



Publication Year	2018
Acceptance in OA	2020-12-22T16:33:04Z
Title	Northwest Africa 6232: Visible-near infrared reflectance spectra variability of an olivine diogenite
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Publisher's version (DOI)	10.1111/maps.13056
Handle	http://hdl.handle.net/20.500.12386/29118
Journal	METEORITICS & PLANETARY SCIENCE
Volume	53

1 Title: **NorthWest Africa 6232: Visible-near infrared reflectance spectra variability of an**
2 **olivine diogenite**

3
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9
10 **Abstract**

11 Visible and near-infrared (VNIR) reflectance is an important spectroscopic technique to identify
12 minerals, and their associations, on planetary bodies surface. Howardite, eucrite and diogenite
13 (HED) are igneous-like meteorites with spectral properties suitable for 4Vesta and Vestoids.

14 Pyroxene and olivine are the two major mafic minerals present in HED which can be identified
15 with VNIR reflectance measurements. Understanding the compositional variability of those
16 phases and their mixtures, can be useful to better understand the evolution of 4Vesta crust. To
17 reach this aim, laboratory activity on different diogenite or eucrite are important to explore their
18 spectral variability and so our capability to retrieve compositional information.

19 Here we report the VNIR reflectance spectral analysis of an harzburgitic olivine diogenite,
20 NorthWest Africa 6232 (probably paired with NorthWest Africa 5480), containing variable
21 amount of olivine as small grains or aggregates. We evidence how the olivine-diogenite spectra
22 parameters (e.g. position) are in accordance between slab and powders. The olivine-diogenite
23 band position shifts from synthetic orthopyroxene in accordance with the presence of olivine and
24 chromite. In particular, the presence of a large olivine clast permits to evidence a linear variation
25 of the band position from synthetic orthopyroxene and olivine, but underestimating the presence
26 of olivine in the olivine-diogenite spot.

27
28 **1. Introduction**

29 Diogenites (D) are achondrites meteorites, like orthopyroxenite and harzburgite, generally
30 associated to a basaltic magmatism linked to the earliest stage of asteroidal melting on a
31 differentiated parent body. They are petrogenetically correlated to eucrite (E), which can be
32 cumulitic or basaltic, and to howardite (H), that are brecciated samples composed by
33 diogenite and eucrite fragments. This suite of meteorites, named HEDs, is considered to be
34 associated to a basaltic magma system on asteroid 4Vesta, which is considered their parent
35 body (e.g. Feierberg and Drake 1980, McSween et al. 2013).

36 Diogenites are often characterized by orthopyroxene (opx), relatively Mg-rich (En₈₄₋₆₆),
37 associated with olivine (ol), spinel (e.g. chromite), sulfides and metals, and minor
38 plagioclase, clinopyroxene, silica phase or rare phosphates (see summary in Mittlefeldt et al
39 1998, Grady et al. 2014). Depending on the modal composition, diogenites can be
40 distinguished in dunitic ($\geq 90\%$ ol), harzburgitic (ol + opx) and orthopyroxenitic ($\geq 90\%$ opx),
41 respectively (Beck and McSween 2010).

42 The presence of ol has been considered an important marker for the 4Vesta evolution (Pieters
43 et al. 2005). Ol has been along searched within diogenitic terrains, but none of these regions
44 (e.g. Rheasilvia) seems to have spectral evidence of this mineral phases (Ammannito et al.
45 2013a). Conversely it is discussed the presence of Ol in relative high abundance in northern
46 regions, like Bellicia and Aruntia craters (Ammannito et al. 2013b) associated with

47 howardite-like lithologies enriched in eucrite (Zambon et al., 2014; 2016). Other regions with
48 lower ol amount have been discussed by Ruesch et al. (2014), Palomba et al. (2015), Poulet
49 et al. (2015) and Zambon et al. (2016). Several of these ol-bearing regions seems to be
50 correlated with diogenitic material (Zambon et al. 2016).

51 The correlation between HED and 4Vesta is strongly suggested by VNIR reflectance
52 spectroscopy. Several powdered portions of HED have been measured, as a bulk, showing
53 reflectance spectra dominated by two crystal field absorptions around 1 and 2 μm (e.g.
54 Duffard et al., 2005; Burbine et al., 2009; Beck and McSween, 2010). These absorptions are
55 associated to pyroxene (px) (Burns 1993), the spectrally dominating phase in both diogenites
56 and eucrites.

57 The compositional variation from diogenites to eucrites, due to both mineral phases and
58 mineral chemistry, can be outlined also in VNIR reflectance. In fact, the crystal field
59 absorptions due to transitional elements (i.e. Fe, Ti) are active in the VNIR, and so diagnostic
60 to recognize silicates present on igneous material.

61 A shift from of the absorption positions low to high wavelength, for both 1 and 2 μm bands
62 (band I and II, respectively) have been highlighted (e.g. Mittlefehldt et al 1998). This trend
63 can be mainly identified with the increasing of iron and calcium in eucrite-px with respect to
64 diogenite-px (Burbine et al. 2009, Beck et al. 2011). Anyway the presence of significant
65 amount of other phases, e.g. plagioclase in eucrite and, in particular, of ol in diogenite (but
66 also in some eucrites) could influence the reflectance spectra.

67 Recently, the presence of ol on 4Vesta for the first time indicated in Ammannito et al.
68 (2013b) stimulated the discussion about the capability to retrieve the presence of ol in a
69 mafic mixed material.

70 The major evidence attributed to the olivine was a clear asymmetry present at longer
71 wavelengths with respect to the band center around 1 μm (see Ammannito et al 2013b),
72 similar to that singled out by generic ol-px mixtures. No ol absorption has been evidenced
73 (Ammannito et al. 2013b; Poulet et al. 2015) from VIR data (onboard Dawn, e.g. De Sanctis
74 et al. 2010), but studying spectral parameters (Ruesch et al. 2014; Thangjam et al 2014;
75 Palomba et al. 2015) and modeling the spectra by radiative transfer (Poulet et al. 2015) or
76 linear modeling (Zambon et al. 2016) variable abundance of ol has been retrieved on
77 different site.

78 Anyway most of these methods have been tested considering mixtures of ol and px, where
79 often ol was more forsteritic (Fo~86-90%) and px more enstatitic than in diogenite. Few
80 work considered powders of HED with ol enriched samples or referred to them (e.g. Li and
81 Milliken 2015; Beck et al. 2013).

82 Beck et al. (2013) working with a systematic ol (Fo90) and px (En76) powder mixtures
83 highlighted a linear trend between the 1 and 2 μm Band Area Ratio (B.A.R) and the px%.
84 Such trend was already evidenced by Cloutis et al (1986) for a Fo89-En86 set of ol-px
85 mixtures, grinded at different sizes. Cloutis et al (1986) discussed also how this trend was not
86 size dependent. Beck et al. (2013), studying some harzburgitic diogenite meteorites,
87 demonstrated that the B.A.R was not so different from a orthopyroxentic diogenite, and
88 compatible with relative low ol amount (<30%), although they emphasized the heterogenous
89 distribution of ol within the same diogenite sample.

90 Moreover, a correlation between the band I position and the B.A.R parameter has been
91 evidenced by Cloutis et al. (1986) and Gaffey et al. (1993), even if varying the mineral
92 composition, mineral assemblages and grain size this trend can vary (Pieters et al. 2005).

93 Recently, Li and Milliken (2015) working with a radiative transfer model show a good fit
94 some fine powder spectra of ol-bearing diogenite. The authors worked with retrieved optical
95 constant from spectra of compositional reasonable endmembers with fine size. They reported
96 a good accordance (within 5%) of olivine amount.
97 So studying opportune material as analogue mixtures or HED meteorites in details can
98 contribute to better understand the ol spectral influence on px absorptions with suitable
99 mineral chemistry; and consequently to investigate in higher detail the amount of olivine on
100 Vesta terrains.
101 Spectrally investigating meteorites samples as powders implies that few sample can be
102 studied. Moreover, powders homogenize the distribution of the mineral phases present in the
103 sample (which can be highly variable) losing information about sample heterogeneity (at
104 least at the observing scale). In addition, looking for HED analogues, the difference in
105 composition with respect to terrestrial rocks avoids or complicates to obtain systematic
106 mineral mixtures with suitable Fo/Fa and En, Fs, Wo. Moreover the presence of plagioclase
107 (in particular for eucrite) and other minor, but effective, constituent (like chromite, sulfides
108 and metal) are not considered.
109 A different opportunity to enlarged the number of samples but in particular the spectral
110 variability due to all the rock constituent on HED is to analyze spectral properties of
111 representative slices (slab), well characterized from a petrographic and mineral chemistry
112 point of view.
113 Slab spectra suffer the effects of petrographic characteristics and effect due to the optical
114 coupling which can strongly influence the slope and absorption spectral contrast. However,
115 bulk rock spectra can contribute to the spectral description of a natural rock suite, adding
116 spectral information needed for the interpretation of remote sensing or in situ high-spatial
117 resolution hyperspectral data.
118 Few works in the literature discuss the spectral variation between slab and powders from the
119 same rocks, Harloff and Arnold (2000) and Pompilio et al (2007), evidence how spectral
120 contrast and slope can vary, even if the dominating spectral features relate to crystal field are
121 always evident. Carli et al. (2014) highlighted how in co-genetic mafic/pl-bearing rock
122 powders and slabs permit to define the same lithological units from VNIR spectra. Moreover,
123 different works emphasize how coarsening the particle or grain size do not strongly effect the
124 band center of minerals (e.g. Craig et al., 2008; Serventi et al. 2013;2016). This appears true
125 also for large sizes up to slabs (e.g. Carli et al., 2014; 2015) even if it has been evidenced
126 how coarsening the sizes the most abundant minerals became more effective even if less
127 absorbing (e.g. pl versus px, see Serventi et al., 2013, Carli et al. 2014). Conversely, the band
128 depth varies with the size (e.g. Craig et al 2007; 2008) even if systematic trend can be always
129 recognized for the different sizes with respect the mineral abundances or volumetric iron
130 (Carli et al. 2014).
131 In this manuscript we described the spectral properties of an harzburgitic olivine-diogenite,
132 NorthWest Africa 6232 (NWA6232) classified by A. Irving and S. Kuehner (see, Garvie
133 2012) and probably paired with NorthWest Africa 5480 (NWA 5480, comment submitted by
134 A. Irving on Meteoritical Bulletin Database). We considered spectra of both powders and
135 two slabs, for which we acquired several spectra with particular attention to few spots with ol
136 or px dominated region. Besides, due to the presence of a coarse ol clast we discuss the
137 implication for the retrieving of compositional information from harzburgitic diogenite
138 considering spectral parameters unaffected by the size.

139 **2. Methods and Analytical approach**

140 **2.1. Sample Preparation and characterization**

141 Two slices of NWA6232 harzburgitic olivine diogenite, belonging to the Natural History
142 Museum of the Università degli Studi di Firenze (cat. n. RI-3225), have been analyzed.

143 Both slices (here labelled NWA6232_A and NWA6232_B) have been considered as slab
144 samples for reflectance investigation. Additionally, from the second slice a thin section
145 was obtained for petrographic and minerochemical analyses. Moreover, from a
146 representative portion of the diogenite NWA6232_B we produced powders at different
147 grain size.

148 Asperities left by the saw were not present on measured cut surface samples, so we do
149 not treated slabs further and, therefore, the slab do not show a mirror-like surface.

150 To preserve the original meteorite composition in powdered samples, the rocks were first
151 ground to prepare the <1.00 mm coarse grain size class. The coarse powders were then
152 quartered and each fraction was ground under smaller grain size classes, <0.050, <0.075,
153 <0.100, <0.125, <0.150, <0.180, <0.200, <0.250 mm.

154 Mineral assemblages and rock textures were first observed, on thin section, through a
155 Zeiss Axioplan II optical microscope. Then, scanning electron microscope images and
156 elemental maps were acquired, on both the first slab and the thin section, at the MEMA
157 laboratories of the University of Firenze by means of a Zeiss EVO MA15 equipped with
158 OXFORD INCA 250 microanalysis. In order to get the relative modal abundance of the
159 main mineral, the elemental maps (Si, Al, Mg, Fe, Ca, Mn, Cr, S) were processed with
160 the specific INCA software module. Finally the minero-chemical analyses of the main
161 phases (namely olivine and pyroxene) were performed, at the microanalysis laboratory of
162 the IGG-CNR by means of Electron Microprobe JEOL JXA-8600 equipped with four
163 Wavelength Dispersive Spectrometers. The modal and mineral chemistry analyses are
164 reported in Tables 1, 2.

165 **2.2. Sample Reflectance Measurements**

166 Bidirectional spectra of slabs and powders, at different grain sizes, were acquired using a
167 Fieldspec Pro ® spectrophotometer mounted on a goniometer at S.LAB. laboratory, at
168 “Institute for Space Astrophysics and Planetology”, IAPS-INAF, Rome. The spectra were
169 acquired with a spectral resolution of ~3 nm in the VIS and ~10–12 nm in the NIR, a
170 spectral resolution of 1 nm, with $i = 30^\circ$ and $e = 0^\circ$. The source used was a quartz
171 tungsten halogen (QTH) lamp and the spot illuminated has a diameter of ca. 6 mm. The
172 standard reference calibration was performed with a Spectralon optical standard
173 (registered trademark of Labsphere, Inc.) both for slab and powder measurements.

174 Therefore each powder grain size class (<0.050, <0.075, <0.100, <0.125, <0.150, <0.180,
175 <0.200, <0.250 mm) contains a range of grain dimensions beneath the upper limit to
176 maintain the compositional homogeneity. The slab samples are considered as analogs of
177 centimeter-size natural rock grains and compact multimineral aggregates in the regolith
178 (Carli and Sgavetti 2011). Studying both powders and slabs spectra evidences how varies
179 the influence of the optical coupling with respect to the mineral absorptions. This aspect
180 is very important (see also Carli and Sgavetti 2011) to understand spectral information of
181 multi-crystal grains, which can be present in a regolith. By the way we can investigate the
182 spectral heterogeneity of samples at the scale of the illuminated spot.

183 Moreover, the first slice (NWA6232_A) contains an olivinic clast with dimension closer
184 to 6mm, so we acquired spectra along a cross line starting from the adjacent diogenite

185 portion and finishing into this clast. This set of measurements were then used to
186 extrapolate areal abundance of olivine with respect the diogenite sample from a spectral
187 parameters analysis.
188

189 2.3. Correlation between spectral parameters and composition

190 Absorptions related to the crystal field of HEDs have been deeply investigated, and they
191 are in general due to the presence of pyroxenes. Different parameters, in particular, band
192 center position (B.C.), band depth (B.D.) and the B.A.R are frequently applied to
193 correlate spectral properties with the different lithologies, i.e. eucrite, diogenite and
194 howardite. The same parameters can be also calculated in presence of different amount of
195 olivine and can give also indication of the different amount of pyroxene and olivine.
196 Knowing the mineral chemistry and the petrography of our samples allows to better
197 explain the properties of acquired spectra from both powder and slab. Furthermore, it can
198 permit a comparison of the olivine diogenite with the spectral properties of the rock
199 forming minerals with the appropriate composition analyzed in the literature (e.g.
200 pyroxenes from Klima et al. 2007; olivine from King and Ridley, 1987, Sunshine and
201 Pieters, 1998, Isaacson et al. 2014).

202 Therefore, in section 3.3 we correlate the B.C. to the mineral chemistry of px and ol, and
203 the two B.C.s each other. B.D.s and shoulder position (maximum between Band I and
204 Band II) have also take into account to evidence the spectral variability. In addition, we
205 correlate also the spectral parameters of a cross in-out to an olivine clast evidencing the
206 spectral changes respect to the ol amount into the illuminated spot. This has been done
207 considering both shift of B.C.I and B.A.R, and their variability with ol% into observed
208 spot. We will refer as ol-cross to the spectra acquired along this cross.

209 The ol clast % in the illuminated spot has been calculated considering the clast as circular
210 (as the spot), so we calculated the integrated area between the two circle, moving on the
211 clast into the light spot along the diameter.

212 All the spectral parameters have been calculated after continuum removed. The
213 continuum is considered as a wavelength's function line segments that join the
214 reflectance maxima in the spectrum (Clark and Roush 1984). The reflectance maxima are
215 chosen for each case depending on the single spectrum.
216

217 3. Results

218 3.1. NWA6232, petrography and mineralogy

219 NWA6232 has been classified by A. Irving and S. Kuehner (Garvie, 2012) as a diogenite
220 but few characteristics have been reported by these authors. It is probably paired with
221 NWA 5480, a pristine harzburgitic diogenite characterized by an highly deformed texture
222 explained by plastic deformation that occurred after crystallization at mantle pressures
223 (Tkalcic et al., 2013 ; Peslier et al., 2015) or as an impact-melt breccia from a target
224 composed of olivine and pyroxene-rich lithologies (Yamaguchi et al., 2015). Here we
225 have described macroscopically the two slices, then a thin section of a representative
226 portion of one slice (NWA6232_B) has been investigated in detail under optical
227 microscope.

228 The thin section shows an heterogeneous overall texture characterized by a cumulitic
229 intergrowth of olivine and orthopyroxene dominated zones (Fig. 1). Olivine ranges in
230 size from tens of μm to mm: smaller grains are poikilitically included in orthopyroxene,
231 while the largest grains are aggregates of smaller grains with variable orientation, which
232 often display rounded edges and are most anhedral (Fig. s1, supplementary online).
233 Orthopyroxene grains are typically subhedral and range from hundreds of μm to mm in
234 size. They are riddled with poikilitic olivine and do not show any alignment. Chromite
235 occurs as subhedral grains, 100 μm wide and with resorbed margins or as blebs < 10 μm
236 wide. Troilite grains, often <10 μm in size, are scattered throughout the thin section. The
237 hand size slice (NWA6232_B) shows also a centimetric grey area characterized by a
238 concentration of pyroxene, not present in the thin section. The other slice of the sample,
239 NWA6232_A has been observed and analyzed by means of SEM. The cut surface
240 displays an heterogenous texture similar to the one observed in the thin section,
241 although a cm-sized clast of olivine is clearly distinguishable. BSE-SEM images and
242 compositional maps (Fig. s2 and s3) performed on the slice allowed to determine the
243 following average modal abundances of the phases of the diogenite: orthopyroxene 72%,
244 olivine 26%, troilite 1%, chromite 1% and rare Fe,Ni alloy (see Table 1). The olivine
245 clast appears homogeneous, although several chromite grains (circa 3%) are scattered
246 throughout the clast (Fig. s4).

247
248

3.2. VNIR reflectance data of NWA6232

249 Twenty spectra have been, here, acquired for each slab sample to cover the entire surface,
250 a cross of thirteen spectra have been also acquired from outside to inside the ol-clast (see
251 table 3). In addition we acquired spectra for each powder grain size.
252 Reflectance spectra (Fig. 2b,c,d,e) show clearly the two absorption bands diagnostic of
253 pyroxene for all the powder's spectra and for slab's spectra, with the exception for
254 spectra around the above described olivine clast in NWA6232_A (Fig. 2a, and green
255 dashed circle in Fig. 1a). A small portion of NWA6232_B shows two deeper absorption,
256 this area seems to be characterized by higher concentration of pyroxene. In this
257 manuscript, for clarity, we named ol-diogenite the collected spectra scattered overall the
258 sample, ol-clast the spectra acquired on the 6 mm clast, ol-rich the spectra where
259 diogenite reflectance properties are influenced by ol, px-rich the spectrum that is
260 characterized by the strongest band I and II absorption.
261 Spectra dominated by pyroxene absorptions show also two weak absorption at 0.505 and
262 0.547 μm , associated with spin-forbidden Fe^{2+} absorption (e.g. Burns 1993; Klima et al.
263 2007). A third weak absorption around 0.428 μm is evident only for the higher
264 reflectance slab spectra and powders spectra (Fig. 3). Spectra dominated by olivine
265 absorption show weak bands at 0.458 and at 0.496 μm , which can be correlated with
266 spin-forbidden in olivine, and a third absorption around 0.529 μm (Burns et al. 1993).
267 The absorption around 0.5 μm is of particular interest because ol and px spin-forbidden
268 are almost overlapped around those wavelengths. In fact, powder spectra show an
269 asymmetric absorption, as well as ol-diogenite slab spectra, whereas ol-rich spots show a
270 doublet minima (e.g. dark green spectra in Fig. 3b). Px-rich and Ol-clast spectra instead
271 show the two different expected absorptions. Moreover, the ol-clast spectra have a wide
272 and relatively weak absorption towards 2 μm which is not expected in ol spectra, but it

273 can be due to a small contribute of px, in particular, chromite (Burns et al. 1993; Cloutis
274 et al. 2014).

275 Here, we focus on the two stronger absorptions at 1 and 2 μm to discuss the spectral
276 variability with respect to the two dominating mineral phases. To reach this aim, aside
277 from the spectra acquired on powdered sample and on two slabs (Fig. 3), we
278 systematically measured spectra from a cross out to in the ol clast, described above,
279 which have a size closer to the illuminated spot (Fig. 4).

280

281 3.3. Compositional variation by VNIR analysis

282 In this section, we report the result from spectral parameters and we compare it with the
283 mineral chemistry, modal composition and phases distribution.

284 The band center for powders and the two slices (without ol dominating spots) have been
285 plotted as averaged values in Fig. 5a,b with respect to the ferrosilite content (Fs%) in
286 pyroxene. The position of Band I (B.C.I) shows a very reduced shift between powder and
287 the two slices with a small standard deviation. Differently, powder Band II (B.C.II)
288 spectra shows a shift to slight higher wavelengths compare to the two slices' spectra,
289 which show higher standard deviation, even though within one sigma.

290 We have also considered the B.C.I and II of three synthetic pyroxenes from Klima et al.
291 (2007) with mineral chemistry close to those present in NWA6232. The samples are
292 named 002, 003, 027, in their paper, with Fs% varying from 20-30% (Klima et al. 2007).
293 The px's B.C.I are 10 nm lower than NWA6232's B.C.I. This can be correlated with the
294 presence of widespread crystals of olivine spread out in the diogenite. B.C.II of px shows
295 position closer to those of the averages of slices spectra, whereas also in this case
296 powder's spectra show a slightly shift towards higher wavelength.

297 The diagram B.C.I vs B.C.II permit to describe the spectral variability of pyroxene from
298 low-Ca to high-Ca (e.g. Cloutis and Gaffey 1991), and it has been used to plot HED
299 spectra and differentiate between diogenite and eucrite (e.g. Moskovitz et al., 2010). The
300 compositional variation from high-Mg and low-Ca px in diogenite towards Fe- and Ca-
301 enriched px in eucrite reflects an almost linear variation of B.C.I and B.C.II.

302 In Fig. 5c we plotted the averages B.C.I vs B.C.II for two slices, the powders and the
303 Klima's px, for all we report the error bars representative of the standard deviation. It's
304 clear that each spectrum, despite a range of variations, in particular for B.C.II is
305 compatible with low calcium pyroxene. Nevertheless, B.C.I is slightly shift to longer
306 wavelength and powder spectra show both centers at slightly higher wavelengths. If we
307 compare these positions with HED spectra from literature (see dark and light grey box for
308 diogenite and eucrite, after Moskovitz et al., 2010), we can see a good correspondence
309 between band centers and diogenite field for slabs' spectra, except for ol-dominated
310 spectra. The powders B.C.s are still in diogenite field but shifted towards eucrite field.

311 In Fig. 5c, we plot also the B.C.I position for olivine with closer fayalite (Fa%) value
312 (from King and Ridley 1987; Sunshine and Pieters, 1998; Isaacson et al., 2014). The
313 green lines represent the band center position (solid, Sunshine and Pieters, 1998; dot,
314 Isaacson et al., 2014) calculated by Modified Gaussian Model, as Gaussian minimum
315 position (Sunshine et al 1990), and dashed line is the band center calculated as the
316 minimum after continuum removed by King and Ridley (1987). The ol-rich and -clast
317 spectra show B.C. close to the expected value for an 29 Fa%. These spectra show also a
318 second band around 2 μm , but shifted to higher values with respect to other diogenite

319 spectra, in this olivine dominated spot (ol-clast) the second band could probably be
320 assigned to the presence of chromite (e.g. Cloutis et al. 2004) as reveal by SEM images.
321 Considering the composition of px in NWA6232 and the spectra of pxs with analogue
322 composition from Klima et al. (2007), we can assigned the shoulder at longer wavelength
323 for the Band II between 2.45 and 2.50 μm (e.g. continuum removed spectra in Fig. 4c).
324 For this reason, we considered, for powder and slab spectra, the maximum for the
325 continuum between this wavelength range, varying for each spectrum, depending from
326 the spectral shape and slope. So we can be confident that the shift in band center, after
327 continuum removed, should be attribute to local variation in mineral assemblages (Fig.
328 4c).

329 Fig. 6 shows the variation of 1) Band Depth (B.D.), 2) the Shoulder Position (B.S.) vs.
330 B.C. for Band I and Band II and the 3) Band Area ratio (B.A.R.) for all the measured
331 spectra of NWA6232_A and NWA6232_B.

332 Band I depth varies from 0.2 to 0.5 (Fig. 6a), except for the px-dominated area (B.D.I
333 ~ 0.7 , as well as, B.D.II; Fig. 6b), without any correlation with band position. B.D.I and II
334 of powder spectra are higher than those for slab spectra, but their depth are smaller with
335 respect px-rich spot. Spectra dominated by ol-clast have a B.D.I around 0.5-0.6, and for
336 the ol-cross the band depth seems to be correlated with the center position.

337 B.D.II seems to have a weak correlation with the position, decreasing the depth the
338 absorption moves from lower wavelength, where band II is dominated by pyroxene, to
339 longer wavelength, where probably increase ol and opaque phases (e.g. chromite), as
340 suggested by ol-cross data. In fact, we can see the presence of two cluster indicating px-
341 dominated spectra (ol clast $< 10\%$, see table 3) and ol-influenced spectra.

342 B.S. is not a direct indicator of absorption, but in mixing material can give useful
343 indication as demonstrated also by Serventi et al. (2013).

344 B.S. slightly moves from 1.3 to 1.5 μm (Fig. 6c) with a weak linear correlation with
345 respect to px dominated B.C.I, whereas ol-influenced spectra move to high values (1.7
346 μm). Ol-cross data evidence as moving from diogenite to the ol clast there is a quick shift
347 to longer wavelength of the B.S. up to 1.7 μm . This wavelength is reached for 006-007
348 spectra, which show a 39-48% of ol-clast (see table 3). B.S. vs. B.C.II (Fig. 6d),
349 differently, show essentially two populations, with high values for ol clast $> 50\%$ (B.C. II
350 $> 2.0 \mu\text{m}$) or region with B.C.II at ca. 1.9 and B.S. at ca. 1.4 μm .

351 In Fig. 6e the B.C.I is plotted vs. the B.A.R parameter for the spectra acquired in the
352 cross-in to olivine clast, superimposed to the results from Gaffey et al. (1993) modified
353 after Pieters et al. (2005). Gaffey et al. (1993) trend was obtained by Cloutis et al. (1986)
354 for powders' mixture (at three grain sizes 38-53, 63-90, 90-125 μm) of olivine (Fs89) and
355 pyroxene (En86) with different mineral chemistry respect to NWA6232. Cloutis et al
356 (1986) evidence how no-size effect where present. However, considering a modified
357 B.A.R, and considering different compositions of px and ol, the variation of spectral
358 parameters from the general trend was evident for some of the few investigated cases.

359 The presence of an ol-clast with a dimension closer to the illuminated spot can be used
360 for a more quantitatively evaluation of the olivine influence on reflectance spectra when
361 present with variable abundance into diogenite. Fig.6e shows a similar general behavior
362 with respect to the one evidenced by Gaffey et al. (1993), with differences which could
363 be related to the different size and in particular to mineral association.

364 Moreover, we measured the B.A.R also for powder spectra of NWA6232 and their values
365 are in good agreement with respect to the values for the ol-diogenite spectra of the ol-
366 cross (spot 000, 001 and 002, table 3).

367 Then, we have calculated the ol clast abundance as the ol area % presents in our spot (see
368 section 2.3) to evaluate the variation of those spectral parameters which can be attributed
369 to compositional information, such as B.C.I and B.A.R. We did this for all the thirteen ol-
370 cross spectra measured at different steps (see table 3).

371 In Fig. 7a,b B.C.I and B.A.R. are plotted vs. the area of olivine present in the spot. It
372 results clear that the variation in B.C.I, already evidenced in Fig. 6, is correlated with the
373 variation of the area of olivine clast into the spot, with an almost linear trend ($R^2=0.981$).
374 The B.A.R., considered by Cloutis et al. (1986) to be a possibly indicator to discriminate
375 $px/(px+ol)$, shows, in Fig. 7b, a strong reduction from values >1 to 0.2 for only 30% of
376 ol-clast (000 to 004 spectra). Increasing the ol abundance B.A.R shift towards 0.1 for
377 100% of olivine clast in the spot.

378 From Fig. 5 we have seen that the diogenite B.C.I is shifted to values higher than
379 pyroxene composition, and this could be in accordance with the widespread presence of
380 olivine grains (from tens of micron to mm) in NWA6232 (see section 3.1 and Fig. s1). To
381 investigate the influence of olivine present into the diogenite we have considered the opx
382 B.C.I from Klima et al. (2007). Then we have on one side hypothesized a variable
383 abundance of olivine also in ol-diogenite spectra (Fig. 7c), and on the other side we have
384 considered the averaged abundance (25%) we obtained from SEM images. Considering a
385 possible B.C.I linear trend from synthetic pyroxene to ol-clast we have seen that the best
386 fit required an ol abundance for NWA6232 ol-diogenite spectra of 8% ($R^2=0.988$), with a
387 variation from 5 to 11% of ol with $R^2>0.985$. Olivine abundance retrieved from SEM
388 elementary maps image analysis indicates a higher value of olivine, which is variable
389 within the different images but always upper than 20%. So the B.C.I shift of circa 10 nm
390 from opx to ol-diogenite spectra (where circa 25% of olivine is present) then the position
391 shift with an almost linear trend to 1.068 μm when the olivine clast is completely into the
392 spot (011-012 have the almost same B.C.I position).

393 This is reasonable considering that opx crystal field absorption is strongly than co-genetic
394 ol (e.g. Serventi and Carli, 2017) and opx absorption at circa 1 μm insists within the lower
395 wavelength portion within the ol absorption.

397 **4. Discussion and implications for olivine detection on parental bodies**

398 NWA 6232 is an olivine diogenite, characterized by an average abundance of ol close to
399 25%, present in size from tens of μm to mm, with smaller grains that are poikilitically
400 included in opx and largest ones that are aggregates of several crystals. In one of the two
401 samples a clast of ol crystal aggregates has dimension of circa 6 mm in diameter.

402 So, considering a spot of the same size we can evidence how vary the spectral properties
403 and in particular some spectral parameters with the olivine abundance. The ol-opx
404 variability has been already discussed in some cases (e.g. Cloutis et al., 1986; Beck et al.,
405 2013), working with mineral mixtures, in the past, but often with ol and opx composition
406 different from those expected for HED. Few cases investigate powder of ol-bearing
407 diogenites but with only low range of relative ol abundance, even if this variability can be
408 high on the same sample in abundance as well as crystal size.

409 Therefore, to investigate a slab becomes an important tool for up-grading the spectral
410 variability of our meteorites samples, working with the opportune mineral composition,
411 and mineral association as expected for their parental bodies. Moreover, due to the
412 expected sample heterogeneity, we can evidence systematic variation on spectral
413 properties and particularly in some spectral parameters (e.g. band position), which are no
414 or few affected by the crystal or grain sizes. In our case, it plays an important role the
415 presence of two regions, ol-dominated and px-dominated. In particular we took care
416 about the ol-dominated region where a clast with dimension similar to our observing spot
417 is present.

418 In general we have observed that spectra of ol-diogenite, for both slab or powders, are
419 characterized by the two absorption bands indicative of pyroxene (Fig. 2c,e). The spectral
420 features vary slightly in the wavelength region between 1.0 and 1.5 μm in accordance
421 with a variable amount of olivine into the different spots (Fig. 2b). Only ol dominated
422 spectra show a 1 μm absorption clearly indicative of this mineral (Fig. 2a), even if the ol-
423 cross spectra show how a systematic variation is present varying the areal abundance of
424 olivine in the spectra (Fig. 4b). Spin forbidden absorption seems to be present (already
425 evidenced for HED, or px and ol, in the literature, e.g. Burns 1993; Hiroi et al. 2001,
426 Klima et al., 2007; Isaacson et al., 2014). They are different in position for ol and px (Fig.
427 3a,b), but one absorption is centered at circa 0.5 μm for both ol and px, and it seems like
428 it varies with the ol/px ratio.

429 The primary absorptions are around 1 and 2 μm , their position permit to superimpose
430 NWA6232 into the Diogenite field (Fig. 5c), with some difference between slabs and
431 powders, with the last that show centers at slightly longer wavelength. The average value
432 for the slab spectra is closer to the synthetic pyroxene B.C. with Fs 25%, even if B.C.I is
433 always shifted of $\sim +10\text{nm}$. Ol-clast spectra still show a residual BII which could be
434 related to few amount of pyroxene into the spot, but because it is shifted towards longer
435 wavelength, we can suppose that chromite plays a role (Fig. 5c and see Fig. s4).

436 We have seen that the Band I can be considered a useful indicator for discussing the ol/px
437 relative abundance, as already indicated in the literature (e.g. Cloutis et al., 1986). Being
438 the depth influenced also by the grain size, we highlighted that band center is an
439 important parameter for this goal. In fact, comparing the B.C. with B.A.R (as in Pieters et
440 al., 2005), we can see that our spectra closely follow the general trend, considering the
441 difference in ol-px mineral chemistry and size effect. Ol dominated spot have also
442 chromite grains within ol-clast, and ol-diogenite spectra are characterize by an averaged
443 25% of olivine widespread in the sample, so it is not a single opx endmember. Moreover,
444 comparing the shift of the B.C.I varying the areal abundance of the ol clast, into the
445 measured spot, we can see a linear trend (Fig. 7a); whereas the B.A.R reaches values very
446 closed to the 100% of ol (Fig. 7b), already for 30% of ol-clast. Then, considering the opx
447 endmember position (Fig. 7c) we can see that the ol abundance expected for the ol-
448 diogenite spectra, considering the best linear fit, should be 8%, with a range 5-11% with
449 very high R^2 .

450 Anyway, analyzing our samples with SEM images (X-ray elementary maps) we have
451 calculated a range of widespread ol grain into NWA 6232 between 20-35%. This
452 indicates that increasing ol into our spot, the opx absorption strongly dominate the
453 spectral parameter until 25-30% of olivine then band center start to follow a linear shift
454 increasing the ol.

455 B.A.R, as well as the position of the B.S. between Band I and II, seem to be useful
456 indicator of ol presence since they shift to values closer to those for the ol-clast spectra
457 for ~ 50% of olivine (30% of ol clast, see fig. 6c and 7b).

458 These results can be considered a first test to evidence the spectral variability of an
459 olivine diogenite as well as the ol/opx ratio with composition compatible for the
460 diogenite. Therefore, them seem to evidence how persisting into slab analysis of HED, as
461 well as other meteorites, e.g. associated to asteroids V and S, could contribute to better
462 define spectral indicator for studying the composition of those bodies. In fact, often we
463 referee to terrestrial analogues which have different mineral chemistry, as well as mineral
464 assemblages, with respect to the composition of those meteorites and so their parental
465 bodies. Even if those analogues can be suitable guideline they cannot take into account
466 the spectral variability of the investigated samples and bodies.

467 Because to implement suitable systematic mixture of mineral powders with similar
468 composition to those present for example into the HED is not an easy task to pursue, so
469 to take advantage of the heterogeneity of natural sample could be an useful tool to
470 enlarge the knowledge about spectral trends for these materials.

471

472 5. Conclusions

473 NWA6232 is an olivine diogenite characterized by an average 25% of olivine, with an
474 heterogeneous texture. Olivine is present in euhedral and subhedral crystals from μm to
475 mm in scale, often poikilitically included in orthopyroxene crystals. Clast of mm sizes of
476 olivine and orthopyroxene were also present. This heterogeneity have been considered to
477 investigate the VNIR reflectance variability from the slab surfaces of two different slices.
478 In general, the reflectance of the ol-diogenite is characterized by the two absorptions
479 around 1 and 2 μm due to the presence of the orthopyroxene. The orthopyroxene rich
480 area spot and the powder samples prepared from a representative portion of one slice
481 show absorption on the same positions but with different intensity. The band center
482 positions are close to those of synthetic pyroxene with similar composition from Klima et
483 al. (2007), even if shifted at higher wavelengths, in accordance with the presence of
484 widespread olivine in NWA6232.

485 Then we used the presence of a rounded ol-clast of circa 6mm size in diameter to
486 evaluate also the spectral variability varying the ol abundance within the measured spot.
487 The spectra acquired in the ol-clast show clearly the wide absorption band at $\sim 1 \mu\text{m}$
488 typical of olivine, moreover a residual absorption at $\sim 2 \mu\text{m}$ is still present due to the
489 presence of chromites crystal within the ol-clast. The position of the olivine absorption is
490 in accordance with those from the literature with similar composition (e.g. Isaacson et al.
491 2014).

492 Spectral parameters like B.A.R and B.S. showed that a shift towards the values
493 attributable to the ol-clast is already reached for 30% of the clast into the spot.

494 Conversely, we have seen that the B.C.I position is in accordance with the trend present
495 in Pieters et al. (2005) evidenced for ol-px mineral mixtures, once compare with B.A.R
496 values. In addition, B.C.I position shows a linear trend from the synthetic orthopyroxene
497 to olivine clast with respect to the olivine areal %, suggesting a 8% of olivine present into
498 the ol-diogenite. This value is underestimated from the 20-35% range measured by SEM
499 image analysis for different images acquired from the samples. This results indicate how

500 pyroxenes absorption dominates the spectra until ~30% of the olivine abundance, for En-
501 Wo and Fa composition suitable for diogenites.
502 Those results evidence the importance to work on slab spectra. The spectral variability of
503 HED slices should be considered to enlarge the number of studied samples and to use the
504 heterogeneity of those meteorites to investigate much more in details spectral parameters
505 trends and property, considering minerals composition suitable to the different diogenites
506 and eucrites.
507

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7. Figure Captions

647 Figure 1 – It shows the two slab samples a) NWA6232_A and b) NWA6232_B. Powders
648 and a thin section have been produced from NWA6232_B representative of the ol
649 diogenite. In a) is shown the ol clast with a green circle whereas in b) an arrow indicates a
650 portion of opx enriched portion. C) Polarizing optical microscope image of thin section:
651 grey crystals are orthopyroxene; pink to blue crystals are olivine; the outlined area is
652 poikilitic olivine in an orthopyroxene crystal; transmitted light, crossed polars.

653 Figure 2 – Selected spectra of slabs, a-d), and powders at variable grain size are plotted in
654 e). a) ol-clast spectra (NWA6232_A), b) spectra characterized by ol-richer portions, c) ol-
655 diogenite spectra, d) spectra related to the opx rich portion of NWA6232_B. e) from
656 bottom to top <50, <75, <100, <125, <150, <180, <200, <250 μm .

657 Figure 3 – Spin-forbidden in the visible spectral range. a) selected spectra from different
658 spot, green spectra are related to higher abundance of olivine, violet spectra indicate ol-
659 diogenite or px-rich portion. b) continuum removed spectra to highlight the differences,
660 powder continuum removed spectra are reported as comparison.

661 Figure 4 – ol-cross section and spectra. In a) is showed the portion from which we moved
662 out to in the ol-clast. In b) all spectra are showed (see table 3) and in c) continuum
663 removed spectra of the first, last and one intermediate spectra.

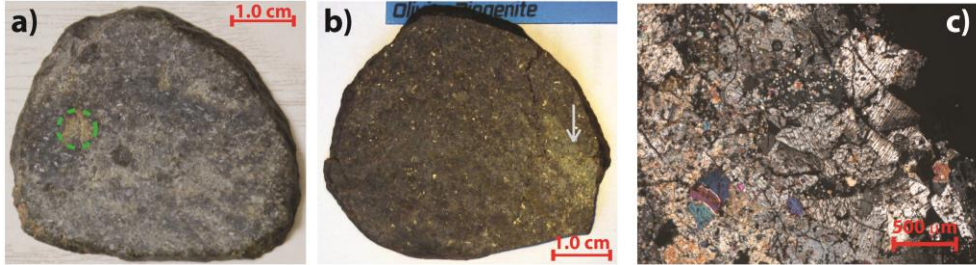
664 Figure 5 – a,b) averaged Band Centers are related to the Fs% of diogenite opx, with the
665 band center of the closest synthetic opx from Klima et al. (2007) for a comparison. c)
666 Band I center is plotted versus Band II center, average values for the two slabs, powders
667 and synthetic opx are present as well as outliers ol-rich and ol-clast position. Green line
668 represent the position of B.C.I for ol with similar composition, dashed: King and Ridley
669 et al. 1987, solid: Sunshine and Pieters 1998, and dot: Isaacson et al., 2014. Error band
670 are the standard deviation of the average.

671 Figure 6 – Band depth I, II (a,b) and Band Shoulder (c,d) are plotted vs the Band Center
672 I, II. Band Center I of ol-cross spectra has been plotted vs. the B.A.R, moreover we have
673 plotted the averaged values for powders, which is very close to the ol-diogenite (000,
674 001) spectra. See text for more details.

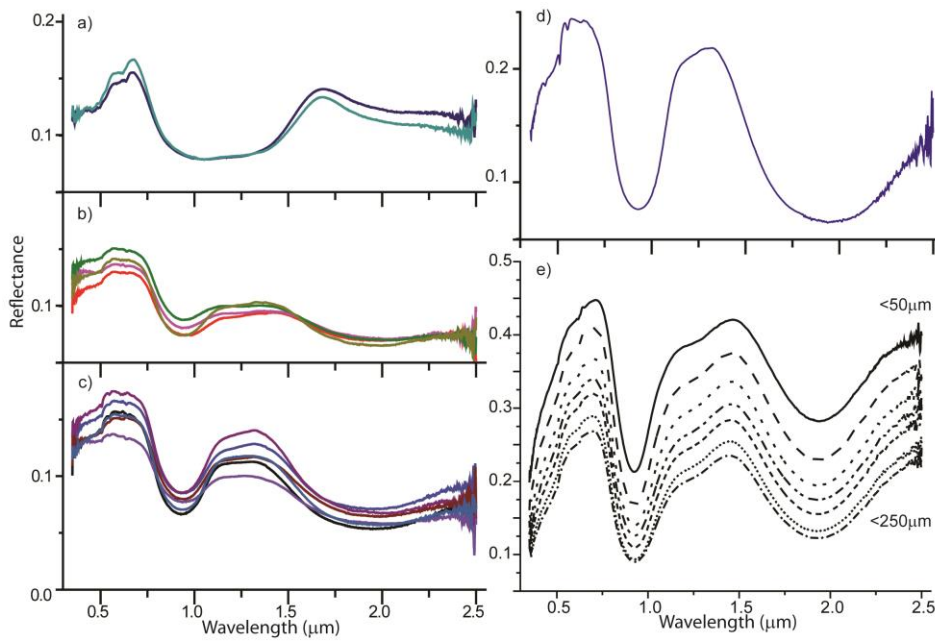
675 Figure 7 – Ol-clast abundance within the spot has been compare with the Band Center I
676 (a) and B.A.R (b). Band Center shows a linear relationship. c) Band I center has been
677 plotted in function of the ol abundance, taking into account the synthetic px has free-ol
678 endmember. The trend see in a), related to green square shift towards higher abundance
679 of ol (green diamonds, in fact spot 000 is not anymore 0% of ol). Considering that the
680 best linear fit should be obtain for an 8% of widespread ol into the diogenite, but SEM

681 images analysis reveal an higher value, ~25%. We plot also the averaged values for
682 powders (orange cross) and ol-diogenite slabs (blu triangle). See text for more details.
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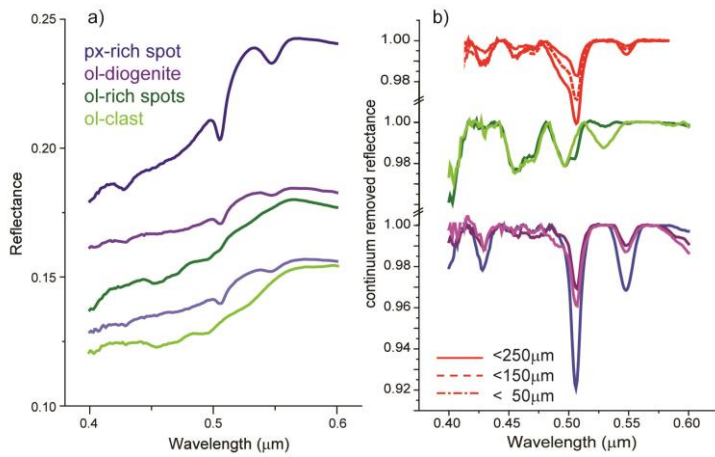
Figure:



685
686 **Figure 1**
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689 **Figure 2**
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692 **Figure 3**

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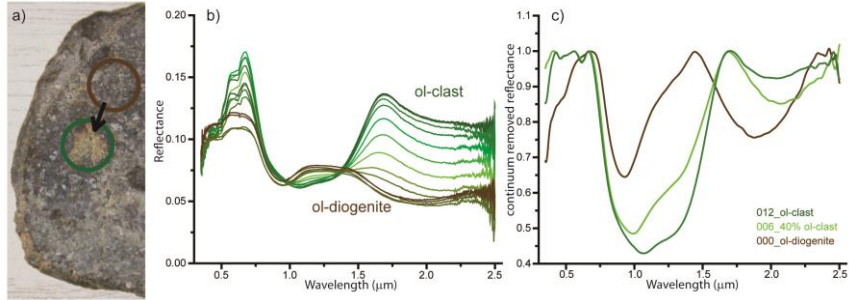
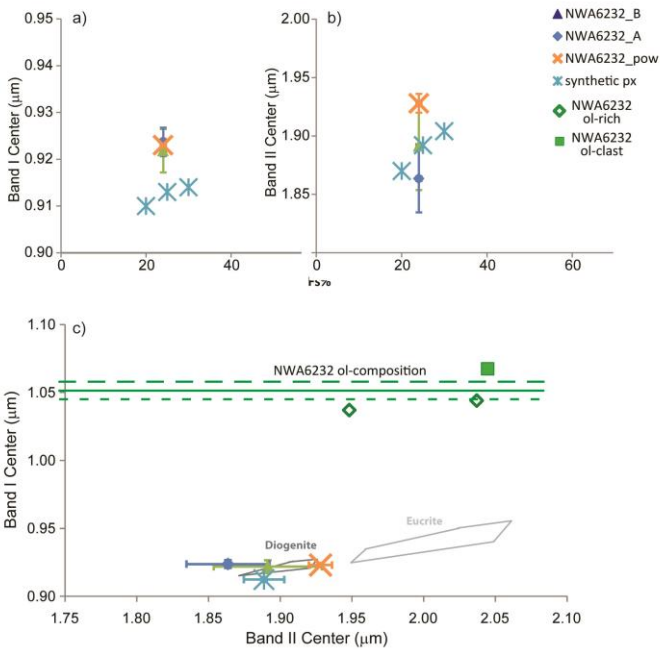
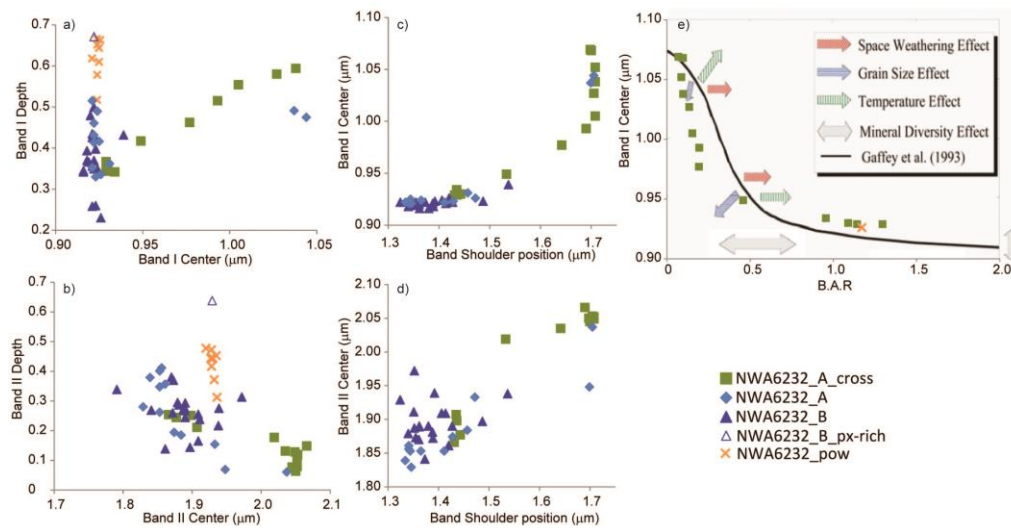


Figure 4



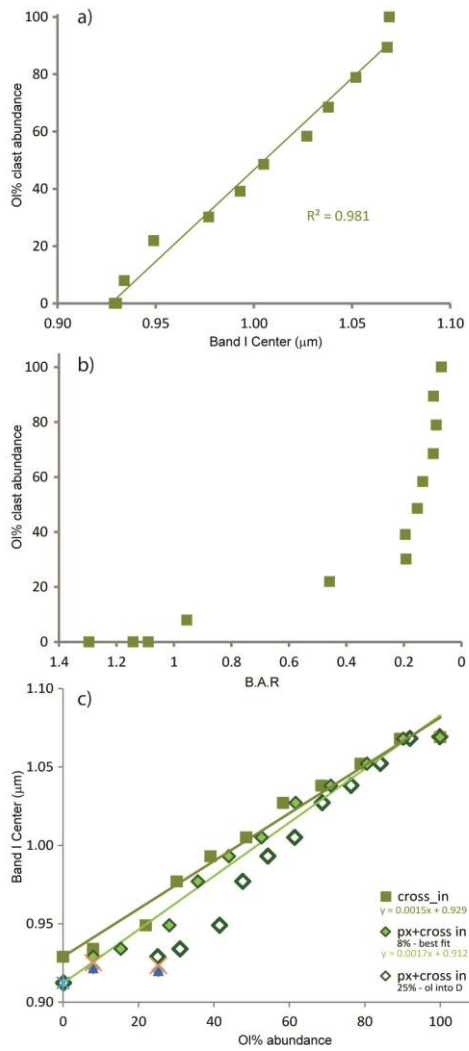
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Figure 5



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Figure 6



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703 **Figure 7**

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707 **Tables:**

Table 1. relative abundance retrieved from SEM image analysis. See text for more details.

	modal distribution ol-diogenite						modal distribution ol-clast				
	mean	st.dev	spot 1	spot 2	spot 3	spot 4	mean	st.dev	spot 5	spot 3	spot 4
Olivine	25.7	6.1	34.5	22.4	25.0	20.8	96.5	1.9	98.6	94.8	96.0
Pyroxene	71.8	5.6	63.7	72.6	74.3	76.5	rare				
Chromite	0.9	0.3	1.1	1.1	0.5	0.8	2.9	1.7	0.8	3.8	3.9
Troilite	1.2	0.9	0.7	1.9	0.3	2.0	0.7	0.7	0.5	1.4	0.1
Fe,Ni alloy	rare						rare				

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Table 2. Mineral chemistry for the major phase as retrieved from microprobe analysis

	pyroxene			olivine	
	mean	st.dev.		mean	st.dev.
SiO2	54.7	0.6	SiO2	37.4	0.5
TiO2	0.1	0.1	TiO2	0.0	0.1
Al2O3	0.4	0.0	Al2O3	0.0	0.0
Cr2O3	0.5	0.2	Cr2O3	0.1	0.1
FeO	15.7	0.5	FeO	26.2	0.8
Mno	0.5	0.1	Mno	0.6	0.1
MgO	27.1	0.3	MgO	35.8	0.5
CaO	1.0	0.1	CaO	0.1	0.1
Na2O	0.0	0.0	Na2O	0.0	0.1
K2O	0.0	0.1			
Total	100.1	0.7	Total	100.2	0.8
Wo	2.0	0.2	Fo%	70.5	0.9
En	73.8	0.8	Fa%	29.5	0.9
Fs	24.1	0.6			
N° Mg	75.4	0.7	N° Mg	70.9	0.9

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Table 3. Steps from out to in the clast of olivine in NWA6232_A, and relative % of olivine clast into the spot

spot	Ol cross	
	step (mm)	Area ol clast%
000	8.0	0.0
001	7.0	0.0
002	6.0	0.0
003	5.0	7.9
004	4.0	21.9
005	3.5	30.2
006	3.0	39.1
007	2.5	48.5
008	2.0	58.3
009	1.5	68.5
010	1.0	78.9
011	0.5	89.4
012	0.0	100.0

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