# Middle Pleistocene (MIS 14) environmental conditions in the central Mediterranean derived from terrestrial molluscs and carbonate stable isotopes from Sulmona Basin (Italy)

Giovanni Zanchetta[1*], Monica Bini[1], Biagio Giaccio[2], Giuseppe Manganelli[3], Andrea Benocci[4], Eleonora Regattieri[5,6], Andre C. Colonese[7], Chiara Boschi[6], Cristian Biagioni[1]

[1]Dipartimento di Scienze della Terra, University of Pisa, Via S. Maria 53, 56126 Pisa, Italy
[2]Istituto di Geologia Ambientale e Geoingegneria, IGAG-CNR, Via Salaria km. 29.4, 00015 Monterotondo Rome, Italy
[3]Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente, Via Mattioli 4 53100 Siena, Italy
[4]Museo di Storia Naturale dell'Accademia dei Fisiocritici, Piazzetta Gigli 2 53100 Siena, Italy
[5]Institute of Geology and Mineralogy, University of Cologne, Zülpicher Str. 49a, 50674 Cologne, Germany
[6]Istituto di Geoscienze e Georisorse, IGG-CNR, Via Moruzzi 1, 56126 Pisa, Italy
[7]Department of Archaeology, BioArCh, University of York, Wentworth Way, York YO10 5DD England (UK).
*Corresponding author: zanchetta@dst.unipi.it

## Abstract

A paleosol from the Middle Pleistocene lacustrine-fluvial succession of Sulmona Basin, central Italy, was analysed for the land snail shell content, and the stable isotope composition of the shells and associated pedogenic carbonates. The paleosol – known as Fiorata Paleosol – is covered by a thick tephra layer dated to ca. 527 ka allowing the pedogenetic horizons to be correlated to the marine isotope stage (MIS) 14-early MIS 13 interval. The terrestrial mollusc assemblage contained few individuals and was characterized by a low number of species which predominantly indicate open and dry habitats, thus suggesting that Fiorata Paleosol likely developed during glacial conditions of the MIS 14. The $\delta^{13}C$ values of pedogenic carbonates and terrestrial shells indicate prevailing $C_3$-type vegetation, probably marked by some degree of water stress. Calculation of the $\delta^{18}O$ precipitation values, derived from pedogenic carbonates and shell $\delta^{18}O$ values, indicate that the average temperature was 3-5°C lower than present day. This study highlights how paleosols, despite offering only snapshots of past climate and environments, provide valuable complementary information to paleoclimatic data obtained in the adjacent lacustrine intervals, specifically for the Sulmona successions.

*Keywords:* tephra layers; paleosol; $C_3$-type vegetation; Glacial

## 1. Introduction

Stable isotopes (e.g. $^{13}C/^{12}C$ and $^{18}O/^{16}O$) of pedogenetic carbonate (Cerling, 1984; Jiamao et al., 1991; Cerling and Quade, 1993; Zanchetta et al., 2000) and terrestrial mollusc shells (e.g. Balakrishnan et al., 2005a; Colonese et al., 2007, 2010; Murelaga et al., 2012; Yanes et al., 2011; Paul and Mauldin, 2013. Prendergast et al., 2016) can provide valuable snapshots of past environments, notably vegetation type (e.g. $C_3/C_4$ ratios, Cerling and Quade, 1993; Zanchetta et al., 2006), and past precipitation regimes (Lecolle, 1985; Zanchetta et al., 2005; Baldini et al., 2007; Hassan, 2015; Prendergast et al., 2017). Despite representing important sources of complementary paleoclimatic information, combined studies on molluscan assemblages and stable isotope analysis of pedogenic and shell carbonates are scarce (e.g. Zanchetta et al., 2006; Leone et al., 2000; Balakrishnan et al., 2005a).

Furthermore, whilst the Holocene and Late Pleistocene terrestrial mollusc assemblages of the Mediterranean and continental Europe are rather well known and studied (e.g. Kerney, 1976; Esu, 1981; Rousseau et al., 1992; Limondin-Lozouet and Antoine, 2006; Limondin-Lozouet et al., 2017), the Middle Pleistocene successions are relatively rare and often chronologically poorly constrained (e.g. Rousseau and Keen, 1989; Limondin-Lozouet and Preece, 2004). In particular, terrestrial molluscs of glacial periods have been previously described for the Last Glacial in Europe from loess successions (e.g. Ložek, 1990; Rousseau et al., 1990; Moine, 2008), but for older glacial intervals our knowledge is essentially fragmentary and incomplete.

In this paper we discuss the terrestrial mollusc assemblages and stable isotope geochemistry ($^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios) of their shells and of associated pedogenic carbonates from a Middle Pleistocene paleosol developed within a fluvial to lacustrine succession at the Sulmona Basin (Abruzzo, central Italy, Fig. 1). The lacustrine successions have been extensively investigated and yielded important insights into past climate conditions in the Central Mediterranean between the late Early to the Late Pleistocene (Giaccio et al., 2015; Regattieri et al., 2015, 2016, 2017). However, stratigraphic evidence indicates that the lake level was substantially lower during some glacial intervals, and subaerial processes (fluvial-colluvial deposition, erosion and/or pedogenesis) dominated with respect to the lacustrine sedimentation (Giaccio et al., 2015; Regattieri et al., 2015,2016,2017). For such a sub-aerial stratigraphic intervals, pedogenic horizons thus represent the unique alternative sources of information to complement paleoclimatic inferences derived from lacustrine sediments at Sulmona Basin.

## 2. Site description

The Sulmona Basin (Fig. 1) is an intramontane depression formed during the Plio-Quaternary extensional tectonic phase that dissected the earlier orogenic, fold-and-thrust-belt system of the Apennine chain (e.g. Patacca and Scandone, 2007). The progressive formation of the basin was driven by the Sulmona or Morrone NW–SE-trending fault system (Galli et al., 2015), accommodating the volume for the accumulation of a thick Quaternary succession (e.g. Cavinato and Miccadei, 2000; Giaccio et al., 2012, 2013b). The Pleistocene succession is subdivided in three main unconformity-bounded alluvial–fluvial–lacustrine units; SUL-6, SUL-5 and SUL 4-3 (Figs. 1, 2). Each unit is constrained by tephrochronology, including direct $^{40}Ar/^{39}Ar$ dating of the tephra layers, and magnetostratigraphy (Giaccio et al., 2012, 2013a, 2013b; Sagnotti et al., 2014; Giaccio et al., 2015; Regattieri et al., 2015, 2016, 2017; Figs. 1, 2). The paleosol discussed in this paper (hereafter referred to as Fiorata Paleosol, from the toponymal of the type section; Fig. 1) occurs immediately above the lower boundary of SUL-5 and formed on the gravel-sand succession which fills a deep fluvial incision carved into the underlying SUL-6 unit (Figs. 1, 2). The pedogenic horizon consists of ca. 40-50 cm of gray-dark-grayish brown (10YR 4/2 -4/1 dark) silty to coarse massive sands A horizon (Fig. 2). The lower boundary fades in the lower fluvial interval through a massive, bioturbated C horizon. Thin root traces are preserved in the upper horizon, sometimes with walls impregnated by oxides. Small carbonate concretions are also visible. The Fiorata Paleosol is directly capped by a syn-depositionally reworked tephra layer (SUL5b-12 in Fig. 2) up to 0.5 m-thick of fine lapilli to coarse ash made up of green, porphyritic and finely grained micro-scoria (Fig. 2). Some fine volcanic ash fills small burrows and/or root traces within the upper soil horizon. Based on its peculiar foiditic composition of the glass from the layer and its stratigraphic order with respect other marker tephras, SUL5b-12 (Fig. 2) was correlated to the Tufo di Bagni Albule eruption by Giaccio et al. (2013a), from Colli Albani volcanic district dated by $^{40}Ar/^{39}Ar$ to 527±2 ka (Marra et al., 2009).

A detailed description of climatic and hydrological settings of the Sulmona Basin can be found in Regattieri et al. (2015, 2016, 2017) and is only briefly summarized here. The Sulmona meteorological station (ca. 400 m a.s.l.) records a mean annual temperature of 13.7°C, and an average rainfall of ca. 700 mm. Precipitation is strongly influenced by local topography and by the rising margin of the tectonic basin, reaching values of about 1200 mm at mountain summits. Winter precipitation is largely regulated by conditions in the North Atlantic and the North Atlantic Oscillation (López-Moreno et al., 2011). The meteoric precipitation at the L'Aquila Station (ca. 710 m a.s.l., ca. 60 km NW from Sulmona) has an average $\delta^{18}O$ value of - 7.13 ‰ (Longinelli and Selmo, 2003). The measured isotopic altitudinal gradient ($\delta^{18}O$/100 m) ranged from - 0.23 to - 0.13 ‰/100 m (e.g. Barbieri et al., 2005; Giustini et al., 2016).

## 3. Material and Methods

Two distinct sedimentary samples (SUL-16/01 and SUL-16/02) of ca. 10 kg each were collected from two different localities along the section exposing the Fiorata Paleosol at a distance of ca. 100 m, and ca. 10-15 cm below the paleosol top (Figs. 1 and 2). At these two sampling sites no differences in the paleosol profile were observed. Samples were first dried at room temperature for several days and then disaggregated using a very dilute solution of $H_2O_2$ (ca. 5%) and deionized water. The material was gently washed and sieved using 2000, 1000, 500 and 250 μm mesh screens, and all the identifiable shells and fragments were picked out under a binocular microscope and counted using the convention of Sparks (1961), where every gastropod apex is recorded to give a minimum number of individuals. The higher systematics followed Bouchet and Rocroi (2005) except for the helicoideans, for which the revision by Razkin et al. (2015) was adopted. The taxonomy and nomenclature of the extant species followed Welter-Schultes (2012).

During mollusc picking, small carbonate concretions (mm-sized) were also found and selected for isotopic analysis. Whole, well preserved shells of a helicelline geomitrid species and small carbonate concretions were soaked in a solution of distilled water and $H_2O_2$ (30%) and sonicated to remove contaminants. Samples were then dried, powdered and homogenized for stable isotope analyses. Samples of helicelline shells were also checked for mineralogical composition using X-ray diffraction (XRD). XRD was performed using a Bruker D2 Phaser diffractometer (30 kV, 10 mA) operating in Bragg-Brentano geometry (Θ-Θ scan mode) and equipped with a 1-dimensional Lynxeye detector. Ni-filtered Cu *K*α radiation was used. Data were collected in the scan range 4-65° in 2Θ, with scan step of 0.02° and counting time of 0.1 s/step. Data were processed through the software Diffrac.Eva (Bruker AXS Inc., 2015). Similarly, carbonate concretions were checked for mineralogical composition using XRD and inspected using a SEM-EDS for microscopic observation (Philips SEM 515 coupled with an EDS EDAX-DX micro-analyser).

Stable oxygen ($\delta^{18}O$) and carbon ($\delta^{13}C$) isotope ratios were determined using a Gas Bench II (Thermo Scientific) coupled with an IRMS Delta XP (Finnigan Mat) at the IGG-CNR in Pisa (Italy). Each carbonate sample of ca. 0.15 mg was dissolved in $H_3PO_4$ (100%), for 1 h at 70 °C in a sealed vial flushed with helium. The headspace gas ($CO_2$) was entrained in a helium stream, automatically dried and purified and then injected into the continuous flow isotope ratio mass spectrometer via an active open split. Sample results were corrected using the international standard NBS-19 and a set of internal standards (two marbles, MOM and MS, and a carbonatite NEW12, previously calibrated using the international standards NBS-18 and NBS-19, e.g. Negri et al., 2015) and normalized to the V-PDB international standard and expressed in the well-known δ-notation.

All samples were analysed in duplicate and analytical uncertainties for replicated analyses of $\delta^{18}O$ and $\delta^{13}C$ were ±0.15 ‰ or better. The $\delta^{18}O$ values of water are reported as V-SMOW.

## 4. Results

### *4.1 The terrestrial mollusc assemblage*

A very low number of terrestrial mollusc shells were recovered from the sampled sediments. These are all gastropods, no bivalves were found. Sample SUL-16/01 was virtually devoid of fossil remains, whereas sample SUL-16/02 contained less than 20 shells/kg. Despite the relatively low number of individuals, the counts can be considered representative for ecological analyses due to the amount of material sieved. All the shell remains belonged to terrestrial molluscs (Table 1), and only scarce fragments of unidentifiable micromammal bones were recovered.

Six species of terrestrial molluscs were recovered (Tab. 1; Fig. 3), two of which could not be identified to species level. The enid *Jaminia* sp. is represented by two shell apices only. As the extant species of this genus can be distinguished from the extinct Quaternary *Jaminia malatestae* (Esu, 1988) only based on the shell aperture it was not possible to identify these specimens to species level. The helicelline geomitrid, the most represented species in the paleosol, belongs to a group whose genus level taxonomy is entirely based on anatomical characters of the soft-parts. Therefore it was also not possible to make a more detailed taxonomic identification for this taxon. Shell features of the Sulmona geomitrid matched those of species in genera *Candidula*, *Cernuella*, *Helicella*, *Helicopsis*, *Xerocrassa* and *Xerosecta* (see the thorough iconographic survey on European species by Welter-Schultes, 2012). It could be hypothesized that the Fiorata Paleosol species corresponded to *Helicopsis striata* (Müller, 1774), a small European xerophilous geomitrid often associated with *Pupilla muscorum*.

From an ecological perspective, the identified species can be associated with dry to mesophilous open habitats (Tab. 1). *Pomatias elegans* is a medium-sized European prosobranch snail living among litter, humus and plant debris in many different dry to mesophilous habitats with some plant cover and preferably on calcareous substrates. *Truncatellina cylindrica* is a very minute European-Mediterranean pulmonate snail living among humus and leaf litter in dry to mesophilous habitats with some plant cover. The extant *Jaminia* species are small to medium-sized European calciphile pulmonates living on the soil surface or among rocks in dry, open grasslands and limestone reliefs. The Middle and Late Pleistocene *Jaminia malatestae* has been reported in open-dry paleoenvironments from the central-southern Italian peninsula during cold climatic periods (Di Vito et al., 1998; Marcolini et al., 2003; D'Amico and Esu, 2011; Limondine-Louzet et al., 2017).

*Pupilla muscorum* is a very small Holarctic pulmonate snail usually living among humus, leaf litter and rock debris in dry, cool, open habitats, preferably on calcareous substrates. *Vallonia costata* is a very small Holarctic snail, living among humus, litter, moss and plant debris in mesophilous open or sparsely vegetated habitats. This is also valid for the helicelline geomitrid, which is typical of dry, open, sunny habitats (indeed its shell is a typical "chaliconcha" following the shell classification by Sacchi, 1952).

*4.2 Mineralogical and isotopic analyses*

The XRD analysis confirmed that the terrestrial shells preserved their primary aragonite mineralogy, as also suggested by their well-preserved aspect (Fig. 4b). Only one sample had a considerable amount of calcite (ca. ¼) and thus it was excluded from further isotopic analysis. However, we suspect that this was due to the presence of thin and superficial encrustations of pedogenic carbonates. Oxygen isotope composition of terrestrial shells ranged from - 4.26 ‰ to - 2.55 ‰, whereas their carbon isotope composition ranged from - 9.42 ‰ to - 8.34 ‰ (Table 2).

Pedogenic carbonates were mm-sized, often elongated fine-grained concretions, preserving small cylindrical holes, sometimes ramified. Most were consistent with "hypocoatings-type" (Fig. 4c) carbonate concretions (e.g. Barta, 2011). The XRD analysis indicated that the small pedogenic concretions were mostly formed of calcite, along with minor quartz inclusions and traces of feldspars and micas (Fig. 4a), as further confirmed by SEM-EDS. Microscopic investigations did not show clear evidence of several phases of calcite depositions supporting their origin as impregnations around pores (i.e. small roots) of the soil matrix (Barta, 2011). Oxygen isotope composition of pedogenic carbonates ranged from - 7.60 ‰ to - 6.54 ‰, whereas their carbon isotope composition ranged from - 10.02 ‰ to - 9.52 ‰ (Table 2).

## 5. Discussion

*5.1 Chronology and paleoenvironmental significance of the mollusc assemblage*

The deep unconformity at the base of SUL-5, which cuts up to ~50 m of the underlying unit SUL-6 (Figs. 1 and 2), filled by fluvial gravels and sands, and capped by the Fiorata Paleosol, indicates a pronounced and long phase of lake low-stand associated to the complete desiccation of the lacustrine system. Based on the available chronological and stratigraphic constraints (Figs. 1 and 2), this subaerial phase can be roughly dated between ~650 ka and ~530 ka, or between MIS 16 and MIS 14. However, the Fiorata Paleosol documents only the final stages of this long subaerial phase, and the timing of the end of the soil-forming phase can be precisely constrained by the deposition of the thick tephra layer correlated to the Tufo di Bagni Albule, dated to 527±2 ka (Fig. 2). Recently, a tephra layer dated to 531±5 ka, and tentatively correlated to the Tufo di Bagni Albule, has also been identified in the archaeological succession of Valle Giumentina (layer T109b, Villa et al., 2016), located ~15 km NE of Sulmona Basin). According to the MIS chronology (e.g. Railsback et al., 2015), the Fiorata Paleosol can therefore be correlated with the period corresponding to MIS 14 (Fig. 2) and/or to the MIS 14-MIS 13 transition . However, the non-marine fauna is suggestive of an open-dry environment and more indicative of a glacial phase, better corresponding to a later phase of the glacial MIS 14.

The fauna is characterized by a low number of species and shares some general similarities with other terrestrial mollusc assemblages from the central Italian Peninsula considered typical of colder and drier conditions of glacial periods (e.g. Esu, 1981; Di Vito et al., 1998; Limondin-Lozouet et al., 2017; Boretto et al., 2017). Similarly, the terrestrial molluscs from Sulmona Basin indicate open and moderately dry habitats, as inferred from the presence of mesophilous and slightly thermophilous components (Table 1, i.e. *Pomatias elegans*). The presence of more thermophilous elements among the terrestrial molluscs correlated to glacial phases in the central Mediterranean, typically absent in coeval assemblages in central Europe, has already been noted by Sarti et al. (2005). This probably indicates the less extreme character, in terms of temperature, of these assemblages compared to the glacial counterparts of central to southern Europe. Interestingly, rare remains of *P. elegans* have also been found in the Valle Giumentina succession in the upper “glacial” assemblages (VG3 and VG4 biozones, Limondin-Lozouet et al., 2017), which for the generally low number of species (indicating dry and open habitats), resembles Fioratta Paleosol assemblage. However, VG3 and VG4 biozones are stratigraphically above the tephra dated to 531±5 ka at Valle Giumentina and tentatively correlated to the Tufo di Bagni Albule (unfortunately, there is no support chemical data for this layer), and therefore they do not precisely match the chronological interval documented by the Fiorata Paleosol. Conversely, the assemblages below the T109b tephra (VGM2 biozone) is characteristic of interglacial conditions, as documented by a larger number of species indicating forest environment and mild climate. As such we are inclined to conclude that the malacological record from Valle Giumentina is not chronologically synchronous with the Fiorata Paleosol assemblage (i.e. glacial MIS 14), therefore preventing a detailed correlation among the two records.

### *5.2 Stable isotope geochemistry*

The shells and pedogenic carbonates have very distinctive $\delta^{18}O$ and $\delta^{13}C$ values (Fig. 4), which also differ from the values obtained from lacustrine carbonates dated to MIS 11 and MIS 12 in the same basin (Regattieri et al., 2016), as well from clastic marine carbonates from the substratum (Regattieri et al., 2016; Villa et al., 2016). Along with the mineralogical evidence for the preservation of the shell mineralogy, the isotopic distribution provides robust evidence that terrestrial carbonates were not isotopically altered by diagenesis. This also indicates that pedogenic carbonates were not significantly contaminated by clastic carbonate.

Aragonite is usually enriched in $^{18}O$ and $^{13}C$ compared to calcite (Tarutani et al., 1969; Grossman and Ku, 1986; Romanek et al., 1992; Kim and O'Neil, 1997), but the difference observed between pedogenic carbonates and shells is not simply related to different isotopic fractionation factors. Terrestrial shells have $\delta^{13}C$ values higher than pedogenic carbonate by ca. 1 ‰. This value is slightly lower than those expected for calcite and aragonite precipitating close to isotopic equilibrium from the same solution (ca. 1.7 ‰, Romanek et al. 1992). We noticed, however, that analyses of aragonite and calcite in biogenic carbonates yielded differences in values closer to ca. 1 ‰ (Lécuyer et al., 2012). The $\Delta$ ($\delta^{18}O_{aragonite}$-$\delta^{18}O_{calcite}$) values show some differences according to the equations used (e.g. usually lower than 1 ‰, Tarutani et al., 1969; Grossman and Ku, 1986; Patterson et al., 1993; Kim and O'Neil, 1997; Lécuyer et al., 2012), but these differences are always lower than those observed between the $\delta^{18}O$ of aragonitic shells and pedogenetic carbonates in our record (ca. 4 ‰, Fig. 4). This difference can be explained by kinetic (vital) offset compared to equilibrium conditions for terrestrial mollusc shells, and to different environmental water sources from which the two carbonate polymorphs precipitate (i.e. the shell and the pedogenic carbonate).

The $\delta^{18}O$ values of terrestrial gastropod shells is proven to be related to the $\delta^{18}O$ values of environmental waters absorbed/ingested by the snails (e.g. water vapour, dew, local meteoric precipitation, e.g. Lécolle, 1985; Goodfriend et al., 1989; Zanchetta et al., 2005; Prendergast et al., 2015), and to isotopic effects linked to the exchange of fluid between the external environment (through the body of the snails) and internal fluid (Balakrishnan and Yapp, 2004), which are influenced by relative humidity (Balakrishnan and Yapp, 2004) and temperature. Therefore, no simple isotopic equilibrium with meteoric water could be assumed. However, empirical relations between the $\delta^{18}O$ values of meteoric water and the shells have been found within living populations (e.g. Lécolle, 1985; Goodfriend and Ellis, 2002; Zanchetta et al., 2005; Yanes et al., 2008; Prendergast et al., 2015), although in very arid lands a direct correlation is often not particularly robust (Goodfriend et al., 1989). Considering the data available from different living populations, there is no conclusive evidence that oxygen isotopic composition of shells is species-dependent (e.g. Lécolle, 1985; Goodfriend and Ellis, 2002; Zanchetta et al., 2005; Baldini et al., 2007; Yanes et al., 2008, 2009; Colonese et al., 2013ab, 2014). However, some significant differences have been reported in the literature in oxygen isotope composition between land snail populations living in the same place (Goodfriend and Magaritz, 1987; Yanes et al., 2011). Rather than a real species offset, these differences could be related to factors like duration of activity, life cycle, use of different water sources (dew, ingested food, rainfall) and/or the time of shell deposition compared to life cycle (e.g. Goodfriend and Magaritz, 1987). Ecological niches, occupied by different populations living in the same site, can additionally influence the final oxygen isotope composition of the shells (Goodfriend et al., 1989; Balakrishnan et al., 2005b; Yanes et al., 2008, 2009; Colonese et al., 2013b, 2014). The most complete model to interpret oxygen isotope composition of terrestrial gastropod shells, assuming no species offset, is that proposed by Balakrishnan and Yapp (2004). The model indicates that the steady-state $\delta^{18}O$ value of shell carbonate depends upon temperature, relative humidity, $\delta^{18}O$ of the input liquid water and $\delta^{18}O$ of ambient water vapour. However, quantitative prediction using this model involves several assumptions, which complicate its applicability to past samples (Balakrishnan et al., 2005a; Colonese et al., 2013a).

For living populations in Italy, Zanchetta et al. (2005) found an empirical relation between isotopic composition of precipitation ($\delta^{18}O_p$) and isotopic composition of shell ($\delta^{18}O_s$):

$$\delta^{18}O_p = 0.65 \times \delta^{18}O_s \boxtimes 5.44 \; (r^2 = 0.79) \qquad (1)$$

If relation (1) is assumed valid also for the past and for Sulmona settings, the average values of the oxygen isotope composition of meteoric water during the period of shell calcification can be calculated to be - 7.8±0.5 ‰.

Oxygen isotope composition of pedogenic carbonate is mostly related to local rainfall (Cerling, 1984), with additional evaporative effects in the soil and the effect of temperature-related isotopic fractionation during calcite precipitation. Using Cerling's (1984) data on modern soils, Jiamao et al. (1997) proposed the following relationship between $\delta^{18}O$ values in water and soil carbonate, which incorporates the evaporative effect in soils (Zanchetta et al., 2000) and the effect of the temperature in the fractionation factor:

$$\delta^{18}O_P = -1.361 + 0.955 \times \delta^{18}O_{CaCO3} \; (r^2 = 0.98) \qquad (2)$$

Boretto et al. (2017) found that equation (2) is a good predictor of isotopic composition of current $\delta^{18}O_P$ along the Tuscan coast. Assuming that equation (2) can also be applied to older pedogenic carbonates, it provides an average $\delta^{18}O$ precipitation value of ⊠ 8.3±0.4 ‰. This $\delta^{18}O$ value is similar, though lower, to those obtained from the Fiorata Paleosol shells, a fact that mutually supports the two estimations. We note that the equations (1) and (2) have been obtained using the annual average $\delta^{18}O$ value of local rainfall, so in principle the calculated values should be interpreted accordingly. However, terrestrial molluscs form their shells predominantly during wetter and/or warmer conditions (Balakrishnan and Yapp, 2004), therefore, the isotopic signal would be skewed toward the growth period (Kehrwald et al., 2010). If the warmer part of the year (e.g. spring/summer) was the principal season for the shell growth, higher $\delta^{18}O$ values of meteoric precipitation would be expected (Rozanski et al., 1993; Fricke and O'Neil, 1999) as, indeed, observed. Today in the Mediterranean, during the hottest part of summer land snails aestivate (e.g. Yurena et al., 2011), and are mostly active during spring and early autumn. However, during periods with a potentially cooler and wetter climate (i.e., glacial events), summer would be the greatest period of activity for land snails.

While pedogenic carbonates may precipitate from soil water which is more representative of the annual average recharge conditions (Cerling, 1984), Breecker et al. (2009) observed that pedogenic carbonates in very dry environments form during warmer, drier periods and from soil solution mostly recharged during wetter periods. If the soil water solution from which carbonate precipitates represents the colder months of recharge, this would explain the lower estimated $\delta^{18}O$ for precipitation compared to that obtained for shells. On the other hand, pedogenic carbonates can be the result of repeated events of carbonate deposition (and eventually re-dissolution), and thus their isotopic composition represents the weighted average of multiple events over a certain period of time. The mm-size of hypocoatings (Fig. 4c), and absence of clear evidence of phases of growth and dissolution, suggest that they form over a relatively short time (less than centuries, e.g. Retallack, 2005). Similarly, shells dispersed within soil horizons are not necessarily coeval, but may represent a different period of burial. All these factors can complicate the proposed interpretation, however, the relatively narrow $\delta^{18}O$ values measured also suggest that conditions did not change significantly during the soil formation.

The most striking feature is that the estimated $\delta^{18}O$ values of precipitation are, on average, lower than the values measured today at L'Aquila station ( - 7.13 ‰), also considering a small altitudinal correction for the Sulmona basin (ca. - 0.15 ‰). Lower $\delta^{18}O$ of precipitation during glacial/stadial conditions is expected at latitudes where isotopic composition of meteoric precipitation is strongly related to temperature (Rozanski et al., 1993). In the central Mediterranean a dependence between precipitation $\delta^{18}O$ and surface temperature ($\delta^{18}O$/T) has been found to be ca.

+0.2 ‰/°C, and this relation can be assumed also for the last two glacial periods (Bard et al., 2002). Therefore, the differences between present day $\delta^{18}O$ values of precipitation and the predicted average $\delta^{18}O$ value from pedogenic carbonates would account for ca. 5°C lower temperature at the time of soil carbonate formation, perhaps representing winter recharge; whereas the Fiorata Paleosol shells indicate less than 3°C lower temperature, probably due to expression of the warmer season.

It has been suggested that in the central Mediterranean most of the $\delta^{18}O$ signal in Quaternary continental carbonates is dominated by the "amount effect" of rainfall (ca. - 2 ‰/100 mm; Bard et al., 2002). This assumption has been used specifically for lakes for which additional evaporative-enrichment effects have been suggested during drier periods (Zanchetta et al., 1999,2007a; Roberts et al., 2008; Giaccio et al., 2015; Regattieri et al., 2015,2016), and for speleothem carbonate (Bar-Matthews et al., 2000; Regattieri et al., 2014; Zanchetta et al., 2007a,2016), for which the evaporative effect could be considered minor. Oxygen isotope composition of authigenic, bio-mediated calcite from lacustrine intervals from the Sulmona Basin unequivocally indicate that carbonates tend to have higher $\delta^{18}O$ values during colder and drier periods (Regattieri et al., 2015,2016,2017; Giaccio et al., 2015). Higher $\delta^{18}O$ values of lacustrine calcite during colder and drier periods at Sulmona probably result from the combination of several factors. During a glacial period $^{16}O$-enriched water is stored in continental ice (the "ice volume effect", e.g. Mix and Ruddiman, 1984) leading to $^{18}O$-enriched ocean waters; this enrichment is propagated into the hydrological cycle. The most obvious local effect is the lower temperature of carbonate precipitation, with related changes in the fractionation factor (Kim and O'Neil, 1997 and references therein), even though the occurrence of algal blooms responsible for calcite precipitations cannot occur for too lower temperatures. Moreover, drier conditions during glacial periods could enhance evaporation, causing enrichment in $^{18}O$ in residual water (Gonfiantini, 1986).

While environmental conditions derived from the terrestrial mollusc assemblages and from the general stratigraphic features are consistent with a general reduction in the amount of precipitation, both shell and pedogenic carbonates predict considerably lower $\delta^{18}O$ values in meteoric precipitation. This clearly challenges the assumption that the rainfall amount exerts a dominant effect on the isotopic composition of continental carbonates in the Mediterranean area, at least for the interval considered.

A possible explanation to reconcile these discordant interpretations is that terrestrial carbonates show distinct responses to precipitation regimes. Lakes and speleothems tend to have recharge systems that average and mix rainfall over the catchment area, and thus are more sensitive to the total amount of precipitation. Terrestrial gastropod shells, instead, are more susceptible to local precipitation and humidity during the period of growth. Pedogenic carbonates would be more sensitive to local rainfall and specific periods of recharge of soil interstitial water. For instance, the pedogenic carbonates of the Fiorata Paleosol would have been influenced by a shift in large-scale atmospheric circulation. This may have taken the form of frequent incursions of cold air masses, depleted in $^{18}O$, deriving from northern latitudes of continental Europe, producing mostly snow precipitation (Enzi et al., 2014). Melting snow can have a different soil infiltration pattern compared to rainfall. This may have led to carbonates mostly recharged by $^{18}O$-depleted waters. Shells may have formed during warmer parts of the year but during wetter precipitation events characterised by particularly lower-than-average $\delta^{18}O$ values (e.g. Colonese et al., 2007, 2013).

It is important to emphasize that the empirical equations discussed herein may not be widely applicable to past climates, in particular for glacial periods for which different synoptical climate conditions would have existed (Kuhlemann et al., 2008; Kehrwald et al., 2010).

On the other hand, the MIS 14 is a particularly weak glacial in many records (Lang and Wolff, 2011), as shown by the global benthic stack of Lisieki and Raymo (2005) or ice core temperatures (Jouzel et al., 2007). The pollen record at Thenaghi Philippon in Greece did not show a very prominent decrease in arboreal vegetation for MIS 14, even though phases of increased grasses due to drier and colder conditions were recognized (Tzedakis et al., 2006). This is also evident in Lake Ohrid where MIS 14 seems one of the less expressed glacial periods of the record (Franke et al., 2016).

Carbon isotope composition of both shells and pedogenic carbonates is indirectly related to vegetation cover, but with different and complex relationships. Terrestrial molluscs form their shells mainly from respired $CO_2$, and shell $\delta^{13}C$ values mostly reflect the stable carbon isotope composition of ingested vegetation (e.g. Goodfriend et al., 1989; Stott, 2002; Metref et al., 2003; Balakrishnan et al., 2005b; Liu et al., 2007; Prendergast et al., 2017). However, depending on the species and environmental settings (calcareous areas) shell $\delta^{13}C$ values may also be affected by the ingestion of soil carbonates (Yates et al., 2002; Romaniello et al., 2008; Yanes et al., 2008; Colonese et al., 2014). Moreover, different feeding behavior and food preferences may variably affect shell $\delta^{13}C$ values (Colonese et al., 2014). Using vegetation as the unique $CO_2$ source for shell carbon isotopes, Stott (2002) found a strong positive linear relationship between plant and shell $\delta^{13}C$ ($\delta^{13}C_{shell}$):

$$\delta^{13}C_{diet} = 1.35 \times \delta^{13}C_{shell} - 11.73 \qquad (3)$$

The equation (3) has been obtained for *Cornu aspersum* and the applicability to other species might be questionable. However, applied to our shell $\delta^{13}C$ values, it provides an average value for the ingested food of - 23.7±0.6 ‰. The average value for $C_3$ plants is ca. - 27 ‰ (e.g. Deines, 1980), and the calculated values of ingested vegetation are consistent with carbon isotope values obtained from $C_3$ vegetation from moderately dry conditions. Carbon isotope composition of $C_3$ vegetation in drier environments can be significantly higher than plants from wet environments (e.g. Kohn, 2010). Specifically in the Mediterranean, remarkable differences in $\delta^{13}C$ of $C_3$ plants are observed related to changes in water-use efficiency, which also varies largely between species, with higher $^{13}C/^{12}C$ ratio measured in drier areas (Hartman and Danin, 2010; Prendergast et al., 2017). Moreover, in the Mediterranean area similar shell $\delta^{13}C$ values have been reported in ecosystems dominated by $C_3$ plants (Goodfriend et al., 1989; Colonese et al., 2014; Prendergast et al., 2015).

For pedogenic carbonates there are theoretical equations which can be applied for calculating the $\delta^{13}C$ values of vegetation from which it is precipitated and the relative amount of $C_3$ and $C_4$ vegetation. According to Wang and Zheng (1989) the $\delta^{13}C$ values of vegetation over a soil can be estimated from the carbon isotope composition of pedogenic carbonate, with the following equation:

$$x= (11.9 + \delta^{13}C_{pedogenic})/14 \quad (4)$$

Applying the equation (4) to our carbonate $\delta^{13}C$ values, a proportion of $C_4$ plants ranging from 30 to 38 % is obtained. $C_4$ vegetation is relatively rare in southwestern Europe and mostly belonging to herb and shrubs (Pyankov et al., 2010), as such these estimations seem particularly high. Indeed, these estimations are based on the assumption that $C_3$ plants have a mean carbon isotopic value of ca. - 27 ‰, which is only a first-order estimation, whereas higher values of prevailing $C_3$ vegetation can be obtained by water stress, as previously discussed.

Considering the $C_4$ estimation from the isotopic composition of pedogenic carbonate, Breecker et al. (2009) observed that in dry environments pedogenic carbonates form predominantly during warm and dry conditions, and during periods of low soil respired-$CO_2$, thus overestimating the presence of $C_4$ vegetation. This supports the observation obtained from shell $\delta^{13}C$ values that the relatively high $\delta^{13}C$ values in pedogenic carbonates at Sulmona derive from $C_3$ vegetation enriched in $^{13}C$ during dry seasons. The integration of these two sources of paleoenvironmental information offers stronger arguments for interpreting past vegetation cover during soil formation, notably in Mediterranean areas, where the isotope ecology of modern and fossil shells is relatively well known.

## 6. Conclusion

Chronological, stratigraphic, and paleontological data indicate that the paleosol at the base of SUL5 in the Sulmona Basin sedimentary succession was formed during drier and probably colder conditions at the time of the MIS 14 glacial phase. The local mollusc assemblage indicates an open, dry environment. Carbon isotope compositions of pedogenic carbonates and shells consistently suggest prevailing $C_3$ vegetation adapted to dry environments. Inferred oxygen isotope composition of past rainfall from shells and pedogenic carbonates indicates that precipitation was generally $^{18}O$-depleted over the region compared to present-day. While this could imply a decrease in the atmospheric temperature of ca. 3-5°C compared to present day, this also conflicts with the current interpretation of speleothems and lake $\delta^{18}O$ values in the central Mediterranean. For example, lower $\delta^{18}O$ values in carbonates (arising from lower precipitation $\delta^{18}O$ values) should reflect increased rainfall, due to the amount effect. But increased rainfall is not supported in our record according to the paleontological data and/or the carbon isotope composition of carbonates. We propose that more frequent incursions of $^{18}O$-depleted cold air masses deriving from northern latitudes of continental Europe, along with a general context of reduced precipitation, would have influenced the isotopic composition of pedogenic carbonates and terrestrial shells. This work highlights the importance of integrating isotopic approaches on terrestrial carbonates (molluscs and pedogenic carbonates) to derive more robust interpretative frameworks on past climate and environments in the Mediterranean region.

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Figure and table captions

Figure 1. Location map, geological sketch map and general stratigraphy of the area. SC1 hole is discussed in Sagnotti et al., 2014 and Regattieri et al., 2015.

Figure 2. General stratigraphy of the lacustrine succession of the Sulmona Basin, with details of Fiorata paleosol succession and age constraints for the formation of the soil. Main tephra layers are indicated along with $^{40}Ar/^{39}Ar$ dating. The isotopic curve is from Lisieky and Raymo (2005). Tephrostratigraphy and $^{40}Ar/^{39}Ar$ dating from Giaccio et al. (2012; 2013a; 2013b; 2015); Sagnotti et al. (2014); Regattieri et al. (2015; 2016; 2017).

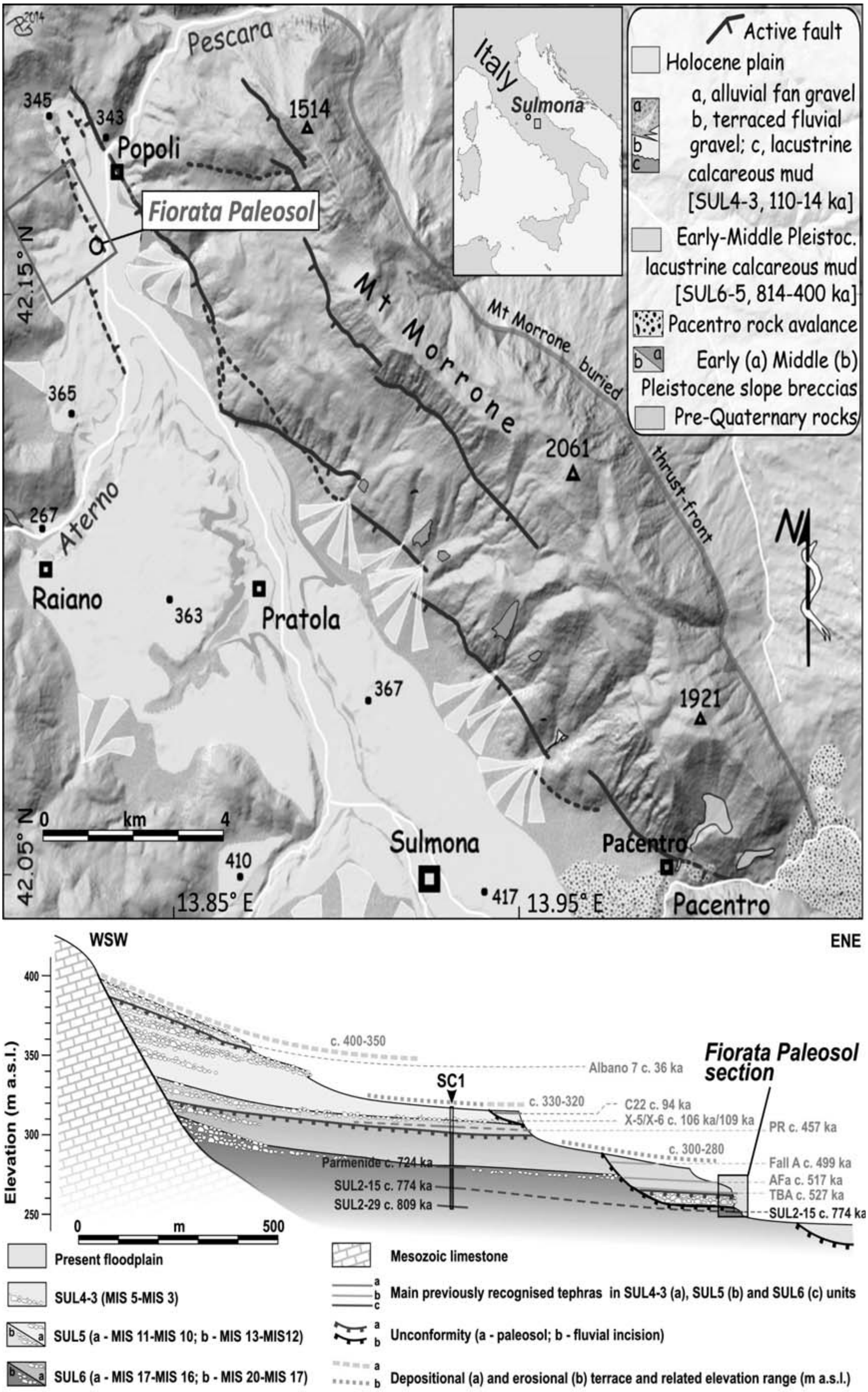
Figure 3. The most represented land snail species in Fiorata paleosol: *Pupilla muscorum* (top), *Vallonia costata* (middle) and an unidentified geomitrid helicelline (bottom).

Figure 4. Example of X-ray powder diffraction patterns of the small pedogenic concretions (a) and terrestrial shells (b). Main diffraction lines are shown ($d_{hkl}$ in Å). In (a), colors refer to diffraction lines of different minerals: blue = calcite; red = quartz; yellow = mica; and green = feldspar. In (b), all the diffraction lines belong to aragonite; (c) details of pedogenic concretions, showing typical shape of hypocoating.

Figure 5. Carbon and oxygen isotopic data from lacustrine deposits of Sulmona Basin (Regattieri et al., 2016), shell and pedogenic carbonate from Fiorata paleosol (this work); and clastic carbonate (Villa et al. 2016; Regattieri et al., 2016). VG: Valle Giumentina.

Table 1. Landsnails species and their ecological requirement.

Table 2. Stable isotope composition of land snail shells and pedogenic carbonate from the Fiorata Paleosol.



Active fault
Holocene plain
a, alluvial fan gravel
b, terraced fluvial gravel; c, lacustrine calcareous mud [SUL4-3, 110-14 ka]
Early-Middle Pleistoc. lacustrine calcareous mud [SUL6-5, 814-400 ka]
Pacentro rock avalance
Early (a) Middle (b) Pleistocene slope breccias
Pre-Quaternary rocks
Italy
Sulmona
Pescara
Popoli
Fiorata Paleosol
Mt Morrone
Mt Morrone buried thrust-front
Aterno
Raiano
Pratola
Sulmona
Pacentro
42.15° N
42.05° N
13.85° E
13.95° E
km
WSW
ENE
Elevation (m a.s.l.)
SC1
Fiorata Paleosol section
c. 400-350
Albano 7 c. 36 ka
c. 330-320
C22 c. 94 ka
X-5/X-6 c. 106 ka/109 ka
PR c. 457 ka
c. 300-280
Fall A c. 499 ka
AFa c. 517 ka
TBA c. 527 ka
SUL2-15 c. 774 ka
Parmenide c. 724 ka
SUL2-15 c. 774 ka
SUL2-29 c. 809 ka
Present floodplain
SUL4-3 (MIS 5-MIS 3)
SUL5 (a - MIS 11-MIS 10; b - MIS 13-MIS12)
SUL6 (a - MIS 17-MIS 16; b - MIS 20-MIS 17)
Mesozoic limestone
Main previously recognised tephras in SUL4-3 (a), SUL5 (b) and SUL6 (c) units
Unconformity (a - paleosol; b - fluvial incision)
Depositional (a) and erosional (b) terrace and related elevation range (m a.s.l.)


Fig.1

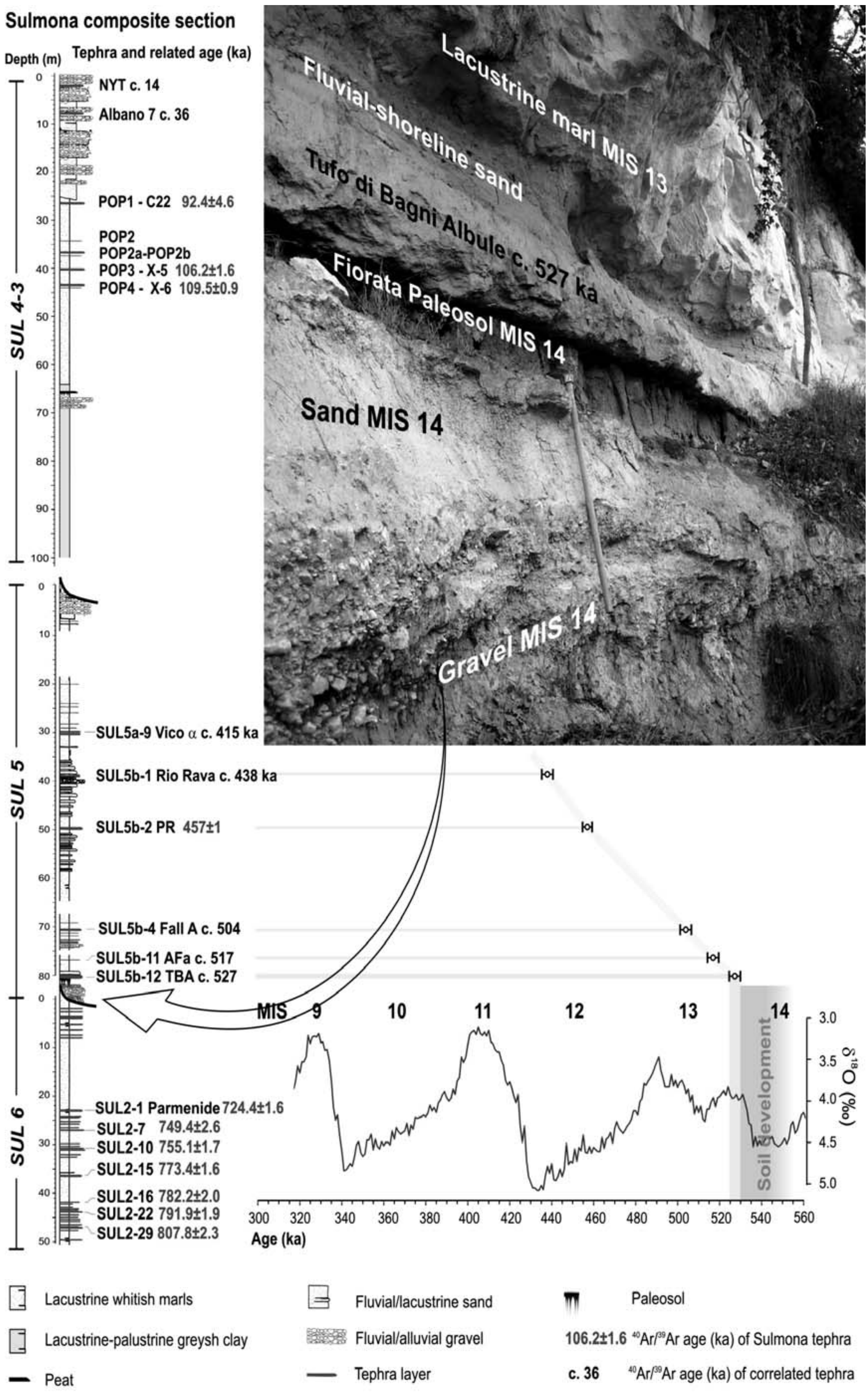
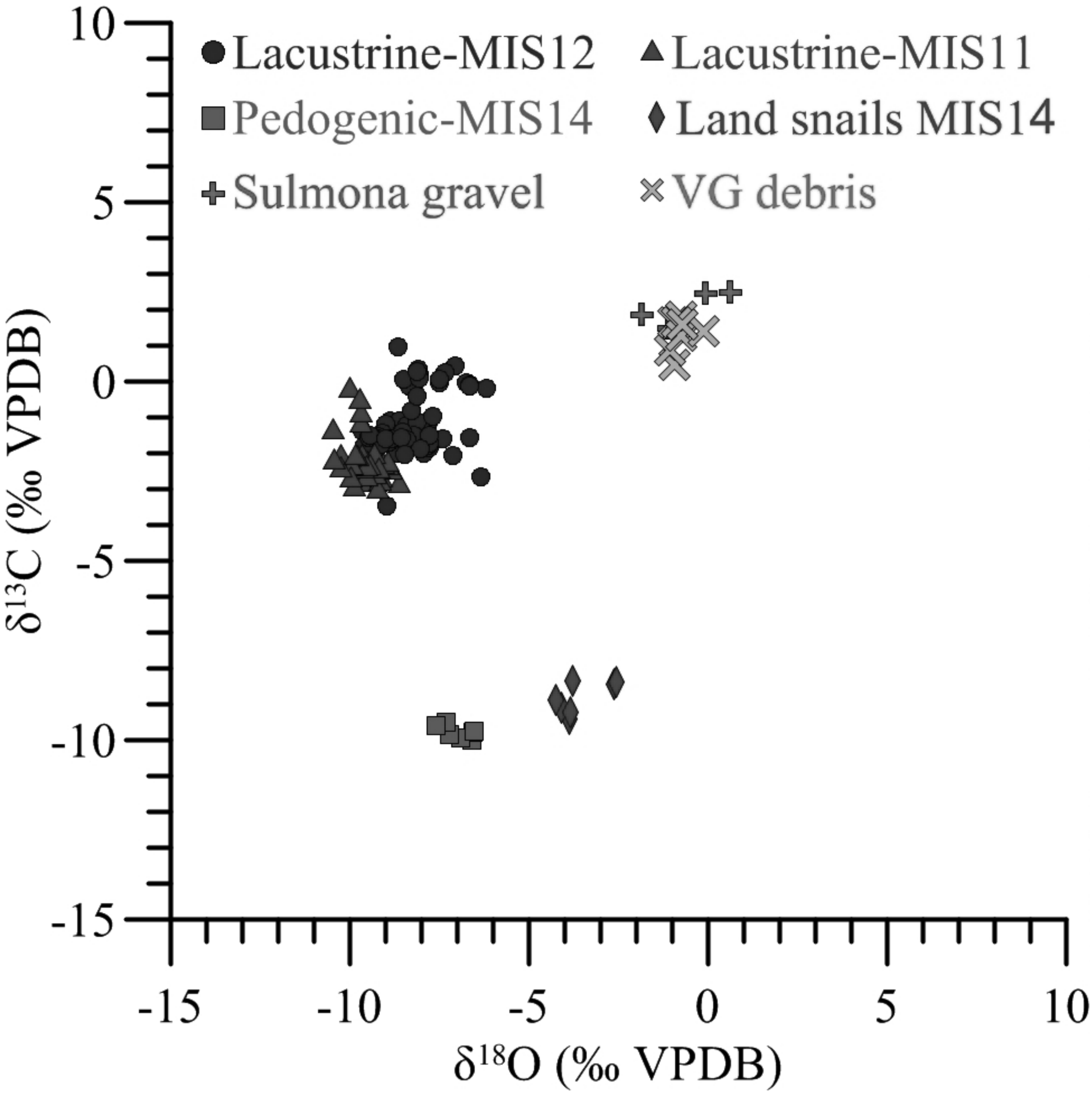

Sulmona composite section
Depth (m)
Tephra and related age (ka)
SUL 4-3
NYT c. 14
Albano 7 c. 36
POP1 - C22 92.4±4.6
POP2
POP2a-POP2b
POP3 - X-5 106.2±1.6
POP4 - X-6 109.5±0.9
SUL 5
SUL5a-9 Vico α c. 415 ka
SUL5b-1 Rio Rava c. 438 ka
SUL5b-2 PR 457±1
SUL5b-4 Fall A c. 504
SUL5b-11 AFa c. 517
SUL5b-12 TBA c. 527
SUL 6
SUL2-1 Parmenide 724.4±1.6
SUL2-7 749.4±2.6
SUL2-10 755.1±1.7
SUL2-15 773.4±1.6
SUL2-16 782.2±2.0
SUL2-22 791.9±1.9
SUL2-29 807.8±2.3
Lacustrine marl MIS 13
Fluvial-shoreline sand
Tufo di Bagni Albule c. 527 ka
Fiorata Paleosol MIS 14
Sand MIS 14
Gravel MIS 14
MIS 9 10 11 12 13 14
Soil development
δ18O (‰)
Age (ka)
Lacustrine whitish marls
Lacustrine-palustrine greysh clay
Peat
Fluvial/lacustrine sand
Fluvial/alluvial gravel
Tephra layer
Paleosol
106.2±1.6 40Ar/39Ar age (ka) of Sulmona tephra
c. 36 40Ar/39Ar age (ka) of correlated tephra

Fig.2



Lacustrine-MIS12
Lacustrine-MIS11
Pedogenic-MIS14
Land snails MIS14
Sulmona gravel
VG debris
10
5
0
-5
-10
-15
δ13C (‰ VPDB)
-15
-10
-5
0
5
10
δ18O (‰ VPDB)

| Species and higher systematics | Material | Main habitats |
| --- | --- | --- |
| **Caenogastropoda, Hypsogastropoda, Pomatiidae** | | |
| *Pomatias elegans* (Müller, 1774) | 2 sps: one operculum of a juvenile and one last whorl fragment of an adult/subadult | dry to mesophilous woodland edges and glades |
| **Heterobranchia, Pulmonata, Orthurethra, Vertiginidae** | | |
| *Truncatellina cylindrica* (Férussac, 1807) | 2 sps: two incomplete shells | mesophilous open habitats |
| **Heterobranchia, Pulmonata, Orthurethra, Pupillidae** | | |
| *Pupilla muscorum* (Linnaeus, 1758) | > 16 sps: many well preserved shells | dry to mesophilous open habitats |
| **Heterobranchia, Pulmonata, Orthurethra, Valloniidae** | | |
| *Vallonia costata* (Müller, 1774) | 32 sps many badly preserved shells | mesophilous open habitats and woodlands |
| **Heterobranchia, Pulmonata, Orthurethra, Enidae** | | |
| *Jaminia* sp. | 2 sps: two shell apices | dry open habitats |
| **Heterobranchia, Pulmonata, Sigmurethra, Geomitridae, Helicellinae** | | |
| Unidentified helicelline geomitrid | > 70 sps: many fragmentary shells | dry open habitats |

Table 1. Landsnails species and their ecological requirement.

| Sample label | $\delta^{13}C$ ‰ (V-PDB) | $\delta^{18}O$ ‰ (V-PDB) |
|---|---|---|
| Pedogenic carbonate | | |
| SUL14-1 | -10.02 | -6.58 |
| SUL14-2 | -9.80 | -6.57 |
| SUL14-3 | -9.95 | -6.90 |
| SUL14-4 | -9.52 | -7.22 |
| SUL14-14a | -9.52 | -7.31 |
| SUL14-12 | -9.77 | -6.54 |
| SUL14-13 | -9.60 | -7.60 |
| ***Average (±1 st dev)*** | ***-9.79 ± 0.18*** | ***-6.96±0.42*** |
| *Land snail shell* | | |
| SUL14-6 | -9.42 | -3.88 |
| SUL14-7 | -9.11 | -4.10 |
| SUL14-8 | -8.45 | -2.63 |
| SUL14-9 | -8.34 | -3.77 |
| SUL14-10 | -8.89 | -4.26 |
| SUL14-11 | -9.23 | -3.85 |
| SUL14-11a | -8.39 | -2.55 |
| ***Average (± 1 st dev)*** | ***-8.83 ± 0.44*** | ***-3.10 ± 0.69*** |

Table 2 Stable isotope composition of land snail shells and pedogenic carbonate from the Fiorata paleosol

Highlights

Mollusks association from Fiorata Paleosol indicates dry climate during late MIS14.

Carbon isotopes of pedogenic carbonates and land shells support the notion of dry climate.

Oxygen isotope composition of pedogenic carbonate and shells suggest lower 3-5 °C temperature than present.