

Sedimentary Geology

Palynology and thermal maturity assessment of the Permian succession in the Monte Leoni area (Middle Tuscan Ridge, inner Northern Apennines, Italy): new constraints for the stratigraphy and metamorphic evolution of the Tuscan Domain --Manuscript Draft--

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Abstract:	The reconstruction of the upper Palaeozoic sedimentary evolution of Western Mediterranean area is suffering for scarce age documentation of its stratigraphic units. This is also the consequence of the metamorphism and deformation they experienced during the Alpine tectonic events. Based on palynology and thermal maturity assessment, we contribute to this issue reporting biostratigraphic and sedimentological results in key-outcrops of the upper Palaeozoic successions of southern Tuscany (Italy), thus offering new data for the Palaeozoic units of the inner Northern Apennines, as well as for their palaeogeographic and palaeotectonic evolution predating the opening of the Alpine Neotethys. This study is focused on the Falsacqua Formation mainly consisting of quartzitic phyllite, sandstone and carbonate, representing the basal succession of two tectonic units exposed in the Middle Tuscan Ridge, and which age attribution was strongly debated in literature and referred to late Carboniferous-early Permian or Devonian. Palynological data document the first finding of a microflora of middle-late Permian age adding key constraints for age attribution. This age assignment permits to correlate the Falsacqua Formation with the coeval ones of southern Tuscany (i.e., Farma and Poggio al Carpino formations) and Elba Island (Rio Marina Formation) that are characterized by a similar microfloral content. Optical thermal maturity index as Spore Color Index is around 9 to 10 and suggests a T peak of about 300-350°C while the Raman spectroscopy on Carbonaceous material indicates a T peak around 375°C for both tectonic units. These data provide new constraints for the maximum T values occurred during the syn-collisional metamorphism developed in this sector of the Northern Apennines.
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UNIVERSITÀ DEGLI STUDI
DI PERUGIA

Perugia, May 12th, 2022

Dear Editor,

Please find the manuscript “Palynology and thermal maturity assessment of the Permian succession in the Monte Leoni area (Middle Tuscan Ridge, inner Northern Apennines, Italy): new constraints for the stratigraphy and metamorphic evolution of the Tuscan Domain” by Amalia Spina, Andrea Brogi, Enrico Capezzuoli, Gennaro Ventruti, Martina Zucchi, Mauro Aldinucci, Simonetta Cirilli, Andrea Schito, Domenico Liotta

Our paper focuses on the use of the palynological approach to analyze a metapelitic Palaeozoic unit (i.e., the Falsacqua Formation) exposed in the Monte Leoni area (Northern Apennines, Italy) and affected by low-grade metamorphism. The results of the study are discussed both in terms of maximum T attained during the metamorphism and the stratigraphic correlation of the Falsacqua Formation with coeval successions of the Northern Apennines.

All the authors agree to submit this paper and contributed to realize it.

Thank you for your consideration and we look forward to receiving your response.

Sincerely,

Amalia Spina

Highlights

- Age determination of the Falsacqua Formation by palynological studies
- Stratigraphic correlation of the Falsacqua Formation with coeval successions of the Northern Apennines;
- Thermal maturity of the Falsacqua Formation by different optical and geochemical approach
- Permian palaeogeography of Northern Apennines stratigraphic sequences

1 Palynology and thermal maturity assessment of the Permian succession in the Monte Leoni
2 area (Middle Tuscan Ridge, inner Northern Apennines, Italy): new constraints for the
3 stratigraphy and metamorphic evolution of the Tuscan Domain

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21
22 **Abstract**

23 The reconstruction of the upper Palaeozoic sedimentary evolution of Western Mediterranean area
24 is suffering for scarce age documentation of its stratigraphic units. This is also the consequence of
25 the metamorphism and deformation they experienced during the Alpine tectonic events. Based on

palynology and thermal maturity assessment, we contribute to this issue reporting biostratigraphic and sedimentological results in key-outcrops of the upper Palaeozoic successions of southern Tuscany (Italy), thus offering new data for the Palaeozoic units of the inner Northern Apennines, as well as for their palaeogeographic and palaeotectonic evolution predating the opening of the Alpine Neotethys. This study is focused on the Falsacqua Formation mainly consisting of quartzitic phyllite, sandstone and carbonate, representing the basal succession of two tectonic units exposed in the Middle Tuscan Ridge, and which age attribution was strongly debated in literature and referred to late Carboniferous-early Permian or Devonian. Palynological data document the first finding of a microflora of middle-late Permian age adding key constraints for age attribution. This age assignment permits to correlate the Falsacqua Formation with the coeval ones of southern Tuscany (i.e., Farma and Poggio al Carpino formations) and Elba Island (Rio Marina Formation) that are characterized by a similar microfloral content. Optical thermal maturity index as Spore Color Index is around 9 to 10 and suggests a T peak of about 300-350°C while the Raman spectroscopy on Carbonaceous material indicates a T peak around 375°C for both tectonic units. These data provide new constraints for the maximum T values occurred during the syn-collisional metamorphism developed in this sector of the Northern Apennines.

Keywords: Palynology, thermal maturity, Raman Spectroscopy, Permian, Northern Apennines, Gondwana.

45 **1. Introduction**

46 Since the last century, the palynological method has supported a wide range of researches in the
47 field of biostratigraphy, with a sensitive fallout on palaeoenvironmental, palaeoclimatological,
48 palaeogeographical and palaeotectonic reconstructions (e.g., Tyson, 1995, 1996; Batten, 1996;
49 Tyson et al., 2005; Traverse, 2007; Spina and Vecoli, 2009; Machado et al., 2010; Cirilli et al., 2015,
50 2018; Spina, 2015; Mendonça Filho and Gonçalves, 2017; Galasso et al., 2019a). The fundamental
51 role exerted by palynomorphs (organic walled organisms including spores/pollen and marine
52 organic elements) for biostratigraphic investigations derives from their high potentiality of
53 preservation even within medium and high-grade metamorphic rocks with temperature and pressure
54 higher than 350 °C and 14 kbar, respectively (Hanel et al., 1999; Bernard et al., 2007). Indeed, most
55 of the mineralized micro and macrofossils are not commonly preserved in metasediments and may
56 be unrecognizable in deformed rocks. Accordingly, as palynomorphs are the unique fossils
57 preserved, their importance is paramount for dating the host sediments, providing the
58 chronostratigraphic constraints to reconstruct: (i) the depositional and palaeogeographic setting; and
59 (ii) the geometrical relations among different stratigraphic and/or tectonic units (Pacltová, 1986;
60 Pflug and Reitz, 1992; Hanel et al., 1999; Brogi et al., 2021; Capezzuoli et al., 2021). Palynomorphs
61 are also commonly used in thermal maturity studies (geo-thermometry and hydrocarbon source rock
62 potential; Tissot and Welte, 1984; Hartkopf-Fröder et al., 2015; Schito et al., 2017a; 2022;
63 Riboulleau et al., 2018; Spina et al., 2018a; 2021). One of the important features of their external
64 organic wall is the internal re-ordering of the molecular structure as a consequence of thermal stress
65 during burial (depth and duration, geothermal flux, fluid geochemistry). In many palynomorphs,
66 these processes result in colour alteration that is directly related to the attained maximum
67 temperature. Different methods were developed for thermal maturity assessment. These mainly
68 consist of optical and geochemical analyses (Tissot et al., 1987; Sweeney and Bunharm, 1990;
69 Vandenbroucke and Largeau, 2007). Among them, the most popular is the Rock Eval Pyrolysis,

commonly used to measure quantity, quality, and thermal maturity of organic matter in rock samples (Peters and Cassa, 1994). Rock Eval Pyrolysis data are generally integrated with optical methods, such as Vitrinite Reflectance and Spore Colour Index (SCI) data, to construct geochemical well logs (Spina et al., 2018a; 2021; Riboulleau et al., 2018; Sorci et al., 2020). Other methods are FTIR and Raman spectroscopy, progressively acquiring great importance for hydrocarbon exploration and for palaeoenvironmental and geodynamic reconstructions, too (Negro et al., 2006; Fraser et al., 2014; Lagabriele et al., 2016; Beyssac et al., 2019; Schito et al., 2022). Raman spectroscopy especially, has revealed to be a promising tool to study the structural order of carbonaceous material in metamorphism (Beyssac et al., 2002; Lahfid et al., 2010; Ferralis et al., 2016; Lünsdorf et al., 2017) and also in the diagenetic realm (Liu et al., 2013; Hinrichs et al., 2014; Schmidt et al., 2017; Hackley and Lünsdorf, 2018; Khatibi et al., 2018; Schito et al., 2017a; 2017b; 2019; Muirhead et al., 2020; 2021; Schito and Corrado, 2020).

In this paper, we adopt the palynological approach to analyze a metapelitic Palaeozoic unit (i.e., the Falsacqua Formation) exposed in the Monte Leoni area, located in the Middle Tuscan Ridge (hereafter MTR; Figs. 1 and 2). This formation represents the deepest outcropping succession of the two tectonic units (Giorgetti et al., 1998; Fig. 3). These are both affected by low-grade metamorphism and are part of the inner Northern Apennines tectonic pile (Costantini et al., 1988; Carmignani and Kligfield, 1990; Carosi et al., 2002; Brogi et al., 2005). The results of this study are discussed both in terms of maximum T attained during the metamorphism and the stratigraphic correlation of the Falsacqua Formation with coeval successions of the Northern Apennines.

2. Geological setting

The Palaeozoic-Triassic metamorphic successions (i.e., pre-Verrucano and Verrucano units; Rau and Tongiorgi, 1974; Costantini et al., 1988; Lazzarotto et al., 2003; Perrone et al., 2006; Molli et al., 2020) of inner Northern Apennines are exposed in limited areas: in the Tuscan Archipelago

95 (Elba and Giglio Islands, Bortolotti et al., 2001; Lazzarotto et al., 1964; Rossetti et al., 1999), and
 96 in the MTR, a N–S trending regional morphotectonic feature ranging from the Apuan Alps, to the
 97 north, to the Argentario and Monti Romani, to the south (Fig. 1). In these areas, Meso-Cenozoic
 98 carbonate and terrigenous succession (i.e., the Tuscan Domain) deposited on the Adria continental
 99 margin during the earlier events of the Alpine neo-Tethys opening (Bernoulli et al., 2001). The
 100 Tuscan Units, together with their oceanic and transitional counterparts (Ligurian and Sub-Ligurian
 101 Units, respectively), were stacked during the late Oligocene-early Miocene Northern Apennines
 102 collisional event (Vai and Martini, 2001). This process produced diffuse HP-LT metamorphic
 103 conditions (Theye et al., 1997; Rossetti et al., 1999; 2002; Brunet et al., 2000; Molli, 2008; Brogi
 104 and Giorgetti, 2012; Bianco et al., 2015; 2019), later overprinted by greenschist metamorphic facies
 105 (Franceschelli et al., 1986).

106 In particular, in the Monte Leoni area (Figs. 2 and 3) two Tuscan tectonic Units have been described
 107 (Giorgetti et al., 1998; Brogi, 2008), both consisting of Palaeozoic marine successions overlain by
 108 Triassic continental deposits (Verrucano Group) and Meso-Cenozoic marine carbonate succession
 109 (Lazzarotto et al., 2003; Aldinucci et al., 2005). These tectonic units (Fig. 3) were deformed under
 110 slightly different metamorphic conditions (Giorgetti et al., 1998): (a) the outer and easternmost unit
 111 (Monte Leoni-Montagnola Senese Unit - LMS) experienced pressure of 8-10 kbar and temperature
 112 of 400-420 °C, while (b) the inner and westernmost unit (Montepescali-Monte Quoio-Iano Unit -
 113 MQI) experienced less pressure (8-9 kbar) and a maximum T of 360 °C. Their juxtaposition is
 114 ascribed to late Oligocene-early Miocene based on radiometric ages (Brunet et al., 2000) and
 115 regional considerations (Bertini et al., 1991; Carmignani et al., 1994), although their present-day
 116 geometry is deriving by the extensional tectonics acted during the middle-late Miocene (Brogi,
 117 2008). This polyphase deformation gave rise to superimposed structures and related metamorphic
 118 events (Meccheri et al., 1987; Moretti, 1991; Giorgetti et al., 1998; Aldinucci et al., 2005; Brogi,

2006). Thus, at outcrop scale, the main schistosity developed during the metamorphic peak and bedding are the recognizable foliations.

3. Lithostratigraphy of the Falsacqua Formation

The lower stratigraphic portion of the Falsacqua Formation just crops out in limited exposures of the eastern LMS unit, where it results characterized by quartzitic phyllite (Fig. 4a) with minor alternation of metasilstone and metasandstone beds. This succession is overlain by alternations of unfossiliferous metacarbonate and phyllite levels with occasional thin layers of metasandstone and metasilstone. The metacarbonate levels, exposed in both MQI and LMS units, are organized in laminated, decimeters-thick beds formed by microsparitic grey limestone and dolostone with scattered mica and silt- to fine sand-sized quartz grains (Fig. 4b, d). These metacarbonate beds become progressively thinner until disappearing and being substituted by alternations of gray quartz-micaceous metasandstone, fine gray quartzite, metasilstone and dark phyllite (Fig. 4c, e). These lithotypes are generally arranged in normally graded beds, up to 1.5 m thick. Bedding surfaces are each other parallel, with evidence of seafloor erosion as represented by occasional, small-scale scours. Furthermore, tractional sedimentary structures, such as plane-parallel lamination, are locally present. Metaconglomerate lenses or centimetric-thick beds are also present.

This formation is overlain by Triassic continental deposits (i.e., the Verrucano Group), represented by fluvial-alluvial fan deposits (Civitella Marittima Formation: Aldinucci et al., 2003, 2005). The passage from Palaeozoic to Triassic is always hidden by vegetation, although it is supposed to be discontinuous (Aldinucci et al., 2005).

4. Material and methods

4.1 Organic matter concentration

Ten samples were collected in the cropping out successions belonging to both the tectonic units exposed in the Monte Leoni. Seven samples, among which three from the medium stratigraphic portion (FALS 02, 04, 10) and four from the upper one (FALS 01, 06, 07, 11) derive from the eastern LMS unit, while three samples, among which two (FALS 12 and 14) from the medium stratigraphic portion and one (FALS 13) from the upper one, are from the western MQI one (Tab. 1; Fig. 3). Sampling was performed in the available exposures preferring the dark levels (phyllite, metasiltite and limestone) which are the most promising lithologies for organic matter analysis. Samples were then processed at the Sedimentary Organic Matter Laboratory of the Department of Physics and Geology of University of Perugia (Italy) - following the technical procedures proposed by Traverse (2007) and Buratti and Cirilli (2011). Twenty grams of each sample were crushed and processed using hydrochloric acid (HCl, 37%) and hydrofluoric acid (HF, 50%) and sieved with a 10 µm filter. The organic residue was mounted in a slide for thermal maturity studies. The remain part was treated with Schultz solution in order to lighten dark-hued palynomorphs, then sieved with a 10 µm filter and mounted in a slide for biostratigraphic studies. The palynological slides are stored at the Sedimentary Organic Matter Laboratory of the Department of Physics and Geology of University of Perugia (Italy).

159

160 **4.2 Spore Color Index (SCI)**

Miospore colour was analysed by standard optical methods as Spore Color Index (SCI; Fisher et al., 1980) in order to evaluate the organic matter thermal maturity (Tab. 1). Microscope used was Leica DM1000. This method is fundamentally characterized by the colour changing (from yellow pale to black) of miospores with increasing thermal increments in the low thermal maturity range. Following the proper standardization, arbitrary numerical values (a ten-point scale) were applied to the colour change sequence. In the present study, SCI was evaluated mainly from the colour of smooth, unfolded and unornamented miospore specimens as *Punctatisporites* spp. and *Calamospora*

spp. in unoxidized residues based on a visual comparison to Munsell colour standards as proposed by Traverse (2007). Approximately, ten miospores per sample were analyzed in order to estimate SCI. Organic matter from palynomorphs-productive samples was also analyzed for SCI optical analysis.

4.3 MicroRaman spectroscopy

Among the collected samples, three of them (FALS 01, FALS 04 from eastern LMS unit and FALS 12 from western MQI unit; Tab. 1; Fig. 3) were chosen to perform MicroRaman spectroscopy in order to estimate thermal maturity. Micro-Raman spectra were recorded at ambient conditions with a LabRAM HR Evolution Horiba in a backscattering geometry at the Department of Earth Science and Environmental Sciences (University of Bari, Italy). This spectrometer is equipped with an Ultra-Low Frequency (ULF) notch filter and an electrically cooled charged coupled device (CCD) detector. Raman spectra were excited by a He/Ne ($\lambda = 632.8$ nm) laser source using a 50X long working distance objective and a 600 grooves/mm grating. The instrument was calibrated using the 520.4 cm^{-1} line of a Si wafer before performing the Raman analyses. The laser power was set at 25% of the maximum output power to avoid photochemical damages to the sample (Beyssac et al., 2002; Lunsdorf et al., 2017; Schito et al., 2017b). This was checked by visual inspection and spectroscopic changes over the period of laser irradiation. To obtain a better signal to noise ratio several scans with an acquisition time of 60 sec in the $1000\text{--}1800\text{ cm}^{-1}$ region, were acquired, and the average spectra were used for the analysis. A band fitting analysis using a pseudo-Voigt function with the minimum number of the component was done using the GRAMS 9.2 software package. The spectra were corrected for the fluorescence background by subtracting a polynomial baseline. The area (integrated intensity), intensity (height), center position, and full width at half maximum (FWHM) were determined for all bands.

4.4 Raman spectrum of carbonaceous material

Raman spectroscopy is a well consolidated method to estimate thermal maturity of carbonaceous material (CM), since the CM Raman signal exhibits systematic changes, from disordered organic material to well-ordered graphite, with increasing of metamorphic degree (Beyssac et al., 2002; Lahfid et al., 2010; Kouketsu et al., 2014; Lunsdorf et al., 2017). In general Raman spectrum of CM consists of a first order region between 1100 to 1800 cm^{-1} and a second order region between 2500 to 3100 cm^{-1} (Tuinstra and Koenig, 1970; Nemanich and Solin, 1979; Pasteris and Wopenka, 1991; Beyssac et al., 2002). The first order region, where we focused in this work, is dominated by the G band and D bands. The G band is named for graphite, as it corresponds to the narrow band at around 1580 cm^{-1} (e.g., Wang et al. 1990) visible in the Raman spectrum of well-crystallized graphite. This G-band is due to a doubly-degenerated in-plane C–C stretching mode with E_{2g} symmetry (e.g., Tuinstra and Koenig, 1970). D-band are labelled as disorder since are associated to the crystal defects occurring in the structure. In particular, the D1 band, generally observed in carbonaceous material at about 1355 cm^{-1} , can be explained by an increased structural disorder of the sp^2 carbon network. With increasing degree of disorder, additional Raman bands appear at around 1620 cm^{-1} (D2-band), 1510 cm^{-1} (D3-band), and 1245 cm^{-1} (D4-band). The assignment of these D bands is still a matter of debate (Schito et al., 2017b; Henry et al., 2019).

5. Results

In this section the results of the palynological study and thermal maturity analyses obtained from the samples belonging to the MQI and LMS Units (Figs. 2 and 3) are reported.

5.1 Palynological assemblage

Samples from the easternmost unit (Tab. 1; Fig. 3) are characterized by a scarce microfloristic content (Fig. 5a). Nonetheless, different taeniate bisaccate pollen as *Striatopodocarpites* spp. (S.

218 *cancellatus*, *S. communis*, *S. fusus*) and *Protohaploxylinus limpidus* in assemblage with non taeniate
 219 as *Alisporites nuthallensis* and *A. splendens* and *Limitisporites* sp. cf. *monstruosus* were
 220 documented. Monosaccate pollen grains as *Potonieisporites novicus* and *Plicatipollenites* sp. and
 221 trilete spores as *Densoisporites playfordii* and *Kraeuselisporites* sp. cf. *rallus*, *Punctatisporites*
 222 *fungosus*, *Punctatisporites* spp. and *Calamospora* spp. also occurred in assemblage with monolete
 223 as *Thymospora opaqua* and the *incertae sedis* organic microfossil *Reduviasporonites chalastus*.
 224 Palynological assemblages from the westernmost unit (Tab. 1; Fig. 3) are characterized by a similar
 225 microflora (Fig. 5b). Taeniate bisaccate pollen as *P. limpidus*, *P. microcorpus*, *S. cancellatus* and *S.*
 226 *communis* and *Taeniaesporites* sp. cf. *noviaulensis* occur together with non taeniate as *A.*
 227 *nuthallensis* and *A. splendens*. Monosaccate as *P. novicus* and *Plicatipollenites malabarensis* were
 228 also recognized. Smooth spores as *Punctatisporites* spp., *Calamospora* spp., and other not
 229 determined because strongly degraded, were found in assemblage with *T. opaqua* and *R. chalastus*.

230

231 **5.2 Thermal maturity of organic matter**

232 **Optical analysis**

233 Samples from the eastern unit show value of SCI values around 9/10 (dark brown to black colour;
 234 Tab.1). Organic-wall of the smooth spores from the samples of the western unit (Tab .1) show the
 235 same dark brown to black colour. These SCI values correspond to a Vitrinite Reflectance of 2.5%
 236 (Hartkopf-Fröder et al., 2015) indicating the metagenesis stage of the organic matter thermal
 237 maturity (Fig. 6).

238 **Geochemical analysis**

239 Thermometry from Raman spectroscopy of carbonaceous material is calibrated using the first
 240 order region dominated by the G band and D bands. A series of geothermometers based on the
 241 correlation between Raman parameters (area and/or intensity of the G and D bands) and
 242 paleotemperatures, estimated in metamorphic rocks by other analytical methods (e.g., Fe-Mg

exchange reactions), were already proposed by using green (514 to 532 nm) lasers (see Henry et al., 2019 for a review). Values of some Raman parameters (in particular, their position and relative intensities) depend on the wavelength of the laser source (Quirico et al., 2005) and thus most of the existing correlation could be useless for the present work where spectra have been acquired using a red (632 nm) laser. Nevertheless, Kouketsu et al. (2014) experimentally demonstrated that the full width of the D1 band (FWMH-D1) parameter remain constant when different laser sources are used. By this, we adopted the peak-fitting procedures described by Kouketsu et al. (2014), based on the FWHM of D1:

251

$$T\text{ }^{\circ}\text{C} = -2.15 (\text{FWMH-D1}) + 478$$

The applicable temperature range for this equation is between 150–400°C thus resulting appropriated for our goals, according to Temperature evaluations given by Theye et al. (1997) and Giorgetti et al. (1998).

On first sight, the spectra for all the analyzed samples look quite similar. Raman spectra acquired from FALS 04 samples display a broad peak at $\sim 1600\text{ cm}^{-1}$ that can be decomposed into G- and D2-bands, and a prominent D1 peak at $\sim 1330\text{ cm}^{-1}$. About FALS 01 sample, an additional weaker D3 band at 1440 cm^{-1} is necessary in the fitting the spectrum, indicating a higher disorder degree (Fig. 7).

Considering the FWHM of the D1 band and by applying Equation 1, FALS 01 and FALS 04 samples (eastern unit) yielded a temperature of 352 °C and 373 °C, respectively. Similarly, to this last temperature value, FALS 12 sample (western unit) yielded 375 °C. The error associated with this geothermometer based on FWHM-D1 is of about $\pm 30\text{ }^{\circ}\text{C}$ (Kouketsu et al., 2014).

265

266 6. Discussion

The discussion is divided in three different parts, focusing on the age determination and regional correlation, thermal maturity and paleogeographic implications.

6.1. Age of the Falsacqua Formation: stratigraphic and palaeoenvironmental correlation with coeval formations

Lithological features and microfloristic content show strong similarities among the analyzed samples from both western and eastern units (Fig. 3), documenting a middle-late Permian age for the two units. A microflora similar the one of the Falsacqua Formation was also documented in other successions of southern Tuscany and Tuscan Archipelago (Cirilli et al., 2002; Aldinucci et al., 2008; Spina et al., 2019; Brogi et al., 2021; Fig. 7). Specifically, pollen as *Alisporites nuthallensis* was recorded in assemblage with *A. splendens* in the Poggio al Carpino and Rio Marina formations (Lazzarotto et al., 2003; Spina et al., 2019). This latter pollen grain was also documented in the Gavorrano Monzogranite hosting rock and in the Farma and Carpineta formations with *Protohaploxypinus limpidus* and *Protohaploxypinus* spp., *Taeniaesporites noviaulensis* and *Striatopodocarpites* spp. (Aldinucci et al., 2008; Brogi et al., 2021). In the Rio Marina and Poggio al Carpino formations, spore as *Densoisporites playfordii* also occurs (Spina et al., 2019). Other spores as *Kraeuselisporites rallus* and *Thymospora opaqua*, occurring in the Falsacqua Formation, are also present in the Carpineta, Mt. Calamita, Rio Marina formations and Gavorrano Monzogranite hosting rock (Aldinucci et al., 2008; Spina et al., 2019; Brogi et al., 2021). *Reduviasporonites chalastus* is present in all the Permian Tuscan successions palynologically studied up to now. Other important affinities are recognized with the Lopingian microflora from Southern Alps (Italy), where the occurrence of *A. splendens*, *Alisporites* spp., *P. limpidus*, *Protohaploxypinus* spp., *S. fusus*, *S. cancellatus* and *Striatopodocarpites* spp. and *R. chalastus* were documented from some key sections bracketing the Permian-Triassic boundary (Clement-Westerhof, 1974; Visscher and Brugman, 1988; Cirilli et al., 1998; Spina et al., 2015; Nowak et al., 2019; Gibson and Bodman, 2021; Gibson and

Wellman, 2021) before the first occurrence of the conodont *Hindeodus parvus* which marks the base of the Triassic System (Yin et al., 2001).

Coeval Lopingian assemblages, showing the same microfloristic content by the presence of *A. nuthallensis*, *A. splendens*, *P. limpidus*, *R. chalastus*, *Taeniaesporites* spp. were also documented from other European countries as England (Clarke, 1965, Warrington and Scrivener, 1990; Warrington, 2005; 2008; Gibson and Wellman, 2021), Ireland (Visscher, 1971), Germany (Leschik, 1956; Grebe, 1957; Schaarschmidt, 1963), Hungary (Haas et al., 1988); Barents Sea (Mangerud, 1994; Mangerud et al., 2021); Greenland (Piasecki, 1984; Twitchett et al., 2001) and Russia (Utting et al., 1997). Other similarities concern the microflora from Gondwana. The microflora from the Falsacqua Formation shows the close compositional characteristics evidenced by the presence of several pollen grains as *A. nuthallensis*, *P. limpidus*, *P. novicus*, *S. cancellatus*, *S. fusus*, and *T. novaiulensis* and the *incertae sedis* *R. chalastus*, with Guadalupian OSPZ 5 and 6 biozones recorded in Northern Gondwana regions as Iran, Oman, Pakistan, Saudi Arabia and Southern Turkey (Balme, 1970; Stephenson et al., 2003; Stephenson 2006; 2008; 2016; Stolle, 2007; Stolle et al., 2011; Spina et al., 2018a; 2020; 2021). In particular, the monolete spore *Thymospora opaqua* were documented only in these Gondwanan regions and in Tuscan assemblages (Spina et al., 2019; Brogi et al., 2021). Cavate trilete spore as *Densoisporites playfordii* with bisaccate as *T. noviaulensis* were recorded in the late Permian of West Pakistan (Balme, 1970; Hermann et al., 2012). Close microfloristic composition also characterizes the same time interval of the Mozambique (Galasso et al., 2019a, b) and Israel (Eshet, 1990; Stephenson and Korngreen, 2020). Based on the correlation with coeval microflora recorded from both independently and not-independently successions, the palynological assemblage yielded from the Falsacqua Formation is herein assigned to the Guadalupian-Lopingian (i.e., middle-late Permian) time interval.

This finding has remarkable stratigraphic and palaeoenvironmental implications, as it enables to correlate the biomineralized fossils barren Falsacqua Formation with other coeval formations

317 exposed in Southern Tuscany, such as the Farma Formation (Aldinucci et al., 2008), the Poggio al
318 Carpino Formation (Lazzarotto et al., 2003), the Arenarie del Monte Argentario Formation (Cirilli
319 et al., 2002), the Gavorrano Monzogranite hosting rock (Brogi et al., 2021), as well as the Rio Marina
320 and Mt. Calamita formations in the Elba Island (Tuscan Archipelago; Spina et al., 2019). Among
321 these formations, a remarkable lithostratigraphic similarity does exist between the Falsacqua
322 Formation and its age-equivalent counterpart exposed just few 10 km northward in the Monticiano-
323 Roccastrada Ridge, namely the Farma Formation. In terms of depositional setting, the latter has been
324 related by Aldinucci et al. (2008) to a relatively distal setting (i.e., below storm-wave base level) of
325 a river-dominated delta, where hyperpycnal, high-density turbiditic flows deposited mostly
326 structureless with normally graded sandstones locally topped by few centimeters of a current-ripple
327 laminated division. In this setting, background sedimentation was represented by suspension fallout
328 of fines from both the tail of the above-mentioned hyperpycnal flows and low-density river-borne
329 plumes. Accordingly, although poor outcrop conditions at Monte Leoni area prevents any detailed
330 sedimentological investigation, the Falsacqua Formation, characterized by the same lithological
331 features of the Farma Formation, could be deposited within similar palaeoenvironmental conditions,
332 thus representing the submerged domain of a river-dominated delta. In this setting, the phyllite and
333 metacarbonate typifying the lowermost exposed portion of the Falsacqua Formation could have
334 resulted from the most distal portion of the above-mentioned deltaic system or its deactivation/lateral
335 shifting, with the latter being part of an articulated belt of coarse-grained, river-dominated deltas
336 (e.g. Poggio al Carpino, Arenarie del Monte Argentario and Rio Marina formations; Cirilli et al.,
337 2002; Lazzarotto et al., 2003; Spina et al., 2019, Molli et al., 2020; Capezzuoli et al., 2021). Such a
338 deltaic sedimentation was most likely accommodated by SW–NE-oriented, pull-apart basins
339 developed within a large-scale transtensional zone (Rau 1990; Cortesogno et al. 1998; Molli et al.,
340 2020) at the beginning of the Alpine sedimentary cycle.

341

6.2 Thermal maturity of organic matter and palaeotemperature

The colour of spormorphs of the Falsacqua Formation is generally dark brown to black corresponding to SCI values 9/10. This range indicates the metagenesis stage of organic matter thermal maturity (Hartkopf- Fröder et al., 2015; Fig. 6) and corresponds to a vitrinite reflectance value between 2,5% and 4% within the epizone (according to the definition of Frey, 1987) and equivalent to a palaeotemperature interval of 300-350°C. Paleotemperature calculated by means of the FWMH-D1 value according to Kouketsu et al.'s correlation (2014), allows to better constrain the maximum T during the metamorphic peak. In our case (Fig. 7), the measured T peak values are similar for the two tectonic units exposed in the Monte Leoni. Samples belonging to the eastern unit indicate a T peak of about 375 °C, as well as the sample analyzed from the western unit reaching about the same value and highlighting no noticeable temperature difference between the two studied units. Nevertheless, Giorgetti et al. (1998) estimated different T peak values for the western and eastern units: 400-420°C and 350-360°C, at a P of 8-10 kbar, respectively. However, considering the maximum error of $\pm 30^{\circ}\text{C}$ associated with the geothermometer we applied, according to Kouketsu et al. (2014), the resulting peak temperature might have reached values close to those proposed by Giorgetti et al. (1998).

6.3 Some considerations about the palaeogeography

Based on microfloristic findings from coeval middle-upper Permian successions of southern Tuscany (Cirilli et al., 2002; Lazzarotto et al., 2003; Aldinucci et al., 2008; Spina et al., 2019; Brogi et al., 2021; Fig. 8), we performed a correlation with microflora recorded from different areas belonging to the Permian Euramerica and Gondwana phytogeographical provinces (Utting and Piasecki, 1995; Stephenson, 2018). Microflora from Tuscany generally share different compositional characteristics, like the dominance of bisaccate pollen as *Lueckisporites virkkiae*, *Taeniaesporites*, *Protohaploxypinus*, *Striatopodocarpites* and rare *Vittatina* with those from the

367 Euramerica palaeofloristic province, in particular Southern Alps and Western Europe (Zechstein) as
368 well as U.S.A. Other common features were noted also in other studies (Spina et al., 2019; Brogi et
369 al., 2021) with the microflora documented from Northern Gondwana regions (Saudi Arabia, Iran,
370 Oman, Pakistan, Jordan, Iraq, Israel and North Africa; e.g., Stephenson. 2018). In particular, spore
371 as *Thymospora opaqua* and *Vittatina costabilis* are considered as endemic of these countries. The
372 Tuscan assemblage shows a diffused, mixed flora exhibiting common features with both
373 Euramerican palaeofloristic and Northern Gondwana provinces. These features can be explained by
374 the near-equatorial position of Adria microcontinent, very close to the Middle East regions as also
375 proposed by Molli et al (2020).

376

377 **7. Conclusions**

378 The microfloristic content of the analysed succession of Monte Leoni supports for a middle-late
379 Permian age (Guadalupian-Lopingian), therefore correlating the Falsacqua Formation to most of
380 other Paleozoic successions exposed in the inner Northern Apennines (e.g., Farma Formation, Rio
381 Marina, Mt. Calamita, Farma, Arenarie del Monte Argentario formations). Like all these units, also
382 the Falsacqua Formation is interpreted as deposited in the submerged domain of a river-dominated
383 delta developed in a transtensional setting.

384 The thermal maturity of the organic matter highlights a similar maximum T value for the two
385 tectonic units exposed in the Monte Leoni. These values correspond to the maximum T reached at
386 the metamorphic peak during the orogenesis and are slightly different from those obtained, for the
387 same tectonic units, by other authors through the metamorphic assemblage defining the main
388 schistosity (S1 foliation).

389 Optical analysis related to the thermal maturity of organic matter indicated SCI values of 9/10
390 corresponding to a palaeotemperature of 300-350°C in both western and eastern units. These T
391 values are not confirmed by the geothermometer based on the Raman spectra indicating higher

temperatures around 375 °C. The slight discrepancy about the palaeotemperature results between optical and Raman analysis, could be linked by the effects of P values (up to 10 kbar) as estimated by Giorgetti et al. (1998). High pressure could retard the organic maturation reflected in the colour of palynomorphs but not in the sporopollenin composition. Based on this consideration, in rock deposits experienced by high pressure and relatively high temperature, the optical analysis of palynomorphs could be not confident.

The middle-upper Permian Tuscan microflora is marked by common features with both Euramerican and Northern Gondwana provinces. These ‘mixed’ features confirm the suggestion by Molli et al. (2020) who indicated a near-equatorial position of Adria microcontinent, as part of the Northern Gondwana regions.

Finally, our results confirm and underline the key role of organic matter studies to provide fundamental inputs for reconstructing geological and palaeoenvironmental settings. Its potentiality for the studies of metasedimentary units around the world is probably greater than currently stated. Although difficult and many times unsuccessful, palynological processing of metasediments can provide information that would otherwise be inaccessible.

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421

422 Figure 1: a) Location of the Apennine Range in the Mediterranean Sea and b) distribution of main
423 metamorphic units, including Palaeozoic rocks (in purple), along the Tyrrhenian side of the Northern
424 Apennine.

425 Figure 2: Detail of the Middle Tuscan Ridge. The location of the studied area (shown in Fig. 3) is
426 also evidenced.

427 Figure 3: Geological map of the Monte Leoni area and location of the collected samples

428 Figure 4: a) Quartzitic phyllite cropping out in eastern LMS Unit and forming the lowermost portion
429 of the Falsacqua Formation; b) laminated, dark gray metacarbonate levels of the eastern LMS Unit;
430 c) alternations of metasandstone and metasilstone level of the uppermost portion of the Falsacqua
431 Formation - eastern LMS Unit; d) deformed alternation of metacarbonate and phyllite levels
432 cropping out in the eastern MQI Unit; e) also in the eastern MQI Unit, toward the top of the
433 succession metacarbonate disappears and alternation of metasandstone and metasilstone became
434 dominant.

435 Fig. 5: a) Sporomorphs from the Falsacqua Formation (eastern unit). Scale bar indicates 10 μ m. 1.
436 *Striatopodocarpites cancellatus* (Balme and Hennelly) Hart 1963; 2, 7. *Alisporites splendens* (Jizba)
437 Foster 1979; 3. *Protohaploxypinus microcorpus* (Schaarschmidt) Clarke 1965; 4. *Limitisporites* sp.
438 cf. *monstruosus* (Luber and Waltz) Hart 1965; 5, 8. *Striatopodocarpites fusus* (Balme and Hennelly)
439 Potonie 1958; 6. *Striatoabieites* sp.; 9. *Kraeuselisporites* sp. cf. *rallus* Balme 1970; 10.
440 *Reduviasporonites chalastus* (Foster) Elisk 1999; 11. *Densoisporites playfordii* Balme 1970; 12.
441 *Cycadopites* sp.; 13, 14. *Thymospora opaqua* Singh 1964; 15, 16. *Punctatisporites fungosus* Balme
442 1970; b) Sporomorphs from the Falsacqua Formation (western unit). Scale bar indicates 20 μ m with
443 exception of 6) where it is 10 μ m. 1. *Protohaploxypinus limpidus* (Balme and Hennelly) Balme and
444 Playford 1967; 2. *Platysaccus* sp.; 3. *Striatopodocarpites cancellatus* (Balme and Hennelly) Hart
445 1963; 4. *Alisporites nuthallensis* Clarke 1965; 5. *Taeniaesporites* sp. cf. *noviaulensis* Leschik 1956;

446 6. *Vittatina costabilis* Wilson 1962; 7. *Osmundacites* sp.; 8. *Potoniesporites novicus* Bharadwaj
447 1954; 9. *Alisporites* sp. cf. *opii* Daugherty 1941.

448 Figure 6 - Correlation chart between the miospores colour of Falsacqua Formation, Spore Color
449 Index, vitrinite reflectance and temperature used in assessing organic maturation (based and
450 modified from Fraser et al., 2014; Hartkopf-Froder et al., 2015 with references).

451 Fig. 7: Representative results of peak fitting on Raman spectra of carbonaceous material in FALS
452 01, FALS 04 and FALS 12 samples.

453 Fig. 8: Sporomorphs recorded in the middle-upper Permian Tuscan successions which also occur in
454 other Europaeen and northern Gondwana key sections and areas. Tuscany: 1: Arenarie del Monte
455 Argentario Formation (Cirilli et al., 2002); 2: Poggio al Carpino Formation (Lazzarotto et al., 2003);
456 3: Farma Formation (Aldinucci et al., 2008); 4: Carpineta Formation (Aldinucci et al., 2008); 5: Le
457 Cetine Formation (Spina et al., 2019); 6: Falsacqua Formation (this study); 7: Gavorrano
458 Monzogranite hosting rock (Brogi et al., 2021); 8: Rio Marina Formation (Spina et al., 2019); 9: Mt.
459 Calamita Formation (Spina et al., 2019); Western Europe: 10: Southern Alps (Cirilli et al., 1998;
460 Cassinis et al., 2000; Visscher and Brugman, 1988; Hartkopf-Fröder et al., 2001; Spina et al., 2015;
461 Nowak et al., 2019); 11: England, Ireland, Germany, Greenland (Grebe, 1957; Clarke, 1965;
462 Twitchett et al., 2001; Gibson and Wellman, 2021); 12: Arctic Domain: Russia, Arctic Canada,
463 Alaska (Jansonius, 1962; Piasecki, 1984; Utting et al., 1989; 1997; Utting, 1994; Mangerud, 1994;
464 Utting et al., 2004); 13: Northern Gondwana margin: Saudi Arabia, Oman, Iran, Jordan, Pakistan,
465 Southern Turkey (Balme, 1970; Eshet, 1990; Grignani et al., 1991; Stephenson et al., 2003;
466 Stephenson, 2006; 2008; Jan et al., 2009; Stephenson and Powell, 2013; 2014; Spina et al., 2018b;
467 2020; 2021; Stephenson and Korngreen, 2020).

468 Table 1: Analyzed samples and related geographical coordinates and palynological and
469 spectroscopic analysis.

470

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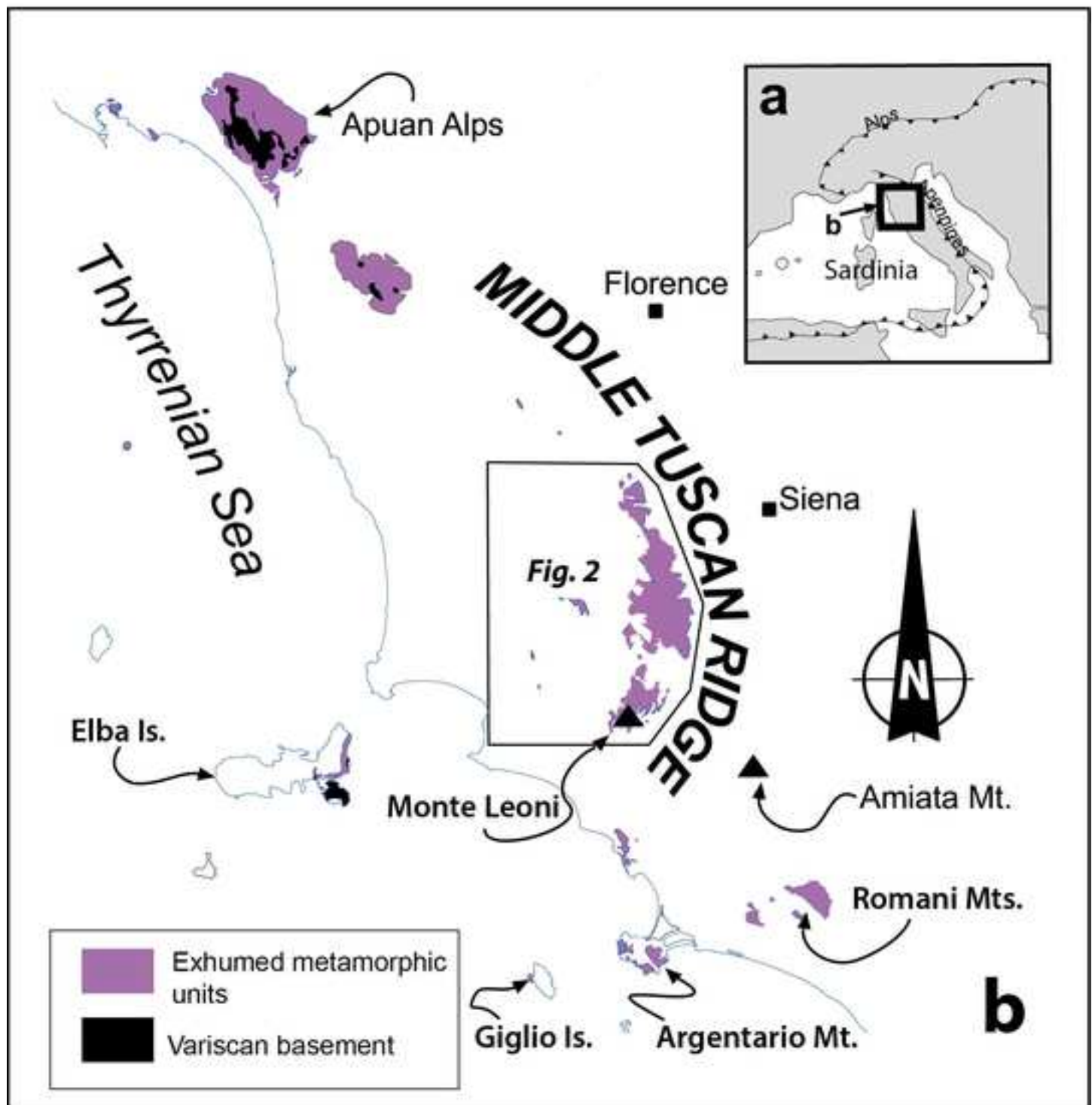
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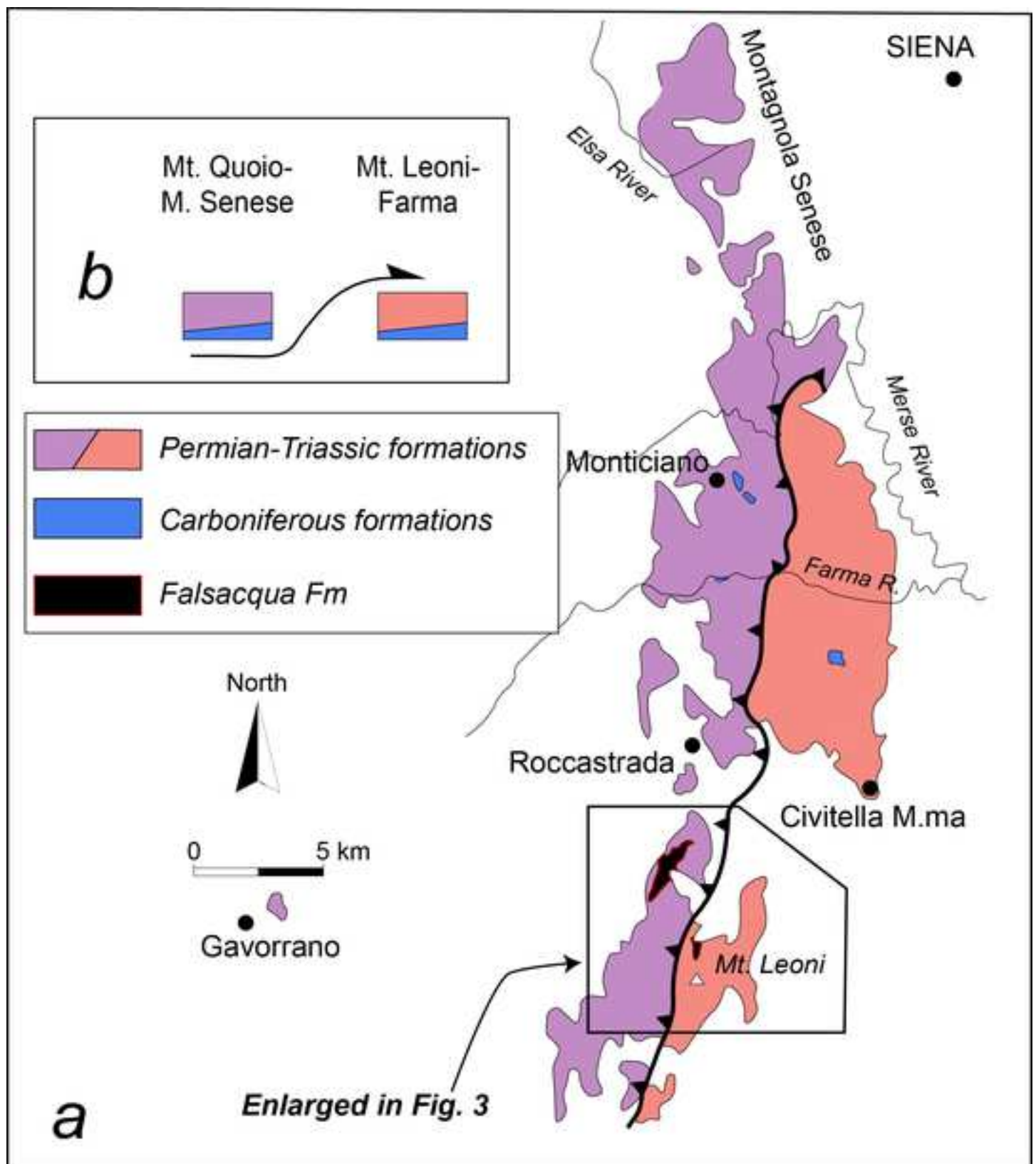
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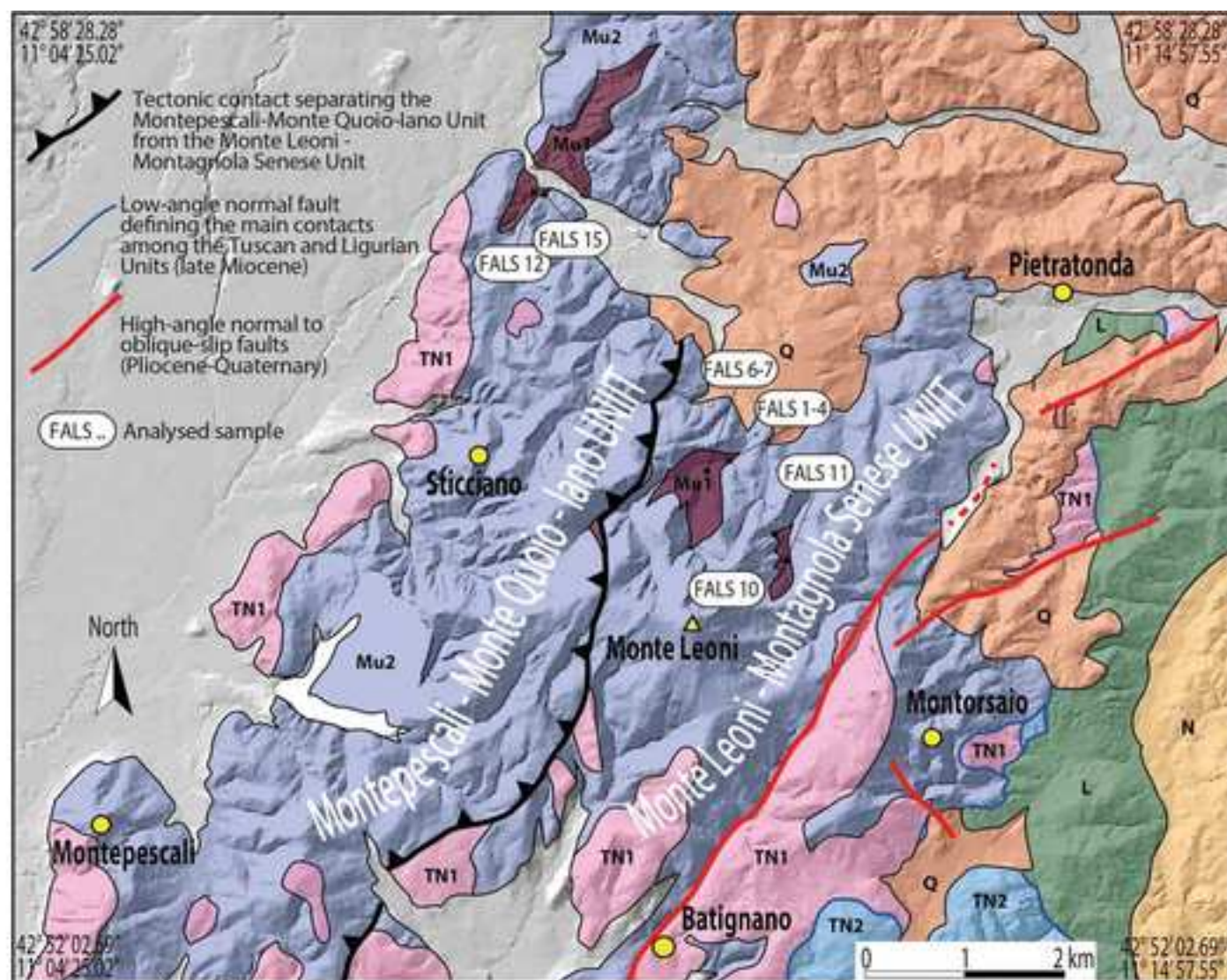
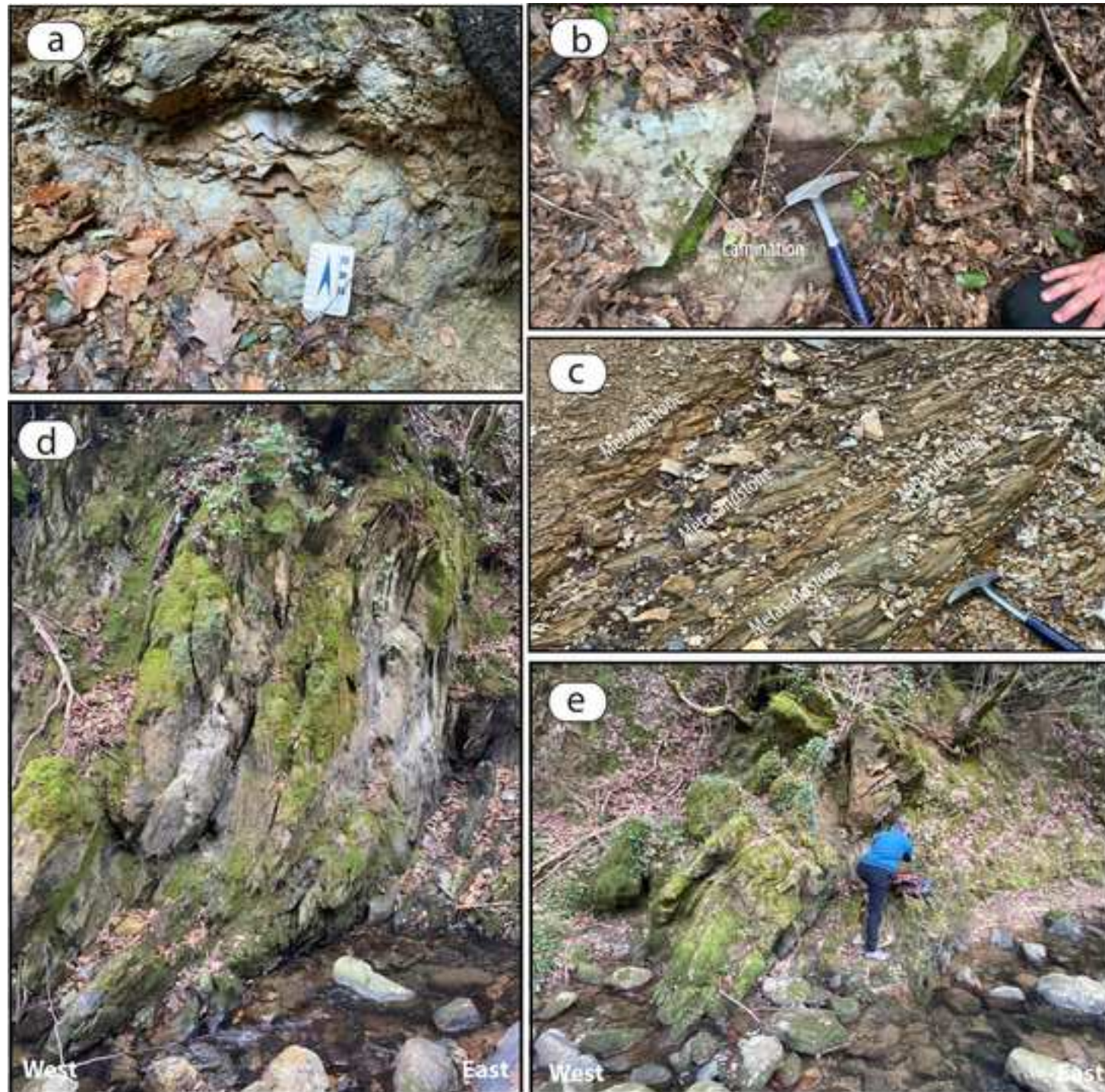


Figure 4



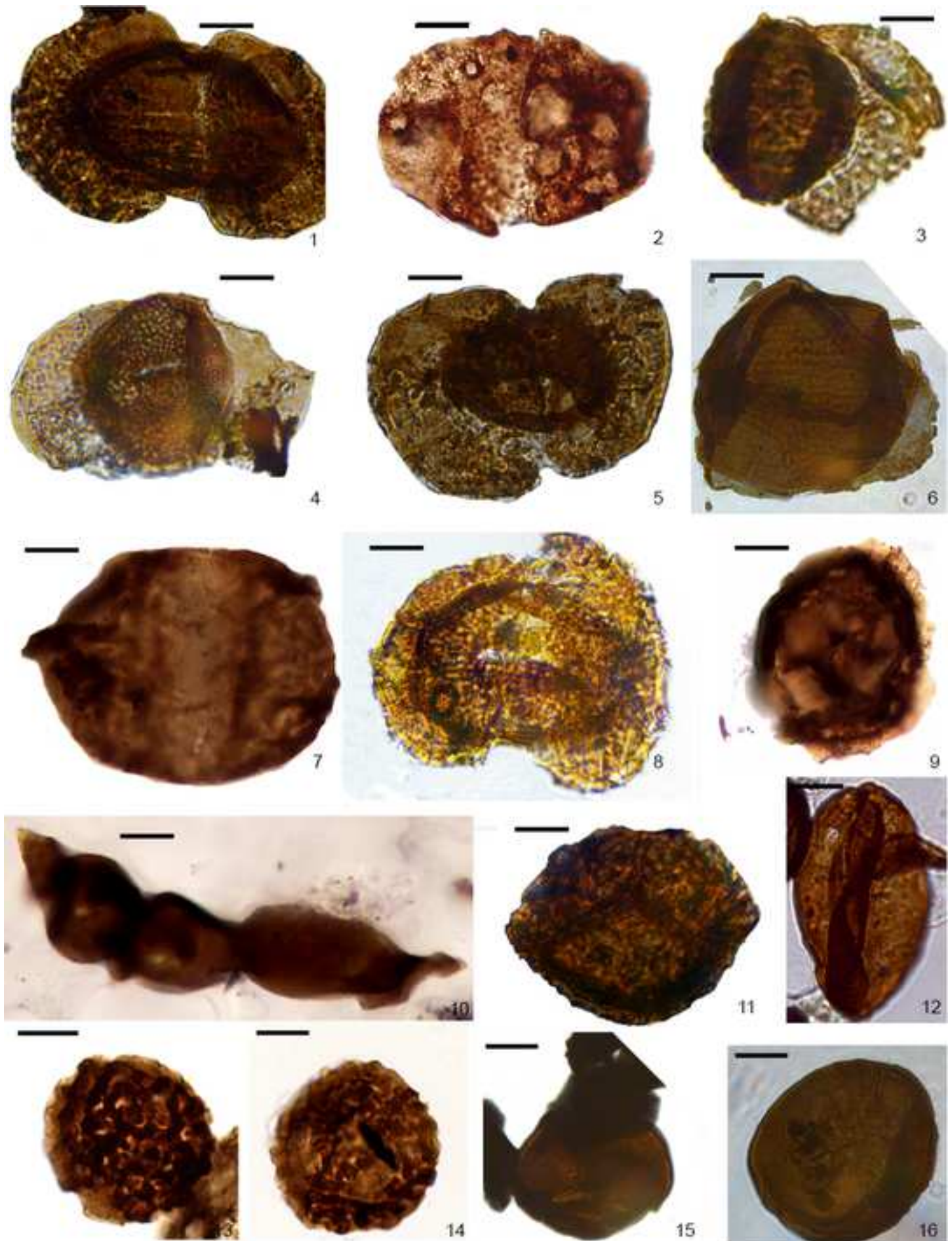
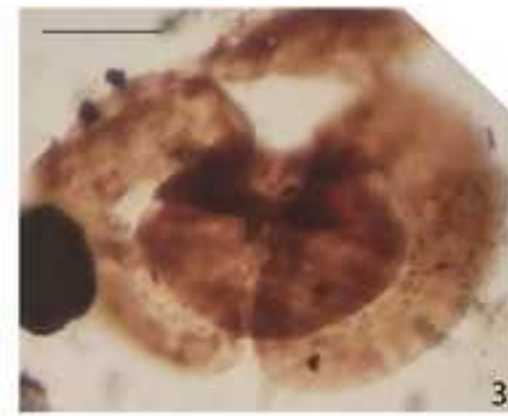
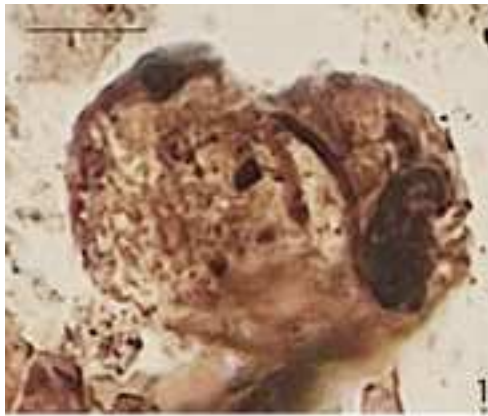


Figure 5b

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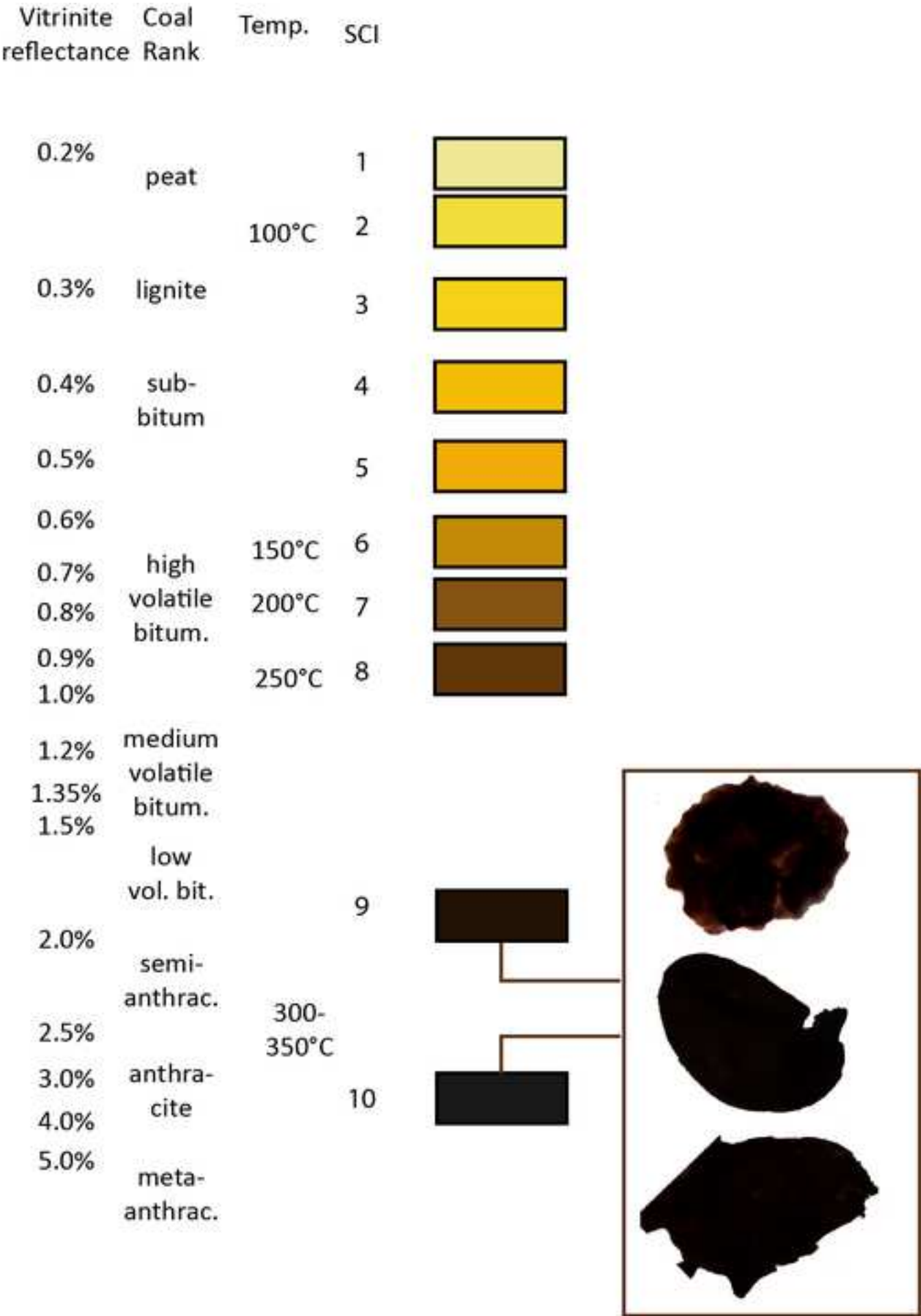
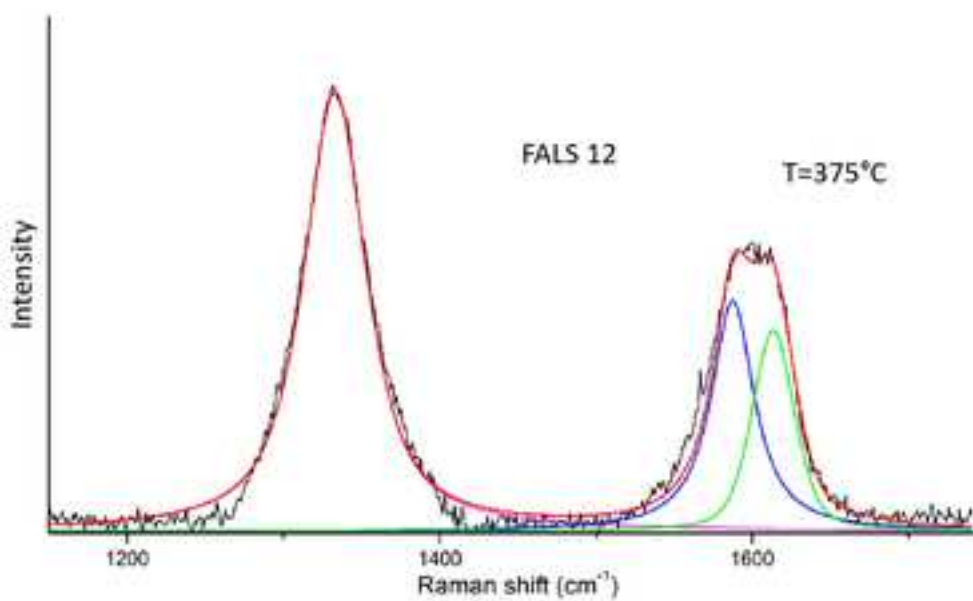
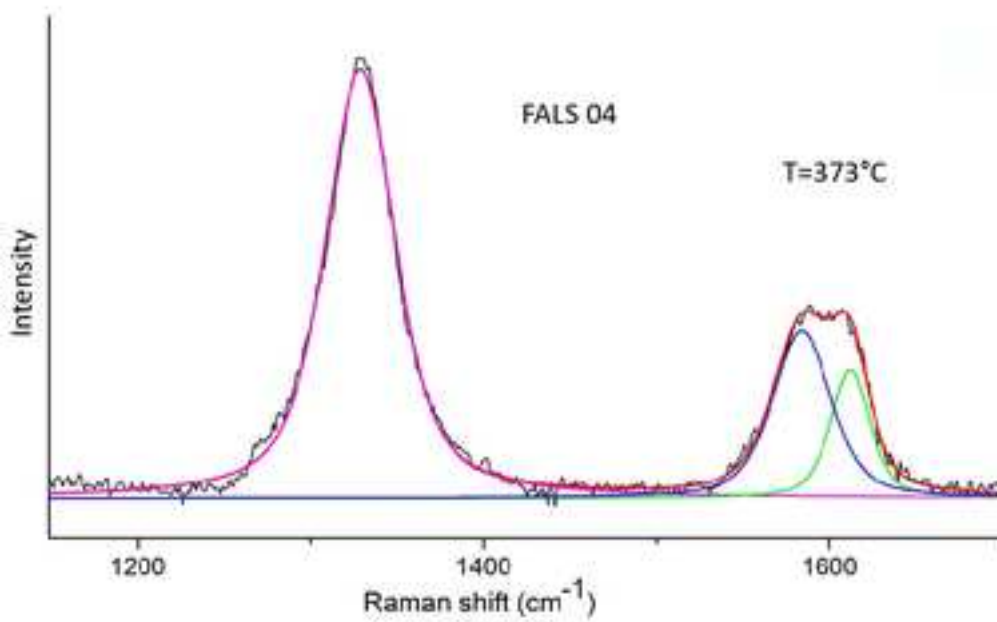
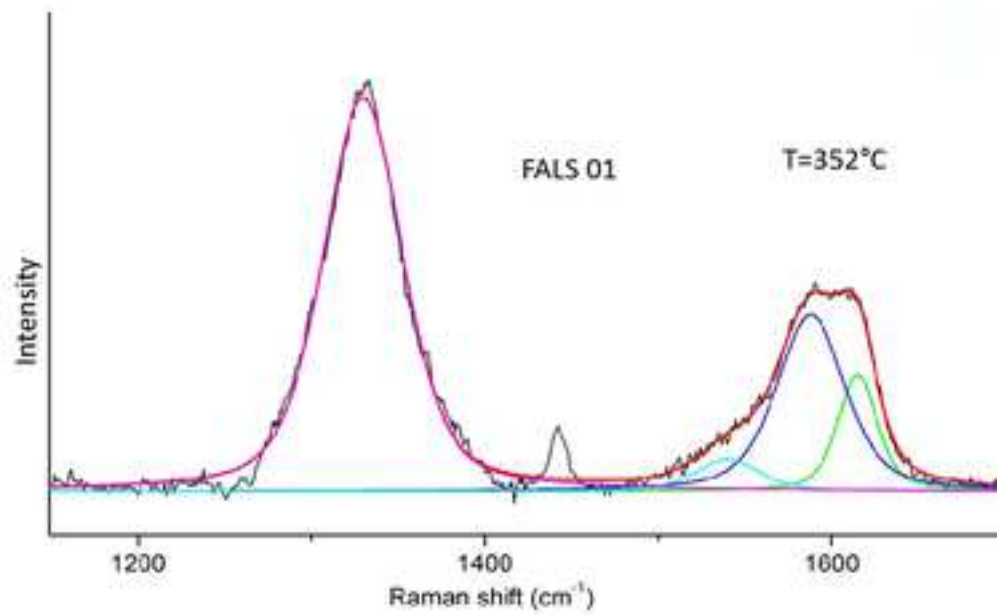


Figure 7



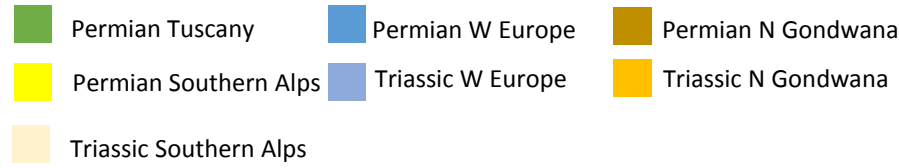
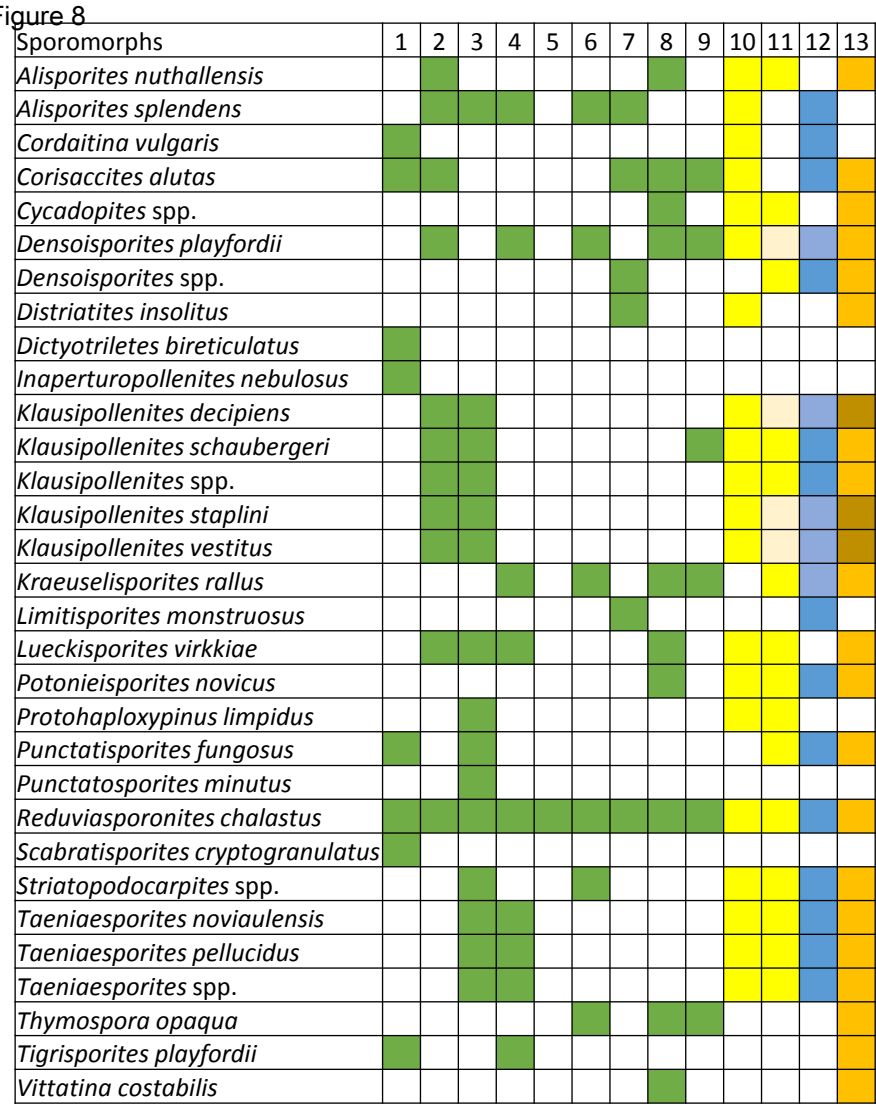


Table 1

Unit	sample	latitude	longitude	sporomorphs content	lithology	processed for palnology	Thermal maturity	
							SCI	RAMAN
Eastern Unit	FALS 01	42°55'8.11"N	11°10'31.54"E	productive	black limestone	x	x	x
	FALS 02	42°55'11.73"N	11°10'30.92"E	barren	metasandstone	x		
	FALS 04	42°55'10.88"N	11°10'31.20"E	productive	black phyllite/metasilite	x	x	x
	FALS 06	42°54'41.87"N	11°11'8.03"E	barren	black limestone	x		
	FALS 07	42°54'41.47"N	11°11'7.53"E	barren	black limestone	x		
	FALS 10	42°54'45.39"N	11°10'57.92"E	productive	black phyllite/metasilite	x	x	
	FALS 11	42°54'42.44"N	11°11'8.38"E	productive	black limestone	x	x	
Western Unit	FALS 12	42°57'9.50"N	11° 9'22.74"E	productive	black phyllite/metasilite	x	x	x
	FALS 13	42°57'9.53"N	11° 9'22.76"E	productive	black limestone	x	x	
	FALS 14	42°57'9.84"N	11° 9'21.76"E	productive	black phyllite/metasilite	x	x	

Declaration of interests

☒The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: