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3 **Thermal Infrared Emissivity of Felsic-rich to Mafic-rich Analogues of Hot**
4 **Planetary Regoliths.**

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16

17 **Abstract**

18 Atmosphere-less inner Solar System bodies such as Mercury and several high-
19 eccentricity Near Earth Objects use to undergo to a wide range of surface
20 temperatures. The work shows how the thermal expansion induced by strong diurnal
21 insolation affects the thermal infrared spectra of felsic-rich to mafic-rich regoliths.
22 1400-700 cm⁻¹ spectra of granular plagioclase-pyroxene mixtures were measured in
23 laboratory at five temperatures between 295 K (ambient) and 725 K, simulating
24 different daily surface temperatures of the Solar System. At the same time, the work
25 describes for the first time how two minerals with different thermal expansion
26 coefficients combined in the same granular sample reveal in a non-ambient thermal
27 infrared spectrum. Spectra of plagioclase-rich analogues, on one hand, appear

dominated by felsic features regardless the surface daily temperature, and do not exhibit short-wavenumber absorptions of pyroxenes at all. When perceivable, on the other hand, the 920-cm^{-1} clinopyroxene absorption, which use to be unaffected by thermal variations, proves instead to be a proxy for the solid-solution composition (i.e. Mg-Fe relative content). On the contrary, hints on the plagioclase solid solution occurring at ambient temperatures (i.e. Ca-Na relative content) disappear over 525 K. For all the mixtures, the position of the Christiansen Feature is linearly dependent on the plagioclase-pyroxene content as well as on the temperature, proving to be a reliable tool to obtain the relative mineralogical content when the surface temperature is known. As a whole, in order to decipher planetary hyperspectral data, the surface temperature acquisition seems to be mandatory, as well as the comparison with analogue spectra obtained under realistic temperature conditions.

Keywords: planetary - silicate – plagioclase – pyroxene - emissivity – temperature

1. Introduction

Compositional studies of planetary surfaces are mostly realized by means of the collection and interpretation of the released electromagnetic radiations. Ground-based, orbit and lander hyperspectral instruments covering a wide range of wavelength has allowed unveiling, locally or globally, the chemical and mineralogical surface properties of several rocky planetary bodies. Among these techniques, the thermal infrared (TIR, $100\text{-}5000\text{ cm}^{-1}$) spectroscopy allows to recognize the mineralogical structures of the outer shell of crystalline assemblages. This capability mainly relies on the characteristic spectral features arising by cation–anion and lattice vibrations of crystalline structures in the middle portion of electromagnetic spectrum (Farmer, 1974). This technique works very effectively for silicates (Hamilton, 2010), for which

a few mineral groups - such as plagioclase feldspars - can be deficient in transition elements and use to provide weak diagnostic features along shorter wavelengths (i.e. visible and near-infrared wavelength).

By using TIR spectroscopy, compositional mapping is conducted at different scales on several rocky bodies in the Solar System, primarily on the Earth surface where remote sensing techniques can be easily combined with field data (Salisbury, J.W., D'Aria, 1994). Earth-based observations in the TIR have been performed to investigate surface components of both Main-belt and Near-Earth asteroids (e.g., Lim et al., 2005; Vernazza et al., 2010) or inner planets (e.g., Sprague et al., 2009). On the other hand, large-scale and global mapping are easier accomplished with orbital surveys. Global mineral maps have been produced for example using Mars thermal infrared data from the Mars Global Surveyor Thermal Emission Spectrometer (TES, Christensen et al., 2001) and the Mars Odyssey Thermal Emission Imaging System (THEMIS, Christensen et al., 2005), and using lunar data from the Lunar Reconnaissance Orbiter (LRO) Diviner (Greenhagen et al., 2010). A new frontier of the Solar System exploration is the return of solid samples from asteroids, which is accomplished through a preliminary global survey to find suitable sampling sites and minimize risks during the surface campaign. For instance, Near Earth Asteroid (101955) Bennu is the target of the Origins, Spectral Interpretation, Resource Identification, and Security–Regolith Explorer (OSIRIS-REx) asteroid sample return mission (Lauretta et al., 2017). During the first two-year orbit period (2018-2019), the global survey of Bennu is correlated by the OSIRIS-REx Thermal Emission Spectrometer (OTES, Christensen et al., 2018) that provides the surface mineralogy through 100-1750 cm^{-1} emissivity spectra.

77 In order to succeed in the interpretation, the correlation of remote sensing data
78 to a solid laboratory background is crucial. A great effort has been done to directly
79 obtain the emissivity of a sample radiative surface, and specific laboratory setups and
80 databases have been built up to sustain the remote Solar System exploration. In
81 support of NASA Mars missions, an extensive library containing thermal emission
82 spectra of coarse-grain rocks and minerals undergone 350 K has been supplied by the
83 Arizona State University (ASU, Christensen et al., 2000). Matching orbital spectra
84 with the ASU laboratory spectra (Hamilton and Christensen, 2000) allowed mapping
85 silicate assemblages on the Mars surface (Bandfield et al., 2000; Ramsey and
86 Christensen, 1998). Similar analysis techniques were applied on lunar soils, using
87 LRO Diviner radiometer channels (Paige et al., 2010) to investigate a diagnostic
88 emissivity maximum called Christiansen Feature (CF, Conel, 1969). CF positions
89 detected by Diviner were compared to the CF positions of well-characterized lunar
90 samples and analogues, obtaining a global map of the silicate dominant phases
91 (Greenhagen et al., 2010). Lunar environment, as long as other airless environments,
92 promotes strong thermal gradients within the shallow radiative depth, affecting CF
93 positions (Glotch et al., 2010). Being feldspar CFs proper proxies of primary
94 anorthositic crust, plagioclase analogues were widely studied in laboratory along the
95 TIR range under different environment conditions (Donaldson Hanna et al., 2012),
96 then used for Moon Mineralogy Mapper data interpretation (Donaldson Hanna et al.,
97 2014).

98 In support of the future employ of BepiColombo Mercury Radiometer and
99 Thermal Infrared Spectrometer (MERTIS, Hiesinger and Helbert, 2010) on the ESA-
100 JAXA BepiColombo mission, the Planetary Spectroscopy Laboratory (PSL,
101 www.dlr.de/pf) of the German Aerospace Center (DLR) has developed a simulator

chamber that allows to increase the temperature of the sample radiative depth up to ~775 K – comparable to the maximum temperature reachable at the equator of Mercury - in a vacuum environment. A Fourier spectrometer equipped with a nitrogen cooled detector coupled to the chamber allows measuring emissivity of a variety of particle sizes of possible surface Mercury analogs. Those measurements, along more traditional low-temperature emissivity measurements in purged environment, constitute the Berlin Emissivity Database (Maturilli et al., 2008). Recent works that combine accurate lattice data to PSL emissivity spectra of olivine and clinopyroxenes (Ferrari et al., 2014; Helbert et al., 2013) demonstrate that the thermal expansion promoted by intense daily insulation of a planetary surface (e.g., of Mercury) induces variations on spectral features. Though those spectral variations are strictly correlated to the temperature variation and totally reversible, they provide a temporary mismatch between space data and traditional databases, affecting the correct interpretation of the surface composition as much as irreversible transformations (e.g., spectral flattening due to shock impacts) affect possible structural inferences (e.g., particle size). Basic variations characterized in PSL spectra during the thermal expansion imply the shift of most features, simulating an increasingly size of the main cations, and the quasi-steady state of others, the latter of which can be considered baselines for any interpretation. A more difficult interpretation of the spectra, of course, arises from the simultaneous presence of different minerals during thermal expansion, since each mineral bears a different thermal expansion coefficient.

In this work we examine the TIR spectral variations of bimodal mixtures of plagioclase and pyroxene, which most likely could be present on a planetary silicate surface, in addition to the temperature-dependent spectral variations of the single constituents, regardless their formational mechanism. The study is specifically

focused on absorption features with wavenumbers between 1400 and 700 cm⁻¹ (7-14 μm), where the most prominent silicate bands are observed. In this range, absorptions mainly occur by the stretching vibrations of the cation-oxygen (Si/Al-O) tetrahedra. With increasing temperature, though tetrahedra represent the stiffer configuration of silicate, the entire structure uses to adjust in order to maintain the linkage between different polyhedra layers. This adjustment results in a change of bond lengths of Si/Al and surrounding oxygens, a change reflected in the stretching potential of each of those bonds. In order to investigate how those variations promoted by thermal expansion affect the 1400-700 cm⁻¹ spectral range, we measured at different steps of temperature - up to 725 K – the emissivity of co-genetic silicates with different weight ratio, reduced to suitable particle sizes for the regolith of a rocky planetary body.

2. Methods

2.1 Selection, preparation and characterization of the samples

To better constrain the effect of different variables acting on surface materials it is useful to consider *ad hoc* samples to separate as much as possible the single components. Bimodal mixtures with variable abundance of co-genetic endmembers at constrained particle sizes is suitable for this purpose.

Plagioclase and pyroxene are among the most diffuse silicates of the Solar System. In particular, terrestrial planet that underwent to a primordial differentiation accumulated floating plagioclases dragging low amounts of mafic minerals on the outermost shell (e.g., Halliday, 2001; Tonks and Melosh, 1993; Wetherill, 1980). In addition, plagioclase and pyroxene are the most abundant phases of lava flow rocks, which are currently considered the main constituents of the Mercury's crustal surface (Namur and Charlier, 2017 and reference therein), and S-type asteroids (e.g., Nakamura et al., 2011). Therefore anorthosites-kindred materials represent a suitable

analogue of an elementary bimodal combination of differently polymerized silicates bearing different thermal expansion coefficients.

The set of considered mineral endmembers consists of single phases occurred in a natural anorthosite sample belonging to the gabbro-anorthosite Nordingrå complex (Sweden, Lindh et al., 2001). This massif displays a high percentage of outcropping leucogabbro and true anorthosite with respect to other rapakivi-type massifs - possibly depending on a multiple intrusion mechanism - favouring the collection of feldspar-rich samples. Typical Nordingrå-complex anorthosite is coarse-grained and has a plagioclase content higher than 90 wt%. Plagioclase crystals can reach 1–4 cm in length: their compositional range is An_{48-67} , with labradorizing cores. Clinopyroxene (Di_{60}) and olivine are the main primary mafic minerals, frequently substituted by uralitic hornblende. Brown biotite and opaque minerals as ilmenite and magnetite occur as inclusions.

A unique bulk sample of anorthosite was used to provide co-genetic single-mineral phases suitable for weighted linear mixtures. The sample bulk composition was analysed by X-ray powder diffraction at the Department of Geosciences of the University of Padua. Data were recorded on a PANalytical θ - θ diffractometer (Cu radiation) equipped with a long fine-focus Cu X-ray tube operating at 40 kV and 40 mA and a real-time multiple strip (RTMS) detector (X'Celerator). The scan was performed over the range $3-80^\circ 2\theta$ with a step size of $0.017^\circ 2\theta$ and a counting time of 150 s/step. The program High Score Plus (PANalytical) was used for phase identification and quantitative phase analysis with Rietveld refinement (Rietveld, 1967). A pseudo-Voigt function was employed for the profile shapes. Refined parameters were scale factors, zero-shift, background, lattice constants, and profile parameters (Gaussian and Lorentzian coefficients). Results of the analysis are

reported in Table 1SM. Plagioclase solid solution ranges between andesine and labradorite (An₇₀₋₃₀), and represents the 83 wt% of the analysed material. Clinopyroxene (ferroan diopside 6 wt%) is partially substituted by uralitic amphibole (actinolite) and chlorite. Quartz and ilmenite are detectable, whereas shallow peaks of low-calcium pyroxene and biotite are observable but not quantifiable.

The bulk sample was divided into two equal volumes that were mechanically ground in a jaw crusher toward 1 mm, obtaining two partitions of anorthosite *talquale*. Those partitions represent samples where the relative abundance of plagioclases and clinopyroxenes are 93% and 7%, respectively. In order to separate pyroxenes from the silicic minerals, a mechanical separation of additionally-reduced grain sizes (e.g., by Frantz Magnetic Separator) was considered ineffective because of the widespread presence of amphiboles. Then 0.5 to 1-mm plagioclase and pyroxene crystals were separated by hand-picking from one of the two anorthosite-*talquale* partitions. Though sericitization was diffuse, preserved crystals of the required phases were still available. Plagioclase crystals displayed diffuse labradorescence, and the occasional quartz were accompanied by chalcopyrite-pyrite coatings. Well-shaped augites were distinguishable by elongated amphiboles and tabular brown biotite. Mafic crystals were often accompanied by euhedral small apatites, which have been carefully discarded.

Crystals of the two picked phases were analysed by the wavelength-dispersive system (WDS) method. The analyses were carried out using a CAMECA CAMEBAX SX50 electron microprobe, with a fine-focused beam (~1 µm diameter), an acceleration voltage of 20 kV and a beam current of 20 nA, with 10 s counting times for both peak and total background. Ten analytical spots per sample were acquired. X-ray counts were converted to oxide wt% using the PAP correction program supplied

by CAMECA (Pouchou and Pichoir, 1991). Results of the analyses are reported in Table 2SM. Plagioclase solid solution ranges between An₄₅ and An₆₅, possibly confirming crystal cores enriched in Ca, whereas clinopyroxenes display lower content of Ca, and much variable Mg# (i.e. 0.33-0.52) with respect to the value reported by Lindth et al. (2001).

All partitions (i.e. anorthosite *talquale*, plagioclase and clinopyroxene phases) are further reduced in a dry planetary ball mill using sintered aluminium oxide balls, and sieved to <63 and 63-125 µm size fractions. In the attempt to reduce size-distribution differences induced by hardness, final samples were obtained mixing a part of <63-µm fraction and a part of 63-125-µm fraction, in a weight ratio of 1:1. The particle-size fraction of <125 µm, provided for the spectroscopic measurements, cannot be totally immune to thermal gradient and multiple scattering effects in the TIR range (Maturilli et al., 2006 and reference therein), nevertheless it approaches the finest Moon and Mercury's regolith size (Emery et al., 1998; McKay et al., 1980). In particular, the <63-µm fraction is numerically dominated by finest particles, possibly reaching the 70 wt% constituted by particles <5 µm in diameter. Such finest particulate, smaller than the studied wavelength range, uses to coat larger particles dominating the spectral behaviour of the overall sample (Salisbury and Wald, 1992).

Two suitable analogues of bi-components were obtained mixing 90 wt% of plagioclases with 10 wt% of clinopyroxene, partly comparable with the anorthosite *talquale* (i.e. 93% and 7%, respectively), and mixing 50 wt% of plagioclase with 50 wt% of clinopyroxenes. This intermediate assemblages can be associated to a first case study where plagioclase and mafic materials are mixed in equal abundances similar to some of the normative Mercury-like terrain (e.g., E. Vander Kaaden et al., 2017). The achieved samples set, which includes the Nordingrå-complex anorthosite

(*anorth*), the plagioclase endmember (*pl100*), the pyroxenes endmember (*pl000*), the 90-wt% plagioclase mixture (*pl090*) and the 50-wt% plagioclase mixture (*pl050*), is summarized in [Table 1](#). Samples available for measurements were placed into

(i) teflon cups, operating for vacuum reflectance measurements, with a 10 mm internal diameter and 2 mm thick bottom, filling the cups for the whole available volume, and

(ii) stainless steel cups operating for vacuum high-temperature measurements, with a 50 mm internal diameter, 5 mm thick bottom and 20 mm in height, filling the cups for the first 3 mm.

Filled cups were placed in a dryer chamber.

2.2 Experimental setup

The spectral measurements were performed at the PSL. The instrument used was a Bruker Vertex 80V FTIR spectrometer operated under vacuum, with liquid nitrogen cooled HgCdTe detector and KBr beamsplitter. Emissivity and reflectance spectra were acquired between 750 and 1400 cm^{-1} , at a spectral resolution of 4 cm^{-1} .

The external evacuated planetary simulation chamber was used to measure emissivity. The setup provides that the steel cup containing the sample is heated via an induction system and the radiance is collected by an Au-coated parabolic 90° off-axis mirror and reflected to the spectrometer. Samples were heated once and emissivity was measured under a medium vacuum of 0.7 mbar at 425 K, 525 K, 625 K and 725 K with increasing temperatures, then during the cooling maintaining the temperature at 525 K. Measurements of the calibration body were taken at the same temperatures as the sample. Within the chamber, an iron buffer was provided in order to avoid any possible iron oxidation during the annealing. The intent of this setup was

to reach the maximum temperature variation achievable by the PSL setup within the range suggested for terrestrial planet surfaces, preventing any possible variation of the sample during the heating. The sample radiance $I_{(T)}$ and the calibration body radiance $CB_{(T)}$ were collected at each scheduled step of temperature T . For each sample, 5 scans were averaged to produce a single spectrum. The absolute emissivity of the sample $\epsilon_{a(T)}$ is derived using the $\epsilon_{a(T)} = I_{(T)} / CB_{(T)} \cdot E_{CB}$, where E_{CB} is the calibration body emissivity curve. More details regarding the setup and the calibration technique are discussed in Ferrari et al. (2014).

A Bruker A513 accessory was used for bi-conical (illumination=emission=13°) reflectance measurements (Maturilli et al., 2014) at room temperature. The bi-directional reflectance of each sample (R) was collected in medium vacuum at 295 K within the same range of wavelength. A derived emissivity ϵ_d is obtained following the Kirchhoff's law [$\epsilon_d = 1 - R$] for a comparison with the measured ϵ_a at low temperature.

3. Results

In this work the influence of the simulated environment on measured spectra is described in terms of spectral contrast referring to the imposed vacuum, and of absorption band wavenumber position referring to induced thermal expansion. In the 700-1400 cm^{-1} wavenumber range, the spectral contrast between the CF and the first group of absorption features, as well as the wavenumber position of the CF relative to the absorption bands, are strongly affected by the decreasing pressure and the increasing thermal gradients (Donaldson Hanna et al., 2012 and reference therein; Logan et al., 1973). Concerning the spectra of end-member phases, emissivity absorption minima previously described in the literature as diagnostic are identified as (i) reststrahlen bands (here referred as RB) due to the Si-tetrahedral fundamental

vibrations (Lyon, 1962), and (ii) transparency features (TF) caused by volume scattering characteristic of fine particle sizes (Maturilli et al., 2006; Salisbury and Walter, 1989). Reststrahlen bands have long been identified as diagnostic of composition (e.g., Lyon, 1962).

Measured spectra are shown in [Figures 1 and 2](#), including reflectance-derived emissivity (orange line). [Figure 1](#) shows the spectra of the Nordingra-complex anorthosite (*anorth*), which represents a relative abundance of 93% of plagioclases and 7% of clinopyroxenes ([Table 1](#)). In [Figure 2](#), spectra of plagioclase (*pl100*) and pyroxenes (*pl000*) end-members and samples obtained by mixing (*pl090* and *pl050*, [Table 1](#)) are displayed, from left to right, with increasing pyroxene content and decreasing degree of polymerisation of the silicate structures, i.e. decreasing cumulative number of oxygens shared by tetrahedra. The polymerisation uses to strengthen the structure, increasing the CFs values and the spectral contrasts (e.g., Logan et al., 1973), and driving the main absorption features toward higher wavenumbers (or higher frequencies of vibration, requiring more energy to vibrate; Farmer, 1974; Salisbury and Walter, 1989). All spectra of measured emissivity display an ubiquitous rise at 1370 cm^{-1} due to a shallow absorption of the calibration body. Documented diagnostic features of reflectance-derived emissivity spectra collected at 295 K are listed in [Table 2](#), in terms of CF locations and absorption-band minima positions, and in [Table 3](#) as emissivity values. Corresponding diagnostic features of measured emissivity spectra are listed in [Table 4](#), in terms of CF locations and absorption-band minima positions, and in [Table 5](#) as emissivity values.

The end-member phases are considered reference samples for the spectral interpretation. From higher to lower wavenumbers, the spectral features attribution of the plagioclase end-member (*pl100*, [Figure 2](#)) includes the CF, two close reststrahlen

bands (RBs) between 1100 and 1200 cm^{-1} followed by a third one located at ~ 1000
 cm^{-1} , and a transparency feature (TF). The shallow RB located at 920 cm^{-1} , which is
equally characteristic of plagioclase solid solutions, appears overlapped with the deep
TF of plagioclase-bearing samples. Concerning low-temperature spectra (i.e. spectra
collected at 295 and 425 K), the split of the high-wavenumber broad reststrahlen band
in two minima and the occurrence of the TF at $\sim 870 \text{ cm}^{-1}$ are characteristics of Na-
rich plagioclase solid solutions (Donaldson Hanna et al., 2012; Hamilton and
Christensen, 2000), and consistent with the andesine content of *pl100* sample (Table
1SM). Similarly, the spectral features attribution of the clinopyroxenes end-member
(*pl000*, Figure 2) includes the CF, three RBs at ~ 860 , ~ 950 and $\sim 1100 \text{ cm}^{-1}$, and a TF.
Concerning low-temperature spectra (i.e. spectra collected at 295 and 425 K), the
asymmetry of the first RB and the location of the third RB at $\sim 870 \text{ cm}^{-1}$ are
characteristic of Fe-rich augites (Hamilton, 2000), and consistent with $\text{Mg}_{0.33}$ - and
 $\text{Mg}_{0.52}$ -clinopyroxenes of *pl000* sample (Table 2SM). Consistently with the different
degree of polymerisation, plagioclase RBs occur at higher wavenumbers with respect
to the pyroxene ones because of their higher number of oxygens shared by two
tetrahedral (Smith and Brown, 1988). In general, low-temperature TFs are deeper than
RBs.

Low-temperature spectra of synthetic anorthosite (*pl090*) and anorthosite
talquale (*anorth*) appear strongly influenced by the plagioclase content, displaying as
well the CF, the two close RBs followed by a third one and the TF (Figure 1 and 2).
Comparing the two samples, variations of the absorption positions can be attributed to
a different wt.% of the main phases and to the secondary phases detectable in the
parental body. *Anorth* sample, indeed, implies a 6 wt.% content of quartz, which
spectrally shifts the CF toward lower wavenumbers and increases the separation

between the first two RBs with respect to *pl090* sample (Wald and Salisbury, 1995). On the other hand, low-temperature spectra of the synthetic gabbro (*pl050*), which is constituted by the same weight of plagioclase and clinopyroxene, show a series of features of more complex interpretation (Figure 2). Christiansen features of *pl050* spectra appear sharper than CFs of all other samples. The spike shape depends on the presence of equal amount of two minerals that significantly differ along this short range. The sum of the optical contributions does not perform with a broadening of the CF, which on the contrary manifests where the refractive index of both minerals approaches the medium refractive index (overlapping zone). *Pl050* spectra show reststrahlen bands of both end-members (Figure 2 and Table 2 and 4), with the last one (the fourth RB) coinciding with the TF characteristic of plagioclases and followed by the TF characteristic of pyroxenes. A general shift of all absorption bands toward lower wavenumbers (i.e. lower vibrational frequencies) with decreasing plagioclase content accommodates the contribution of less polymerized materials as pyroxenes.

The overall low spectral contrast that occurs between CFs and Si(/Al)-tetrahedral absorption bands (RBs), which is quantifiable around 2-5 percent variation, and the persistence of transparency features in low-pressure environments (Figure 1 and 2) are due to the dominant fine fraction of all samples that induces a volume scattering regime (Maturilli et al., 2006; Salisbury and Wald, 1992). End-member spectra tend to display greater spectral contrast than mixtures in which they occur (e.g., Hamilton and Christensen, 2000). Absolute emissivity collected at low temperature (i.e. 425 K) and derived emissivity (reflectance collected at 295 K) show comparable features, though for the absolute-emissivity measurements the spectral contrast appears attenuated and the CFs of plagioclase-rich samples tend to broad and shift toward higher wavenumbers with respect to the derived-emissivity CFs (Figures

1,2). A decreased spectral contrast can be attributed to substantial differences in the measure techniques, e.g. to a less stable vacuum state of the emissivity measurements. A lower vacuum, indeed, uses to promote a general decline of the spectral contrast (e.g., Donaldson Hanna et al., 2012). The shift shown by the CFs of plagioclase-rich samples is most likely due to the stronger thermal gradient promoted by the increased temperatures along the radiative depth (Salisbury and Walter, 1989). Conversely, no shift ($< \text{cm}^{-1}$) occurs for CF peak of *pl000* sample (Figure 2), which toward higher wavenumbers displays a broad shoulder that possibly depends on a preferential orientation of the particles with respect of the radiative surface, an expected behaviour for chain silicates such as pyroxenes. Being *pl050* sample composed by 50-wt% of both end-members, the CF position of its spectra is strongly influenced by the effective composition of the radiative surface, therefore it could be difficult to compare spectra originated from different sample cups.

Concerning the emissivity spectra shape, with increasing temperatures two main variations are observed (Figures 1, 2): (i) the spectral contrast between CFs and the RBs increases; (ii) the emissivity maximum located around 800 cm^{-1} notably decreases, resulting in an increase of negative slope between the two maxima. Donaldson Hanna et al. (2012) highlighted that an increase of the spectral contrast is correlated to an increase of the vacuum level. Therefore, the overall increase of spectral contrast with increasing temperature of Figs. 1 and 2 measurements could be partially influenced by an increased vacuum within the emissivity chamber.

As well as done for the end-members, the main spectral features of emissivity spectra (i.e. CFs, RBs and TFs) can be discussed in function of temperature and plagioclase's relative abundance.

CFs tend to shift toward higher wavenumbers with increasing temperatures (Figures 1,2,3). In particular, plagioclase-rich CFs shift from 1280-1291 cm^{-1} to 1300-1314 cm^{-1} , with an average shift of 20 cm^{-1} from 425 K to 725 K. CF's pyroxene end-member located at 1160 cm^{-1} displays no significant changes up to 625 K, then shifts of about 30 cm^{-1} to the highest temperature (Figure 3). On the other hand, synthetic-gabbro spectra show a systematic shift of the CF, gaining 30 cm^{-1} (i.e. from 1240 cm^{-1} to 1273 cm^{-1}). The greater CF shifts of pyroxene-rich spectra are consistent with results of Logan et al. (1973). The systematic shift of plagioclase-bearing CFs with increasing temperature is even better highlighted in Figure 3, where each "temperature" set of measurements (differentiated by colours) shifts consistently toward higher wavenumbers. Similarly to the absorption features, the CF position uses to shift toward lower wavenumbers with decreasing polymerization, i.e. from plagioclase to pyroxene (Farmer, 1974): CFs shown in Figure 3 consistently shift. Due to the fact that up to 725 K the position of all measured CFs does not overlap, this features are considered diagnostic of the plagioclase-pyroxene ratio.

In order to compare the behaviour of the main absorption bands consequently to the temperature and compositional variations, the reststrahlen bands of all emissivity spectra have been grouped depending on their wavenumber occurrence (Figures 1,2). Within the 1400-700 cm^{-1} range, four wavenumber windows have been reasonably identified as representative of RBs occurrence for our samples' set (grey windows, Figures 1,2). The first two windows refer to the two close high-wavenumber RBs that characterize the plagioclase end-member spectra: the 1160-1190 cm^{-1} window (labelled *a* in Figures 1,2) includes all the first RBs developed along the entire temperature range by samples containing plagioclase, the 1080-1150 cm^{-1} window (labelled *b* in Figures 1,2) comprehends the second RBs of samples containing

plagioclase as well as the first RBs of the pyroxene end-member, which occurs between 1085 and 1105 cm^{-1} (Figures 1,2,4). The third window, located in the 940-1000 cm^{-1} range (labelled *c* in Figures 1,2), refers to the third RBs of samples containing plagioclase and the second RBs of the pyroxene end-member, which overlap in the synthetic-gabbro sample spectra (i.e. *pl050*). The fourth window, located in the 850-880 cm^{-1} range (labelled *d* in Figure 2), refers to the third RBs of the pyroxene end-member, which likewise occurs in *pl050*.

RBs occurring at $\sim 920 \text{ cm}^{-1}$ (Figures 1,2), which are characteristic of plagioclase solid solutions, appear strongly affected by the TF of plagioclase-bearing samples and therefore less reliable. Their positions do not show significant shifts with increasing temperature or plagioclase content (Table 4). Nevertheless, their spectral slope tends to increase with increasing temperature (Table 5), allowing to prevail on the TF over 725 K.

Figure 4 allows a comparison of the main emissivity RB minima's shifts as function of the temperature variation and of the plagioclase content. High-wavenumber RBs located within the *a* window - and characteristic of samples containing plagioclase - systematically shift toward lower wavenumbers (i.e. negative shift, Figure 4a) with increasing temperatures, disappearing over 525 K in the plagioclase end-member (*pl100*) spectra and over 625 K in the synthetic anorthosite (*pl090*) spectra. Shifts of those RBs are linear and can be quantified in a decrease of 8-10 cm^{-1} per 100 K/degrees of increasing temperature (i.e. $\sim 10^{-1} \text{ cm}^{-1} \text{ K}^{-1}$). On the other hand, at the same temperature, plagioclase-rich absorptions occurring within this first window shift toward higher wavenumbers with increasing plagioclase content (i.e. with a positive shift, Figure 4d): in this specific comparison the anorthosite *talquale* (*anorth*) features are interpreted to be dependent on the 83 wt.% of

plagioclase that constitutes the sample. Whereas the synthetic-gabbro (*pl050*) group displays a negative shift with respect to the anorthosite *talquale* absorptions for most of the temperature steps (Figure 4d), being influenced by the high content of pyroxene that uses to show the first absorption at lower wavenumbers.

Concerning the *b* window, with increasing temperature RBs display negative shifts as well (Figure 4b), but to a lesser extent with respect to the higher-wavenumber RBs: shifts tend to increase with increasing content of pyroxene from 2-3 cm⁻¹ per 100 K for *pl100* and *anorth* minima (i.e. 0 to 6 wt.% of pyroxene, respectively) to 5-6 cm⁻¹ every 100 K for *pl050* and the pyroxene end-member (*pl000*) minima. Within the *b* window, shifts are again strongly controlled by the pyroxene content: an increase of pyroxene of 10 wt.% in plagioclase-rich samples corresponds to a maximum shift of 8 cm⁻¹; an additional increase of 40 wt.% (*pl050*) corresponds to an additional shift of about 35 cm⁻¹ (Figure 4e), whereas an additional increase of 50 wt.%, which correspond to the *pl000* sample, corresponds to a maximum increase of 10 cm⁻¹. The gabbroic-like features, indeed, are conditioned by the lower-wavenumbers attitude of the pyroxene end-member. Even in this case, it seems to be clear the influence of the pyroxene on the absorption positions.

The *c* window includes the third RBs of plagioclase-bearing spectra and the second RBs of the pyroxene end-member (Figures 1,2). With the first 100-K increase, at 525 K the plagioclase-bearing features appear all shifted of different amount to gather in a narrow interval between 985 and 989 cm⁻¹, whereas further increases of temperature does not provide substantial changes on their positions (Figure 4c). On the contrary, the third RB of *pl000* linearly shifts toward lower wavenumbers with a decrease of ~4 cm⁻¹ per 100 K. With increasing temperature, the divergence of RB's positions depending on the sample composition suggests that RBs occurring within

this window are strongly affected by the plagioclase content, which works as a stiffener. On the other hand, low-temperature absorptions enclosed in the *c* window tend to shift toward lower wavenumbers with increasing pyroxene content (Figure 4f), roughly coupling the shift amount between *pl050* and *pl000* and confirming the dominance of plagioclase within this range.

Concerning the third RB of the pyroxene end-member (*d* window, Figure 2), which occurs as a fourth absorption in the *pl050* spectra, it seems to undergo as well a negative shift of 9 cm⁻¹ with the first 100 K of temperature increase, and then notably decreases the shifts to 3 cm⁻¹ per 100 K from 525 K to 725 K (Table 4).

Figure 5 allows a comparison of the main RB spectral contrasts (i.e. the differences between the CF emissivity and the absorption-minima emissivity) as a function of the temperature variation and of the plagioclase content. Spectral contrasts between CFs and RBs increase both with increasing temperature, smoothing differences due to the wavenumber position, and with increasing plagioclase content. The increase reduces the evidence of the TFs and it appears linear and proportional to the plagioclase content, being spectral contrasts of plagioclase-rich RBs twice the pyroxene-rich values at low temperatures, and three times at high temperatures. Even in this case, anorthosite-*talquale* RBs act as though the sample is composed by 83 wt.% of plagioclase, confirming the contribution of other components on the spectral contrast. The minimum increase of spectral contrast occurs in pyroxene end-member (*pl000*) spectra. The correlation between spectral contrast and plagioclase-pyroxene ratio suggests that spectral contrast is not solely affected by vacuum efficiency, which increases with increasing temperatures, but can be related to the mineralogy as well. The mineralogical composition, indeed, can affect the thermal conductivity and the average size of the sieved particulate. Concerning this work, a generally lower

spectral contrast of pyroxene's RBs is consistent with an enrichment in finer particulates during the grinding (e.g., Logan et al., 1973), which is corroborated by the presence of deeper TFs (Figure 2).

4. Discussion

In this work, in most cases, the position of the CF tends to shift toward higher wavenumbers with increasing temperatures and toward lower wavenumbers with decreasing polymerization (i.e. from plagioclase to pyroxene) (i) linearly and (ii) without superimpositions, becoming a useful proxy even for mixtures, not only for plagioclases.

With increasing temperatures, in the 900-1200 cm^{-1} range, all RBs of the considered samples show a shift of their position and a deepening with respect to the CF emissivity values. Highest shifts are negative and occur at higher wavenumbers of plagioclase-bearing spectra, but their extent does not depend on the plagioclase wt.%. Those shifts, associated with an increased spectral contrast, are the most prominent variations that, for example, an instrument like MERTIS can encounter for regoliths dominated by plagioclase-clinopyroxene assemblages on the hot surface of Mercury. Notably, at very high temperatures plagioclase-rich spectra lack of the high-wavenumber RBs, similarly to those of the pyroxene end-member, therefore any compositional interpretation must refer to the following RB positions. More moderate negative shifts of the RB positions occur at lower wavenumbers, within the *b* window (Figure 2), with extents that seem to be proportional to the pyroxene content. A relationship between the RB's shift amount and the thermal expansion coefficient (α_V) of the single-phase mineral has been observed by Helbert et al. (2013) and Ferrari et al. (2014) in silicate spectra. Within similar temperature ranges, a $\text{An}_{46}\text{-Ab}_{34}$ plagioclase - which is comparable to the *pl100* composition - has a α_V of $2.2 \times 10^{-5} \text{ K}^{-1}$

(Tribaudino et al., 2010), whereas a Fe-rich clinopyroxene - Mg# 0.17, which is closer to the *pl000* composition - has a α_v of $2.7 \times 10^{-5} \text{ K}^{-1}$ (Ferrari et al., 2014). In this work, the RB of *pl100* that occurs within the *b* window displays an average shift of about 2 cm^{-1} per 100 K, whereas that one of *pl000* display an average shift of about 6 cm^{-1} , consistently with the idea that greater coefficients use to promote greater shifts. In any case, the position of the *b*-window RB, when complemented by the surface temperature, is useful to distinguish anorthosite-like mixtures (i.e. felsic-rich regolith) from the gabbroic-like or basaltic-like ones (i.e. more mafic compositions). This is also the case of MERTIS that, having a spectral resolution ranging from 9 to 20 cm^{-1} in this spectral range, is sensitive both to great plagioclase-pyroxene ratio variations and to major temperature changes of the Mercury surface. On the other hand, RBs occurring at moderate to high temperatures at even lower wavenumbers (*c* window of Figure 2) are diagnostic of the plagioclase presence but cannot provide further information on the plagioclase-pyroxene ratio. The adjacent RBs, occurring at $\sim 920 \text{ cm}^{-1}$, would be instead indicative of plagioclase-rich mixtures but are strongly affected by the closer TF. A distinction between anorthositic- and gabbroic-like regolith could be achieved through the spectral contrast at very high temperatures, but it would require a suitable knowledge of the involved surface parameters (grain size distribution, pressure, thermal gradient etc.) and possibly more analogue measurements. Lowest shifts are negative and occur at lower wavenumbers of pyroxene-rich spectra (i.e. within the *d* window). More precisely, the lowest shifts occur in the third RB of *pl000*, consistently with Ferrari et al. (2014). Concerning both the position and the spectral contrast, during MERTIS detection this feature would appear unaffected by the increase of temperature, therefore it is eligible to indicate pyroxene-rich regolith.

5. Conclusions

1400-700 cm^{-1} emissivity spectra of bimodal mixtures of plagioclase and pyroxene measured between 425 K and 725 K have been examined in order to evaluate changes due to temperature and plagioclase-pyroxene ratio variations. In particular, the distinction of a plagioclase-rich regolith from more mafic compositions (e.g., gabbroic as well as basaltic) has been assessed, determining which features can be diagnostic during the remote sensing investigation of hot planetary surfaces. Results suggest that, regardless the surface daily temperature, spectra of anorthositic-like regolith can be distinguished from those of gabbroic-like regolith by the lack of absorptions at 850-880 cm^{-1} , which are characteristic of pyroxene-rich mixtures. In addition, a more robust distinction can be achieved cross-checking the wavenumber of the Christiansen features and the wavenumber of reststrahlen absorptions located between 1080 and 1150 cm^{-1} with the temperature of the radiative surface. Noteworthy, spectra of plagioclase-rich regolith measured at high surface temperatures can lack of the first reststrahlen band, suggesting the contribution of a Ca-rich plagioclase instead of a more correct intermediate plagioclase solid solution. At high temperatures, on the other hand, the increase of spectral contrast of the reststrahlen absorptions to the detriment of the transparency feature makes items more readable, and the spectral contrast itself could be used to distinguish deeper plagioclase-rich absorptions. To be remarked that MERTIS laboratory performances (D'Amore et al., 2018) show signal-to-noise ratio greater than 200 in the 1000-1200 cm^{-1} range, meaning that the noise level is lower than 0.5%. Such a performance would fully enabling MERTIS to detect on the hot surface of Mercury most of the variations shown in this work. On the other hand, the interpretation of the hyperspectral data returned by MERTIS as well as by any other TIR spectrometer will

benefit from laboratory spectra obtained under realistic temperature conditions, especially in cases where instruments measure the surface temperature independently with an integrated radiometer. Ongoing work focuses on both extending such measurements to more complex planetary-body analogues as well as a theoretical understanding of the thermal effects based on ab-initio calculations.

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References

- Bandfield, J.L., Hamilton, V.E., Christensen, P.R., 2000. A Global View of Martian Surface Compositions from MGS-TES. *Science* (80-.). 287, 1626–1630. <https://doi.org/10.1126/science.287.5458.1626>
- Christensen, P.R., Bandfield, J.L., Hamilton, V.E., Howard, D.A., Lane, M.D., Piatek, J.L., Ruff, S.W., Stefanov, W.L., 2000. A thermal emission spectral library of rock-forming minerals. *J. Geophys. Res.* 105, 9735–9739. <https://doi.org/10.1029/1998JE000624>
- Christensen, P.R., Bandfield, J.L., Hamilton, V.E., Ruff, S.W., Kieffer, H.H., Titus, T.N., Malin, M.C., Morris, R. V., Lane, M.D., Clark, R.L., Jakosky, B.M., Mellon, M.T., Pearl, J.C., Conrath, B.J., Smith, M.D., Clancy, R.T., Kuzmin, R.O., Roush, T., Mehall, G.L., Gorelick, N., Bender, K., Murray, K., Dason, S., Greene, E., Silverman, S., Greenfield, M., 2001. Mars Global Surveyor Thermal Emission Spectrometer experiment: Investigation description and surface science results. *J. Geophys. Res. Planets* 106, 23823–23871. <https://doi.org/10.1029/2000JE001370>

574 Christensen, P.R., Hamilton, V.E., Mehall, G.L., Pelham, D., O'Donnell, W., Anwar,
 575 S., Bowles, H., Chase, S., Fahlgren, J., Farkas, Z., Fisher, T., James, O., Kubik,
 576 I., Lazbin, I., Miner, M., Rassas, M., Schulze, L., Shamordola, K., Tourville, T.,
 577 West, G., Woodward, R., Lauretta, D., 2018. The OSIRIS-REx Thermal
 578 Emission Spectrometer (OTES) Instrument. *Space Sci. Rev.* 214, 87.
 579 <https://doi.org/10.1007/s11214-018-0513-6>

580 Christensen, P.R., McSween, H.Y., Bandfield, J.L., Ruff, S.W., Rogers, A.D.,
 581 Hamilton, V.E., Gorelick, N., Wyatt, M.B., Jakosky, B.M., Kieffer, H.H., Malin,
 582 M.C., Moersch, J.E., 2005. Evidence for magmatic evolution and diversity on
 583 Mars from infrared observations. *Nature* 436, 504–509.
 584 <https://doi.org/10.1038/nature03639>

585 Conel, J.E., 1969. Infrared Emissivities of Silicates: Experimental Results and a
 586 Cloudy Atmosphere Model of Spectral Emission from Condensed Particulate
 587 Mediums. *J. Geophys. Res.* 74, 1614–1634.
 588 <https://doi.org/10.1029/JB074i006p01614>

589 D'Amore, M., Helbert, J., Maturilli, A., Varatharajan, I., Ulmer, B., Säuberlich, T.,
 590 Berlin, R., Peter, G., Hiesinger, H., Martinez, S., Casale, M., Ortiz de Landaluze,
 591 I., Walter, I., 2018. Data processing of the Mercury radiometer and thermal
 592 infrared imaging spectrometer (MERTIS) onboard Bepi Colombo, in: Strojnik,
 593 M., Kirk, M.S. (Eds.), *Infrared Remote Sensing and Instrumentation XXVI*.
 594 SPIE, p. 16. <https://doi.org/10.1117/12.2321051>

595 Donaldson Hanna, K.L., Cheek, L.C., Pieters, C.M., Mustard, J.F., Greenhagen, B.T.,
 596 Thomas, I.R., Bowles, N.E., 2014. Global assessment of pure crystalline
 597 plagioclase across the Moon and implications for the evolution of the primary

598 crust. J. Geophys. Res. Planets 119, 1516–1545.
 599 <https://doi.org/10.1002/2013JE004476>

600 Donaldson Hanna, K.L., Thomas, I.R., Bowles, N.E., Greenhagen, B.T., Pieters,
 601 C.M., Mustard, J.F., Jackson, C.R.M., Wyatt, M.B., 2012. Laboratory emissivity
 602 measurements of the plagioclase solid solution series under varying
 603 environmental conditions. J. Geophys. Res. E Planets 117, 1–7.
 604 <https://doi.org/10.1029/2012JE004184>

605 E. Vander Kaaden, K., M. McCubbin, F., R. Nittler, L., N. Peplowski, P., Z. Weider,
 606 S., A. Frank, E., J. McCoy, T., 2017. Geochemistry, mineralogy, and petrology
 607 of boninitic and komatiitic rocks on the mercurian surface: Insights into the
 608 mercurian mantle. Icarus 285, 155–168.
 609 <https://doi.org/10.1016/j.icarus.2016.11.041>

610 Emery, J.P., Sprague, A.L., Witteborn, F.C., Colwell, J.E., Kozlowski, R.W.H.,
 611 Wooden, D.H., 1998. Mercury: Thermal Modeling and Mid-infrared (5–12 μm)
 612 Observations. Icarus 136, 104–123. <https://doi.org/10.1006/ICAR.1998.6012>

613 Farmer, V.C., 1974. The Infrared Spectra of Minerals. Mineralogical Society of Great
 614 Britain and Ireland. <https://doi.org/https://doi.org/10.1180/mono-4>

615 Ferrari, S., Nestola, F., Massironi, M., Maturilli, A., Helbert, J., Alvaro, M.,
 616 Domeneghetti, M.C., Zorzi, F., 2014. In-situ high-temperature emissivity spectra
 617 and Thermal expansion of C2/c pyroxenes: Implications for the surface of
 618 Mercury. Am. Mineral. 99, 786–792. <https://doi.org/10.2138/am.2014.4698>

619 Glotch, T.D., Lucey, P.G., Bandfield, J.L., Greenhagen, B.T., Thomas, I.R., Elphic,
 620 R.C., Bowles, N., Wyatt, M.B., Allen, C.C., Hanna, K.D., Paige, D.A., 2010.
 621 Highly silicic compositions on the moon. Science (80-.). 329, 1510–1513.

622 <https://doi.org/10.1126/science.1192148>

623 Greenhagen, B.T., Lucey, P.G., Wyatt, M.B., Glotch, T.D., Allen, C.C., Arnold, J.A.,
624 Bandfield, J.L., Bowles, N.E., Hanna, K.L.D., Hayne, P.O., Song, E., Thomas,
625 I.R., Paige, D.A., 2010. Global silicate mineralogy of the moon from the diviner
626 lunar radiometer. *Science* (80-.). 329, 1507–1509.
627 <https://doi.org/10.1126/science.1192196>

628 Halliday, A.N., 2001. In the beginning. . . *Nature* 409, 144–145.
629 <https://doi.org/10.1038/35051685>

630 Hamilton, V.E., 2010. Thermal infrared (vibrational) spectroscopy of Mg-Fe olivines:
631 A review and applications to determining the composition of planetary surfaces.
632 *Chemie der Erde* 70, 7–33. <https://doi.org/10.1016/j.chemer.2009.12.005>

633 Hamilton, V.E., 2000. Thermal infrared emission spectroscopy of the pyroxene
634 mineral series. *J. Geophys. Res. E Planets* 105, 9701–9716.
635 <https://doi.org/10.1029/1999JE001112>

636 Hamilton, V.E., Christensen, P.R., 2000. Determining the modal mineralogy of mafic
637 and ultramafic igneous rocks using thermal emission spectroscopy. *J. Geophys.*
638 *Res.* 105, 9717. <https://doi.org/10.1029/1999JE001113>

639 Helbert, J., Nestola, F., Ferrari, S., Maturilli, A., Massironi, M., Redhammer, G.J.,
640 Capria, M.T., Carli, C., Capaccioni, F., Bruno, M., 2013. Olivine thermal
641 emissivity under extreme temperature ranges: Implication for Mercury surface.
642 *Earth Planet. Sci. Lett.* 371–372, 252–257.
643 <https://doi.org/10.1016/j.epsl.2013.03.038>

644 Hiesinger, H., Helbert, J., 2010. The Mercury Radiometer and Thermal Infrared
645 Spectrometer (MERTIS) for the BepiColombo mission. *Planet. Space Sci.* 58,

646 144–165. <https://doi.org/10.1016/J.PSS.2008.09.019>

647 Laurretta, D.S., Balram-Knutson, S.S., Beshore, E., Boynton, W. V., Drouet
648 d’Aubigny, C., DellaGiustina, D.N., Enos, H.L., Golish, D.R., Hergenrother,
649 C.W., Howell, E.S., Bennett, C.A., Morton, E.T., Nolan, M.C., Rizk, B., Roper,
650 H.L., Bartels, A.E., Bos, B.J., Dworkin, J.P., Highsmith, D.E., Lorenz, D.A.,
651 Lim, L.F., Mink, R., Moreau, M.C., Nuth, J.A., Reuter, D.C., Simon, A.A.,
652 Bierhaus, E.B., Bryan, B.H., Ballouz, R., Barnouin, O.S., Binzel, R.P., Bottke,
653 W.F., Hamilton, V.E., Walsh, K.J., Chesley, S.R., Christensen, P.R., Clark, B.E.,
654 Connolly, H.C., Crombie, M.K., Daly, M.G., Emery, J.P., McCoy, T.J.,
655 McMahon, J.W., Scheeres, D.J., Messenger, S., Nakamura-Messenger, K.,
656 Righter, K., Sandford, S.A., 2017. OSIRIS-REx: Sample Return from Asteroid
657 (101955) Bennu. *Space Sci. Rev.* 212, 925–984. [https://doi.org/10.1007/s11214-](https://doi.org/10.1007/s11214-017-0405-1)
658 017-0405-1

659 Lim, L.F., McConnochie, T.H., Bell, J.F., Hayward, T.L., 2005. Thermal infrared (8-
660 13 μ m) spectra of 29 asteroids: The Cornell Mid-Infrared Asteroid Spectroscopy
661 (MIDAS) survey. *Icarus* 173, 385–408.
662 <https://doi.org/10.1016/j.icarus.2004.08.005>

663 Lindh, A., Andersson, U.B., Lundqvist, T., Claesson, S., 2001. Evidence of crustal
664 contamination of mafic rocks associated with rapakivi rocks: An example from
665 the Nordingrå complex, Central Sweden. *Geol. Mag.* 138, 371–386.
666 <https://doi.org/10.1017/S0016756801005672>

667 Logan, L.M., Hunt, G.R., Salisbury, J.W., Balsamo, S.R., 1973. Compositional
668 implications of Christiansen frequency maximums for infrared remote sensing
669 applications. *J. Geophys. Res.* 78, 4983–5003.

670 <https://doi.org/10.1029/JB078i023p04983>

671 Lyon, R.J.P., 1962. Evaluation of Infrared Spectrophotometry for Compositional
672 Analysis of Lunar and Planetary Soils. Tech. report, Stanford Res. Inst.

673 Maturilli, A., Helbert, J., Moroz, L., 2008. The Berlin emissivity database (BED).
674 Planet. Space Sci. 56, 420–425. <https://doi.org/10.1016/j.pss.2007.11.015>

675 Maturilli, A., Helbert, J., St. John, J.M., Head, J.W., Vaughan, W.M., D'Amore, M.,
676 Gottschalk, M., Ferrari, S., 2014. Komatiites as Mercury surface analogues:
677 Spectral measurements at PEL. Earth Planet. Sci. Lett. 398, 58–65.
678 <https://doi.org/10.1016/j.epsl.2014.04.035>

679 Maturilli, A., Helbert, J., Witzke, A., Moroz, L., 2006. Emissivity measurements of
680 analogue materials for the interpretation of data from PFS on Mars Express and
681 MERTIS on Bepi-Colombo. Planet. Space Sci. 54, 1057–1064.
682 <https://doi.org/10.1016/j.pss.2005.12.021>

683 Mckay, D.S., Heiken, G., Basu, A., Blanford, G., Simon, S., Reedy, R., French, B.M.,
684 Papike, J., 1980. The lunar regolith, in: The Lunar Sourcebook. pp. 285–356.

685 Nakamura, T., Noguchi, T., Tanaka, M., Zolensky, M.E., Kimura, M., Tsuchiyama,
686 A., Nakato, A., Ogami, T., Ishida, H., Uesugi, M., Yada, T., Shirai, K., Fujimura,
687 A., Okazaki, R., Sandford, S.A., Ishibashi, Y., Abe, M., Okada, T., Ueno, M.,
688 Mukai, T., Yoshikawa, M., Kawaguchi, J., 2011. Itokawa dust particles: A direct
689 link between S-type asteroids and ordinary chondrites. Science (80-.). 333,
690 1113–1116. <https://doi.org/10.1126/science.1207758>

691 Namur, O., Charlier, B., 2017. Silicate mineralogy at the surface of Mercury. Nat.
692 Geosci. 10, 9–13. <https://doi.org/10.1038/ngeo2860>

693 Paige, D.A., Siegler, M.A., Zhang, J.A., Hayne, P.O., Foote, E.J., Bennett, K.A.,

694 Vasavada, A.R., Greenhagen, B.T., Schofield, J.T., McCleese, D.J., Foote, M.C.,
 695 DeJong, E., Bills, B.G., Hartford, W., Murray, B.C., Allen, C.C., Snook, K.,
 696 Soderblom, L.A., Calcutt, S., Taylor, F.W., Bowles, N.E., Bandfield, J.L.,
 697 Elphic, R., Ghent, R., Glotch, T.D., Wyatt, M.B., Lucey, P.G., 2010. Diviner
 698 Lunar Radiometer Observations of Cold Traps in the Moon's South Polar
 699 Region. *Science* (80-.). 330, 479 LP-482.

700 Pouchou, J.-L., Pichoir, F., 1991. Quantitative Analysis of Homogeneous or Stratified
 701 Microvolumes Applying the Model "PAP," in: *Electron Probe Quantitation*.
 702 Springer US, Boston, MA, pp. 31–75. [https://doi.org/10.1007/978-1-4899-2617-](https://doi.org/10.1007/978-1-4899-2617-3_4)
 703 [3_4](https://doi.org/10.1007/978-1-4899-2617-3_4)

704 Ramsey, M.S., Christensen, P.R., 1998. Mineral abundance determination:
 705 Quantitative deconvolution of thermal emission spectra. *J. Geophys. Res. Solid*
 706 *Earth* 103, 577–596. <https://doi.org/10.1088/1475-7516/2016/07/026>

707 Rietveld, H.M., 1967. Line profiles of neutron powder-diffraction peaks for structure
 708 refinement. *Acta Crystallogr.* 22, 151–152.
 709 <https://doi.org/10.1107/S0365110X67000234>

710 Salisbury, J.W., D'Aria, D.M., 1994. Emissivity of terrestrial materials in the 3-5 μm
 711 atmospheric window. *Remote Sens. Environ.* 47, 345–361.
 712 [https://doi.org/doi.org/10.1016/0034-4257\(94\)90102-3](https://doi.org/10.1016/0034-4257(94)90102-3)

713 Salisbury, J.W., Wald, A., 1992. The role of volume scattering in reducing spectral
 714 contrast of reststrahlen bands in spectra of powdered minerals. *Icarus* 96, 121–
 715 128. [https://doi.org/10.1016/0019-1035\(92\)90009-V](https://doi.org/10.1016/0019-1035(92)90009-V)

716 Salisbury, J.W., Walter, L.S., 1989. Thermal infrared (2.5-13.5 μm) spectroscopic
 717 remote sensing of igneous rock types on particulate planetary surfaces. *J.*

718 Geophys. Res. 94, 9192–9202. <https://doi.org/10.1029/JB094iB07p09192>

719 Smith, J. V., Brown, W.L., 1988. Feldspar Minerals : Volume 1 Crystal Structures,
 720 Physical, Chemical, and Microtextural Properties. Springer Berlin Heidelberg.

721 Sprague, A.L., Donaldson Hanna, K.L., Kozlowski, R.W.H., Helbert, J., Maturilli, A.,
 722 Warell, J.B., Hora, J.L., 2009. Spectral emissivity measurements of Mercury’s
 723 surface indicate Mg- and Ca-rich mineralogy, K-spar, Na-rich plagioclase, rutile,
 724 with possible perovskite, and garnet. Planet. Space Sci. 57, 364–383.
 725 <https://doi.org/10.1016/j.pss.2009.01.006>

726 Tonks, W.B., Melosh, H.J., 1993. Magma ocean formation due to giant impacts. J.
 727 Geophys. Res. Planets 98, 5319–5333. <https://doi.org/10.1029/92JE02726>

728 Tribaudino, M., Angel, R.J., Cámara, F., Nestola, F., Pasqual, D., Margiolaki, I.,
 729 2010. Thermal expansion of plagioclase feldspars. Contrib. to Mineral. Petrol.
 730 160, 899–908. <https://doi.org/10.1007/s00410-010-0513-3>

731 Vernazza, P., Carry, B., Emery, J., Hora, J.L., Cruikshank, D., Binzel, R.P., Jackson,
 732 J., Helbert, J., Maturilli, A., 2010. Mid-infrared spectral variability for
 733 compositionally similar asteroids: Implications for asteroid particle size
 734 distributions. Icarus 207, 800–809. <https://doi.org/10.1016/j.icarus.2010.01.011>

735 Wald, A.E., Salisbury, J.W., 1995. Thermal infrared directional emissivity of
 736 powdered quartz. J. Geophys. Res. Solid Earth 100, 24665–24675.
 737 <https://doi.org/10.1029/95JB02400>

738 Wetherill, G.W., 1980. Formation of the Terrestrial Planets. Annu. Rev. Astron.
 739 Astrophys. 18, 77–113. <https://doi.org/10.1146/annurev.aa.18.090180.000453>

740

741 **Table 1 Suppl. Mat.** Results of the X-ray powder diffraction analysis of the Nordingrå-complex
742 anothosite sample.

Mineral	wt. %
Andesine, labradorite	83
Quartz	6
Diopside - ferroan	6
Actinolite	3
Ilmenite	<1
Clinochlore	<1

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Table 2 Suppl. Mat. Electron microprobe analysis (oxide wt. %) and formula in atoms per formula unit based on six oxygen atoms for the crystals studied in this work. Standards (analytical crystals, spectral lines) used were albite (Amelia plagioclase, TAP, K α) for Na, MgO (TAP, K α) for Mg, Al₂O₃ (TAP, K α) for Al, diopside (TAP, K α) for Si and (PET, K α) for Ca, MnTiO₃ (PET, K α) for Ti and (LIF 220, K α) for Mn, Cr₂O₃ (LIF 220, K α) for Cr, Fe₂O₃ (LIF 220, K α) for Fe, and orthoclase (PET, K α) for K.

Sample	Plagioclase	Plagioclase (core)	Clinopyroxene Mg#0.52	Clinopyroxene Mg#0.33
Oxide wt. %				
Na ₂ O	6.05	4.29	0.21	0.13
MgO	0.02	0.02	10.00	6.49
Al ₂ O ₃	26.56	29.28	1.75	0.77
SiO ₂	56.84	52.67	50.50	49.99
K ₂ O	0.57	0.43	-	-
CaO	9.07	12.34	20.65	20.57
TiO ₂	0.04	0.06	0.64	0.33
Cr ₂ O ₃	0.01	0.01	0.03	0.01
MnO	0.01	0.01	0.38	0.44
FeO	-	-	16.44	21.97
Fe ₂ O ₃	0.30	0.33	-	-
Total	99.45	99.44	100.60	100.70
Formula				
Ca	0.44	0.60	0.85	0.87
Na	0.53	0.38	0.02	0.01
K	0.03	0.02	-	-
Mn	-	-	0.01	0.01
Fe ²⁺	-	-	0.53	0.72
Fe ³⁺	0.01	0.01	-	-
Mg	-	-	0.56	0.38
Ti	-	-	0.02	0.01
Cr	-	-	-	-
Al	1.42	1.58	0.08	0.04
Si	2.57	2.40	1.94	1.97
Total	4.00	4.00	4.00	4.01

753 **Table 1.** Samples obtained by bulk sample separation and mixing of the two main phases,
754 plagioclases and clinopyroxene.

Sample	Label	Plagioclase	Clinopyroxene
		wt. %	wt. %
Anorthosite	<i>anorth</i>	83 (93 _{pl-cpx})	6 (7 _{pl-cpx})
Plagioclase	<i>pl100</i>	100	-
Synthetic anorthosite	<i>pl090</i>	90	10
Synthetic gabbros	<i>pl050</i>	50	50
Clinopyroxene	<i>pl000</i>	-	100

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Table 2. Positions of Christiansen features, Reststrahlen bands and Transparency features of reflectance-derived emissivity spectra collected at 295 K.

Sample	Label	Feature position											
		cm ⁻¹											
		CF	CF	RB	RB	RB	RB	RB	RB	RB	RB	TF	TF
Anorthosite	<i>anorth</i>	1265	-	1188	1120	-	-	1001	-	-	-	874	-
Plagioclase	<i>pl100</i>	1263	-	1180	1136	-	-	1003	-	920	-	874	-
Synthetic anorthosite	<i>pl090</i>	1259	-	1178	1132	-	-	1001	(941)	923	-	877	-
Synthetic gabbros	<i>pl050</i>	1246	-	1173	-	1101	-	-	958	912	-	879	-
Clinopyroxene	<i>pl000</i>	-	1159	-	-	-	1097	-	960	-	866	-	831
				<i>a</i>	<i>b</i>			<i>c</i>			<i>d</i>		

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761 **Table 3.** Emissivity of Christiansen features, Reststrahlen bands and Transparency features of reflectance-derived emissivity spectra collected at

Sample	Label	Emissivity											
		CF	CF	RB	RB	RB	RB	RB	RB	RB	RB	TF	TF
Anorthosite	<i>anorth</i>	0.983	-	0.955	0.954	-	-	0.956	-	-	-	0.951	-
Plagioclase	<i>pl100</i>	0.996	-	0.963	0.962	-	-	0.958	-	0.958	-	0.952	-
Synthetic anorthosite	<i>pl090</i>	0.993	-	0.957	0.956	-	-	0.955	(0.954)	0.954	-	0.954	-
Synthetic gabbros	<i>pl050</i>	0.983	-	0.964	-	0.950	-	-	0.939	0.939	-	0.938	-
Clinopyroxene	<i>pl000</i>	-	0.984	-	-	-	0.958	-	0.964	-	0.961	-	0.960
				<i>a</i>	<i>b</i>			<i>c</i>			<i>d</i>		

762 295 K.

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765 **Table 4.** Positions of Christiansen features, Reststrahlen bands and Transparency features of emissivity spectra collected at different
766 temperatures.

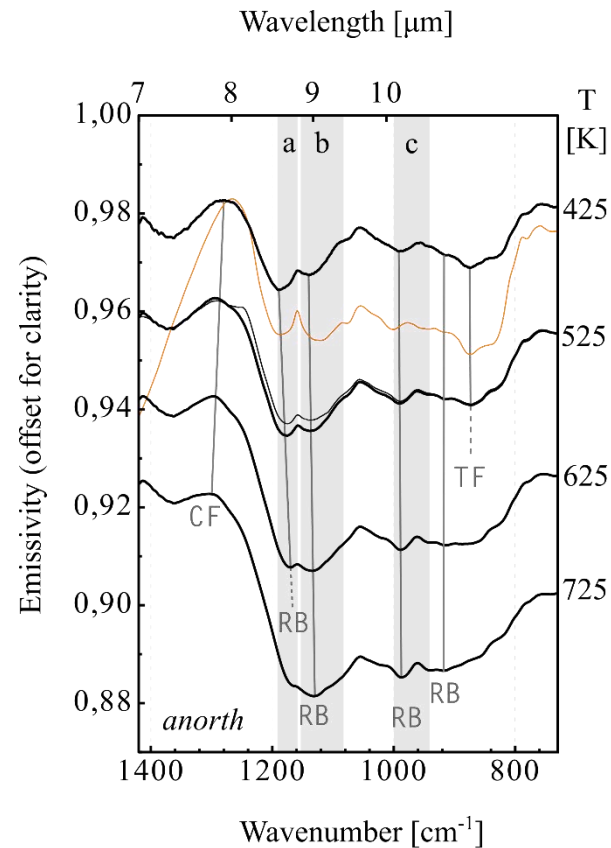
Sample	Label	Temp.		Feature position										
		K												
		CF	CF	RB	RB	RB	RB	RB	RB	RB	RB	RB	TF	TF
Anorthosite	anorth	425	1280	-	1188	1140	-	-	992	-	915	-	875	-
		525	1295	-	1175	1139	-	-	989	-	914	-	874	-
		625	1296	-	1172	1136	-	-	989	-	914	-	878	-
		725	1305	-	1165	1133	-	-	987	-	918	-	-	-
Plagioclase	pl100	425	1291	-	1179	1146	-	-	986	-	912	-	874	-
		525	1294	-	1173	1146	-	-	989	-	914	-	872	-
		625	1303	-	-	1140	-	-	989	-	913	-	875	-
		725	1314	-	-	1136	-	-	985	-	915	-	-	-
Synthetic anorth.	pl090	425	1287	-	1185	1148	-	-	985	-	913	-	876	-
		525	1287	-	1172	1142	-	-	988	-	914	-	874	-
		625	1294	-	1166	1139	-	-	988	-	914	-	875	-
		725	1300	-	-	1132	-	-	988	-	914	-	-	-
Synthetic gabbro	pl050	425	1240	-	1188	-	1111	-	976	-	906	875	-	823
		525	1248	-	1180	-	1108	-	985	-	908	860	-	823
		625	1262	-	1170	-	1104	-	985	-	908	859	-	820
		725	1273	-	1163	-	1096	-	984	-	908	859	-	819
Clinopyroxene	pl000	425	-	1160	-	-	-	1106	-	959		872	-	811
		525	-	1162	-	-	-	1103	-	954		863	-	811
		625	-	1163	-	-	-	1095	-	950		860	-	807
		725	-	1187	-	-	-	1086	-	947		857	-	805

Table 5. Emissivity of Christiansen features, Reststrahlen bands and Transparency features of spectra collected at different temperatures.

		Temp.			Emissivity									
		K												
Sample	Label	CF	CF	RB	RB	RB	RB	RB	RB	RB	RB	RB	TF	TF
Anorthosite	anorth	425	0.987	-	0.968	0.971	-	-	0.976	-	0.975	-	0.973	-
		525	0.985	-	0.957	0.958	-	-	0.963	-	0.964	-	0.963	-
		625	0.988	-	0.953	0.952	-	-	0.956	-	0.957	-	0.957	-
		725	0.982	-	0.943	0.940	-	-	0.944	-	0.946	-	-	-
Plagioclase	pl100	425	0.995	-	0.967	0.969	-	-	0.971	-	0.967	-	0.964	-
		525	0.994	-	0.958	0.959	-	-	0.960	-	0.958	-	0.955	-
		625	0.996	-	-	0.949	-	-	0.949	-	0.947	-	0.947	-
		725	0.992	-	-	0.936	-	-	0.934	-	0.932	-	-	-
Synthetic anorth.	pl090	425	0.992	-	0.968	0.969	-	-	0.971	-	0.968	-	0.966	-
		525	0.989	-	0.957	0.957	-	-	0.958	-	0.956	-	0.954	-
		625	0.987	-	0.947	0.946	-	-	0.947	-	0.945	-	0.945	-
		725	0.992	-	-	0.942	-	-	0.939	-	0.936	-	-	-
Synthetic gabbro	pl050	425	0.984	-	0.976	-	0.978	-	0.979	-	0.976	0.974	-	0.974
		525	0.980	-	0.969	-	0.969	-	0.972	-	0.969	0.968	-	0.967
		625	0.984	-	0.968	-	0.966	-	0.968	-	0.965	0.964	-	0.964
		725	0.981	-	0.962	-	0.958	-	0.961	-	0.958	0.958	-	0.958
Clinopyroxene	pl000	425	-	0.989	-	-	-	0.976	-	0.980	-	0.974	-	0.972
		525	-	0.984	-	-	-	0.968	-	0.974	-	0.969	-	0.966
		625	-	0.985	-	-	-	0.967	-	0.971	-	0.965	-	0.963
		725	-	0.983	-	-	-	0.961	-	0.965	-	0.959	-	0.957

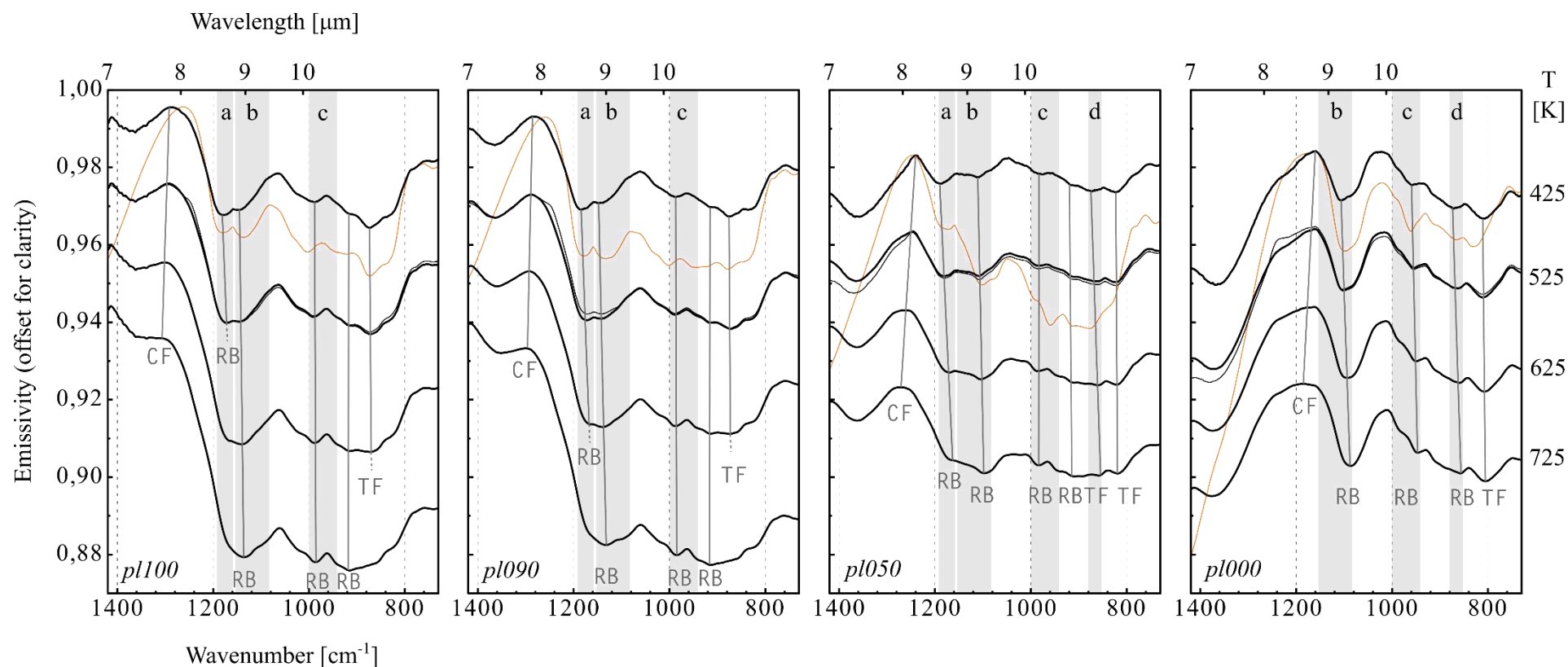
*a**b**c**d*

768 **Figure 1.** Anorthosite *talquale* emissivity spectra (ϵ_a , black lines) collected at 4 temperatures are shown alongside derived emissivity (ϵ_d , orange
769 lines) collected at 295 K; emissivity spectra were collected with increasing temperatures (black thick lines), then during the cooling maintaining
770 the temperature at 525 K (black thin line). Wavelength ranges where RBs occur are indicated by coloured windows.

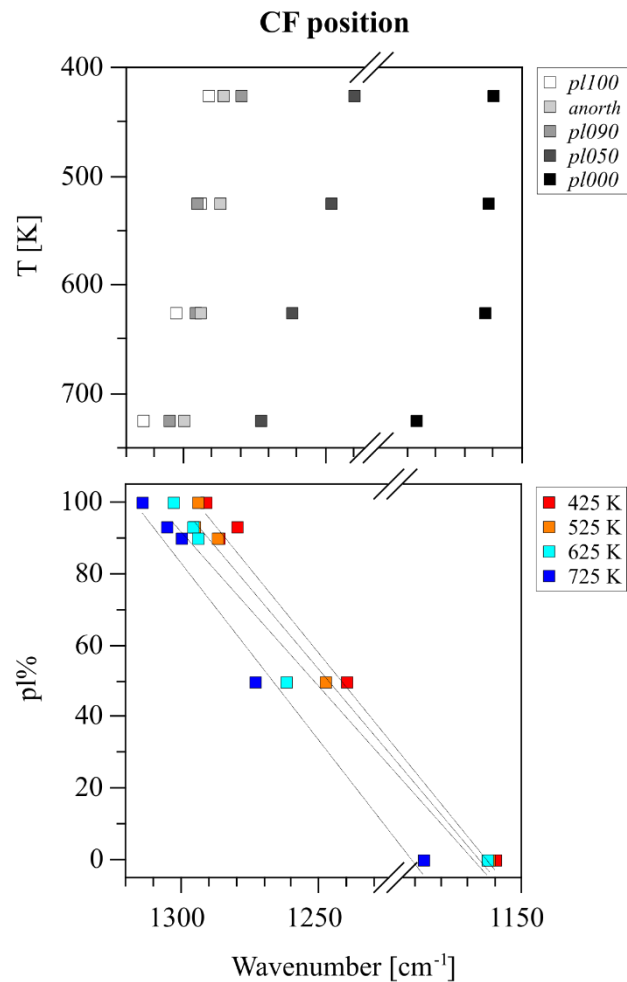


771

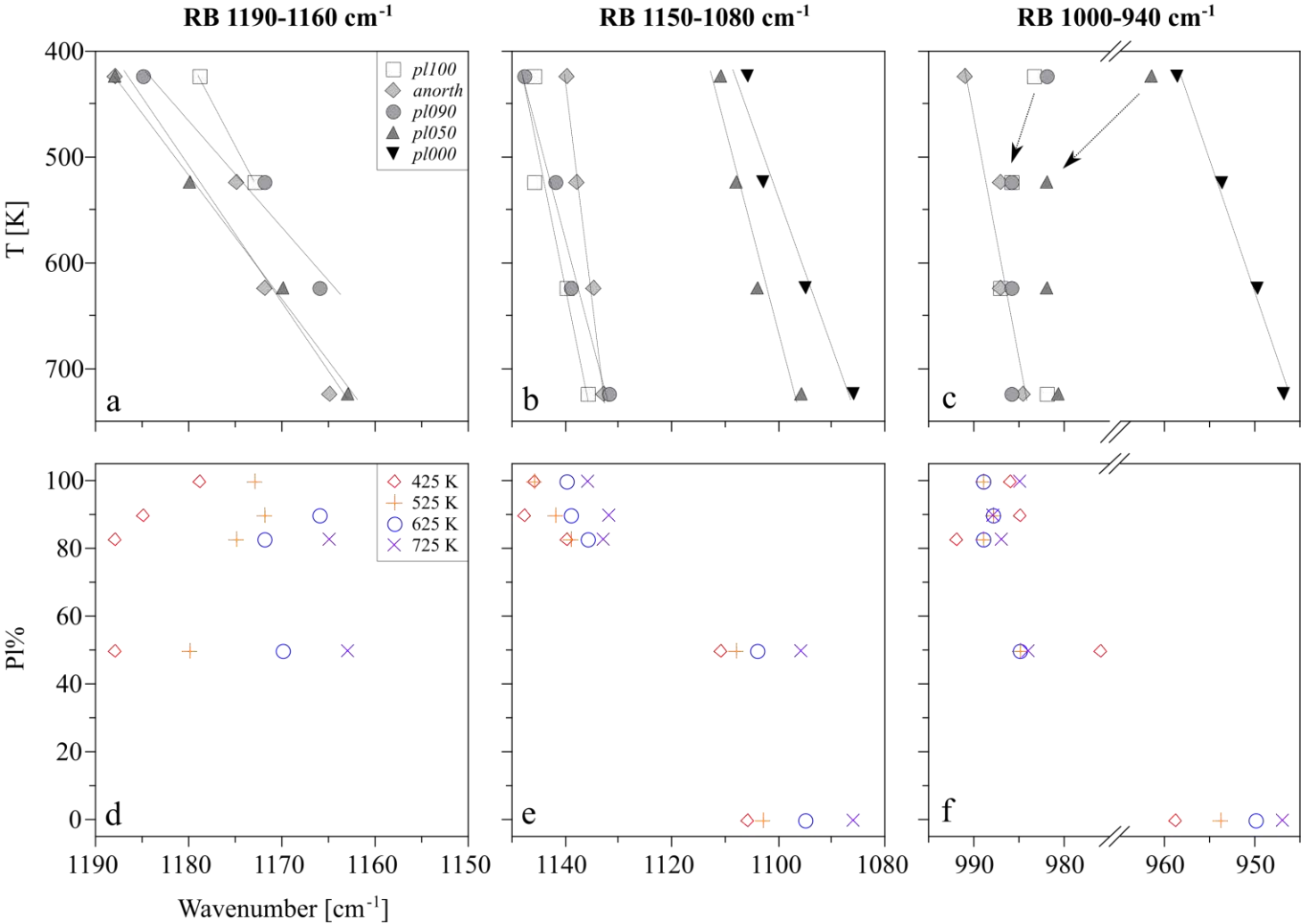
773 **Figure 2.** Endmembers and mixtures emissivity spectra (ϵ_a , black lines) collected at 4 temperatures are shown alongside derived emissivity (ϵ_d ,
774 orange lines) collected at 295 K; emissivity spectra were collected with increasing temperatures (black thick lines), then during the cooling
775 maintaining the temperature at 525 K (black thin line). Results are shown, from left to right, with decreasing degree of polymerization.
776 Wavelength ranges where RBs occur are indicated by grey windows and labelled a, b, c and d.



779 **Figure 3.** Comparison between emissivity CF positions collected at 425 K, 525 K, 625 K and 725 K (upper panel) and in function of the
780 plagioclase content (lower panel).



782 **Figure 4.** RBs positions in function of the temperature (upper panels a-c) and the plagioclase content (lower panels d-f): RBs are grouped in
783 function of the wavelength range where they occur.



785 **Figure 5.** RBs depths in function of the temperature (upper panels a-c) and of the plagioclase content (lower panels d-f): RBs are grouped in
786 function of the wavelength range where they occur.

