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Spectroscopic studies of materials relevant for the hydrological evolution of Mars

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Abstract. Due to the present climatic conditions, liquid water is unstable on the Martian surface. For this reason the search for signs of the stable presence of surficial liquid water in the past is an extremely important issue which can give precious information about the geological and climatic evolution of Mars and could have very important implications on the possibility that life developed at some stage on the planet. The Astrophysics Group of the University of Lecce has been involved for many years in laboratory studies about particulate samples of minerals (such as hematite, carbonates, sulphates and other evaporites), whose origin is linked with the presence of bodies of standing water, as well as of materials (in particular olivine) at least partially subject to aqueous alteration. The experimental data are used as input parameters in radiation transfer models in order to produce synthetic Martian spectra to be compared with the observational data. This comparison could give important clues about the composition of Martian soil and aerosol. In this work we will review our spectroscopic studies of materials relevant to the search for the past existence of liquid water on the Martian surface, with particular emphasis on the recent laboratory work on the aqueous alteration of olivine.

1. Introduction

In spite of a great deal of work on the subject, our understanding of early Mars climatic history remains still fuzzy. The present day hyperarid climate, characterized by an annually averaged surface temperature close to 210 K and an atmospheric pressure of about 6 mbar, makes Mars a very inhospitable world. However, data from several robotic (both orbiter and lander) missions have demonstrated convincingly that Mars was once a warmer and wetter place (Mars Pathfinder Rover team 1997; Phillips et al. 2001; Craddock & Howard et al. 2002). In particular, early Mars may have experienced episodes of relative mild climate as a result of thicker greenhouse atmosphere able to produce surface temperatures and atmospheric pressures high enough to make liquid water stable on the planet surface (Forget et al. 2004). Important remnants of this period are scattered spots of the Martian surface where geological structures like fluvial valleys probably due to atmospheric precipitation (Mangold et al. 2004), deltas (Ori, Marinangeli & Baliva 2000; Malin & Edgett 2003) and recently exhumed deposits of water-related minerals are present. In particular both hematite and sulfates have been observed in Terra Meridiani, in Aram Chaos and in various areas of the

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Valles Marineris system (Christensen et al. 2001; Gendrin et al. 2005). In the same locations outcrops of clays and other hydrated materials seem also to be present (Milliken et al. 2005). Furthermore, according to Poulet et al. (2005), in a region North-East of Syrtis Major called Nili Fossae, serpentine, a typical product of the aqueous alteration of olivine, is likely present. Only carbonates deposits, predicted by several geochemical models (Pollack et al. 1987; Schaefer 1990) and since long time searched for by various researchers, up to now escaped any observation. In this context, laboratory work, as well as theoretical studies are mandatory in order to confirm the recent discoveries of water-related minerals and to perform a systematic search for carbonates. For this purpose since many years the Astrophysics Group of the University of Lecce has started a research program aimed to study the optical properties of minerals relevant for Martian studies. In particular we focused our attention on those materials which could have experienced interaction with water, either during the formation or subsequently. The main goal is to use the laboratory data as input parameters in radiation transfer models in order to produce synthetic Martian spectra to be compared with the observational data, supplied by the spectrometers (TES, PFS and OMEGA) which are now orbiting on board Mars Global Surveyor and Mars Express spacecrafts around Mars. This comparison could give important clues about the composition of Martian soil and aerosol. In the present work we will review the results of our recent experimental and theoretical studies. In the following section we will briefly discuss our research on the spectral behaviour of water-related minerals, while in the third section we will focus on the very recent laboratory work on olivine samples weathered by aqueous alteration.

2. Water-related minerals

Among the materials whose formation process normally requires the presence of liquid water, the Astrophysics Group of the University of Lecce has focused its attention on the optical properties of limestone, gypsum and hematite. In particular the optical constants of a particulate sample of limestone, a typical carbonate material mainly composed of calcite ($CaCO_3$), have been determined in the 1.5 - 62.5 μm range. These results have been used in a tentative fit of Martian spectra measured by ISO and they seem to indicate the possible presence of carbonates in the Martian aerosol (Orofino et al. 1998, 2002). The same data, together with the optical constants of submicron gypsum ($CaSO_4 \cdot 2(H_2O)$) particles determined in our laboratory (Marzo et al. 2004) have also been used in a radiative transfer model in order to obtain synthetic spectra of Mars to be compared with the spectra of the planet provided by the instruments at work on Mars. The results of this work are the main subject of a paper in preparation (Fonti et al. in prep).

Among the materials of Martian interest, hematite is certainly one of the most important. Hematite is a ferric oxide (α-Fe_2O_3) naturally occurring in two forms, mainly depending on the granulometry of the samples. Because of the visual colour of Mars, red hematite and others ferric oxides have long been suggested as surface materials, especially for brighter, redder regions of the planet. In addition, in some scattered spots of the Martian surface hematite particles with size even greater than those of red hematite (typically > 10 μm) are present. Due to its colour, this kind of coarser-grained hematite is called grey hematite. Christensen et al. (2000, 2001) found evidence for a large deposit of grey hematite in a low albedo area in the Sinus Meridiani region of Mars. Coarse hematite is considered strong evidence for longstanding water, which led to the decision to land the rover Opportunity there. On the contrary, it is unknown whether the formation of fine-grained hematite requires abundant water. In this respect, studies are needed in order to definitely distinguish fine-intimate from coarse hematite. For this reason in our laboratory we analyzed a sample of submicron hematite particles in the 6.25-50 μm range in order to study the influence of particles size and shape on the infrared spectra. Moreover we have derived the optical constants of this particulate sample and we have compared our results with those published for bulk samples

of hematite. Synthetic absorption spectra of hematite have been calculated by means of these sets of n and k, choosing the appropriate particle shape distributions, in order to well reproduce the experimental extinction spectrum. An important result of our study is the fact that shape effects could play an important role for the interpretation of astronomical spectra (Jurewicz et al. 2003).
In the case of hematite, as a consequence of the production of small irregularly-shaped particles by mechanical grinding, a model based on a collection of randomly oriented ellipsoids can reproduce the experimental extinction spectrum better than the Mie theory spherical approximation (Marra et al. 2005).

3. Aqueous alteration

Aqueous alteration is a process that changes the physical and chemical properties of a rock forming material, due to its interaction with liquid water. Aqueous alteration is a common process in some bodies of the Solar System. In fact it has been observed on Earth, in the interplanetary dust particles (MacKinnon & Rietmeijer 1987; Sanford 1987) and in the meteorites (Zolensky & McSween 1988). In particular aqueous alteration also occurred in an important group of Martian meteorites collectively called SNC meteorites. Carbonates and other evaporitic minerals (such as halite, gypsum and anhydrite), oxides (magnetite and hematite) and phyllosilicates are the main secondary minerals present in these meteorites (Treiman 1993; Gillet et al. 2001). Among phyllosilicates, serpentine and iddingsite are the main product of aqueous alteration of olivine, while smectite clay and hisingerite are the most abundant products of the alteration of pyroxene. The location (Treiman 1993), the isotopic composition (Sutton et al. 2002) and the age of the secondary materials found in the Martian meteorites strongly suggest that alteration is preterrestrial.

While the presence of the products of aqueous alteration in the SNC meteorites is well assessed, it is not clear if such materials are present in form of massive deposits or outcrops on the surface of Mars. The problem of the existence of massive outcrops of olivine on the Martian surface is a very interesting issue which is still far to be clear. Olivine ($(Mg, Fe)_2SiO_4$) is a rock-forming mineral, very abundant on Earth, consisting of an isomorphic mixture between two silicate end-members: forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4). The crystals have a typical green colour, more or less dark depending on the fayalite content. Terrestrial olivine is basically forsteritic in composition and it is the main constituent of mafic effusive rocks, such as gabbri, basalts, and peridotites.

In Table 1 are listed the bands present in the spectra of pure unaltered olivine, compared with those present in the spectra of altered olivine, in the range $0.2 \div 5.5\ \mu$m.

Table 1. Spectral position of the bands exhibited by unaltered and altered olivine.

Unaltered Olivine	Altered Olivine
-	0.46 μm
-	0.65 μm
1.00 μm	1.00 μm
-	2.20 μm
2.75 μm	-
-	2.90 μm
-	4.28μm
-	4.80 μm
5.5 μm	-

The common alteration products of olivine on Earth are iddingsite and Mg-phyllosilicates mostly serpentine, but also chlorite and talc. Iddingsite is a reddish-brown mineraloid made of a mixture of phyllosilicates (montmorillonite and chlorite), iron oxides (goethite and hematite), quartz and calcite (Burns 1986). Generally serpentine is the main final product of hydrothermal alteration of olivine; Takatori et al. (1993) have, indeed, synthesized serpentine samples from olivine powders sealed in pure water and heated in autoclaves at 400 °C and 500 bars for 1 week. On the contrary iddingsite is the main final product of alteration of olivine by water at low temperature, probably less than 70 °C (Treiman 1993; Romanek et al. 1996).

In the earlier stages of aqueous alteration, olivine can be still pure, in the sense that the alteration products have not appeared yet, even at a microscopic scale. At these stages the aqueous alteration is mainly linked to the characteristic features at about 0.46 and 0.65 μm due to oxidised iron present in olivine. In this case also the hydration bands, due to OH^- and H_2O, often appear in the range 0.9 ÷ 2.8 μm (in particular at about 1.4, 1.9 and 2.3 μm).

We produced several grain samples starting from commercially available bulk samples of olivine called Eifel, after the site they have been collected (Krantz GmbH, Germany). The geological setting of Eifel region (Mader & Teyssen 1985) is consistent with an aqueous alteration of the samples under study. The grains have then been selected in six different size ranges:

a) greater than 426 μm;
b) between 426 and 300 μm;
c) between 300 and 200 μm;
d) between 200 and 106 μm;
e) between106 and 50 μm;
f) smaller than 50 μm.

Scanning Electron Microscope (SEM) images obtained at different magnifications show that in addition to olivine grains with a smooth surface, it is possible to observe a small group of particles characterized by a rough surface. It is possible that the latter represents a product of aqueous alteration of the pristine olivine grains. The qualitative Energy Dispersive X-ray (EDX) elemental analysis confirms the different composition of the two kinds of grains.

For the reflectance measurements we used a Perkin Elmer Lambda 900 (PE-L900) spectrophotometer in the range UV/Vis/NIR (0.2 ÷ 2.5 μm) equipped with an integrating sphere of 150 mm in Spectralon.

In Fig. 1 we present all the spectra relative to the six granulometry classes in the whole spectral range of interest. As it can be seen, all the spectra exhibit a band at 0.65 μm and a shoulder at 0.46 μm on the steep slope from 0.3 to 0.5 μm. These features confirm that the samples are actually altered.

From Fig. 1 it is also immediately evident that the grain size has a strong influence on the appearance of the spectra: the continuum level increases and the spectral contrast decreases as the grain size becomes smaller. Such an effect is particularly evident for the steep rise from 0.3 to 0.5 μm, for the deep absorbing band around 1 μm and for the wide knee at about 1.6 μm. At the same time we note an overall flattening of the reflectance from 0.5 to 2.5 μm.

Some interesting effects are worth to be addressed for their potential use in the interpretation of the observed Martian spectra. If we focus our attention (see Fig. 1) on the structures between 0.5 and 0.8 μm, we clearly see that they undergo evident changes. Such changes are a consequence of the modifications induced by the varying grain size in the steep rise from 0.3 to 0.5 μm, and in the absorption band at 1 μm as well as in the weaker bands at 0.45 and 0.65 μm. Even if the modifications in the appearance of the spectra are linked to changes in the absorption efficiency of the samples, they can more easily be tracked focusing on the two spectral structures separating the weak 0.65 μm band from the main band at 1 μm on one side and from the shoulder at 0.45 μm on the other. The position of these two structures is 0.56 and 0.73 μm respectively and it is almost perfectly stable for all the samples we examined. In order to find a quantitative relation between the shape of the measured spectrum and the grain size (s), we can define the parameter $\Delta(s)$:

$$\Delta(s) = R(0.56) - R(0.73)$$

where R(0.56) and R(0.73) are the measured reflectivity at 0.56 and 0.73 μm respectively. In Fig. 2 we plot the value of Δ versus the logarithm of what we conventionally assumed as the average grain size of each of the six chosen size classes, that is the size value at one third of the width of each class. In addition we assumed as zero the lower size value of the first class. As it can be seen, the experimental points are reasonably well fitted by a linear function.

The error bars reported in Fig. 2 have been evaluated taking into account all the experimental uncertainties. In particular, as far as the average grain size is concerned, a rather large value (±15 %) has been adopted, because of the difficulty to determine the actual size distribution within each interval. Much more

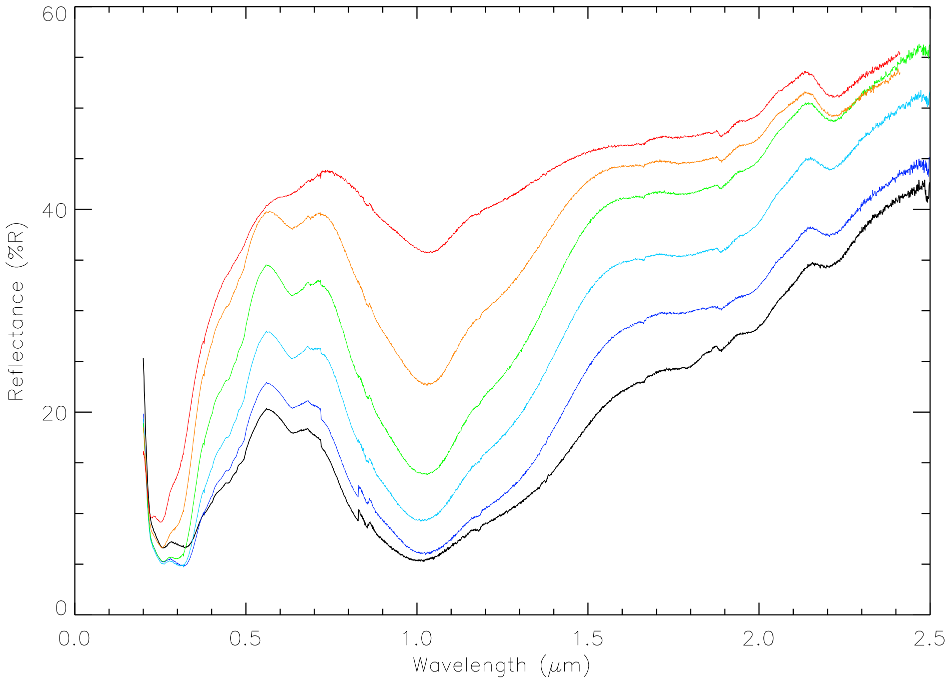

Fig. 1. Spectra of samples of olivine particles collected in the different grain size: greater than 426 μm (black line); 426 ÷ 300 μm (blue line); 300 ÷ 200 μm (cyan line); 200 ÷ 106 μm (green line); 106 ÷ 50 μm (orange line); smaller than 50 μm (red line). The steep rise shortward of 0.2 μm and the two tiny structures between 0.8 and 0.9 μm are instrumental effects.

straightforward is the evaluation of the error bar on the Δ parameter, which has been directly derived from the uncertainty on the measured reflectance ± 0.5 %, given by the manufacturer of the integrating sphere.

The calculated value of the correlation coefficient is $r = 0.99$, which implies that a linear correlation could be a quite good approximation of the actual relation between the parameter Δ, directly derived from the spectrum, and the grain size. If this is the case, it would be possible to derive from a spectral measurement the average particle size of the observed planetary regolith in an independent way. In fact, since the parameter Δ has been defined as the difference between two intensities relative to the same spectrum, the information contained in Fig. 2 would not be affected by all the other effects mentioned above (i.e. viewing geometry, relative abundance of olivine, etc.), which usually tend to confuse the information about the grain size.

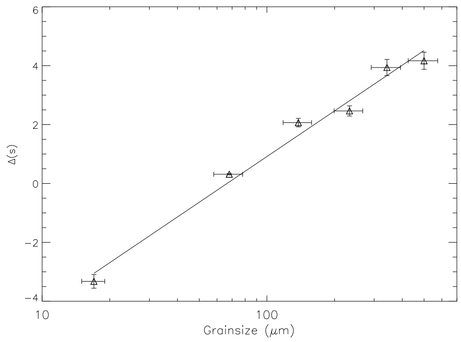

Fig. 2. Correlation between grain size and the parameter Δ (see text for the definition).

In conclusion the spectroscopic study of altered olivine particles, which is the subject of a paper by Orofino et al. (2005), provides some peculiar signatures which can be very useful for the identification of such material in space and for Martian studies, in particular about the geology, chemistry and physics of Mars. Indeed if the olivine signature at about 0.65 μm will be found in the observed spectra of Mars, it will be possible to draw some conclusions on the Martian paleoclimate as well as on the size of regolith particles which will be useful for subsequent studies of the surface.

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