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(Article begins on next page)

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Olivine thermal emissivity under extreme temperature ranges: implication for Mercury surface

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Due to its proximity to the Sun and a weak exosphere, the surface of Mercury is subjected to temperature variation up to 625 K during a hermean day. Minerals elastically expand and contract adjusting their crystal structure through time and from place to place as a function of temperature variations. This significantly influences the interpretation of remote sensing data by instantaneously and reversibly modifying the mineral spectral signatures, which are intimately related to the crystal structure. Here we show, for the first time, how the thermal emissivity spectra of a Mg-rich olivine (i.e. $Mg_{1.84}Fe_{0.16}SiO_4$) significantly changes as a function of temperature. An increase of 420 K modifies the olivine spectrum shifting in wavelength its emissivity features, simulating the spectrum of an olivine strongly enriched in iron (Fe abundance close to 20%). This "chameleon-like behaviour" indicates that the spectroscopic investigations of the surface of Mercury must take into account the local time dependency to properly infer the compositions of planetary materials by remote sensing acquisition of future space missions.

It is well known that the surface of Mercury shows extremely large temperature variations at specific locations[1].This is due to its closeness to the Sun but also to its slow rotation (one hermean day last 88 terrestrial days) which allows the surface temperature of the side of the planet facing the Sun to reach equilibrium with the solar flux while its dark side is much colder; the surface temperature can vary over a hermean day between about 70 and 700 K[1] at different latitudes. These temperature variations significantly affect the crystal structure and density of minerals and rocks present on the surface of a planet[2].

As a consequence, several kinds of remote information linked to mineral structures, including relative spectral signatures, are strictly dependent on the environmental conditions and vary according to the surface temperature. By "looking at the planet" in remote sensing, Mercury may change its outer face through time and from place to place as a function of solar irradiation. If this is not taken into account it could led to important misinterpretations and could limit our capability of inferring compositions and rheological properties of materials from remote sensing acquisition.

Thus, we need to investigate the *in situ* behaviour of geological materials, i.e. under extreme temperature environments, and improve the geological interpretation and compositional inferences by applying the knowledge acquired to the analysis of the available remote sensing data.

In this light, here we present a new *in situ* multi-methodological laboratory approach comprehensive of high-temperature X-ray diffraction (single-crystal and powder materials) and high-temperature thermal infrared (TIR) spectroscopy in the range 1400 to 700 cm^{-1} (7 to 14 µm). Such range is the same that will be investigated by the Mercury Radiometer and Thermal Infrared Spectrometer[3] (MERTIS) on board of BepiColombo Mercury Planetary Orbiter spacecraft. In such wavelength range, the spectra can be used very effectively to identify the fine-scale structural properties of silicates (e.g. stretching and bending motions in the silicon-oxygen anions, metal – oxygen and lattice vibrations[4]). In addition, for some important mineral family, like olivine, the emissivity peak positions are a good indicator of the composition[5,6]. TIR spectroscopy was performed at the Planetary Emissivity Laboratory in Berlin (PEL), which has been built up over the

last 5 years to study systematically the effect of temperature on TIR spectral signatures in the 1400-700 cm^{-1} (7-14 µm) range[7].

In this work we investigated an olivine sample having composition $Mg_{1.84}Fe_{0.16}SiO_4$ (Fo_{92})[8,9,10,11].Olivine has been chosen as one of the major component of Earth's mantle, of many meteorites classes and has been identified on the surfaces of planetary bodies, and in the spectra of astronomical targets[3]. Moreover, the presence of olivine has been considered in several petrological models of Mercury[12,13,14,15] and should likely be a primary mineralogical phase in the wide volcanic plains recently discovered on its surface[16], particularly if the new MESSENGER X-ray observations pointing to a basic to ultrabasic compositions for these effusions are taken into account[17]. The olivine studied here occurs in high-pressure ultramafic nodules from the Newer Volcanics of Mt. Leura[8,9] (Victoria, Australia) and was fully characterized by single-crystal X-ray diffraction and powder X-ray diffraction. The chemistry has been assumed to be identical to that published for the same sample by 9, as confirmed by the X-ray structure refinement of our sample and by the excellent agreement between the unit-cell parameters obtained by our characterization and their data (Supplementary Tables 1, 2, 3).

The minerals present on the Mercury surface undergo temperature variations that depend on solar irradiation. Known thermal models[18,19] of Mercury show that at the equator a point on the surface is subjected to a temperature variation of about 420 K between sunrise days and the midday.

In order to evaluate how olivine would behave on the Mercury surface under such significant temperature variations, we have measured its volume - and density - change as a function of temperature (Fig. 1a) (see Methods Summary). In detail, we have measured the unit-cell volume between room temperature (the minimum temperature presently achievable by our set-up and at the same time the temperature at which all the TIR mineral databases are available[6,7]) and 773 K, in order to cover most of the possible temperature variations on Mercury surface. The volume change as a function of temperature (Table 1) gave us a measure of the linear volume thermal expansion coefficient $\alpha_V = 3.07(2)\times10^{-5}$ K^{-1} (calculated as: $\alpha_V = [(V-V_0)/V_0]/\Delta T$) in agreement with previous

results[20]. Assuming a temperature variation of 420 K, as for example the temperature variation between sunrise and midday on Mercury at the equator, we calculate a volume variation of 3.77(8) $\mathring{A}^3$ (calculating using the volume thermal expansion coefficient). In Fig. 1b the unit-cell volume is plotted against the composition of olivines for compositions ranging between Fo_{92} and Fo_{62}, the compositional range most representative of the geological environments[21]. It is evident that increasing the iron content the unit-cell volume significantly increases due to the larger cation radius of Fe^{2+} (in octahedral coordination the radius of Fe^{2+} is 0.78 Å against 0.72 Å of $Mg^{(22)}$). Hence, the increase in temperature and the increase in iron have the same effect on olivine, increasing the unit-cell volume. According to the equation $V = 308.6(6) - 0.181(8) \times Fo\%$ [10,11], an increase in temperature by about 420 K corresponds to an increase in iron from Fo_{92} to Fo_{71}.

From such crucial experimental observation we decided to determine the effect of temperature on the TIR spectral signature of olivine, performing measurements in vacuum at different temperatures (see Methods Summary). The olivine sample was hand-reduced to a grain size range between 100 μm and 160 μm which is considered close to a most likely end-member of the Mercury regolith size[23]. In detail, on the same sample we have collected two spectra at two different temperatures between about 350 K and 770 K (the error in temperature calibration is estimated to be up to 5 K) in order to simulate the typical diurnal equatorial temperature variation of the hermean surface.

In order to define the effect of the thermal annealing during the emissivity data collection, the sample was re-analyzed *ex-situ* by X-ray powder diffraction and single-crystal X-ray diffraction and did not show any significant difference in the unit-cell parameters with respect to the pre-annealing data (Supplementary Table 4). In particular, we can state that the sample did not undergo any iron oxidation due to the temperature effect: in fact, as it is well known, an iron oxidation would have reduced the Fe^{2+} to Fe^{3+} with a consequent reduction of the cation radius from 0.78 Å to 0.645 Å, respectively, and a consequent decrease of the unit-cell parameters.

In Figure 2a the main olivine bands between 1000 and 850 cm^{-1} are shown. Bands 1, 2 and 3 are the most intense in olivine in this spectral range and their exact position is a strong function of the iron

abundance[4]. In the inset 2b we highlight the shift of 7 cm^{-1} in the band 3 position, between the 352 K-spectrum and the 773 K-spectrum. This is a significant result as the same wavenumber shift corresponds to a change in composition from Fo$_{92}$ to Fo$_{71}$ according to the data of Hamilton[4] in Table 6.

On the surfaces of planetary bodies we have rocks and soils and we must then consider the simultaneous presence of different minerals, each with its characteristic thermal expansion coefficient. This would result in a more complex behaviour and in an even more difficult interpretation of the spectra: in fact, for example, a further important mineral assumed to be present on Mercury is the plagioclase and plagioclase have very different thermal expansion coefficients with respect to olivine. Data obtained on several plagioclase compositions[24], using the same equation used considered for olivine, gave thermal expansion coefficients very variable between α_V = 2.8×10^{-5} K^{-1} for pure albite NaAlSi$_3$O$_8$ and α_V = 1.6×10^{-5} K^{-1} (for pure anorthite CaAl$_2$Si$_2$O$_8$ (data calculated between 298 and 774 K). Clinopyroxene and orthopyroxene also have been assumed to be possible phases for Mercury surface[15]: for these minerals different thermal expansion coefficient data have been determined. For compositions between diopside (CaMgSi$_2$O$_6$) and hedenbergite (CaFeSi$_2$O$_6$) literature data show values between $3.3^{(25)}$ and $2.9^{(26)} \times 10^{-5}$ K^{-1}; for orthopyroxenes (between orthoenstatite Mg$_2$Si$_2$O$_6$ and orthoferrosilite Fe$_2$Si$_2$O$_6$) values close to 3.0-3.1×10^{-5} K^{-1} have been determined[27]. Thus, considering such different thermal expansion behaviour, we could easily state that spectral signature collected at room temperature could be totally different from that collected at high temperature.

Our cross-related data by in situ X-ray diffraction and TIR spectroscopy demonstrate that the effect of temperature must be taken into account when interpreting spectral features, in order to correctly determine the abundance and composition of specific mineral phases.

Our results should be considered reliable for all those terrestrial bodies and asteroids, which undergo significant surface temperature variations and that could be characterized by what we called "chameleon-like surface".

METHODS SUMMARY

In situ high-temperature diffraction. In situ X-ray measurements were performed by powder diffraction experiments (5° - 100° in 2θ, continuous scan mode) in the temperature range 295 K - 1273 K to include a possible temperature range encountered on the Hermean surface. Data were collected on a Philips X'Pert diffractometer system (University of Salzburg, Austria), equipped with an Anton PAAR HTK-16 high temperature chamber (Cu Ka radiation, primary and secondary side 0.04 rad Soller slits, secondary graphite monochromator, 4 hours/ measurement). After each temperature increase the sample was allowed to equilibrate for one hour before starting measurement at this temperature. NIST silicon was used as an internal standard; lattice parameters were obtained from whole pattern refinement using the FULLPROF-suite[28] and are reported at each temperature in Table 1.

In situ high-temperature emissivity measurements. Emissivity data were measured in the Planetary Emissivity Laboratory[28] (PEL), at the Institute for Planetary Research of the German Aerospace Center (DLR) in Berlin. The instrument used is a Bruker Vertex 80V, with a liquid nitrogen cooled HgCdTe detector and a KBr beamsplitter. The spectrometer is coupled to an evacuated planetary simulation chamber, having an automatic sample transport system to maintaining the vacuum while changing the samples. Radiance is collected by an Au-coated parabolic 90° off-axis mirror and reflected to the spectrometer entrance port. The sample is heated via a copper induction pancake coil while staying always under 1 mbar of pressure[29]. Measurements of a calibration body are taken at 2 temperatures to derive the instrumental response function. The artefact that in a certain point of the spectrum, called Christiansen feature (CF), emissivity goes to unity is used for the calibration procedure[30] and to determine the temperature of the sample at the emitting skin.

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Supplementary Information is linked to the online version of the paper a www.nature.com/nature.

Acknowledgments

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Author Contributions N.F. refined X-ray data and fitted them to spectroscopic data; S.F. selected, reduced, prepared the samples and collected spectroscopic data; M.A. collected and processed spectroscopic data; M.M. designed the study; G.R. collected and processed X-ray data; M.T.C. discussed thermal models; M.B. analysed the thermal expansion data; J.H., C.C. and F.C. were involved in study schedule; N.F. and S.F. designed the study, analysed data and wrote the paper. All authors discussed the results and commented on the manuscript.