Mem. S.A.It. Suppl. Vol. 16, 113

Memorie della
Supplementi

Spectroscopic analysis of particulate samples of altered olivine for planetological studies

V. Orofino, A. Blanco, M. D'Elia, S. Fonti, and M. Giuri

Physics Department, University of Salento, Via Arnesano, 73100 Lecce
e-mail: vincenzo.orofino@le.infn.it

Abstract. Among the materials of planetological interest, olivine is particularly important due to its ubiquity in the Solar System and to the fact that, in the presence of water, it readily alters to iddingsite and various phyllosilicates. For this reason laboratory studies on olivine samples play an important role in the framework of the research on the geochemical evolution of celestial bodies such as Mars and several asteroids.
In this work we present the results of spectroscopic studies of different particulate samples of three kind of olivine analysed in reflectance in the range 0.2-2.5 μm. Our goal is to study the influence of the grain size on the spectra and in particular on the characteristic of the band at 0.64 μm, which is commonly present in the spectra of altered and unaltered olivine.

Key words. Grains – laboratory – olivine – spectroscopy

1. Introduction

Olivine ($(Mg,Fe)_2SiO_4$), a silicate mineral consisting of an isomorphic mixture of forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4), is a particularly important material of planetological interest, due to its ubiquity in the Solar System. It is well known, in fact, that olivine is present on the surface of Mercury, the Moon, Mars, comets and asteroids, as well as in the meteorites and in the interplanetary dust particles (IDP).

In particular, on Mars and the asteroids the presence of olivine is strictly linked with the geochemical evolution of those bodies and, more precisely, with the occurrence of water on the surface. This is due to the fact that, as we will see in detail in Section 2, olivine readily alters to iddingsite and various phyllosilicate minerals in the presence of water (Colman, 1986). For this reason, as far as Mars is concerned, if large quantities of altered olivine were present in very ancient regions of the planet, this would imply that in the past the Martian climate was wetter and warmer enough to allow the stability of liquid water on the surface of the planet, as suggested by various paleoclimatological models (Pollack et al., 1987). On the other hand, the presence of abundant altered olivine on the surface of asteroids could indicate that, as suggested by Rosenberg et al. (2001), primitive asteroidal bodies, initially made up of ice and anhydrous minerals, underwent extensive aqueous alteration when the ice melted in response to heating, perhaps due to radioactive decay of ^{26}Al (Grimm and McSween, 1989) or possibly to solar electromagnetic induction (Shimazu and Terasawa, 1995).

Send offprint requests to: V. Orofino

Infrared spectroscopy is a powerful tool to study aqueous alteration. In fact the occurrence of this process can be detected by means of the characteristic hydration bands, due to OH and H_2O, that generally appear in the range 0.9-2.5 μm (in particular at about 0.9, 1.4 and 1.9 μm). They are overtones and combinations of fundamentals that occur near 3.0 and 6.0 μm (Clark et al., 1990). In addition hydroxyl is often linked to metals producing a metal-OH bend feature whose position is typically in the 2.2-2.3 μm region (Clark et al., 1990).

Laboratory research on terrestrial particulate olivine samples can allow the interpretation of data coming from space missions. In the present work we show and discuss the experimental results concerning reflectance measurements in the 0.2-2.5 μm wavelength range, made on various olivines showing in particular a typical absorption feature around 0.64 μm which can be associated to an early stage of aqueous alteration of the grains.

2. Aqueous alteration of olivine

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 reactions promote chemical redistribution, changes in petrologic relationships and isotopic fractionation.

In the earlier stages of aqueous alteration the precursor anhydrous material can be still pure, in the sense that the alteration products have not appeared yet, even at a microscopic scale. At these stages aqueous alteration of the original material can be detected only by means of the characteristic hydration bands. Subsequently, alteration materials form veinlets and patches with irregular margins, replacing the precursor material in the body of the original rock, but outside of these very small areas the host rock appears unaltered (Treiman, 1993). At the end of the process the transformation affects large rock masses and the precursor mineral assemblage is destroyed.

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 and Rietmeijer, 1987) and in the meteorites (Zolensky and McSween, 1988). The presence of aqueous alteration has been also inferred for the meteorite parent bodies such as the main-belt C-type asteroids (Vilas et al., 1994) and Mars (Wentworth and Gooding, 1994). In the case of the meteorites of asteroidal origin the most common products of aqueous alteration are (Zolensky, 2001):

a) Ca, Mg, and Fe sulphates;
b) nepheline;
c) oxides (in particolar magnetite);
d) hydroxides;
e) Ca, Mg, and Fe carbonates;
f) phyllosilicates (serpentine from olivine; other clays from pyroxenes).

In the case of the Martian meteorites (the so called SNC meteorites - McSween, 1994) the main products of aqueous alteration are (Gillet et al., 2001):

a) carbonates;
b) sulphates and other salts (gypsum, anhydrite, halite);
c) phyllosilicates (iddingsite).

In both cases, as well as on Earth, the common alteration products of olivine are iddingsite and phyllosilicates (mostly serpentine, but also smectite, 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 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), while serpentine is the main final product of hydrothermal alteration of olivine (Takatori et al. 1993). However, in the literature the term ”serpentine” is often used in a very general way in order to identify also the initial stages of the aqueous alteration of olivine, characterized by the occurrence of the hydration bands.

3. Laboratory measurements

We have produced several grain samples starting from commercially available bulk samples of three different kinds of olivine collected from:

a) the Eifel region, Germany (Hentschel, 1983; Mader and Teyssen, 1985);

b) the Twin Sisters Range, Washington, USA (King and Ridley, 1987);

c) the Jackson County, North Carolina, USA (Huang and Keller, 1970).

Eifel olivine was supplied by Krantz GmbH (Germany), while Twin Sisters and Jackson olivines were supplied by Ward's LLC (USA).

The grinding procedure started directly from rock samples and it has been carried out using a Retsch mechanical mortar grinder to produce a general mixture of sand and dust. The grains have then been selected using a set of sieves that allowed us to divide the samples in six different size ranges:

(a) between 1000 and 425 μm;
(b) between 425 and 300 μm;
(c) between 300 and 200 μm;
(d) between 200 and 106 μm;
(e) between 106 and 50 μm;
(f) smaller than 50 μm.

The above size ranges, whose limiting values are imposed by the commercially available sieves, have been chosen in order to cover the whole size range of the Martian regolith, ranging from micrometer particles up to sand, as inferred from thermal inertia measurements (Jakosky et al., 2000).

The morphological investigation of the dust particles has been done using a scanning electron microscope (SEM, JEOL JSM6480LV) equipped with an energy dispersive X-ray (EDX) detection system (iXRF System, SphinX 130) for the semiquantitative elemental analysis of the grain samples. For Jackson olivine such kind of analysis indicates an elemental composition consistent with pure olivine particles characterized by a very strong forsteritic component. On the other hand the elemental composition of the other two kinds indicates the presence of highly forsteritic olivine grains with impurities of Al, K and Ca (for Eifel olivine) and Al and Cr (for Twin Sisters olivine).

The size distributions of the grains in the various size ranges have been evaluated by means of the Malvern Mastersizer 2000 granulometer, which recovers the dimensional information by analyzing the diffraction pattern of laser beam. The result is a volume size distribution from which the average diameter D of our samples in the six size ranges can be evaluated.

In order to perform the various set of reflection measurements, we have deposited the particulate samples in a 4 mm deep aluminium support with a diameter of about 35 mm. We have filled the aluminium support with the dust and then we have levelled the surface by hand with a blade. In this case the sample has a flat surface quite useful for bi-directional and biconical reflectance measurements, since, as our previous results seem to suggest (Orofino et al., 2006), the flattening procedure does not induce a noticeable preferred orientation to the mineral grains.

For the reflectance measurements we have used a Perkin Elmer Lambda 900 (PE-L900) spectrophotometer in the range UV/Vis/NIR (0.2-2.5 μm) equipped with a Labsphere integrating sphere of 150 mm in Spectralon. The instrument provides directly the relative directional-hemispherical spectral reflectance at 8°; to obtain the absolute reflectance, the normalization to the reference spectrum of the Spectralon is needed.

4. Results and conclusions

In Fig. 1 we present all the spectra relative to the six grain size fractions obtained for the samples of Twin Sisters olivine, which seems to be most altered among the three analysed kinds olivine. Similar spectra are exhibited by the samples of Jackson olivine, while Eifel olivine samples have a slightly different spectral behaviour (see Fig. 4 of Orofino et al., 2006).

As it can be seen in the Fig. 1, the main feature present in all the spectra is that at about 1.0 μm due to ferrous iron in olivine (Burns, 1970). Very interesting are also the bands at 0.64, 1.4, 1.9 and 2.3 μm, as well as the shoulder at 0.45 μm on the steep spectral slope from 0.3 to 0.5 μm.

As mentioned in Sect. 1, the aqueous alteration of our samples is clearly suggested by the bands at 1.4, 1.9 and 2.3 μm. In particu-

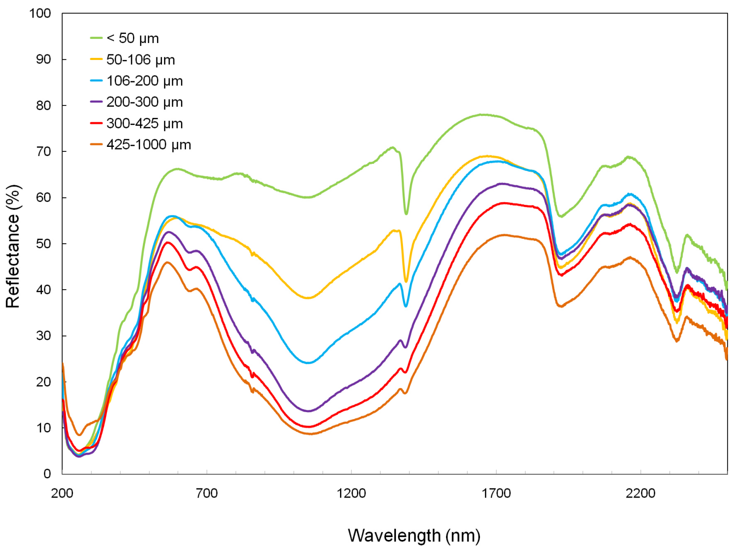

Fig. 1. Reflectance spectra of Twin Sister olivine in the selected size ranges.

lar, according to Clark et al. (1990), the feature at 1.4 μm is related to the first overtone of stretching of the O-H bond; the second band is due to a combination of asymmetric O-H stretching with bending of the H-O-H bond, while the feature at 2.3 μm is due to bending of metal-OH bonds (perhaps Mg-OH). These bands are of comparable intensity for Twin Sisters and Jackson olivines, while are appreciably weaker for Eifel olivine, suggesting that the first two kinds are more altered than the German olivine. In particular the strong band at 1.9 μm in the spectra of the two American olivines is indicative of the presence of molecular water in the samples.

On the contrary the nature of the absorption features at 0.64 μm is still a matter of debate. Probably the most likely origin of this band is a spin-forbidden Fe^{2+} transition, as suggested by King and Ridley (1987). However, due to the altered nature of our samples, it is likely that a fraction of the transitions originating the 0.64 μm band is also due to Fe^{3+} ions; in other words the band could be partially due also to oxidized iron present in the olivine grains, as a result of their aqueous alteration.

¿From Fig. 1 it is immediately evident that the grain size has a strong influence on the appearance of the spectra; in fact, the continuum level increases and the spectral contrast decreases as the grain size becomes smaller.

In particular, we focused our attention on the two spectral structures (reflectance maxima) separating the weak 0.64 μm band from the shoulder at 0.45 μm on one side and from the main band at 1.0 μm on the other. These structures, in fact, undergo evident changes, both in position and in relative intensity, clearly connected to the different grain size. The two structures will be conventionally referred in the following as 0.56 μm (λ_1) and 0.7 μm (λ_2) features, respectively.

The influence of the grain size on the position on the two features can be studied plotting their peak wavelengths λ_1 and λ_2, against the average diameter D of the particles in the various size ranges. For the three kind of olivines this is shown in Fig. 2, where the behaviour of λ_2 is reported. Note the very similar trends shown by Twin Sisters and Jackson olivines, which are the most altered ones. The peak wavelength λ_1 (not shown here) exhibits a sim-

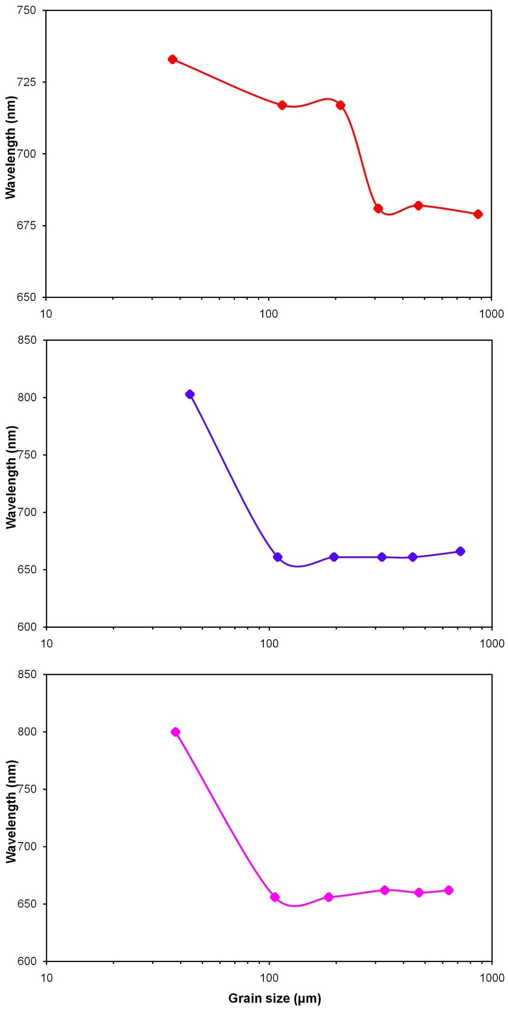

Fig. 2. Peak position of the 0.7 μm feature vs the mean diameter of the grains for Eifel (upper panel), Twin Sisters (middle panel) and Jackson (lower panel) olivines. The dots are comparable with the experimental errors.

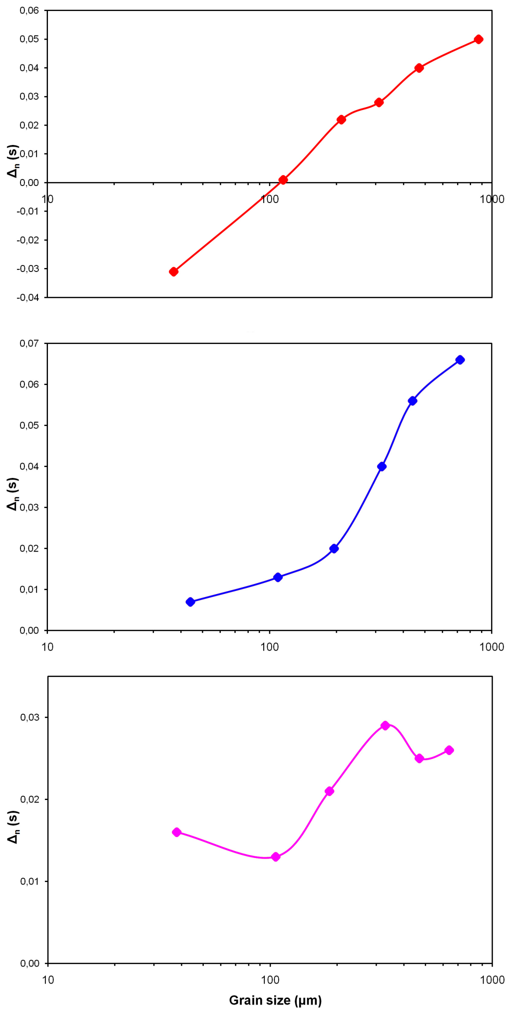

Fig. 3. Same as the previous figure, but for the Δ_n parameter. Eifel olivine (upper panel), Twin Sisters olivine (middle panel), Jackson olivine (lower panel).

ilar behaviour but its variations are smaller than those shown by the second maximum.

In order to study the dependence on the grain size of the relative intensity of the two features at 0.56 and 0.7 μm we can introduce the spectral parameter Δ_n defined by Orofino et al. (2006) as:

$$\Delta_n(\mathrm{D}) = [\mathrm{R}(\lambda_1)\text{-}\mathrm{R}(\lambda_2)]/[\mathrm{R}(\lambda_1)+\mathrm{R}(\lambda_2)] \quad (1)$$

where $\mathrm{R}(\lambda_1)$ and $\mathrm{R}(\lambda_2)$ are the measured reflectivity of the two maxima at 0.56 and around 0.7 μm, respectively.

In Fig. 3 the parameter Δ_n has been plotted versus the average grain size D for the three olivines. As one can see, a common trend exists for all the three olivines: Δ_n increases as D increases. But, apart from this very general trend, the differences among the various types are not negligible.

It is worthwhile to note that the band at 0.64 μm with its two maxima at 0.56 and 0.7 μm has been observed in several reflectance spectra of asteroids, as well as in some Martian spectra taken by the OMEGA spectrometer (Mustard et al., 2005). In these cases the exact position of the two reflectance maxima, as well as their relative intensity, can give information about the grain size of the regolith present in the celestial object under study.

Acknowledgements. This research has been partially supported by Italian Space Agency (ASI) and the Italian Ministry of University and Research (MUR).

References

Burns, J.A. 1986, Icarus 66, 1
Burns, R.G. 1970, Mineralogical Applications of Crystal Field Theory. Cambridge University Press, New York.
Clark, R.N. et al. 1990, J. Geophys. Res. 95, 12653-12680
Colman, S.M. 1986. Rates of Chemical Weathering of Rocks and Minerals. Academic Press, Orlando, FL.
Gillet, Ph. et al. 2001, Meteor. & Planet. Sci. 36, Suppl., A66 (Abstract ♯5177)
Grimm, R. E., & McSween, H. Y. 1989, Icarus 82, 244-280
Hentschel, G. 1983, Der Aufschluss 34, 391-396
Huang, W.H., & Keller, W.D. 1970, Amer. Mineral. 55, 2076-2094
Jakosky, B.M. et al. 2000, J. Geophys. Res. 105, 9643-9652
King, T.V.V., & Ridley, W.I., 1987, J. Geophys. Res. 92, 11457-11469
MacKinnon, I.D.R., & Rietmeijer, F.J.M. 1987, Rev. Geophys. 25, 1527-1553.
Mader, D., & Teyssen, T. 1985, Sediment. Geol. 41, 1-74
McSween, H.Y. 1994, Meteoritics 29, 757-779
Mustard, J. F. et al. 2005, Science 307, 1594-1597
Orofino, V. et al. 2006, Planet. Space Sci. 54, 784-793
Pollack, J.B. et al. 1987, Icarus 71, 203-224
Romanek, C.S. et al. 1996, 27th Annual Lunar and Planetary Science Conference, pp. 1099-1100
Rosenberg, N. D. et al. 2001, Lun. Planet. Sci. Conf. XXXII, Abstract ♯1406
Shimazu, H., & Terasawa, T. 1995, J. Geophys. Res. 100, 16923-16930
Takatori, T. et al. 1993, 24th Annual Lunar and Planetary Science Conference, pp. 1389-1390
Treiman, A.H. 1993, Geochim. Cosmochim. Acta Suppl. 57, 4753-4754
Vilas, F. et al. 1994, Icarus 109, 274-283
Wentworth, S.J., & Gooding, J.L. 1994, Meteoritics 29, 860-863
Zolensky, M.E. 2001, XI Ann. V.M. Goldschmidt Conf., Abstract ♯3052
Zolensky, M., & McSween, H.Y. 1988. Kerridge, J.F., Matthews, M.S. (Eds.), Meteorites and the Early Solar System. The University of Arizona Press, Tucson, pp. 114-143.