

**Revision 1**

**In-situ high-temperature emissivity spectra and thermal expansion of *C2/c* pyroxenes:  
implications for the surface of Mercury.**

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**Abstract**

This work was carried out within the framework of the European Space Agency – Japanese Aerospace Exploration Agency BepiColombo space mission to Mercury and intends to provide valid tools for the interpretation of spectra acquired by the MErcury Radiometer and Thermal Infrared Spectrometer (MERTIS) on board of BepiColombo.

Two *C2/c* augitic pyroxenes, with different Mg/Fe ratios and constant Ca contents, were investigated by in-situ high-temperature thermal infrared spectroscopy and in-situ high-temperature single-crystal X-ray diffraction up to temperatures of about 750 and 770 K, respectively.

The emissivity spectra of the two samples show similar band center shifts of the main three bands toward lower wavenumbers with increasing temperature. In detail, with increasing temperature bands 1 and 2 of both samples show a much stronger shift with respect to band 3, which remains almost unchanged. Our results indicate that the center positions of bands 1 and 2 are strong functions of the temperature, whereas the center position of band 3 is a strong function of the Mg# [with Mg# = Mg/(Mg + Fe<sup>2+</sup>) atomic ratio].

26 The analysis of the thermal behavior gives similar thermal expansion volume coefficients,  $\alpha_V$ , for  
27 the Mg-rich and Fe-rich samples, with  $\alpha_V = 2.72(8)$  and  $2.72(7) \times 10^{-5} \text{ K}^{-1}$ , respectively, using the  
28 Berman (1988) equation. This correspondence totally explains the band center shifts similarity between  
29 the two samples.

30 Our data suggest that MERTIS spectra will be able to provide indications of *C2/c* augitic pyroxene  
31 Mg# and will allow a correct interpretation that is independent on the spectra acquisition temperature.

32 **Keywords:** high temperature, TIR emissivity, thermal expansion, clinopyroxenes, Mercury.

### 33 Introduction

34 Ca-rich pyroxenes (clinopyroxenes, cpx) are among the most abundant silicate minerals of the  
35 Earth's crust and upper mantle. This has prompted investigations on their existence as a main  
36 constituent of other planetary body's shells. Recently terrestrial, lunar and meteoritic clinopyroxenes  
37 have been extensively investigated under different conditions of temperature and pressure by  
38 diffraction and spectroscopic techniques (e.g., Tribaudino et al. 2002; Nestola et al. 2008), following  
39 their important role for planetary geology.

40 Contextually, several ground-based telescopic observations that comprehend visible, near- and mid-  
41 infrared spectroscopy (0.4-14  $\mu\text{m}$ ) pointed out that Ca-rich (and low-Fe) clinopyroxenes could be  
42 common constituent minerals of the surface of Mercury, with diopside and augite considered as good  
43 possible candidates (i.e., Sprague et al. 2002, 2007, 2009).

44 The on-going Mercury Surface Space ENvironment GEochemistry and Ranging (MESSENGER)  
45 NASA mission (Solomon et al. 2001) have further improved the overall knowledge of this planet by  
46 the interpretation of a wider range of spectra (e.g., Visible and Near Infra-Red spectra, X-ray spectra  
47 and Gamma-ray spectra). In particular, for the dominant terrains of the surface of Mercury, Warell et  
48 al. (2010) indicate that Mg-rich clinopyroxenes could reach 30% of (Hapke-modeled, Warell and  
49 Davidsson 2010) mineral modal abundance.

50 The next European Space Agency and Japan Aerospace Agency mission to Mercury, named  
51 BepiColombo, will carry on board the Mercury Radiometer and Thermal Infrared Spectrometer  
52 (MERTIS) (Hiesinger and Helbert 2010) that will be able to provide Thermal Infra-Red (TIR)  
53 emissivity spectra from 7 to 14  $\mu\text{m}$  ( $1400\text{-}700\text{ cm}^{-1}$ ). This wavelength range is very useful to identify  
54 the fine-scale structural properties of several silicates (e.g., stretching and bending motions in the  
55 silicon-oxygen anions, metal-oxygen and lattice vibrations). In addition, for mineral families such as  
56 pyroxenes, the emissivity band positions are a good indicator of the composition (Hamilton 2000).

57 Previous spectra interpretations of Mercury have not considered the possible effects induced by the  
58 extreme daily surface temperature range on the surface minerals. Indeed, the temperature of the surface  
59 of Mercury can range in 44 earth-days between 70 and 725 K, depending on latitudes and longitudes  
60 (Strom and Sprague 2003). Known thermal models (Vasavada et al. 1999; Bauch et al. 2011) show that  
61 a point on the equatorial surface is subjected to a temperature variation greater than 400 K between the  
62 sunrise and the midday. These temperature variations significantly affect the crystal structure and  
63 density of minerals and, at the same time, should affect the TIR spectral signature of each single  
64 mineral present on the surface of the planet. This behavior has been recently demonstrated for  
65 plagioclases and olivines, which show significant TIR spectral signature changes under the typical  
66 temperature variation of the surface of Mercury (Helbert and Maturilli 2009; Helbert et al. 2013), and  
67 could be even predicted for other silicates.

68 To our knowledge, emissivity measurements of Ca-rich pyroxenes within the TIR range have been  
69 always conducted at room conditions (Christensen et al. 2000; Hamilton et al. 2000). In this work we  
70 have measured the thermal expansion and the TIR emissivity spectra in vacuum at high temperature of  
71 two Ca-rich clinopyroxenes with a strong different Fe content and similar Ca amount, in order to  
72 provide possible spectral signature changes occurring at the most likely environment of the surface of  
73 Mercury. Considering that MERTIS will collect TIR emissivity spectra likely from a clinopyroxene-  
74 bearing regolith, our work could improve the interpretation of the returned data.

75

## Methodology

### 76 Sample characterization

77 Well-preserved natural crystals of diopside were selected from the Montefiascone Volcanic  
78 Complex (Di Battistini et al. 1998). The samples analyzed were provided by the Museum of  
79 Mineralogy of the University of Padua (Omboni mineral collection) and labeled as DiMDCV. Crystals  
80 of hedenbergite, coming from the Elba Island (Tuscany region, Italy) and belonging to a private  
81 collection, were labeled HeE0125. Both phases were fully characterized at room conditions at the  
82 Department of Geosciences of the University of Padua (Italy) by the following techniques.

83 (i) Minerals were firstly analyzed by the Wavelength-Dispersive System (WDS) method. The  
84 analyses were carried out using a CAMECA CAMEBAX SX50 electron microprobe, with a fine-  
85 focused beam (~1 $\mu$ m diameter), an acceleration voltage of 20 kV and a beam current of 20 nA, with 10  
86 seconds counting times for both peak and total background. X-ray counts were converted to oxide wt%  
87 using the PAP correction program supplied by CAMECA (Pouchou and Pichoir 1991). Standards,  
88 spectral lines and analytical crystals used were albite (Amalia plagioclase, TAP, K $\alpha$ ) for Na, MgO  
89 (TAP, K $\alpha$ ) for Mg, Al<sub>2</sub>O<sub>3</sub> (TAP, K $\alpha$ ) for Al, diopside (TAP, K $\alpha$ ) for Si, (PET, K $\alpha$ ) for Ca and Ti,  
90 MnTiO<sub>3</sub> (LIF 220, K $\alpha$ ) for Mn, Cr<sub>2</sub>O<sub>3</sub> (LIF 220, K $\alpha$ ) for Cr and Fe<sub>2</sub>O<sub>3</sub> (LIF 220, K $\alpha$ ). Results of the  
91 analyses are reported in Table 1.

92 (ii) X-ray powder diffraction was performed in order to identify minor phases present in the  
93 selected natural samples. Data were recorded on a Panalytical  $\theta$ - $\theta$  diffractometer (Cu radiation)  
94 equipped with a long fine focus Cu X-ray tube operating at 40kV and 40mA and a real-time multiple  
95 strip (RTMS) detector (X'Celerator). The scan was performed over the range 3-80° 2 $\theta$  with a step size  
96 of 0.017° 2 $\theta$  and a counting time of 150 s/step. The program High Score Plus (PANalytical) was used  
97 for phase identification, quantitative phase analysis with Rietveld refinement (Rietveld 1967) and cell  
98 parameters determination with Le Bail method (Le Bail et al. 1988). A pseudo-Voigt function was

99 employed for the profile shapes. Refined parameters were scale factors, zero-shift, background, lattice  
100 constants, and profile parameters (Gaussian and Lorentzian coefficients). Diffractograms are reported  
101 in Supplementary Figure 1 and results of the analyses are reported in Table 2. HeE0125 sample shows  
102 traces of actinolite and gypsum in amount lower than 1%.

103 (iii) Single-crystal X-ray diffraction was performed on both samples by a STOE STADI IV 4-circle  
104 diffractometer equipped with Mo source (conditions: 50 kV, 40 mA) and an Agilent CCD in order to  
105 obtain a reliable cation distribution combining the X-ray with the EMPA data. The single crystals used  
106 for this analysis were twin- and inclusion-free and had a sharp optical extinction. Their size ranged  
107 from  $120 \times 120 \times 100 \mu\text{m}^3$  (DiMDCV) to  $450 \times 200 \times 100 \mu\text{m}^3$  (HeE0125). Weighted structural  
108 refinements based on  $F_o^2$  were performed using the SHELX-97 package (Sheldrick 1997) in the  $C2/c$   
109 space group starting from the coordinates of Finger and Ohashi (1976). The atomic scattering factors  
110 were taken from the International Tables for X-Ray Crystallography (Wilson 1995). Neutral vs. ionized  
111 scattering curves were refined for the oxygen (O and  $O^{-2}$ ) and silicon (Si and  $Si^{2+}$  atoms). Fully ionized  
112 scattering factors were used for  $Al^{3+}$ ,  $Ti^{4+}$ ,  $Cr^{3+}$ ,  $Mg^{2+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Mn^{2+}$ ,  $Ca^{2+}$ ,  $Na^+$ . Anisotropic thermal  
113 parameters were obtained for all atoms of the two samples. For crystal DiMDCV a residual electron-  
114 density maximum, located at  $0.67 \text{ \AA}$  from the M2 site, was observed in the difference-Fourier map; the  
115 same maximum was not found in the HeE0125 sample. The maximum found in the DiMDCV sample  
116 is known for Ca-rich  $C2/c$  pyroxenes. It has been observed in previous studies (Rossi et al. 1987;  
117 Oberti and Caporuscio 1991; Boffa Ballaran et al. 1998; Domeneghetti et al. 2005) and ascribed to the  
118 possible presence of Mg and  $Fe^{2+}$  at the M2 site, giving rise to the so called “M2' split position”.  
119 Therefore, a further set of refinements was performed using  $Mg^{2+}$  and  $Fe^{2+}$  scattering factors for the  
120 isotropic M2' site. The analytical results are reported in Table 3, bond-lengths are reported in Table 4.

## 121 **High-temperature in-situ single-crystal X-ray diffraction**

122 The same two fragments analyzed by single-crystal X-ray diffraction at room conditions were used  
123 for the in-situ high-temperature measurements. The high-temperature experiments were performed at  
124 the Department of Earth Sciences and Environment of the University of Pavia (Italy). Each crystal was  
125 loaded in a 0.5 mm inner diameter quartz vial 26 mm long closed at the top by using an oxy-methane  
126 flame. In order to avoid any possible Fe oxidation during the annealing, an iron wire was loaded as  
127 buffer in the vial together with the crystal. A small amount of quartz wool was used in order to avoid  
128 any mechanical stress, and any contact between the iron wire and the crystal. After alternately washing  
129 with Ar flux and evacuating, the vial was sealed at the open end (bottom) by using an oxy-methane  
130 flame.

131 The vial was then mounted into a short metal goniometer head on a Philips PW1100 diffractometer  
132 operated with FEBO software (a locally developed control software) working with MoK $\alpha$  radiation at  
133 55 kV and 30 mA and using a 0.5 mm short collimator. A microfurnace was mounted on the  
134 diffractometer. It consists of an H-shaped Pt–Rh resistance and a Pt:Pt-Rh thermocouple fixed inside a  
135 steel cylindrical cage 1 inch wide closed with a Kapton film, calibrated as in Cámara et al. (2012). The  
136 experimental setting described allows to collect diffraction data up to  $\theta_{\max} = 33^\circ$ . The UB matrix was  
137 determined by peak search and indexing of the 24 most intense reflections. The UB matrix and unit-cell  
138 parameters were firstly refined by measuring the Bragg angles of the selected 24 most intense  
139 reflections, using horizontal and vertical slits. Afterward, the Philips LAT procedure was used to obtain  
140 accurate and precise lattice constants and the UB matrix. The LAT procedure allowed the position of  
141 different reflections (with different  $nd$ -values), at positive and negative  $\omega$ - $2\theta$ , to be measured. The  
142 reflection is firstly centred by using the vertical and horizontal slits, then a scan in  $\omega$ - $2\theta$  is performed  
143 and the observed maxima are calculated. The observed  $nd$ -values were fitted producing a relative  $d$ -  
144 value and its estimated standard deviations.

145 The procedure was repeated on both crystals for each temperature step (Table 5) on a group of 60  
146 selected reflections. Lattice parameters were calculated by least-squares fitting of all the observed d-  
147 values and are reported in Table 5.

#### 148 **Sample preparation for Thermal Infra-Red (TIR) emissivity measurements**

149 Regarding the particulate mineral samples, the selected range of particle size and porosity can affect  
150 the observed emissivity spectral features, which are the result of both the absorption coefficient and the  
151 refractive index. This influence depends on the dominant scattering, which is just due to the  
152 dimensional relationship between the grain-size and the incident wave. Thus, coarse particulates are  
153 dominated by surface scattering, which leads to enhanced reststrahlen bands in the emissivity spectra.  
154 Fine particulate (< 65  $\mu\text{m}$ ) materials, on the other hand, are dominated by volume scattering - waves  
155 are refracted into particle interiors and then scattered or refracted back out, which leads to a reduced  
156 contrast in the reststrahlen bands accompanied by the appearance of additional features (Maturilli et al.  
157 2008). Concerning remote sensing applications, understanding this effect is fundamental to distinguish  
158 features due to scattering effects from those due to the composition.

159 Emery et al. (1998) defined the size of the fine loose rocks (regolith) that constitute the surface of  
160 Mercury most likely to range between 30  $\mu\text{m}$  and 100  $\mu\text{m}$ . DiMDCV and HeE0125 samples have been  
161 reduced in a jaw crusher and then sieved under 125  $\mu\text{m}$ , allowing us to work very close to the  
162 presumable size of Mercurian regolith. The selected particle range cannot be totally immune to thermal  
163 gradient effects and volume scattering in the TIR range, which should be remarkable in the finest  
164 particles of the surface of Mercury proposed in the literature (e.g., Maturilli et al. 2006); therefore, it  
165 currently represents the most likely particle range identifiable by space mission on the surface of  
166 Mercury.

167 The produced particulates have been placed into specific stainless steel cups, with a 50 mm internal  
168 diameter, 5 mm thick bottom and 20 mm in height, filling the cups for the first 2 mm, and then heated

169 in oven at 325 K for almost 12 hours, in order to minimize the presence of intragrain water. The cups  
170 were at last placed in a dryer chamber.

### 171 **High-temperature in-situ Thermal Infra-Red (TIR) emissivity spectroscopy**

172 This kind of analysis is possible by means of vibrational spectroscopy, whose basic principle is that  
173 vibrational motions occur in a crystal lattice at particular frequencies, strictly associated to the crystal  
174 structure and elemental composition (Farmer 1974; Christensen et al. 2000). The spectral  
175 measurements have been performed at the Planetary Emissivity Laboratory (Institute of Planetary  
176 Research, Deutsches Zentrum fuer Luft- und Raumfahrt, Berlin) (Maturilli et al. 2008). The instrument  
177 used is a Bruker Vertex 80V, with a liquid nitrogen cooled HgCdTe detector and a KBr beamsplitter.  
178 The spectrometer is coupled to an evacuated planetary simulation chamber, having an automatic  
179 sample transport system (carousel) to maintain the vacuum while changing the samples. The steel of  
180 the sample cups is heated via a copper induction pancake coil, ensuring that the surroundings remain  
181 cold into the chamber. The emissivity measurements can be carried out at different temperatures, which  
182 in this study are 343 K and 723 K, and under 1 mbar of pressure (Helbert et al. 2013), acquiring spectra  
183 between 1 and 16  $\mu\text{m}$  at a resolution of 4  $\text{cm}^{-1}$ . Radiance is collected by an Au-coated parabolic 90°  
184 off-axis mirror and reflected to the spectrometer entrance port. Measurements of a calibration body at  
185 exactly the same sample temperature (T) are taken so that an absolute emissivity of the sample can be  
186 derived by applying the empirical formula  $E=I(T)/BB(T)*E_{BB}$ , where I(T) is the sample radiance  
187 measured at temperature T, BB(T) is the calibration body radiance measured at the same temperature  
188 T, and  $E_{BB}$  is the calibration body emissivity curve.

189 In this work, the two prepared cups have been placed together on the carousel and then heated one at  
190 a time. For each sample, the first emissivity measurement was carried out at 343 K, and the second at  
191 723 K, in order to reach the maximum temperature variation achievable by the PEL set-up within the



192 range suggested for the surface of Mercury (Vasavada et al. 1999; Bauch et al. 2011). The acquired  
193 emissivity spectra are shown in Figure 1.

## 194 **Results and discussion**

### 195 **Chemical composition and single-crystal X-ray diffraction**

196 The chemical compositions of our two samples were determined by EMPA analyses as described in  
197 the experimental section. The relative chemical formulas based on six oxygen atoms are the following:

198 sample DiMDCV:  $\text{Ca}_{0.94}\text{Na}_{0.01}\text{Fe}^{\text{tot}}_{0.08}\text{Mg}_{0.95}\text{Cr}_{0.01}\text{Ti}_{0.01}\text{Si}_{1.92}\text{Al}_{0.08}\text{O}_6$

199 sample HeE0125:  $\text{Ca}_{0.99}\text{Na}_{0.01}\text{Mn}_{0.02}\text{Fe}^{\text{tot}}_{0.82}\text{Mg}_{0.16}\text{Si}_{1.98}\text{Al}_{0.02}\text{O}_6$

200 The main difference between the two samples is related to the Mg-Fe substitution with an Mg# =  
201 0.92 for DiMDCV and 0.17 for HeE0125.

202 Based on the same approach used in several previous works dedicated to the best refinement  
203 protocol for clinopyroxenes (e.g., Domeneghetti et al. 2005; Nestola et al. 2007) we combined EMPA  
204 and the crystal structure refinement results to obtain a reliable cation distribution for samples  
205 investigated here, obtaining the following cation distribution:

206 DiMDCV:  $^{[\text{M}2+\text{M}2']}\text{(Ca}_{0.95}\text{Mg}_{0.05})^{[\text{M}1]}\text{(Mg}_{0.91}\text{Fe}^{2+}_{0.08}\text{Cr}_{0.01})^{[\text{T}]}\text{(Si}_{1.95}\text{Al}_{0.05})\text{O}_6$

207 HeE0125:  $^{[\text{M}2+\text{M}2']}\text{(Ca}_{0.98}\text{Na}_{0.02})^{[\text{M}1]}\text{(Fe}^{2+}_{0.76}\text{Mg}_{0.16}\text{Fe}^{3+}_{0.05}\text{Cr}_{0.01}\text{Mn}_{0.02})^{[\text{T}]}\text{(Si}_{1.95}\text{Al}_{0.05})\text{O}_6$

208 Charge balance for both the formulae is satisfying: the sample DiMDCV showing 11.96 positive  
209 charges and the sample HeE0125 having 11.99 positive charges.

210 Based on Shannon (1976), the average cation radii of the M2-M2' sites are 1.10 Å and 1.12 Å for  
211 DiMDCV and HeE0125, respectively, with a difference of about 1.8%. The tetrahedral sites, instead,  
212 for both samples are identical in terms of chemistry and thus cation radius. As a consequence, the only  
213 difference affecting the structure of these two clinopyroxenes is related to the M1 site where the strong  
214 Mg/Fe cation substitution occurs. In detail, the average cation radius of the M1 site for the DiMDCV

215 sample is 0.72 Å whereas it is 0.76 for the HeE0125 sample (i.e., a difference by about 5.3%). This  
216 difference is responsible for the strongly increased unit-cell volume at room conditions for the  
217 HeE0125 sample i.e., +2.8% (Table 4) and for the increase by about 2.1% of the <M1-O> distance for  
218 this sample. On the contrary, the <M2-O> distances of the two samples only show a difference by  
219 about 0.7%. No differences are evident for the tetrahedral sites of the two samples investigated.

## 220 **Thermal expansion behavior**

221 Several studies have been dedicated to characterize the high-temperature behavior of *C2/c*  
222 clinopyroxenes belonging to the pyroxene quadrilateral ( $\text{CaMgSi}_2\text{O}_6$  -  $\text{CaFeSi}_2\text{O}_6$  -  $\text{Mg}_2\text{Si}_2\text{O}_6$  -  
223  $\text{Fe}_2\text{Si}_2\text{O}_6$ ) during the last forty years. However, most of such studies were mainly focused on the end-  
224 member compositions, i.e., diopside and hedenbergite (Cameron et al. 1973), diopside (Finger and  
225 Ohashi 1976), hedenbergite (Tribaudino et al. 2008). Despite that augite compositions  
226  $(\text{Ca},\text{Mg},\text{Fe})(\text{Mg},\text{Fe})\text{Si}_2\text{O}_6$  are actually among the most common rock forming pyroxenes, only one  
227 intermediate composition *C2/c* pyroxene has been investigated at high temperature, a synthetic  
228  $\text{Ca}_{0.8}\text{Mg}_{1.2}\text{Si}_2\text{O}_6$  (Benna et al. 1990).

229 In this work we measured at 14 different temperatures and up to 773 K the evolution of the unit-cell  
230 volumes of the two intermediate (augitic) pyroxene DiMDCV and HeE0125 samples. Unit-cell volume  
231 as a function of temperature for both samples is shown in Figure 2. The two T-V curves show similar  
232 trends. The increase in volume up to 773 K is 1.38% and 1.37% for DiMDCV and HeE0125,  
233 respectively, with a negligible difference.

234 In Table 6 the volume thermal expansion coefficients were reported for the two samples investigated  
235 in this work compared with other clinopyroxenes compositions. Data shown in Table 6 were obtained  
236 by using the second order polynomial thermal expansion equation proposed by Berman 1988 (Eq. 1):

237

$$(1) V(T) = V_{298} [1 + a_0(T - T_{298}) + a_1(T - T_{298})^2]$$

238 from which (2)  $\partial V/\partial T = \alpha_{V,T} = a_0 + 2a_1(T - T_{298})$ . The equation (2) applied to our dataset provides the  
239 best fitting with a consistent agreement between observed and calculated unit cell volumes, much  
240 smaller than  $0.1 \text{ \AA}^3$  for all the temperature steps from room  $T$  to the maximum temperature reached in  
241 this work (773 K). In order to compare our results with those present in literature we re-fit data in Table  
242 6, using the same Berman (1988) equation: the thermal expansion coefficients are reported in the same  
243 table.

244 Note that previous works (i.e., Cameron et al. 1973) reported the thermal expansion coefficients for  
245 several  $C2/c$  pyroxenes, including the two end-members diopside and hedenbergite, performing linear  
246 least-square fittings of the unit cell volume by using the following equation:

247 
$$(3) \alpha_x (\text{K}^{-1}) = 1/X_{298} \times (X_T - X_{298}) / (T - 298).$$

248 Equation (3) represents what the authors called “mean thermal expansion coefficient”, where the  
249 terms  $X_{298}$  and  $X_T$  are the values of a single parameter at 298 K (room temperature) and at some higher  
250 temperature  $T$ , respectively. The quantity  $\alpha_x$  represents a percentage increase per degree (actually  
251 percent  $\times 10^{-2}$ /degrees) over the temperature range studied, and it is algebraically equivalent to the rate  
252 of increase with temperature divided by the room temperature value of the parameter. Their mean  
253 thermal expansion coefficients calculated as described above are  $2.98 \times 10^{-5}$  and  $3.33 \times 10^{-5} \text{ K}^{-1}$  for  
254 diopside and hedenbergite, respectively. More recently, Tribaudino et al. (2008) reported the thermal  
255 expansion coefficient,  $\alpha_V$ , for a synthetic pure hedenbergite sample. In that work the thermal expansion  
256 coefficient has been determined by fitting the experimental values of the unit-cell volume at the  
257 different temperatures using the following equation:

258 
$$(4) \ln (V/V_{298}) = \alpha (T - T_{298})$$

259 Equation (4) assumes that the thermal expansion coefficient  $\alpha_V$  is independent from  $T$ . The resulting  
260 volume thermal expansion coefficient  $\alpha_V = 2.92(7) \times 10^{-5} \text{ K}^{-1}$  is therefore very close to that of a linear

261 approximation. However, Cámara et al. (2012) clearly demonstrated that higher order polynomial  
262 equations would be more reliable for almost linear thermal expansion behavior. Thus for our two  
263 samples we did not consider linear approximations.

264 Using the data of thermal expansion in Table 6 it is possible to note a strong scatter in terms of Mg#  
265 versus the relative volume thermal expansion coefficient (Fig. 3), which prevents any extrapolation of  
266  $\alpha_V$  as a function of composition.

267 Applying our high-temperature results to the environment present on the surface of Mercury, we  
268 could assume that possible augitic pyroxenes may undergo a temperature variation of 400 K over a  
269 time of 44 Earth-days. Using the equation (1) for our samples we can calculate a volume variation of  
270  $5.11 \text{ \AA}^3$  for both DiMDCV and HeE0125 samples. If we focus on the Mg-rich sample (the most  
271 probable composition present on the surface of Mercury) we can observe that an increase in unit-cell  
272 volume by  $5.11 \text{ \AA}^3$  could be obtained by an increase of 400 K or by a decrease in the Mg# of 0.20 (i.e.,  
273 from 0.92 to 0.72 in case of the DiMDCV sample). This interpolation has been obtained considering  
274 the unit-cell volume of two end-members diopside and hedenbergite of Finger and Ohashi (1976) and  
275 Tribaudino et al. (2008) respectively, which are reported in Table 6. Concerning TIR data acquired  
276 from satellites, this means that neglecting the effect of the temperature on the surface we could face  
277 significant mistakes in terms of composition. In fact, the available data of TIR spectra on  
278 clinopyroxenes are only refer to relatively low temperature conditions (i.e., 353 K, Christensen et al.  
279 2000).

### 280 **High-temperature thermal emissivity**

281 In Figure 1, the main bands of *C2/c* clinopyroxenes belonging to the pyroxene quadrilateral between  
282  $1250$  and  $850 \text{ cm}^{-1}$  are shown for the two samples studied in this work. We assigned an identification  
283 number (1, 2 and 3) to each remarkable band minima in the investigated region, from the highest  
284 wavenumber to the lowest one, considering remarkable those absorptions greater than 5% of the

285 spectral contrast. Bands 1, 2 and 3 of *C2/c* clinopyroxenes have been previously recognized by  
286 Hamilton (2000) as the most intense in this spectral range, and their exact peak position is strongly  
287 depending on the sample iron abundance. However, a deep comparison between our spectra and those  
288 of Hamilton (2000) is prevented by the use of different spectrometers and measuring techniques, and  
289 significantly different sample grain-sizes. Indeed, the PEL liquid nitrogen cooled detector has a greater  
290 sensitivity with respect to the uncooled detector (Ruff et al. 1997) employed in the comparison work,  
291 and finer sample grain-sizes we chose provide lower spectral contrast comparing to those of Hamilton  
292 (2000) (i.e., 710-1000  $\mu\text{m}$ ). In detail, in Figure 1 we show the PEL spectra collected at 343 K (solid  
293 line) and 723 K (dashed line). For both Mg-rich and Fe-rich samples we detected a shift of the bands,  
294 which can be expected as a function of the thermal expansion data discussed in the previous section. A  
295 detailed analysis of the peak positions is shown in Figure 4. Between 1250 and 850  $\text{cm}^{-1}$ , band  
296 positions of both samples moved toward lower wavenumbers with the temperature increase. In detail,  
297 the band 1 of the DiMDCV sample shifts of 14  $\text{cm}^{-1}$  for DiMDCV sample and of 17  $\text{cm}^{-1}$  for HeE0125  
298 sample as the temperature increases by 380 K. Bands 2 and 3 show smaller shifts but still we still  
299 observe 10  $\text{cm}^{-1}$  for the band 2 and 4  $\text{cm}^{-1}$  for the band 3 of the DiMDCV sample, and 8  $\text{cm}^{-1}$  for the  
300 band 2 and 2  $\text{cm}^{-1}$  for the band 3 of the HeE0125 sample.

301 Our data suggest that changes that occur on spectral signatures of Ca-rich pyroxenes as a function of  
302 temperature can be restricted to specific wavelengths, and are closely related to the thermal expansion  
303 volume coefficients. As shown, the thermal expansion volume coefficient for *C2/c* clinopyroxenes with  
304 similar Ca content is not affected by different Mg/Fe ratios (e.g.,  $\alpha_V = 2.72 \times 10^{-5} \text{ K}^{-1}$  for both samples  
305 investigated,  $0.92 < \text{Mg\#} < 0.17$ ) and, as a consequence, the three bands shift by similar amounts  
306 regardless of the Mg#.

307

## Implications

308 The BepiColombo MERTIS spectrometer will have a spectral resolution ranging from 9 to 20  $\text{cm}^{-1}$   
309 across its spectral range of 1400 to 700  $\text{cm}^{-1}$ . Such resolution will allow measuring at least two of the  
310 three band center shifts detected in this work for each composition, in particular those of bands 1 and 2  
311 (14  $\text{cm}^{-1}$  and 10  $\text{cm}^{-1}$  for DiMDCV sample, and 17  $\text{cm}^{-1}$  of band 1 for HeE0125 sample) that are strong  
312 functions of the temperature. Whenever Ca-rich clinopyroxenes will be interpreted in MERTIS spectra,  
313 each shift of band-1 and band-2 centers toward lower wavenumbers with respect to room temperature  
314 band centers can be correctly attributed to the effects of the higher surface temperatures. The  
315 radiometric channel of MERTIS can provide an independent measure of the surface temperature  
316 imaged by the spectroscopic channel.

317 However, bands 1 and 2 of the Mg-rich augite have no discernible wavenumbers differences to  
318 those of Fe-rich augite, neither at room temperature (1105 vs. 1107  $\text{cm}^{-1}$  for band 1, 953 vs. 949  $\text{cm}^{-1}$   
319 for band 2) nor at high temperature (1091 vs. 1090  $\text{cm}^{-1}$  for band 1, 943 vs. 941  $\text{cm}^{-1}$  for band 2). Our  
320 TIR data show that at any temperature a Mg-rich augite can be distinguished from a Fe-rich augite only  
321 based on band 3 (i.e., 918 vs. 903  $\text{cm}^{-1}$  at 343 K, 914 vs. 901  $\text{cm}^{-1}$  at 723 K). Therefore, the distinctive  
322 absorption band of Ca-rich pyroxenes centered around 910  $\text{cm}^{-1}$  provides a measure for the Mg/Fe  
323 content regardless of the surface temperature, even at Mercury peak surface temperatures.

324 Concerning BepiColombo scientific goals, our results suggest that MERTIS spectra will be able to  
325 provide indications of *C2/c* augitic pyroxene magnesium content and will allow a correct interpretation  
326 for the whole range of surface temperatures of Mercury that MERTIS will encounter.

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### 335 **Appendix A. Supplementary Materials**

336 Supplementary data associated with this article can be found in the online version.

### 337 **References cited**

338 Bauch, K., Hiesinger, H., and Helbert, J. (2011) Insolation and resulting surface temperatures of study  
339 regions on Mercury. Abstract 2257 of the 42<sup>nd</sup> Lunar and Planetary Science Conference, The  
340 Woodlands, Texas.

341 Benna, P., Tribaudino, M., Zanini, G., and Bruno, E. (1990) The crystal structure of  $\text{Ca}_{0.8}\text{Mg}_{1.2}\text{Si}_2\text{O}_6$   
342 clinopyroxenes ( $\text{Di}_{80}\text{En}_{20}$ ) at  $T=-130, 25, 400$  and  $700$  °C. *Zeitschrift für Kristallographie -*  
343 *Crystalline Materials*, 192, 183-199.

344 Berman, R.G. (1988) Internally-consistent thermodynamic data for minerals in the system  $\text{Na}_2\text{O}-\text{K}_2\text{O}-$   
345  $\text{CaO}-\text{MgO}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{TiO}_2-\text{H}_2\text{O}-\text{CO}_2$ . *Journal of Petrology*, 29, 445-522.

346 Boffa Ballaran, T., Carpenter, M., Domeneghetti, M.C., and Tazzoli, V. (1998) Structural mechanisms  
347 of solid solution and cation ordering in augite-jadeite pyroxenes: I. A macroscopic perspective.  
348 *American Mineralogist*, 83, 419-433.

349 Cámara, F., Gatta, G.D., Meven, M., and Pasqual, D. (2012) Thermal expansion and high temperature  
350 structure evolution of zoisite by single-crystal x-ray and neutron diffraction. *Physics and Chemistry*  
351 *of Minerals*, 39, 27-45.

352 Cameron, M., Sueno, S., Prewitt, C.T., and Papike, J.J. (1973) High temperature crystal chemistry of  
353 acmite, diopside, hedenbergite, jadeite, spodumene, and ureyite. *American Mineralogist*, 58, 594-

- 354 618.
- 355 Christensen, P.R., Bandfield, J.L., Hamilton, V.E., Howard, D.A., Lane, M.D., Piatek, J.L., Ruff, S.W.,  
356 and Stefanov, W.L. (2000) A thermal emission spectral library of rock-forming minerals. *Journal of*  
357 *Geophysical Research*, 105, 9735-9739.
- 358 Di Battistini, G., Montanini, A., Vernia, L., Bargossi, G.M., and Castorina, F. (1998) Petrology and  
359 geochemistry of ultrapotassic rocks from the Montefiascone Volcanic Complex (central Italy):  
360 magmatic evolution and petrogenesis. *Lithos*, 43, 169-195.
- 361 Domeneghetti, M.C., Zema, M., and Tazzoli, V. (2005) Kinetics of Fe<sup>2+</sup> - Mg order-disorder in *P2<sub>1</sub>/c*  
362 pigeonite. *American Mineralogist*, 90, 1816-1823.
- 363 Emery, J.P., Sprague, A.L., Witteborn, F.C., Colwell, J.E., Kozłowski, R.W.H., and Wooden, D.H.  
364 (1998) Mercury: Thermal modeling and Mid-infrared (5-12 μm) observations. *Icarus*, 136, 104-123.
- 365 Farmer, V.C. (1974) *The infrared spectra of minerals*. The Mineralogical Society, Monograph 4,  
366 London.
- 367 Finger, L.W. and Ohashi, Y. (1976) The thermal expansion of diopside to 800 °C and a refinement of  
368 the crystal structure at 700 °C. *American Mineralogist*, 61, 303-310.
- 369 Hamilton, V.E. (2000) Thermal infrared emission spectroscopy of the pyroxene mineral series. *Journal*  
370 *of Geophysical Research*, 105, 9701-9716.
- 371 Helbert, J. and Maturilli, A. (2009) The emissivity of a fine-grained labradorite sample at typical  
372 Mercury dayside temperatures. *Earth and Planetary Science Letters*, 285, 347-354.
- 373 Helbert, J., Nestola, F., Ferrari, S., Maturilli, A., Massironi, M., Redhammer, G.J., Capria, M.T., Carli,  
374 C., Capaccioni, F., and Bruno, M. (2013) Olivine thermal emissivity under extreme temperature  
375 ranges: Implication for Mercury surface. *Earth and Planetary Science Letters*, 371-372, 252-257.



- 376 Hiesinger, H., Helbert, J., and the MERTIS Co-I Team (2010) The Mercury Radiometer and Thermal  
377 Infrared Spectrometer (MERTIS) for the BepiColombo mission. *Planetary and Space Science*, 58,  
378 144-165.
- 379 Le Bail, A., Duroy, H., and Fourquet, J.L. (1988) Ab-initio structure determination of  $\text{LiSbWO}_6$  by X  
380 Ray powder diffraction. *Material Research Bulletin*, 23, 447-452.
- 381 Maturilli, A., Helbert, J., Witzke, A., and Moroz, L. (2006) Emissivity measurements of analogue  
382 materials for the interpretation of data from PFS on Mars Express and MERTIS on Bepi-Colombo.  
383 *Planetary and Space Science*, 54, 1057-1064.
- 384 Maturilli, A., Helbert, J., and Moroz, L. (2008) The Berlin emissivity database (BED). *Planetary and*  
385 *Space Science*, 56, 420-425.
- 386 Nestola, F., Tribaudino, M., Boffa Ballaran, T., Liebske, C., and Bruno, M. (2007) The crystal structure  
387 of pyroxenes along the jadeite-hedenbergite and jadeite-aegirine joins. *American Mineralogist*, 92,  
388 1492-1501.
- 389 Nestola, F., Boffa Ballaran, T., Liebske, C., Thompson, R., and Downs, R.T. (2008) The effect of the  
390 hedenbergitic substitution on the compressibility of jadeite. *American Mineralogist*, 93, 1005-1013.
- 391 Oberti, R. and Caporuscio, F.A. (1991) Crystal chemistry of clinopyroxenes from mantle eclogites: a  
392 study of the key role of the M2 site population by means of crystal-structure refinement. *American*  
393 *Mineralogist*, 76, 1141-1152.
- 394 Pouchou, J. L. and Pichoir, F. (1991) Quantitative analysis of homogeneous or stratified microvolumes  
395 applying the model "PAP". In K. Heinrich and D. Newbury, Eds., *Electron Probe Quantitation*, p.  
396 31-76, Plenum Press, New-York.
- 397 Rietveld, H.M. (1967) Line profiles of neutron powder-diffraction peaks for structure refinement. *Acta*  
398 *Crystallographica*, 22, 151-152.

- 399 Rossi, G., Oberti, R., Dal Negro, A., Molin, G.M., and Meilini, M. (1987) Residual electron density at  
400 the M2 site in *C2/c* clinopyroxenes: relationships with bulk chemistry and sub-solidus evolution.  
401 *Physics and Chemistry of Minerals*, 14, 514-520.
- 402 Ruff, S.W., Christensen, P.R., Barbera, P.W., and Anderson, D.L. (1997) Quantitative thermal  
403 emission spectroscopy of minerals: A laboratory technique for measurement and calibration.  
404 *Journal of Geophysical Research*, 102, 899-913.
- 405 Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in  
406 halides and chalcogenides. *Acta Crystallographica*, A32, 751-767.
- 407 Sheldrick, G.M. (1997) SHELX, programs for Crystal Structure Analysis (Release 97-2). Institut für  
408 Anorganische Chemie der Universität, Göttingen, Germany.
- 409 Solomon, S.C., McNutt, R.L., Gold, R.E., Acuña, M.H., Baker, D.N., Boynton, W.V., Chapman, C.R.,  
410 Cheng, A.F., Gloeckler, G., Head, J.W., Krimigis, S. M., McClintock, W.E., Murchie, S.L., Peale,  
411 S.J., Phillips, R.J., Robinson, M.S., Slavin, J.A., Smith, D.E., Strom, R.G., Trombka, J.I., and Zuber,  
412 M.T. (2001) The MESSENGER mission to Mercury: scientific objectives and implementation.  
413 *Planetary and Space Science*, 49, 1445-1465.
- 414 Sprague, A.L., Emery, J.P., Donaldson, K.L., Russell, R.W., Lynch, D.K., and Mazuk, A.L. (2002)  
415 Mercury: Mid-infrared (3-13.5  $\mu\text{m}$ ) observations show heterogeneous composition, presence of  
416 intermediate and basic soil types, and pyroxene. *Meteoritics and Planetary Science*, 37, 1255-1268.
- 417 Sprague, A.L., Warell, J., Cremonese, G., Langevin, Y., Helbert, J., Wurz, P., Veselovsky, I., Orsini S.,  
418 and Milillo, A. (2007) Mercury's surface composition and character as measured by ground-based  
419 observations, *Space Science Reviews*, 132, 399-431.
- 420 Sprague, A.L., Donaldson Hanna, K.L., Kozlowski, R.W.H., Helbert, J., Maturilli, A., Warell, J.B., and  
421 Hora, J.L. (2009) Spectral emissivity measurements of Mercury's surface indicate Mg- and Ca-rich

422 mineralogy, K-spar, Na-rich plagioclase, rutile, with possible perovskite, and garnet. Planetary and  
423 Space Science, 57, 364–383.

424 Strom, R.G. and Sprague, A.L., Eds. (2003) Exploring Mercury: The Iron Planet, Springer/Praxis, New  
425 York.

426 Tribaudino, M., Nestola, F., Cámara, F., and Domeneghetti, M.C. (2002) The high-temperature  $P2_1/c$ -  
427  $C2/c$  phase transition in Fe-free pyroxene ( $\text{Ca}_{0.15}\text{Mg}_{1.85}\text{Si}_2\text{O}_6$ ): Structural and thermodynamic  
428 behavior. American Mineralogist, 87, 648-657.

429 Tribaudino, M., Nestola, F., Bruno, M., Boffa Ballaran, T., and Liebske, C. (2008) Thermal expansion  
430 along the  $\text{NaAlSi}_2\text{O}_6$ - $\text{NaFe}^{3+}\text{Si}_2\text{O}_6$  and  $\text{NaAlSi}_2\text{O}_6$ - $\text{CaFe}^{2+}\text{Si}_2\text{O}_6$ . Physics and Chemistry of  
431 Minerals, 35, 241-248.

432 Vasavada, A.R., Paige, D.A., and Wood, S.E. (1999) Near surface temperatures on Mercury and the  
433 Moon and the stability of polar ice deposits. Icarus, 141, 179-193.

434 Warell, J. and Davidsson, B. (2010) A Hapke model implementation for compositional analysis of  
435 VNIR spectra of Mercury. Icarus 209, 164-178.

436 Warell, J.B., Sprague, A.L., Kozłowski, R.W.H., Rothery, D.A., Lewis, N., Helbert, J., and Cloutis, E.  
437 (2010) Constraints on Mercury's surface composition from MESSENGER and ground-based  
438 spectroscopy. Icarus, 209, 138-163.

439 Wilson, A.J.C., Ed. (1995) International Tables for Crystallography Vol. C, Dordrecht: Kluwer  
440 Academic Publishers.

#### 441 **Table and Figure captions**

442 Table 1. Electron microprobe analysis (oxide wt%) and formula in atoms per formula unit based on six  
443 oxygen atoms for the crystals studied in this work.

444 Table 2. Unit cell parameters determined by X-ray powder diffraction using the Le Bail method (Le  
445 Bail et al. 1988) for the crystals studied in this work.

446 Table 3. Unit cell parameters and structural refinement details for the single crystals studied in this  
447 work.

448 Table 4. Bond-lengths (Å) for the crystals studied in this work.

449 Table 5. Unit-cell volumes as a function of temperature for samples DiMDCV and HeE0125.

450 Table 6. Thermal expansion coefficients for different *C2/c* pyroxenes obtained using the Berman  
451 (1988) equation. See the text for  $\alpha_V$  and  $a_1$ .

452 Figure 1. Emissivity spectra collected in vacuum between 1250  $\text{cm}^{-1}$  and 850  $\text{cm}^{-1}$  at 343 K and 723 K:  
453 diopside (upper) sample DiMDCV; hedenbergite (lower) sample HeE0125. The significant absorption  
454 bands of this wavenumbers range are labeled with numbers 1, 2 and 3.

455 Figure 2. Unit-cell volume as a function of temperature for samples DiMDCV and HeE0125.

456 Figure 3. Volume thermal expansion coefficient as a function of Mg# number for different *C2/c*  
457 clinopyroxenes.

458 Figure 4. Band shifts as a function of temperature (full stars at 343 K and empty stars at 723 K for the  
459 DiMDCV (Mg-rich cpx) sample and the HeE0125 (Fe-rich cpx) sample between 1250 and 850  $\text{cm}^{-1}$ .

460 Supplementary Figure 1. Powder X-ray diffraction of DiMDCV sample (upper) and HeE0125 sample  
461 (lower). Reference peaks of diopside (card 98-001-7094 of ICSD database) are shown in blue color,  
462 reference peaks of magnesian hedenbergite (card 01-087-0702 of ICSD database) are shown in red

463 color. Concerning diffractogram of HeE0125 sample, letters A and G indicate the amphibole's and the  
464 gypsum's peaks, respectively.

**Revision 1**

**Table 1**

<b>Sample</b>	<b>DiMDCV</b>	<b>HeE0125</b>
<b>Oxide wt. %</b>		
<b>Na<sub>2</sub>O</b>	0.11	0.16
<b>MgO</b>	17.46	2.70
<b>Al<sub>2</sub>O<sub>3</sub></b>	1.89	0.37
<b>SiO<sub>2</sub></b>	52.60	48.33
<b>CaO</b>	24.07	22.60
<b>TiO<sub>2</sub></b>	0.26	0.01
<b>Cr<sub>2</sub>O<sub>3</sub></b>	0.31	0.01
<b>MnO</b>	0.07	0.70
<b>FeO<sub>tot</sub></b>	2.68	24.12
<b>Total</b>	99.45	99.00
<b>Formula</b>		
<b>Ca</b>	0.94	0.99
<b>Na</b>	0.01	0.01
<b>Mn</b>	-	0.02
<b>Fe</b>	0.08	0.92
<b>Mg</b>	0.95	0.16
<b>Ti</b>	0.01	-
<b>Cr</b>	0.01	-
<b>Al</b>	0.08	0.02
<b>Si</b>	1.92	1.98
<b>Total</b>	4.00	4.00

**Table 2**

<b>Unit-cell</b>	<b>DiMDCV</b>	<b>HeE0125</b>
<i>a</i> (Å)	9.7443(1)	9.8268(2)
<i>b</i> (Å)	8.9147(1)	9.0045(1)
<i>c</i> (Å)	5.2591(1)	5.2527(1)
$\beta$ (°)	106.004(10)	105.023(1)
<i>V</i> (Å <sup>3</sup> )	439.135	448.899

**Table 3**

<b>Crystal data</b>	<b>DiMDCV</b>	<b>HeE0125</b>
Crystal system	Monoclinic	Monoclinic
Unit-cell parameters		
<i>a</i>	9.751(2) Å	9.838(1) Å
<i>b</i>	8.905(2) Å	9.009(1) Å
<i>c</i>	5.264(1) Å	5.2585(6) Å
$\beta$	106.08(2)°	105.00(1)°
Unit-cell volume	439.18 Å <sup>3</sup>	450.15 Å <sup>3</sup>
Space group	<i>C2/c</i>	<i>C2/c</i>
<i>Z</i>	4	4
<b>Data collection</b>		
Instrumentation	Four-circle STOE-STADI IV	
Temperature (K)	298(1)	
Radiation, wavelength (Å)	MoK $\alpha$ , 0.71073	
$2\theta_{\max}$ (°)	85.90	85.96
<i>h, k, l</i> ranges	-8 +18, -13 +15, -8 +8	-14 +15, -13 +16, -10 +2
Omega scan width (°), exposure time (s)	1, 20	1, 20
Unique reflections ( <i>R</i> <sub>int</sub> )	1129 (0.030)	1136 (0.068)
Unique reflections <i>F</i> > 4 $\sigma$ ( <i>F</i> )	710	722
<b>Structure refinement</b>		
Structure solution and Refinement software	SHELX	
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	
Data/restraints/parameters	1129/17/83	1136/17/83
<i>R</i> <sub>1</sub> [ <i>F</i> > 4 $\sigma$ ( <i>F</i> )]	0.0224	0.0508
<i>R</i> <sub>1</sub> all	0.0541	0.0778
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.062	0.999
Weighting scheme	$\frac{\exp(2.55 \times s^2)}{\sigma^2(F_o^2)}$ where <i>s</i> = sin( $\theta$ )/ $\lambda$	$\frac{\exp(2.55 \times s^2)}{\sigma^2(F_o^2)}$ where <i>s</i> = sin( $\theta$ )/ $\lambda$

$R_{\text{int}} = \frac{\sum |F_o^2 - F_c^2(\text{mean})|}{\sum F_o^2}$   
 $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$   
 $\text{Goof} = \{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$ , where *n* = number of reflections, *p* = number of refined parameters



**Table 4**

	<b>DiMDCV</b>	<b>HeE0125</b>
<b>Si-O2</b>	1.590(1)	1.585(1)
<b>Si-O1</b>	1.609(1)	1.608(1)
<b>Si-O3</b>	1.668(1)	1.670(1)
<b>Si-O3</b>	1.688(1)	1.690(1)
<b>&lt;Si-O&gt;</b>	1.639	1.638
<b>M1-O2</b>	2.046(1) ×2	2.078(1) ×2
<b>M1-O1</b>	2.056(1)×2	2.123(1) ×2
<b>M1-O1</b>	2.124(1)×2	2.155 (1) ×2
<b>&lt;M1-O&gt;</b>	2.075	2.119
<b>M2-O2</b>	2.334(1) ×2	2.348(1) ×2
<b>M2-O1</b>	2.364(1) ×2	2.359(1) ×2
<b>M2-O3</b>	2.560(1) ×2	2.611(1) ×2
<b>M2-O3</b>	2.718(1) ×2	2.730(1) ×2
<b>&lt;M2-O3&gt;</b>	2.494	2.512

**Table 5**

Temperature (K)	$V(\text{\AA}^3)$	$V(\text{\AA}^3)$
	<b>DiMDCV</b>	<b>HeE0125</b>
298	437.27(7)	449.74(8)
323	437.55(8)	450.05(6)
323 <sup>a</sup>	437.58(8)	450.00(7)
373	438.22(7)	450.60(8)
423	438.92(8)	451.20(7)
473	439.40(7)	451.85(7)
498 <sup>a</sup>	439.69(8)	452.32(8)
523	440.06(9)	452.61(8)
573	440.68(10)	453.23(9)
623	441.31(8)	453.84(9)
673	442.06(9)	454.58(8)
698 <sup>a</sup>	442.47(9)	454.92(8)
723	442.77(8)	455.36(7)
773	443.39(9)	455.98(8)

Note: the uncertainty on the temperature is estimated to be 1 K. <sup>a</sup>Data measured during the cooling.

**Table 6**

<b>Sample</b>	<b>Unit-cell <math>V</math> (<math>\text{\AA}^3</math>)</b>	<b><math>\alpha_V</math> (<math>\times 10^{-5} \text{ K}^{-1}</math>)</b>	<b><math>a_1</math> (<math>\times 10^{-9}</math>)</b>	<b>References</b>
DiMDCV	437.33(3)	2.72(8)	5.0(1.9)	This work
HeE0125	449.75(3)	2.72(7)	5.0(1.6)	This work
Diopside	438.78(37)	3.36(41)	-0.4(4)	Cameron et al. (1973)
Diopside	439.09(17)	2.77(2)	8.3(3)	Finger and Ohashi (1976)
Hedenbergite	450.69(23)	2.35(24)	5.1(2.3)	Cameron et al. (1973)
Hedenbergite	450.94(15)	3.3(2)	-4.8(2.6)	Tribaudino et al. (2008)









