite.   The descriptions provided suggest that these two opals are derived from biogenic opal diagenesis.

The RELAB library provides the spectra of 9 opals (the spectra are presented in Figure   V-2):
- 4 come from different areas of the Taupo hydrothermal system (New Zealand; Goryniuk (2004)
- 1 comes from deep marine sediments.
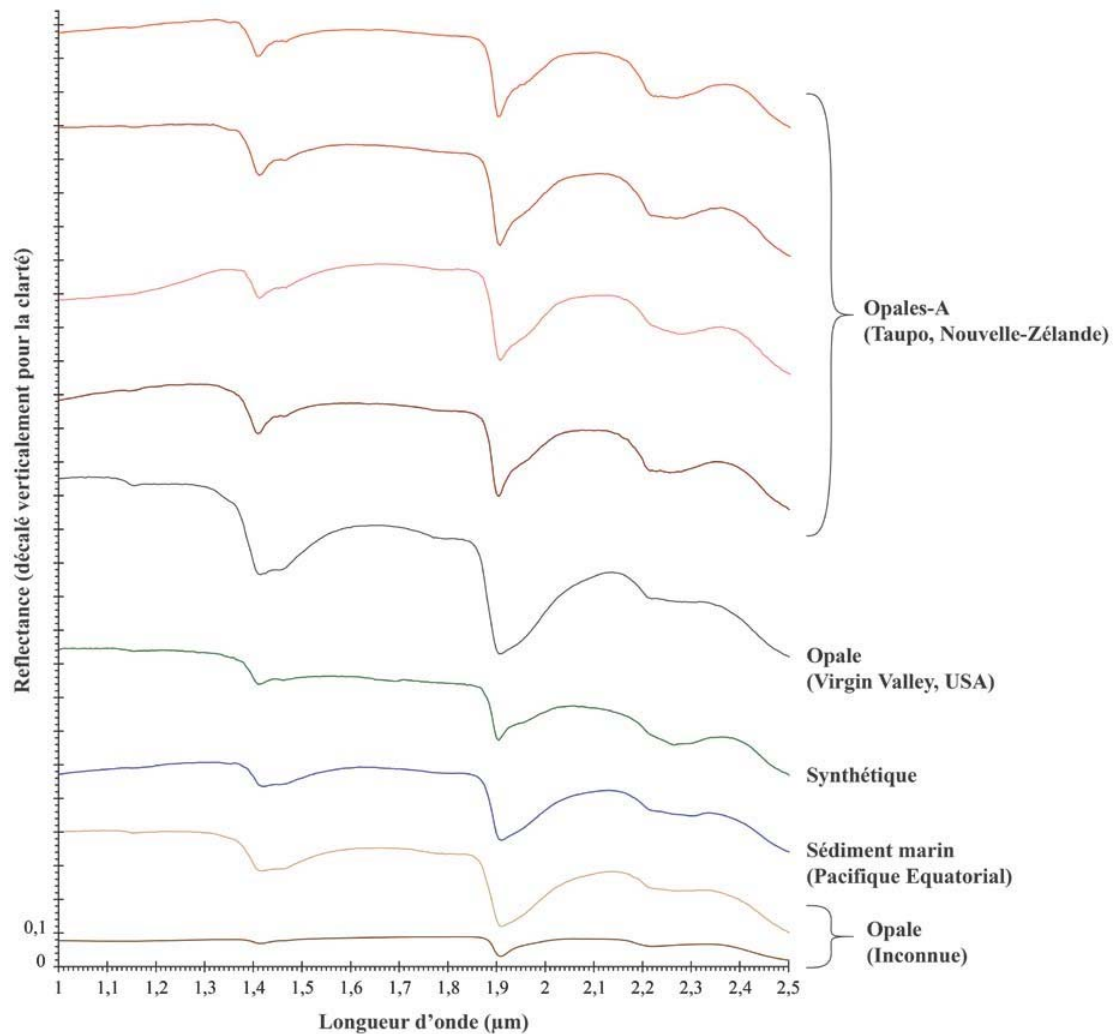- 1 is from Virgin Valley
- 1 synthetic
- 2 are of unknown origin.

Figure V-2: Spectra of opals from the RELAB spectral library used as a reference for Martian silica spectra.

These spectral libraries (USGS and RELAB) have several weak points. On the one hand, some of the samples are poorly characterized at the level of their structure (opal-A or -CT). On the other hand, the samples do not transcribe the wide variety of contexts in which silica can be found. Biogenic opal is well represented (the two USGS opals and one RELAB opal), as is hydrothermal opal (4 RELAB opals). But it is not presented opals from context of meteoric alteration, which is nevertheless part of the important processes of creation of opal. In addition, the results presented in Chapter Four show that the context of precipitation plays a role in the shape of the band, so it is important to consider the majority of training contexts.

The sampling used in Chapter Four could bring a variety of complementary silica to these spectral libraries.

d)   Applications of spectral criteria

It is important to take precautions with regard to the use of spectral criteria acquired under terrestrial conditions for Martian detections (Bishop and Pieters, 1995; Rice et al., 2013). Martian conditions (especially low pressure) have the effect of modifying the hydration of   silica, thus the bands of silica in the near infrared (used in identification). Laboratory experiments under Martian conditions show that molecular water is evacuated in the same way as heating (Milliken et al., 2008; Rice et al., 2010b, 2013).

As shown earlier, it is possible to extract information about the mineralogical phase through spectra in the near-infrared region.

i)   *Instrumental* detectability

1.   Spectral resolution

The second essential question before the application of terrestrial spectral criteria is to check whether the criteria are visible with the instruments used. For an orbital use of the criteria developed in Chapter Fourth, the finest spectral resolution is that of CRISM (6.55 nm; Murchie et al. 2007). However, this resolution does not allow the position criterion of the apparent maximum on the band to be applied to 1.9µm (5200^{cm-1}).   Indeed, this criterion implies a variation of a few cm-1 whereas CRISM cannot differentiate, in this spectral range, two points separated by less than ≈ 20 $^{cm-1}$. This criterion could therefore not be used with CRISM. For the CRC, it is likely that the problem is identical because it is based on a precise positioning of the apparent maximum. In addition, atmospheric correction involves variations in CO_2 bands close to the 2µm zone. In particular, the correction of the band at 1.955µm (i.e., 5115 cm-1) is critical because the CRC involves taking the absorption of the band at 5100   cm-1 (Figure V-3).

CRISM being the   spectro-imager using the finest spectral resolution, these criteria are not usable for orbital detections.
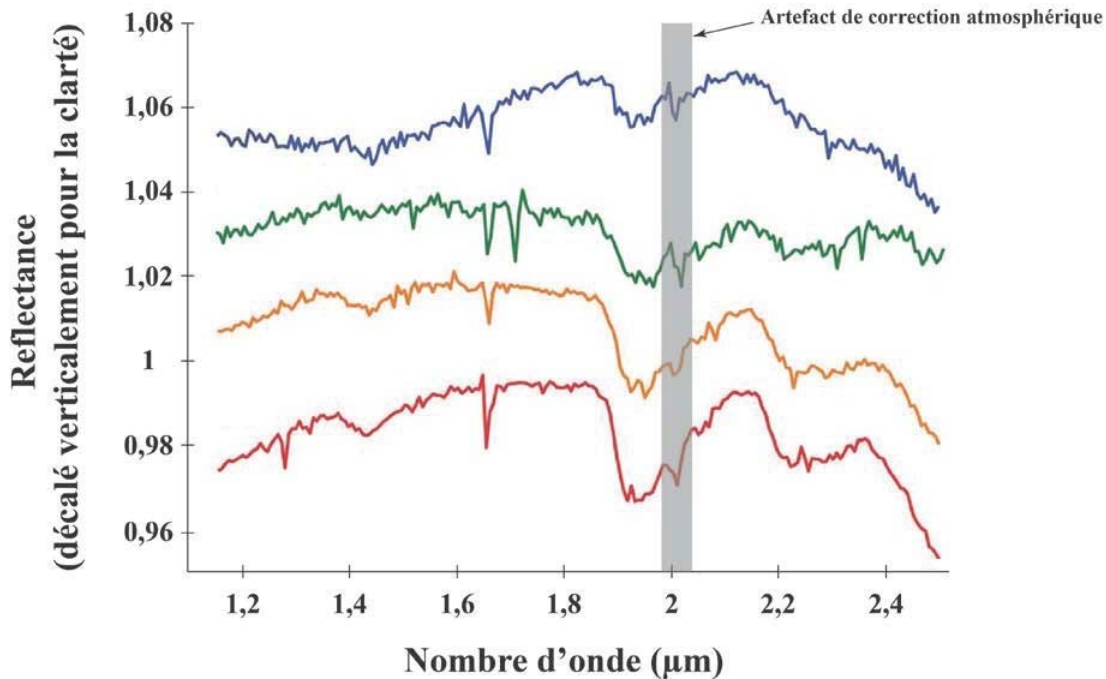
Figure V-3: Spectra acquired by CRISM on silica showings near Antoniadi Crater (modified from Smith and Bandfield 2012) and corrected according to the volcano-scan method of McGuire et al. (2009). The spectrum shows an artifact due to this correction on the low-frequency (high-wavelength) part of the 1.9μm band.

2. *Spatial resolution, mixing problem.*

Spatial resolution also involves detectability issues. Indeed, even with the best spatial resolution currently available for the orbital (18 m per pixel) it is rare to observe deposits of pure amorphous silica over such an area. It is therefore likely that silica is mixed with other minerals with absorption bands at the same wavelengths. In the area of one pixel (several hundred square meters), two phases can coexist. These different phases are mixed either in a "surfacing" way (for example, on 20 m² of the pixel, 10 m² of a pure phase, and 10 m² of a second) or intimately (mixing of two phases even at a reduced spatial scale, typically, the mixture of two powders). The infrared signature of surface mixtures is the average of the spectra of each component of the mixture, weighted to the surface proportion of each constituent (so-called linear mixture). However, for intimate mixtures, mixing does not necessarily behave linearly due to factors such as grain size and diffusion of different components (Nash and Conel,1974; Hapke, 1981; Mustard and Pieters, 1989; Bishop and Dummel, 1996).

It is therefore important to constrain the threshold at which the concentration of amorphous silica is sufficient to be detected via spectro-imagers. Intimate mixtures of montmorillonite, kaolinite, obsidian and opal-A show that these mixtures behave linearly in the 0.3 – 2μm range (McKeown et al., 2011). However, for the 2-2.5μm range, these mixtures no longer behave linearly. It has also been shown that a silica film of several tens of microns covering grains also shows an amorphous silica signature (Minitti et al., 2007; Seelos et al., 2010). Knowing that the infrared signatures studied here are limited to pure hydrated silica, mixing with other minerals involves different band shapes. The mixtures therefore have a strong impact on infrared mineral characterization.

ii)   Method coupling

The spectral criteria developed here can be used exclusively for silica. In this case, it is essential to check that the surface is exclusively, or at least primarily, made of silica. For this, the coupling between different techniques is essential. As preliminary results, it was acquired the powder spectrum of 3 silica (having 3 different band shapes) and fresh tuff harvested   in Ethiopia (Timkete Bahir deposit). ; Figure V-4). In the near infrared, the water in silica has a signal very close to that contained in rhyolite. Only the band around 2.2µm (4500^{cm-1}) seems to be different between opals and rhyolitic tuff. This implies that it would be impossible to discriminate opal deposits from rhyolite tuff from Wegel Tena-like deposits (pedogenetic) using only the near infrared.

In this case, the use of other methods, in particular mid-and far-infrared spectroscopy, makes it possible to discriminate between these two types of mineralogy (Lyon, 1965; Michalski, 2003). However, currently, probes do not have a spectrometer with sufficient spatial resolution for efficient coupling between near-infrared and longer-wavelength intragroup spectro-imagers.
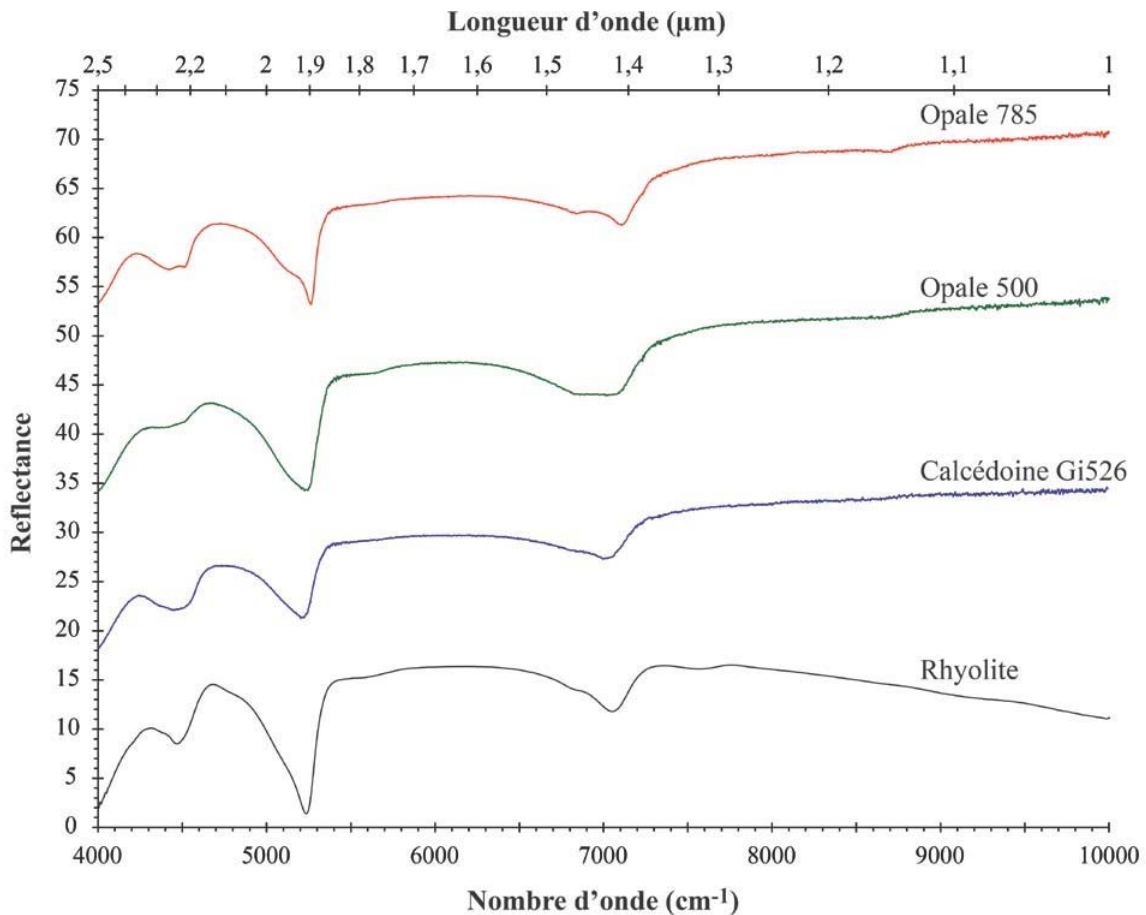

Figure V-4: Reflectance spectra of silica and rhyolite powders. The silica corresponds to the samples used in Chapter Four.   The difference between rhyolitic tuff and   *silica for bands at 5200 and 7000^{cm-1}(1.9 and 1.4µm) is not significant.*

In the current state of knowledge, mid and far infrared have not shown a criterion for differentiating opals from different precipitation media. The coupling between the infrared ranges would therefore constrain the nature and geological environment of silica deposit.

Orbital spectral imaging has observed that hydrated silica is present in many areas of Mars. However, the determination of the silica structure, as well as the deposition environment, is subject to many problems intrinsic to the technique. Indeed, the atmosphere and dust are natural obstacles to obtaining a fully exploitable silica signal. The definite advantage of orbital detections is the extent of the surface area studied. This technique makes it possible to observe large areas (several 100 m² to several km²) and to map them to the infrared signatures and spectral morphologies observed. However, it is interesting to determine areas with signatures suggesting silica deposits, for future investigations via *in-situ analyses*.

2°)   *In-situ* analyses

Various missions have been (and   will be) launched on the surface of Mars to determine its geology and   deduce the conditions that prevailed there (also to determine if life could have developed there). Although these analyses are restricted to restricted areas, they have the advantage of being less affected by the atmosphere. In addition, rovers have a wider range of mineralogical analysis methods (both chemistry and structure).

a)   Spectro-imaging

The first detection of hydrated silica in *situ* was made by a spectro-imager on board the Spirit rover in Gusev Crater (Squyres et al., 2008). The Miniature Thermal Emission Spectrometer (Mini-TES) has acquired   spectra between 450 and 1500 cm-1 with a spectral resolution of 10 [cm-1]. It has a spatial resolution between 7 and 18 cm per pixel for an area 10 m away (Christensen, 2003). Mini-TES has the spectral ability to distinguish different silica phases by their signatures in the mid- and far-infrared (Lippincott et al., 1958; Michalski, 2003).

The other spectro-imagers currently on board do not cover the spectral range in which the main characteristic absorptions of silica are visible, or of the water it contains. Indeed, the multispectral camera Panoramic Camera (Pancam), aboard the Mars Exploration Rovers (SED: Spirit and Opportunity) has two channels at 0.934 and 1.009µm (at ≈ 10700 and 9900 cm^{-1}; Bell et al. 2003). On Mars Science Laboratory (MSL, aka Curiosity), the Mast-Mounted Cameras (Mast-cams) have two filters to watch at 0.935 and 1.035µm (≈ 10700 and 9660 [cm-1]; Malin et al. 2010). Although there is a harmonic of water bands in silica around 0.95µm (≈ 10530[cm-1], which has not been studied here), Rice et al. (2013) showed that this band was neither diagnostic of hydrated silica, nor visible with these onboard instruments.

b)   Other on-board instruments

Rovers have other instruments that allow the identification of silica. On the MERs, the analysis by spectro-imagers can be associated with chemical analyses by microanalysis X (Chapter Seconde-II-1°) a) . Indeed, the first detections by silica spectral imaging in Gusev Crater were coupled with APXS analyses (Alpha Particle X-ray Spectrometer; Rieder et al.

2003) allowing to conclude that silica was pure up to 80-98% weight (Ruff et al., 2011). This type of analysis constrains chemistry, but it is not possible to deduce the silica polymorph involved.

Mars Science Laboratory (MSL, aka Curiosity) has a much larger array of instruments for mineralogical analysis. An APXS is also present on MSL, with improvements compared to those on board on the MER, allowing chemical analyses on an area of about 20 cm² (Gellert et al., 2009). APXS is based on the principles of microanalysis X (Chapter Two-II-1°) a) which does not normally analyze light or volatile elements, but simulation techniques make it possible to deduce the hydration of the target (Campbell et al., 2008). The proportion of water in silica can make it possible to deduce some clues about the siliceous phase analyzed (opals have higher water concentrations than chalcedony). Chemistry is also accessible through Chemical & Camera (ChemCam), which is based on the principles of Laser Induced Breakdown Spectroscopy (LIBS, Maurice et al. 2012; Wiens et al. 2012). This method consists of pulverizing, via a powerful laser, a part of the sample that will be transformed into plasma, whose emitted radiation will be analyzed. This spectroscopy makes it possible to have the chemistry of the target on an area of less than 1 mm². These techniques therefore make it possible to determine the presence of silica, but hardly the phase. For this, the CheMin instrument makes it possible to acquire diffractograms of minerals. Based on X-ray diffraction, which makes it possible to know the structural parameters of minerals, it is possible to deduce in which form silica is (Blake et al., 2009, 2012). MSL is therefore the rover currently best able to detect and analyze silica on Mars effectively. However, no available instrument allows to deduce the process of formation (at the time of the available infrared spectroscopy).

c) Future missions

i) ExoMars

The European Space Agency's (ESA; in collaboration with Ros cosmos, the Russian space agency) program plans to launch an orbiter and a rover. On the latter, several instruments are dedicated to the analysis of mineralogy. Two spectro-imagers are planned for mineralogical analysis. ISEM (Infrared Spectroscopy for ExoMars) and MicrOmega can acquire spectra in the ranges 1.1-3.3μm (3030-9090 cm-1) and 0.9-3.5 (2850-11100 cm-1) μm respectively (Pilorget et al., 2012; Korablev et al., 2014). Although the spectral resolution is quite low (≈25 cm-1 for ISEM, ≈ 20 cm-1 for MicrOmega), these analyses overcome the problems induced by atmospheric corrections and spatial resolution. In addition to infrared analysis, the rover will be equipped with the Raman Laser Spectrometer (RSL; Rull et al. 2011) which makes it possible to acquire Raman spectra, with which it is possible to deduce the structure (see Chapter Second 2°). This mission also aims to collect samples for a return to Earth. This rover will therefore have a sufficient instrumental range for a finer study of Martian silica.

ii) March2020

The US Mars2020 mission, scheduled for launch in 2020, consists of a rover, resembling the current MSL. The rover will host the French SuperCam instrument, an improved version of ChemCam. This instrument is a coupling of LIBS (like ChemCam, allowing to have the precise chemistry), Raman (for the structure) and infrared analysis (Maurice et al., 2015). In addition to the Raman spectroscopy (characterizing the silica polymorph), this instrument may be able to allow a calculation of the CRC (thanks to infrared analysis), thus identifying clues on

the formation of these silica. This instrument has all the assets to collect the maximum information that silica can provide.

On this rover, it is also planned to embark an instrument to acquire chemistry by X-ray microanalysis (called PIXL for Planetary Instrument for X-ray Litho-chemistry; Allwood et al. 2015).

Martian silica has already been identified on Mars, mainly thanks to spectro-imagers on board orbital probes. These detections have shown that silica is associated with various minerals, as well as with several types of morphology. However, the problems intrinsic to this method do not make it possible to identify more precisely the silica phase detected, let alone to deduce the genesis process. Indeed, the criteria developed in this thesis work are not usable by these instruments. Orbital spectral imaging is therefore limited for the identification of the phases and processes of silica genesis on Mars.

On the other hand, instruments on board the ships on the surface of Mars could allow further investigation. Currently, it is the Curiosity rover (MSL) that has the instrumental range best able to extract the maximum amount of information from silica (the structure via CheMin and the chemo via ChemCam). However, no tool can deduce its genesis environment by infrared spectroscopy. The future rovers, ExoMars and Mars2020 have all the analysis devices to deduce the structure (especially thanks to the Raman) and the genesis environment (with infrared spectro-imagers). Questions about some Martian silica outcrops will therefore have to wait for the new rovers to find answers.