Soil development on sediments and evaporites of the Messinian crisis

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Abstract: Vast areas in the Mediterranean are characterised by evaporite deposits of the Messinian crises (c. 6–5.3 Ma BP). During this period, large deposits were built up in shallow lagoon-like systems and are now found in southern Italy, Albania, Cyprus and Turkey. So far, soil formation on evaporites has been studied predominantly in subarid to arid environments. Although the formation of soils has received new significance, little is known about the evolutionary trajectories on evaporites of the Mediterranean. We therefore studied soil formation in the Caltanissetta basin (Sicily) where evaporites are most widespread. The lithologies included the sequence: marine clay deposits, laminated marl (diatomite; Tripoli sediments), Calcare di Base (limestone), detritic deposits, gypsum (selenite). The chemical signature (immobile elements, rare earth elements) indicated that they all have a similar origin. Surprisingly, both an increasing Corg and carbonate content in the soils caused a decrease in the $\delta^{13}\text{C}$ signal in carbonates and in part in the bulk soil. The low $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of carbonates in the parent material indicate a high rock-water (or meteoric water) interaction that has occurred during sedimentation and diagenesis. Organic matter was oxidised into the shallow lagoon-like systems and its carbon incorporated in the limestone. Elemental leaching from silicates during pedogenesis was most intense in the soils that developed on clays and Tripoli sediments. Vertisols and Mollisols have evolved, together with a high amount of oxyhydroxides (non-crystalline and crystalline forms) and kaolinite. Only weak soil formation was recognisable at sites having gypsiferous parent material. The presence of a high amount of selenite hindered a more advanced evolution. The soils developed on detritic and gypsiferous material exhibited some palygorskite that was inherited from the parent material. At sites having selenite or limestone, shallow Aridisols or Mollisols are found. Weathering is weakly pronounced, e.g. indicated by a high proportion of trioctahedral minerals. Besides inheritance from the parent material, smectite and kaolinite are also actively formed in the soils with increasing weathering. Plagioclase and mica are the main sources of smectite and K-feldspar is a main source of kaolinite neo-formation. The evaporite deposits vary greatly within short distances causing a high spatial diversity of soils. Consequently, soil quality strongly varies, which challenges agricultural use. Well-developed soil profiles and advanced weathering stages are only possible when marine clays, Tripoli sediments or detritic deposits are the parent material. Limestone (Calcare di Base) and gypsiferous sediments (selenite) strongly limit soil formation and mineral transformation.

DOI: <https://doi.org/10.1016/j.catena.2019.104368>

Posted at the Zurich Open Repository and Archive, University of Zurich

ZORA URL: <https://doi.org/10.5167/uzh-177652>

Journal Article

Accepted Version

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Originally published at:

Egli, Markus; Plötze, Michael; Tikhomirov, Dmitry; Kraut, Tatjana; Wiesenberg, Guido L B; Lauria, Gabriele; Raimondi, Salvatore (2020). Soil development on sediments and evaporites of the Messinian crisis. *Catena*, 187:104368.

DOI: <https://doi.org/10.1016/j.catena.2019.104368>

1 **Soil development on sediments and evaporites of the Messinian crisis**

2

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30 **Abstract**

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32 (c. 6 – 5.3 Ma BP). During this period, large deposits were built up in shallow lagoon-like systems
33 and are now found in southern Italy, Albania, Cyprus and Turkey. So far, soil formation on
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36 evaporites of the Mediterranean. We therefore studied soil formation in the Caltanissetta basin
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38 deposits, laminated marl (diatomite; Tripoli sediments), Calcare di Base (limestone), detritic
39 deposits, gypsum (selenite). The chemical signature (immobile elements, rare earth elements)
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41 content in the soils caused a decrease in the $\delta^{13}C$ signal in carbonates and in part in the bulk soil.
42 The low $\delta^{13}C$ and $\delta^{18}O$ values of carbonates in the parent material indicate a high rock-water (or
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50 material exhibited some palygorskite that was inherited from the parent material. At sites having
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52 e.g. indicated by a high proportion of trioctahedral minerals. Besides inheritance from the parent
53 material, smectite and kaolinite are also actively formed in the soils with increasing weathering.
54 Plagioclase and mica are the main sources of smectite and K-feldspar is a main source of kaolinite
55 neo-formation.

56 The evaporite deposits vary greatly within short distances causing a high spatial diversity of soils.
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58 profiles and advanced weathering stages are only possible when marine clays, Tripoli sediments

59 or detritic deposits are the parent material. Limestone (Calcare di Base) and gypsiferous
60 sediments (selenite) strongly limit soil formation and mineral transformation.

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62 **Key Words:** Soil formation, evaporites, clay mineralogy, weathering, diatomite, stable isotopes,
63 carbonates

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66 **1. Introduction**

67 Significant domains of the Mediterranean area are characterised by shallow-water evaporites
68 deposited during the transition of the Miocene to the Pliocene, often during the third stage of the
69 Messinian salinity crisis. These deposits are well preserved (Manzi et al., 2016). During the
70 Messinian salinity crisis (MSC), many carbonate and evaporite deposits were formed in the
71 Mediterranean area. These deposits were bonded to carbonate platforms and coral reef
72 complexes that were widely distributed (Caruso et al., 2015). According to Manzi et al. (2016), the
73 MSC crisis took place particularly between 5.97 and 5.33 Ma BP. The transition from open marine
74 conditions to hypersaline environments occurred between 7 and 5.7 Ma BP (Caruso et al., 2015).
75 Messinian offshore evaporites can be found from Sicily to Calabria, in the Ionian basin, Albania,
76 along the Mediterranean ridge, Cyprus and southern Turkey. These deposits usually consist of
77 pre-evaporitic limestone units, lower evaporites (1st cycle), upper evaporites (2nd cycle), and clays
78 or limestones (Trubi) on top of them. The lower evaporites contain limestone and/or a lower
79 gypsum deposition-series (consisting of up to 16 cycles) where large halite and K-Mg salt lenses
80 may also be included (Manzi et al., 2011). The upper evaporites consist of the upper gypsum-
81 series and gypsum turbidites (Manzi et al., 2011). Many of these deposits were built up in rather
82 shallow lagoon-like systems. After the uplift of these sediments, erosion and incision processes
83 resulted in a smooth, hilly landscape. Within a relatively short distance, the different evaporite units
84 appear at the surface and are the basis for soil formation.

85 Soils on evaporite series in the Mediterranean area have only rarely been investigated. Some
86 studies have been realised on moderately comparable geological situation where claystones,
87 gypsiferous marlstone, limestones and silt- and sandstones were encountered (e.g., Lafuente et

88 al., 1999; Moazallahi and Farpoor, 2012; Tazike et al., 2017). Usually, such investigations were
89 carried out in arid or semiarid climates. As a consequence of the dry climate, rather weakly- to
90 moderately-developed soils were found that also exhibited a particular mineralogical composition
91 (e.g. often palygorskite was reported; e.g., Tazike et al., 2017). In several cases, the soils were
92 significantly influenced by aeolian input. Large parts of central Sicily are constituted of the
93 previously-mentioned evaporite series. The evaporite series in Sicily (Catalano, 1986; Manzi et al.,
94 2011), with its outcropping lithologies, occupy a prominent area. These evaporites have a great
95 importance for forestry (Fierotti et al., 1995) and agronomy (Raimondi et al., 2000) because they
96 determine the properties of soils that evolve on them. In addition, the run-off waters circulate
97 soluble salts (chlorides and sulphates) that influence the properties of the adjacent substrates and
98 soils (Raimondi et al., 1999; Puccio and Raimondi, 2017) and the productivity of plants. Moreover,
99 the water of the hydrographic network that either begins or crosses these substrates (e.g. the
100 Salito river, the Platani-Sicilia river basin, the Salso-Sicilia river) loses the required quality for
101 drinking water (for man and animals) or irrigation (Ballatore et al., 1968a,b).

102 It is, however, also true that very fertile soils evolve on some outcrops of these lithotypes at lower
103 altitudes having a high capacity for agricultural use (Lauria and Raimondi, 2018). Within the
104 context of global warming and food security, the formation of soils and their evolutionary trajectories
105 have received a new significance. So far, a systematic study on the evolution of these soils and of
106 their characteristics has never been done.

107 We therefore aimed at investigating the main soil evolutionary trajectories as a function of the
108 various evaporitic deposits. We had to assume that in this Mediterranean area soil evolution —
109 depending on the substrate — can reach advanced stages having a high proportion of kaolinite
110 and smectite. Furthermore, soil evolution should be distinctly different at a very small scale
111 because of the distinctly different main chemical composition of the substrates.

112

113

114 **2. Materials and methods**

115 **2.1. Study area**

116 The study area is near Canicatti in the central to southern part of Sicily. The investigated soils are
117 at an altitude between 320 – 380 m a.s.l. (Table 1; Fig. 1) and are characterised as Mollisols,
118 Vertisols, Entisols or Aridisols. The climate is Mediterranean having an average annual
119 precipitation of about 500 mm. These soils evolved on typical sediments deposited before and
120 during the Messinian Crisis: clayey marine sediments (the ‘Argille’ sites), diatom sediments
121 (‘Tripoli’), limestone (Calcare di Base, ‘Calcare’ site), detritic deposits (‘Detriti’ site) and gypsiferous
122 sediments (‘Gessi’ site).

123 The Caltanissetta basin is the one in which the evaporites are most widespread. This basin has
124 been described as a vast foredeep area in front of a northern upraising mountain range (Fig. 1).

125 The Tripoli deposits (lowest units) consist of a succession of laminated white diatoms rich in
126 coccolithophores and dinoflagellates with remains of teleostean fish, sometimes alternating with
127 bituminous pelite and laminated diatomite marls having a whitish colour and abundant planktonic
128 foraminifera. The Tripoli formation has a thickness that usually does not exceed 40 m (in some
129 cases it reaches 70 – 80 m). The age is lower Messinian.

130 The Messinian Crisis was responsible for a huge accumulation of evaporites throughout the whole
131 Mediterranean domain (Caruso et al., 2015). The Evaporites can be subdivided into a 1st (lower
132 evaporites) and 2nd cycle (upper evaporites). In Sicily, the 1st cycle consists mostly of “Calcare di
133 Base”, interbedded with gypsum layers. The Messinian deposits accumulated in three main
134 depozones of the Apenninic-Maghrebien foredeep system (Manzi et al., 2011), one of which was
135 the Caltanissetta Basin in which the study site is situated. Depending on the position in the
136 depozones, carbonate (breccia), sulphiferous carbonates (sulphur limestone) etc. can be found.

137 The lower evaporites contain gypsum (Lower Gypsum; Manzi et al., 2011; Caruso et al., 2015) up
138 to 300 m thick that is associated with halite.

139 The formation of the Calcare di Base and the sulphur deposits predates the deposition of the
140 Upper Gypsum unit (Caruso et al., 2015). The Upper Evaporites (Upper Gypsum; Manzi et al.,
141 2011) are made of a cyclic succession of up to 300 m-thick gypsum and fine clastic deposits that
142 grade progressively upward to hyper- and hyposaline sediments of the “Lago-Mare” that were
143 deposited before the Zanclean marine reflooding of the Mediterranean Basin (Caruso et al., 2015).

144 The Upper Gypsum unit, overlying the Lower Gypsum unit along an irregular stratigraphic contact,

possibly complicated by the dissolution of underlying halite bodies (Manzi et al., 2009), consists of cyclically stacked primary gypsum and marl beds capped by the siliciclastic Arenazzolo Formation that are overlain by the Pliocene marine Trubi Formation (carbonates; Manzi et al., 2011).

2.2. Sampling strategy

In total, eight profiles (all at a similar altitude of about 300 – 400 m a.s.l.) were sampled (Fig. 2). With this approach, 1 – 3 soil profiles per geological substrate in close vicinity to each other were investigated. The soil profiles were sampled based on their horizonation and, where possible, down to the C horizon. About 1 – 2 kg per soil horizon (continuous sampling over the horizon) were taken using open pits or freshly created trenches. Furthermore, soil cylinders (100 cm³, Eijkelkamp) were used to determine bulk density of the soil material (fine earth). Undisturbed soil samples (at least 2 per horizon) were extracted from each soil horizon.

2.3. Physical and chemical analyses

All bulk samples were sieved to <2 mm (fine earth) after oven drying (40 °C) for 48 hours. Particle-size distribution of the fine-earth was measured using a combined method consisting of wet-sieving the coarser particles (2000 – 32 µm) and determining the finer particles (< 32 µm) by means of an X-ray sedimentometer (SediGraph 5100). Because some of the samples contained gypsum, a pre-treatment using a BaCl₂ solution was necessary (according to Vieillefon, 1979).

Soil pH (in 0.01 M CaCl₂) was determined on air-dried fine-earth samples using a soil:solution ratio of 1:2.5. The oxalate-extractable Al, Fe and Mn content was determined following the standard method of McKeague et al. (1971). Element concentrations were analysed using atomic absorption spectroscopy (AAnalyst 700, Perkin Elmer). The oxalate (Al_o, Mg_o, Fe_o) treatment usually extracts weakly- and poorly-crystalline phases and some of the organic phases (Mizota and van Reeuwijk, 1989). In addition, the total amount of pedogenic (crystalline and non-crystalline) Fe-, Al- and Mn-phases was determined using a dithionite extraction (Borggaard, 1988). The total carbon (C) and nitrogen (N) contents and δ¹³C were determined using elemental analysis isotope ratio mass spectrometry (EA-IRMS). The measurements were performed using a Thermo Fisher Scientific Flash HT Plus elemental analyser equipped with a thermal conductivity detector and coupled to a

174 ConFlo IV to Delta V Plus isotope ratio mass spectrometer. The isotopic values were calculated
175 against working in-house standards (Caffeine (Sigma), Chernozem (Black Carbon Reference
176 Materials)), which were themselves calibrated against international reference materials (Caffeine
177 (IAEA 600), Benzoic acid (IAEA 601), Cellulose (IAEA CH3), ammonium sulfate (IAEA N1), Urea
178 (IVA)). The carbonate was determined using a Thermo Fisher Scientific GasBench II connected to
179 a Delta V Plus isotope ratio mass spectrometer using a slightly modified method compared to
180 Breitenbach and Bernasconi (2011). Aliquots of samples and standards containing 20-100 µg
181 carbonate C were weighed into exetainer vials, closed and automatically flushed with He for 10
182 minutes. 25–50µl phosphoric acid was added manually by using a syringe. Samples were
183 measured at least 60 minutes after acid addition, which was sufficient to release all carbonate C
184 from calcium carbonate, aragonite and dolomite (Breitenbach and Bernasconi, 2011). The
185 carbonate C concentrations as well as $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values were calibrated against a secondary
186 standard (Merck CaCO_3) and international reference material (IAEA NBS18 Calcite). Organic
187 carbon was obtained by the difference between the total and inorganic carbon.
188 The determination of the loss on ignition (LOI; organic matter and adsorbed water) was performed
189 by igniting 2 g of oven-dried fine earth at 550 °C for 16 h.
190 The analysis of the total elemental content in the fine earth (major and minor compounds and REE
191 (rare Earth elements) such as La, Ce, Pr, Nd and Sm) was done by means of X-ray fluorescence
192 (XRF). Soil material (c. 5 g) was milled to < 50 µm and analysed as loose powder in sample cups
193 using an energy dispersive X-ray fluorescence spectrometer (SPECTRO X-LAB 2000, SPECTRO
194 Analytical Instruments, Germany).

195

196 2.4. Soil clay mineralogy

197 The clay fraction of the soils was obtained after removal of organic matter with dilute (3 %) and Na-
198 acetate buffered H_2O_2 (pH 5) and then by dispersion with Calgon and sedimentation in water (Egli
199 et al., 2001).

200 Oriented specimens on glass slides were analysed using a Rigaku SmartLab Automated
201 Multipurpose X-ray Diffractometer equipped with a 3kW sealed tube X-ray generator having a
202 standard Cu target. Using $\text{Cu-K}\alpha$ radiation generated at 40 kV and 30 mA, the slides were

scanned in the range of 3 – 15° 2θ with a step of 0.01° 2θ and a speed of 2° 2θ per minute. The following sample treatments were performed prior to X-ray diffraction (XRD) scanning: Mg-saturation, glycerol solvation (Gly) and K-saturation. After the first XRD scan, the K-saturated samples were heated for 2 h at 335 and 550 °C, and rescanned after each heating step. The d(060) region was investigated on randomly oriented specimens in the angle range of 58 to 64° 2θ with steps of 0.01° 2θ at a speed of 1° 2θ per minute. The XRD data of oriented specimens were corrected for Lorentz and polarisation factors (Moore and Reynolds, 1997) following Egli et al. (2001). Peak separation and profile analysis were carried out with Origin PFM™ following Lanson (1997) and Egli et al. (2001).

For quantitative X-ray analyses, randomly oriented Ca-exchanged samples (Zhang et al., 2003) were scanned from 4 to 80° 2θ with steps of 0.02° 2θ at 2 s intervals using a Bragg-Brentano X-ray diffractometer (Bruker AXS D8 Advance, Germany). The instrument worked with CoKα radiation and was equipped with an automatic theta compensating divergence slit, primary and secondary soller slits and a LynxEye line detector. The qualitative phase analysis was carried out using the software package DIFFRAC.EVA V4.3 (Bruker AXS). The quantitative mineralogical composition of the inorganic part of the material was determined using Rietveld analysis of these XRD patterns with the program Profex/BGMN V3.14.3 (Döbelin and Kleeberg, 2015).

220

221 2.7. Chemical weathering indices and semi-quantitative and relative dating

To characterise mineral alteration and chemical weathering in soils, several indices were used. Among them were the weathering index WIP according to Parker (1970) and the molar ratio of (K+Ca) / Ti with Ti being the immobile element (Egli and Fitze, 2000; Stiles et al., 2003), K and Ca the weatherable elements. To better characterise silicate weathering, this coefficient was modified into (K+Na)/Ti, because the investigated soils are rich in carbonate and, therefore, large parts of Ca may derive from carbonate leaching biasing the original index.

The WPI is defined by (molar weight percentage):

$$229 \quad WIP = 100 \left[\frac{2Na_2O}{0.35} + \frac{MgO}{0.9} + \frac{2K_2O}{0.25} + \frac{CaO}{0.7} \right] \quad (1)$$

230

231 CaO refers to the silicate proportion of Ca.

232 In addition, the open-system mass transport function τ (Chadwick et al., 1990; Egli and Fitze,
233 2000) was determined. Relative elemental losses in the soil column can be calculated as follows:

234
$$\tau = \left(\frac{C_{j,w} \cdot C_{i,p}}{C_{i,w} \cdot C_{j,p}} \right) - 1 \quad (2)$$

235 where: i denotes the immobile element (Ti), $C_{j,p}$ (g/kg) is the concentration of element j in the
236 unweathered parent material, and $C_{j,w}$ is the concentration of element j in the weathered product
237 (g/kg).

238

239

240 **3. Results**

241 3.1. General soil characteristics

242 The Tripoli and the Argille sites exhibited the thickest soil columns with up to 270 cm (Tripoli 2).
243 Depending on the site conditions (erosive vs. less erosive site), the thickness of the Tripoli soils
244 varied considerably, showing an A-B-C or only A-C soil horizon sequence. The Calcare and Gessi
245 soils were often shallower and had a thickness of roughly 70 cm. The rock surface at the Gessi site
246 exhibited some karstic features and fractures giving sometimes rise to the accumulation of more
247 weathered soil material in pockets below a less weathered material (Table 2, Fig. 2). In addition,
248 the Gessi site is within an area having many rock outcrops. Owing to the rock outcrops and
249 steeper slope, part of the rainwater is lost with lateral flow. Consequently, less water is available
250 for soil formation and plant growth giving rise to arid conditions (Aridisol). The Argille sites have
251 Vertisols. Due to land use, the Argille site 7 has an additional layer (an Entisol) overlaying the
252 Vertisol (Table 1).

253 All soils are characterised by a pH-value in the neutral to slightly alkaline range (7.3 – 7.9; Table
254 2). As a consequence, all soils contain carbonate (Table 3). The carbonate content is low in the
255 Argille 5, 6 and Gessi soils. The Detriti and Argille 7 sites contain relatively strongly varying
256 carbonate contents. This is, among other things, due to anthropogenic activities. The highest
257 carbonate contents were measured in the Tripoli soils and at the Calcare site. Several soils have a
258 calcic horizon and secondary carbonates. The original composition of the Tripoli deposits (diatoms)

contains little carbonate (about 4%) and about 70 – 75% SiO₂ (Table 3). A considerably high gypsum content (Table 3) was measured in the whole soil profile at the Gessi site. A small amount of gypsum was also traceable in the subsoil of Argille 5 and 6 (Table 3).

Not surprisingly, the Argille soils are characterised by a very high clay content (up to more than 70%). The Tripoli soils are considerably less clayey, but have a high silt content. The Gessi soil has a more silt-sandy character.

The relatively homogeneous and deep distribution of organic carbon along the soil profiles of Argille 5, 6, 7 and Detriti exhibits their vertic characteristics. The Argille soils clearly produce the highest amount of oxalate-extractable Fe and Al indicating an active weathering environment (Table 4, Fig. 3a). In this respect, the Detriti soil is moderately comparable to the Argille soils. Crystalline Fe-forms — derived from the difference of the dithionite minus the oxalate-extractable Fe-forms — are detected in all soils. However, the Argille soils (Argille 5 and 6) exhibit by far the highest amount of crystalline Fe-forms with up to 13 g/kg. A low content of crystalline Fe is measured at the Gessi, Calcare and Detriti sites. The Tripoli soils were in a similar range and sometimes exhibited a slightly higher content of crystalline Fe-forms. The oxalate-extractable Si contents are low; however, the molar ratio Al/Si-ratio is often between 1 and 2 indicating the presence of a small amount of ITM (imogolite type materials; Parfitt and Hemni, 1982).

The production of oxalate- and dithionite-extractable Fe or Al, however, also depends on the total amount of Fe and Al present in the soils. The ratio of the dithionite- or oxalate-extractable content of Fe and Al to the corresponding total content does not vary that greatly among the different soils. In average, about 14.5% ($\pm 6\%$) of Fe is present in a pedogenic form.

Each of the soil profiles (average value) exhibited quite a similar trend of incompatible elements when plotted in the line plot of Figure 4. For several elements, the enrichment is more than a factor 100 when compared to the primitive mantle (data from Sun and McDonough, 1989). A particular enrichment can be detected for the elements Rb, Ba, Th, U and Pr, whereas Nb, Sr and Zr exhibit a distinctly lower enrichment. Compared to the primitive mantle, the content is similar or slightly depleted for Ti. In several cases the unweathered Tripoli material shows the lowest enrichment (Fig. 4). The highest enrichment is mostly found for Argille (5 – 7). Although there is some variability (the contents differ sometimes more than one order of magnitude) in the enrichment of

288 the elements Rb, Ba and Th, the general trend over all considered elements looks similar for all
289 soils. Consequently, they all must have a common origin — a confirmation of their autochthonic
290 formation.

291 The comparison of several immobile elements (Fig. 5) points in a similar direction. These elements
292 can be used to trace, among other things, the input of allochthonous material (e.g. aeolian
293 contribution) to soils (Dahms and Egli, 2016). The elements Ti, Zr, Nb, Ce, and Y have a relatively
294 high ionic potential and are considered to be chemically immobile under most near-surface
295 environments (Hutton, 1977; Muhs and Benedict, 2006). According to Muhs and Benedict (2006),
296 Ti and Nb are found in ilmenite, rutile, anatase, titanomagnetite, sphene, and biotite. Zr is mostly
297 present in the mineral zircon and the REEs (rare Earth elements) Ce and Y are related to a wide
298 variety of minerals such as phyllosilicates (micas, chlorite, other clay minerals), sphene,
299 amphiboles and apatite (Muhs and Benedict, 2006). The ratios demonstrate (Fig. 5) that — with
300 some exceptions — there is a relatively small variability within the soils. The chemical background
301 of the soil horizons obviously does not vary appreciably. Potential aeolian contributions must
302 therefore originate from local sources. There is, however, a certain offset of the unaltered Tripoli
303 rock material (high in Si and low in carbonates) with respect to the Ce/Y ratio. The Gessi soil
304 already had a slightly lower Ti content when compared to the other samples (Fig. 5). The CB and B
305 horizons of the Gessi soil had, furthermore, a distinctly higher Na content than the other soils. As a
306 consequence, the (K+Na)/Ti and the WIP were distinctly higher when compared to the other
307 samples. A part of Na is probably included in some sulphates or other easily soluble components.
308 This assumption is substantiated by the fact that the most weathered horizon (A) of the Gessi site
309 is close to all other data points. With increasing weathering, the easily soluble Na distinctly
310 diminishes and, therefore, the WIP and (K+Na)/Ti change.

311

312 3.2. Soil clay mineralogy

313 The X-ray diffractograms of typical samples (Tripoli 1, Argille 6) after glycerol-, Mg- and K-
314 saturation and after heating at 335 °C and 550 °C are given in Figure 6. After glycerol saturation,
315 the Tripoli samples exhibited basal reflections at 0.72, near 0.90, 1.00, 1.10 (1.08 – 1.12) and 1.71
316 nm. The peak near 1.71 nm indicates smectite (Fig.. 6). The peak at 0.91 nm is probably due to a

317 reflection ($d(002)$) of the 1.71 nm peak. The peak at 1.00 nm indicates mica and the 1.08, 1.12 and
 318 1.32 nm irregularly interstratified minerals (e.g. mica/smectite; Fig. 6). However, the peak near
 319 1.08 nm also could be caused by palygorskite, which usually has its typical positions at 1.05, 0.449
 320 and 0.323 nm (Bakhshandeh et al., 2011). Indeed, the quantitative analysis of minerals in the clay
 321 fraction indicated that the Tripoli, Argille 7, Calcare and particularly the Gessi samples contain a
 322 minor content of palygorskite (Table 5). The peak near 1.41 nm (Mg saturation) of the A1 horizon
 323 of Tripoli 1 (Fig. 6) remains after K saturation. With heating, this peak collapsed indicating the
 324 presence of some HIS (hydroxy-interlayered smectite) or HIV (hydroxy-interlayered vermiculite).
 325 HIS or HIV cannot be detected in the C2 horizon of the Tripoli soil which demonstrates that HIV is
 326 formed pedogenically. In general, the XRD-pattern between the subsoil and topsoil do not change
 327 distinctly. In the Tripoli soil, some HIV and some additional interstratified clay minerals have been
 328 formed actively during pedogenesis whereas barely recognisable changes could be detected in the
 329 Argille soil. The Argille soil is affected by vertic processes leading to a homogenisation of the top-
 330 and subsoil. Consequently, the mineralogical changes are only minor. Compared to the Tripoli
 331 soils, the Argille soils contain a distinctly higher content of kaolinite (cf. Fig. 6, Table 5). The Tripoli
 332 soils have a higher content of interstratified minerals.

333 The evaluation of XRD patterns in the d_{060} region of phyllosilicates ($58 - 64^\circ 2\theta$ region) confirmed
 334 the presence of both trioctahedral and dioctahedral phases in the subsoil and topsoil (Fig. 7).
 335 Trioctahedral species are represented by peaks in the range $59 - 61^\circ 2\theta$ (Mavris et al., 2011) and
 336 dioctahedral species are found, correspondingly, in the range $61 - 63^\circ 2\theta$. A significant part of the
 337 peaks near 0.1537 and 0.1533 nm can be attributed to quartz. The peaks near 0.1520 nm are,
 338 thus, more indicative of changes in trioctahedral species. The Tripoli soils exhibited only minor
 339 changes in trioctahedral species from the C to the A horizon (with probably even a slightly higher
 340 contribution of trioctahedral species in the A horizon). The proportion of trioctahedral species in the
 341 Argille soils seemed to decrease with pedogenesis indicating an active weathering of some
 342 trioctahedral mica. The contribution of the peak in the range of 0.1495 – 0.1498 nm (kaolinite and
 343 smectite) increased with progressive soil evolution. This mica is either transformed into smectite or
 344 into interstratified mica/smectite. The soil Gessi exhibits even in the A horizon a distinct peak at
 345 0.1538 nm and therefore has a higher content of trioctahedral mica than all the other investigated

soils. The ratio of tri- to dioctahedral minerals is similar for the Calcare site (data not shown). The peaks near 0.1520 (all samples) and 0.1500 can probably be attributed to Fe-rich dioctahedral phases (Fanning et al., 1989; nontronite) and montmorillonite, respectively (Moore and Reynolds, 1997). The peak near 0.1484 nm is assigned to kaolinite (or beidellite). This peak is most pronounced in the Argille soils.

The quantitative mineral analysis (Table 5) revealed that the relative proportion of smectite is high (33 – 60 %). The kaolinite content is highest in the Argille soils (15 – 31 %). All soils contain some mica. The Tripoli and Calcare soils show a high content of calcite (12 – 24 %). The presence of a small amount of palygorskite is also noticeable in the Tripoli, Argille 7, Calcare, Detriti and particularly Gessi soils, together with traces of cristobalite in the Argille soils. The Rietveld fits of X-ray diffraction patterns of typical samples (Tripoli 2, Argille 6) are given in Figure 8.

The isotopic compositions (C and O) of the bulk soil (only $\delta^{13}\text{C}$) and carbonates show a relatively high variability (Fig. 9), particularly at the sites Argille and Tripoli. This variability seems less for the sites Calcare, Gessi and Detriti which is however also a consequence of the rather low number of samples for these sites. In general, the least negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ ratios in carbonates were detected in the Argille soils. The differences among the sites in the $\delta^{13}\text{C}$ values of the bulk soil are not that evident; except for Gessi having the lowest values.

4. Discussion

4.1. Parent material and chemical characteristics of the soils

The highest Al-, Fe- and Si-contents are found in the Argille soils. Although the Tripoli material consists predominately of siliceous material, the parent material already contains a mixture of carbonates and diatom sediments. Two processes potentially led to the formation of this mixture: i) a syngenetic deposition of carbonates having diatoms or ii) an accumulation of carbonates after deposition and a partial isomorphic substitution of the laminated structure of the diatom Tripoli deposits over time. The deposition of the major part of the early Messinian Tripoli took place in near-normal marine conditions (Bellanca et al., 2001) giving rise to a repetition of sedimentary triplets composed of homogeneous marls, laminated marls and diatomites. This resulted in a

375 mixture of Si- rich and carbonate-rich material. The Tripoli grades upward in the lithological
376 sequence into the Calcare di Base which displays the first evidence of evaporite precipitation
377 (Bellanca et al., 2001). Not the Tripoli soils, but the Argille and Detriti soils have now the highest Si,
378 Al and Fe content. The carbonate content is highest in the Tripoli and Calcare soils.

379 Low $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the carbonates would indicate a relatively high rock-water (or
380 meteoric water) interaction (Martín-Martín et al., 2015). This interaction may also lead to pedogenic
381 carbonates. The present-day rainwater composition in Sicily has for an altitude of about 450m a.s.l.
382 a $\delta^{18}\text{O}$ of about -7‰ (Liotta et al., 2006). Already during sedimentation and subsequent
383 diagenesis, the carbonate fraction showed a considerable variability in the oxygen and carbon
384 isotopic ratios ($\delta^{13}\text{C}$ in carbonates: approx. -20 to $+2\text{‰}$, and $\delta^{18}\text{O}$: -11 to $+3\text{‰}$; Caruso et al.,
385 2015). However, most values of $\delta^{18}\text{O}$ of the bulk carbonate in sediments are in between -3.80 and
386 $+2.15 \text{‰}$ suggesting that the carbonates formed predominantly in marine environments that were
387 episodically affected by significant contributions of meteoric waters (Caruso et al., 2015). The $\delta^{18}\text{O}$
388 values (carbonates) of the soils clearly reflect this marine origin, although some samples of all sites
389 are outside this range and seem therefore to be affected by meteoric water — which, in the context
390 of weathering, is not very surprising. Pedogenic carbonates reflect soil genesis processes and
391 record soil-forming factors and palaeoenvironmental conditions. Because (pedogenic) carbonates
392 have variable physical and chemical properties, soil genesis and palaeoenvironmental conditions
393 are registered, among other things, in the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signal (Zamanian et al., 2016).

394 With an increasing C_{org} content in the soil, the bulk $\delta^{13}\text{C}$ values approach an average value in the
395 range of about -10 to -20‰ (Fig. 9a,d). A similar trend on the $\delta^{13}\text{C}$ of carbonates can be observed
396 with an increasing CaCO_3 content (Fig. 9b). These trends are most obvious for the Argille soils and
397 Tripoli 1 and 2 (when considered individually). The other soils fit into the general trend pattern
398 (e.g., the site Detriti aligns well to Argille), although with the single soil profiles no particular shift
399 can be detected (due to the low number of observations). The $\delta^{13}\text{C}$ of the bulk soil does not much
400 change with an increasing carbonate content (Fig. 9). This all seems surprising. However, Caruso
401 et al. (2015) already measured in the carbonate-containing sediments values $\delta^{13}\text{C}$ values that were
402 generally negative (often between -0.4 to -18.4‰). These authors interpreted this as an

incorporation of carbon from the oxidation of organic matter that characterises water column eutrophication. The bedrock of the site Calcare has a $\delta^{13}\text{C}$ value of -1.1‰ and the Tripoli bedrock between -3.66 and -6.61‰; Table 2) which fit into the range reported by Caruso et al. (2015). Consequently, both organic carbon and carbonates contribute to a decreasing $\delta^{13}\text{C}$ value with increasing concentration. As shown in Table 1 and Figure 9d, The increasing organic carbon content decreases the $\delta^{13}\text{C}$ value of the soils. In addition, the dissolution of primary carbonates and its reprecipitation as secondary carbonate (pedogenic carbonate) shifts their $\delta^{13}\text{C}$ ratio to more negative values (Gocke et al., 2011). According to Hasinger et al. (2015), the $\delta^{13}\text{C}$ signal of secondary carbonates in soils is influenced by factors such as dissolved inorganic carbon, dissolved organic carbon, rain water, root respiration and organic matter decay. Towards the surface, plant-derived carbon products (over root respiration, organic matter decay) or even CO_2 from the atmosphere are dissolved in soil water and increasingly influence the precipitation products of secondary carbonates (Fig. 9d). All these processes give rise to a specific fractionation of carbon isotopes. In some soils, the $\delta^{13}\text{C}$ is less negative in the soil column compared to the parent material which would indicate such an effect. Argille 5 and 6 have a relatively low CaCO_3 content. From the subsoil to the topsoil, the $\delta^{13}\text{C}$ values of both the bulk soil and carbonates tend to more negative values which points to an increasing proportion of pedogenic carbonates that is influenced by vegetation and plant-derived carbon.

Assuming that the $\delta^{13}\text{C}$ signal of the bulk soil can be represented $\delta^{13}\text{C}(\text{bulk}) = \alpha \times \delta^{13}\text{C}_{\text{org}} + [(1 - \alpha) \times \delta^{13}\text{C}_{\text{inorg}}]$, with α = the proportion of org. C on total C, then the average $\delta^{13}\text{C}$ signal of soil organic matter in the topsoil (A horizon) is $-24.8 \pm 2.4\text{‰}$. Consequently, C3 plants and their products determine together with (secondary) carbonates (having a lower value; approx. -2 to -11‰) the $\delta^{13}\text{C}$ signal of the topsoils.

426

4.2. Chemical weathering and soil mineralogy

Chemical weathering of silicates seems to be most pronounced in the Tripoli and Argille soils (Figs. 5 and 10). The Calcare, Gessi and Detriti sites exhibited almost no element leaching (from silicates) or both — accumulation and depletion — having an almost zero net-effect (Fig. 10). As a

consequence, the Argille and Tripoli sites have the most reactive soils. If, however, the WIP and (K+Na)/Ti ratio are considered, then the soil material of the Calcare and Detriti sites is in a similar range as are the Tripoli and Argille soils (Fig. 5).

As previously mentioned, the Argille soils gave rise to the highest oxyhydroxide production over the entire duration of soil formation and seem to weather actively by releasing a high amount of easily weatherable Fe. This process led to the formation of weakly crystalline but also to crystalline Fe forms (goethite, hematite). Hematite is present only in traces (very weak peak at 0.27 nm the X-ray diffractograms, but a prominent peak at 0.254 nm that is, however, also due to goethite; Chernyshova et al., 2007). The presence of goethite is more likely (Table 5). The highest content of kaolinite was detected in the Argille soils. Kaolinite strongly correlates with the oxalate-extractable and also dithionite-extractable Fe and, thus, is formed in an actively weathering and already strongly-altered environment. However, not all kaolinite found in the soils is due to neoformation. A distinct proportion is inherited from the parent material (cf. Table 5). Also the content of smectite positively and significantly correlates with the amount of pedogenic Fe-forms. It is noteworthy that the release of pedogenic Fe-forms depends on the Fe-content of the parent material (Table 4). Therefore, the highest content of smectite is measured in the Argille and Detriti soils. The smectite contents of the Tripoli, Calcare and Gessi soils are comparable. A distinct part of the smectite is inherited from the parent material. In Mediterranean to subarid and arid environments, the inheritance of clay minerals from the parent material is the most important source (Tazikeh et al., 2017). Due to the close correlation with pedogenic Fe-forms that usually increase from the subsoil or C-horizon to the topsoil, an active formation of smectites in the soil seems to take place. In addition, the negative correlation (or rather trend; because R^2 is rather low) of smectite with mica (Fig. 3f) and less evident with plagioclase (Fig. 3e) points to a neoformation of smectites in the soils. Besides inheritance, a potential source of smectite formation seems therefore mica and plagioclase (Mavris et al., 2011). In Mediterranean soils, smectite may be transformed to interstratified kaolinite-smectite and later to kaolinite (Barbera et al., 2008). However, this process could not be detected in the investigated soils. Part of the kaolinite also seems to be neo-formed in the soils, evidenced by the negative correlation (Fig. 3d) to K-feldspar. The hydrolysis of silicates in water results in an acid (silicic acid) and a base (hydroxy-Al-Si,

460 kaolinite; Churchman, 2012). Although some kaolinite may derive from Sahara dust input, active
461 formation of this mineral also takes place in the soils as shown by other investigations (Barbera et
462 al., 2008). Smectite and kaolinite are often inherited from the parent material and seem
463 thermodynamically stable in such environments (Scalenghe et al., 2016). Except at the Gessi and
464 Detriti sites, the soils contain some ITM. These soils probably have received some fine ash input
465 from Etna-eruptions — as reported also for soils in northwest Sicily (Egli et al., 2013), or even
466 earlier from the Monti Iblei.

467 Noteworthy is also the presence of some palygorskite (Table 5) in some of the investigated soils,
468 particularly at the Gessi site. Palygorskite is usually found in arid to subarid climates (Owliaie et al.,
469 2006; Bakhshandeh et al., 2011; Moazallahi and Farpoor, 2012) having a neutral to alkaline
470 environment (Churchman and Lowe, 2012 and references therein). Usually, gypsiferous soils show
471 more pedogenic palygorskite when compared to calcareous soils (Owliaie et al., 2006).
472 Neoformation of palygorskite, as a result of calcite and gypsum precipitation, seems to be a major
473 pathway for the occurrence of this mineral (Owliaie et al., 2006). Gypsum leads to a higher Mg/Ca
474 ratio that favours palygorskite formation. Other factors that promote palygorskite formation are a
475 high pH and a high Si solubility (Khademi and Mermut, 1998). Singer (1984) also proposed that
476 palygorskite may form from precursor minerals such as smectite. Palygorskite may also be
477 inherited from the parent material (Singer 2002; Churchman and Lowe, 2012). In the investigated
478 soils, we detect a negative correlation between the carbonate and palygorskite content. This
479 negative correlation consequently does not support the idea that palygorskite is actively formed in
480 the soils. We therefore have to assume that palygorskite is inherited from the parent material and
481 particularly conserved in the gypsum-containing soil (Gessi).

482

483

484 **5. Conclusions**

485 The chemical data, isotopic measurements and clay mineral analyses enable — together with
486 existing data from previous work — the construction of general model of soil evolution on
487 evaporites of the Messinian Crisis. According to Caruso et al. (2015), the Calcare di Base units
488 (limestones) were deposited under conditions that were controlled by multistaged, diagenetic and

489 epigenetic changes in response to large fluctuations of the depositional conditions that were
490 related to climatic changes. With time, a lagoon-like landscape developed. The almost complete
491 disappearance of marine microorganisms in the upper part of the Tripoli formation and the wide
492 range of stable isotope variations of the carbonate fraction in the overlying carbonate layers reflect
493 the transition to semi-closed or closed sub-basins affected by fluctuations from highly evaporated
494 hypersaline solutions to freshwater (Caruso et al., 2015; Manzi et al., 2011) and organic carbon
495 input (from surrounding, vegetated areas). As evidenced in Figures 4 and 5, the different parent
496 materials limestone of the Calcare di Base, Tripoli (diatoms), clays (Argille soils), Detriti and
497 gypsiferous material (Gessi), all have a common source, are autochthonous sediments and are not
498 (or only marginally) influenced by aeolian inputs.

499 The marine clay deposits led mostly to the formation of Vertisols, characterised by a high smectite
500 and kaolinite content. A distinct part of the clay minerals is inherited from the parent material, but
501 also weathering and soil formation contributed to mineral transformations. We hypothesise the
502 following transformations: i) plagioclase (?) → smectite, ii) mica → interstratified mica-smectite →
503 smectite, iii) K-feldspar → kaolinite, iv) weathering of mica and formation of weakly crystalline
504 oxyhydroxides (Fe, Al) → hematite, goethite.

505 The Tripoli sediments (diatoms) were mixed with carbonates (either syn- or epigenetic). Typically,
506 Mollisols have developed from this type of parent material. Smectite, and to a lower extent
507 kaolinite, are the main clay minerals. Traces of palygorskite have been detected. This mineral is
508 predominantly inherited from the parent material. The release of Fe^{2+} from primary minerals is less
509 pronounced, leading to a lower content of oxyhydroxides in the soil. In general, the same mineral
510 transformation processes as in the clay deposits (see above) occur.

511 A shallow Mollisol has developed on Calcare di Base (Calcare site). The main clay mineral is
512 smectite. Besides kaolinite and mica, traces of palygorskite were also found. The weathering stage
513 of this soil is lower than most others which is expressed, among other things, by the relatively high
514 proportion of trioctahedral mica.

515 The Detriti site has a Mollisol that exhibited a relatively high release of oxyhydroxides (particularly
516 Al). Element losses along the soil profile are, however, rather marginal. The most prominent clay
517 mineral is clearly smectite. Kaolinite and mica play a subordinate role. In addition, palygorskite was

518 also detected. Regarding the weathering stage, the Detriti soil seems to be in between the Argille
519 and Tripoli soils.

520 Only weak soil formation was recognisable at the Gessi site. The presence of a high gypsum
521 content (12 – 36 %) has hindered a more advanced weathering of the substrate. Chemical
522 weathering of silicates was the lowest compared to the other soils. Only a small amount of
523 oxyhydroxides has been released due to weathering. The most important clay mineral is smectite.
524 Kaolinite, mica and palygorskite are minor components. While kaolinite and smectite may have
525 been formed partially during pedogenesis, palygorskite has been inherited from the parent material
526 and conserved.

527 The deposits of this evaporite series vary within short distances, which leads to a high soil spatial
528 variability. Advanced soil evolutionary stages (high proportion of kaolinite and smectite) can only be
529 encountered on clay deposits and the Tripoli series (diatoms).

530

531

532 **Acknowledgements**

533 We would like to thank to two unknown reviewers for their helpful comments on an earlier version
534 of the manuscript and Alan Rogers for polishing the English.

535

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Highlights

1. The evaporite deposits of the Messinian crises have a similar origin
2. A high rock- meteoric water interaction occurred during sedimentation and diagenesis
3. Weathering is most advanced on clay and Tripoli deposits
4. With increasing weathering, smectite and kaolinite are actively formed in the soils
5. In part, palygorskite is present and was inherited from the parent material

Table 1
Characteristics of the investigated sites.

Profile	Coordinates	Altitude (m a.s.l.)	MAAT ¹⁾ (°C)	MAP ¹⁾ (mm)	Slope (%)	Exposure	Parent material	Soil units (Soil Taxonomy; Soil Survey Staff, 2014)	Vegetation/ Land use
Tripoli 1	37° 19' 13.12 N / 13° 54' 44.62 E	375	18.0	500	4	N	Tripoli: laminated marl (diatomite)	Aridic Calcixeroll	Uncultivated area
Tripoli 2	37° 19' 12.84 N / 13° 54' 43.88 E	375	18.0	500	4-5	NE	Tripoli: laminated marl (diatomite)	Pachic Calcixeroll	Uncultivated area
Detriti	37° 19' 08.87 N / 13° 54' 41.81 E	379	18.0	500	1-2	S	Detritic deposits of “Calcare di base” (limestone)	Typic Haploxeroll	Vineyard
Calcare	37° 19' 04.64 N / 13° 54' 41.00 E	390	18.0	500	1-2	S	“Calcare di base” (limestone)	Aridic Haploxeroll	Pasture
Argille 5	37° 19' 21.89 N / 13° 56' 03.37 E	310	18.0	500	1	S	Clays and marl (Tortonian)	Chromic Gypsite	Pasture
Argille 6	37° 19' 26.20 N / 13° 55' 41.59 E	321	18.0	500	1	S	Clays and marl (Tortonian)	Chromic Haplosite	Fruit orchard (apricot)
Argille 7	37° 19' 25.66 N / 13° 55' 26.92 E	327	18.0	500	6	N	Crushed limestone (Calcare di base) over clays and marl (Tortonian)	Xeric Torriorthent over a Chromic Haplosite	Vineyard
Gessi	37° 17' 24.28 N / 13° 58' 15.90 E	302	18.0	500	30	S	Gypsum (selenite; Messinian)	Xeric Calcigypsite	Pine forest

¹⁾MAAT (mean annual temperature), MAP (mean annual precipitation), according to Raimondi et al. (2003)

Table 2
 Description of the soil profiles together with some major chemical and physical characteristics

Profile	Horizon	Depth	Munsell colour	Density	Sand	Silt	Clay	pH (CaCl ₂)	C _{org}	N	δ ¹³ C (bulk soil)	CaCO ₃	δ ¹³ C (CaCO ₃)	δ ¹⁸ O (CaCO ₃)
		(cm)	(moist)	g cm ⁻³	%	%	%		%	%	‰	%	‰	‰
Tripoli 1	A1	0-20	10YR5/3	1.16	8.1	37.3	54.6	7.70	1.45	0.11	-13.62	38.6	-10.18	-3.75
	A2	20-60	10YR7/6	1.16	10.5	36.5	53.0	7.68	1.91	0.18	-15.44	36.3	-10.50	-3.24
	Ck	60-150	out of scale	1.11	6.1	65.3	28.6	7.76	0.75	0.03	-10.72	49.8	-10.28	-3.00
	C	>150	out of scale	1.13	4.9	49.9	45.2	7.68	0.41	0.04	-5.96	38.8	-4.94	-1.15
	R1w ¹⁾	> 150						7.82				31.5	-5.09	-2.10
	R2 ²⁾	>150						7.92				4.0	-3.33	0.31
Tripoli 2	A1	0-40	10YR3/2	1.16	15.8	45.1	39.1	7.74	1.62	0.13	-14.15	37.4	-10.05	-3.43
	A2	40-100	10YR3/2	1.18	11.3	39.3	49.4	7.85	1.58	0.10	-13.16	37.7	-9.96	-3.56
	Bw1	100-160	10YR5/6	1.48	24.8	46.5	28.7	7.70	0.70	0.02	-13.33	35.7	-11.72	-4.21
	Bw2	160-270	10YR5/6	1.36	11.3	44.2	44.5	7.72	0.91	0.03	-12.86	36.7	-11.44	-4.37
	CB	>270	10YR5/6	1.50	21.4	44.9	33.7	7.66	0.53	0.03	-11.43	42.4	-10.39	-4.29
Detriti	A1	0-40	10YR2/2	1.00	17.4	34.1	48.5	7.62	2.12	0.16	-15.53	27.0	-8.54	-3.84
	A2	40-80	10YR2/2	1.10	11.3	34.2	54.5	7.65	2.36	0.15	-15.71	24.1	-8.40	-2.93
	A3	80-140	10YR2/2	1.24	21.2	37.1	41.7	7.66	2.04	0.15	-12.98	34.6	-6.81	-2.94
Calcare	A	0-70	10YR2/2	1.13	24.6	41.3	34.1	7.67	3.66	0.30	-13.39	45.8	-5.83	-3.62
	C ³⁾	>70	10YR7/3					8.18				96.9	-1.10	
Argille 5	A	0-30	10YR3/3	1.11	11.2	24.3	64.5	7.58	1.59	0.16	-19.62	7.0	-6.14	-3.69
	Bssz1	30-70	2.5Y4/4	1.19	6.0	23.3	70.7	7.59	0.95	0.10	-15.94	6.7	-4.46	-3.60
	Bssz2	70-110	2.5Y5/4	1.31	8.0	32.0	60.0	7.64	0.60	0.06	-13.36	4.6	-1.16	-2.30

Argille 6	A	0-35	2.5Y4/4	1.16	11.6	28.0	60.4	7.59	0.67	0.06	-10.61	8.6	-1.98	-2.85
	Bss	35-80	2.5Y4/4	1.19	25.2	24.0	50.8	7.60	0.57	0.05	-9.20	7.0	-0.90	-2.78
	Bssg	80-120	2.5Y4/4 / 2.5Y6/2	1.23	10.2	30.3	59.5	7.65	0.45	0.04	-7.85	7.9	0.83	-1.19
Argille 7	Ap1	0-30	10YR3/2	1.12	14.6	30.3	55.1	7.65	2.68	0.11	-12.40	33.4	-8.49	1.16
	Ap2	30-50	10YR5/4	1.21	9.5	37.0	53.5	7.76	1.11	0.06	-11.13	43.5	-7.72	-1.57
	Ap3	50-95	10YR5/6 / 10YR3/2	1.22	14.0	12.5	73.5	7.82	2.32	0.05	-9.44	32.7	-8.58	-3.74
	2Bss	95-115	10YR6/6	1.25	4.6	22.0	73.4	7.73	1.01	0.05	-12.10	20.3	-7.26	-2.67
Gessi	Akzy	0-20	10YR2/2	0.89	27.8	31.7	40.5	7.51	4.16	0.29	-20.84	14.1	-8.19	-4.02
	CBzy	20-40	10YR5/3	1.26	49.8	18.2	32.0	7.30	0.63	0.02	-20.70	2.2	-7.73	-4.02
	Bkzy	40-70	10YR7/4	1.51	34.8	20.6	44.6	7.48	0.76	0.04	-16.62	7.0	-9.33	-5.47

¹⁾weathered diatomite

²⁾unweathered diatomite

³⁾Massive carbonate (rock sample)

Table 3

Main chemical components (given in oxide or carbonate form) of the soil samples (fine earth).

Profile	Horizon	Na ₂ O %	MgO %	Al ₂ O ₃ %	SiO ₂ %	P ₂ O ₅ %	SO ₃ %	K ₂ O %	CaO %	CaCO ₃ %	TiO ₂ %	V ₂ O ₅ %	MnO %	Fe ₂ O ₃ %	ZrO ₂ %	LOI ¹⁾ %
Tripoli 1	A1	0.42	1.87	7.8	36.0	0.146	0.14	1.02	1.23	37.1	0.46	0.02	0.10	3.70	0.012	10.0
	A2	0.67	1.82	7.6	35.7	0.138	0.16	1.08	0.71	35.6	0.48	0.02	0.11	4.03	0.012	11.9
	C1	0.57	2.10	6.3	26.7	0.203	0.11	0.93	3.25	50.6	0.37	0.01	0.15	2.89	0.010	5.8
	C2	1.04	2.06	8.6	33.6	0.161	0.11	1.28	1.97	38.6	0.50	0.04	0.05	4.49	0.011	7.4
	Diatomite	0.72	0.72	2.3	72.9	0.043	0.12	0.42	14.01	4.3	0.17	0.01	0.04	1.26	0.003	3.0
Tripoli 2	A1	0.65	1.88	7.7	35.5	0.149	0.14	1.05	1.51	35.0	0.46	0.02	0.09	3.68	0.012	12.1
	A2	0.50	1.86	7.5	34.2	0.139	0.14	0.97	2.58	36.0	0.45	0.02	0.09	3.57	0.012	12.0
	Bw1	0.53	1.94	9.1	36.1	0.077	0.19	1.22	1.75	35.7	0.60	0.02	0.12	4.51	0.019	8.1
	Bw2	0.56	2.01	9.1	35.2	0.069	0.23	1.15	3.04	35.6	0.54	0.01	0.11	4.13	0.016	8.3
	CB	0.73	1.81	8.0	31.8	0.083	0.19	1.03	2.27	41.4	0.52	0.02	0.10	3.92	0.014	8.1
Detriti	A1	0.65	2.09	10.7	38.4	0.146	0.14	1.14	1.58	26.0	0.64	0.02	0.10	5.12	0.016	13.2
	A2	0.58	2.07	11.0	39.4	0.143	0.14	1.16	2.64	23.3	0.66	0.02	0.11	5.28	0.016	13.5
	A3	0.50	2.06	9.3	33.8	0.156	0.16	1.01	1.45	33.8	0.56	0.02	0.10	4.77	0.014	12.2
Calcare	A	0.65	1.88	6.4	25.0	0.307	0.29	1.00	3.12	46.0	0.37	0.01	0.08	3.22	0.009	11.7
	C	0.95	1.53	0.5	1.4	0.183	0.19	0.04	2.09	90.3	0.02	0.00	0.04	0.22	0.000	2.5
Argille 5	A	0.92	1.79	13.1	52.8	0.092	0.14	1.64	1.44	6.8	0.83	0.02	0.06	6.49	0.019	13.9
	Bssz1	1.01	1.70	12.5	49.2	0.035	3.73	1.51	3.50	6.5	0.77	0.02	0.06	6.11	0.017	13.3
	Bssz2	1.15	1.76	13.1	52.1	0.029	3.35	1.56	3.05	4.4	0.81	0.02	0.04	6.42	0.018	12.2
Argille 6	A	0.88	1.84	14.4	51.4	0.084	0.28	1.34	1.30	8.3	0.93	0.02	0.07	6.53	0.020	12.5
	Bss	0.95	1.73	13.9	51.3	0.065	1.63	1.29	2.35	6.7	0.92	0.02	0.07	6.37	0.019	12.8

	Bssg	1.11	1.76	14.4	50.2	0.050	2.22	1.22	1.97	7.6	0.93	0.02	0.06	6.45	0.020	12.0
Argille 7	Ap1	0.97	5.85	8.1	34.5	0.181	0.28	1.06	1.38	32.8	0.46	0.02	0.12	3.88	0.012	10.4
	Ap2	0.76	3.19	7.8	30.3	0.133	0.17	0.90	0.49	42.5	0.49	0.02	0.11	4.07	0.011	9.1
	Ap3	0.77	6.19	7.8	33.9	0.122	0.30	0.97	0.73	35.0	0.48	0.02	0.12	4.12	0.012	9.4
	Bss	0.76	2.51	12.6	43.9	0.093	0.16	1.17	0.91	19.7	0.79	0.02	0.06	5.55	0.017	11.8
Gessi	A	1.65	2.10	7.8	27.4	0.036	12.84	1.01	9.56	13.7	0.45	0.02	0.05	3.44	0.012	19.9
	CB	4.15	1.70	4.5	5.0	0.001	35.87	0.39	25.08	2.3	0.20	0.01	0.02	1.46	0.004	19.4
	B	3.13	1.80	4.9	11.6	0.001	30.77	0.64	20.33	7.2	0.25	0.01	0.02	1.92	0.007	17.4

¹⁾ LOI (at 550°C): includes soil organic matter and strongly adsorbed water

Table 4

Oxalate (o) and dithionite (d) –extractable fractions of Al, Fe, Mn and Si (only oxalate) in the soils. In addition, the molar ratio of Al(o)/Si(o), an indicator of the presence of imogolite type material, and the content of crystalline Fe forms are given.

Profile	Horizon	Al(o) mg/kg	Fe(o) mg/kg	Mn(o) mg/kg	Si(o) mg/kg	Al(o)/Si(o) ¹⁾	Al(d) mg/kg	Fe(d) mg/kg	Mn(d) mg/kg	Fe(d)-Fe(o) ²⁾ mg/kg	Al(o)/Al(t)) ³⁾	Fe(o)/Fe(t)	Al(d)/Al(t)	Fe(d)/Fe(t)
Tripoli 1	A1	622	611	450	341	1.90	265	2866	367	2255	0.014	0.023	0.006	0.106
	A2	748	647	418	318	2.45	292	2926	387	2279	0.018	0.022	0.007	0.102
	C1	230	577	723	125	1.91	94	1607	487	1030	0.007	0.029	0.003	0.081
	C2	227	767	100	173	1.37	98	5075	99	4308	0.005	0.024	0.002	0.161
Tripoli 2	A1	702	627	488	319	2.29	272	2732	350	2105	0.016	0.023	0.006	0.099
	A2	639	544	465	253	2.62	245	2658	361	2114	0.015	0.021	0.006	0.101
	Bw1	709	445	625	433	1.70	322	3770	507	3325	0.015	0.014	0.007	0.120
	Bw2	688	478	544	322	2.22	332	3589	447	3111	0.014	0.016	0.007	0.120
	CB	552	325	514	282	2.03	249	2681	422	2356	0.013	0.012	0.006	0.095
Detriti	A1	1435	1098	500	491	3.04	609	3981	471	2884	0.024	0.029	0.010	0.107
	A2	1340	1181	520	494	2.83	594	3920	467	2740	0.022	0.031	0.010	0.103
	A3	1067	942	428	423	2.62	511	3822	400	2880	0.021	0.028	0.010	0.112
Calcare	A C	710	610	216	374	1.98	292	2770	224	2160	0.021	0.027	0.009	0.123
Argille 5	A	978	1184	221	519	1.96	325	8653	289	7469	0.014	0.026	0.005	0.187
	Bssz1	612	1114	193	393	1.62	214	9779	282	8665	0.009	0.025	0.003	0.223
	Bssz2	353	978	115	313	1.17	112	12180	180	11202	0.005	0.021	0.002	0.259
Argille 6	A	619	1664	357	336	1.92	151	10935	351	9272	0.008	0.035	0.002	0.231
	Bss	515	1233	253	281	1.91	123	12625	315	11393	0.007	0.026	0.002	0.270

	Bssg	819	1833	360	214	3.99	115	14925	293	13092	0.010	0.039	0.001	0.317
Argille 7	Ap1	562	739	384	461	1.27	246	3441	438	2702	0.013	0.027	0.006	0.125
	Ap2	536	764	435	290	1.92	243	3092	482	2328	0.013	0.026	0.006	0.106
	Ap3	381	755	305	365	1.09	178	3662	352	2907	0.010	0.028	0.005	0.136
	Bss	469	978	289	387	1.26	190	4295	255	3317	0.007	0.024	0.003	0.107
Gessi	A	1134	861	138	416	2.83	609	3190	205	2329	0.027	0.035	0.014	0.129
	CB	522	448	34	185	2.94	262	1122	36	673	0.023	0.046	0.012	0.114
	B	399	614	45	159	2.61	312	1743	53	1129	0.016	0.047	0.012	0.133

¹⁾ molar ratio

²⁾ crystalline Fe-forms

³⁾ total content

Table 5
[Click here to download Table: Table_5.docx](#)

Table 5
 Mineralogical composition ($\pm$ standard error) of the clay fraction of the investigated samples.

Profile	Horizon	Quartz	Cristobalite	K-Feldspar	Na-Plagioclase	Calcite	Dolomite/ Ankerite	Anatase	Kaolinite	Muscovite/ Illite	Smectite	Palygorskite	Goethite
		%	%	%	%	%	%	%	%	%	%	%	%
Tripoli 1	A1	3.6 $\pm$ 0.1		3.2 $\pm$ 0.4	2.1 $\pm$ 0.2	24.1 $\pm$ 0.3		0.5 $\pm$ 0.1	12.3 $\pm$ 0.8	12.8 $\pm$ 1.0	39.8 $\pm$ 1.4	1.0 $\pm$ 0.3	0.5 $\pm$ 0.2
	A2	4.1 $\pm$ 0.3		2.6 $\pm$ 0.4	2.2 $\pm$ 0.2	20.9 $\pm$ 1.0		0.6 $\pm$ 0.1	11.8 $\pm$ 1.0	13.6 $\pm$ 0.9	43.1 $\pm$ 2.3	0.6 $\pm$ 0.2	0.5 $\pm$ 0.2
	C1	4.8 $\pm$ 0.1		3.4 $\pm$ 0.4	2.3 $\pm$ 0.2	12.8 $\pm$ 0.2		0.4 $\pm$ 0.1	9.0 $\pm$ 0.8	14.9 $\pm$ 1.0	49.0 $\pm$ 1.2	2.6 $\pm$ 0.3	0.5 $\pm$ 0.1
	C2	6.1 $\pm$ 0.2		2.8 $\pm$ 0.4	2.4 $\pm$ 0.2	17.2 $\pm$ 1.1		0.4 $\pm$ 0.1	8.5 $\pm$ 0.9	16.5 $\pm$ 1.1	43.4 $\pm$ 1.7	1.9 $\pm$ 0.3	0.6 $\pm$ 0.2
Tripoli 2	A1	3.9 $\pm$ 0.1		3.0 $\pm$ 0.4	2.1 $\pm$ 0.2	23.5 $\pm$ 0.9		0.6 $\pm$ 0.1	12.3 $\pm$ 0.7	13.2 $\pm$ 0.5	40.2 $\pm$ 1.5	0.7 $\pm$ 0.3	0.5 $\pm$ 0.2
	A2	3.6 $\pm$ 0.1		2.3 $\pm$ 0.4	2.3 $\pm$ 0.2	23.7 $\pm$ 0.4		0.6 $\pm$ 0.1	11.0 $\pm$ 0.7	12.5 $\pm$ 0.9	41.9 $\pm$ 1.5	1.7 $\pm$ 0.2	0.4 $\pm$ 0.2
	Bw1	5.2 $\pm$ 0.1		2.5 $\pm$ 0.4	2.1 $\pm$ 0.2	12.0 $\pm$ 0.2		0.7 $\pm$ 0.1	13.0 $\pm$ 0.8	16.0 $\pm$ 0.9	45.8 $\pm$ 1.3	2.1 $\pm$ 0.3	0.6 $\pm$ 0.2
	Bw2	4.9 $\pm$ 0.4		2.6 $\pm$ 0.5	2.0 $\pm$ 0.2	13.1 $\pm$ 0.8		0.8 $\pm$ 0.1	11.9 $\pm$ 1.5	14.8 $\pm$ 1.0	48.3 $\pm$ 1.4	0.6 $\pm$ 0.2	0.8 $\pm$ 0.2
	CB	4.2 $\pm$ 0.1		2.5 $\pm$ 0.5	1.7 $\pm$ 0.2	21.8 $\pm$ 0.3		0.5 $\pm$ 0.1	9.4 $\pm$ 0.6	13.1 $\pm$ 0.8	44.3 $\pm$ 1.0	1.5 $\pm$ 0.3	0.6 $\pm$ 0.2
Detriti	A1	3.2 $\pm$ 0.1		2.0 $\pm$ 0.5	1.3 $\pm$ 0.2	7.8 $\pm$ 0.2		0.8 $\pm$ 0.1	14.7 $\pm$ 0.8	11.9 $\pm$ 0.3	56.8 $\pm$ 1.0	0.9 $\pm$ 0.2	0.6 $\pm$ 0.2
	A2	3.1 $\pm$ 0.1		2.3 $\pm$ 0.5	2.0 $\pm$ 0.2	7.0 $\pm$ 0.2		0.9 $\pm$ 0.1	14.2 $\pm$ 0.8	9.5 $\pm$ 0.3	59.8 $\pm$ 1.0	0.9 $\pm$ 0.1	0.3 $\pm$ 0.1
	A3	3.3 $\pm$ 0.1		2.7 $\pm$ 0.4	1.6 $\pm$ 0.2	10.0 $\pm$ 0.2		0.8 $\pm$ 0.1	12.5 $\pm$ 0.8	9.7 $\pm$ 0.3	57.6 $\pm$ 0.9	1.2 $\pm$ 0.3	0.6 $\pm$ 0.2
Calcare	A	3.0 $\pm$ 0.2		2.1 $\pm$ 0.4	1.8 $\pm$ 0.4	20.5 $\pm$ 0.5		0.8 $\pm$ 0.1	12.2 $\pm$ 1.0	12.5 $\pm$ 1.5	45.7 $\pm$ 3.3	0.7 $\pm$ 0.2	0.5 $\pm$ 0.2
	C												
Argille 5	A	3.3 $\pm$ 0.2	2.9 $\pm$ 0.2	2.1 $\pm$ 0.2	2.4 $\pm$ 0.2	3.3 $\pm$ 0.2		0.8 $\pm$ 0.1	15.4 $\pm$ 0.9	9.8 $\pm$ 1.0	59.5 $\pm$ 1.3	0.0	0.5 $\pm$ 0.2
	Bssz1	13.3 $\pm$ 0.3	3.7 $\pm$ 0.5	3.7 $\pm$ 0.4	5.0 $\pm$ 0.3	9.7 $\pm$ 0.2		0.7 $\pm$ 0.1	14.5 $\pm$ 1.1	15.0 $\pm$ 1.0	33.8 $\pm$ 1.7	0.0	0.6 $\pm$ 0.2
	Bssz2	12.2 $\pm$ 0.2	3.4 $\pm$ 0.5	3.6 $\pm$ 0.4	4.3 $\pm$ 0.3	5.6 $\pm$ 0.2		0.5 $\pm$ 0.1	14.8 $\pm$ 0.9	13.8 $\pm$ 1.0	40.9 $\pm$ 1.7	0.0	0.9 $\pm$ 0.2
Argille 6	A	2.2 $\pm$ 0.1	3.3 $\pm$ 0.3	1.4 $\pm$ 0.2	1.3 $\pm$ 0.2	4.8 $\pm$ 0.1		1.5 $\pm$ 0.1	28.1 $\pm$ 0.9	12.5 $\pm$ 0.6	43.9 $\pm$ 1.3	0.0	1.0 $\pm$ 0.2
	Bss	6.1 $\pm$ 0.1	5.0 $\pm$ 0.6	2.3 $\pm$ 0.2	1.8 $\pm$ 0.2	8.3 $\pm$ 0.2		1.2 $\pm$ 0.1	26.0 $\pm$ 0.8	11.3 $\pm$ 0.9	37.0 $\pm$ 1.2	0.0	1.0 $\pm$ 0.2
	Bssg	2.4 $\pm$ 0.2	3.4 $\pm$ 0.3	2.3 $\pm$ 0.3	1.8 $\pm$ 0.3	4.8 $\pm$ 0.3		1.0 $\pm$ 0.2	31.0 $\pm$ 1.1	7.2 $\pm$ 1.0	45.4 $\pm$ 1.3	0.0	0.7 $\pm$ 0.2

Argille 7	Ap1	4.1±0.2	3.2±0.7	1.9±0.3	8.2±0.3	3.6±0.2	0.6±0.1	12.4±0.9	14.0±1.0	48.8±1.4	2.9±0.5	0.5±0.2
	Ap2	3.2±0.1	2.3±0.5	1.5±0.2	18.4±0.3	1.5±0.3	0.6±0.1	14.4±0.8	10.9±1.0	43.3±1.4	3.4±0.5	0.5±0.2
	Ap3	4.0±0.2	2.3±0.5	1.8±0.3	8.4±0.3	5.0±0.3	0.7±0.1	13.4±0.9	13.6±1.5	49.1±1.2	1.3±0.3	0.4±0.2
	Bss	1.9±0.1	2.1±0.5	1.5±0.2	5.6±0.2	0.2±0.1	0.8±0.1	23.2±0.8	11.1±1.5	51.3±1.2	1.3±0.5	0.6±0.2
Gessi	A	12.5±0.3	3.5±0.6	3.4±0.3	17.5±0.3		0.4±0.1	4.4±1.0	10.9±0.6	44.6±1.3	2.4±0.5	0.4±0.2

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Figure captions

Fig. 1. Schematic geologic map (according to Manzi et al., 2011; modified) of Sicily with the distribution of evaporites, thrusts, main recent volcanic deposits (Mt. Etna) and the study area near Canicatti with the various soil profiles (Gessi, Tripoli 1 & 2, Detriti, Calcare and Argille 5 – 7). The geologic transect shows the main units (gypsiferous deposits are not drawn due to simplicity reasons).

Fig. 2. Investigated soil profiles with soil horizon designation. The insert shows a typically layered diatom sediment piece.

Fig. 3. Bivariate plots with regression lines/curves for a) oxalate-extractable Fe and Al as a function of the soil profile, b) kaolinite of the clay fraction (but given as total amount with respect to the fine earth) and oxalate-extractable Fe, c) smectite of the clay fraction (but given as total amount with respect to the fine earth) and oxalate-extractable Fe, d) kaolinite and K-feldspar (in the clay fraction), e) smectite and plagioclase (in the clay fraction) and f) smectite and mica (in the clay fraction).

Fig. 4. Primitive mantle normalised trace elements as a function of the various soil profiles (average value per profile) represented in a line plot.

Fig. 6. Binary diagram of concentration ratios of a) Ti/Zr vs Ti/Nb, b) Ti/Zr vs Ce/Y, c) Ti/Zr vs the weathering index $(K+Na)/Ti$ and d) Ti/Zr vs the weathering index WIP (weathering index according to Parker, 1970) as a function of the various soil profiles.

Fig. 6. X-ray diffractograms of the clay fraction of the topsoil and subsoil of Tripoli 1 and Argille 6. Gly = glycerol saturation (of Mg-saturated samples), Mg = Mg-saturation, K = K-saturation, 335° = K-saturated and heated sample, 550° = K-saturated and heated sample.

The d -spacings are given in nm.

Fig. 7. Peak separation of X-ray patterns in the $d(060)$ region of some typical soil samples (clay fraction). The peak region between $59 - 61^\circ 2\theta$ can be attributed to trioctahedral mineral and the region $61 - 63^\circ 2\theta$ to dioctahedral species. The square symbols represent the smoothed, measured data and the solid lines correspond to the modelled elementary and summation curve.

Fig. 8. Rietveld plots of the X-ray diffraction patterns of random powders of the clay samples Tripoli2 Bw2 and Argille6 A.

Fig. 9. Comparison between a+b) the $\delta^{13}\text{C}$ value of the CaCO_3 , C_{org} and CaCO_3 content of soil samples, respectively, c) the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ value of CaCO_3 in the soil profiles, d) C_{org} of the soil and the $\delta^{13}\text{C}$ value of the bulk soil and e) the $\delta^{13}\text{C}$ value of the bulk soil and the CaCO_3 content.

Fig. 10. Open-system mass transport function (relative losses) τ of the elements Na and K for the different profiles.