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# Calibration of short-wave infraRed (SWIR) hyperspectral imaging using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to obtain continuous logging of mineral abundances along sediment cores

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1 **Calibration of Short-Wave InfraRed (SWIR) hyperspectral imaging using Diffuse Reflectance**  
2 **Infrared Fourier Transform spectroscopy (DRIFTS) to obtain continuous logging of mineral**  
3 **abundances along sediment cores**

4

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31 Abstract

32

33 Sediment cores are a major source of sub-surface data for a variety of environmental research  
34 endeavors, as well as mining and civil engineering applications. In paleo-environmental studies,  
35 fluctuations in mineral abundances along sediment cores are used to study climate change, sea-level  
36 variations, sediment dynamics, and landscape evolution. Increasing reliance on such proxies spurs  
37 the need for reliable and time-saving analytical tools and procedures. Diffuse Reflectance Infrared  
38 Fourier Transform spectroscopy (DRIFTS) is a rapid, non-destructive and accurate tool for  
39 quantification of mineral abundances. We use DRIFTS to calibrate Short-Wave InfraRed (SWIR)  
40 hyperspectral images (HSI) of a sediment core, in order to convert point-specific DRIFTS  
41 measurement of mineral abundances into a continuous record of mineral abundances along the core.  
42 Initially, single-phase and mineral assemblages of quartz, calcite, and clay mineral are created and  
43 measured by DRIFTS to establish calibration curves to convert DRIFTS data into mineral  
44 abundances, as %<sub>w</sub>t of bulk sediment samples. Mineral abundances are then measured by DRIFTS in  
45 a set of 60 samples from a core drilled into the Albegna River delta, Tuscany, Italy in the Fall of 2020.  
46 SWIR-HSI of the core are then obtained and averaged over the areas corresponding to the samples  
47 taken for point-specific DRIFTS measurements. Least squares regressions are established between  
48 SWIR-HSI and DRIFTS data over these areas. This calibration is then used to convert SWIR-HSI of  
49 the entire core into a continuous prediction of quartz, calcite, and clay minerals abundances along the  
50 core. The continuous record highlights sharp changes in mineral composition, smeared out in the  
51 discontinuous DRIFTS record. The advantages and limitations of the method, as well as its  
52 applicability to other sedimentary environments are discussed.

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58 Keywords: Infrared spectroscopy, hyperspectral imaging, sediment core, chemometrics, minerals,  
59 high resolution analysis

## 60 1. Introduction

61

62 Sediment cores are a major source of sub-surface information in stratigraphic and paleo-  
63 environmental studies. They are used to reconstruct past- climate (Miller et al., 2020), sea-levels  
64 (Kelsey et al., 2015), landscapes (Pennington et al., 2017) archeological environments (Delile et al.,  
65 2018; Salomon et al., 2018); for technical essays in mining and civil engineering (Kahraman et al.,  
66 2016), and for the assessment of natural (Grand Pre et al., 2012) and anthropogenic (Bigus et al.,  
67 2014) hazards. Variations of geochemical and mineralogical abundances along sediment cores are  
68 used as proxies for fluctuations of past climates (Solotchina et al., 2009; Wan et al., 2007; Tamburini  
69 et al., 2003), fluctuations in weathering rate, sedimentation rate, and shifts in depositional patterns  
70 (He et al., 2020; Wang et al., 2016; Hamdan et al., 2018; Lupker et al., 2012; Garzanti et al., 2010;  
71 2011; Martinelli et al., 1993). They are used to assess sediment provenance and thereby track  
72 landscape evolution (Li et al., 2014; Andrews and Eberl, 2012; Liu et al., 2020; Pe-Piper et al., 2016;  
73 Heroy et al., 2003; Wahab and Stanley, 1991). Geochemical and mineralogical quantitative analyses  
74 traditionally resort to precise but time-consuming and expensive analytical methods, such as atomic  
75 absorption spectroscopy - AAS, inductive coupled plasma mass spectroscopy – ICP-MS (Willis,  
76 1986), Scanning electron microscopy - SEM (Schulz et al., 2020), X-Ray diffraction - XRD (Moore and  
77 Robert, 1997) and Raman spectroscopy (Larkin, 2011). The accelerating growth of sediment core  
78 libraries worldwide has motivated the use of faster and less costly analytical approaches, such as  
79 portable X-ray fluorescence - PXRF (Duce et al., 2019), Attenuated Total Reflectance Fourier  
80 Transform Infrared spectroscopy - ATR-FTIRS (Milosevic, 2012), and Diffuse Reflectance Infrared  
81 Fourier Transform spectroscopy - DRIFTS (Frei and MacNeil, 2018). In the meantime, the need for  
82 high-resolution information on finely laminated sediments spurred the adaptation of non-destructive  
83 scanning and imaging techniques to sediment cores (Rothwell and Rack, 2006), most notably XRF  
84 core scanning (Davies et al., 2015), X-Ray tomography (Zonta et al., 2021; Paris et al., 2020), and  
85 hyperspectral imaging - HSI (Jacq et al., 2019a, b). Pioneering HSI on soils (Zaeem et al., 2021) and  
86 lake sediments (Makri et al., 2020; Rapuc et al., 2020; Ghanbari et al., 2020; Jacq et al., 2019a, b;  
87 Van Exem et al., 2018; Rivard et al., 2018; Butz et al., 2017; Aymerich et al., 2016) yields  
88 encouraging results. So far, HSI has been applied to organic-rich and silty-clayey lacustrine  
89 sediments and to nonwater-saturated sedimentary rocks with fairly homogenous grain size distribution

90 along core. The conversion of HSI data into chemical and mineral abundances requires calibration  
91 against standard analytical methods such as ICP-MS (Zaeem et al., 2021; Rivard et al., 2018), Loss  
92 on Ignition – LOI (Jacq et al., 2019b), particle size distribution – PSD (Jacq et al., 2019), and XRD  
93 (Greene et al., 2019).

94 FTIRS has been used for five decades (Srodo, 2002) to determine the abundance of  
95 carbonates (So et al., 2020; Henry et al., 2017), clay minerals (Srodo, 2002; Joussein et al., 2001),  
96 amorphous silica and quartz (Bertaux et al., 1998, Bandopadhyay, 2010; Melucci et al., 2019), other  
97 tectosilicates and sulfates (Muller et al., 2014; Bosch-Reig et al., 2017; Painter et al., 1978), total  
98 organic carbon (Vogel et al., 2008; Rosen et al., 2010; 2011; Hahn et al., 2011), metals (Moros et al.,  
99 2009; Siebielec et al., 2004), and plastic microparticles (Hahn et al., 2019).

100 We used DRIFTS to analyze the evolution of the provenance of sediments deposited during  
101 the Holocene in the delta of the Albegna River, in Tuscany, Italy, starting with a 14 m-long core  
102 obtained in 2020 (sediment core ALB-1). The analysis was conducted on samples, presenting an  
103 average separation of 20 cm. The analysis reveals that the sediment is almost exclusively composed  
104 of quartz, calcite and clay minerals, the abundances of which vary widely along core. In order to  
105 obtain a more continuous record of these variations, we use a high-resolution Short-Wave InfraRed  
106 (SWIR) hyperspectral images (HSI) of sediment core ALB-1, a core retrieved from the delta of the  
107 Albegna River, in Tuscany, Italy, in 2020. The HSI is averaged over the characteristic thickness (3  
108 cm) of each of the DRIFTS samples. A calibration of the HSI data using the DRIFTS data is then  
109 conducted. It allows converting the HSI into a continuous record of mineral abundances at a  
110 resolution of 3 cm. Tectosilicates in general, and quartz in particular, are not detected by SWIR-HIS.  
111 In the case at hand, however, the simplicity of the mineral assemblage allows to adduce quartz  
112 abundance from the abundance of the two other dominant mineral groups. We also attempt to provide  
113 a site-specific prediction of quartz by expecting inverse correlations with calcite or by grain-size  
114 texture effects. Practically, the method involves first the establishment of calibration curves of mineral  
115 assemblages and DRIFTS data using synthetic mixtures of minerals, in order to convert DRIFTS data  
116 into quartz, calcite, and clay content. The calibration is applied to convert the DRIFTS signature of 60  
117 samples from core ALB-1 into mineral abundances. The sediment displays marked variations in grain-  
118 size (from clay to pebble) and of moisture content along core. The SWIR-HSI of untreated core  
119 surfaces is not only sensitive to carbonates and clay minerals content, but also to grain-size and

120 moisture. We consider as work hypothesis that calibration of HSI data with DRIFTS of dry and  
121 powdered samples could improve the continuous mineral logging along sediment cores. This  
122 treatment reveals sharp step-changes in mineral abundances along the core that were poorly visible  
123 in the discontinuous record, revealing the existence of very rapid (< 100 y), irreversible paleo-  
124 environmental changes. After exposing these results, we discuss several aspects of the methodology.  
125 We first discuss our selection of DRIFT spectra peaks to assess mineral abundances and the  
126 replicability of this approach. We then discuss the relevance of the approach presented here to the  
127 establishment of continuous records of mineral abundances in other geological settings. More  
128 generally, we discuss the complementarity, advantages and limits of using a two infrared sensors  
129 approach. Finally, we discuss the origin of the layering documented in core ALB-1 and the processes  
130 that control it.

## 131 **2. General context**

132

133 Core ALB-1 was retrieved in 2020 from the Holocene fluvio-deltaic plain of the Albegna River, in  
134 Tuscany, Italy (Fig.1). With a length of 70 km and a catchment area of 750 km<sup>2</sup>, the Albegna River is  
135 one of the main coastal rivers of Tuscany. The river originates near the Quaternary Monte Amiata  
136 volcano, 1,738 m above sea-level (Fig. 1-A). The river flows south-westwards through Pliocene and  
137 Quaternary basins (Cornamusini et al., 2011; Bossio et al., 2004). It reaches the Tyrrhenian Sea north  
138 of the Giannella sand spit (Fig.1-C). The tides along the Tyrrhenian coast are microtidal averagely  
139 ranging ~ 30 cm (Bertoni et al., 2020). The climate in the area is Mediterranean, with a mean annual  
140 temperature of 13.8 °C along the coastal reaches and of 11°C in the Albegna headwaters. Mean  
141 annual precipitation ranges from 700 mm/year at the coast to 1500 mm/year on Monte Amiata  
142 (Marker et al., 2008). The Albegna River catchment drains Triassic-Cretaceous clayey calcareous  
143 limestones, succeeded downstream by Oligocene sandstone, Miocene lagoonal and marine deposits  
144 and finally Plio-Pleistocene marine clays close to the coast (Fig. 1-B, Cornamusini et al., 2011; Bossio  
145 et al., 2004; Bertini et al., 1967). A sizeable volume of sediments derived from these formations  
146 contributes to the > 30 m-thick Holocene infill of the Albegna lower valley, which was incised during  
147 the last glacial marine low stands (Mazzini et al., 1999). Geochemical and mineralogical data from  
148 widely scattered 30 surface silty-clay samples in the catchments of the Albegna and Fiora Rivers  
149 (Gliozzo et al., 2014) indicate mineral abundances in the range of 15-70% for phyllosilicates, 9- 58%

150 for quartz, and 1-34% for calcite. Phyllosilicates consist mainly of kaolinite, illite, smectite and chlorite.  
151 Feldspars (2-6%), dolomite (0-3%) and hematite (0-1%) are detected but are much less abundant.

### 152 **3. Material and Methods**

#### 153 **3.1. Field drilling**

154

155 Mechanical rotation coring was conducted on the left bank of the Albegna River, +1.5 m above the  
156 mean sea-level, close to the river mouth (Fig. 1C), next to the historic Forte delle Saline Renaissance  
157 fortified tower, and next to the Roman fluvial port of Albinia. The site lies 200 m south of the Albegna  
158 River channel, 500 m east of the sea, and 700 m north of the lagoon of Orbetello. An outer core liner  
159 was used to prevent contamination of core sections by core wall material during drilling operations.  
160 Coring allowed the retrieval of a 14 m-long continuous sedimentary succession. Stratigraphic  
161 description in the field includes estimates of sediment color, texture, hardness, and the presence of  
162 oxidation, shells, and plant fragments. Absolute ages were obtained by accelerator mass  
163 spectrometry radiocarbon dating. The samples were processed in the Center for Radiocarbon dating of  
164 Lyon UMR 5138, and measured at the LMC14 Artemis Laboratory in Saclay, France (Table 1).  
165 Radiocarbon ages were converted into calendar years using the IntCal20 Northern Hemisphere  
166 atmospheric calibration curve (Reimer et al., 2020).

167

#### 168 **3.2. Methodological approach**

169 The approach involves five consecutive steps (Fig.2). The part of the sediment core comprised  
170 between 2 m and 13.5 m below the ground surface was extracted continuously using a 2 cm-wide  
171 plastic U-channel. A total of 11.5 meters, split into 23 U-channel sub-sections (50 cm each) were  
172 entirely scanned by SWIR-HSI (Step 1). U-channels prevent damaging of laminated sequences during  
173 transport, especially highly non-cohesive sand layers. After image acquisitions, sixty samples were  
174 taken from the U-channels (see section 3.2.2.) and measured by DRIFTS (Step 2). Synthetic mineral  
175 mixtures were prepared to calibrate the conversion of these DRIFTS data into mineral abundances  
176 (Step 3). DRIFTS and SWIR-HSI data were then compared over the areas of DRIFTS sampling to  
177 convert SWIR-HSI data into mineral abundances (Step 4). This calibration was then used to obtain a  
178 3 cm-resolution continuous record of mineral abundances along the core (Step 5).

179

180 **3.2.1. Hyperspectral imaging (Step 1)**

181 Short-Wave Infrared (SWIR, Specim Ltd., Finland, OLES22.5) hyperspectral imaging of the sediment  
182 core was obtained following the protocol described in Jacq et al. (2020b). The resulting image is 1 cm  
183 wide and 11.5 m long. It consists of 45 columns and 53,220 lines of 185  $\mu\text{m}^2$ -sized pixels. Each pixel  
184 contains a record of 288 individual spectral channels spanning a range of 3,880-10,354  $\text{cm}^{-1}$ ,  
185 corresponding to a wavelength range of 965 to 2,576 nm, with a 5.6 nm resolution. The spectra were  
186 subsampled between 3,966 and 9,781  $\text{cm}^{-1}$  (1,016-2,526 nm) in order to remove noisy wavelengths.  
187 Reflectance spectra were then converted into pseudo-absorbance values, and pretreated by Standard  
188 Normal Variate and a baseline to be formatted in the same way as the DRIFTS data (Matlab R2020a,  
189 Mathworks, USA). SWIR-HSI spectra are presented in wavelength (nm) units.

190

191 **3.2.2. Sediment core sampling (Step 2)**

192 Magnetic susceptibility logging of the core (Dearing, 1999) was conducted at 3 cm-resolution using a  
193 Bartington MS2 susceptibilimeter and MS2F probe (Oxon, UK) in cgs units (centimeter-gram-second  
194 system) before the sampling of the core. Samples 3cm-thick were collected every 20 cm for DRIFTS  
195 (Figure 2, Step 2). Additional samples were collected in the thinnest stratigraphic units in order to  
196 prevent under-sampling of these units. The samples were dried in an oven at 50°C for seven days.  
197 The proportions of clay-silt, sand, and coarser fractions were measured by wet sieving through 0.063  
198 mm and 2 mm-mesh size stainless steel sieves of 10 g of sediment. The sand fraction was sieved at  
199 0.25, 0.5 and 1 mm to document grain-size distribution in the sand fraction (fine/medium/coarse  
200 sand). Subsamples of 5 g bulk sediment were set aside before the sieving and manually grinded  
201 using an agate mortar into a fine homogenous powder. The powder was dried at 50°C for 24h prior to  
202 spectroscopic measurement.

203

204 **3.2.3. Reference minerals and synthetic mineral assemblages (Step 3-A)**

205 42 synthetic mineral assemblages were produced for the calibration of the DRIFTS data. Powders of  
206 pure quartz ( $\text{SiO}_2$ ), calcite ( $\text{CaCO}_3$ ), kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), montmorillonite  
207 ( $(\text{Na,Ca})_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ ) and illite ( $\text{K,H}_3\text{O}(\text{Al,Mg,Fe})_2(\text{Si,Al})_4\text{O}_{10}[(\text{OH})_2\cdot(\text{H}_2\text{O})]$ ) were used from  
208 previously established mineral spectra databases (Chapkanski et al., 2021a,b). Samples (1 g each) of  
209 pure minerals were prepared by mixing oven-dried spectroscopic-grade potassium bromide (KBr) with



210 quartz (Q) and calcite (Ca). The clay minerals (Cm) were represented by a 1:1:1 mixture of kaolinite,  
211 montmorillonite and illite. Clay species can be successfully discriminated by FTIR spectroscopy  
212 (Srodo, 2002; Joussein et al., 2001), but, because their specific absorption bands overlap, it was  
213 decided to only consider their spectral signature collectively, to avoid any confusion (Muller et al.,  
214 2014). Further combinations were prepared: Q + Ca, Q + Cm, Ca + Cm and Q + Ca + Cm (Table 2).  
215 Precision of  $\pm 0.1$  mg is required when weighing. The powders were mixed by hand using an agate  
216 mortar and pestle for five minutes, in dry conditions. The samples were finally stored in an oven for 12  
217 hours prior to spectroscopic measurement to maintain a low moisture content.

218

#### 219 **3.2.4. DRIFTS analysis (Step 3-B)**

220 Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) was conducted on the  
221 sediment core samples and on the synthetic mixtures. The texture of the powders ensures a good  
222 and homogenous penetration of infrared light into the samples (Bertaux et al., 1998). The mid-  
223 reflected infrared light spectrum of each sample was obtained using a FT-IR Frontier Spectrometer  
224 with a KBr beam splitter, a diffuse reflectance sampling accessory and a TGS detector (PerkinElmer,  
225 Waltham, MA, USA). Spectroscopic measurements were conducted in a temperature- and humidity-  
226 controlled room to ensure stable and constant optical air properties during measurement. 10 mg of  
227 each sample was placed into a micro-cup and scanned from 4,000 to 450  $\text{cm}^{-1}$ , with a 1  $\text{cm}^{-1}$   
228 resolution, corresponding to wavelengths of 2,500 to 22,222 nm. Dried powdered potassium bromide  
229 (KBr) was used as background sample. Supplementary technical details are provided in Chapkanski  
230 et al., (2020). Middle Infrared spectral data feed a data matrix of “n” lines (where “n” is the number of  
231 spectra/samples) and “p” columns (where “p” is the quantity of spectral bands). The reflectance  
232 spectra were converted to absorbance, standardized, and finely baselined using Standard Normal  
233 Variate and Baseline pretreatments (Camo Unscrambler 10.3, Oslo, Norway). DRIFT spectra are  
234 presented in wavenumber ( $\text{cm}^{-1}$ ) units.

235

#### 236 **3.3. Conversion of DRIFT spectra into mineral abundances (Step 3-C)**

237 Absorbance mid-infrared spectroscopy has been applied to the quantification of mineral assemblages  
238 (Srodon, 2002) because the amount of absorbed infrared radiation is proportional to the mineral mass  
239 fraction (%weight), thus obeying to the Lambert-Beer’s law (Pichard and Frohlich, 1986; Bertaux et al.,

240 1998). Therefore, simple linear regressions (Moosavi and Ghassabian, 2018) can be applied to  
241 convert the areas of absorbance peaks into weight concentrations (Table 2). Spectroscopic  
242 measurements were repeated three times on each synthetic mixture to assess reproducibility. The  
243 most discriminating absorbance peaks were selected to quantify the %weight of each mineral species.  
244 The center of these peaks are located as follows: for quartz (Q) at 1,874  $\text{cm}^{-1}$ , 1,160  $\text{cm}^{-1}$ , and 696  
245  $\text{cm}^{-1}$ ; for calcite (Ca) at 2,512  $\text{cm}^{-1}$ , 875  $\text{cm}^{-1}$ , and 848  $\text{cm}^{-1}$ ; and for clay minerals (Cm) at 3,696  $\text{cm}^{-1}$ ,  
246 3,622  $\text{cm}^{-1}$ , and 1,112  $\text{cm}^{-1}$ . The baselined area of these peaks was quantified using the software  
247 PerkinElmer Spectrum (Waltham, MA, USA). Overlapping peak areas between the discriminating  
248 peaks were excluded to avoid over-quantification. Pure mineral end-members were used as zero-  
249 abundance standards for other end-member minerals. For instance, the pure quartz spectrum was  
250 used as standard zero for calcite calibration. Therefore, the linear regression was used to provide Q,  
251 Ca and Cm mineral weight estimates for each sample following: Mineral weight % = (peak area - a)/b.  
252 Linear coefficient of determination ( $R^2$ ), mean values, and the standard deviations of residual values  
253 were used to evaluate the performance of the calibration (Moosavi and Ghassabian, 2018). Best  
254 curve calibrations were obtained at 1,160  $\text{cm}^{-1}$  for quartz, 2,512  $\text{cm}^{-1}$  for calcite, and 3,622  $\text{cm}^{-1}$  for  
255 clays. The calibration was then used to quantify mineral species in the synthetic assemblages in order  
256 to evaluate the performance of the calibration on samples of known composition (Table 2). Finally, the  
257 calibration was used for the quantification of Q, Ca, and Cm abundances in the 60 samples of core  
258 ALB-1.

259

#### 260 **3.4. Calibration of HSI data for mineral abundance prediction (Step 4 and 5)**

261 The hyperspectral image was down-sampled to a 3 cm-core thickness resolution over the areas  
262 occupied by each DRIFTS sample, such as to match the DRIFTS measurements. The DRIFTS-  
263 derived mineral abundance of the 60 sampling depth intervals (Fig. 2) was then matched to the  
264 corresponding SWIR-HSI spectra matrices. The two datasets were then subjected to partial least  
265 squares regressions (Wold et al., 1984) using the software Camo Unscrambler 10.3 (Oslo, Norway) to  
266 relate quartz, calcite and clay mineral abundances to the corresponding SWIR-HSI spectra obtained  
267 by hyperspectral imaging. Linear coefficients of determination ( $R^2$ ) and root mean square errors  
268 (RMSE) were used to evaluate the performance of these regressions and p-values were provided to  
269 verify their statistical significances. Regression coefficient weight vectors of cumulated PLSR

270 components were used to assess the contribution of each wavelength to the correlation. The  
271 calibration was then used to assess the abundance of quartz, calcite, and clay minerals continuously  
272 along core ALB-1 at 3 cm-resolution using the SWIR-HSI spectral dataset, yielding a total of 313  
273 measurements over the 14 m-long core. The same PLSR model was also applied to produce maps of  
274 mineral abundances. The same PLSR model was also applied to all the HSI pixels (45 columns by  
275 53,220 lines) to produce mineral abundance maps and characterize the deposits at resolution of 185  
276  $\mu\text{m}$ .

## 277 **4. Results**

### 278 **4.1. Stratigraphy, grain-size and magnetic susceptibility in core ALB-1**

279 Sediment core ALB-1 intersected three main stratigraphic units (Fig.3). Basal Unit 1 (- 13.5 to - 8.5 m  
280 depth) is relatively homogenous and is composed of up to 70%<sub>wt</sub> fine- to medium-sized grey shelly  
281 sand. Its magnetic susceptibility (MS) is low (0-80 cgs). Shell concentration is highest at its base (sub-  
282 unit 1-A) while the overlying sub-unit 1-B shows coarser and homogenous sands. Unit 2 (- 8.5 to - 3.5  
283 m depth) is extremely heterogeneous and composed of alternations of silty clays and sand layers.  
284 Brownish, poorly magnetic silty clays at the base of unit 2 (in SU2-A) amount to 70%<sub>wt</sub> of the  
285 sediment. The overlying sub-unit 2-B is a succession of grey clayey/shelly sand and gravel.  
286 Magnetic values range from 0 to 300 cgs with marked peaks in coarse sand and gravelly layers. The  
287 topmost sub-unit (2-C) is made of interbedded brown, weathered silty clay and sand layers. A well-  
288 sorted brown medium sand (70%<sub>wt</sub> of the sand fraction) layer marks the top of sub-unit 2C. Magnetic  
289 susceptibility decreases upward throughout unit 2. The last, and topmost stratigraphic unit (SU3)  
290 consists of massive, weathered grey silty clay (90%<sub>wt</sub> of the sediment) dotted by carbonate  
291 concretions near its base (SU3-A). Its upper part (SU3-B) is made of dark brown alternations of silty  
292 clay and sand containing roman pottery sherds with MS values ranging from 0 to 200 cgs.

293

### 294 **4.2. Peak identification of Infrared spectra**

#### 295 **4.2.1. DRIFT spectra of synthetic assemblages**

296 A selection of DRIFT spectra of pure mineral species and species combination is provided on Figure  
297 4. Quartz exhibits distinctive absorbance peaks at 1,872  $\text{cm}^{-1}$ , 1,610  $\text{cm}^{-1}$ , 1,352  $\text{cm}^{-1}$ , 1,160  $\text{cm}^{-1}$ , 813  
298  $\text{cm}^{-1}$  and 696  $\text{cm}^{-1}$ . Calcite is identified by peaks at 2,984  $\text{cm}^{-1}$ , 2,874  $\text{cm}^{-1}$ , 2,512  $\text{cm}^{-1}$ , 1,797  $\text{cm}^{-1}$ ,

299 1,623 cm<sup>-1</sup>, 1,400 cm<sup>-1</sup>, 875 cm<sup>-1</sup>, 848 cm<sup>-1</sup>, and 714 cm<sup>-1</sup>. Clays (kaolinite, montmorillonite, and illite)  
300 absorb mostly at 3,696 cm<sup>-1</sup>, 3,624 cm<sup>-1</sup>, 1,240 cm<sup>-1</sup>, 1,111 cm<sup>-1</sup> and 792 cm<sup>-1</sup>.

301

#### 302 **4.2.2. DRIFT spectra of core samples**

303 Figure 5 provides descriptive statistics (mean, maximum, minimum, Q1 and Q3 quartiles) of all  
304 combined core sample DRIFT spectra in the SWIR and MIR light ranges. Absorbance peaks were  
305 attributed to specific inorganic and organic compounds using previously established mineralogical  
306 spectra database (Chapkanski et al., 2021a,b) as well as extensive spectra libraries (Chukanov and  
307 Chervonnyi, 2016). Clay minerals, especially Kaolinite - Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> and Montmorillonite -  
308 (Na,Ca)<sub>0,3</sub>(Al,Mg)<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub> are associated with absorbance peaks at 3,696 and 3,626 cm<sup>-1</sup> and  
309 around 3,400 to 3,350 cm<sup>-1</sup> in the O - H stretching vibration region. Carbonates, especially calcite  
310 CaCO<sub>3</sub> is associated with absorbance peaks at 2,986 cm<sup>-1</sup>, 2,876 cm<sup>-1</sup>, 2,640 to 2,460 cm<sup>-1</sup>, 1,460 to  
311 1,360 cm<sup>-1</sup> and 874 cm<sup>-1</sup>. Tectosilicates, especially quartz (SiO<sub>2</sub>) clearly absorb at 1,160 and 696 cm<sup>-1</sup>  
312 while peak of feldspars occurs at 1,290 to 1,270 and 795 cm<sup>-1</sup> and could be specifically attributed to  
313 albite NaAlSi<sub>3</sub>O<sub>8</sub> and orthoclase KAlSi<sub>3</sub>O<sub>8</sub>. Inosilicate and nesosilicate minerals could absorb at 970  
314 and 650 cm<sup>-1</sup>. Chlorite and mica groups generated the absorbance peak observed at 1,630 cm<sup>-1</sup>.  
315 Aliphatic C-H bands absorb at 2,930 cm<sup>-1</sup> and unsaturated bands of alkenes C=C absorb at 1,642 cm<sup>-1</sup>  
316 1.

317

#### 318 **4.2.3. Short-Wave Infrared spectra of sediment core images**

319 The SWIR spectra show areas of absorbance related to organic and inorganic compounds (Fig. 5).  
320 The two main absorption peaks near 1,440 nm and 1,925 nm are produced by hydroxyl bonds mainly  
321 induced by moisture (Palmer and Williams, 1974), but they can also be produced by organic and  
322 inorganic compounds, especially clays. Clays show absorption peaks related to Al-OH bonds between  
323 2,200-2,220 nm and to O-H bonds around 1,410 nm, 2,340 nm and 2,450 nm (Madejova et al., 2017).  
324 Carbonates, chlorite and micas also produce multiple absorption peaks around 2,282 and between  
325 2,310-2340 nm, but these often overlap with other compounds, such as organic matter (Cloutis, 1989;  
326 Krupnik and Khan, 2019; Viscarra Rossel and Behrens, 2010). Organic (C-H) bonds produce  
327 numerous absorption peaks, especially around 1,056 nm, 1,146 nm, 1,400 nm, 2,300-2,350 nm and

328 2,400-2,450 nm (Cloutis, 1989). Tectosilicates, including quartz, have no specific absorption peaks in  
329 the investigated spectral range (Krupnik and Khan, 2019).

330

### 331 **4.3. Calibrations of mineral abundances**

#### 332 **4.3.1 Performance of the synthetic sample cross-calibration**

333 Weight concentrations (wt%) of minerals (quartz, calcite and clay minerals) were obtained using linear  
334 regression equations (Fig 6). Predicted values were plotted against known weight concentrations in  
335 order to evaluate the performance of the mineral quantifications (Fig. 6). Quartz, calcite and clay  
336 minerals were successfully predicted in single and multi-phase samples with  $R^2 >$  of 0.9. All  
337 correlations are significant with p-values  $<$  0.05. Mean and standard deviations of residual values  
338 show slight underestimation of the prediction in single and multi-phases (from -0.5 to -1.5). The  
339 standard deviation ranges from 2.2 to 7.

340

#### 341 **4.3.2 Performance of the synthetic sample to core sample DRIFTS calibration**

342 The linear regressions established using our synthetic standards were applied to the mid- infrared  
343 spectrum of the sediment cores samples (total of 60) to calculate quartz, calcite and clay minerals  
344 abundances (Fig. 3.C). Predicted values (in wt%) range between 14 and 64% ( $\pm 0.2$ ) for quartz, 0 and  
345 43% ( $\pm 0.7$ ) for calcite, and 0 and 41% ( $\pm 0.9$ ) for clays. Quartz wt% is positively correlated with  
346 medium (0.48) and fine (0.53) sand fractions and bears negative correlation with the silty-clay (-0.56)  
347 fraction (Table 3). In contrast, clay minerals wt% is highly correlated to the clay-silt fraction (0.91) and  
348 negatively correlated to the medium (-0.78) and fine (-0.52) sand fractions. Calcite wt% shows no  
349 specific correlation with any grain-size fraction.

350

### 351 **4.4 Calculation of mineral abundance along core ALB-1**

#### 352 **4.4.1 Performance of the DRIFTS-core SWIR image calibration**

353 Partial least squares regression (PLSR) was used to create a predictive model of quartz, calcite and  
354 clay abundance at regularly spaced, 3 cm-thick intervals along core ALB-1. The PLSR calibration was  
355 carried out between DRIFTS-derived mineral abundances in the 60 core samples and their SWIR  
356 spectra obtained by hyperspectral imaging (see section 3.4). The PLSR statistical performance is  
357 shown on Fig. 7. Quartz wt%, calcite wt%, and clay minerals wt% are successfully predicted based on

358 the SWIR spectra using seven latent variables (PLS components). In addition to statistical  
359 parameters, the plot analysis of the raw regression coefficients allows for evaluating the influence of  
360 absorbance bands on the PLS regression loading weights (Vogel et al., 2008; Hahn et al., 2011;  
361 2018). High coefficients (either positive or negative) contribute significantly to the prediction of the  
362 major mineralogical components (Fig. 7). Calcite regression coefficients show positive values for  
363 spectral regions specific to carbonates (2,237 nm, 2,500 nm) and organic matter (1,056 nm, 1,146  
364 nm), and negative values for spectral regions induced by clays (1,422 nm, 2,208 nm and 2,415 nm,  
365 Cloutis, 1989; Krupnik and Khan, 2019; Madejova et al., 2018; Viscarra Rossel and Behrens, 2010).  
366 Positive regression coefficients of clay minerals are related to specific wavelengths of phyllosilicates  
367 (1,411 nm, 1,900 nm, 2,202 nm and between 2,380-2,450 nm), while the negative coefficients are  
368 related to hydroxyl bonds probably induced by interstitial moisture between the coarser grains (1,445  
369 nm, 1,838 nm, 1,945 nm) and to chlorites (2,292 nm, Palmer and Williams, 1974; Cloutis, 1989;  
370 Krupnik and Khan, 2019; Viscarra Rossel and Behrens, 2010). Quartz regression coefficients show  
371 positive values for spectral regions specific to hydroxyl bonds (1,445 nm and 1,945 nm) and stand out  
372 for their anti-correlation with carbonates (-0.82) and clay minerals (-0.42), particularly pronounced for  
373 the hydroxyl and carbonates bonds (2,237 nm, 2,500 nm, Fig. 7).

374

#### 375 **4.4.2. Performance of the continuous logging and mineral mapping along core ALB-1**

376 The calibrated PLSR model was applied to each hyperspectral image data averaged over 3 cm bins,  
377 along the sediment (total of 313 bins) in order to assign continuous logging mineral abundances of  
378 quartz, calcite and clay minerals (Fig. 3.D). Predicted values range within 19-58% ( $\pm 4$ ) for quartz, 4-  
379 48% ( $\pm 3$ ) for calcite and 0-37% ( $\pm 3$ ) for clay minerals. They display a high degree of agreement with  
380 DRIFTS-derived abundances. Predicted quartz wt% is positively correlated with fine-sand (0.62) and  
381 total sand (0.60) fractions, and shows negative correlations with clay minerals (-0.68) and the clay-silt  
382 fraction (-0.58, Table 3). Predicted calcite wt% shows no specific correlations with other mineralogical  
383 or physical properties of sediments. Predicted clay minerals wt% show strong correlation with the  
384 clay-silt fraction (0.86) and hydroxyl bonds peak at 1,450 nm (0.68) and are negatively correlated to  
385 the total and medium sand fractions. The basal stratigraphic unit (SU1) is notably rich in quartz and  
386 poor in clay compared to other units. For SU1, differences between SWIR-HSI predicted and DRIFTS  
387 inferred mineral abundances are averagely 0.33, -0.44 and -0.27 for quartz, calcite and clays

388 respectively. The high resolution maps of mineral abundances (Fig.3D) reveal a faint layering  
389 produced by fluctuations in quartz abundance, while calcite and clay content remains fairly stable.  
390 The medium stratigraphic units (SU2) is highly heterogeneous, but it stands out for its higher calcite  
391 content than units SU1 and SU3, and for its higher clay content relative to SU1. For SU2, differences  
392 between predicted and observed mineral abundances are averagely -1.07, 0.26 and -0.35 for quartz,  
393 calcite and clays. SU3 is notably clay-rich and calcite-poor compared to the other units. For this unit,  
394 differences between predicted and observed mineral abundances are averagely 5.07, 0.17 and 1.34  
395 for quartz, calcite and clays respectively.

396

## 397 **5. Discussion**

### 398 **5.1. Peak selection for DRIFTS assessment of mineral abundances and replicability**

399 Numerous studies reported satisfactory mineral calibrations and predictions using Fourier Transform  
400 InfraRed (FTIR) measurements on samples with known mineral contents (Pichard and Frohlich, 1986;  
401 Bertaux et al., 1998; Moosavi and Ghassabian, 2018). Based on these previous approaches, we  
402 converted DRIFTS data into mineral abundances using linear regressions calibrated on single and  
403 multi-phase synthetic mineral assemblages. Qualitatively, quartz, calcite and clay minerals can be  
404 identified easily in the infrared spectra (Fig. 4) owing to their specific peaks. In quantitative  
405 investigations, however, non-overlapping peaks should be selected (Pichard and Frohlich, 1986).  
406 Previous quantitative studies used peaks centered at  $693\text{ cm}^{-1}$  and  $712\text{ cm}^{-1}$  to respectively assess  
407 quartz and calcite abundances (Pichard and Frohlich, 1986). At these wavenumbers, however,  
408 overlaps with clay mineral peaks tend to generate unwanted quantitative distortions, so that better  
409 predictions were obtained using  $1,160\text{ cm}^{-1}$  for quartz and  $2,512\text{ cm}^{-1}$  for calcite. Calcite is the most  
410 abundant carbonate mineral in our sedimentary sequence, but its peak could be produced in other  
411 natural environments by additional carbonates, in particular aragonite (triple bond at  $2,546$ ,  $2,524$  and  
412  $2,500\text{ cm}^{-1}$ ), dolomite ( $2,526\text{ cm}^{-1}$ ) and magnesite ( $2,538\text{ cm}^{-1}$ ). Among clay minerals, slight chemical  
413 variations can induce overlapping bonds (Madejova and Komadel, 2001) and different peak shapes  
414 (Henry et al., 2017). To overcome this problem, we have combined kaolinite, montmorillonite, and illite  
415 absorbances (Muller et al., 2014). The best calibration was obtained using a peak centered at  $3,622$   
416  $\text{cm}^{-1}$ , where the three clay species absorb. The accuracy of the linear regressions (Fig. 6) is  
417 satisfactory, with high  $R^2$  coefficients, low residual values, and therefore a direct relationship between

418 absorbance and mineral abundance. Still, discrepancies between known single-phase mineral  
419 concentrations and DRIFTS-inferred abundances tend to increase at very low (< of 2%) and high (> of  
420 50%) mineral concentration (Henry et al., 2017). Departure from the linear regression at high  
421 concentration could result from the lower density of the synthetic powder at such values, whereas  
422 departures at low concentration could be influenced by detection limits (Vogel et al., 2016). In multi-  
423 phase mineral concentrations, DRIFTS-inferred abundances remain satisfactory (Fig. 6) showing that  
424 the chosen peaks are not influenced by the absorbance of other minerals.

425 PLS regressions have been widely used to calibrate mineral abundances in FTIR spectra (Fernandes  
426 et al., 2020; Hahn et al., 2018; Muller et al., 2014). Predictions often show great performances and  
427 efficiency because the calibrations are based on the entire set of wavenumbers and therefore all  
428 absorbance peaks are considered. However, as certain peaks are common for two or more mineral  
429 phases, leading to over or under estimations (Vogel et al., 2016). Besides, the PLS calibration is  
430 population-specific, and must be rerun on each new dataset requiring the availability of the entire  
431 calibration dataset. However, these later are often inaccessible. To overcome this issue, this study  
432 provides linear regressions that are easily reusable for natural sediment spectra.

433

## 434 **5.2. Calibration of high-resolution imaging SWIR spectra and DRIFTS-inferred mineral** 435 **abundances**

436 In the mid-infrared range used in DRIFTS, absorbance is controlled by vibrations of molecular bonds  
437 and functional groups. Therefore, peaks are very meaningful in the detection of carbonates and  
438 silicates (Fig. 5). By contrast, in the shorter infrared range (SWIR), absorbance is controlled by broad  
439 bonds, overtones and combination of functional groups (Robertson et al., 2016). Consequently, HSI-  
440 derived spectra are not sensitive to certain mineral phases such as tectosilicates (quartz and  
441 feldspar), some oxides, phosphates and sulfides (Krupnik and Khan, 2019). Moreover, spectral  
442 analyses are commonly based on chemometrics which, to overcome the absence of well-defined  
443 peaks, handle the entire range of wavelengths. Here, we use a PLS regression to assess the  
444 relationship between the DRIFTS-inferred mineral abundances and core image spectra, because the  
445 PLS regression allows us to assess the accuracy of the calibration. The analysis of PLS regression  
446 coefficients is commonly used to evaluate the performance of prediction models (Vogel et al., 2008;  
447 Hahn et al., 2011). Models relying on direct relationships between the investigated minerals and the



448 spectra (such as the SWIR-HSI models for calcite and clay minerals) are considered reliable and  
449 replicable because absorbance is directly influenced by specific functional bands in the crystalline  
450 structure of the minerals (Hahn et al., 2011, 2018). In contrast, models based on indirect relationships  
451 (such as the SWIR-HSI model for quartz) rely on inter-correlations between different mineralogical or  
452 physical properties that occur in specific sedimentological configurations and may, therefore, not be  
453 replicable elsewhere. In the present study, the good SWIR-HSI predictions of calcite and clay  
454 minerals result from a direct relationship to their respective functional groups. In the case of the clays,  
455 the correlation ( $> 0.60$ ) that exists between clay minerals and clay-silt texture and hydroxyl bonds (see  
456 section 4.4.1, Table 3) may not result from intrinsic spectral properties of the clays, but rather from  
457 grain-size and moisture effects affecting the SWIR spectra. Nonetheless, dried and ground samples  
458 yield DRIFTS-derived abundance trends and values that are similar to that of the SWIR data implying  
459 that the SWIR-HSI prediction of clay minerals is mainly based on their spectral functional bonds, not  
460 by grain-size or moisture in the core. Similarly calcite predictions show no correlations with the  
461 physical properties of the core. By contrast, the acceptable prediction of quartz abundance by SWIR-  
462 HSI cannot result from the direct measurement of functional groups, as they do not reflect in that  
463 spectral range (see section 4.2.3.). The SWIR-HSI predicted quartz show significant positive  
464 correlations ( $> 0.60$ ) with fine and total sand fractions (Table 3) and negative correlations ( $< -0.6$ ) with  
465 the clay minerals. Moreover, the raw PLSR coefficients of quartz are negatively correlated ( $-0.82$ ) with  
466 the calcite coefficients (Fig. 7). Therefore, quartz prediction by SWIR-HSI is made successful here  
467 owing to its close association to a fine and medium sand characterized by a relatively low calcite and  
468 clay mineral content, as opposed to silty-clay (rich of clay minerals) or shelly (rich of calcite) sediment  
469 with more heterogeneous textures. This association between well sorted, fine-to medium sand, and  
470 abundant quartz is a common characteristics of sediments that however is far from systematic.  
471 Therefore, the use of the methodology should be conducted with care, with a substantial site-specific  
472 foreknowledge of the sediment composition and of its variations. Used inappropriately, the model will  
473 generate significant inaccuracies.

474

### 475 **5.3. Two-sensors infrared approach: complementarity, advantages and limits.**

476 The two-sensor approach relies on the near- and mid-infrared electromagnetic ranges (Fig. 5).

477 DRIFTS provides a precise quantification of quartz, calcite and clay minerals content owing to its high

478 sensitivity to specific functional bands in the mid-infrared range: O-H, N-H, C-H stretching, H-O-H  
479 deformation, CO<sub>3</sub>, Si-O stretching, Si-O-Al and Fe-O (Russell & Fraser, 1994; Chukanov &  
480 Chervonnyi, 2016). The use of dried, ground samples ensures homogeneity and replicability of  
481 measurements. The analysis does not alter the chemistry and mineralogy of the samples, which can  
482 therefore be reused in other analyses. Compared to X-Ray Diffraction, DRIFTS is less sensitive to  
483 mineral phases present in small amount. However, is not subject to analytical biases introduced by  
484 the differential settling or preferred orientations of minerals (Herbert et al., 1992). Besides, owing to its  
485 wide range of wavenumbers (from 4.000 to 450 cm<sup>-1</sup>), DRIFTS provides good qualitative  
486 determination of clay minerals directly on bulk sediments and it is sensitive to both amorphous silica  
487 (Meyer-Jacob et al., 2014; Frohlich, 1989) and organic compounds (Francos et al., 2021; Chapman et  
488 al., 2001). Therefore, it constitutes a relevant alternative to conventional XRD for the calibration of  
489 mineral abundance based on hyperspectral images (Greene et al., 2019). To conduct an optimal HSI  
490 modelling, calibration samples should cover the entire range of mineral concentrations (Vogel et al.,  
491 2008), which is found in the image. To capture the expected range, samples should be collected at  
492 regular, and rather short depth-intervals along the core, generating a sizeable number of samples. To  
493 process such a large number of samples, DRIFTS is also appropriate because it can be carried out on  
494 small (10 mg) samples, because it do not involve hazardous chemical materials nor dangerous  
495 radiation emissions. Sample preparation is quick (~1 min/sample) and simple. The establishment of  
496 the calibration curves using synthetic mixtures is the most time-consuming step, but future users can  
497 simply reuse the linear regression coefficients provided in this study in order to obtain (semi)  
498 quantitative mineral abundances from the DRIFT spectra of natural sediments.

499 Although near-infrared spectra obtained by hyperspectral core-imaging are less sensitive to mineral  
500 composition and not sensitive to tectosilicates, they provide unprecedented time-saving (2 min/meter),  
501 high-resolution investigations (185 μm<sup>2</sup> pixel) in a completely non-invasive and non-destructive  
502 manner. The main challenges arise from the irregular and heterogeneous state of the sediment core  
503 surface, which often presents particle size and humidity variations that strongly impact the near  
504 infrared spectrum, leading to prediction bias (Verpoorter et al., 2014). For this reason, calibrations  
505 with mineral abundance values inferred by the DRIFTS on powdered and dry samples constraint the  
506 PLSR algorithm to specific-absorbance of minerals and reduce the effects of moisture and grain-size.  
507 The latter can be easily detected using two main absorptions bands by O-H bonds around 1,440 nm

508 and 1,925 nm, but also by the rise of the spectra baseline in the Near- and Mid-Infrared ranges (Fig  
509 5). In the present study, low deviations between DRIFTS-inferred and SWIR-HSI predictions of  
510 minerals (< 1.5, see section 4.4.2.) suggest that the heterogeneous grain-size state of the sediment  
511 core surface is overcome by the PLSR modelling. By contrast, the prediction of quartz remains  
512 strongly dependent of site-specific sediment and mineralogical characteristics.

513

#### 514 **5.4. Depositional environments encountered along core ALB-1**

515

516 The palaeovalley of the Albegna River has been incised during the last glacial sea-level low stands; it  
517 was subsequently infilled by marine and fluvial sediments during the Late-glacial to Holocene  
518 transgression (Mazzini et al., 1999). The delta of the Albegna River has progressively prograded and  
519 filled its valley, while a sand-spit was building up farther offshore, progressively isolating a lagoon  
520 from the open sea. The delta is therefore expected to have grown first in an open marine  
521 environment, and then in a lagoonal environment, before reaching the sand spit and shedding its  
522 sediment, along the sand spit foreshore. The core is located within the former lagoon, immediately  
523 behind the sand spit, at a location that probably emerged just as the emerged delta floodplain was  
524 reaching the sand spit,

525 Non-continuous grain-size analysis, continuous magnetic susceptibility, and mineral core-logging  
526 reveal three stratigraphic units, which we subdivided into two-three sub-units (Fig. 3). The lower  
527 sequence SU1 contains thin (1 cm-thick) silty-clay layers interbedded with fine- to medium- grained,  
528 quartz-rich sand containing occasional shells and well-rounded gravel. Considering its age (> 5,300  
529 BCE), unit SU1 can be interpreted as deposited in an open marine environment, during the  
530 transgression and maximum flooding of the Albegna palaeo-valley. The slight upward coarsening,  
531 from SU1-A to SU1-B, may reflect the progradation of the Albegna River delta (Styllas, 2014) after the  
532 maximum flooding. It is associated with a slight but continuous increase in quartz abundance, which  
533 may result from the positive correlation between quartz abundance and sand grain size. The  
534 continuous record (Fig. 3D) reveals an abrupt superposition of the overlying deposits (SU2-1),  
535 composed of organic clays. This facies is reminiscent of the quiet lagoonal environment still found  
536 today in the remain parts of the lagoon, and is therefore interpreted as resulting from the rapid  
537 development of lagoonal conditions behind the sand spit (5,500 to 5,370 BCE) during the Atlantic.

538 This unit is overlaid by extremely heterogeneous sediments (SU2-B) consisting of fine- to medium-  
539 grained sand deposits interbedded with silty-clayey layers. Calcite content is at its highest and  
540 correlates with layers of medium- to coarse-grained sand made of shell fragments. This facies  
541 indicates a highly biologically productive in the shallow lagoon occurring between 4,240 and 4,000  
542 BCE) at the end of the Atlantic. The greater abundance of sand, compared to the lagoon of Orbetello  
543 farther south, indicates the proximity of either an inlet in the sand spit, or/and, most likely, the  
544 increasing proximity of the Albegna River mouth, as the river delta progrades across the lagoon  
545 toward the coring site. Local peaks in magnetic susceptibility are produced by gravely beds rich in  
546 shell fragments and may represent the reworking of the coarsest river sediments. The SU2-B to SU2-  
547 C evolution from a reducing to oxidizing environment (grey to brown-colored sediments) and the  
548 increase in grain-size (from fine-medium- to coarse-grained sand) reflects the progressive shoaling of  
549 the lagoon, as the Albegna River mouth gets closer to the coring site. The highest unit (SU3) is  
550 composed of emerged floodplain sediments, deposited on the banks of the Albegna River, once the  
551 coring site had been integrated into its delta plain between 2,880 and 2,630 cal BC, during the  
552 Subboreal. The overbank deposits consist of weathered silty-clay, rich in clay minerals, cemented by  
553 carbonate concretions deposited near the water table. The top of the core (SU3-B) consists of dark-  
554 brown silty-clay and unsorted sands. Its dark brownish color may reflect more advanced pedogenesis,  
555 in a floodplain progressively less frequently subjected to flooding. However, interpretation is made  
556 difficult by the fact that this sediment has been strongly reworked by anthropogenic activity, which is  
557 attested by the high density of Roman sherds in this top unit.

558

## 559 **5.5. Wider significance**

560 The widespread use of sediment cores for a variety of environmental research, mining and civil  
561 engineering applications provides a favorable context for the development of fast techniques that do  
562 not require time-consuming pretreatments with chemical products. The need for fast and easily  
563 applied techniques encourages approaches based on continuous core-logging calibrated on punctual  
564 analyses (Greene et al., 2019). The two-sensor infrared methodology proposed here, involving  
565 DRIFTS and SWIR-HSI for the continuous logging of mineral abundances along sediment cores,  
566 provides a simple and time-saving approach. Hyperspectral imaging has already demonstrated its  
567 added value in the study of lacustrine environments (Sorrel et al., 2021; Makri et al., 2020; Butz et al.,

2017; Aymerich et al., 2016). Its application to a wider range of sedimentary environments remains to be tested, especially in contexts, such as here, where substantial grain-size variations occur along core. Here our combined two infrared sensor approach shows sharp mineralogical variations between subunits and within subunits. The maps of mineral abundances provide extremely high-resolution horizontal and vertical values of abundances, highlighting laminations and the fine-scale architecture of the sediment layers. Our analysis, albeit restricted to three major mineral species and groups, illustrates variations that can be tied to major changes in the depositional environment (open sea, lagoonal, fluvio-deltaic). We believe that the high resolution prediction of calcite and clay minerals could be easily applied in other sedimentological environments, but for prediction of quartz we rather recommend to use Mid-Wave InfraRed (MWIR: 2,700-5,300 nm) or Long-Wave InfraRed (LWIR: 8,000-12,000 nm) hyperspectral cameras (Contreras Acosta et al., 2020; Lorenz et al., 2019) that are sensible to tectosilicates. To improve processing times, benchtop DRIFTS measurements could be replaced by the emerging hand-operated FTIR, but the use of such non-destructive techniques has to reckon with issues of sample humidity and grainsize variations at the sediment surface. Wider significance of this approach would be found in geoarchaeological stratigraphy (Haburaj et al., 2020; Linderholm et al., 2018) and sequence stratigraphy where hyperspectral imaging could be correlated with Ground Penetrating Radar (GPR) profiles. Moreover, in palaeo-lagoon investigations correlated with seasonal variations of macro- and micro-fauna.

586

587

## 588 **6. Conclusion**

589 This study demonstrates the potential of a two-sensor infrared methodology involving Diffuse  
590 Reflectance Infrared Fourier Transform spectroscopy (DRIFTS) and Short-Wave InfraRed (SWIR)  
591 hyperspectral imaging (HSI) to provide a simple and time-saving approach for continuous logging of  
592 mineral abundances along sediment cores. The DRIFT spectra were used to provide quantitative  
593 estimations for quartz, calcite and clay minerals abundances of single and multi-phase synthetic  
594 mixtures. Therefore, reliable DRIFTS-inferred estimations of these minerals were obtained for 60  
595 sediment samples from a 14 meters-depth core (ALB-1), drilled in the deltaic deposits of the Albegna  
596 River. The mineral abundance values were fused with the SWIR-HSI data in order to establish partial  
597 least squares regression (PLSR) model aiming to assign continuous logging of mineral abundances

598 along the ALB-1 core. The PLSR statistical performance was satisfactory showing high degree of  
599 agreement between the DRIFT-induced and SWIR-HSI predicted results. The same predicting model  
600 was used to compute maps of mineral abundances evidencing the layered structure of mineral  
601 concentrations. The classical sedimentological non-continuous analyses (e.g. grain-size),  
602 complemented by combined DRIFTS and SWIR-HSI approach, bring into focus changes of sediment  
603 dynamics and depositional patterns recorded into the deltaic facies at high-resolution vertical scale.  
604 We contend here that the fused two-sensor infrared approach has a clear potential to help  
605 reconstructing fluvial-deltaic sedimentary successions. Calcite and clay minerals could be reliably  
606 predicted in other sedimentary environments. However, in terms of quartz prediction, the SWIR-HSI  
607 remain limited and it cannot be used for direct spectra modeling of tectosilicates. To overcome this  
608 issue, we rather recommend to use Mid-Wave InfraRed (MWIR: 2,700-5,300 nm) or Long-Wave  
609 InfraRed (LWIR: 8,000-12,000 nm) hyperspectral cameras. However, these latter significantly costlier.  
610 Further analyses are intended in order to provide quantifications of specific phyllosilicates (kaolinite  
611 vs. illite vs. smectite) by DRIFTS in order to test whether they could be reliably predicted by SWIR-  
612 HSI in complex fluvio-deltaic sediment mixtures. Moreover, research involving DRIFT-induced total  
613 organic matter and biogenic silica abundances are currently in progress in order to provide a wider  
614 understanding of the total sample composition.

615

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#### 637 8. Data Availability

638 All the data that support the findings of this study are available from the corresponding author upon  
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928

929 Tables

930 Table 1: Summary of synthetic mixture showing the mineral %wt by sample.

931 Table 2: Radiocarbon age determination of the ALB-1 core sediments.

932 Table 3: Correlation matrix of different mineralogical and physical properties of ALB-1 core sediment  
933 samples.

934

935 Figures captions

936 Figure 1: Location map of the Albegna fluvial-deltaic environment at different spatial scales. (A) the  
937 Albegna watershed limits and relief, (B) the simplified lithological map of the Albegna watershed and  
938 its surroundings and (C) the Albegna low-lying area and the current extensions of the Orbetello  
939 lagoon.

940 Figure 2: Schematic demonstration of the research methodology. Step 1: Scanning of the core by  
941 SWIR-HSI; Step 2: Measurement of core samples by DRIFTS; Step 3: Conversion of core sample  
942 spectra into mineral abundances; Step 4: Combination of SWIR-HSI and DRIFTS spectra over the  
943 area sampled for DRIFTS; Step 5: Calibration of SWIR-HSI data to continuous record of mineral  
944 abundances along the core.

945 Figure 3: Chronostratigraphy of the drill core ALB-1. The figure displays: (A) the texture of sediments,  
946 (B) the magnetic susceptibility and grain-size analyses, (C) the mineral abundances %wt by sample,

947 inferred by DRIFT spectroscopy and (D) the high resolution prediction of mineral abundances  
948 obtained by the calibrated SWIR-HSI.

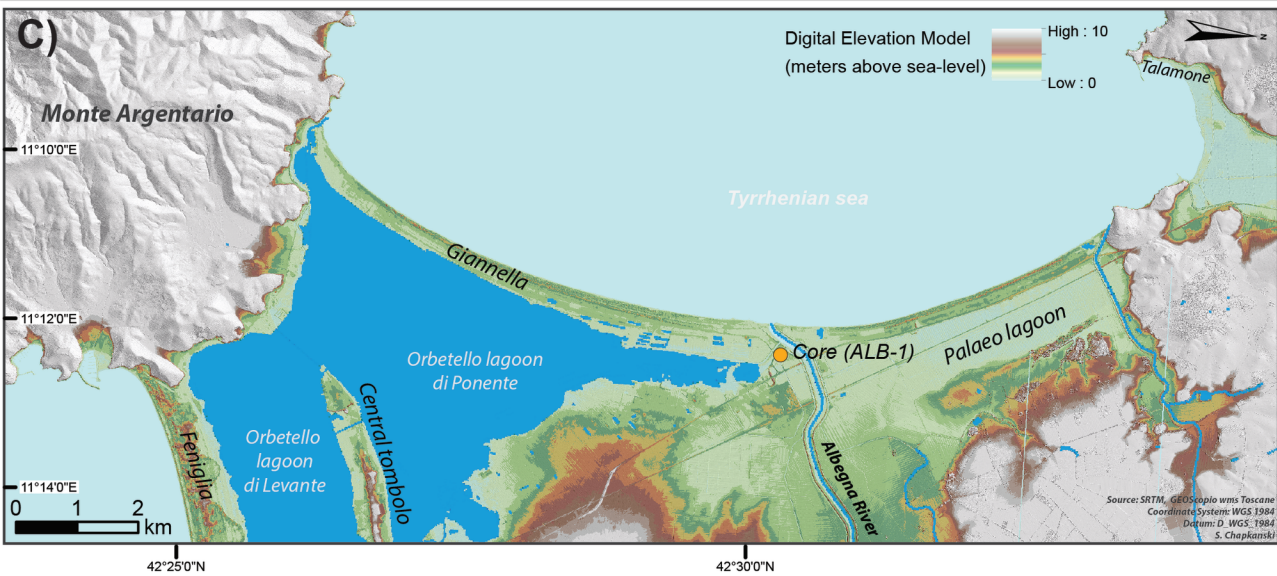
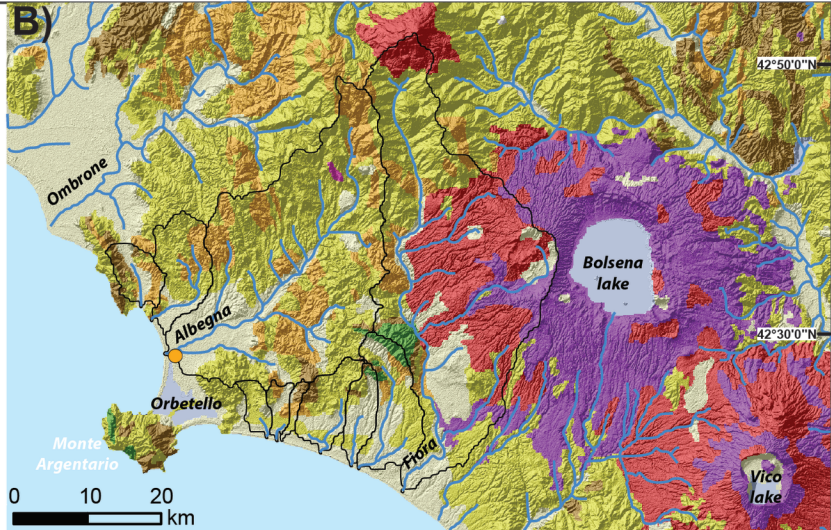
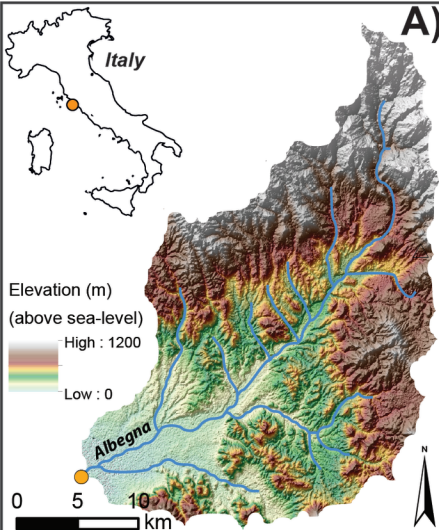
949 Figure 4: Overview spectra obtained from the synthetic mixture samples composed of pure minerals  
950 and potassium bromide (KBr). The red line highlights the peaks, selected for the establishment of the  
951 calibration curves.

952 Figure 5: Descriptive statistics of the short-wave spectra (nm units) obtained by the Hyperspectral  
953 Imaging and the mid-infrared spectra (cm-1 units) obtained by the Diffuse Reflectance Infrared Fourier  
954 Transform Spectroscopy. Grey lines highlight specific absorbance peaks discussed in this study.  
955 Statistics were performed on 60 SWIR-HSI and 60 DRIFTS corresponding spectra of sediment  
956 samples along the entire ALB-1 core.

957 Figure 6: Two-dimensional scatter plot of the DRIFT-inferred mineral %wt and the known mineral  
958 %wt. The regression line has drowned in black and the confident levels (0.95) in grey. Linear  
959 regression equations employed for the mineral %wt estimations are reported.

960 Figure 7: Two-dimensional scatter plot of PLSR-SWIR predicted mineral %wt and the DRIFT-inferred  
961 mineral %wt. The PLSR line is drown in black and the confident levels (0.95) in grey. Raw PLSR  
962 coefficients for each modeled mineral are reported. Most discriminant coefficients (peaks) are  
963 identified and highlighted.

964  
965



# Sediment Core

## Step 1

U-channel core image (11.5 m)

1 pixel = 1 spectrum  
45 columns, 53220 lines  
2394900 pixels of 185 $\mu$ m<sup>2</sup>

Image subsampling

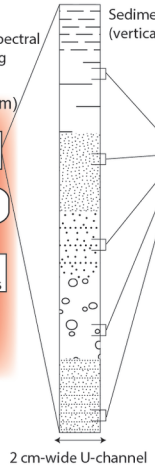
Data matrix

313 lines, 268 columns  
313 spectrum of 288 bands

expand SNV+  
Baseline treatments

Dataset of 313  
SWIR spectra

## Step 4



Sediment samples taken along the core  
(vertical thickness of 3 cm)

2 cm-wide U-channel

## Step 2

60 raw samples

Drying 50°C

Dry sample

Quartering

Sample 5 g

DRIFTS  
measurements

Powder

Grinding

Fraction:  $\leq 1$  mm

Sieving:  $\leq 1$  mm

SNV+Baseline  
treatments

Dataset of 60  
MIR spectra

Q,Ca and Cm wt%  
for 60 samples

Simple linear  
Regression

DRIFTS  
measurements

Peak area  
measurements

Dataset of Q,Ca  
and Cm peak areas

Synthetic mineral mixtures

1 weight %

2 weight %

5 weight %

10 weight %

15 weight %

## Step 3

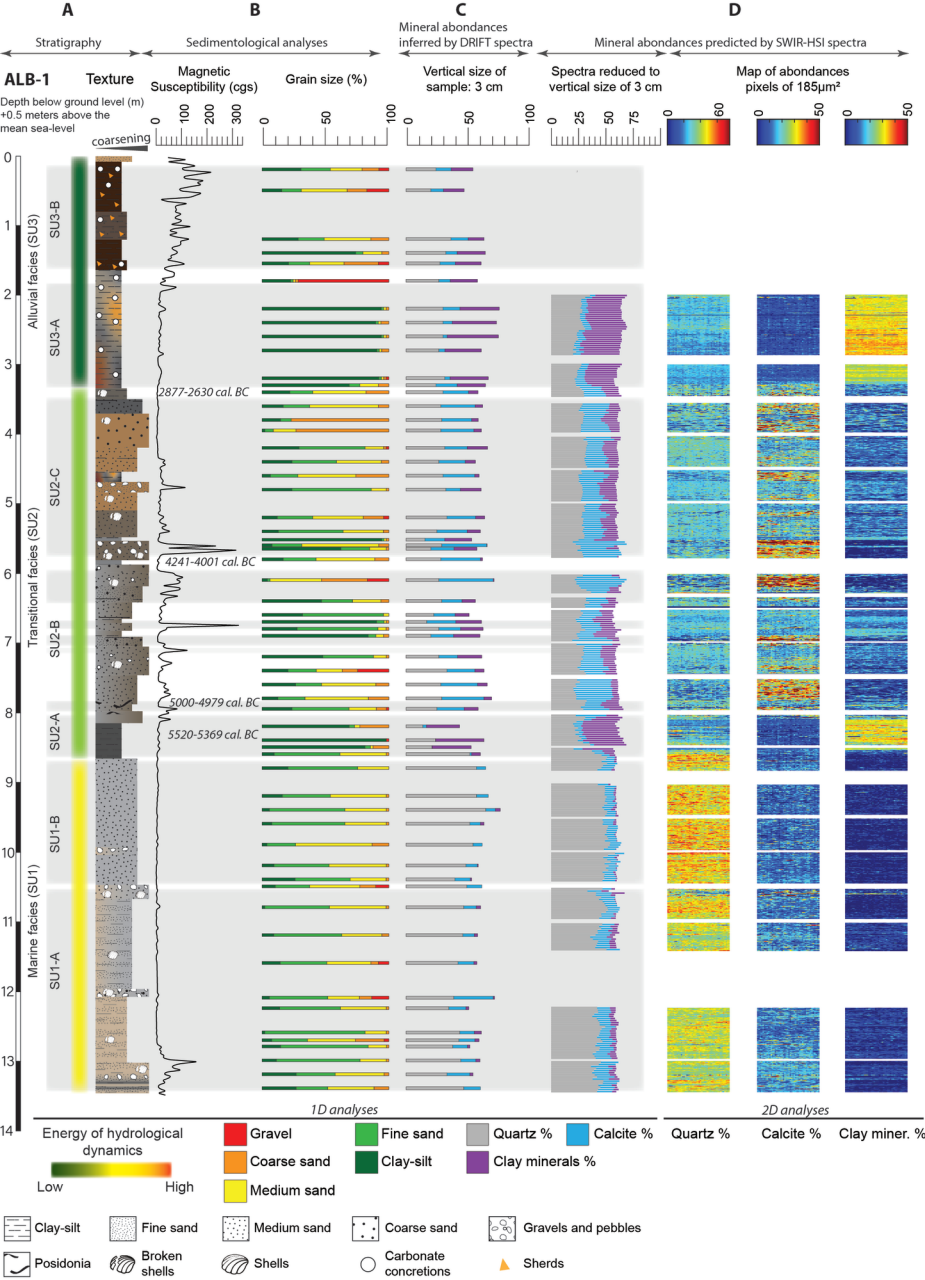
Data fusion  
and calibration

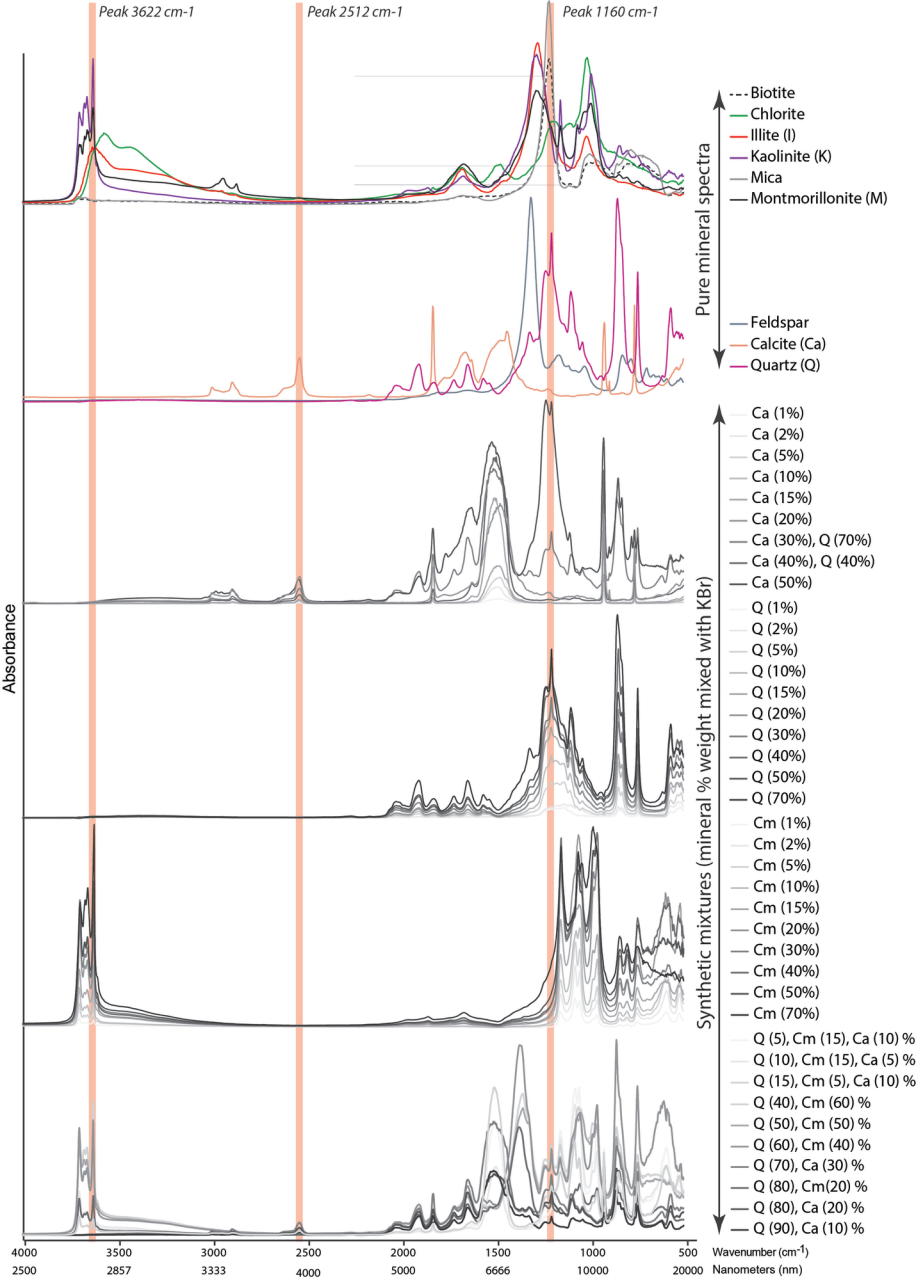
Data matrix for PLSR calibration  
Rows: Q,Ca, Cm wt% and 268 SWIR wavenumbers  
Rows: 60 samples along the core (each 3 cm)

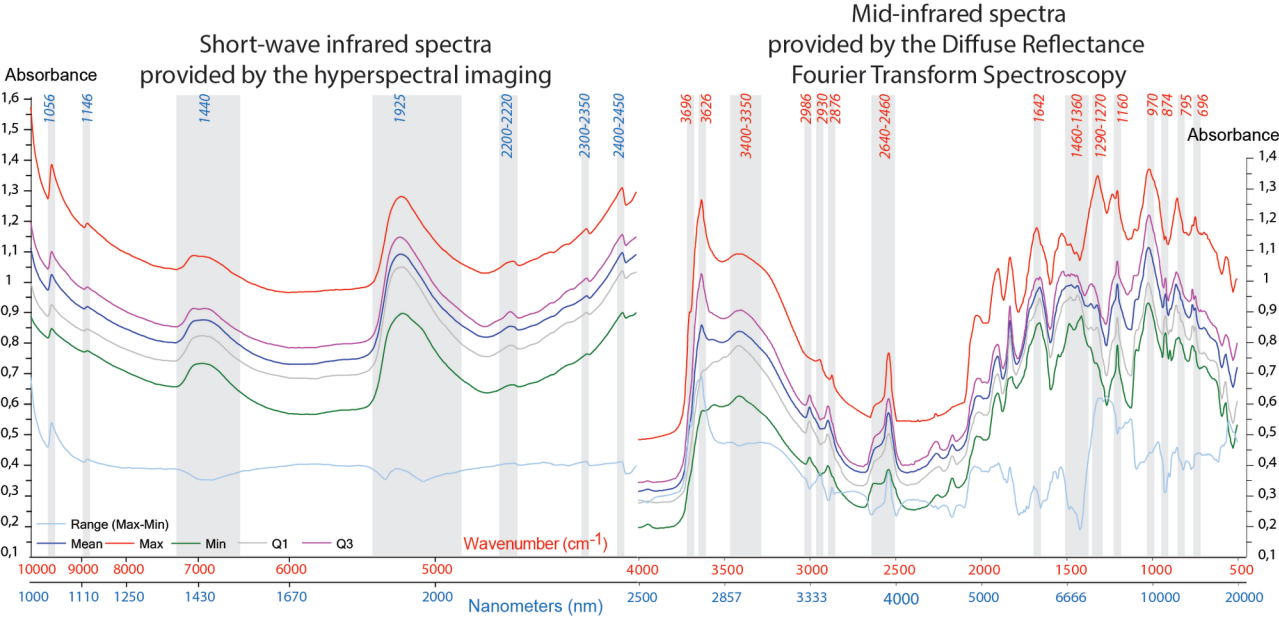
PLSR prediction

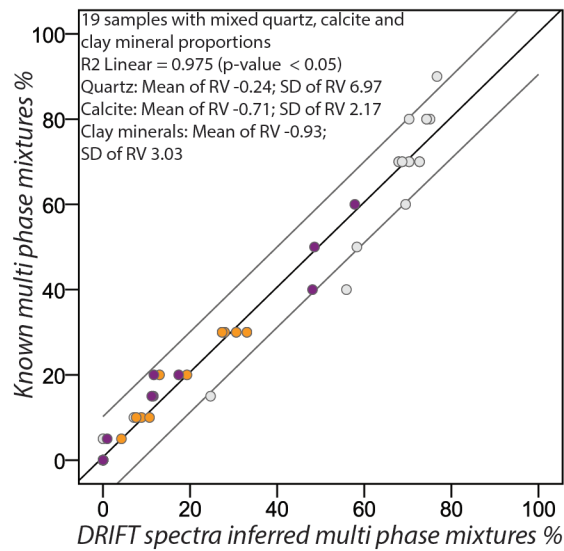
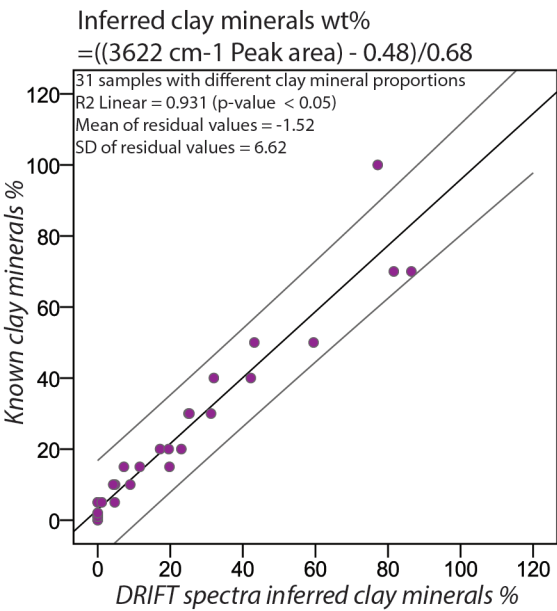
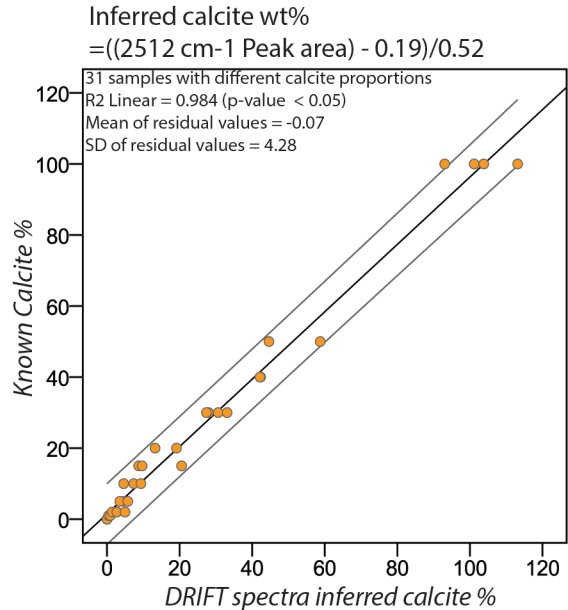
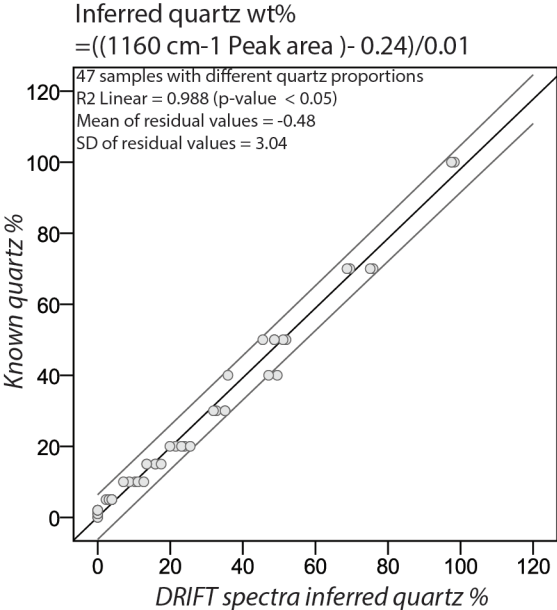
Q,Ca and Cm %  
for 313 samples

## Step 5

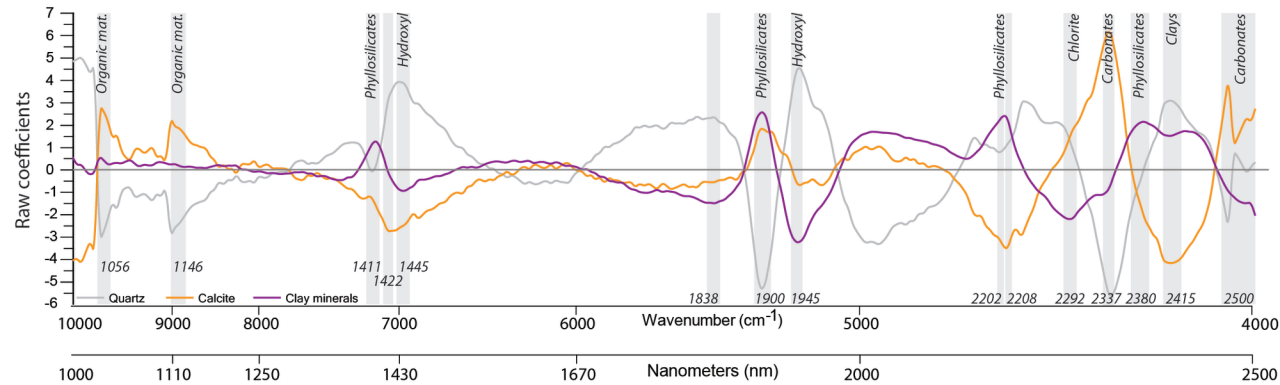
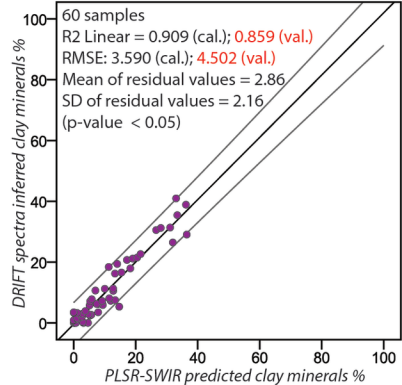
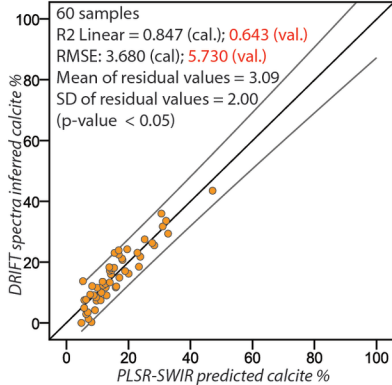
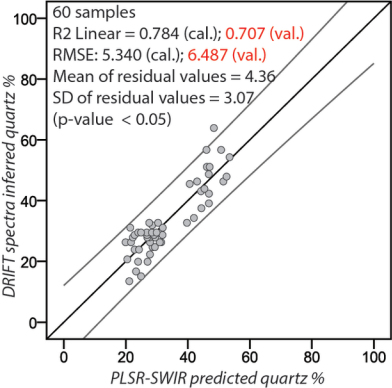












ID	Quartz wt%	Calcite wt%	KaolMontmllite (1:1:1) wt%	KBr wt%
Ca1	0	1		99
Ca2	0	2		98
Ca5	0	5		95
Ca10	0	10		90
Ca15	0	15		85
Ca20	0	20		80
Ca50	0	50		50
Ca100	0	100		0
Cm1	0	0		99
Cm2	0	0		98
Cm5	0	0		95
Cm10	0	0		90
Cm15	0	0		85
Cm20	0	0		80
Cm30	0	0		70
Cm40	0	0		60
Cm50	0	0		50
Cm70	0	0		30
Cm100	0	0		0
Q1	1	0		99
Q2	2	0		98
Q5K15Ca10	5	10		70
Q5	5	0		95
Q10K15Ca5	10	5		70
Q10	10	0		90
Q15K5Ca10	15	10		70
Q15	15	0		85
Q20	20	0		80
Q20Cm80	20	0		0
Q30	30	0		70
Q40Cm60	40	0		0
Q40	40	0		60
Q40Ca40	40	40		20
Q50Cm50	50	0		0
Q50	50	0		50
Q60Cm40	60	0		0
Q70Ca30	70	30		0
Q70	70	0		30
Q80Cm20	80	0		0
Q80Ca20	80	20		0
Q90Ca10	90	10		0
Q100	100	0		0

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Core	Depth (below soil topographic level)	Stratigraphic Units	Laboratory code	Dating support	<sup>14</sup> C age in BP	Age calibrated (Reimer et al., 2020)
ALB-1	349 cm	SU2-C	Lyon-18795	Wood	4155 ± 30	2877 to 2630 BC
ALB-1	597 cm	SU2-C	Lyon-18796	Organic matter	5300 ± 30	4241 to 4001 BC
ALB-1	790-792 cm	SU2-B	Lyon-18797	Charcoal	6015 ± 35	5000 to 4797 BC
ALB-1	823-826 cm	SU2-A	Lyon-18798	Organic matter	6485 ± 35	5520 to 5369 BC

## Correlations

DRIFTS inferred quartz (%)	1.00															
DRIFTS inferred calcite (%)	-0.36	1.00														
DRIFTS inferred clay-minerals (%)	-0.58	-0.39	1.00													
PLSR-SWIR predicted quartz (%)	<b>0.89</b>	-0.36	<b>-0.64</b>	1.00												
PLSR-SWIR predicted calcite (%)	-0.35	<b>0.92</b>	-0.37	-0.39	1.00											
PLSR-SWIR predicted clay-minerals (%)	<b>-0.60</b>	-0.35	<b>0.95</b>	<b>-0.68</b>	-0.39	1.00										
Clay-silt texture (%)	-0.56	-0.36	<b>0.91</b>	-0.58	-0.37	<b>0.86</b>	1.00									
Fine-Sand (%)	0.52	-0.13	-0.52	<b>0.62</b>	-0.10	-0.56	<b>-0.62</b>	1.00								
Medium-Sand (%)	0.48	0.39	<b>-0.78</b>	0.46	0.40	<b>-0.75</b>	<b>-0.74</b>	0.23	1.00							
Coarse-Sand (%)	-0.16	0.39	-0.18	-0.21	0.37	-0.06	-0.25	-0.37	0.01	1.00						
Total sand (%)	0.57	0.32	<b>-0.90</b>	<b>0.60</b>	0.34	<b>-0.86</b>	<b>-0.99</b>	<b>0.65</b>	<b>0.74</b>	0.23	1.00					
Gravel (%)	0.00	0.27	-0.13	-0.07	0.25	-0.12	-0.15	-0.16	0.06	0.16	0.01	1.00				
Magnetic susceptibility	-0.25	0.37	-0.02	-0.22	0.45	-0.11	-0.03	0.04	0.08	-0.08	0.02	0.09	1.00			
Moisture peak at 1935 nm	0.09	0.13	-0.04	0.06	0.17	-0.10	-0.06	-0.06	0.30	-0.25	0.03	0.24	0.23	1.00		
Hydroxyl bonds peak at 1450 nm	-0.41	-0.18	<b>0.69</b>	-0.47	-0.17	<b>0.68</b>	<b>0.73</b>	<b>-0.61</b>	-0.37	-0.20	<b>-0.74</b>	-0.01	0.03	0.44	1.00	