### 1 Revision 1

- 2 VNIR spectral variability of the igneous stratified Stillwater Complex: a tool to map lunar
- 3 highlands
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### 10 Abstract

11 Lunar Highlands are plagioclase-rich terrains produced by crystal floating in a Magma Ocean

system. Lunar samples revealed the presence of anorthositic (plagioclase >90%) samples from the

13 Highlands, associated to more mafic rocks. Recently, remote sensing data permits to map those

14 terrains with high spatial and spectral resolution allowing to detect plagioclase and mafic crystal

15 field (C.F.) absorptions.

16 In this paper we have studied bidirectional spectral characteristics in the visible near-infrared

17 (VNIR) of rocks from the Stillwater Complex, a cumulitic igneous stratified complex, with

18 composition varying from mafic to sialic (e.g. pyroxenite, anorthosite). We investigated both slabs

19 and powders of these rocks to give indication of the spectral variability of rocks analogues of lunar

20 crust, from a mineralogical point of view. Samples have been spectrally separated in four main

21 groups considering the different C.F. absorption association, reflectance and spectral shape for both

slab and powder spectra. More spectral details can be obtained from the analysis of powder spectra

than from the slab spectra.

The composition of rocks can be addressed by studying spectral parameters, as the position and the intensity of the absorption (e.g. band center and band depth). The analysis of our plagioclase-

| 26 | pyroxene bearing samples indicates that mafic composition can be clearly obtained for samples         |
|----|---|
| 27 | characterized by one pyroxene phase, even for few amounts of pyroxene, from powder spectra. On        |
| 28 | the other hands, slab spectra show clear pyroxene absorptions only for rocks with mafic abundance     |
| 29 | at least $> 20\%$ . The intensity of the mafic absorptions of these samples shows a linear trend with |
| 30 | respect to the abundance of pyroxenes (orthopyroxene + clinopyroxene, for samples with ferrosilite    |
| 31 | amount < ca.25%). Considering all pyroxene bearing samples the band depth of slab spectra are         |
| 32 | linearly related to the volumetric distribution of ferrous iron in pyroxenes.                         |
| 33 |   |
| 34 | Key words: LUNAR AND PLANETARY STUDIES: terrestrial anlogues - OPTICAL                                |

- 35 SPECTROSCOPY: VNIR reflectance spectroscopy SURFACE STUDIES: highlands particulate
- 36 and rocks analogues
- 37

### 38 Introduction

39 Lunar highlands have been long considered the product of global Magma Ocean (MO) which

40 produced a wide variety of mafic lithologies in a heterogeneous mantle and a ferroan anorthosite

41 primary crust via the crystallization and floatation of plagioclase (e.g. Smith et al., 1970; Wood et

42 al., 1970; Warren, 1985). It is generally accepted that this body was largely molten during its early

43 evolution (e.g. Warren, 1985), and that the lunar magma ocean (LMO) crystallized from the cooling

44 of the outer portion to form the early crust and the upper mantle (e.g. Warren, 1985).

45 In particular, lunar surface lithology analyses have been often successful in placing the different

46 rocks in the context of the LMO paradigm (Elardo et al., 2012) even if inconsistencies have been

- 47 advanced by several authors (e.g. Walker, 1983; Longhi and Ashwal, 1985), pointing out e.g. that
- 48 several models for the evolution of LMO did not take into account the fact that lunar monomineralic
- 49 rocks are rare (Snyder et al., 1992). Snyder et al. (1992) modeled the crystallization for the LMO

| 50 | suggesting an early transition from olivine, orthopyroxene, to calcic pyroxene (ceasing olivine                 |
|----|---|
| 51 | crystallization). After 65-70% of the LMO crystallized, plagioclase came on the liquidus and began              |
| 52 | to crystallize. This sequence is supposed to be formed from bottom to up the layering of the upper              |
| 53 | mantle and the crust of the Moon. Similar mineral assemblages sequences are recognized in the                   |
| 54 | layered igneous intrusions on the Earth (e.g. Stillwater complex, Duluth Gabbro Complex,                        |
| 55 | Skaaergard intrusion, Snyder et al., 1992). Warren (1985) also evidenced as crystallization of the              |
| 56 | LMO can produce a wide variety of mafic lithologies in a heterogeneous mantle with the formation                |
| 57 | of a ferroan anorthosite crust via flotation of plagioclase rich cumulates.                                     |
| 58 | Recently, data from the multiband imager (M.I.) and the spectral profiler (S.P.) onboard the                    |
| 59 | Japanese SELENE missions and from the Moon Mineralogy Mapper (M <sup>3</sup> ) Nasa-reflectance                 |
| 60 | spectrometer onboard the Indian Chandrayaan spacecraft, have clearly highlighted as C.F.                        |
| 61 | absorption band close to $1.2 \mu m$ is unambiguously recognizable in different regions on the lunar            |
| 62 | crust and is assignable to ferrous iron in plagioclase (Ohtake et al., 2009; Yamamoto et al., 2012;             |
| 63 | Donaldson Hanna et al., in review). Moreover, it has been evidenced that regions close to pure                  |
| 64 | anorthosites show spectral variation similar to those of plagioclase-pyroxene mixtures with variable            |
| 65 | amount of mafic minerals (Matsunaga et al., 2008; Ohtake et al., 2009; Cheek et al., 2011; Pieters et           |
| 66 | al. 2011; Kramer et al., 2013).   |
| 67 | M <sup>3</sup> data also revealed distinctive rock-types along the inner basin ring in the Moscoviense (Pieters |

et al., 2011), designated as "OOS" and dominated by high concentrations of orthopyroxene, olivine, and Mg-rich spinel. These lithologies occur as small areas, each a few km in size, but widely separated within the highly feldspathic setting of the basin rim. Although the abundance of plagioclase is not well constrained, OOS have been classified as pyroxenites and harzburgites due to high mafic mineral content (Pieters et al., 2011). OOS origin appears to be related to one or more magmatic intrusions into the lower crust, perhaps near the crust/mantle interface. The authors hypothesized that processes such as fractional crystallization and gravity settling may provide a

| 75 | mechanism that concentrate the mafic components within zones several km in dimension. The OOS           |
|----|---|
| 76 | are embedded within highly anorthositic material; they may be contemporaneous with crustal              |
| 77 | products from the cooling Magma Ocean (Pieters et al., 2011).   |
| 78 | Even if M <sup>3</sup> , SP and MI data improved the knowledge of lunar composition, the formation      |
| 79 | mechanisms of the lunar crust are still a matter of debate and the determination of the highland        |
| 80 | mineralogical composition, as well as mineralogical variation within the crust, are important for       |
| 81 | understanding the formation model and the subsequent evolution of the lithosphere.                      |
| 82 | On the Earth several large layered intrusions are present and well known from a                         |
| 83 | petrographic/petrologic point of view, e.g. anorthosite kindred intrusion like Bushweld Complex         |
| 84 | (R.S.A.), Stillwater Complex (Montana, USA), Bierkrejm-Sokndal (Norway). The petrographic and           |
| 85 | compositional variations of these intrusions are expression of their petrology and evolution.           |
| 86 | Studying spectral characteristics of well-known terrestrial layered intrusions with petrographic and    |
| 87 | compositional characteristics similar to the lunar crust could be a useful tool to improve              |
| 88 | spectroscopical and compositional knowledge from remote sensing analysis.                               |
| 89 | In this paper we have studied samples from different layers belonging to the Stillwater Complex.        |
| 90 | discussing the spectral variability of rocks from different layers and classifying spectra signature of |
| 91 | both powders and cut-rocks. Even if the lunar surface was considered as characterized by fine           |
| 92 | materials (see e.g. McKay et al., 1974), the development of high spatial resolution spectrometers, as   |
| 93 | well as, possible future rover missions, will permit to map pixels with spectrum dominated by           |
| 94 | exposed rocks (e.g. crater wall). This reason motivated us to study both powders and cut-rocks          |
| 95 | spectra. Moreover, we quantified spectral parameters and compared them with the different mineral       |
| 96 | chemistry and assemblages, to emphasize correlation between spectral variability and the                |
| 97 | mineralogy of rocks genetically related to each other.  |

# 98 Geological setting of Stillwater Complex

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|---|
| The Stillwater Complex (SWC) was emplaced 2.7 Ga BP (see McCallum, 1996), and it crops out on   |
| the northern edge of the Beartooth Range, one of the major exposed blocks in the Wyoming  |
| Archean Province. Several authors studied the mineralogy, petrography and geochemistry of this  |
| cumulitic stratified intrusion in order to investigate the evolution of the system, and the presence of   |
| important mineralization (e.g. Page, 1979; McCallum et al., 1980, Raedeke and McCallum 1980;  |
| Radeke, 1982; Boudreau and McCallum, 1986; Boudreau and McCallum, 1992; Campbell and  |
| Murck, 1993). In particular, Raedeke and McCallum (1980) showed how SWC samples from series   |
| with cumulate plagioclase have trends analogues to lunar highlands samples. These trends can be   |

associated to: 1) a basaltic systems approaching a perfect fractional crystallization; and 2) an 107

equilibrium crystallization of trapped intercumulus liquid for very plagioclase rich Series (see their 108

Figure 2,3). Raedeke and McCallum (1980) also evidenced that applying the model derived for 109

SWC rocks they could explained the major elements variations in the ferroan anorthosite. Some 110

authors (e.g., see McCallum, 1996; and references therein) interpreted the formation of anorthosite 111

at SWC as an accumulation of coalescent pl-rich suspension (rockbergs) forming large scale sorting 112

- similar to that hypothesized for the lunar highlands (Herbert et al., 1977; Shearer et al., 2006). 113
- In this paper we briefly summarized the variations of major/primary minerals, which can be 114

addressed to recognize co-genetic igneous rocks by VNIR spectral reflectance. The SWC's igneous 115

stratigraphy is subdivided into three major zones (Fig.1b), which from base to top are: the Basal 116

Series (BS, not considered in this paper), the Ultramafic Series (UmS) and the Banded Series (BdS). 117

The BdS are then subdivided in three sub-series, Lower Banded Series (LBdS), Middle Bande 118

119 Series (MBdS) and Upper Banded Series (UBdS). Each Series has been further subdivided in zones

- and sub-zones. Series or zones are related to the appearance or disappearance of one or more 120
- cumulus minerals. The layering in all the complex varies from centimeter to metric scale. 121

Figure 1 122

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126 1) The UmS can be subdivided in a Peridotite Zone (PZ) and in a Bronzite Zone (BZ). The base is

127 placed at the first appearance of significant amount of cumulus olivine (ol) and the root corresponds

128 with the crystallization of the cumulus plagioclase (pl). The PZ is characterized by sequences of

129 cyclic peridotite-hazburgite-bronzitite units where ol  $\pm$  orthopyroxene (opx)  $\pm$  chromite are the

130 cumulus phases (Raedeke and McCallum, 1984). Pl occurs as intercumulus phase within 2 and

131 15%. Massive and disseminated chromite can be present in peridotite layers. The rock textures vary

132 from poikilitic to equigranular.

133 The BZ is the upper zone, it is homogeneous, with the opx as cumulus phase (Jackson, 1961). The

intercumulus minerals are pl with small amount of other phases (e.g. clinopyroxene (cpx), quartz,

135 chromite). In the upper zone the intercumulus pl and augite (cpx) became more abundant.

136 In the UmS, Ol vary from forsterite content (Fo, Mg/(Mg+Fe)%) 79 to 90. Mg-rich ol are associated

to chromite, whereas Fe-rich ol are present in the lowermost peridotites. Opx vary from enstatite

138 content (En, Mg/(Mg+Fe+Ca)%) 76 to 86 with a general Mg enrichment, and intercumulus cpx are

in equilibrium with opx composition. Pl shows anorthitic value (An, Ca/(Ca+Na+K)%) between 75

and 80, with few samples showing more albitic or anortitic composition (An from 69 to 86).

2) The BdS start when pl becomes a cumulus major constituent of rocks. The LBdS are composed
of norite and gabbronorite, with minor amount of ol bearing cumulus that host the Johns-Manville
Reef (J-M Reef) a platinoid rich reef. The MBdS are composed of anorthosites, ol-gabbros and
troctolites and the UBdS comprise gabbronorites with minor troctolites and norites (McCallum et
al., 1986).

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a) LBdS are characterized in the lower part by rocks with cumulus opx and pl in cotetic 146 proportion, with 1-10% of cpx in the Norite I zone (N-I) that became a primary cumulus phase in 147 the Gabbronorite I zone (GN-I). Modally graded and rhythmic layering are common. The minerals 148 chemistry is quite homogeneous with opx En75-83 and pl An78-83 (Page and Moring, 1987). 149 Above the GNI zone is the ol-bearing zone I (OB-I) where ol appear as cumulus phase. The upper 150 151 portion of the LBdS is characterized by a uniform member of norite (N-II) and a gabbronorite zone 152 (GN-II) when augite return as cumulus phase. This layering is best developed in norites and 153 gabbronorites that contain pl in excess of cotetic proportions suggesting that the magma may have been slightly undersaturated in pyroxenes (px) (McCallum, 1986). Pl are still quite homogenous in 154 composition with An 75-77, px shows a slightly Mg impoverishment trend except the upper part of 155 156 the GN-II. The LBdS finishes with a small OB-II layer, where pillows of troctolite are set in an anorthositic body. 157

b) The MBdS lithologies have high pl volume (> 82 pl.%) as primary cumulus phase, ol and
augite are the other most common cumulus mafic minerals while opx is rare. Therefore, the major
lithologies are anorthosite, troctolite, ol-gabbro, and rare gabbronorite (±ol). The difference from
the other Banded series is probably due to a change in composition of the magma with respect to the
LBdS and UBdS parental magma (Raedeke, 1982; Irvine et al., 1983).

163 The MBdS starts and finishes with two thick uniform anorthosite zones (An-I and An-II) with the

164 presence of minor amount of oikocrysts or intercumulus crystals of augite, opx or inverted

165 pigeonite. Px-rich and px-poor domains are present in An-I and An-II, suggesting a possible

166 formation due to a coalescence of meter-sized rockbergs of partially consolidated pl cumulates

167 (Haskin and Salpas, 1992). Pl composition are virtually constant with An76-77 on large scale, but

- are more heterogeneous on a cm scale (McCallum et al., 1980). The central area of the MBdS is
- 169 characterized by two ol-bearing zones (OB-III, OB-IV) which are formed by troctolites and
- anorthosites in the lower parts, overlain by ol-gabbro. The uppermost unit in both OB-III and OB-

IV is a ol-gabbronorite where both ol and opx appear to be a cumulus minerals in addition to pl and
augite. There is no systematic variation in mineral composition and pl are similar to An-I and -II
with an average An77 (McCallum et al. 1980, Meurer and Boudreau 1995). Mafic mineralogy of
MBdS show no systematic variation, but a generally iron-richer composition with respect to LBdS
and UBdS.

c) The UBdS begin with a banded troctolite (OB-V zone). This zone is characterized by ol-176 rich lenses along the contact, rising the body shows modally graded layers, cross-bending, scour 177 and fill structures, indicating strong action during the formation. The root of OB-V present a thick 178 anorthosite layer which degrade in a repetitive sequence of anorthosite-norite-gabbronorite. The 179 upper zone of UBdS is a gabbronorite (GN-III). The GN-III starts with a sequence of homogeneous 180 laminated gabbronorite, with pl, augite and low-Ca px in cotetic proportion. The opx result as a 181 cumulus phase in lower part, while in central and upper part it is present as poikilitic crystals 182 183 derived by the inversion of cumulus pigeonite. In GN-III can be present magnetite as post-cumulus phase, irregular pegmatite zone and xenoliths of anorthosite. Pl shows a change from An75 to An62 184 rising along the section, as well as, low-Ca px moves from Mg# (magnesium number) 0.75 to 0.67 185 (Radeke, 1982). 186

#### 187 Methods

188 Twenty samples with different composition have been considered in this work, representing various 189 layers of the complex. Only few samples had a clear indication of the collected site (see Fig.1b and 190 caption). We used the bulk rock composition, mineral chemistry and mineral abundances to 191 correlate the other samples with units (see Fig. 1a,b).

192 Reflectance spectra were measured on rock powders at different grain size (<0.050, <0.125, <0.250

- 193 mm) and on slab samples. The slab samples are considered as analogues of cm size natural rock
- 194 grains and compact multimineral aggregates in the regolith (Carli and Sgavetti, 2011). Studying

both powders and slabs spectra permit to evidence how varies the influence of the optical coupling
with respect to the minerals absorptions. This aspect is very important (interesting reader see also
Carli and Sgavetti, 2011) to understand spectral information of multi-crystal grains which can be
present in a regolith.

199 Powder and slab samples were prepared from the rock portion adjacent to the thin section used for

200 petrographic and chemical analyses. On slab (cut surface) samples, the measured surface was

slightly polished using a silicon carbide abrasive, having particle sizes in the range between 10 and

202 20  $\mu$ m. The abrasion permits the removal of the asperities left by the saw, but does not produce a

203 mirror-like surface. In order to preserve the original rock composition in powdered samples, the

rocks were first ground to prepare the <2.00 mm coarse grain size class. The coarse powders were

then quartered and each fraction was ground under smaller grain size classes, <0.250 mm,

206 <0.125mm and <0.050 mm. Each powder grain size class therefore contains a range of grain

207 dimensions beneath the upper limit, except for the slab.

208 Mineral assemblages and rock textures were described through optical microscopy on thin sections.

209 A point counter was used to measure the relative modal abundance of minerals and according to the

210 IUGS Subcommission on Rock Classification (LeMaitre et al, 2002; Le Bas et al., 1986), the

211 intrusive rocks are classified by the relative modal abundance of the primary mineral. Rock

chemistry was analyzed using a X-ray fluorescence spectrometer (XRF), in use at the XRF

213 laboratory at Geosciences Department of the University of Padova. The chemistry of the principal

214 mineral phases was determined by electron microprobe analyses with a CAMEBACAMECA SX50

215 (EMPA) at the microprobe laboratory of C.N.R.-IGG, Padova. The rock modal and chemical

compositions and mineral chemistry are reported in tables 1, 2 and 3.

217 Slab spectra were measured using diffuse reflectance spectroscopy at IFAC-CNR, Florence, using a

double-beam double-monochromator spectrophotometer (Perkin-Elmer-Lambda 19) with a 60 mm

219 integrating sphere and an halogen lamp as source of irradiation. Spectral resolution and sampling

| 220 | was 1 nm between 0.35 and 2.50 $\mu m$ at room temperature and normal atmospheric pressure. The                     |
|-----|---|
| 221 | illuminated spot was ca. 1 cm <sup>2</sup> , suitable for characterizing rocks with relatively large crystal sizes. |
| 222 | To account for the heterogeneity of the rocks and to assure the spectral and petrographic data                      |
| 223 | comparability, five separate adjacent spots were acquired over about 6-7 cm <sup>2</sup> sample area and            |
| 224 | averaged. A smoothing function based on a Fast Fourier Transform (FFT) algorithm using twenty                       |
| 225 | data points has been applied to the average spectrum, without significant effects on the diagnostic                 |
| 226 | band minimum positions. Bidirectional spectra of powders at different grain sizes were acquired                     |
| 227 | using a Fieldspec Pro spectrophotometer mounted on a goniometer at S.LAB. laboratory, at "Istituto                  |
| 228 | di Astrofisica e Planetologie Spaziali", IAPS- Inaf, Rome. The spectra were acquired with a spectral                |
| 229 | resolution of ~3 nm in the VIS and of ~10-12 nm in the NIR, with i=30° and e=0°. The source used                    |
| 230 | was a QTH (Quartz Tungsten Halogen) lamp and the spot illuminated has an area of ca. 0.5cm <sup>2</sup> .           |
| 231 | The standard reference calibration was performed with a Spectralon® optical standard (registered                    |
| 232 | trademark of Labsphere, Inc.) both for slab and powder measurements.  |

#### 233 Analytical approach

All the samples were spectrally characterized both as slab of rocks and powders (<0.250 mm) to

235 define a spectral classification. C.F. absorptions representative of the dominant mineral phases (Fig.

- 236 2), as well as, spectral shape (defined by the presence of different absorbing phase and the spectra
- slope) were used to identify the different spectral groups. Three major C.F. absorptions at  $\sim 1.00$ ,
- 238 1.25, 2.00 μm, were labeled as Band I, V, and II; very weak IVCT (intervalence charge transfer)
- bands (Band III, IV) were identified at ~  $0.55-0.65 \,\mu$ m. Some samples also show overtone
- absorptions, at ~1.4, 1.9, 2.2-2.3µm, labeled a, b, c, d, due to the presence of mineral alteration, like
- 241 epidote, serpentine, bowlingite, iddingsite.
- 242 <u>Figure 2.</u>
- 243 We then compared the spectral classification with mineral and rock compositions (see section 6.1).

Subsequently for each C.F. absorption we determined band center (B.C.) and band depth (B.D.), 244 after continuum removal by division; and considering a wavelength's function continuum line as 245 segments that join the reflectance maxima in the spectrum (Clark and Roush, 1984). The reflectance 246 maxima are chosen for each samples depending on the single spectrum, they vary from 5 to 8 247 points. The B.C. results in the position of the minimum of each absorptions after the continuum 248 249 removal, and the B.D. is the difference between the continuum reflectance and the B.C. reflectance 250 after the division with the continuum (Clark and Roush, 1984). In particular, we refer to B.C.I and 251 B.D.I for the position and intensity of Band I, and to B.C.II and B.D.II for the Band II. For selected samples characterized primary by pl, opx and cpx we measured spectra of finer grain size, <0.125 252 mm and <0.050 mm, to consider sizes closer to a fine regolith. 253 The B.C. and B.D. of slab and powder spectra were correlated to mineral and rock composition to 254 255 analyze trends and investigate differences between slab and powders spectra and within different

grain size for samples dominated by plagioclase and pyroxenes. In particular, B.C. of C.F.

absorptions can be directly associated with the  $Fe^{2+}$  amount on silicates (e.g. ferrosilite content,

258 Fs%, Fe/(Fe+Mg+Ca), in Cloutis and Gaffey, 1991; Klima et al., 2007; Fa/Fo% in Burns, 1993) or

indirectly to  $Ca^{2+}$  (e.g. px band I and II in Cloutis and Gaffey, 1991); here we related the absorption

260 position to Fs% and Wo% (wollastonite content, Ca/(Fe+Mg+Ca)) to compare the data with Cloutis

and Gaffey (1991). B.D. of px-bearing rocks has been plotted vs. the px abundance and vol. $Fe^{2+}$  in

px, to highlight if the variation in composition of mafic minerals can influence the known

relationship between B.D. and mineralogy (similarly to e.g. Pompilio et al. 2007).

### 264 The Stillwater Complex: mineralogy and petrographic characteristic of investigated samples

265 Petrographic observation under optical microscope were made for twenty samples, recognizing

266 mineral phases and relative abundances. Mineral chemistry and bulk rock were also measured to

- 267 obtain information useful to discuss the VNIR spectral variations and to constrain the unit of
- 268 provenance of some samples (see Fig. 1).

- Seven samples (StC1, StC2, StC3, StC4, StC5, StC6, StC7) representative of the UmS, are
- 270 characterized by cumulus of mafic phases (ol, opx)  $\pm$  chromite, while pl and cpx (augite) are present
- as intercumulus or postcumulus phases. Mineral phases show low amounts of hydrated alteration.
- 272 StC2,4,7 are mela-norites (Fig.3) with high amount of cumulus opx, and a small amount (~13%, see
- table 1) of cumulus ol in StC2. StC1,3,5,6 are characterized by relative higher abundance of
- cumulus ol and a variable but significative presence of cumulus opaque minerals (chromite). StC1
- and StC5 present a poikilitic texture with opx crystals present as oikocrysts surrounding small
- cumulus ol. Chromite abundance vary from 2% (StC5) to 28% (StC1) to 55% (StC6) to 90%
- 277 (StC3).
- 278 <u>Figure 3.</u>
- 279 Other samples are representative of the BdS. Pl is a cumulus phase, present with variable amount, in
- association with mafic minerals, which can be cumulus or intercumulus crystals. On the base of
- 281 mineral association, samples can be divided in:
- Anorthosites (StC9,10,18), very pl-rich rocks (relative pl>90%), with few amount of intercumulus
- cpx, and opx in StC10. Zoisite is present in StC9 and StC18 as plagioclase alteration;
- Leuco-gabbros (StC11,13), very similar to anorthositic samples but with an higher amount of cpx.
- In StC13 is also present low amount of opx either as intercumulus crystals or as exolution in cpx;
- 286 Gabbronorites (StC8,12,14), characterized by the presence of high amount of cumulus pl and
- different opx/cpx ratio. Opx are generally cumulus whereas cpx can be either small cumulus or
- 288 intercumulus phase;
- Mela-norites (StC20,25), characterized by high, iron-bearing opx amount as cumulus phases.
- 290 Despite the relative low amount of pl, the ratio between Mg# of opx and An of pl suggests that they
- are compatible with BdS composition (Fig. 2);

- and Ol-bearing samples (StC16,17,19), characterized by high amount of pl and an amount of
- cumulus of higher than opx+cpx. StC17 and StC19 present high degree of ol alteration (serpentine);
- 294 moreover, StC17 have pl partially altered (epidote).
- Figure 4 shows the general variation of the mineral chemistry. Opx varies from En91 to 61, with
- 296 Mg richer samples from UmS; this variation is recognized also in cpx composition (with En from
- 48 to 39, and Wo 45  $\pm$ 1) and in ol with Fo increasing from 88 for UmS to 76 BdS. Pl shows a
- composition from An70 to An89, with An79-89 for BdS. Moreover pl chemistry shows a variable
- FeO from 0.1 wt.% to 0.5 wt.%, from mafic rich to pl rich rocks, respectively.
- 300 <u>Figure 4.</u>

#### 301 The Stillwater Complex: VNIR spectroscopy results

#### 302 Spectral classification

- 303 We spectrally classified all the samples consisting of rock powders (<0.250 mm), to consider
- spectral characteristics of natural-mixtures of mono-crystal grains (Fig. 5), and spectra measured on
- slabs, to consider spectral characteristics of multi-crystals grains (Fig. 6) (see also Carli et al., in
- 306 *press*). This spectral classification of the SWC samples is based on C.F. absorptions of the primary
- 307 minerals (px, ol, pl, chromite) and, secondary, considering also the spectral slope and reflectance.

Powders spectra (Figure 5) can be classified in four main groups, further subdivided into subgroups,as follows:

The first group (Group 1\_p, Fig. 5a) is characterized by a wide absorption band at ~1.25 μm
 (Band V) and high albedo. These samples are pl-rich rocks, two anorthosites and a leuco gabbros (StC 9, 18 and 11, respectively, see Table 1), which have cpx as only mafic phase.
 Vibrational bands are indicative of zoisite.

| 314 | 2) | The second group (Group 2_p, Fig. 5b) is dominated by the two absorption band at 1.00 and             |
|-----|----|---|
| 315 |    | $2.00\mu\text{m}$ indicative of px. In figure the reflectance is scaled, for clarity, but spectra are |
| 316 |    | ordered from bottom to top following the reflectance (maximum at ca. 0.75 $\mu m$ vary from           |
| 317 |    | 0.27 (StC25) to 0.46 (StC10)) and the spectral contrast is maintained. This group can be              |
| 318 |    | further divided into two subgroups: the Group 2a_p whit spectra characterized by the band I           |
| 319 |    | and II, it is the most populated group; the Group 2b_p (grey labels) show the two px                  |
| 320 |    | absorptions and the evidence of the bandV absorption, indicative of pl. The Group 2b_p is             |
| 321 |    | characterized by the samples within the second group with the highest amount of pl, and               |
| 322 |    | both cpx and opx (StC10,13,14), which have the highest albedo and the lowest px                       |
| 323 |    | absorption's spectral contrasts. Gabbronorite spectra (samples StC8,12,14) are characterized          |
| 324 |    | by px composite bands, with position and asymmetry correlated to the opx/cpx ratio. Some              |
| 325 |    | spectra show small vibrational bands indicative of very small amount of alterations. In the           |
| 326 |    | visible range are also present weak IVCT absorptions.   |
| 327 | 3) | The third group is defined by a wide absorption band from 0.5 to 1.7 $\mu m$ (Fig.5c, Group           |
| 328 |    | $3a_p$ ). StC16 shows a lower spectral contrast due to its modal distribution, when $Fe^{2+}$ is      |
| 329 |    | present in several minerals (e.g. pl, opx, cpx and ol) the contribution of all of this absorbing      |
| 330 |    | phases in contiguous wavelength range reduce the contrast of the composite absorption                 |
| 331 |    | (Carli and Sgavetti, 2011, see their fig. 3,5); whereas StC5 is characterized by a defined            |
| 332 |    | absorption related to Fe <sup>2+</sup> in M1 and M2 site of ol (Burns, 1993). Both samples are        |
| 333 |    | composed of fresh ol. In the Group 3b_p are present spectra with very low albedo and                  |
| 334 |    | spectral contrast, and C.F. absorption features only suggested by a weak inflection centered          |
| 335 |    | at about 1.05 $\mu$ m, representing samples containing strongly serpentinized ol.                     |
| 336 | 4) | The fourth group (Fig. 5d) included spectra dominated by low albedo and a clear influence             |
| 337 |    | of chromite at wavelength higher than 2 $\mu\text{m}.$ This group can be subdivided into two groups.  |
| 338 |    | One is characterized by chromite dominated sample (StC6, Group 4a_p). In Group 4b_p are               |

present StC1 and StC3 spectra showing two absorption bands at 1 and 2 µm, although
weaker then spectra in the second group, reflectance lower than 0.2, and the clear influence
of chromite at wavelength higher than 2 µm (absence of a band shoulder around 2.4-2.5
µm).

343 Figure 5.

Slab spectra can similarly be subdivided into four main groups on the basis of absorption band
association and overall reflectance and spectral contrast (Figure 6). However, the different
processes acting in the bulk samples with respect to the powder samples affect in different ways
albedo, spectral contrast and spectral slope, resulting in different spectral class populations for the
two sets of spectra, particularly for the first two groups.

| 349 | 1) | The first group (Group 1_s) is identified by a wide absorption band with a minimum close         |
|-----|----|--|
| 350 |    | to 1.25 $\mu m$ (BandV), high albedo (Fig. 6a, albedo max in the visible from 0.35 to 0.55), and |
| 351 |    | a general blue slope, typical of slab spectra. The wide absorption band at ${\sim}1.25\mu m$ is  |
| 352 |    | indicative of $Fe^{2+}$ in pl (Burns, 1993). These samples in fact are pl-rich rocks and include |
| 353 |    | three anorthosites (StC9,10,18) and two leuco-gabbros (StC11,13)(see Table 1). StC10,13          |
| 354 |    | (opx-bearing samples) were not included in the corresponding Group 1_p. Vibrational bands        |
| 355 |    | are present indicative of the small amount of pl's alteration, like epidote or sericite.         |
| 356 | 2) | The second group (Fig. 6b) is still the most populated. The spectra are characterized by the     |
| 357 |    | presence of a well developed absorption band or a clear flexures at 1.00 $\mu m$ associated to a |
| 358 |    | wider and weaker band or a subtle flexure in the 2.00 $\mu m$ region indicative of px (Burns,    |
| 359 |    | 1993). The spectra also show intermediate to low albedo. This group can be split into two        |
| 360 |    | subgroups on the basis of the 1 $\mu$ m feature, the spectra with clear band I absorption are in |
| 361 |    | Group 2a_s (black labels) and spectra with band I flexure are in Group 2b_s (grey labels).       |
| 362 |    | The Group 2b_s includes two gabbronorite samplesStC8 and StC14, whereas a third                  |

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| 363 |                | gabbronorite, StC12 (Group 2a_s), show clear absorptions. The different spectral behaviors   |
|-----|----------------|--|
| 364 |                | could be related more with some petrographic variation (e.g. different plagioclase crystal   |
| 365 |                | sizes distributions) than with mineralogical characteristics (abundance or chemistry), which |
| 366 |                | affects and complicates the optical path of the light. This aspect, not discussed in details |
| 367 |                | here, is object of ongoing work. Some spectra show weak vibrational bands indicative of      |
| 368 |                | very small amount of alterations. In the visible range are also present IVCT indicative of   |
| 369 |                | $Fe^{2+}-Fe^{3+}$ or $Fe^{2+}-Ti^{4+}$ .   |
| 370 | 3)             | The third group is characterized by intermediate to low albedo spectra with very subtle      |
| 371 |                | spectral features. However, also these problematic spectra can be tentatively included into  |
| 372 |                | two subgroups. Group 3a_s includes spectra in which a shallow absorption or flexure can be   |
| 373 |                | recognized in the C.F. region from 0.5 to 1.75 $\mu$ m (Fig. 6c, StC5,16). These spectra     |
| 374 |                | represent ol bearing samples. Group 3b_s includes two featureless spectra characterized by a |
| 375 |                | blue, almost flat, slope. They represents strongly altered (StC19) or completely             |
| 376 |                | serpentinized (StC17) ol-bearing samples.  |
| 377 | 4)             | The fourth group shows low albedo (<0.12) spectra with a broad, weak absorption at 2 $\mu m$ |
| 378 |                | towards longer wavelength (Group 4a_s). These samples are characterized by high chromite     |
| 379 |                | abundance (Fig.6d). Samples StC6 shows also an absorption at ca. 1.1 $\mu$ m, as for powder  |
| 380 |                | spectrum (see Group 4a_p), which can be indicative also of ol. Group 4b_s: sample StC1,      |
| 381 |                | with almost 90% of chromite, still show, even if weak, a clear band I absorption, with a     |
| 382 |                | band II broad toward longer wavelengths than those seen for px in Group 2a,b_s.              |
| 383 | Figure         | 6  |
| 505 | <u>i iguit</u> | <u>v.</u>  |

384 Spectral parameters

The strong blue slope that affect all slab spectra prevent the reliable recognition of the band II long wavelength shoulder, thus only the B.C.I and B.D.I parameters were considered (see Fig.5,6). In

| 387 | contrast, powder samples B.C.II and the B.D.II parameters were analyzed, even if some spectra              |
|-----|--|
| 388 | appear to be highly affected by the presence of alteration mineral phases, as indicated by the 1.9 $\mu$ m |
| 389 | overtone band ( $\upsilon 1 + \upsilon 2$ ).   |

In the literature, several papers indicate how mineral and mineral mixture composition can be 390 related to the spectral parameters variations, as: 1) the B.C. absorption bands at 1 or 2  $\mu$ m was 391 392 related to px chemistry, stated as Fs or En content and Wo content (e.g. Cloutis et al., 1991; Burns, 393 1993; Sunshine et al., 1991; Klima et al 2007; 2011); 2) ol B.C. is a function of Fo-Fa value (Burns, 1970; Cloutis et al. 1986); 3) the B.C. at ~1.25 was assigned to  $Fe^{2+}$  in pl with position varying with 394 the amount of iron in the crystal structure (Bell and Mao, 1973; Serventi et al., 2013). Mineral 395 abundances have been successfully related to the band intensity (expressed as B.D. or Band Area) 396 397 for different type of mixtures. Cloutis et al. (1986) found a linear relationship between Band Area Ratio (Band II Area/Band I Area; BAR) vs. px/(px+ol) for some px-ol mixtures. Pompilio et al. 398 (2007) described as B.D. of opx mixed with pl or dark materials varies linearly with the relative 399 abundance of opx, and a similar behavior was expressed by the B.D.I of slab spectra of rocks 400 characterized by opx± pl, ilmenite. Serventi et al. (2013) studying mixtures of pl and mafic material 401 402 demonstrating the unexpected spectroscopic effects of PL chemistry superimposed on the expected 403 effects due to modal composition in these mineral mixtures. Moreover, Serventi et al. (2013) 404 pointed out that B.D.I for opx rich end members shows linear variation vs. the amount of 405 volumetric iron in pl.

406 So, B.C. is often related to mineral chemistry, here we considered a weighted Fs% and Wo% value,

407 that is a weighted content of the Fs and Wo of both pyroxenes in samples (e.g.  $cpx\%*Fs\%^{cpx} +$ 

408 opx%\*Fs%<sup>opx</sup>), in order to partially compare our results with Cloutis and Gaffey (1991).

Figure 7 shows the B.C.I variation vs. the Fs% weighted for all the grain sizes. In particular, Fig. 7a

displays the band center for the < 0.050 mm class and three fields can be recognized: 1) StC2, 4, 7, 8

and 12, centered between 0.9 and 0.93  $\mu$ m, indicate opx-rich samples (opx/cpx>1) and the center

4/30

moves to longer wavelength with increasing Fs%, with the exception of StC12, composed with 412 considerable amount of cpx; 2) StC10, 13 and 14 are centered at longer wavelength, 0.95-0.98 µm, 413 due to the opx/cpx<1. In this field there is not a clear variation trend with mafic composition; 3) 414 StC18, opx-free, is centered at 1.05  $\mu$ m. Fig. 7b compares the <0.050 and <0.125 mm classes, 415 showing that coarsening the grain size B.C.I slightly move towards longer wavelength (as seen also 416 417 e.g. by Serventi et al. 2013 for mafic and pl phases, and Clenet et al., 2011 for ol). The shift is very 418 reduced for samples with almost mono px phase, whereas is higher in samples belonging to the second field (St13, 10 and 14). Fig. 7c shows that, with the exception of StC18, the position 419 difference between the <0.125 and the <0.250 mm classes is strongly reduced. In the figure are also 420 plotted the ol-rich sample (StC5, 16) centers that fall in the third field. StC20 and 25 are composed 421 with very high amount of iron-rich opx: the centers fall in the first field but the wavelength are 422 lower than expected, probably due to the saturated bottom-flat absorption band. Fig. 7d finally 423 shows the behavior of slab spectra: centers are at shorter wavelength with respect to the 0-250 um 424 powders (with the exception of StC20, 25), probably due to the saturation effect in slabs (see Carli 425 and Sgavetti, 2011). Fig. 7d also shows the pl-rich samples (StC10,13,18,9,11), centered at longer 426 wavelength than the px-rich samples, between 1.20 and 1.30  $\mu$ m, due to the strongly influence of pl 427 absorption on coarsest grain sizes. 428

429 <u>Figure 7.</u>

430 Figure 8 shows the B.C.I vs. the weighted Wo%. In particular it shows that: 1) with increasing the

431 Wo% content, B.C.I generally moves to longer wavelength, from the opx-rich samples to the cpx-

rich (StC10, 13, 14 and 18); 2) coarsening the powders grain size, centers move toward longer

433 wavelength; and 3) St5 and 16, representative of ol-rich samples, fall outside the variation trend.

- Figure 9 shows the B.C.II vs. the Fs% (Fig. 9a) and Wo% (Fig 9b) weighted for all the powder
- grain sizes. Several samples show position centered at about  $1.9 \,\mu\text{m}$ , due to the vibrational
- 436 processes indicative of alteration superimposed to the px C.F. absorptions. Only some opx-rich

437 samples have B.C.II no affected by the 1.9  $\mu$ m, those samples show a clear trend respect Wo% for 438 values <5% (see Fig. 9c).

- 439 <u>Figure 8.</u>
- 440 <u>Figure 9.</u>

B.D. is the expression of the intensity of the absorption band, which is related to the probability of 441 electronic transitions between different crystal field states occur (Burns, 1993). This parameter 442 depends on different chemical and physical properties which affect the optical absorption. In 443 particular it can be affected by: variation in the abundance of the absorbing elements in a mineral 444 (e.g.  $Fe^{2+}$  in px); variation of ratio between minerals in a mixture (e.g. opx/cpx); and variation of 445 grain or particle sizes. Because all of these aspect are acting on the B.D. with different contribution 446 in our paper we have considered the variation of B.D. with respect to the mineral abundance and 447 considering the  $Fe^{2+}$  influence. For this reason, B.D.I and II are plotted vs. the abundance of px 448 (Fig. 10a,b and Fig. 11a) and vs. the volumetric Fe<sup>2+</sup> in px (Fig. 10c,d and Fig. 11b). Moreover we 449 have plotted it for the different studied grain sizes. 450 B.D.I of powder spectra shows a linear trend with very high correlation vs. the Opx%+Cpx% 451 (Fig.10a) with angular coefficient similar for different grain sizes (0.0054 to 0.006). Also, B.D.I 452 increases with coarsening the powder size, while it decreases in slabs. Including the iron-richer 453 samples (StC20 and St25) for the <0.250 mm size, values are still correlated (Fig. 10b). Slab spectra 454

455 show a linear relationship with a lower confidence ( $R^2=0.71$  with respect to  $R^2 > 0.94$  for powders)

- 456 and a very low angular coefficient (0.0025). Considering StC20 and StC25,  $R^2$  further diminishes to
- 457 0.65 due to the saturated px absorption.
- 458 In Figure 10c, B.D.I shows a liner relationship with very high coefficient value (0.93 for slab and
- 459 0.98 for finest powders) with respect to vol.Fe<sup>2+</sup> in px; however, Fig. 10d shows that powder
- samples with grain size < 0.250 mm show a worse R<sup>2</sup> (0.76) when we include the iron-rich px

bearing StC20 and StC25 samples and can be better fitted with a second degree polynomial relation,

- 462 with a  $R^2$  of 0.86.
- 463 <u>Figure 10.</u>

464 In figure 11, B.D.II shows linear relationships with a slightly lower  $R^2$  value for <0.250 mm grain

- size considering iron rich px spectra with respect to selected samples.
- 466 <u>Figure 11.</u>
- 467 **Discussion**

1) Stillwater Complex samples show a high variation of pl/mafic material and both pl and mafic

- 469 minerals have variable chemistry among layers of the plutonic system. Figure 12 shows the pl/mafic
- 470 variation for all samples; even if pl-mafic composition in SWC samples varies, the trend of mineral
- abundance with respect to sample's Fe<sub>tot</sub> are comparable to those of mineral mixtures studied by
- 472 Serventi et al. (2013; see their Fig. 2). In particular, Fig. 12b shows that pl-rich rocks contain the
- iron-richest pl, while mafic-rich samples consist of the iron-poorest pl.

474 <u>Figure 12.</u>

A rock powder spectrum, though different from that of a mineral mixture with the same chemistry 475 476 and modal composition as the rock, however often displays the diagnostic absorption bands of the most abundant component minerals. The spectra measured on samples of a rock suite as the 477 intrusive Stillwater Complex can be usefully classified into groups, each including spectra with 478 same association of absorptions or spectral shape. This provides a "spectral classification" that 479 facilitates the comparison with the petrographic classification and the correlation with the intrusion 480 stratigraphy, and, finally, allows the recognition of a "spectroscopic stratigraphy" of the Complex 481 (e.g., Ferrari et al. 1996; Longhi et al., 2001). Slab spectra suffer the effects of petrographic 482 characteristics (e.g. crystal size and its distribution, cumulus/intercumulus phases, poikilitic 483 textures, etc.) which strongly influence the slope and absorption spectral contrast, up to even 484

suppress some absorption features. However, bulk rock spectra can contribute to the spectral
description of a natural rock suite, adding spectral information needed for the interpretation of
remote sensing or in-situ high spatial resolution hyperspectral data.

Almost mono-mineralic rocks are characterized by the component mineral phase signature, and the 488 spectral variation is mainly related to the different grain sizes. On the other hand, the spectra of bi-489 mineral or multi-mineral rocks are characterized by composite bands, due to absorption processes 490 acting on few tens of micron (e.g. opx and augite). Here, we have considered <0.250 mm powder 491 and slab spectra to define the spectral characteristics of samples and pooling in spectral groups 492 depending on C.F. absorption, reflectance and shape. For selected samples, characterized by pl-px 493 association, we have also acquired spectra of smaller grain sizes to discuss spectral parameter 494 variation related to the sizes. 495

496 2) Both powder and slab spectra have been classified into four predominant spectral groups. Two

497 groups show a dominant C.F. associations (Band V due to pl, Group 1\_p,\_s, or Band I and II due to

498 px, Group 2a,b\_p,\_s). The Goup 1\_p\_s are characterized by samples from BdS. Group 2a,b is

499 composed by samples from both UmS and BdS, with variable px amount and composition (see

table 1 and 3). Note that, StC2, despite the presence of 13% of ol, can't be differentiated from the

others. Group 2b\_p show also the evidenced for a the Band V due to pl over the absorption Band I

and II. Group 3a\_p, s is indicative of ol samples (StC5 from UmS and StC16 from BdS), whereas

samples with ol highly altered are featureless (Group 3b\_p\_s); those samples are from ol-bearing

zones of MBdS or UBdS. Group 4a\_p,\_s is characterized by spinel bearing evidence due to the

spinel absorption at circa 2.0  $\mu$ m towards the infrared (absence of a shoulder at 2.2-2.5  $\mu$ m

wavelength region), a general low reflectance and reduced spectral contrast (Group 4a\_p,s). In the

507 Group 4b\_p,\_s are still present samples with the clear influence of spinel but also Band I and II. All

samples of the Group 4 are from UmS.

| 509 | Although the groups recognized for slab and powders are similar, some differences are evident. Pl |
|-----|---|
| 510 | rich rocks show clear Band I and II where mafic minerals are present as both opx and cpx for      |
| 511 | powder spectra (sample StC10,13) while considering slab spectra only Band V is detectable. Group  |
| 512 | 2a is composed by the same samples for both powder and slab spectra (with the only exception of   |
| 513 | StC8), as well as, Group 3a and 3b. Group 4 includes samples StC1,3,6 and showing spinel          |
| 514 | signature. Group 4_p_s are characterized of spectra dominated by the spinel absorption (StC6 for  |
| 515 | powder and StC3,6 for slab), whereas in Group 4b_p,_s are present spectra with px absorptions     |
| 516 | influenced by chromite absorption, StC1 and StC3(even if the chromite abundance is $> 90\%$ ) for |
| 517 | powder and only StC1 for slab.  |

3) The spectral variation of B.C.I, II and V and B.D.I and II, have been quantitatively described by 518 the analysis of spectral parameters, thus allowing the comparison with compositional information in 519 order to quantify the spectral parameters. In the SWC suite, B.C.I variation reflects the mineral 520 521 chemistry variation even if not all the mineral components can be resolved. Figure 7 shows how 522 samples with one mafic phase (opx or cpx) have band center comparable with px of Cloutis and 523 Gaffey (1991) for the finer powder grain sizes. Opx rich samples have B.C.I comparable to Cloutis and Gaffey (1991) also for <0.250mm, whereas in anorthosite sample StC18, which presents cpx as 524 mafic phase, B.C. is shifted to longer wavelength due to the strong effect of the high pl (94%) 525 526 abundance. Sample with gabbronoritic composition and opx/cpx > 1 (StC8, StC12) show B.C.I dominated by opx for all the powder grain sizes; samples with opx/cpx < 1 are closer to 527 intermediate cpx (~Wo. 30%, Cloutis and Gaffey 1991) with positions moving to longer 528 529 wavelength, towards augitic composition, coarsening the grain size. Figure 8 shows as B.C.I in pxbearing samples follows a trend similar to Cloutis and Gaffey (1991) with respect to the Wo%. Both 530 Fig. 7c and Fig. 8 display how powder spectra of StC9-StC11 (BandV) and ol-rich samples (StC5, 531 532 StC16) are far from px positions, behavior emphasized for slab spectra. Slab spectra also show a shift to slightly longer wavelength even for some px-bearing samples (StC8,20,25). 533

In particular, in the SWC we observe that coarsening the grain size the composite band absorptions become more affected by most abundant mineral phases, even if less absorbing (e.g. B.C.I move to higher wavelength or is made up by band V). This behavior can be probably related to different optical paths, and different behavior of single mineral phases with respect to the incident light. Pl absorption becomes, generally, more influent for bigger particle size, in agreement with Serventi et al. (2013).

540 B.D.I of ol-free samples (both including and excluding StC20, 25, Figures 10a,b) show linear

relationship (high  $R^2$ ) with respect to the pxs abundance, with angular coefficient that slightly

542 increases with the grain size (B.D.I are almost identical for all the grain sizes). Considering slab

spectra, the B.D.I still varies linearly (even if with lower  $R^2$ ) and StC20 and StC25 are outliers (Fig.

544 10a,b). We investigated also the relationship of B.D.I vs. the volumetric  $Fe^{2+}$  in pxs: for slabs, it

shows a linear relationship with  $R^2 = 0.93$ , considering all the samples (Fig. 10c), whereas, for

546 powder spectra, the trend is described by second degree law (with  $R^2=0.86$ , Fig. 10d).

It has been demonstrated in the literature that slab spectra have lower albedo and reduced spectral
contrast (Pompilio et al. 2007, Harloff and Arnold 2001). Considently, in the SWC sample set the

overall reflectance reduction linearly increases with increasing the modal % of absorbing minerals,

indicated by the variation of the angular coefficient. Moreover, in slabs spectra we cannot

discriminate the px absorptions for samples with less than 20% opx+cpx. Powders B.D.II also

shows a linear relationship for all the powders with only StC25 as outlier in coarser powders (fig

11). Even this trend shows a slight increasing of the angular coefficient coarsening the powder size.

The B.D.I and II behavior of powders shows how, despite possible mineral chemistry variations in

rocks co-genetically related, the intensity of the absorption is strictly related to the rock composition

556 (mineral abundance, Fig. 10a,b), even if samples with very high iron-rich mafic concentration show

- 557 band depth slightly higher than predicted (probably rocks from enriched residual magma). The
- importance of mineral chemistry in addition to the mineral abundance is strongly evidenced on slab

559 spectra which show saturated band minima, resulting in a B.D. linearly related with the ferrous iron volumetric distribution (Fig. 10c). Moreover, B.D. for different grain sizes are almost unchanged, 560 with the band depth slightly increasing coarsening the grain in agreement with the observation of 561 Harloff and Arnold (2001) for similar grain sizes of px or basalts. 562 Integrating the spectral classes with the spectral parameters analysis assigns a geologic significance 563 to the spectral classes. Within each class, the absorption band association and variation of band 564 centers and band depths give information on the rock composition, allowing the correlation with 565 the igneous stratigraphy as derived from field survey. Figure 13 shows the stratigraphic distribution 566 of the spectral classes, based on both powder and slab spectra. We can observe that UmS and LBdS 567 are represented by Group 2 spectra for both powder and slab, with Group 2b p present in the 568 MBdS. The PZ is also characterized by Group 3a and Group 4 consistently with the alternation of 569 peridotite-harzburigte-bronzitite and with localized layers enriched in chromite. Whereas the Group 570 571 1 is indicative of the MBdS for slab spectra, and only of the AnI and AnII for powder spectra, due

to the plagioclase Band V. Group 3b indicates the ol-bearing layers of the MBdS, which are high

573 altered in serpentine.

574 <u>Figure 13.</u>

#### 575 Implications

576 M3 and S.P. analyses revealed that anorthositic lunar highlands can be associated to local regions 577 with high mafic content (e.g. Ohtake et al., 2009; Pieters et al., 2011). Minerals like px, ol, as well 578 as spinels, were detected in lunar samples (see e.g. summary in Lucey et al. 2006) and have been 579 recently mapped by remote sensing data (e.g. Pieters et al., 2011). Spectral signature of the 580 principally rock forming minerals can be described for both rocks and powders with a definition of 581 the rocks variability in the intrusive complex. Mineral composition and mineral abundance variations are useful information that can help to understand if rocks could be associated geneticallyeach-other.

SWC samples are representative of a set of the major petrographic and mineral variation present in 584 a layered intrusion. Understanding the VNIR spectra variation will help us to improve our 585 capability to classify and discuss spectral signatures indicative of geological variations on planetary 586 surfaces. In this paper we in particular investigated the spectral variability of an anorthositic 587 kindred. The spectral analysis of a number of both powder and slab samples showed that the 588 spectral variability permits us to classify the rock suite on the basis of the spectral band association, 589 590 revealing the dominant mineralogy (Fig. 5,6). Powder spectra (similar to a finest regolith) gives more information than slab spectra (representative of coarse regolith, e.g. higher amount of 591 outcrops). Hyperspectral imaging data contains the influence of both composition and physical 592 properties of each pixel. Because the presence of fine to coarse materials influences the 593 594 compositional analysis, an accurate spectral description associated to a morphological interpretation 595 is needed to avoid wrong "spectral lithology" classification (done considering absorption identification and quantitative absorption analysis, e.g. B.C. and B.D.). Thus hyperspectral imaging 596 analysis will be improved once the correlation of spectral features from fine to coarse material will 597 be better understood. 598

599 In our work we have shown how B.C.I is closer to the dominated absorbing mineral, or the position

600 is intermediate between expected B.C.I of the present phases, which are affecting the absorption

band (Fig. 7,8). Moreover, B.C. is not affected by grain size in almost mono-mineralic samples.

Differently, coarsening the grain size the B.C. of multi-mineral samples shifts from wavelengths

603 indicative of increasing Ca-px, or of the presence of ol or pl. Moreover, in VNIR reflectance

spectra of pl-rich rocks mafic minerals are less evident increasing the grain size.

B.D.I and II show a clearly linear relationship between co-genetically related rocks, so a trend of

spectral variation among different portion of a geological system can be regarded as the possible

expression of a mafic intrusive complex (Fig. 10,11). If bigger outcrops affect a pixel's spectral information (here represented by slab spectra), we should expect a trend with lower B.D., indicated by very low angle coefficient. Moreover where rock spectra (i.e. slab) are investigated, mafic absorption will be clear only for abundances, at least, higher than 20% (Fig. 10). We have seen that where spectra show a possible band saturation a linear trend is present with respect to a volumetric variation on mineral composition ( $Fe^{2+}afu*%px$  in our case, Fig. 10c), maybe indicative of a compositional variation on the magma chamber.

- Further work will investigate the spectra applying a Gaussian modeling (e.g. MGM, Sunshine et al.,
- 615 1990, Clenet et al., 2013; EGO, Pompilio et al., 2009) to define and discuss the different absorption
- 616 processes that form composite bands.

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### 784 Figure's Captions:

- Figure 1 a) Mg# of opx vs. An# of pl, distribution of Series and Zones, modified after McCallum
- (1996). Samples studied in this paper are plotted (red and blue diamond). b) samples are distributed
- vs. the stratigraphy of the igneous layering as defined by McCallum et al. (1980) and Radeke and
- 788 McCallum (1984). Samples StC2, StC4, StC7, StC8, StC12, StC13, StC14, StC16, StC17, StC20
- and StC25 (italic) are positioning following the Mg# vs. An#, mineral chemistry, mineral
- assemblages and petrographic characteristics. Other samples are placed in noted zone. In a): UmS,
- 791 Ultramafic Series; LBdS, MBdS, UBdS, Lower, Middle, Upper Banded Series; N, Norite Zone;
- 792 GN, Gabbronorite Zone; OB, olivine-bearing Zone.
- Figure 2 shows all the absorptions identified in our samples. C.F. absorption are listed as I, II, III,
- IV, V; vibrational absorption are listed as 'a' (e.g. O-H-O), 'b' (e.g. OH-), 'c, d' (e.g. M-OH). See
  text for more details.
- Figure 3 Gabbroic rocks diagram (after Streickeisen (1976)). The mineral abundances have been
- restimated by point counter analysis of representative thin sections, the number of points varies with
- the crystal sizes of each samples, but we counted from ca. 600 to 800 points for sample (see also
- Table 1). a) all the samples are plotted, except the StC3 sample because it contains opaques >90%;
- b) pl-px rocks are plotted. In both boxes the pl vertex shows anorthositic rocks, whereas in the
- 801 opposite side are present the ultramafic rocks.
- Figure 4 a) mafic mineral compositions are showed. Opx vary from En91 to En61 and cpx from
- 803 En48 to En39 (Wo ~45). Olivines vary from 88 to 76 Fo%. All minerals show an iron enrichment
- from UmS to BdS. b) plagioclase diagram, An varies from 70 to 89, with UmS pl in general more
- albitic than BdS pl. Multiple measurements are plotted for each samples in a) and b).

806 Wo=wollastonite%, Di=diopside%, Hd=Hedembergite%, En=Enstatite%, Fs=Ferrosilite%;

- 807 Fo=Fosterite%; Or=Ortoclase%, Ab=Albite%, An=Anortite%
- Figure 5 Powder (<0.250 mm) spectra divided in four main groups considering different C.F.
- absorption, reflectance and spectral shape. a) pl rich rocks (Group 1a\_p), higher reflectance spectra,
- dominated by band V; ; b) px rich samples, spectra dominated by band I and II (Group 2a\_p), and
- spectra showing an association of Band I, V, II (Group 2b p, samples StC10,13,14, grey lebel); c)
- ol bering rocks, two spectra show ol band I absorption (Group 3a p), two spectra are almost
- featureless, low albedo (Group 3b\_p), reflectance of StC17 is shifted of 3%; d) chromite bearing
- rocks: Group 4a p is dominate by chromite spectra, with a weak 1µm band which can be affected
- also by ol. Group 4b p, px-chromite samples have clear band I, and band II spectrally affected by
- the chromite absorption towards infrared. Reflectance of StC1 is shifted of + 5% for clarification.
- 817 See text for more details.
- Figure 6 Slab spectra divided in four main groups considering different C.F. absorptions,
- reflectance and spectral shape. a) pl rich rocks, higher reflectance spectra dominated by band V
- 820 (Group 1\_s); b) px rich rocks, spectra dominated by band I and II; c) ol bearing rocks, spectra
- showing blue slope and a weak (Group 3a s) or absent (Group 3b s) band I, reflectance shift: StC5
- +10%, StC16 +5%, StC19 -5%, for clarity; d) low albedo spectra with very low absoprtion contrast,
- 823 chromite bearing samples (Group 4a s). Group 4b s show px-chromite samples, absorbing contrast
- and reflectance are lower than px-bearing sample in Group 2\_s. Reflectance of StC6 is shifted of –
- 825 5% for clarification. See text for more details.
- 826 Figure 7 B.C. I vs. pyroxenes composition, expressed as Fs. We have considered a weighted value
- 827 due to the presence of both opx and cpx, to compare with Cloutis and Gaffey (1991), grey symbols.
- 628 Grain sizes < 0.050 mm and < 0.125 mm were produced only for selected samples. a) powder
- 829 (<0.050 mm) spectra, a color density bar is used to show the difference of Fs value for opx and cpx
- on samples with both pyroxenes. The color variation is indicative of the px abundances (dark blue
- end indicates the Fs% of the most abundant px, light end the Fs% of the less abundant px); b)
- powders <0.125 mm compare to a) plot; c) powders <0.250 compare to b) plot, more samples are
- studied, pl rich samples StC9 and StC11 are not plotted here (B.C.V at  $\sim 1.27 \,\mu$ m); d) Slab spectra
- compare to powder spectra, all samples are plotted, pl rich samples are dominated by band V
- position (>1.050  $\mu$ m). The box in a,b,c indicate, from bottom to top, the groups 1, 2, 3 discussed in
- the spectral parameters section.

Figure 8 – B.C.I vs. pyroxene composition, expressed as weighted Wo%. Powder spectra show a

B.C. closer to pyroxene of Cloutis and Gaffey (1991). Ol rich samples are out from the trend. See

- 839 the text for more details.
- Figure 9 B.C.II plotted vs weighted Fs.% (a) and Wo% (b). The B.C. position is affected by the
- 841 OH- vibrational band at 1.9 $\mu$ m. c) enlarged view of b) (grey dashed box) with wo < 20%; it shows
- the B.C.II for opx-rich samples with  $<250 \mu m$  size, for which we have the highest number of
- samples. The B.C.II moves towards higher wavelengths increasing Wo% content.
- Figure 10 B.D.I vs. pyroxene abundance (a, b), vs. total volumetric  $Fe^{2+}$  ( $Fe^{2+}$  afu (opx)\*opx%+
- Fe<sup>2+</sup> afu (cpx)\*cpx%; c,d). a) here are not considered the spectra of StC20, 25. b) all samples.
- Powder B.D.I is linearly related to the px abundance, whereas slab B.D.I shows low  $R^2$ . c) slabs
- 847 B.D.I are linearly related with high  $R^2$  vs. the volumetric iron. d) powder of spectra are not linearly
- related to the volumetri iron, the trend can be described with a second polynomial equation. See text
- for more details. In a) selected samples are labeled, in b) are labeled StC20,25. In c), d) samples are
- in the same order of a) from left to right, with StC20,25 that have the two highest total volumetric
- iron values.
- Figure 11 B.D.II of powders are linearly related to the px abundance. a) selected samples, b) all
  samples (see also Fig. 10a,b).
- Figure 12 pl-mafic abundance vs. FeOtot from XRF (see table 2). a) pl abundance decrease
- increasing the iron bulk in the samples, mafic mineralogy shows the opposite behavior. b) show as
- pl ferrous iron abundance (from EMPA, see table 3) varies from high abundance for pl-rich rocks to
- low  $Fe^{2+}$  abundance for pl-poor samples.
- Figure 13 The stratigraphy of the igneous layering (e.g. defined by McCallum et al. (1980) and
- Radeke and McCallum (1984)) vs. the spectral stratigraphy from the spectral groups for both
- powder and slab. The Groups 1 and 2 divided the stratigraphy in two bigger layers for slab spectra.
- 861 Whereas for powder: Group 1 is characterized by samples from the Anorthosite I and II Zone, and
- Ol-bearing Zone is covered by Group 2b\_p and Group 3b\_p. Group 4 and Group 3a samples are
- from Peridotite Zone. '?' indicates the UBdS where we have one samples with very high ol
- alteration, not representative of original mineralogy.



























| Mineral abundance |       |       |       |       |       |         |            |           |
|-------------------|-------|-------|-------|-------|-------|---------|------------|-----------|
| sample            | Pl    | Срх   | Opx   | Ol    | Op    | Zoisite | Alteration | n.° point |
| StC1              | 5.10  | 0.00  | 47.00 | 19.70 | 28.30 | 0.00    | Rare       | 792       |
| StC2              | 12.40 | 0.00  | 73.70 | 13.30 | 0.60  | 0.00    | Rare       | 676       |
| StC3              |       |       |       |       | >90   |         | Rare       | 601       |
| StC4              | 11.00 | 2.80  | 85.90 | 0.30  | 0.00  | 0.00    | Rare       | 775       |
| StC5              | 6.80  | 3.10  | 25.70 | 62.30 | 2.00  | 0.00    | Few        | 762       |
| StC6              | 0.00  | 0.00  | 0.00  | 45.10 | 54.90 | 0.00    | Rare       | 603       |
| StC7              | 16.50 | 1.00  | 82.10 | 0.40  | 0.00  | 0.00    | Rare       | 711       |
| StC8              | 54.50 | 10.00 | 35.00 | 0.00  | 0.10  | 0.50    | Rare       | 804       |
| StC9              | 79.00 | 5.20  | 0.00  | 0.00  | 0.00  | 15.70   | Pl         | 705       |
| StC10             | 94.20 | 4.30  | 0.80  | 0.00  | 0.00  | 0.70    | Rare       | 718       |
| StC11             | 84.20 | 15.80 | 0.00  | 0.00  | 0.00  | 0.00    | Rare       | 755       |
| StC12             | 60.60 | 17.30 | 22.10 | 0.00  | 0.00  | 0.00    | Rare       | 720       |
| StC13             | 81.30 | 15.50 | 3.10  | 0.00  | 0.00  | 0.10    | Rare       | 686       |
| StC14             | 69.00 | 21.20 | 9.70  | 0.00  | 0.00  | 0.00    | Rare       | 739       |
| StC16             | 81.30 | 5.50  | 2.40  | 10.80 | 0.00  | 0.00    | Few-Ol     | 779       |
| StC17             | 46.30 | 7.30  | 3.70  | 34.30 | 0.00  | 8.40    | Pl; Ol     | 630       |
| StC18             | 94.10 | 4.10  | 0.00  | 0.00  | 0.00  | 1.80    | Few-Pl     | 713       |
| StC19             | 58.40 | 5.50  | 0.00  | 35.70 | 0.50  | 0.00    | Ol         | 622       |
| StC20             | 13.20 | 4.60  | 63.90 | 1.00  | 0.50  | 0.50    | Rare       | 613       |
| StC25             | 9.90  | 1.40  | 88.70 | 0.00  | 0.00  | 0.00    | Rare       | 653       |

Table 1 – Stillwater Complex samples: minerals abundance from point counting under optical microscope. Op. indicates opaque minerals. Alteration col. indicates sample alteration.  $n^{\circ}$  poi indicates the total number of counted points.

|  | STC1   | STC2  | STC3   | STC4  | STC5  | STC6   | STC7  | STC8  | STC9  | STC10 | STC11 | STC12 | STC13 | STC14 | STC16 | STC17 | STC18 | STC19 | STC20 | STC25 |
|--|--------|-------|--------|-------|-------|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| $SiO_2$  | 32.34  | 52.19 | 19.66  | 54.82 | 41.57 | 11.51  | 54.55 | 51.10 | 48.51 | 49.26 | 49.14 | 50.38 | 49.37 | 50.41 | 46.83 | 45.06 | 48.70 | 43.41 | 51.48 | 54.18 |
| $\mathrm{TiO}_2$                                   | 0.22   | 0.12  | 0.32   | 0.12  | 0.04  | 0.47   | 0.11  | 0.15  | 0.07  | 0.11  | 0.11  | 0.10  | 0.12  | 0.14  | 0.05  | 0.04  | 0.09  | 0.06  | 0.23  | 0.11  |
| $Al_2O_3$  | 7.52   | 2.85  | 12.51  | 3.91  | 3.14  | 11.76  | 5.41  | 16.83 | 31.57 | 27.23 | 30.75 | 20.39 | 26.57 | 21.07 | 26.74 | 21.15 | 29.44 | 16.57 | 9.22  | 3.89  |
| $Fe_2O_{3tot}$                                     | 16.48  | 10.80 | 19.71  | 10.15 | 13.77 | 29.52  | 9.34  | 7.06  | 1.18  | 3.03  | 1.49  | 4.95  | 3.22  | 4.45  | 4.36  | 8.09  | 1.79  | 11.15 | 14.30 | 9.63  |
| MnO  | 0.17   | 0.18  | 0.17   | 0.19  | 0.17  | 0.16   | 0.18  | 0.13  | 0.02  | 0.05  | 0.02  | 0.10  | 0.06  | 0.09  | 0.06  | 0.10  | 0.03  | 0.14  | 0.22  | 0.17  |
| MgO  | 27.86  | 31.03 | 20.07  | 27.33 | 38.56 | 18.22  | 25.69 | 12.40 | 0.84  | 3.29  | 1.04  | 9.61  | 3.76  | 7.71  | 6.73  | 13.77 | 2.05  | 18.12 | 16.58 | 27.36 |
| CaO  | 1.63   | 2.79  | 1.18   | 3.35  | 1.85  | 0.43   | 4.45  | 10.70 | 16.13 | 15.79 | 15.76 | 13.15 | 15.55 | 15.46 | 13.68 | 10.84 | 15.92 | 8.90  | 6.27  | 3.45  |
| Na <sub>2</sub> O                                  | 0.10   | 0.23  | 0.06   | 0.26  | 0.25  | 0.03   | 0.42  | 1.11  | 2.17  | 1.86  | 2.21  | 1.33  | 1.84  | 1.48  | 1.78  | 1.25  | 2.25  | 0.94  | 0.37  | 0.31  |
| K <sub>2</sub> O                                   | 0.02   | 0.04  | 0.01   | 0.04  | 0.03  | 0.01   | 0.06  | 0.08  | 0.09  | 0.08  | 0.12  | 0.06  | 0.10  | 0.13  | 0.06  | 0.04  | 0.08  | 0.05  | 0.49  | 0.05  |
| P <sub>2</sub> O <sub>5</sub>                      | 0.01   | 0.01  | 0.00   | 0.01  | 0.01  | 0.01   | 0.01  | 0.01  | 0.01  | 0.01  | 0.02  | 0.01  | 0.01  | 0.01  | 0.01  | 0.01  | 0.01  | 0.01  | 0.01  | 0.01  |
| Tot.   | 86.4   | 100.2 | 73.7   | 110.2 | 99.4  | 72.1   | 100.2 | 99.6  | 100.6 | 100.7 | 100.7 | 100.1 | 100.6 | 100.9 | 100.3 | 100.4 | 100.4 | 99.4  | 99.2  | 99.2  |
|  |        |       |        |       |       |        |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| Cr (ppm)   | 113464 | 3149  | 195794 | 3167  | 5090  | 211616 | 3274  | 635   | 65    | 302   | 53    | 615   | 259   | 660   | 75    | 57    | 122   | 230   | 1476  | 3410  |
|  |        |       |        |       |       |        |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| L.O.I.   | 0.44   | 1.25  | -0.40  | 0.79  | 4.55  | 0.37   | 1.20  | 1.23  | 0.70  | 0.54  | 0.68  | 0.83  | 0.59  | 0.92  | 2.67  | 5.16  | 1.60  | 7.75  | 1.90  | 0.76  |
| FeO  | 4.41   | 8.30  | 2.64   | 8.21  | 10.44 | 1.75   | 6.61  | 4.76  | 0.88  | 2.22  | 1.10  | 3.87  | 2.56  | 3.96  | 3.02  | 4.77  | 1.55  | 5.20  | 8.97  | 7.72  |
| Fe <sub>2</sub> O <sub>3</sub>                     | 11.58  | 1.58  | 16.78  | 1.03  | 2.17  | 27.58  | 2.00  | 1.77  | 0.20  | 0.56  | 0.27  | 0.65  | 0.38  | 0.05  | 1.00  | 2.79  | 0.07  | 5.37  | 4.33  | 1.05  |
| $\Sigma$ (FeO<br>+Fe <sub>2</sub> O <sub>3</sub> ) | 15.99  | 9.88  | 19.42  | 9.24  | 12.61 | 29.33  | 8.61  | 6.53  | 1.08  | 2.78  | 1.37  | 4.52  | 2.94  | 4.01  | 4.02  | 7.56  | 1.62  | 10.57 | 13.30 | 8.77  |

XRF - bulk rock composition

Table 2 – Bulk rock chemistry from XRF measurements for major elements and chromium. We report the L.O.I. (loos on ignition) and the amount of ferrous and ferric iron from chemical analysis (Pratt and Wilson wet chemical methods).

| orthopyr         | roxene |        |        |          |        |              |            |            |        |        |        |        |        |        |
|------------------|--------|--------|--------|----------|--------|--------------|------------|------------|--------|--------|--------|--------|--------|--------|
|                  | St1    | St2    | St3    | St4      | St5    | St7          | St8        | St10       | St12   | St13   | St14   | St16   | St20   | St25   |
| SiO2             | 57.14  | 56.90  | 58.60  | 56.23    | 56.89  | 56.54        | 55.54      | 53.99      | 55.95  | 56.43  | 55.50  | 55.86  | 53.74  | 53.31  |
| TiO2             | 0.08   | 0.11   | 0.07   | 0.13     | 0.08   | 0.11         | 0.19       | 0.23       | 0.15   | 0.14   | 0.16   | 0.26   | 0.18   | 0.17   |
| Al2O3            | 1.48   | 1.64   | 0.82   | 1.26     | 1.54   | 1.35         | 1.02       | 0.90       | 1.01   | 1.22   | 0.95   | 1.23   | 1.02   | 0.82   |
| Cr2O3            | 0.57   | 0.54   | 0.39   | 0.51     | 0.55   | 0.56         | 0.16       | 0.05       | 0.15   | 0.52   | 0.21   | 0.05   | 0.26   | 0.14   |
| FeO*             | 7.44   | 9.41   | 5.16   | 10.67    | 8.93   | 10.23        | 13.76      | 20.62      | 13.45  | 10.49  | 14.86  | 13.67  | 18.18  | 22.94  |
| MnO              | 0.18   | 0.22   | 0.13   | 0.24     | 0.21   | 0.23         | 0.29       | 0.41       | 0.30   | 0.24   | 0.34   | 0.31   | 0.32   | 0.40   |
| MgO              | 31.92  | 30.72  | 35.37  | 30.52    | 30.77  | 30.28        | 27.54      | 23.12      | 28.59  | 30.47  | 26.88  | 28.66  | 24.80  | 21.65  |
| CaO              | 1.70   | 1.29   | 0.51   | 0.87     | 1.86   | 1.38         | 2.21       | 1.33       | 1.00   | 1.14   | 1.50   | 1.10   | 1.24   | 1.04   |
| Na2O             | 0.02   | 0.01   | 0.03   | 0.01     | 0.02   | 0.01         | 0.03       | 0.04       | 0.02   | 0.03   | 0.02   | 0.01   | 0.02   | 0.03   |
| К2О              | 0.01   | 0.01   | 0.01   | 0.01     | 0.02   | 0.01         | 0.01       | 0.01       | 0.01   | 0.01   | 0.01   | 0.00   | 0.01   | 0.00   |
| Totale           | 100.56 | 100.84 | 101.07 | 100.44   | 100.86 | 100.71       | 100.74     | 100.70     | 100.62 | 100.69 | 100.44 | 101.16 | 99.77  | 100.50 |
|                  |        |        |        |          |        |              |            |            |        |        |        |        |        |        |
| Fe3+             | 0.00   | 0.00   | 0.000  | 0.00     | 0.00   | 0.00         | 0.00       | 0.00       | 0.00   | 0.00   | 0.00   | 0.00   | 0.01   | 0.00   |
| Fe2+             | 0.22   | 0.27   | 0.146  | 0.31     | 0.26   | 0.30         | 0.41       | 0.63       | 0.40   | 0.31   | 0.44   | 0.40   | 0.55   | 0.71   |
|                  |        |        |        |          |        |              |            |            |        |        |        |        |        |        |
| Wo               | 3.29   | 2.52   | 0.94   | 1.68     | 3.59   | 2.69         | 4.33       | 2.68       | 1.95   | 2.20   | 2.97   | 2.14   | 2.47   | 2.11   |
| En               | 85.46  | 83.17  | 91.47  | 82.17    | 82.84  | 81.77        | 74.65      | 64.75      | 77.54  | 81.88  | 74.01  | 77.17  | 69.05  | 61.33  |
| Fs               | 11.18  | 14.29  | 7.48   | 16.12    | 13.48  | 15.49        | 20.92      | 32.41      | 20.45  | 15.81  | 22.95  | 20.64  | 28.39  | 36.45  |
|                  |        |        |        |          |        |              |            |            |        |        |        |        |        |        |
| mg**             | 88.43  | 85.34  | 92.44  | 83.60    | 86.00  | 84.07        | 78.12      | 66.64      | 79.13  | 83.82  | 76.33  | 78.89  | 70.87  | 62.72  |
|                  |        |        |        |          |        |              |            |            |        |        |        |        |        |        |
| clinopyro        | oxene  |        |        |          |        |              |            |            |        |        |        |        |        |        |
|                  | St3    | St4    | St5    | St7      | St8    | St9          | St10       | St12       | St13   | St14   | St16   | St18   | St19   | St20   |
| SiO2             | 54.54  | 53.56  | 53.19  | 54.12    | 53.45  | 52.73        | 52.58      | 53.92      | 52.60  | 53.27  | 52.81  | 52.60  | 52.43  | 52.76  |
| TiO2             | 0.18   | 0.28   | 0.39   | 0.16     | 0.43   | 0.46         | 0.46       | 0.32       | 0.42   | 0.38   | 0.56   | 0.56   | 0.91   | 0.46   |
| AI2O3            | 1.81   | 2.10   | 2.69   | 1.67     | 1.82   | 2.10         | 1.74       | 1.68       | 1.94   | 1.74   | 2.29   | 2.25   | 2.71   | 1.73   |
| Cr2O3            | 0.99   | 0.92   | 1.17   | 1.12     | 0.34   | 0.08         | 0.06       | 0.34       | 0.26   | 0.34   | 0.10   | 0.17   | 0.34   | 0.39   |
| FeO*             | 2.41   | 4.40   | 3.80   | 3.77     | 5.70   | 8.02         | 9.08       | 5.72       | 8.13   | 6.73   | 6.03   | 7.46   | 5.90   | 6.88   |
| MnO              | 0.05   | 0.10   | 0.13   | 0.05     | 0.17   | 0.21         | 0.24       | 0.14       | 0.20   | 0.17   | 0.18   | 0.19   | 0.14   | 0.16   |
| MgO              | 17.22  | 16.29  | 16.38  | 16.38    | 15.61  | 14.43        | 14.02      | 16.14      | 14.69  | 15.60  | 15.62  | 14.83  | 15.72  | 15.31  |
| CaO              | 22.97  | 22.79  | 22.39  | 23.11    | 22.71  | 21.61        | 22.19      | 22.10      | 21.89  | 21.81  | 22.36  | 22.33  | 22.07  | 22.29  |
| Na2O             | 0.47   | 0.35   | 0.48   | 0.29     | 0.27   | 0.21         | 0.21       | 0.20       | 0.28   | 0.23   | 0.28   | 0.24   | 0.31   | 0.20   |
| K2O              | 0.00   | 0.02   | 0.01   | 0.00     | 0.00   | 0.01         | 0.01       | 0.00       | 0.01   | 0.02   | 0.01   | 0.00   | 0.00   | 0.02   |
| Totale           | 100.65 | 100.81 | 100.64 | 100.66   | 100.51 | 99.85        | 100.57     | 100.57     | 100.43 | 100.31 | 100.24 | 100.62 | 100.52 | 100.19 |
| <b>-</b> 3+      |        |        |        | <b>.</b> |        | <b>C C C</b> | <i>c</i> - | <i>c</i> - |        |        | 0.00   |        |        |        |
| Fe <sup>-</sup>  | 0.00   | 0.00   | 0.01   | 0.00     | 0.00   | 0.01         | 0.01       | 0.00       | 0.02   | 0.00   | 0.02   | 0.02   | 0.01   | 0.02   |
| Fe <sup>∠+</sup> | 0.07   | 0.13   | 0.11   | 0.11     | 0.17   | 0.24         | 0.27       | 0.17       | 0.23   | 0.21   | 0.17   | 0.21   | 0.17   | 0.19   |
| Wo               | 46.25  | 46.02  | 45.67  | 46.81    | 45.99  | 44.69        | 45.13      | 44.73      | 44.50  | 44.34  | 45.35  | 45.36  | 44.93  | 45.19  |

| En | 48.25 | 45.78 | 46.50 | 46.16 | 44.00 | 41.56 | 39.68 | 45.47 | 41.56 | 44.13 | 44.08 | 41.93 | 44.54 | 43.21 |
|----|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Fs | 3.79  | 6.93  | 6.05  | 5.95  | 9.01  | 12.95 | 14.41 | 9.05  | 12.91 | 10.68 | 9.55  | 11.83 | 9.37  | 10.89 |
|    |       |       |       |       |       |       |       |       |       |       |       |       |       |       |

# mg\*\* 92.72 86.86 88.48 88.58 83.01 76.24 73.36 83.50 76.34 80.55 82.19 77.98 82.62 79.88

| plagiocla        | ase    |        |        |        |        |        |        |        |        |        |        |        |        |       |        |
|------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-------|--------|
|                  | St2    | St4    | St5    | St7    | St8    | St9    | St10   | St12   | St13   | St14   | St16   | St18   | St19   | St20  | St25   |
| SiO2             | 51.31  | 49.28  | 50.07  | 50.53  | 49.07  | 48.57  | 49.15  | 48.82  | 48.68  | 48.81  | 48.33  | 48.98  | 47.84  | 44.18 | 48.80  |
| TiO2             | 0.05   | 0.02   | 0.03   | 0.03   | 0.03   | 0.00   | 0.03   | 0.03   | 0.03   | 0.02   | 0.00   | 0.03   | 0.03   | 0.04  | 0.00   |
| Al2O3            | 31.03  | 32.03  | 31.68  | 31.36  | 32.78  | 32.75  | 31.96  | 32.73  | 32.28  | 32.53  | 33.18  | 32.19  | 33.38  | 32.35 | 33.10  |
| FeO              | 0.16   | 0.17   | 0.14   | 0.33   | 0.36   | 0.47   | 0.50   | 0.37   | 0.36   | 0.35   | 0.40   | 0.44   | 0.34   | 0.35  | 0.19   |
| CaO              | 14.61  | 16.10  | 15.62  | 14.97  | 16.19  | 16.17  | 16.26  | 16.38  | 16.32  | 16.22  | 16.42  | 16.34  | 16.97  | 19.67 | 16.58  |
| Na2O             | 3.28   | 2.50   | 2.80   | 2.95   | 2.21   | 2.27   | 2.39   | 2.12   | 2.30   | 2.28   | 2.06   | 2.36   | 1.80   | 1.33  | 2.13   |
| K2O              | 0.12   | 0.13   | 0.07   | 0.14   | 0.10   | 0.08   | 0.08   | 0.07   | 0.09   | 0.10   | 0.06   | 0.07   | 0.07   | 0.01  | 0.08   |
| Totale           | 100.56 | 100.23 | 100.41 | 100.31 | 100.75 | 100.36 | 100.37 | 100.52 | 100.06 | 100.31 | 100.45 | 100.40 | 100.41 | 99.48 | 100.89 |
|                  |        |        |        |        |        |        |        |        |        |        |        |        |        |       |        |
| Fe <sup>2+</sup> | 0.01   | 0.01   | 0.01   | 0.01   | 0.01   | 0.02   | 0.02   | 0.01   | 0.01   | 0.01   | 0.02   | 0.02   | 0.01   | 0.08  | 0.01   |
|                  |        |        |        |        |        |        |        |        |        |        |        |        |        |       |        |
| Ab %             | 28.70  | 21.78  | 24.38  | 26.08  | 19.67  | 20.16  | 20.92  | 18.89  | 20.21  | 20.19  | 18.45  | 20.60  | 16.00  | 10.96 | 18.75  |
| An %             | 70.61  | 77.50  | 75.21  | 73.08  | 79.74  | 79.39  | 78.60  | 80.72  | 79.27  | 79.23  | 81.19  | 78.99  | 83.61  | 89.00 | 80.80  |
| Or %             | 0.69   | 0.72   | 0.41   | 0.84   | 0.59   | 0.45   | 0.48   | 0.40   | 0.52   | 0.58   | 0.36   | 0.41   | 0.39   | 0.04  | 0.45   |

olivine

|                  | St1    | St2    | St5    | St6    | St16   | St19   |
|------------------|--------|--------|--------|--------|--------|--------|
| SiO2             | 41.36  | 40.77  | 40.88  | 41.42  | 39.33  | 39.73  |
| TiO2             | 0.02   | 0.02   | 0.01   | 0.01   | 0.02   | 0.04   |
| Al2O3            | 0.00   | 0.01   | 0.01   | 0.01   | 0.01   | 0.27   |
| FeO              | 11.70  | 14.97  | 14.67  | 11.51  | 21.44  | 20.69  |
| MnO              | 0.18   | 0.22   | 0.20   | 0.13   | 0.29   | 0.28   |
| MgO              | 47.28  | 44.40  | 44.92  | 47.74  | 39.75  | 39.47  |
| CaO              | 0.03   | 0.03   | 0.04   | 0.03   | 0.04   | 0.33   |
| Totale           | 100.57 | 100.41 | 100.73 | 100.87 | 100.89 | 100.81 |
|                  |        |        |        |        |        |        |
| Fe <sup>2+</sup> | 0.24   | 0.31   | 0.30   | 0.24   | 0.46   | 0.44   |
|                  |        |        |        |        |        |        |
| Fo               | 87.65  | 83.90  | 84.34  | 87.97  | 76.53  | 77.05  |
| Fa               | 12.16  | 15.87  | 15.45  | 11.90  | 23.15  | 22.64  |
|                  |        |        |        |        |        |        |
| mg**             | 87.81  | 84.10  | 84.52  | 88.08  | 76.77  | 77.29  |

Table 3 - Microprobe average measurements of mineral phases present in our Stillwater Complex samples. Opx,cpx recalculated on base of 6 oxygen, Pl on base of 8 oxygen, Ol on base of 4 oxygen. Fe<sup>2+</sup> and Fe<sup>3+</sup> are recalculated in a.f.u. StC11 and St17 where not measured, those

samples are from the same layers and with very similar characteristics of StC9 and StC19, respectively.