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(Article begins on next page)

1 **Redox-driven changes in organic C stabilization and Fe**
2 **mineral transformations in temperate hydromorphic soils**

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4 Beatrice Giannetta^{a,b}, Danilo Oliveira de Souza^c, Giuliana Aquilanti^c, Luisella Celi^a,
5 Daniel Said-Pullicino^a

6

7 *^aDepartment of Agricultural, Forest and Food Sciences, University of Torino, Largo*
8 *Paolo Braccini 2, 10095 Grugliasco, Italy*

9 *^bDepartment of Biotechnology, University of Verona, Strada Le Grazie 15, 37134*
10 *Verona, Italy (Present address)*

11 *^cELETTRA Sincrotrone Trieste S.C.p.A., S.S. 14 Km 163.5, 34149 Basovizza, Trieste, Italy*

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15 Corresponding author. E-mail address: beatrice.giannetta@univr.it

16

17 **Abstract**

18 Paddy soils experience long-term redox alternations affecting the interactions between
19 the biogeochemical cycling of iron (Fe) and carbon (C). Differences in particle
20 aggregation and soil organic matter (SOM) turnover are likely to both affect and be
21 affected by the trajectory of Fe mineral evolution/crystallinity with redox fluctuations.
22 We hypothesized that the legacy effects of redox cycling under paddy management
23 affects particle aggregation, the distribution and mineralogy of Fe (hydr)oxides between
24 particle-size fractions, and the interaction with SOM stabilization. Moreover, we
25 expected underlying processes to be different in paddy eluvial and illuvial horizons,
26 particularly due to the different inputs and redox conditions these horizons experience.
27 To test these hypotheses, we evaluated the distribution of Fe species and organic C
28 between different aggregate and particle-size fractions in topsoil (eluvial) and subsoil
29 (illuvial) horizons of soils under long-term paddy and non-paddy management in NW
30 Italy, as well as mineralogical changes in Fe phases by Fe K-edge Extended X-ray
31 Adsorption Fine Structure (EXAFS) and X-ray Absorption Near Edge Structure
32 (XANES) spectroscopy. Our findings indicate that although paddy topsoils are depleted
33 in hydrous Fe oxides with respect to non-paddy soils, they can stabilize important
34 amounts of C through mineral associations, particularly with finer particle-size fractions
35 rich in less crystalline Fe phases. We also show that redox cycling can influence
36 microaggregate stability and consequently the distribution of Fe phases and OC between
37 intra and inter-microaggregate fractions. On the other hand, illuvial horizons under paddy
38 management were enriched in short-range ordered hydrous Fe oxides and this contributed
39 to enhanced microaggregate formation and C stabilization with respect to non-paddy
40 subsoils.

41

42 **Keywords:** paddy soils, eluvial and illuvial horizons, physical fractionation, EXAFS,
43 XANES, linear combination fitting.

44 **1. INTRODUCTION**

45 Paddy soils make up the largest anthropogenic wetlands on earth and store a large
46 proportion of the global terrestrial carbon (C) stocks, representing a major terrestrial C
47 pool, (ca.10 Pg) (Kirk, 2004). The greater soil organic C (SOC) accumulation rates in
48 paddy topsoils with respect to non-paddy ones are generally assumed to be due to limited
49 mineralization under anoxic soil conditions resulting from frequent field flooding (Cheng
50 et al., 2009; Kalbitz et al., 2013; Kögel-Knabner et al., 2010; Pan et al., 2004). Although
51 numerous studies attribute organic matter (OM) accumulation in paddy soils to this
52 mechanism, there is growing evidence questioning this assumption (Huang and Hall,
53 2017).

54 Organic matter turnover and stabilization in paddy soils are strongly linked to the
55 dynamic interactions with redox-active minerals, in particular iron (Fe) oxyhydroxides
56 (Huang and Hall, 2017; Hall et al., 2018; Huang et al., 2020). Short-range-ordered (SRO)
57 minerals (e.g., ferrihydrite) are able to stabilize more OC than well-ordered minerals (e.g.,
58 goethite, hematite and lepidocrocite) due to their larger surface area, and thus play a more
59 important role in soil C storage mechanisms (Kramer and Chadwick, 2018; Lalonde et
60 al., 2012; Torn et al., 1997). The role of SRO-Fe oxy-hydroxides in the preservation of
61 SOC in paddy soils and OC persistence in deeper mineral horizons have been well-
62 documented (Chorover et al., 2004; Huang and Hall, 2017; Kramer et al., 2012; Lalonde
63 et al., 2012; Said-Pullicino et al., 2021; Wissing et al., 2014, 2013). However, further
64 insights into the effects of redox alternations on Fe phase composition, crystal order and
65 depth distribution, as well as the link between microaggregate formation and
66 (de)stabilization, and OC stabilization mechanisms are necessary. Overall, depending on
67 soil hydrology, paddy cultivation generally leads to a depletion in pedogenic Fe oxides in
68 the topsoil due to their reductive dissolution and Fe leaching under reducing conditions,
69 that is often accompanied by a relative increase in the proportion of SRO Fe oxides (Kölbl
70 et al., 2014, Winkler et al., 2016). On the other hand, paddy subsoils are generally
71 characterized by Fe oxide accumulation (Kölbl et al., 2014). In addition, redox
72 fluctuations can potentially increase or decrease Fe crystallinity, depending on the
73 environmental context (Coby et al., 2011; Ginn et al., 2017; Riedel et al., 2013; Thompson
74 et al., 2006).

75 In upland soils SRO-Fe oxides can also promote aggregation (Oades and Waters,
76 1991, Xue et al., 2019), which indirectly enhances OM stability (Balesdent et al., 2000;
77 Totsche et al., 2018). However, redox fluctuations are expected to influence aggregate

78 formation and stability with implications on the physical and chemical processes
79 regulating OM stabilization. Selective microbial reduction and reprecipitation of Fe
80 phases due to repeated redox cycles could therefore lead to a change in their distribution
81 between different aggregate size classes. Recent studies have shown that a portion of Fe
82 phases in soil can be protected from reductive dissolution (e.g., dithionite extraction)
83 presumably due to their physical protection within microaggregates or co-precipitation
84 with SRO aluminosilicates (Coward et al., 2018; Filimonova et al., 2016), suggesting the
85 importance of aggregation/precipitation reactions. On the other hand, several studies
86 showed that the reductive dissolution of Fe oxides involved in aggregate binding can
87 disrupt aggregate stability (Huang et al., 2018; Henderson et al., 2012; De-Campos et al.,
88 2009). Detailed chemical and size related characterization of soil aggregates and their
89 depth distribution in rice paddies are scarce, even though such information is fundamental
90 for further understanding the mechanisms controlling the biogeochemical cycling of
91 elements in these agro-ecosystems.

92 The objectives of this work were to compare Fe mineral evolution and OC cycling in
93 the topsoil and subsoil of a temperate paddy soil and an adjacent upland soil. We
94 hypothesized that (1) in paddy topsoils, Fe redox cycling can lead to a depletion of
95 pedogenetic Fe (hydr)oxides, promote microaggregate breakdown, and cause a
96 redistribution of Fe phases with a relative increase in the proportion of SRO oxides and
97 OC associated with the finest “free” particle-size fractions; and (2) the enhanced inputs
98 of dissolved/colloidal Fe and OC entering the paddy subsoil through percolation can
99 favour the accumulation of SRO Fe phases that contribute to the formation of stable
100 microaggregates and C retention in illuvial horizons. To test these hypotheses, we
101 evaluated the effects of redox cycling on the mineralogical changes and
102 distribution/redistribution of Fe species (i.e., Fe in clays, SRO Fe(III) oxides such as
103 ferrihydrite and organic Fe(III) complexes or more well-ordered Fe oxides), and OC
104 between different intra- and inter-microaggregate particle-size fractions in topsoil
105 (eluvial) and subsoil (illuvial) horizons of soils under long-term paddy (P) and non-paddy
106 (NP) management in NW Italy. In order to study Fe transformations a combination of Fe
107 K-edge Extended X-ray Adsorption Fine Structure (EXAFS) and X-ray Absorption Near
108 Edge Structure (XANES) spectroscopy have been applied.

109

110 **2. MATERIALS AND METHODS**

111 **2.1 Site description and sample collection**

112 The study site is located in Zeme (Province of Pavia, NW Italy) (45°11'31.8"N;
113 8°40'3.7"E), in the plains of the River Po, between the Sesia and Agogna rivers and has a
114 temperate climate, with a mean annual temperature of 12.5°C and mean annual
115 precipitation of 950 mm. Soils develop on alluvial sediment with a maximum elevation
116 of 80 m a.s.l., characterized by a high groundwater level during spring, up to 30-50 cm
117 below surface. Two adjacent plots were identified for this study, one under maize (*Zea*
118 *mays*) monocropping (NP, non-paddy) (45°11'33.6"N 8°40'06.1"E; 1.35 ha; Endogleyic
119 Fluvisol) and another under paddy rice (*Oryza sativa*) monocropping (P, paddy
120 management) established about 30 years ago (45°11'29.4"N 8°40'04.5"E; 4.43 ha; Haplic
121 Gleysol). These non-calcareous soils generally had an acidic pH, low contents of OC and
122 pedogenic Fe, and a sandy loam texture. A full description of the soil profiles and basic
123 properties of the soil horizons under non-paddy and paddy management, as well as
124 agricultural practices adopted are reported in Said-Pullicino et al. (2021). In March 2018,
125 towards the end of the winter fallow period, topsoil and subsoil samples were collected
126 from the Ap1, Ap2 and Bgw horizons in the non-paddy field and from the Arp1, Arp2,
127 Arpd, Brd1 and Brd2 horizons in the paddy field from three replicated soil pits in each
128 plot, and subsequently air dried and homogenized by passing through a 2-mm sieve. In
129 this context, differences in analyzed soil properties under these contrasting cropping
130 systems were attributed to the legacy of past management (non-paddy vs. paddy), and as
131 such, were considered to be influenced by the long-term effects of different water
132 management during the cropping season (irrigated vs. flooded) on soil redox conditions
133 (rather than the specific redox conditions at the time of sampling). Moreover, this
134 approach also integrated other effects, such as the slightly different quantity and quality
135 of annual OM inputs with the incorporation of maize or rice crop residues, that were
136 considered secondary and therefore not discussed in the present work.

137

138 **2.2 Microaggregate separation and particle-size fractionation**

139 The fractionation scheme adopted was intended to separate particle-size fractions
140 distinguishing between those particles that constituted part of the stable microaggregates
141 (intra-microaggregate particles size fractions) and particles of similar dimensions not
142 involved in microaggregation (inter-microaggregate particle size fractions). This
143 fractionation was carried out in three principal steps as illustrated in Figure S1:

- 144 (i) Soil microaggregates (53-200 µm) were first separated from all soil samples by
145 means of a custom-built, mechanical wet sieving microaggregate isolator similar to

146 the Yoder sieve apparatus used for measuring aggregate stability, as follows.
147 Aliquots of bulk soil (< 2 mm; 24 g) were transferred into 200 μm bucket sieves
148 and immersed in large beakers filled with deionized water. Rotation of the buckets
149 for 60 min in the presence of six metal beads was sufficient to break all
150 macroaggregates. The coarse sand and particulate OM fraction (CSa+POM)
151 remaining in the buckets was collected while the microaggregates and fine sand
152 (53-200 μm) were separated from the suspension by passing through a 53 μm sieve.
153 (ii) The microaggregates and fine sand were resuspended in 200 ml water to which 15
154 drops of 1 M NaCl were added, rinsed until the supernatant had an $\text{EC} \leq 100 \mu\text{S}$
155 cm^{-1} , and subsequently sonicated with 400 J ml^{-1} to break microaggregates and
156 ensure complete clay dispersion. Particle-size fractionation of the intra-
157 microaggregate soil particles was carried out by sedimentation based on Stokes law
158 to obtain coarse silt (20-53 μm ; mCSi), fine silt (2-20 μm ; mFSi) and clay (<2 μm ;
159 mCl) fractions within microaggregates. Finally, the fine sand fraction (FSa, 53-200
160 μm) was separated by passing through a 53 μm sieve.
161 (iii) The suspension remaining from (i) above, containing the inter-microaggregate and
162 free soil particles (< 53 μm) was concentrated by repeated centrifugation (10,000
163 rpm) and supernatant siphoning, after addition of 2 ml of 1 M NaCl, taking care not
164 to lose any fine mineral particles. The sediment was thereafter rinsed (until the
165 supernatant had an $\text{EC} \leq 100 \mu\text{S cm}^{-1}$), resuspended in 200 ml deionized water, and
166 subsequently sonicated with 400 J ml^{-1} to ensure complete clay dispersion. Particle-
167 size fractionation was carried out by sedimentation as described in (ii) above to
168 obtain coarse silt (CSi), fine silt (FSi) and clay (Cl) fractions between
169 microaggregates.
170 Each fraction was transferred into a pre-weighted container, freeze-dried, weighed and
171 subsequently ground to < 0.5 mm for subsequent analysis.

172

173 **2.3 OC and Fe contents characterization**

174 Total OC content of the eight size fractions was determined by high temperature
175 combustion using an elemental analyzer (NA 2100, Carlo Erba, Milan, Italy). Poorly
176 crystalline Fe (Fe_o) was determined by extraction with 0.2 M ammonium oxalate at pH 3
177 as described by Schwertmann (1964), while more ordered Fe oxides (Fe_d) were
178 determined by extraction with 0.3 M citrate-bicarbonate solution in the presence of
179 sodium dithionite as described by Mehra and Jackson (1960). Metal concentrations in the

180 extracts were determined by atomic absorption spectroscopy (AAAnalyst 400, Perkin
181 Elmer). The ratio of the Fe_o/Fe_d , indicative of the contribution of the short-range ordered
182 phases to total pedogenic oxides, or as the metric of Fe phase crystallinity, as well as their
183 difference to estimate the content of more crystalline oxides (Fe_c), were calculated.

184

185 **2.4 Fe K-edge XANES and EXAFS spectroscopy**

186 X-ray absorption spectroscopic (XAS) analyses of FSa, CSi, mCSi, FSi, mFSi, Cl
187 and mCl fractions were carried out at the XAFS beamline at Elettra Sincrotrone (Trieste,
188 Italy) (Aquilanti et al., 2017; Di Cicco et al., 2009). The samples were prepared as pressed
189 powders (*ca.* 15 mg) between Kapton® tape. Fe spectra were recorded in transmission
190 mode using Si (111) monochromator, which was calibrated to the first-derivative
191 maximum of the K-edge absorption spectrum of a metallic Fe foil (7112 eV). Spectra
192 were acquired over an energy range between 6812-7660 eV with a variable step size (5
193 eV on the pre-edge region, 0.2 eV on the XANES region and a k constant step after
194 XANES equal to 0.03 \AA^{-1}) and integration time of 2 sec per point. The monochromator
195 was detuned to exclude higher order harmonics. Two to six scans were collected and
196 averaged to increase the signal-to-noise ratio. Prior to sample analysis, radiation damage
197 was evaluated by recording a series of scans for a test sample over a duration similar to
198 that required for actual spectra acquisition, and then comparing all XANES and EXAFS
199 features of this sequence. We found that for the analytical conditions applied no photo-
200 reduction due to the beam was observed. It is worth to note that a remarkable feature of
201 XAFS beamline at Elettra is the unfocused beam, which makes the photon flux evenly
202 spread over a large area of the sample minimizing (and in our case, preventing) any beam
203 damage.

204 As previously described in Giannetta et al. (2020a, b), a suite of linear combination fitting
205 (LCF) techniques designed to identify the major Fe components in the studied samples
206 by comparison with the spectra of well characterized standards, was employed to analyze
207 both the XANES and EXAFS data. Additional methods of analysis, such as Principal
208 Component Analysis (PCA) (Table S1) and Target transformation, were used as a
209 complementary tool during linear combination analysis.

210 XANES pre-edge peak analysis at the Fe K-edge was used to identify differences in the
211 relative oxidation state between samples. Although redox conditions during sample
212 collection and handling are known to affect Fe speciation (Prietz et al., 2009), we
213 attributed differences in Fe oxidation states to the legacy effects of long-term soil

214 management, rather than to the specific influence of reducing soil conditions during rice
215 cropping. The energy position, intensity, and shape of the XANES are governed by the
216 oxidation state and the specific bonding environment of the irradiated Fe atoms
217 (coordination type, bonding symmetry, length to neighboring atoms (Westre et al., 1997;
218 Wilke et al., 2001). Particularly, the pre-edge peak centroid energy position (PCE) allows
219 a comparative evaluation of the oxidation state of Fe with values ranging between
220 7113.20 eV for Fe(II) and 7114.55 eV for Fe(III), and can be used for the quantification
221 of Fe(II)/Fe(III) ratios of different Fe bearing minerals in soils with reasonable accuracy.
222 According to Wilke et al. (2001) a linear relationship between the PCE and Fe(II)/Fe(III)
223 ratio can be assumed, if the symmetry around Fe atoms remains the same for all samples.
224 The pre-edge peak model and centroid determination was based on the considerations
225 found on Wilke et al. (2001). Two pseudo-Voigt functions were considered as a
226 component and their energy position, intensity and width were determined after the
227 baseline extraction, which serves to remove the main absorption edge. Accordingly, it
228 was assessed considering positions of individual components weighted by its respective
229 intensity after the fit. A set of standard samples were also analyzed in the same way in
230 order to get a reference value for Fe(II) and Fe(III) energy positions, respectively, 7113.20
231 and 7114.55 eV. Siderite was used for Fe(II) whereas the average values of ferrihydrite,
232 goethite, hematite were used as Fe(III) standards. The choice of these particular minerals
233 was based on their probable presence in our samples according LCF results. The relative
234 contribution of specific Fe compounds or compound classes to soils was also assessed by
235 LCF performed on the entire XANES spectrum. Quantitative LCF was used for the
236 speciation of different organic and inorganic Fe-bearing compounds. LCF on all
237 normalized spectra was performed with the spectra of illite, smectite, nontronite,
238 ferrihydrite, goethite, hematite, lepidocrocite, magnetite, maghemite, smectite, pyrite,
239 purpurite, and Fe(III) citrate. The energy range for the fitting was 7105-7145 eV and the
240 number of components to be include in a fit was determined after PCA on each group of
241 samples (from the same horizon). Eventually, target transformations were used as a
242 further parameter in the choice of the LCF result.

243 LCF analyses of k^3 -weighted Fe and EXAFS spectra were performed over a k range
244 of 2–10 \AA^{-1} . EXAFS data processing (e.g., background removal, normalization and
245 deglitching) and spectra generation were carried out with the software Athena. The
246 qualitative speciation of Fe in the bulk soils and size-fractions by Fe K-edge EXAFS was
247 carried out by comparison with several standards. Fe(III)-citrate is generally used as an

248 analog model compound for Fe(III)-OM complexes because it consists of Fe bound
249 directly to OC (O'Day et al., 2004). We assumed that Fe EXAFS can be more suitable to
250 quantify specific Fe oxyhydroxides (e.g. ferrihydrite, goethite, and hematite) and distinct
251 Fe-organic compounds. Fe K-edge XANES can better estimate the relative contribution
252 of different mineral classes and groups of organic compounds with different oxidation
253 states of the Fe atom (e.g. Fe sulphides, Fe oxyhydroxides, Fe(II) and Fe(III)-organic
254 complexes in mineral mixtures and soil samples.

255 The qualitative analysis of the nature of backscattering atoms in higher coordination
256 shells was conducted using the Morlet wavelet transform (WT) method as implemented
257 in the Igor Pro developed by (Funke et al., 2005). This method complements the
258 conventional Fourier transform (FT) analysis and reveals the energies where back
259 scattering takes place that give rise to the FT peaks. The WT modulus was analyzed and
260 compared with the WT modulus for reference samples with contribution from C and/or
261 Fe backscattering in the second coordination shell.

262

263 **3. RESULTS**

264 **3.1 OC distribution in the different aggregate and particle-size fractions**

265 Across all soil samples 40-60 % of total OC was associated with the finest particle-size
266 fractions (<2 μm ; Cl + mCl), while 20-40 % of total OC was associated with the coarser
267 fractions and particulate OM (>53 μm ; FSa + CSa+POM). Arp1 and Arp2 topsoil
268 horizons of the P soil generally showed higher OC contents across most particle-size
269 fractions with respect to the corresponding Ap1 and Ap2 horizons of the NP soil (Figure
270 1), in line with the higher total SOC contents of topsoils under paddy management.
271 However, the most significant differences were observed for the 2-20 μm (FSi + mFSi)
272 and >53 μm (FSa + CSa+POM) fractions in the more superficial horizon, that were on
273 average 2.1 and 1.4-fold greater under P compared to NP management, respectively. OC
274 associated with the finest particle fractions (Cl + mCl) that represented the greatest
275 proportion of SOC, were only marginally though significantly higher in the P with respect
276 to the NP soil in the first 15 cm of soil depth.

277 Paddy management also influenced the distribution of OC between intra- and inter-
278 microaggregate particle-size fractions in the topsoil. Whereas P management resulted in
279 a relatively higher intra:inter-microaggregate OC ratio for the fine silt-sized fraction (2-
280 20 μm), lower ratios were generally observed for the clay-sized fraction with respect to
281 NP soils (Figure 2a). In fact, on average 82 % of silt-associated OC in the P topsoils was

282 retained within microaggregates (c.f. 70 % in NP topsoils), while only 58 % of the total
283 OC associated with clay-sized particles was intra-microaggregate OC with respect to 72
284 % in the NP soil.

285 Subsoil horizons under P management were particularly enriched in OC associated
286 with the finest soil fractions (mCl + Cl; ~2.7-fold), with respect to the corresponding
287 horizons in the NP soil (Figure 1). Moreover, in the paddy illuvial Brd1 horizon, up to 60
288 % of the clay-sized OC fraction was associated with stable microaggregates, compared to
289 only 40 % in the Bgw horizon of the NP soil (mCl/Cl OC = 2.6 and 0.8, respectively).
290 Although significantly less OC was associated with the silt-sized compared to the clay-
291 sized particles in P subsoils (Figure 1), this former fraction showed the highest intra:inter-
292 microaggregate OC ratio (Figure 2a).

293

294 **3.2 Fe distribution in the different aggregate and particle-size fractions**

295 Most of the pedogenic Fe in NP topsoils (53-58 %) was associated with the finest soil
296 particles (<2 μm), primarily with intra-microaggregate clay particles (Figure 3a). Only
297 around 25% of this Fe was oxalate-extractable as most Fe was in the form of more
298 crystalline phases (Figures 3c and e). A substantial proportion of pedogenic Fe in these
299 topsoils (around 28 %) was also associated with the coarser sand-sized fractions
300 (CSa+POM and FSa) with an average Fe_o/Fe_d ratio of 0.5 (Table 1). In contrast, P topsoils
301 were greatly depleted in pedogenic Fe showing around 70% less Fe associated with finer
302 clay-sized and coarser sand-sized fractions with respect to the corresponding horizons in
303 the NP soils, leading to a more even distribution of pedogenic Fe across particle-size
304 fractions (Figure 3b). However, these observed differences in total pedogenic Fe contents
305 did not seem to greatly influence the distribution of Fe between inter and intra-
306 microaggregate Cl fractions, while a relative increase in intra-microaggregate Fe_d was
307 observed for the FSi fraction (Figure 2b). On the other hand, the distribution between
308 more and less crystalline phases was influenced by management as clay and sand-sized
309 fractions showed a greater proportion of oxalate-extractable Fe and higher Fe_o/Fe_d ratios
310 (up to 0.8) with respect to NP topsoils (Table 1).

311 Subsoil horizons in P and NP profiles showed evident management-related differences in
312 the distribution of pedogenic Fe between aggregate and particle-size fractions. Whereas,
313 NP subsoil samples from the Bgw horizon showed lower total pedogenic Fe contents with
314 respect to the overlying Ap soil horizons (Fig. 3a) albeit very similar intra:inter-
315 microaggregate Fe_d (Figure 2b) and Fe_o/Fe_d ratios (Table 1) across fractions, P subsoils

316 showed higher total pedogenic Fe contents and oxalate-extractable Fe with respect to both
317 P topsoils (Arp1 and Arp2 horizons) and the corresponding subsoil horizon in the NP soil
318 (Bgw). The most enriched Brd1 illuvial horizon in the P soil had pedogenic Fe contents
319 associated with the fine silt and clay-sized fractions that were respectively 3 and 6-fold
320 higher compared to the corresponding subsoil Bwg horizon in the NP soil. The substantial
321 enrichment in pedogenic Fe associated with the finest soil fraction ($< 2 \mu\text{m}$) of the Brd1
322 horizon was mainly due to an increase in Fe_c (Figure 3d) that was also responsible for the
323 lower Fe_o/Fe_d ratio observed with respect to the topsoils (Table 1). Although only limited
324 changes in the distribution of pedogenic Fe between intra and inter-microaggregate
325 fractions across different particles sizes was observed with soil depth in the P soil, the
326 fine silt and clay-sized fractions of the Brd1 showed slightly higher intra:inter-
327 microaggregate Fe_d ratios with respect to the corresponding subsoil horizon in the NP soil
328 (Figure 2b).

329

330 **3.3 Fe speciation in the different aggregate and particle-size fractions**

331 NP soils showed minor variations in centroid position values with soil depth although
332 clear differences were observed between particle-size fractions (Figure 4). PCE values
333 tended to increase with decreasing particle size with a maximum difference of around 0.7
334 eV between FSa and CI fractions, albeit no differences between intra- and inter-
335 microaggregate fractions were observed (Figures 4 and S2; Table S2). Mean PCE values
336 for the clay-sized fractions around 7114.59 eV suggest that Fe-containing mineral phases
337 in this fraction were mostly oxidized. On the other hand, an increasing contribution of
338 Fe(II) was observed for the FSa and CSi fractions with PCE values around 7113.93 eV.
339 Similar differences in PCE values between particle-size fractions were also observed in
340 the P soils, although in contrast to NP soils, clear trends with soil depth were noted (Figure
341 4). Across all particle-size fractions, lower PCE values were generally obtained for
342 topsoils with respect to subsoil horizons suggesting a greater contribution of Fe(II) to total
343 Fe in the superficial horizons. The difference in PCE values between topsoils and subsoils
344 was generally less pronounced for the finest clay-sized fractions (0.15 eV) with respect
345 to the other fractions (0.18-0.34 eV), suggesting a greater contribution of reduced Fe in
346 the coarse-sized fractions separated from P topsoils.

347 The deconvolution of the XANES spectra in the energy range between 7105 eV and 7145
348 eV of both NP and P soils by LCF (Table 2) showed that Fe phases were adequately
349 described by three or four components. The major differences in the relative contribution

350 of different Fe phases were linked to the different particle-size fractions rather than soil
351 management and depth. According to the LCF results (Table 2), in the NP soil the FSa
352 fractions contained relatively high proportions of chlorite (32-34%) that tended to
353 decrease with decreasing particle-size, and siderite (26-33%) that was absent in the other
354 fractions. Other minor phases in this fraction included illite (13-21%) and hematite (20-
355 22%). Similarly, Fe phases in the coarse silt-sized fractions (CSi and mCSi) were also
356 represented by chlorite (22-27%), illite (34-66%) and hematite (13-27%). Minor
357 proportions of magnetite were also detected in this fraction (5-14%). Fine silt-sized
358 fractions (FSi and mFSi) generally showed smaller proportions of chlorite (12-27%) and
359 illite, though other Fe-containing minerals like smectite and nontronite were detected, as
360 well as minor contributions (<10%) from organically complexed Fe(III). In contrast to
361 the other fractions, the finest clay-sized fractions (Cl and mCl) were characterized by the
362 absence of illite and the presence of relatively high amounts of nontronite that represented
363 up to 79-83% of the Fe phases. This particle-size fraction also contained variable
364 contributions from Fe oxide phases (e.g., lepidocrocite and ferrihydrite) as well as
365 organically complexed Fe(III). Overall, in NP, the major differences in the relative
366 contribution of different Fe phases were linked to the different particle-size fractions
367 rather than depth.

368 In the P soils, the FSa fraction contained similar contents of chlorite (32-34%), and
369 siderite (27-32%) as observed for the same fraction in NP. Other minor phases in this
370 fraction included illite and hematite. Fe phases in the coarse silt-sized fractions were also
371 represented by chlorite (18-27%), illite (39-75%) and hematite (9-23%) though with
372 slightly different relative contributions. As for NP soils, fine silt-sized fractions (FSi and
373 mFSi) generally contained chlorite (23-29%) and illite, smectite (16-57%) and nontronite
374 (7-32%), as well as minor contributions (<10%) from organically complexed Fe(III). The
375 clay-sized fractions were characterized by the absence of illite and the presence of
376 relatively high amounts of nontronite that represented up to 79-84% of the Fe phases.
377 This particle-size fraction also contained variable contributions from Fe oxide phases
378 (e.g. lepidocrocite and ferrihydrite) as well as organically complexed Fe(III). These were
379 most abundant in P subsoils.

380

381 **3.4 Fe EXAFS linear combination fitting and WT results**

382 EXAFS spectra of all size-fractions were accurately reconstructed by three or four
383 components, and quantitative results of the LCF evidenced that Fe phases in all NP and

384 P soils were mainly characterized by the presence of chlorite, ferrihydrite, lepidocrocite,
385 and Fe(III)-citrate (Figure 5, Tables 3 and S3).

386 LCF results for the size fractions, with the only exception of FSa, using three components
387 are reported in Figure 6 and the sample fit (dotted lines) is labeled with the R-factor. Fe
388 K-edge EXAFS spectra showed features at $\sim 4.0 \text{ \AA}^{-1}$ (maximum 1), $\sim 6.5 \text{ \AA}^{-1}$ (maximum
389 2), $\sim 7.5 \text{ \AA}^{-1}$ (maximum 3), $\sim 8.5 \text{ \AA}^{-1}$ (maximum 4). The maximum at 4.0 \AA^{-1} has different
390 features in ferrihydrite and lepidocrocite (insert in Figure 5). The maximum at 7.5 \AA^{-1} is
391 characteristic of ferrihydrite, whereas the small maximum at 8 \AA^{-1} is typical of
392 lepidocrocite and magnetite, and a broad one describes Fe(III)-citrate spectrum. The
393 maximum at 8.5 \AA^{-1} is also a characteristic feature of ferrihydrite. The maximum at 10
394 \AA^{-1} is only characteristic of lepidocrocite (insert in Figure 5). The maxima at 6.5 and 7.5
395 \AA^{-1} (as also at 8.5 \AA^{-1}) are characteristic of ferrihydrite (Figure 5).

396 Quantitatively, NP soils evidenced an increase in the relative abundance of ferrihydrite
397 and Fe(III)-citrate phases with decreasing particle size, together constituting around 20-
398 24 % and 9-21%, respectively in the coarse silt (CSi, mCSi) and both 31-43% in the clay-
399 sized (Cl, mCl) fractions, with no evident trends with soil depth (Table 3). On the other
400 hand, the relative abundance of chlorite was lower in the clay-sized fractions (4-15 %)
401 with respect to the other fractions (30-49%), while lepidocrocite accounted for around
402 11-19% of Fe phases across size fractions. Only the coarser FSa fraction was
403 characterized by the presence of more crystalline Fe phases like hematite and goethite.
404 Similarly, P soils showed an increasing abundance of ferrihydrite and Fe(III)-citrate
405 phases with decreasing particle size, from 8-31 % and 9-29 % in the coarse-silt fractions
406 (CSi, mCSi) to 9-41 % and 22-46 % in the clay-sized (Cl, mCl) fractions, respectively.
407 Chlorite ranged from 9 to 66 % and lepidocrocite from 11 to 19 % across size fractions.
408 However, in contrast to NP soils, P soils evidenced lower contents of ferrihydrite in the
409 topsoils and more pronounced variations in the relative abundance of ferrihydrite, more
410 crystalline Fe phases and Fe(III)-citrate with soil depth (Table 3). Considering exclusively
411 the finest clay-sized fraction, the relative content of ferrihydrite increased from around
412 14-20 % in the Arp1 and Arp2 horizons to 40% in the Brd1 horizon, while Fe(III)-citrate
413 decreased from 41-46 % in the topsoils to 30% in the subsoils. Magnetite (up to 15 %)
414 was also detected associated with the clay-sized fractions in the Brd2 horizon.

415 A key in the study of Fe associated with OM by EXAFS is a proper analysis of the
416 second coordination shell. In traditional analysis of EXAFS spectra it is difficult to
417 separate the contributions from different backscattering atoms in higher coordination

418 shells present at similar bonding distances from the central Fe atom. Complementary to
419 LCF, WT provides useful information simultaneously resolving data in both wave space
420 (k) and interatomic distance (R) space, and the resulting k - R maps are helpful for
421 improving the fitting model and understanding elemental speciation in the sample. In
422 addition, WT analysis was used to qualitatively test the presence of Fe back-scatterers in
423 the second coordination shell of Fe. The Morlet wavelet transforms of k^3 -weighted Fe K-
424 edge EXAFS spectra of the samples over a $R + \Delta R$ -range of 2.2-4.0 Å was calculated and
425 the resulting wavelet plots compared with those of Fe(III) reference compounds
426 (ferrihydrite, Fe(III)-citrate, chlorite). Figure S3 shows the WT plots of the standards. In
427 the ferrihydrite plot, the Fe shell contributes a strong feature at 7-8 Å⁻¹ and 2.75 Å
428 (Daugherty et al., 2017). In the Fe(III)-citrate standard, the absence of Fe backscattering
429 is accompanied by new features at distances of 2.0–2.5 Å and indicates back-scattering
430 from lighter atoms, in agreement with single and multiple backscattering from C/O in the
431 second and third coordination shells of tris(oxalato)Fe(III) (Daugherty et al., 2017;
432 Karlsson and Persson, 2010). Moreover, these features appear at lower energies (3–4 Å⁻¹)
433 than those of Fe.

434 The WT of the EXAFS data ($\eta=8$, $\sigma=1$) of the CSi, FSi, Cl and relative aggregated
435 fractions showed that both the intensity caused by light back-scatterers at low k -values
436 and by heavier atoms at higher k varied among the samples (Figure 6), compared to the
437 WT plots of standards (Figure S3). A general trend was observed with decreasing particle-
438 size from the CSi to the Cl fraction in the NP topsoil horizons (Ap1 and Ap2; Figure 6a).
439 The clay samples generally have more intense maxima near 8 Å⁻¹, typical of ferrihydrite.
440 A slight increase in the Fe-SOM signal contribution at above 2.2 Å and 2–4 Å⁻¹ is also
441 present, as reported in the EXAFS LCF results, while the CSi fractions clearly match with
442 the high chlorite content. In the Bgw fraction the increasing content of ferrihydrite (up to
443 50% considering 3 components) is evident in the intense peak at 8 Å⁻¹ in the Cl and mCl.
444 Although an increase in Fe oxides and organically-complexed forms occurred from the
445 coarse to the fine fractions, significant differences were not found ranging from the
446 topsoil to the subsoil in NP soil.

447 Considering the equivalent topsoil horizons under P management, spectra of the Arp1
448 and Arp2 horizons are characterized by features indicating an increase in Fe-SOM and
449 ferrihydrite with decreasing particle-size from the CSi to the Cl fraction (Figure 6b). In
450 addition, the mCl fraction, as also reported in the LCF performed using three components,
451 clearly matches lepidocrocite features. In the Arpd horizon of the P soil the increasing

452 contribution of ferrihydrite (from 21 to up to 28% from the CSi to the Cl fraction) and
453 Fe-SOM (from ca. 18 to ca. 38% from the CSi to the Cl fraction) are also reported in the
454 WT of the EXAFS data. In the Brd1 horizon the higher Fe(III)-SOM content in the Cl
455 with respect to the mCl fraction is evident. As also evidenced by the LCF, CSi contains
456 less ferrihydrite than mCSi. Compared to the Brd1 horizon, in the Brd2 horizon the
457 ferrihydrite content decreased, whereas the increased Fe(III)-SOM contents, in all the
458 fractions, appear as a clear feature.

459

460 **4. DISCUSSION**

461 **4.1 Influence of paddy management on OC distribution in the aggregate and** 462 **particle-size fractions in topsoils and subsoils**

463 The larger accumulation of OM in soils under paddy management with respect to other
464 arable ecosystems has been widely recognized to contribute to the C sink functions of rice
465 agro-ecosystems (Kalbitz et al., 2013; Kögel-Knabner et al., 2010; Wissing et al., 2011).
466 This has often been attributed to the retarded decomposition of OC under waterlogged
467 conditions during several months of paddy field flooding every year (Sahrawat, 2004),
468 although enhanced soil microaggregation (Wissing et al., 2014) and specific organo-
469 mineral associations have also been shown to drive OC accrual in these soils (Winkler et
470 al., 2019). Apart from confirming the greater OC contents in P with respect to NP topsoils,
471 this study also suggests that retarded decomposition could be partly responsible for the
472 higher contents of particulate OM associated with the coarser size fractions under paddy
473 management. This is in line with the findings of Chen et al. (2021) who showed that SOC
474 sequestration in paddy soils is partly linked to the accumulation of crop residue-derived
475 labile C. Although paddy management resulted in a greater amount of particulate OM
476 responsible for around 25 % of total SOC, mineral-associated OM still represented the
477 greatest proportion of SOC. The interaction of OC with soil minerals and its subsequent
478 stabilization against microbial mineralization largely depend on soil redox conditions
479 (Eusterhues et al., 2014). In fact, long-term paddy management favored OC stabilization
480 through this mechanism as P soils showed higher amounts of OC associated with the finer
481 soil fractions with respect to NP soils, not only in the topsoil but also in the subsoil.
482 Moreover, our results evidenced that whereas the clay-sized fraction is the main OC sink
483 in both paddy topsoil and illuvial horizons (40 and 47-62 %, respectively), OC associated
484 with the fine silt-sized fraction can also represent a substantial proportion of total SOC in
485 P topsoils (on average 23 % of total SOC). This was assumed to be linked to the presence

486 of a substantial proportion of pedogenetic Fe oxides (26 %) in this fraction probably due
487 to their redistribution from the finer to coarser fractions with repeated cycles of Fe(III)
488 reduction and re-oxidation/precipitation that characterize these topsoils.

489 OC stabilization in the paddy soils was not only affected by particle size but also
490 related to redox-driven changes in microaggregate formation and stability. Paddy
491 management resulted in relatively lower contents of OC associated with the intra-
492 microaggregate clay-sized particles in the topsoil with respect to the NP soil, but favored
493 the presence of OC associated with the intra-microaggregate fine silt-sized particles.
494 Aggregate stability may be somewhat compromised in soils subjected to alternating redox
495 conditions possibly due to the disruptive energy occurring upon slaking (Six et al., 2000),
496 and reductive dissolution of Fe oxides that are known to serve as binding agents holding
497 aluminosilicate particles together (Blankinship et al., 2017; De-Campos et al., 2009). Our
498 results suggest that clay-sized particles are more prone to dispersion during
499 microaggregate breakdown under alternating redox conditions probably due to their more
500 negative surface charge and greater susceptibility of the SRO-Fe oxides holding
501 aluminosilicate particles together to microbial reduction. In contrast, the higher amount
502 of OC associated with silt-sized particles within microaggregates under paddy
503 management suggests that this size fraction could be less susceptible to aggregate
504 breakdown under anoxic conditions and therefore represent an important pool of stable
505 OC in these soils. This is also corroborated by the higher ratio of intra:inter-
506 microaggregate pedogenic Fe and lower Fe_o/Fe_d ratio observed for the silt-sized with
507 respect to the clay-sized fractions in the P topsoils. Our findings therefore partially
508 confirm our first hypothesis that paddy management may affect the distribution of OC
509 between different particle-size fractions due to the influence of redox cycling on
510 aggregate stability. Huang et al. (2018) previously reported how management-induced
511 soil aggregate turnover and OC stabilization was strongly linked to Fe cycling in a rice-
512 wheat crop rotation, particularly when exogenous OM was applied. Similarly, De-
513 Campos et al. (2009) showed that the reductive dissolution of poorly ordered Fe oxides
514 involved in aggregate binding may lead to changes in the morphology of soil particles,
515 favour colloid dispersion and contribute to a decrease in aggregate stability under anoxic
516 conditions. However, notwithstanding the depletion of total pedogenetic Fe in the topsoil
517 (about 50% less Fe_d), more OC is stabilized by association with the finest soil particles
518 both within and outside microaggregates (about 25% more OC) with respect to non-paddy
519 soils. In paddy topsoils coprecipitation, known to retain more OC with respect to surface

520 adsorption on Fe (hydr)oxides and leading to the formation of Fe-OM associations with
521 a high C/Fe ratio (Sodano et al., 2017), may in fact represent an important mechanism for
522 protected OM from microbial degradation (Ginn et al., 2017) and thus contribute to OC
523 accumulation. This was also confirmed by EXAFS LCF that evidenced a substantial
524 proportion of Fe-OM phases (up to 45%) and ferrihydrite (up to 20%) in the clay-sized
525 fractions (Table 3).

526 The significant enrichment in OC associated with intra-microaggregate clay-sized
527 particles in the P subsoil horizons when compared to the corresponding horizons in the
528 NP soil suggest that microaggregate formation and stabilization in the subsoil may also
529 contribute to the preservation of OC and could be linked to the mobilization of dissolved
530 OC and Fe from the topsoil during the rice cropping season when the paddy fields are
531 flooded (Said-Pullicino et al., 2016), confirming our second hypothesis. In a previous
532 study (Said-Pullicino et al., 2021) we provided evidence that colloid transport, together
533 with the percolation of Fe^{2+} and subsequent precipitation of SRO oxides in the oxic
534 subsoil horizons, could contribute to the accumulation of Fe and OC in the illuvial
535 horizons. In the present study, we are further showing that these redox-driven dynamics
536 may also contribute to microaggregate formation and soil OC stabilization in the deeper
537 soil horizons of temperate paddy soils.

538

539 **4.2 Fe mineral transformations and distribution in the different aggregate and** 540 **particle-size fractions**

541 As expected, paddy management resulted in a general depletion in both SRO and
542 crystalline Fe oxides in the topsoil with respect to the non-paddy soil, probably due to the
543 reductive dissolution of Fe oxides and subsequent leaching into the subsoil with repeated
544 redox cycles, as suggested by Said-Pullicino et al. (2021). Nonetheless, the higher Fe_o/Fe_d
545 ratio of the clay-sized fractions (Table 1) indicate a relative increase in SRO Fe oxides
546 associated with this fraction primarily in the form of ferrihydrite and Fe-OM complexes
547 (Table 3). In redox-active paddy topsoils, repeated reductive dissolution of both
548 crystalline and less ordered Fe oxides under anoxic conditions with subsequent release of
549 high concentrations of dissolved Fe^{2+} and DOC (Bertora et al., 2018; Said-Pullicino et
550 al., 2016), followed by the oxidative re-precipitation with the re-establishment of oxic
551 conditions or in the O_2 -rich rice rhizosphere, can lead to the formation of new mineral
552 phases, mainly SRO oxides more or less associated with phyllosilicate particles (Sodano
553 et al., 2016) or Fe-OC coprecipitates (Sodano et al., 2017). The presence of minor

554 amounts of lepidocrocite (around 12-15 %) also suggests that the Fe²⁺-catalyzed
555 recrystallization or solid state transformations of ferrihydrite to more thermodynamically
556 stable phases can also occur to some extent. Chen and Thompson (2021) report that the
557 nature of the new Fe minerals formed as a result of Fe(II) oxidation may be directed by
558 the relative presence of OM and Fe phases in the soil, that can either hinder or promote
559 crystal growth and the formation of more crystalline phases, respectively. It is thus highly
560 likely that in the studied soils that are relatively poor in pedogenic Fe but that hold
561 important amounts of OM (Said-Pullicino et al., 2021), the trajectory of Fe minerals under
562 paddy management tends towards the relative accumulation of SRO Fe(III) phases. Our
563 results further show that redox-driven Fe phase transformations may also involve changes
564 in microaggregate stability that consequently influences the association of new mineral
565 phases with more aggregated (for fine silt-sized) or dispersed (for clay-sized) mineral
566 particles (Figure 2b). EXAFS LCF suggests that hydrous Fe minerals present in the clay
567 and silt-sized fraction of paddy topsoils are mainly represented by ferrihydrite (about 18
568 and 14 %, respectively) and Fe-OM phases (about 45 and 30 %, respectively) confirming
569 the role these size-fractions may play in OC retention.

570 The lower PCE values generally observed across particle-size fractions in paddy topsoils
571 with respect to both paddy subsoils and non-paddy topsoils (Figure 4) suggest that in this
572 redox-active horizon a proportion of Fe in the mineral phase may remain in its reduced
573 form even after field drainage. XANES LCF suggests that this may be due to the reduction
574 of structural Fe present in phyllosilicate structures (nontronite and smectite in the finer
575 fractions, and chlorite in the coarser fractions) under anaerobic conditions (Table 2).
576 Various studies have shown that the biological reduction of Fe(III) in phyllosilicates like
577 nontronite (Zhao et al., 2013) and illite-smectite mixed layers (Shelobolina et al., 2012)
578 is possible in soils subject to reducing conditions (Liao et al., 2019; Neumann et al., 2015;
579 Ribeiro et al., 2009; Dong et al., 2009 and references therein) to an extent that depends
580 on the location of Fe(III) within the clay structure (Shi et al. 2021). However, the similar
581 proportions of nontronite in P and NP topsoils suggest that this redox-cycling under paddy
582 management did not lead to *in situ* loss of structural Fe. Similar results were obtained by
583 Vogelsang et al. (2016) after one year of incubation of nontronite in a paddy soil. Akter
584 et al. (2018) have also shown that reduction of octahedral Fe³⁺ in clay minerals and their
585 interstratified forms could be responsible for accepting electrons during OM
586 mineralization under anaerobic conditions. Vertical redox gradients and OM contents in
587 hydromorphic soils can therefore exert a major control on the oxidation state of structural

588 Fe in phyllosilicates and other Fe containing minerals (Chen et al. 2017). However, with
589 the re-establishment of oxic conditions, structural Fe in clay minerals can be rapidly
590 reoxidized (within days) to Fe(III) through abiotic or biotic oxidation, as reported for
591 chlorite and nontronite-associated Fe(II) by Zhang et al. (2011) and Shi et al. (2021). It is
592 however possible that in under oxic conditions reduced Fe was preferentially reoxidized
593 in smaller particles having higher contact surfaces with O₂ while reoxidation was slower
594 in larger size fractions and within microaggregates. This would partially explain the
595 increasing presence of reduced Fe(II) with increasing particle size in the redox-dynamic
596 topsoils, even if the soils were already oxic during sampling. The lower PCE values in
597 the coarser soil fractions may also be due to the precipitation of Fe(II) carbonates.
598 XANES LCF evidenced that the precipitation of siderite is evidently not associated with
599 the fine particle-sizes like most other secondary minerals, but eventually other
600 mechanisms (e.g., linked with high rates of CO₂ production during the mineralization of
601 particulate OM) may drive their precipitation on coarser fractions (Table 2). However,
602 due to the presence of similar proportions of siderite in the coarse fractions of both paddy
603 and non-paddy topsoils and subsoils we cannot exclude a lithogenic origin of this mineral.
604 Siderite oxidation kinetics are known to be relatively slow as structurally bound Fe(II) in
605 carbonates are not particularly electro-active due to the low Fe(II) surface density, and
606 rates of oxidation are generally slower with increasing nominal particle size (Hoving et
607 al. 2017) or due to surface passivation of the mineral by organic ligands (Rothwell and
608 Kretzschmar, 2020). Nonetheless, the different trend in PCE values for this fraction in
609 paddy and non-paddy soils suggests that redox-cycling in the former can affect the
610 oxidation state of Fe phases along the soil profile and that Fe K-edge XANES can
611 adequately evaluate these changes.

612 Our results also evidenced that paddy illuvial horizons just beneath the plough pan can
613 accumulate remarkable amounts of Fe (hydr)oxides particularly associated with the finest
614 particle fractions and also contribute to microaggregate formation and stabilization
615 (Figure 3). This is consistent with the inputs of colloidal and/or dissolved Fe from the
616 topsoil and the larger Fe oxide stocks in the subsoil (about 40 % higher) with respect to
617 adjacent non-paddy soils reported for temperate paddy soils by Said-Pullicino et al.
618 (2021). EXAFS LCF suggested that most of the Fe phases associated with the finest
619 particle fractions in the Brd1 horizon were represented by ferrihydrite (40%) and Fe-OM
620 forms (30%) confirming that these subsoil horizons can play an important role in OC
621 accumulation in rice paddy soils. However, we did not observe substantial differences in

622 the mineral composition of pedogenetic Fe phases in paddy and non-paddy subsoils
623 (Table 3). Nor was the transformation of ferrihydrite into more crystalline phases
624 particularly expressed because interaction with dissolved OM could have inhibited the
625 Fe²⁺-catalyzed transformation into more crystalline phases even in the subsoil.
626 Nonetheless, the increasing trend in PCE with soil depth under paddy but not under non-
627 paddy management (Figure 4) clearly suggests that redox cycling in paddy topsoils
628 contribute reduced Fe forms, while Fe phases in the subsoil are mostly oxidized, except
629 for the coarser-size fractions where siderite was detected (Table 2). In these paddy fields,
630 subsoil horizons just beneath the plough pan generally remain prevalently oxic even when
631 the topsoils are flooded, as the rising ground water table during spring and summer (up
632 to around 40 cm below the soil surface) does not limit oxygen diffusion until late in the
633 cropping season (mid-July).

634 **4.3 Potential and limitation of Fe K-edge XANES and EXAFS for Fe speciation in soil fractions**

635 This work together with the results of previous studies carried out on well-defined binary
636 and ternary mixtures of different Fe-bearing minerals (e.g., Wilke et al., 2001; O'Day et
637 al., 2004; Prietzel et al., 2007) showed that Fe K-edge XANES can provide an estimate
638 of the relative contribution of different mineral classes and groups of organic compounds
639 with different oxidation state of the Fe atom (e.g., Fe(II) sulphides versus Fe(III)
640 oxyhydroxides; Fe(II)-organic complexes versus Fe(III)-organic complexes) by
641 calculating the PCE and applying LCF to the entire XANES spectrum. In soils this
642 evaluation is complicated by the presence of mixed Fe phases that form during
643 pedogenesis. Therefore, accurate quantification of different Fe phases in soils by Fe K-
644 edge XANES will probably always remain difficult to achieve particularly in
645 environments experiencing dynamic redox conditions. At present, LCF conducted on the
646 XANES spectrum in an energy range between 7105 and 7145 eV allows the quantification
647 of specific minerals in soils approximately, but not accurately. The accuracy of the results
648 of the LCF procedure is strongly affected by the correctness of the applied set of predictor
649 variables. LCF on the XANES spectrum revealed a systematic influence of increasing
650 oxidizing conditions on the Fe speciation in the topsoil and the subsoil of paddy soil: the
651 contribution of Fe(III) compounds increased with soil depth and decreasing particle size
652 fractions, especially in the aggregated ones. This study highlights the potential of Fe K-
653 edge XANES for the determination of Fe speciation in redoximorphic soils and soil
654 fractions, despite its present problems and limitations. With Fe K-edge XANES, the
655 proportion of Fe(II) and Fe(III) and the relative contribution of different Fe compounds

656 in soil samples and soil aggregates can be evaluated. However, although Fe K-edge
657 XANES can estimate fairly well the relative contribution of different mineral classes and
658 groups of organic compounds with different oxidation states of the Fe atom in mineral
659 mixtures and soil samples, it fails to quantify specific Fe oxyhydroxides (e.g., ferrihydrite,
660 goethite, and hematite) or distinct Fe-organic compounds. Thus, a combination with Fe
661 EXAFS, as also WT, allows the speciation of Fe in different fractions and aggregates in
662 soils subjected to dynamic redox conditions.

663

664 **5. CONCLUSIONS**

665 Evaluating the mechanisms for OC stabilization in paddy soils still deserves attention
666 particularly due to the complex interactions between C cycling and changes in the
667 contents and mineralogy of hydrous Fe oxides in redox-active systems. In this study, we
668 linked the enhanced stabilization of OC in temperate paddy soils to the redox-driven
669 changes in Fe phases (evaluated by Fe K-edge XANES and EXAFS spectroscopy) and
670 their distribution between aggregate and particle-size fractions. Our findings have shown
671 that although paddy topsoils show higher contents of particulate OC in the coarser size-
672 fractions with respect to non-paddy soils, most of the SOC is associated with the finer
673 soil fractions, not only in the topsoil but also in the subsoil. This suggests that the
674 management-induced differences in C stocks is not primarily due to the limited
675 decomposition of crop residues under paddy management, but rather to the redox-driven
676 changes in the association of OC with soil minerals. We show that OC stabilization
677 through interaction with minerals is also affected by microaggregate stability. Paddy
678 management may lead to microaggregate breakdown with a preferential release of clay-
679 sized particles rich in both SRO Fe oxides and OC, while intra-microaggregate fine silt-
680 sized particles may also serve as an important OC sink. Long-term alternating redox
681 conditions generally resulted in paddy topsoil horizons that were depleted in pedogenic
682 Fe with respect to non-paddy soils, and led to a redistribution of Fe phases across different
683 particle size fraction often as less crystalline phases (primarily ferrihydrite and Fe-OM
684 associations). Nonetheless, the higher C contents indicate that higher C loadings can be
685 achieved under these redox-dynamic environments. Moreover, illuvial horizons under
686 paddy management were enriched in SRO hydrous Fe oxides and this contributed to
687 enhanced microaggregate formation and C stabilization with respect to non-paddy
688 subsoils.

689

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Figure captions

Figure 1. Soil OC distribution between different aggregate and particle-size fractions in the (a) non-paddy and (b) paddy soils as a function of soil depth. CSa+POM, coarse sand and particulate OM; FSa, fine sand; CSi, coarse silt; FSi, fine silt; Cl, clay. Black bars represent the proportion of fraction OC within microaggregates for the coarse silt (mCSi), fine silt (mFSi), and clay (mCl) fractions. Error bars represent the standard error.

Figure 2. Intra:inter-microaggregate ratio of (a) OC and (b) pedogenic Fe (Fe_d) associated with coarse silt (CSi), fine silt (FSi), and clay (Cl) particle-size fractions as a function of depth for non-paddy and paddy soils.

Figure 3. Distribution of dithionite-citrate-bicarbonate-extractable Fe (Fe_d ; a, b), oxalate-extractable Fe (Fe_o ; c, d), and crystalline Fe (hydr)oxides (Fe_c ; e, f) between different aggregate and particle-size fractions in the non-paddy (a, c, e) and paddy (b, d, f) soils as a function of soil depth. CSa+POM, coarse sand and particulate OM; FSa, fine sand; CSi, coarse silt; FSi, fine silt; Cl, clay. Black bars represent the proportion of fraction pedogenic Fe within microaggregates for the coarse silt (mCSi), fine silt (mFSi), and clay (mCl) fractions.

Figure 4. Changes in the Fe-K edge XANES pre-edge centroid position for (a) fine sand (FSa), inter and intra-microaggregate coarse silt (CSi and mCSi), (b) inter and intra-microaggregate fine silt (FSi and mFSi), and (c) inter and intra-microaggregate clay (Cl and mCl) fractions in non-paddy and paddy soils as a function of soil depth.

Figure 5. k^3 -weighted EXAFS spectra of the coarse silt (CSi), fine silt (FSi), clay (Cl), coarse silt in aggregates (mCSi), fine silt in aggregates (mFSi), clay in aggregates (mCl) fractions of Ap1, Ap2, Bgw horizons of non-paddy soil and Arp1, Arp2, Arpd, Brd1 and Brd2 horizons of paddy soil. The red dotted lines represent the linear combination fits of the sample spectra ($n=3$). R-factors for the fits are displayed.

Figure 6. High-resolution WT plots of of the coarse silt (CSi), fine silt (FSi), clay (Cl), coarse silt in aggregates (mCSi), fine silt in aggregates (mFSi), clay in aggregates (mCl) fractions of non- paddy (a) and paddy (b) soils. Data are plotted as a function of k (\AA^{-1})

on the x axis and R (Å) on the y axis in the range 2.2–4.0 (Å).

Figure 1

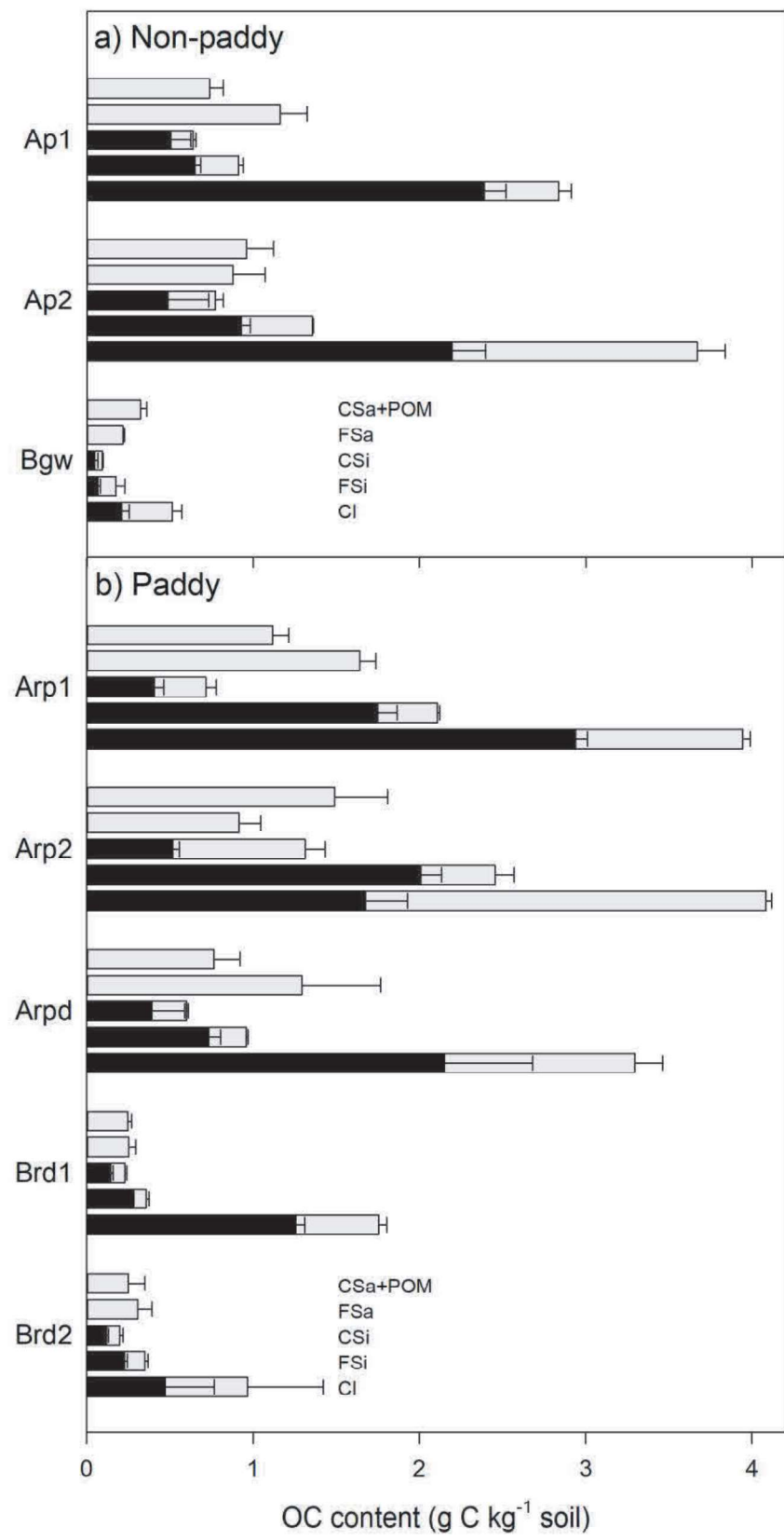


Figure 2

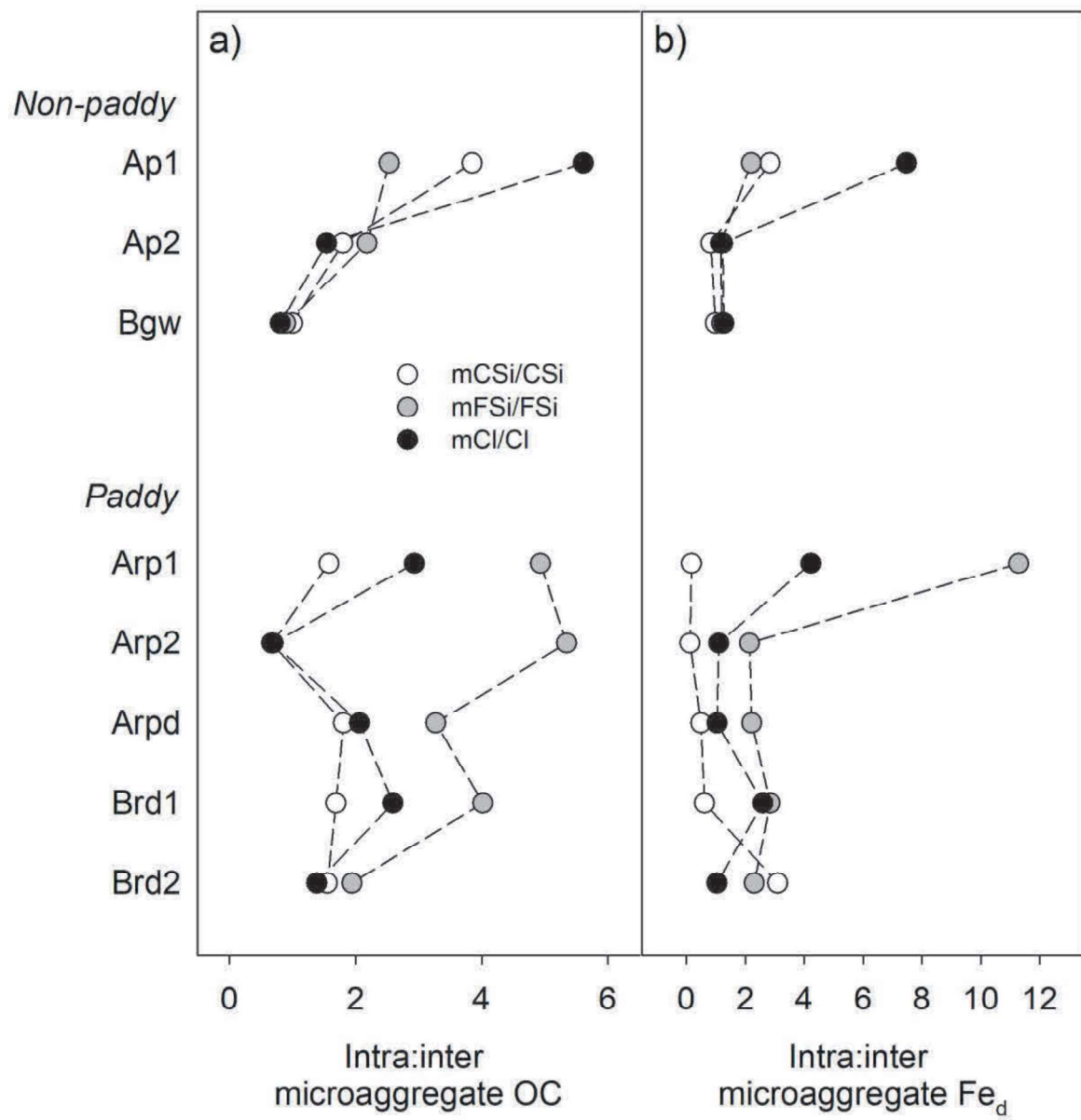


Figure 3

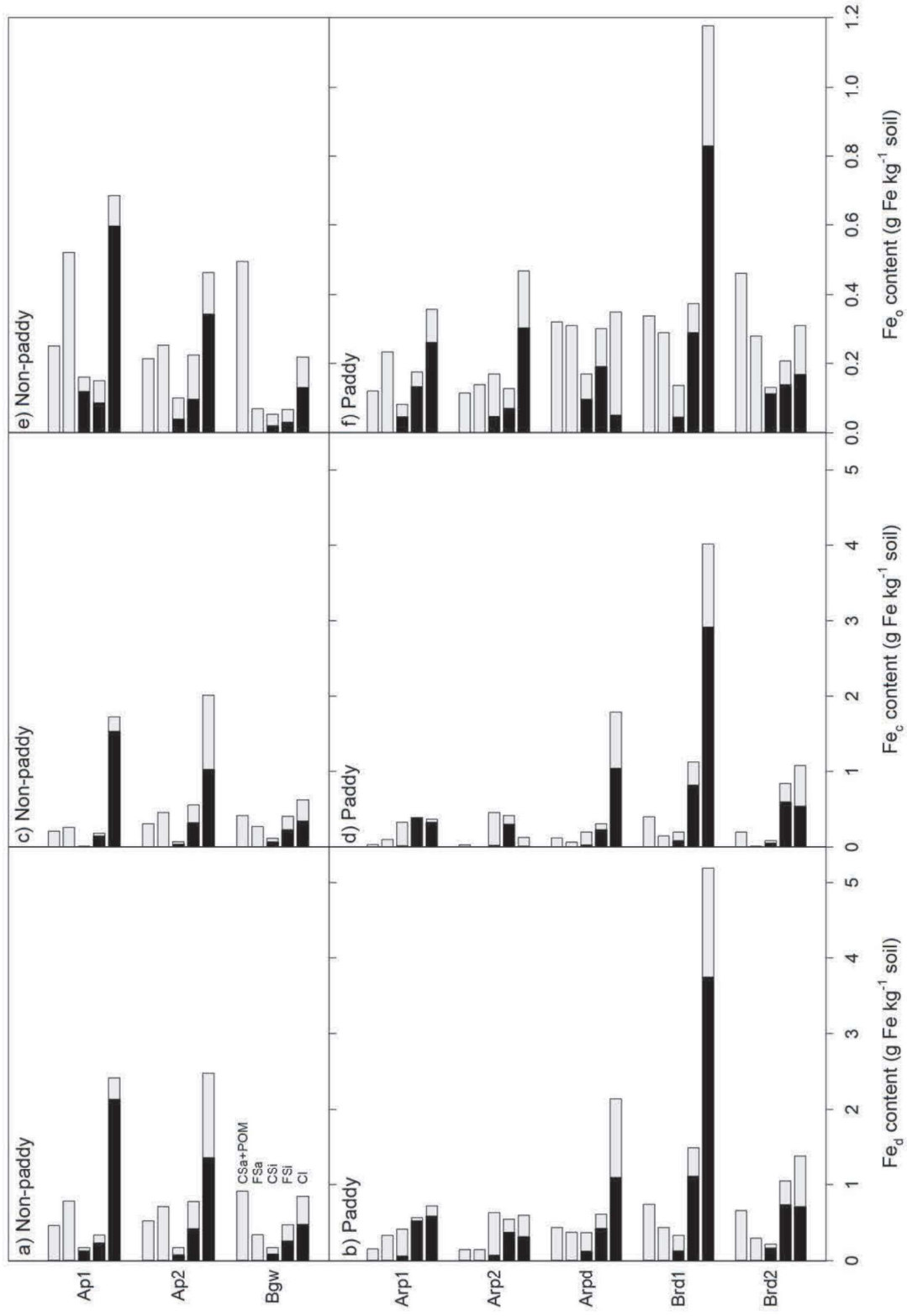


Figure 4

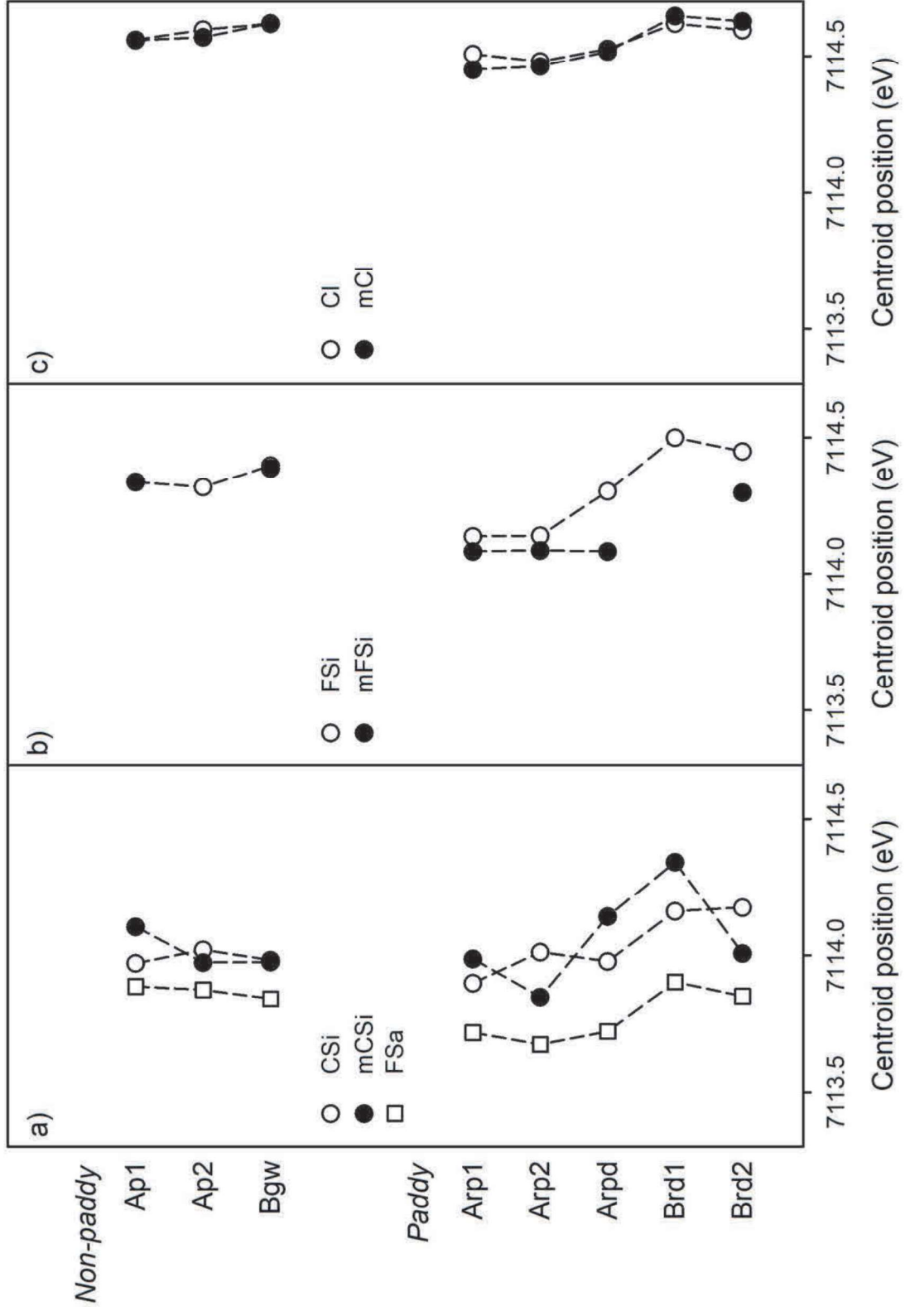


Figure 5

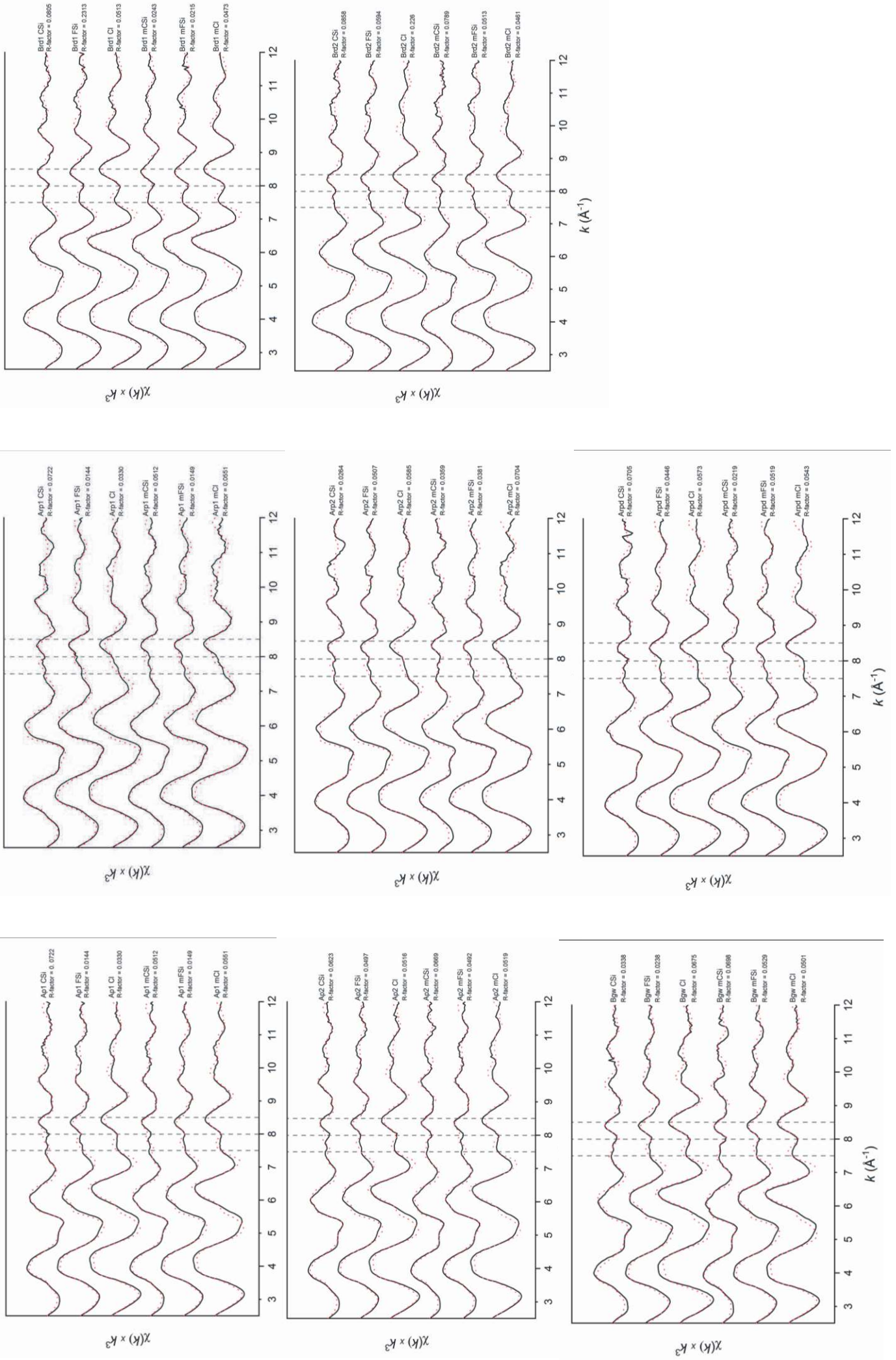
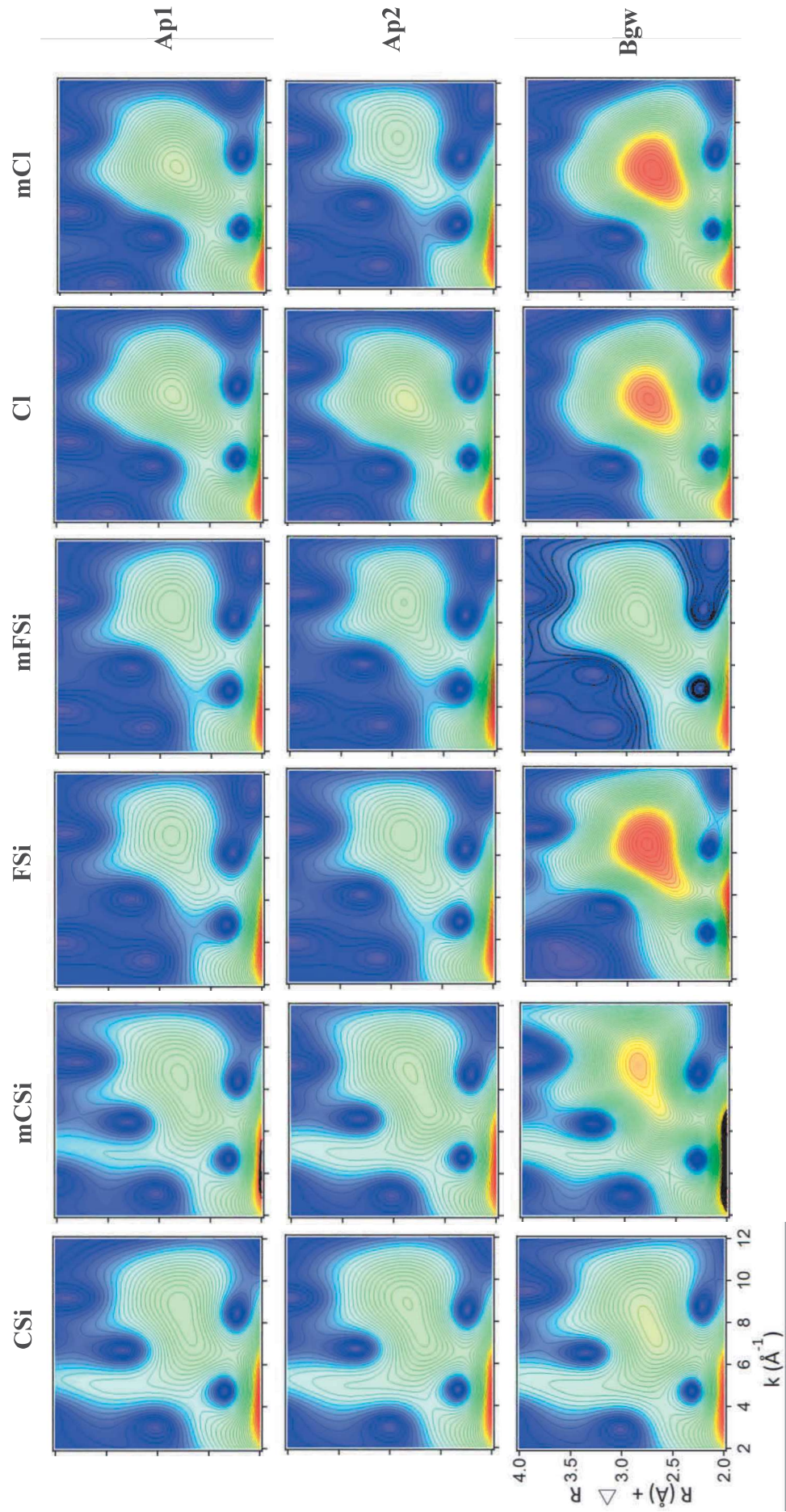


Figure 6

a)



b)

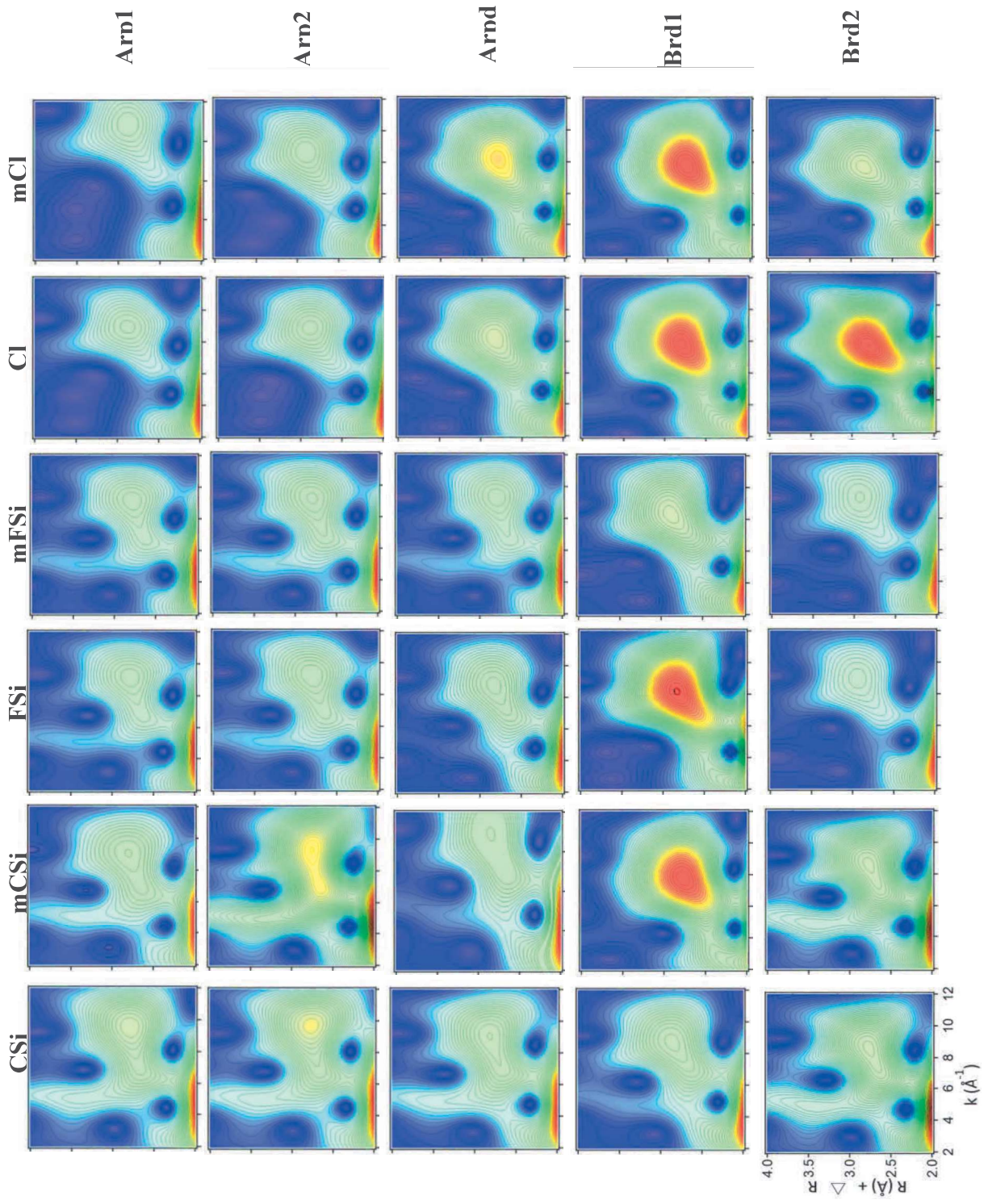


Table 1. Ratio of oxalate-extractable Fe (Fe_o) to dithionite-citrate-bicarbonate-extractable Fe (Fe_d) in different particle-size fractions for each horizon in the non-paddy and paddy soils.

Soil/Horizon	CSa+POM	FSa	CSi + mCSi	FSi + mFSi	Cl + mCl
Non-paddy					
Ap1	0.5	0.7	0.9	0.4	0.3
Ap2	0.4	0.4	0.6	0.3	0.2
Bgw	0.5	0.2	0.3	0.1	0.3
Paddy					
Arp1	0.8	0.7	0.2	0.3	0.5
Arp2	0.8	1.0	0.3	0.2	0.8
Arpd	0.7	0.8	0.5	0.5	0.2
Brd1	0.5	0.7	0.4	0.3	0.2
Brd2	0.7	1.0	0.6	0.2	0.2

CSa+POM, coarse sand and particulate OM; FSa, fine sand; CSi, inter-microaggregate coarse silt; mCSi, intra-microaggregate coarse silt; FSi, inter-microaggregate fine silt; mFSi, intra-microaggregate fine silt; Cl, inter-microaggregate clay; mCl, intra-microaggregate clay fraction.

Table 2. Results for the LCF performed on the Fe K-edge XANES data of the fine sand (FSa), coarse silt (CSi), fine silt (FSi), clay (Cl), coarse silt in aggregates (mCSi), fine silt in aggregates (mFSi), clay in aggregates (mCl) fractions of Ap1, Ap2, Bgw horizons of non-paddy soil and Arp1, Arp2, Arpd, Brd1, and Brd2 horizons of paddy soil.

	Chi2	Component 1	%	Component 2	%	Component 3	%	Component 4	%	Sum
Ap1 FSa	0.033087096	Chlorite	32	Siderite	26	Illite	21	Hematite	20	100
Ap1 CSi	0.019310413	Chlorite	26	Illite	48	Hematite	21	Magnetite	5	100
Ap1 mCSi	0.008858912	Chlorite	22	Illite	66	Hematite	13			100
Ap1 FSi	0.008196354	Chlorite	27	Smectite	42	Nontronite	19	Lepidocrocite	11	100
Ap1 mFSi	0.006696096	Chlorite	26	Smectite	47	Illite	23	FeIII citrate	4	100
Ap1 Cl	0.010688951	Chlorite	8	Jacobsite	13	Nontronite	79			100
Ap1 mCl	0.010184488	Chlorite	8	Jacobsite	13	Nontronite	79			100
Ap2 FSa	0.039485435	Chlorite	33	Siderite	33	Illite	13	Hematite	20	100
Ap2 CSi	0.022535003	Chlorite	27	Illite	46	Hematite	27			100
Ap2 mCSi	0.027156644	Chlorite	26	Illite	37	Hematite	23	Magnetite	14	100
Ap2 FSi	0.006497925	Chlorite	25	Illite	26	Smectite	42	FeIII citrate	7	100
Ap2 mFSi	0.427969307	Chlorite	12	Jacobsite	38	Nontronite	50			100
Ap2 Cl	0.009034114	Chlorite	11	Smectite	65	Lepidocrocite	24			100
Ap2 mCl	0.013101914	Chlorite	11	Nontronite	84	Lepidocrocite	5			100
Bgw FSa	0.038458154	Chlorite	34	Siderite	29	Illite	14	Hematite	22	100
Bgw CSi	0.032032481	Chlorite	26	Illite	36	Hematite	27	Magnetite	11	100
Bgw mCSi	0.026492885	Chlorite	25	Illite	34	Hematite	26	Magnetite	14	100
Bgw FSi	0.007402408	Chlorite	26	Smectite	61	Goethite	9	FeIII citrate	4	100
Bgw mFSi	0.007050961	Chlorite	23	Smectite	25	Illite	42	FeIII citrate	9	100
Bgw Cl	0.013186125	Chlorite	8	Nontronite	77	Ferrihydrite	15			100

Bgw mCl	0.014873833	Chlorite	10	Nontronite	83	FeIII citrate	7	100
Arp1 FSa	0.027628912	Chlorite	33	Siderite	29	Illite	19	100
Arp1 CSi	0.01276442	Chlorite	27	Illite	64	Magnetite	9	100
Arp1 mCSi	0.009723367	Chlorite	24	Illite	68	Hematite	9	100
Arp1 FSi	0.009919808	Chlorite	29	Illite	26	Smectite	22	100
Arp1 mFSi	0.008831991	Chlorite	29	Illite	42	Smectite	22	100
Arp1 Cl	0.010773327	Chlorite	19	Smectite	80	FeIII citrate	1	100
Arp1 mCl	0.010542052	Chlorite	16	Jacobsite	5	Nontronite	79	100
Arp2 FSa	0.034934128	Chlorite	33	Siderite	32	Hematite	22	100
Arp2 CSi	0.01158174	Chlorite	27	Illite	60	Hematite	11	100
Arp2 mCSi	0.047753368	Chlorite	26	Illite	40	Magnetite	34	100
Arp2 FSi	0.00624999	Chlorite	26	Illite	52	Smectite	22	100
Arp2 mFSi	0.006762771	Chlorite	26	Illite	58	Smectite	16	100
Arp2 Cl	0.008425091	Chlorite	19	Smectite	74	Lepidocrocite	7	100
Arp2 mCl	0.007167858	Chlorite	18	Smectite	65	Ferrihydrite	17	100
Arpd FSa	0.032190435	Chlorite	34	Siderite	32	Illite	14	100
Arpd CSi	0.017333956	Chlorite	27	Illite	47	Hematite	18	100
Arpd mCSi	0.005592672	Chlorite	19	Illite	75	Fe III citrate	6	100
Arpd FSi	0.007043644	Chlorite	28	Smectite	33	Nontronite	25	100
Arpd mFSi	0.008959662	Chlorite	28	Illite	44	Smectite	21	100
Arpd Cl	0.008911101	Chlorite	12	Jacobsite	11	Nontronite	78	100
Arpd mCl	0.009600908	Chlorite	11	Jacobsite	12	Nontronite	77	100
Brd1 FSa	0.029485302	Chlorite	32	Siderite	27	Illite	19	100
Brd1 CSi	0.008067183	Chlorite	20	Illite	63	Hematite	17	100
Brd1 mCSi	0.004323186	Chlorite	19	Illite	53	Smectite	14	100
Brd1 FSi	0.005927233	Chlorite	23	Smectite	35	Nontronite	32	100
Brd1 mFSi	0.066203605	Chlorite		Smectite		Nontronite		
						FeIII citrate	9	
						FeIII citrate		

Brd1 Cl	0.015676096	Chlorite	10	Nontronite	84	FeIII citrate	6		100
Brd1 mCl	0.014728171	Chlorite	9	Nontronite	83	Fe(III)-citrate	8		100
Brd2 FSa	0.031482016	Chlorite	32	Siderite	31	Illite	16	Hematite	20
Brd2 CSi	0.00581651	Chlorite	18	Illite	75	Maghemite	7		100
Brd2 mCSi	0.022010179	Chlorite	25	Illite	39	Hematite	23	Magnetite	12
Brd2 FSi	0.008325141	Chlorite	26	Smectite	57	Goethite	17		100
Brd2 mFSi	0.007011355	Chlorite	25	Illite	28	Smectite	40	FeIII citrate	6
Brd2 Cl	0.012284473	Chlorite	9	Nontronite	81	Ferrihydrite	11		100
Brd2 mCl	0.010851395	Chlorite	10	Smectite	66	Lepidocrocite	24		100

Table 3. Results for the four-components LCF performed on the k^3 - weighted Fe K-edge EXAFS data of the fine sand (FSa) coarse silt (CSi), fine silt (FSi), clay (Cl), coarse silt in aggregates (mCSi), fine silt in aggregates (mFSi), clay in aggregates (mCl) fractions of Ap1, Ap2, Bgw horizons of non-paddy soil and Arp1, Arp2, Arpd, Brd1, and Brd2 horizons of paddy soil. Results are expressed in percentage of the fitting components corresponding to experimental spectra of model compounds reported by O'Day et al. (2004) chlorite, ferrihydrite, lepidocrocite, and Fe(III)-citrate.

	R-factor	Component 1	%	Component 2	%	Component 3	%	Component 4	%	Sum
Ap1 FSa	0.079749	Chlorite	44	Magnetite	8	Goethite	33	Lepidocrocite	15	100
Ap1 CSi	0.0429419	Chlorite	46	Ferrihydrite	21	Lepidocrocite	17	FeIII citrate	17	100
Ap1 mCSi	0.0343152	Chlorite	44	Ferrihydrite	20	Lepidocrocite	15	FeIII citrate	21	100
Ap1 FSi	0.0339569	Chlorite	35	Ferrihydrite	19	Lepidocrocite	13	FeIII citrate	33	100
Ap1 mFSi	0.0289672	Chlorite	34	Ferrihydrite	22	Lepidocrocite	13	FeIII citrate	31	100
Ap1 Cl	0.0350046	Chlorite	13	Ferrihydrite	31	Lepidocrocite	14	FeIII citrate	43	100
Ap1 mCl	0.0339516	Chlorite	13	Ferrihydrite	31	Lepidocrocite	13	FeIII citrate	42	100
Ap2 FSa	0.0945382	Chlorite	49	Illite	19	Hematite	13	Lepidocrocite	19	100
Ap2 CSi	0.0425902	Chlorite	49	Ferrihydrite	20	Lepidocrocite	16	FeIII citrate	15	100
Ap2 mCSi	0.0529809	Chlorite	49	Ferrihydrite	24	Lepidocrocite	17	FeIII citrate	11	100
Ap2 FSi	0.0316848	Chlorite	35	Ferrihydrite	22	Lepidocrocite	13	FeIII citrate	30	100
Ap2 mFSi	0.0324117	Chlorite	36	Ferrihydrite	21	Lepidocrocite	12	FeIII citrate	31	100
Ap2 Cl	0.0406223	Chlorite	15	Ferrihydrite	36	Lepidocrocite	11	FeIII citrate	38	100
Ap2 mCl	0.0405023	Chlorite	13	Ferrihydrite	35	Lepidocrocite	12	FeIII citrate	40	100
Bgw FSa	0.0561351	Chlorite	47	Illite	14	Hematite	14	Lepidocrocite	25	100
Bgw CSi	0.0293375	Chlorite	48	Ferrihydrite	24	Lepidocrocite	19	Fe III citrate	9	100
Bgw mCSi	0.0565707	Chlorite	48	Ferrihydrite	24	Lepidocrocite	17	Fe III citrate	11	100
Bgw FSi	0.0119554	Chlorite	30	Ferrihydrite	25	Lepidocrocite	15	Fe III citrate	30	100
Bgw mFSi	0.0302615	Chlorite	32	Ferrihydrite	25	Lepidocrocite	14	Fe III citrate	29	100
Bgw Cl	0.0484722	Chlorite	4	Ferrihydrite	42	Lepidocrocite	17	FeIII citrate	37	100

Bgw mCl	0.02219	Chlorite	12	Ferrihydrite	43	Lepidocrocite	15	Fe III citrate	31	100
Arp1 FSa	0.1303528	Chlorite	45	Illite	16	Ferrihydrite	28	Lepidocrocite	12	100
Arp1 CSi	0.0431159	Chlorite	54	Ferrihydrite	8	Lepidocrocite	14	FeIII citrate	23	100
Arp1 mCSi	0.0394779	Chlorite	46	Ferrihydrite	15	Lepidocrocite	16	FeIII citrate	23	100
Arp1 FSi	0.0128322	Chlorite	43	Ferrihydrite	9	Lepidocrocite	13	FeIII citrate	34	100
Arp1 mFSi	0.0117425	Chlorite	45	Ferrihydrite	13	Lepidocrocite	13	FeIII citrate	29	100
Arp1 Cl	0.0513891	Chlorite	26	Ferrihydrite	14	Lepidocrocite	14	FeIII citrate	46	100
Arp1 mCl	0.0461159	Chlorite	25	Ferrihydrite	16	Lepidocrocite	14	FeIII citrate	45	100
Arp2 FSa	0.1116709	Chlorite	50	Magnetite	10	Hematite	13	Lepidocrocite	27	100
Arp2 CSi	0.0604463	Chlorite	51	Ferrihydrite	13	Lepidocrocite	17	FeIII citrate	18	100
Arp2 mCSi	0.0320848	Chlorite	56	Ferrihydrite	16	Lepidocrocite	19	FeIII citrate	9	100
Arp2 FSi	0.0339822	Chlorite	46	Ferrihydrite	19	Lepidocrocite	11	FeIII citrate	24	100
Arp2 mFSi	0.0130281	Chlorite	46	Ferrihydrite	15	Lepidocrocite	14	FeIII citrate	26	100
Arp2 Cl	0.0395401	Chlorite	25	Ferrihydrite	20	Lepidocrocite	14	FeIII citrate	41	100
Arp2 mCl	0.0545088	Chlorite	23	Ferrihydrite	21	Lepidocrocite	15	FeIII citrate	42	100
Arpd FSa	0.1353997	Chlorite	44	Magnetite	11	Ferrihydrite	35	FeIII citrate	10	100
Arpd CSi	0.0491993	Chlorite	41	Ferrihydrite	23	Lepidocrocite	19	FeIII citrate	18	100
Arpd mCSi	0.0141161	Chlorite	41	Ferrihydrite	21	Lepidocrocite	18	FeIII citrate	21	100
Arpd FSi	0.0246098	Chlorite	36	Ferrihydrite	21	Lepidocrocite	16	FeIII citrate	27	100
Arpd mFSi	0.0442138	Chlorite	41	Ferrihydrite	13	Lepidocrocite	16	FeIII citrate	31	100
Arpd Cl	0.035265	Chlorite	18	Ferrihydrite	26	Lepidocrocite	18	FeIII citrate	38	100
Arpd mCl	0.0274329	Chlorite	17	Ferrihydrite	28	Lepidocrocite	20	FeIII citrate	35	100
Brd1 FSa	0.0858789	Chlorite	49	Nontronite	27	Hematite	13	Magnetite	11	100
Brd1 CSi	0.0526621	Chlorite	35	Ferrihydrite	29	Lepidocrocite	16	FeIII citrate	20	100
Brd1 mCSi	0.0123727	Chlorite	31	Ferrihydrite	31	Lepidocrocite	16	FeIII citrate	22	100
Brd1 FSi	0.2231373	Chlorite	66	Goethite	21	Lepidocrocite		FeIII citrate	13	100
Brd1 mFSi	0.011673	Chlorite	27	Ferrihydrite	30	Lepidocrocite	13	FeIII citrate	30	100

Brd1 Cl	0.0242448	Chlorite	10	Ferrihydrite	40	Lepidocrocite	19	FeIII citrate	31	100
Brd1 mCl	0.0230121	Chlorite	9	Ferrihydrite	41	Lepidocrocite	19	FeIII citrate	31	100
Brd2 FSa	0.0843658	Chlorite	51	Nontronite	31	Hematite	10	Magnetite	8	100
Brd2 CSi	0.0699578	Chlorite	36	Ferrihydrite	24	Lepidocrocite	12	Fe III citrate	29	100
Brd2 mCSi	0.0539459	Chlorite	47	Ferrihydrite	24	Lepidocrocite	14	Lepidocrocite	15	100
Brd2 FSi	0.0467505	Chlorite	29	Ferrihydrite	24	Lepidocrocite	11	Fe III citrate	36	100
Brd2 mFSi	0.0382681	Chlorite	36	Ferrihydrite	23	Lepidocrocite	11	Fe III citrate	30	100
Brd2 Cl	0.1897291	Chlorite	41	Goethite	22	Magnetite	15	FeIII citrate	22	100
Brd2 mCl	0.0416766	Chlorite	11	Ferrihydrite	40	Magnetite	6	Fe III citrate	43	100

