

1 **The role of trapped fluids during the development and deformation of**
2 **carbonate/shale intra-wedge tectonic mélange**

3

4 Luca Smeraglia^{1,2,3*}, Luca Aldega⁴, Stefano M. Bernasconi⁵ Andrea Billi¹, Chiara Boschi⁶, Antonio
5 Caracausi⁷, Eugenio Carminati^{1,4}, Stefania Franchini^{1,4}, Andrea Luca Rizzo⁷, Federico Rossetti⁸,
6 Gianluca Vignaroli⁹

7

8 1. Consiglio Nazionale delle Ricerche, IGAG, c.o. Dipartimento di Scienze della Terra, Sapienza Università di Roma,
9 P.le Aldo Moro 5, 00185 Roma, Italy

10 2. formerly at Dipartimento di Scienze della Terra, Sapienza Università di Roma, P.le Aldo Moro 5, 00185, Roma, Italy

11 3. formerly at Chrono-Environnement, Université de Bourgogne Franche-Comté, 16 Route de Gray, 25000 Besançon,
12 France.

13 4. Dipartimento di Scienze della Terra, Sapienza Università di Roma, P.le Aldo Moro 5, 00185, Roma, Italy

14 5. Geological Institute, ETH Zürich, Sonneggstrasse 5, 8092 Zürich, Switzerland

15 6. Istituto di Geoscienze e Georisorse, Consiglio Nazionale delle Ricerche, Via Moruzzi 1, 56124 Pisa, Italy

16 7. Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Via Ugo La Malfa 153, 90146 Palermo, Italy

17 8. Dipartimento di Scienze, Università Roma Tre, Largo San Leonardo Murialdo, 1, 00146, Roma, Italy

18 9. Dipartimento di Scienze Biologiche, Geologiche e Ambientali, BiGeA, Università di Bologna, 40126 Bologna, Italy

19

20 Luca Smeraglia: luca.smeraglia@cnr.it

21 Luca Aldega: luca.aldega@uniroma1.it

22 Andrea Billi: andrea.billi@cnr.it

23 Stefano Bernasconi: stefano.bernasconi@erdw.ethz.ch

24 Chiara Boschi: chiara.boschi@igg.cnr.it

25 Antonio Caracausi: antonio.caracausi@ingv.it

26 Eugenio Carminati: eugenio.carminati@uniroma1.it

27 Stefania Franchini: stefania.franchini@uniroma1.it

28 Andrea Luca Rizzo: andrea.rizzo@ingv.it

29 Federico Rossetti: federico.rossetti@uniroma3.it

30 Gianluca Vignaroli: gianluca.vignaroli@unibo.it

31

32 *Corresponding author: Dipartimento di Scienze della Terra, Sapienza Università di Roma, Piazzale Aldo

33 Moro 5, 00185 Roma, Italy. Phone +39 06 49914156

34 E-mail address: luca.smeraglia@cnr.it (Luca Smeraglia)

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54 **Abstract:** In contrast to the numerous studies on exhumed tectonic mélanges along subduction
55 channels, in accretionary wedge interiors, deformation mechanisms and related fluid circulation in
56 tectonic mélanges are still underexplored. Here we combine structural and microstructural
57 observations with geochemical (stable and clumped isotopes and isotope composition of noble
58 gases in fluid inclusions of calcite veins) and geochronological data (U-Pb dating) to define
59 deformation mechanisms and syn-tectonic fluid circulation within the Mt. Massico intra-wedge
60 tectonic mélange, located in the inner part of the central-southern Apennines accretionary wedge,
61 Italy. This mélange developed at the base of a clastic succession, and shear deformation was
62 characterized by disruption of the primary bedding, mixing, and deformation of relicts of competent
63 olistoliths and strata within a weak matrix of deformed clayey and marly interbeds. Recurrent
64 cycles of mutually overprinting fracturing/veining and pressure-solution processes generated a
65 block-in-matrix texture. The geochemical signatures of syn-tectonic calcite veins suggest calcite
66 precipitation in a closed system from warm (108-147 °C) paleofluids, with $\delta^{18}\text{O}$ composition
67 between +9‰ and 14‰, such as trapped pore water from diagenesis after extensive ^{18}O exchange
68 with the local limestone host rock ($\delta^{18}\text{O}$ values between +26‰ and +30‰) and/or derived by clay
69 dehydration processes (at $T > 120$ °C). The $^3\text{He}/^4\text{He}$ ratios in fluid inclusions trapped in calcite
70 veins are lower than 0.1 Ra, hence He was exclusively sourced from the crust, excluding mantle-
71 derived fluids. We conclude that: (1) intraformational rheological contrasts, inherited trapped fluids,
72 and low-permeability barriers such as clay-rich stylolites, can favour the development of fluid
73 overpressure and the generation of intra-wedge tectonic mélanges; (2) clay-rich intra-wedge
74 tectonic mélanges may generate efficient barriers within accretionary wedges for vertical and lateral
75 redistribution of fluids from reservoirs outside the mélange. We highlight that the integration of
76 geochemical and geochronological methods can be a powerful approach to better constrain, in the
77 future, the burial-thermal evolution of fold and thrust belts and sedimentary basins.

78

79 **Keywords:** tectonic mélange; fold and thrust belt; fault-fluid interaction; stable and clumped
80 isotopes; noble gases; U-Pb dating

81

82 **1. Introduction**

83 Décollements and thrust faults are major structures that control the internal architecture of
84 fold-and-thrust belts (e.g. [Morley et al., 2017](#)). In particular, décollements commonly generate
85 along evaporite- or clay-rich formations, control the style and timing of folding and tectonic
86 imbrication, and may act as barriers or conduits for crustal flow of fluids, including hydrocarbons.
87 Décollements can often act as channelized paths for fluid redistribution within the crust (e.g.
88 [Vrolijk et al., 1988](#); [Vannucchi et al., 2008](#)).

89 The shearing of clay-rich and initially layered formations along décollements can generate
90 tectonic mélanges through primary bedding disruption, pressure-solution, veining, and
91 offscraping/mixing of blocks from competent formations located above and below the décollement
92 horizon (see [Festa et al., 2012](#) for review). Such deformations can lead to block-in-matrix fabrics,
93 consisting of competent blocks scattered in a weak matrix, which are typically characterized by
94 heterogeneous mechanical and permeability properties (e.g. [Fagereng, 2011](#)). Outcrop,
95 microstructural, and geochemical characterizations of tectonic mélanges can contribute to constrain
96 their spatio-temporal evolution as well as the mechanical properties and hydrogeological
97 characteristics (paleofluid flow).

98 In this context, several studies focused on tectonic mélanges exhumed from basal
99 décollements at the subduction interface along the toe of accretionary wedges and from subduction
100 channels (e.g. [Meneghini et al., 2009](#); [Vannucchi et al., 2008](#); see [Festa et al., 2012](#) for review),
101 where deformation can reach metamorphic conditions (e.g. [Fagereng and Cooper, 2010](#)). Only few
102 studies focused on intra-wedge tectonic mélanges developed at diagenetic P-T conditions along
103 décollements at the base of thrust sheets (e.g. [Vannucchi and Bettelli, 2002](#); [Codegone et al., 2012](#);
104 [Deweever et al., 2013](#); [Ogata et al., 2012](#); [Smeraglia et al., 2019](#)). However, intra-wedge tectonic

105 mélanges may strongly affect the mechanical behavior of inner décollements, thus influencing
106 accretionary wedge geometry and kinematics, and can modulate the transport of fluids (i.e. water,
107 hydrocarbon) across fold-and-thrust belts. Therefore, the understanding of mechanical and
108 hydrological properties of exhumed mélanges is fundamental to unravel fluid (paleo)pathways and
109 assess potential reservoirs for geofluid (i.e. hydrocarbon) accumulation in fold-and-thrust belts.

110 For these reasons, here we combine outcrop and microstructural observations with
111 geochemical analyses (stable and clumped isotopes and isotope composition of noble gases in fluid
112 inclusions of calcite veins) to unravel the deformation mechanisms, paleohydrology (i.e., fluid
113 conduit/barrier behavior), and the temperature conditions during fluid flow within a 150 m-thick
114 intra-wedge tectonic mélange in the Mt. Massico Ridge (e.g. [Billi et al., 1997](#); [Vitale et al., 2018](#);
115 [Smeraglia et al., 2019](#)), which is located in the inner sector (Tyrrhenian side) of the central-southern
116 Apennines fold-and-thrust belt. In this area, outcrop conditions allowed the reconstruction of syn-
117 tectonic paleofluid circulation and the unraveling of progressive intra-wedge mélange deformation,
118 from the undeformed host rock to the finite fabric development by tectonic deformation.

119

120 **2. Geological background**

121 *2.1 Central-southern Apennines*

122 The central-southern Apennines are a late Oligocene to present fold-and-thrust belt generated
123 by the eastward rollback of the west-dipping subduction of the Adriatic plate below the European
124 continental margin ([Fig. 1a](#); e.g., [Carminati et al., 2012](#)). Orogenic accretion was accomplished
125 through and accommodated by a set of NE-verging thrust systems, which scraped off pre- and syn-
126 orogenic deposits of the Adriatic plate ([Fig. 1b](#)). The pre-orogenic deposits consist of ~4,000-5,000
127 m-thick Upper Triassic-Middle Miocene carbonate platform deposits (i.e. Apennine platform; e.g.
128 [Vezzani et al., 2010](#); [Vitale and Ciarcia, 2018](#)) and of ~100 m-thick middle Miocene hemipelagic
129 marls deposited in a transitional foreland-to-foredeep environment (e.g., [Vezzani et al., 2010](#)). The
130 syn-orogenic deposits consist of up to ~3,100 m-thick upper Miocene siliciclastic sandstones, marls,

131 and claystones deposited in a foredeep environment (e.g., Vitale and Ciarcia, 2018). Thrust faults
132 developed during wedge accretion and juxtaposed pre-orogenic deposits onto syn-orogenic
133 sediments, generating stacks of imbricate thrust sheets from the surface down to depths of ~10 km
134 (Fig. 1a,b; e.g. Mostardini and Merlini, 1986; Vezzani et al., 2010). Since early Pliocene time, the
135 internal and axial part of the central-southern Apennines belt underwent tectonic uplift and regional
136 extension, related to the opening of the Tyrrhenian backarc basin and accommodated by the
137 development of NW-SE-oriented extensional faults (Fig. 1a,b; Malinverno and Ryan, 1986).

138

139 *2.2 The Mt. Massico ridge*

140 Mt. Massico is a NNE-SSW-trending ridge located in the innermost part of the central-
141 southern Apennines (Fig. 1a; e.g. Billi et al., 1997; Luiso et al., 2018; Vitale et al., 2018). It is
142 bounded by NE-striking active extensional faults and surrounded by the Quaternary Garigliano and
143 Volturno river plains, the Roccamonfina volcano (Quaternary), and the Tyrrhenian Sea basin (Figs.
144 1a and 2a).

145 In the central and northeastern parts of the Mt. Massico ridge, Upper Triassic to Upper
146 Cretaceous carbonates are exposed (Fig. 1a; Vitale et al., 2018) and arranged to form a ENE-
147 verging asymmetric anticline with an upright forelimb and a WSW-dipping (40°-50°) backlimb
148 (Fig. 1a). In the forelimb, a thrust juxtaposes Upper Cretaceous limestones onto Tortonian syn-
149 orogenic sandstones (see Figure 2 in Sgrosso, 1974). The WSW-dipping backlimb continues in the
150 southwestern part of the ridge, where middle-upper Miocene sediments are exposed (Fig. 2a,b).

151 This succession lies paraconformably atop Upper Cretaceous limestones and begins from the
152 bottom with ~50 m-thick bryozoan-rich limestones of the Cusano Fm., followed upward by
153 hemipelagic marls of the Longano Fm., with a preserved thickness of less than 1-3 meters (Sgrosso,
154 1974; Vitale et al., 2018) (Fig. 2a). Both these formations were deposited in a foreland environment
155 and are Serravallian in age (Sgrosso, 1974). Above the hemipelagic marls, the sedimentary
156 succession evolves into the Tortonian-lower Messinian siliciclastic/carbonaticlastic deposits of the

157 Caiazzo Fm. (hereafter called clastic deposits, [Fig. 2a,b](#)), which are interpreted as wedge-top basin
158 deposits ([Vitale et al., 2018](#)). The clastic deposits are made up of: (1) massive-to-bedded
159 siliciclastic sandstones with clayey, marly, and calcarenite interbeds and (2) polymictic
160 breccias/conglomerates characterized by Mesozoic-Cenozoic carbonate blocks and siliciclastic
161 clasts (up to a few dm³ in volume), including also clasts of volcanic, intrusive, and metamorphic
162 rocks ([Fig. 2a](#)) ([Sgrosso, 1974](#)). The clastic deposits are unconformably overlain by well-bedded
163 lower Messinian calcarenites ([Fig. 2a](#)). Intercalated within the clastic deposits are hundreds of
164 olistoliths, from a few dm³ to several thousands of m³ in volume. Olistoliths consist of Mesozoic-
165 Cenozoic limestones and exotic rocks not exposed in the local sedimentary succession (hereafter
166 named exotic olistoliths), such as marbles and recrystallized carbonates as well as volcanic,
167 intrusive, and metamorphic rocks, and deep basinal Paleocene limestone blocks ([Sgrosso, 1974](#); [Di](#)
168 [Girolamo et al., 2000](#); [Vitale et al., 2018](#)). The total thickness of the upper Tortonian-lower
169 Messinian succession is ~800 m ([Smeraglia et al., 2019](#)).

170

171 2.3 The Mt. Massico *mélange*

172 The about ~150 m thick basal portion of the clastic deposits and the underlying hemipelagic
173 marls are strongly deformed, showing a block-in-matrix fabric typical of tectonic *mélanges* ([Fig.](#)
174 [2a,b](#); [Vitale et al., 2018](#); [Smeraglia et al., 2019](#)). Based on new geological mapping (see also [Vitale](#)
175 [et al., 2018](#) for new stratigraphic constraints), structural analysis, U-Pb dating (syn-tectonic calcite
176 ages of 10.5 ± 2.5 My, 7.0 ± 1.6 My, and 5.1 ± 3.7), and thermal modelling constrained by mixed
177 layers illite-smectite, [Smeraglia et al. 2019](#) proposed that the Mt. Massico tectonic *mélange*
178 developed, since late Messinian times, by out-of sequence thrusting of multiple thrust sheets above
179 the clastic deposits located in the backlimb of the Mt. Massico anticline ([Fig. 9a-c](#)) and by
180 localization of deformation at the base of clastic deposits. In this context, the original stratigraphic
181 boundary between the clastic deposits/hemipelagic marls deposits and the underlying limestones
182 was sheared as a *décollement* horizon and an intra-wedge tectonic *mélange* developed due to the

183 strong rheological contrast between the weak clastic deposits and the competent limestones. This
184 mélange is characterized by a pervasive S-C and S-CC' fabrics showing a coherent transport
185 direction towards ESE, accommodated by partitioned reverse and dextral transpressive tectonics
186 (Fig. 2a; Smeraglia et al., 2019).

187

188 3. Methods

189 Aiming at characterize the structurally-controlled fluid circulation and the geochemical
190 signature of the syn-tectonic fluids in the transition from the undeformed host rock to the tectonic
191 mélange formation, we focused our structural and geochemical studies within the San Sebastiano
192 and Mt. Cicoli areas (Fig. 2). In these areas, it is in fact possible to observe the progressive
193 transition from poorly deformed clastic deposits to moderately and strongly deformed parts of the
194 tectonic mélange along the boundary with the underlying bryozoan-rich limestones of the Cusano
195 Fm. (Fig. 2a). To achieve this purpose we integrated: (1) geological field mapping at 1:10,000
196 scale, and available maps (Billi et al., 1997; Vitale et al., 2018; Smeraglia et al., 2019), to unravel
197 the structural architecture and the deformation history of the intra-wedge tectonic mélange; (2)
198 microstructural (optical microscope) analyses to unravel the deformation mechanisms acting during
199 mélange generation; (3) Stable carbon and oxygen and carbonate clumped isotopes to reconstruct
200 the origin and precipitation temperatures of the paleofluid circulating during mélange generation;
201 (4) H₂O+CO₂, N₂, and minor gaseous species (He, Ne, and Ar concentrations and isotope ratios) in
202 fluid inclusions on previously U-Pb dated syn-tectonic carbonate samples/veins (ages of 10.5 ± 2.5
203 My, 7.0 ± 1.6 My, and 5.1 ± 3.7; Smeraglia et al., 2019) . Sample preparation and analytical details
204 are described in the [Supplementary Material](#).

205

206 4. Results

207 4.1 Outcrop observations

208 A progressive transition in shear strain localization is observed when moving across strike
209 along the studied area. Within the poorly deformed clastic deposits, bedding is still observable (Fig.
210 3a,b). The competent sandstones beds and the marly-shaly interbeds are gently folded and/or cut by
211 low-displacement reverse faults displaying a ramp-and-flat geometry, with the flat segment located
212 within marly and shaly interbeds (Fig. 3b). The marly and shaly interbeds are characterized by a
213 weak and bedding-parallel scaly foliation (Fig. 3a,b); however, in places, an incipient S-C fabric
214 characterized by bedding-parallel S planes and bedding-oblique C planes occurs dismembering the
215 sandstone interbeds (Fig. 3a).

216 We recognized a up ~100 m-thick zone, referred as moderately deformed zone of the tectonic
217 *mélange*, exposed within a diffuse boundary between the poorly deformed clastic deposits and the
218 strongly deformed part of the tectonic *mélange* (Fig. 2). This zone is characterized by still
219 detectable primary structures such as bedding, but competent strata (i.e. sandstones and calcarenites
220 interbeds) show pinch-and-swell and boudin-like geometries. Pervasive and anastomosing bedding-
221 parallel scaly foliation occurs within marly and shaly interbeds (Fig. 3c,d) and, in places, S-C
222 fabrics can be observed (Fig. 3e). With increasing deformation, primary foliation is dismembered
223 and relicts of bedding are scattered within the scaly foliation generating a block-in-matrix fabric
224 (Fig. 3d-e). In particular, such relicts show bedding-perpendicular calcite veins (Fig. 3d,e).

225 The strongly deformed part of the tectonic *mélange*, up to ~50 m-thick, shows well-developed
226 S-C and S-CC' tectonites and sedimentary structures are completely obliterated by tectonic fabric
227 (Figs. 3f-h and 4a,b). In particular, the WNW- to WSW-dipping S- and C-surfaces show dip angles
228 ranging ~60°-70° and ~10°-30°, respectively, with kinematic indicators showing mainly reverse
229 dip-slip to right-lateral transpressional movements (Fig. 2a). Marls and shales are affected by S-C
230 foliations and clasts of competent rocks (i.e. sandstones and calcarenites) are deformed in
231 sigmoidal-lozenge-shaped structures consistent with the overall sense of shear (Figs. 3f-g and 4a-c).
232 Stylolites and slickenfibers are aligned parallel respect to S and C planes, respectively, whereas
233 sigmoidal clasts of competent rocks are permeated by calcite veins (Figs. 3g,h and 4d).

234 With increasing deformation, the sigmoidal relicts of sedimentary structures are progressively
235 thinned and completely obliterated by S-C foliation so that it is difficult to distinguish them from
236 the pervasive scaly foliation at the naked eye (Fig. 4c). In places, foliated marls and shales wrap
237 olistoliths inherited from clastic deposits. The olistoliths preserve their original (from irregular to
238 rounded) shapes, generating a block-in-matrix fabric (Fig. 4e-g). Convolute/contorted foliations
239 also occur (Fig. 4h). Their origin is not clear and it cannot be excluded that they may be relicts of
240 soft sediment (fluid escape) structures. When observable, the boundary between the tectonic
241 mélangé and the underlying bryozoan-rich limestones (not affected by deformation and with
242 sedimentary structures and fossils still recognizable) is sharp.

243

244 *4.2 Microstructural observations*

245 We focused our microstructural observations on the strongly deformed parts of the tectonic
246 mélangé, with special focus on the sigmoidal-lozenge clasts of competent rocks (i.e. sandstones and
247 calcarenites), since they are cohesive and can be easily cut for thin section preparation.

248 The sigmoidal-lozenge clasts are characterized by pervasive stylolites, parallel to S, C, and C'
249 planes (Fig. 5a-c). Stylolites evolve from rough, teeth-shaped, and indented morphology (Figs. 5a-c
250 and 6a-b) to smooth, continuous, and thick (up to 1 mm) dissolution seams (Figs. 5a-c and 6c) filled
251 by insoluble material (i.e. clay minerals and oxides), small clasts of host rock limestones, and
252 fragments of calcite veins (Fig. 6c). Stylolites and dissolution seams bound sigmoids defining a
253 fabric sub-parallel to S, C, and C' planes (Figs. 5a-c and 6a,b). Sigmoids consist of host rock
254 commonly with deformed microfossils, and/or reworked calcite veins (Fig. 6a,b).

255 We identify fibrous and blocky calcite veins. Fibrous veins are oriented perpendicular to
256 stylolites and are characterized by fibrous crystals perpendicular to vein margins (Fig. 6 d-f).
257 Crystals are deformed by stylolites (Figs. 6d-f and 7a). The slickenfibers observed at the outcrop
258 scale along S, C, and C' planes are characterized, at the microscale, by fibrous veins located along
259 stylolite jogs, characterized by fibrous crystals parallel to stylolites (Fig. 6b,f). In places, fibrous

260 veins occur within thick dissolution seams (Fig. 7a,b). In this case, vein margins and fibrous
261 crystals are roughly parallel and perpendicular to dissolution seam margins, respectively (Fig. 7a,b).
262 Blocky veins are filled by blocky to elongated-blocky calcite crystals and are oriented parallel,
263 perpendicular, or oblique to stylolites (Fig. 7c,d).

264 Concerning the relative timing of structures, we observed mutual crosscutting relationships
265 between veins and stylolites (Figs. 5c and 7f). In particular, blocky veins perpendicular to stylolites
266 cut or are deformed by stylolites and/or by blocky/fibrous veins oriented oblique to stylolites (Figs.
267 5 and 7c-f). Fibrous veins parallel and/or perpendicular to stylolites are deformed by stylolites
268 and/or by blocky veins oriented oblique to stylolites (Figs. 5, 7a,b, and 6d-f)

269

270 *4.3 Stable and clumped isotopes*

271 Results from stable and clumped isotopes analyses are shown in Fig. 8 and listed in Table S1
272 and S2. Results are reported in the conventional δ notation with respect to the Vienna Pee Dee
273 Belemnite (VPDB) for $\delta^{13}\text{C}$ and Vienna Standard Mean Ocean Water (VSMOW) for $\delta^{18}\text{O}$.
274 Clumped isotopes are reported in the Carbon Dioxide Equilibrium Scale (Dennis et al. 2011).

275 The host rock $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, measured on limestones interbeds within clastic deposits,
276 range between -0.5‰ and +1.5‰, and between +26‰ and +29.5‰, respectively. Such values are
277 typical of Miocene marine carbonates in the Apennines, Italy (e.g., Hilgen et al., 2005).

278 Blocky veins $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values range between 0‰ and +0.8‰ and between +22.3‰ and
279 +27‰, respectively, with one blocky vein showing $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values overlapping those of the
280 host rock. Fibrous veins $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values range between -0.4‰ and +1.6‰ and between
281 +22.4‰ and +27.8‰, respectively. Three fibrous veins show $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values overlapping
282 those of the host rock. Overall, both blocky and fibrous veins show $\delta^{13}\text{C}$ values overlapping with
283 those of the host rock and an average $\delta^{18}\text{O}$ depletion of ~4‰ respect to the host rock.

284 Clumped-isotope data from blocky veins (four samples) and fibrous veins (five samples)
285 yields $\Delta 47$ values between 0.424 and 0.482 (Table S2). These values correspond to temperatures

286 between 108 ± 13 °C and 147 ± 20 °C (Fig. 8b and Table S1), using the equation of Bernasconi et
287 al. (2018). The calculated $\delta^{18}\text{O}$ paleofluid compositions, using the O'Neil et al. (1969) equation
288 developed for calcite precipitation temperature in the 0-500 °C range, range between 9.1‰ and
289 13.7‰ (Fig. 8b and Table S1).

290

291 4.4 Noble gas analysis

292 The concentrations of $\text{CO}_2+\text{H}_2\text{O}$, N_2 , light noble gases (He, Ne, Ar), and $^3\text{He}/^4\text{He}$, $^4\text{He}/^{20}\text{Ne}$,
293 $^{40}\text{Ar}/^{36}\text{Ar}$ isotopic ratios in fluid inclusions hosted in syntectonic calcite veins (samples 239, 257
294 and 260) are reported in Table S3.

295 $\text{CO}_2+\text{H}_2\text{O}$ and N_2 show concentrations ranging between 1.1×10^{-6} and 8.3×10^{-6} mol/g and
296 between 3.1×10^{-7} and 6.7×10^{-7} mol/g, respectively. The N_2/Ar ratios range between 3092 and 3633.
297 These values are much more higher than the N_2/Ar ratio in the atmosphere (84.1) and the N_2/Ar
298 ratio in air-saturated water at standard temperature and pressure (38). The $^{40}\text{Ar}/^{36}\text{Ar}$ ratios vary from
299 367.3 to 389.9, slightly higher than the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio in atmosphere (298.6).

300 He/Ar and He/ N_2 ratios range between 0.06-0.14 and $2.1-3.8 \times 10^{-5}$, respectively, and are 1-2
301 orders of magnitude higher than the theoretical values in the atmosphere and in the air-saturated
302 water. The $^4\text{He}/^{20}\text{Ne}$ ratios range between 51.7 and 96.5 and are more than two orders of magnitude
303 higher than the typical $^4\text{He}/^{20}\text{Ne}$ ratio in air saturated water (0.268), consistently with fluids trapped
304 at great depth. All these ratios testify an excess of He and N_2 respect to the typical concentrations in
305 atmosphere-derived fluids. The $^3\text{He}/^4\text{He}$ ratios, corrected for the air contamination (R/Ra ratio)
306 range between 0.05 and 0.09, consistently with those of crustal fluids, thus excluding a contribution
307 of He derived from atmospheric air and ^3He from the mantle (Fig. 8d).

308 The $^3\text{He}/^4\text{He}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ ratios are useful tracers to ascertain the origin of the fluids
309 producing the mineralization. However, one condition is that these materials must contain volatiles
310 trapped during precipitation processes and that their isotopic compositions have not been modified
311 over time. Significant post precipitation processes that may affect the noble gases content in the

312 fluid inclusions regard the addition of (1) ^4He , ^{40}Ar produced from the radiogenic decay of U, Th
313 and K, and (2) cosmogenic ^3He derived from the exposure to cosmic ray.

314 In order to estimate the contribution of radiogenic ^{40}Ar into the fluid inclusions, we computed
315 the $^{40}\text{Ar}^*$, which is the amount of ^{40}Ar corrected for the atmospheric contributions ($^{40}\text{Ar}^* =$
316 $^{40}\text{Ar}/^{36}\text{Ar}_{\text{Measured}} - ^{40}\text{Ar}/^{36}\text{Ar}_{\text{Atmosphere}} \times ^{36}\text{Ar}_{\text{Measured}}$). The amounts of $^{40}\text{Ar}^*$ range between 8.99×10^{-11}
317 to 1.38×10^{-10} mol/g (Table S3). The amounts of the measured ^4He and measured $^{40}\text{Ar}^*$ do not
318 show any correlations with the ages of the veins (Fig. S2a,b), thus excluding the accumulation of
319 radiogenic He and Ar produced in the veins by the U, Th and K decay during time.

320 All calcite veins have been collected in outcrops whose time of exposure to the cosmic ray at
321 the surface is not evaluable; hence, the potential contribution of cosmogenic ^3He trapped in the fluid
322 inclusions is difficult to be assessed. However, there is no correlation between the amount of ^3He
323 and the ages of calcite veins (Fig. S2c), which can supports a progressive accumulation over time of
324 cosmogenic ^3He and subsequent migration into the fluid inclusions.

325 On the basis of the average U and Th amounts in the veins of calcite (1.58 and 2.28 ppm for
326 sample 257; 0.35 and 0.01 ppm for sample 239; 0.17 and 0.02 ppm for sample 260; Table S4) is
327 possible to compute the potential $^4\text{He}/^{40}\text{Ar}^*$ ratio produced by the decay of U and Th. The
328 computed $^4\text{He}/^{40}\text{Ar}^*$ ratios range between 10 and 100. These values are much higher than the same
329 ratios in the fluid inclusions (0.61, 0.35, and 0.40 for samples 257, 239, and 260, respectively, Table
330 S3). This suggests that the fluid inclusions are not modified by the contributions of both of
331 radiogenic ^4He and ^{40}Ar produced within the rocks. We conclude that the isotopic ratios of He and
332 Ar in the fluid inclusions are representative of the pristine isotopic signatures of the trapped fluids.

333

334 5. Discussion

335 5.1 *Mélange evolution and deformation mechanisms*

336 Since late Messinian times, the Mt. Massico tectonic mélange developed by out-of sequence
337 thrusting of multiple thrust sheets above the clastic deposits and by localization of deformation at

338 the base of clastic deposits (Fig. 9a-c; Smeraglia et al., 2019). Therefore, when out-of sequence
339 deformation initiated, WSW-ENE shortening affected W-SW-dipping (30°-55°) Meso-Cenozoic
340 carbonates and middle-upper Miocene clastic deposits, tilted by previous thrust-related folding (Fig.
341 2a,b and 9b; Smeraglia et al., 2019). In this context, both layer-perpendicular/oblique shortening
342 and layer-parallel extension occurred in the early phases of deformation (Fig. 10a,b). Layer-
343 perpendicular/oblique shortening was driven by sub-horizontal tectonic compression and produced
344 bedding-parallel foliation by pressure-solution and stylolites generation in the marly and shaly
345 interbeds (Figs. 3a,b). Layer-parallel extension produced dismembering, boudinage, and fracturing
346 of competent bedding (i.e. sandstones and calcarenites interbeds; Fig. 3c).

347 With increasing deformation, the hemipelagic marls between the clastic deposits and
348 bryozoan-rich limestones were scraped off and mixed within the base of clastic deposits, the
349 competent beds were almost completely dismembered, although some relicts of bedding were
350 scattered within the shaly/marly matrix (Figs. 3d, 4e-g, and 10c,d). In this framework, S-C
351 tectonites and block-in-matrix fabric developed within the strongly deformed parts of the tectonic
352 mélange by brittle-ductile processes such as pressure-solution, fracturing/veining, and frictional
353 sliding, with absence of evident cataclasis of the host rock (Fig. 10c,d). The absence of cataclasis is
354 related to the occurrence of widespread pressure solution processes, triggered and enhanced by
355 clay-rich host rocks (marls and shales; Renard et al., 1997), which promoted the dissipation of
356 tectonic stress through host rock dissolution, at slow strain rates rather, than frictional processes
357 (i.e. fracturing, grain rotation, abrasion) commonly occurring during cataclasis in competent rocks,
358 such as pure carbonates (e.g. Billi, 2010). In particular, pressure-solution was more pervasive in
359 weak marly and shaly interbeds than in calcarenite interbeds, producing a network of stylolites
360 aligned along S, C, and C' planes. Stylolites developed through host rock dissolution and insoluble
361 materials (i.e. mainly phyllosilicates) concentrated within dissolution seams (Figs. 3f-h and 4a-c)
362 (e.g. Tessei et al., 2013). Fracturing/veining processes, coupled with pressure-solution, affected the

363 relicts of competent rocks (Figs. 3f-h, 4a-d, and 10c,d). These types of deformation mechanisms
364 commonly occur during tectonic mélangé generation (e.g., Festa et al., 2012 for review).

365

366 5.2 Vein development within the mélangé

367 The occurrence of veins perpendicular to stylolites suggests that both structures formed under
368 the same stress regime, characterized by compression sub-perpendicular to the stylolites, thus
369 generating mode I vein opening perpendicular to stylolites to regulate their evolution through time
370 (Figs. 5a-c, 6d, 7c-f, and 11; e.g., Gratier et al., 2013). Veins parallel to stylolites (Figs. 6f and 7a,b)
371 indicate opening direction parallel to the maximum compression direction and suggests vein
372 opening under an unfavorable stress regime (i.e. opening direction should be perpendicular with
373 respect to the maximum principal stress). In particular, development of fibrous veins (shear
374 veins/slickenfibers) characterized by fibrous crystals perpendicular to the maximum principal stress
375 have been observed in tectonic mélangé and have been related to shear along pre-existing weak
376 planes such as clay-rich stylolites, assisted by fluid overpressure (Fagereng et al., 2010).
377 Alternatively, the unfavorable orientations between veins and tectonic stresses can be explained by
378 episodic stress rotation within the mélangé, vein reworking/rotation during deformation, and/or
379 overpressured fluids that may have opened pre-existing discontinuities, such as stylolites. Although
380 stylolites are commonly considered efficient barriers to fluid flow (Toussaint et al., 2018 for
381 review), veins developed along stylolites (Fig. 7a,b) suggest that they can be preferential pathways
382 for fluid redistribution, consistently with recent experimental and field evidence (e.g., Heap et al.,
383 2014; Bruna et al., 2019). In particular, the low-permeability network generated by stylolites can
384 favor fluid overpressure rise.

385 Stylolite steps filled by calcite crystals (Fig. 6f) suggest opening of voids (i.e. extensional
386 pull-apart) due to slip along undulated stylolites, which promoted calcite precipitation into newly
387 created space, a mechanism commonly occurring during slickenfiber generation (e.g. Fagereng and
388 Byrnes, 2015). This mechanism indicates that frictional sliding occurred along S-, C-, and C'-planes

389 by smoothing the tooth-shaped margins of stylolites and slip along thick clay-rich dissolution seams
390 (Fig. 10d; Tesei et al., 2013).

391 Fibrous crystals (Figs. 6d-f and 7a,b) generated through multiple and micrometer-thick
392 opening increments (e.g., Bons et al., 2012), is incompatible with coeval growth of blocky and/or
393 elongated-blocky crystals that typically develop in fluid-filled spaces generated by a single opening
394 increment larger than that of fibrous veins (e.g. Bons et al., 2012). These different deformation
395 mechanisms suggest various slip rates and deformation behaviors within the *mélange*. Continuous
396 deformation may have occurred within the ductile clay-rich matrix, while discontinuous slip may
397 have occurred during fibrous and blocky vein generation in more competent carbonate-rich blocks
398 (e.g. Fagereng, 2011). In particular, fibrous veins suggest discontinuous creep at very slow slip
399 rates. On the contrary, impulsive deformation at high and fast slip rates may have occurred during
400 blocky vein generation generated by impulsive crackle-like brecciation (e.g. Woodcock et al., 2014;
401 Fagereng and Byrnes, 2015). In both cases, fracturing/veining were probably assisted by fluid
402 overpressure, consistently with crackle-like brecciation (Fig. 5) and the dense network of clay-rich
403 stylolites, which may have created impermeable barriers and fluid pressure rises over time (Moore
404 and Vrolijk, 1992).

405 Crosscutting relationships between structures show recurrent cycles of mutually overprinting
406 brittle (fracturing/veining and frictional sliding) and ductile (pressure-solution) processes indicate a
407 multiphase deformation history (Figs. 5, 6, 7, and 11). Stylolite formation through fibrous veins
408 (Fig. 6d,e) indicate the interruption of the fracturing event and the onset of a new pressure-solution
409 phase, indicating alternating phases of frictional sliding and dissolution processes (Fig. S1; e.g.,
410 Tesei et al., 2013; Giorgetti et al., 2016). Reworking of inherited veins also occurred (Figs. 10b and
411 11). This inference is consistent with previous U/Pb dating on three calcite-filled veins within the
412 tectonic *mélange* showing ages of 10.5 ± 2.5 My, 7.0 ± 1.6 My, and 5.1 ± 3.7 My, respectively
413 indicating multiple events of calcite precipitation during deformation (Smeraglia et al., 2019).

414

415 5.3 Fluid source and syn-tectonic fluid circulation

416 Geochemical data indicate calcite precipitation at temperatures between ~100 and ~150 °C
417 from retained pore water, such as marine water retained in the clastic sediments during diagenesis,
418 modified or completely buffered by isotope exchange with the host rock. We base this interpretation
419 on the following evidence:

420 (1) The calculated $\delta^{18}\text{O}$ paleofluid composition, which was in equilibrium with the calcite at
421 the time of mineral growth, ranges between +9.1‰ and +13.7‰ (Fig. 8b). These values indicate
422 ^{18}O enrichment suggesting extensive oxygen exchange between the fluids and the limestone
423 interbeds of clastic deposits. In particular, most of the calculated $\delta^{18}\text{O}$ paleofluid compositions
424 ranging between +9‰ and +11‰ (Fig. 8b), indicate high water/rock ratios and paleofluids with
425 nearly constant $\delta^{18}\text{O}$ composition, which were responsible for calcite precipitation at progressive
426 increasing temperatures from 108 to 146 °C (Fig. 8b).

427 (2) Data from fluid inclusions in veins suggest an excess of radiogenic He and Ar in fluids
428 circulating during the precipitation of calcite, indicating a source of both He and Ar other than the
429 atmosphere and the mantle. In particular, the $^3\text{He}/^4\text{He}$ ratios are lower than 0.1 R/Ra (Fig. 8d and
430 Table S3) indicating a crustal fluid. In addition, these values are similar to those of crustal-derived
431 fluids (with limited or negligible mantle contribution) enriched in ^4He recorded in natural gaseous
432 emissions of the central-northern Apennines (e.g., Buttitta et al., 2020).

433 (3) The R/Ra ratios of calcite veins are lower than those calculated from actual springs along
434 the Mt. Massico ridge and related to the Roccamonfina volcano (0.39 Ra to 1.99 Ra, typical of
435 mantle-derived fluids; Cuoco et al., 2017), located ~20 towards the NE respect to the study area
436 (Fig. 1), thus excluding the contribution of mantle-derived fluids circulating within the tectonic
437 mélange. In addition, the volcanic activity at Roccamonfina occurred between ~0.6 and ~0.1 My,
438 ~5 My after the latest tectonic activity documented at Mt. Massico (U-Pb vein dated at 5.1 ± 3.7
439 My, Smeraglia et al., 2019), further excluding the mixing of mantle-derived fluids from
440 Roccamonfina with crustal fluids circulated within the tectonic mélange.

441 However, we cannot completely exclude that also meteoric water partly infiltrated within the
442 tectonic mélangé during deformation and/or exhumation, and was modified by ^{18}O isotope
443 exchange with the host rock, acquiring the calculated $\delta^{18}\text{O}$ paleofluid composition.

444 Based on geochemical and geological data, we suggest that syn-tectonic fluid circulation
445 within the Mt. Massico mélangé occurred in a closed system, without a strong connection with
446 external reservoirs (i.e. meteoric or mantle-derived fluids). We therefore propose that during
447 sedimentary and tectonic burial, marine-derived fluids trapped within sandstones and shale
448 interlayers were progressively heated up to 147 °C. During deformation, regional tectonic
449 shortening caused sandstones and shale compaction, porosity reduction, and, eventually, expulsion
450 of previously stored fluids and calcite precipitation into newly-created fractures. In addition, the
451 progressive smectite to illite conversion through mixed layers illite-smectite occurring from
452 temperatures of 60-70 °C to 210 °C (Aldega et al., 2017), may have triggered additional source for
453 local fluids due to water expulsion during clay dehydration (e.g. Moore and Vrolijk, 1992).

454 Syn-tectonic fluid circulation in closed systems has been already observed in tectonic
455 mélangé exposed in various fold-and-thrust belts (i.e. Apennines, Pyrenees) developed within
456 sedimentary succession with alternating of sandstones, marls, and shale (e.g., Vannucchi et al,
457 2010; Gabellone et al., 2013; Lacroix et al., 2014). The Mt. Massico mélangé did not acted as a
458 conduit for external fluids as observed within intra-wedge tectonic mélangé in the Apennines
459 (Meneghini et al., 2012), Sicilian (Dewever et al., 2013), Thailand (Hansberry et al., 2015), and
460 Japan (Raimbourg et al., 2015) fold-and-thrust belts. We explain this difference suggesting that
461 meso- and microstructures of the Mt. Massico mélangé, such as clay-rich stylolites and marls-shale
462 interlayers (Figs. 3, 4, 6, and 7), created efficient low-permeability barriers, which prevented the
463 ingress of fluids from external reservoirs. Otherwise, the occurrence of regional thrusts, both below
464 and above the Mt. Massico tectonic mélangé, may have acted as regional conduits for the drainage
465 of external fluids within the accretionary wedge and away from the tectonic mélangé.

466 We observe an inverse correlation between fluid temperature and ages of calcite veins,
467 showing an increase of calcite precipitation temperature with decreasing ages (Fig. 8c; U-Pb data
468 from Smeraglia et al., 2019). The vein formed at 10.5 ± 2.5 My at temperature of 108 °C suggests
469 an early phase of deformation during wedge accretion (e.g. Tavani et al., 2015). This is not
470 consistent with the burial history proposed by Smeraglia et al. (2019), which shows much lower
471 temperature for the base of the clastic deposits than that recorded by clumped isotopes before the
472 onset of thrusting at 10.5 ± 2.5 My (i.e. Tortonian time; see Fig. 13a in Smeraglia et al., 2019). This
473 can be explained by the lateral and upward migration of deep-seated warm fluids, previously stored
474 in areas already affected by tectonic burial (e.g., Minshull et al., 1989), which circulated within the
475 clastic deposits at shallow depths during the Tortonian. The occurrence pre-Tortonian tectonic
476 burial is highlighted by the borehole stratigraphy of Mara 01 well, located towards the SW respect
477 the Mt. Massico, showing the thrusting of Triassic deposits above Paleocene-Eocene deposits (See
478 Fig. 2 in Smeraglia et al., 2019)

479 Veins formed at 7.0 ± 1.6 My and 5.1 ± 3.7 My at temperatures of 121 and 147 °C,
480 respectively, are consistent with the progressive burial due to thrust sheet emplacement above the
481 mélangé (Smeraglia et al., 2019). However, we point out that most of precipitation temperatures are
482 fully consistent with the maximum burial temperature of 140 °C at depths of ~4 km experienced by
483 the mélangé, calculated by 1D thermal modelling constrained by mixed layers illite-smectite
484 (Smeraglia et al., 2019). This indicates that fluid expulsion occurred under maximum burial
485 condition, suggesting that tectonic overburden promoted and/or triggered fluid overpressure and
486 hydrofracturing.

487

488 **Conclusions**

489 Structural and microstructural observations combined with geochemical data (stable and
490 clumped isotopes and isotope composition of noble gases in fluid inclusions of calcite veins) along

491 the carbonate/shale-bearing tectonic *mélange* within the central Apennines accretionary wedge (Mt.
492 Massico *mélange*) show that:

493 (1) Intra-wedge tectonic *mélange* generates along pre-existent intra- and interformational
494 rheological contrast occurring along carbonate/shale sedimentary successions. In particular,
495 deformation is localized at the boundary between weak (Tortonian clastic deposits and hemipelagic
496 marls) and competent (Meso-Cenozoic limestones) rocks. The development of tectonic *mélange*
497 occurred by disruption of the primary bedding, mixing, and deformation of relicts of competent
498 blocks (i.e., olistoliths and relicts of competent strata) within a weak matrix (i.e., deformed shaly
499 and marly interbeds), through recurrent cycles of mutually overprinting brittle (fracturing/veining
500 and frictional sliding) and ductile (pressure-solution) processes, indicating a polyphase deformation
501 history characterized by fast to slow strain rates.

502 (2) The geochemical signatures of syn-tectonic calcite veins indicate calcite precipitation
503 from warm (108-147 °C) and modified pore fluids, by isotope exchange with the local host rock.
504 Fluid circulation occurred mostly in a closed system dominated by the expulsion and redistribution
505 of pore fluids trapped during sedimentation/diagenesis and/or derived by clay dehydration processes
506 (at $T > 120$ °C), without the interaction of externally derived fluids (i.e. meteoric and/or mantle-
507 derived fluids). A minor contribution from lateral-upward migration of deep-seated warm fluids,
508 previously stored in areas affected by tectonic burial located towards the SW from the Mt. Massico,
509 is inferred in the early phase of the deformation of tectonic *mélange*. Low-permeability barriers,
510 generated by clay-rich stylolites, promoted the generation of fluid overpressure, which were mostly
511 expelled at maximum burial conditions (T 140 °C and depth of ~4 km) in the final stage of *mélange*
512 deformation. Therefore, clay-rich intra-wedge tectonic *mélanges*, along *décollement* zones, may
513 generate efficient barriers within accretionary wedges for vertical and lateral redistribution of fluids
514 from reservoirs outside the *mélange*.

515

516 We highlight that the integration of geochemical (stable and clumped isotopes, analysis of
517 gaseous species in fluid inclusions) and geochronological (U-Pb dating) methods can be a powerful
518 approach to better constrain the burial-thermal evolution and the fluid storage capacity of fold and
519 thrust belts and sedimentary basins, including the associated fault network.

520

521 **Acknowledgements**

522 This work has been funded by: Progetti di Ateneo Sapienza 2017 to E. Carminati, Progetti di
523 Ateneo Sapienza 2016 to L. Aldega, and Progetto di Avvio alla Ricerca 2016 Sapienza to L.
524 Smeraglia. We thank D. Mannelta and TSLab & Geoservices for thin sections, A. Conti, F. Di
525 Fiore, and S. Fabbi constructive discussions and help during fieldwork and sampling and M. Jaggi
526 for the isotope analyses. We are grateful to M. Tantillo for analyzing the chemistry of CO₂+H₂O,
527 N₂, and the isotope composition of light noble gases.

528

529 **References**

- 530 Aldega L., Carminati E., Scharf A., Mattern F. & Al-Wardi M. (2017). Estimating original
531 thickness and extent of the Semail Ophiolite in the eastern Oman Mountains by paleothermal
532 indicators. *Marine and Petroleum Geology*, 84, 18-33.
- 533 Bernasconi, S. M., Müller, I. A., Bergmann, K. D., Breitenbach, S. F., Fernandez, A., et al. (2018).
534 Reducing uncertainties in carbonate clumped isotope analysis through consistent
535 carbonate-based standardization. *Geochemistry, Geophysics, Geosystems*, 19(9), 2895-2914.
- 536 Billi, A. (2010). Microtectonics of low-P low-T carbonate fault rocks. *Journal of Structural*
537 *Geology*, 32(9), 1392-1402.
- 538 Billi, A., Bosi, V., & De Meo, A. (1997). Caratterizzazione strutturale del rilievo del M. Massico
539 nell'ambito dell'evoluzione quaternaria delle depressioni costiere dei fiumi Garigliano e
540 Volturno (Campania settentrionale). *Il Quaternario*, 10(1), 15–26.

- 541 Bons, P. D., Elburg, M. A., & Gomez-Rivas, E. (2012). A review of the formation of tectonic veins
542 and their microstructures. *Journal of Structural Geology*, *43*, 33-62.
- 543 Bruna, P. O., Lavenu, A. P., Matonti, C., & Bertotti, G. (2019). Are stylolites fluid-flow efficient
544 features?. *Journal of Structural Geology*, *125*, 270-277.
- 545 Buttitta, D., Caracausi, A., Chiaraluca, L., Favara, R., Morticelli, M. G., & Sulli, A. (2020).
546 Continental degassing of helium in an active tectonic setting (northern Italy): the role of
547 seismicity. *Scientific Reports*, *10*(1), 1-13.
- 548 Carminati, E., Lustrino, M., & Doglioni, C. (2012). Geodynamic evolution of the central and
549 western Mediterranean: Tectonics vs. igneous petrology constraints. *Tectonophysics*, *579*,
550 173–192. <https://doi.org/10.1016/j.tecto.2012.01.026>
- 551 Codegone, G., Festa, A., & Dilek, Y. (2012). Formation of Taconic mélanges and broken
552 formations in the Hamburg Klippe, central Appalachian orogenic belt, eastern Pennsylvania.
553 *Tectonophysics*, *568*, 215-229.
- 554 Cuoco, E., Minissale, A., Tamburrino, S., Iorio, M., & Tedesco, D. (2017). Fluid geochemistry of
555 the Mondragone hydrothermal systems (southern Italy): water and gas compositions vs.
556 geostructural setting. *International Journal of Earth Sciences*, *106*(7), 2429-2444.
- 557 Dennis, K. J., Affek, H. P., Passey, B. H., Schrag, D. P., & Eiler, J. M. (2011). Defining an absolute
558 reference frame for ‘clumped’ isotope studies of CO₂. *Geochimica et Cosmochimica Acta*,
559 *75*(22), 7117-7131.
- 560 Dewever, B., Swennen, R., & Breesch, L. (2013). Fluid flow compartmentalization in the Sicilian
561 fold and thrust belt: Implications for the regional aqueous fluid flow and oil migration history.
562 *Tectonophysics*, *591*, 194-209.
- 563 Di Girolamo, P., Sgrosso, I., De Gennaro, R., & Giurazzi, S. (2000). Metamorphic rocks in
564 Campania (southern Italy); The “Mondragone marbles”. *Bollettino della Societa Geologica*
565 *Italiana*, *119*(3), 761–766.

- 566 Fagereng, Å. (2011). Fractal vein distributions within a fault-fracture mesh in an exhumed
567 accretionary mélange, Chrystalls Beach Complex, New Zealand. *Journal of Structural*
568 *Geology*, 33(5), 918-927.
- 569 Fagereng, Å., & Byrnes, G. (2015). A range of fault slip styles on progressively misoriented planes
570 during flexural-slip folding, Cape Fold Belt, South Africa. *Journal of Structural Geology*, 70,
571 156-169.
- 572 Fagereng, Å., & Cooper, A. F. (2010). The metamorphic history of rocks buried, accreted and
573 exhumed in an accretionary prism: An example from the Otago Schist, New Zealand. *Journal*
574 *of Metamorphic Geology*, 28(9), 935–954. <https://doi.org/10.1111/j.1525-1314.2010.00900.x>
- 575 Fagereng, Å., Remitti, F., & Sibson, R. H. (2010). Shear veins observed within anisotropic fabric at
576 high angles to the maximum compressive stress. *Nature Geoscience*, 3(7), 482.
- 577 Festa, A., Dilek, Y., Pini, G. A., Codegone, G., & Ogata, K. (2012). Mechanisms and processes of
578 stratal disruption and mixing in the development of mélanges and broken formations:
579 Redefining and classifying mélanges. *Tectonophysics*, 568, 7-24.
- 580 Gabellone, T., Gasparri, M., Iannace, A., Invernizzi, C., Mazzoli, S., & D'antonio, M. (2013).
581 Fluid channeling along thrust zones: the Lagonegro case history, southern Apennines, Italy.
582 *Geofluids*, 13(2), 140-158.
- 583 Giorgetti, C., Collettini, C., Scuderi, M. M., Barchi, M. R., & Tesei, T. (2016). Fault geometry and
584 mechanics of marly carbonate multilayers: An integrated field and laboratory study from the
585 Northern Apennines, Italy. *Journal of Structural Geology*, 93, 1-16.
- 586 Gratier, J. P., Thouvenot, F., Jenatton, L., Tourette, A., Doan, M. L., & Renard, F. (2013).
587 Geological control of the partitioning between seismic and aseismic sliding behaviours in
588 active faults: Evidence from the Western Alps, France. *Tectonophysics*, 600, 226-242.
- 589 Hansberry, R. L., Collins, A. S., King, R. C., Morley, C. K., Gize, A. P., Warren, J., ... & Hall, P. A.
590 (2015). Syn-deformation temperature and fossil fluid pathways along an exhumed detachment
591 zone, khao khwang fold-thrust belt, Thailand. *Tectonophysics*, 655, 73-87.

592 Heap, M. J., Baud, P., Reuschlé, T., & Meredith, P. G. (2014). Stylolites in limestones: Barriers to
593 fluid flow?. *Geology*, 42(1), 51-54.

594 Hilgen, F., Aziz, H. A., Bice, D., Iaccarino, S., Krijgsman, W., Kuiper, K., ... & Zachariasse, W. J.
595 (2005). The global boundary stratotype section and point (GSSP) of the Tortonian stage
596 (Upper Miocene) at Monte Dei Corvi. *Episodes-Newsmagazine of the International Union of*
597 *Geological Sciences*, 28(1), 6-17.

598 Lacroix, B., Travé, A., Buatier, M., Labaume, P., Vennemann, T., & Dubois, M. (2014).
599 Syntectonic fluid-flow along thrust faults: Example of the South-Pyrenean fold-and-thrust
600 belt. *Marine and Petroleum Geology*, 49, 84-98.

601 Luiso, P., Paoletti, V., Nappi, R., La Manna, M., Cella, F., Gaudiosi, G., & Iorio, M. F. M. (2018).
602 A multidisciplinary approach to characterize the geometry of active faults: The example of
603 Mt. Massico, Southern Italy. *Geophysical Journal International*, 213(3), 1673–1681.
604 <https://doi.org/10.1093/gji/ggy080>

605 Malinverno, A., & Ryan, W. B. (1986). Extension in the Tyrrhenian Sea and shortening in the
606 Apennines as result of arc migration driven by sinking of the lithosphere. *Tectonics*, 5(2),
607 227–245. <https://doi.org/10.1029/TC005i002p00227>

608 Meneghini, F., Marroni, M., Moore, J. C., Pandolfi, L., & Rowe, C. D. (2009). The processes of
609 underthrusting and underplating in the geologic record: Structural diversity between the
610 Franciscan Complex (California), the Kodiak Complex (Alaska) and the Internal Ligurian
611 Units (Italy). *Geological Journal*, 44(2), 126–152. <https://doi.org/10.1002/gj.1144>

612 Meneghini, F., Botti, F., Aldega, L., Boschi, C., Corrado, S., Marroni, M., & Pandolfi, L. (2012).
613 Hot fluid pumping along shallow-level collisional thrusts: the Monte Rentella Shear Zone,
614 Umbria Apennine, Italy. *Journal of Structural Geology*, 37, 36-52.

615 Minshull, T., & White, R. (1989). Sediment compaction and fluid migration in the Makran
616 accretionary prism. *Journal of Geophysical Research: Solid Earth*, 94(B6), 7387-7402.

617 Moore, J. C., & Vrolijk, P. (1992). Fluids in accretionary prisms. *Reviews of Geophysics*, 30(2),
618 113-135.

619 Morley, C. K., von Hagke, C., Hansberry, R. L., Collins, A. S., Kanitpanyacharoen, W., & King, R.
620 (2017). Review of major shale-dominated detachment and thrust characteristics in the
621 diagenetic zone: Part I, meso- and macro-scopic scale. *Earth-Science Reviews*, 173, 168–
622 228. <https://doi.org/10.1016/j.earscirev.2017.07.019>

623 Mostardini, F., & Merlini, S. (1986). Appennino centroemeridionale. Sezioni geologiche e proposta
624 di modello strutturale. *Memorie della Societa Geologica Italiana*, 35, 177–202.

625 O'Neil, J. R., Clayton, R. N., & Mayeda, T. K. (1969). Oxygen isotope fractionation in divalent
626 metal carbonates. *The Journal of Chemical Physics*, 51(12), 5547-5558.

627 Ogata, K., Pini, G. A., Carè, D., Zélic, M., & Dellisanti, F. (2012). Progressive development of
628 block-in-matrix fabric in a shale-dominated shear zone: Insights from the Bobbio Tectonic
629 Window (Northern Apennines, Italy). *Tectonics*, 31, TC1003. [https://doi.org/10.1029/](https://doi.org/10.1029/2011TC002924)
630 2011TC002924

631 Raimbourg, H., Augier, R., Famin, V., Gadenne, L., Palazzin, G., Yamaguchi, A., & Kimura, G.
632 (2014). Long-term evolution of an accretionary prism: The case study of the Shimanto Belt,
633 Kyushu, Japan. *Tectonics*, 33(6), 936-959.

634 Renard, F., Ortoleva, P., & Gratier, J. P. (1997). Pressure solution in sandstones: influence of clays
635 and dependence on temperature and stress. *Tectonophysics*, 280(3-4), 257-266.

636 Sgrosso, I. (1974). I rapporti tra la piattaforma carbonatica Campano-Lucana e la piattaforma
637 Abruzzese-Campana al Monte Massico (Caserta). *Bollettino della Societa Geologica Italiana*,
638 93(4), 1197–1209.

639 Smeraglia, L., Aldega, L., Billi, A., Carminati, E., Di Fiore, F., Gerdes, A., ... & Vignaroli, G.
640 (2019). Development of an Intrawedge Tectonic Mélange by Out-of-Sequence Thrusting,
641 Buttressing, and Intraformational Rheological Contrast, Mt. Massico Ridge, Apennines, Italy.
642 *Tectonics*, 38(4), 1223-1249.

- 643 Tavani, S., Storti, F., Lacombe, O., Corradetti, A., Muñoz, J. A., & Mazzoli, S. (2015). A review of
644 deformation pattern templates in foreland basin systems and fold-and-thrust belts:
645 Implications for the state of stress in the frontal regions of thrust wedges. *Earth-Science*
646 *Reviews, 141*, 82-104.
- 647 Tesei, T., Collettini, C., Viti, C., & Barchi, M. R. (2013). Fault architecture and deformation
648 mechanisms in exhumed analogues of seismogenic carbonate-bearing thrusts. *Journal of*
649 *Structural Geology, 55*, 167-181.
- 650 Toussaint, R., Aharonov, E., Koehn, D., Gratier, J. P., Ebner, M., et al. (2018). Stylolites: A review.
651 *Journal of Structural Geology 114*, 163-195.
- 652 Vannucchi, P., & Bettelli, G. (2002). Mechanism of subduction accretion as implied from the
653 broken formations in the Apennines, Italy. *Geology, 30*(9), 835–838.
654 [https://doi.org/10.1130/0091-7613\(2002\)030<0835:MOSAAL>2.0.CO;2](https://doi.org/10.1130/0091-7613(2002)030<0835:MOSAAL>2.0.CO;2)
- 655 Vannucchi, P., Remitti, F., & Bettelli, G. (2008). Geological record of fluid flow and seismogenesis
656 along an erosive subducting plate boundary. *Nature, 451*(7179), 699–703.
657 <https://doi.org/10.1038/nature06486>
- 658 Vannucchi, P., Remitti, F., Bettelli, G., Boschi, C., & Dallai, L. (2010). Fluid history related to the
659 early Eocene-middle Miocene convergent system of the Northern Apennines (Italy):
660 Constraints from structural and isotopic studies. *Journal of Geophysical Research, 115*,
661 B05405. <https://doi.org/10.1029/2009JB006590>
- 662 Vezzani, L., Festa, A., & Ghisetti, F. C. (2010). Geology and tectonic evolution of the
663 Central-Southern Apennines, Italy, Special Paper (Vol. 469, pp. 1–58). America: Geological
664 Society. <https://doi.org/10.1130/2010.2469>
- 665 Vitale, S., & Ciarcia, S. (2018). Tectono-stratigraphic setting of the Campania region (southern
666 Italy). *Journal of Maps, 14*(2), 9–21. <https://doi.org/10.1080/17445647.2018.1424655>
- 667 Vitale, S., Prinzi, E. D., Ciarcia, S., Sabbatino, M., Tramparulo, F. D. A., & Verrazzo, G. (2018).
668 Polyphase out-of-sequence thrusting and occurrence of marble detritus within the wedge-top

669 basin deposits in the Mt. Massico (southern Apennines): Insights into the late Miocene
670 tectonic evolution of the central Mediterranean. *International Journal of Earth Sciences*.
671 <https://doi.org/10.1007/s00531-018-1664-0>

672 Vrolijk, P., Myers, G., & Moore, J. C. (1988). Warm fluid migration along tectonic melanges in the
673 Kodiak accretionary complex, Alaska. *Journal of Geophysical Research: Solid Earth*, 93(B9),
674 10313-10324.

675 Woodcock, N. H., Miller, A. V. M., & Woodhouse, C. D. (2014). Chaotic breccia zones on the
676 Pembroke Peninsula, south Wales: Evidence for collapse into voids along dilational faults.
677 *Journal of Structural Geology*, 69, 91-107.

678

679 **Figure Captions**

680 **Figure 1.** (a) Simplified geological map of the central-southern Apennines (Italy) showing main
681 thrusts and location of the study area. (b) Schematic geological cross-section through the
682 central-southern Apennines (modified after [Mostardini and Merlini, 1986](#)). (c) Geological
683 cross-section through the Mt. Massico ridge (i.e., the study area).

684

685 **Figure 2.** (a) Detailed geological map of the southwestern part of the Mt. Massico ridge with
686 location of key outcrops where the tectonic mélangé is exposed. Schmidt nets (lower
687 hemisphere) showing the attitude of S-C planes with related slip vectors within the tectonic
688 mélangé. Modified after [Smeraglia et al. \(2019\)](#) (b) Geological cross-sections across the Mt.
689 Massico ridge.

690

691 **Figure 3.** Outcrop-scale structural features of the Mt. Massico tectonic mélangé. (a,b) The poorly
692 deformed clastic deposits showing bedding and incipient foliation. Note folded strata and
693 low-displacement faults showing ramp and flat geometry. (c) The moderately deformed zone
694 showing competent strata (i.e. sandstones and calcarenites interbeds) characterized by pinch-

695 and-swell and boudine-like geometries. **(d)** Relict of competent strata. **(d)** Detail of competent
696 strata (Fig. 3c) showing veins perpendicular to bedding and S-C foliation. **(f,g)** The strongly
697 deformed part of the tectonic *mélange* showing S-C foliation within marls and shale and relict
698 of competent strata (limestones and sandstones) showing sigmoidal shapes. **(h)** Relict of
699 competent limestones showing stylolites along S- and C-planes. Inset shows the Schmidt nets
700 (lower hemisphere) showing the attitude of S-C planes with related slip vectors.

701

702 **Figure 4.** Outcrop-scale structural features of the Mt. Massico tectonic *mélange*. **(a-c)** The strongly
703 deformed part of the tectonic *mélange* characterized by S-C and S-CC' tectonites within marls
704 and shale and relict of competent strata (limestones and sandstones) showing sigmoidal
705 shapes. **(d)** Relict of competent limestones showing a pervasive network of calcite veins. **(e-**
706 **h)** Inherited competent (limestones) olistoliths scattered within the weak (marls and shale)
707 scaly foliation, generating the block-in-matrix fabric typical of tectonic *mélange*. **(h)**
708 Contorted and convoluted foliation within the S-C tectonite.

709

710 **Figure 5.** High-resolution hand sample scan of relicts of competent limestones showing sigmoidal
711 shapes. Stylolites are aligned along S-, C- and C'-planes. Calcite veins are oriented parallel,
712 perpendicular, and/or oblique with respect to stylolites. No stylolites affecting calcite veins
713 and calcite veins cutting through stylolites occur.

714

715 **Figure 6.** Microstructures from the tectonic *mélange*. **(a-c)** Stylolites affecting host rock relicts and
716 calcite veins. Note the insoluble materials (clays and oxides) filling up to 1-mm thick
717 dissolution seams. **(d,e)** Fibrous veins characterized by fibrous calcite crystals with long axis
718 oriented roughly parallel to stylolites. Note stylolites affecting fibrous veins. **(f)** Fibrous
719 crystals developed along stylolites jogs along C-plane. Fibrous crystals with long axis
720 oriented roughly parallel to stylolites.

721

722 **Figure 7.** Microstructures from the tectonic mélange. **(a,b)** Fibrous veins characterized by fibrous
723 calcite crystals with long axis oriented perpendicular to stylolites. Note that this type of
724 fibrous veins develop within stylolites. **(c,d,e,f)** Blocky veins characterized by blocky calcite
725 crystals. Blocky veins are oriented parallel, perpendicular, and/or oblique respect to stylolites.
726 Note stylolites affecting blocky veins and mutual crosscutting relationships between blocky
727 veins.

728

729 **Figure 8.** **(a)** $\delta^{13}\text{C}$ (‰ V-PDB) versus $\delta^{18}\text{O}$ (‰ V-SMOW) diagram from blocky and fibrous veins
730 and host rocks in the Mt. Massico tectonic mélange. Notice the average $\delta^{18}\text{O}$ depletion of
731 $\sim 4\text{‰}$ between mélange-related mineralizations and host rock. **(b)** Oxygen isotope
732 fractionation during equilibrium precipitation: $\delta^{18}\text{O}$ of fault-related mineralizations and
733 paleofluid compositions (curves) as a function of temperature. The $\delta^{18}\text{O}$ calculated paleofluid
734 compositions (between 9‰ and 14‰) indicate strong ^{18}O exchange with the local limestone
735 host rock. Notice that warmer fluids have similar $\delta^{18}\text{O}$ paleofluid composition suggesting that
736 the same paleofluid was the source for calcite precipitation at increasing temperatures and
737 depths. **(c)** Temperature ($^{\circ}\text{C}$, clumped isotopes) versus age (My, U-Pb dating, data from
738 [Smeraglia et al., 2019](#)) diagram for three dated veins. Notice the increase in paleofluid
739 temperature with decreasing ages, that indicates progressive tectonic burial during
740 discontinuous thrust sheet emplacement through time. **(d)** $^4\text{He}/^{20}\text{Ne}$ ratio versus $^3\text{He}/^4\text{He}$
741 (R/Ra) ratio diagram. Note that the calcite veins are in the range of R/Ra values typical of
742 crustal fluids of the central Apennines.

743

744 **Figure 9.** **(a)** Large-scale tectonic setting of the Apennine subduction (modified after [Scrocca et al.,](#)
745 [2005](#)) and location of the Mt. Massico structure within the accretionary prism. **(b-c)**
746 Simplified sketch showing the main sedimentary and tectonic events in the Mt. Massico area

747 (Modified after Smeraglia et al., 2019): (b) During late Tortonian-early Messinian times,
748 orogenic compression generated a fault propagation anticline located in the northeastern part
749 of the Mt. Massico ridge, juxtaposing pre-orogenic limestones in the hangingwall with syn-
750 orogenic Tortonian sandstones in the footwall. (c) During late Messinian-early Pliocene
751 times, out-of-sequence thrusting occurred and a ~3,300 m-thick stack of imbricate thrust
752 sheets thrust onto the Tortonian-lower Messinian clastic deposits and calcarenites. At this
753 stage the tectonic mélangé develop at the base of the clastic deposits. Notice that remnants of
754 such thrust sheets are located in the Mt. Petrino area (Fig. 2).

755

756 **Figure 10.** Simplified evolution of the Mt. Massico tectonic mélangé (See Fig. 10b,c for the
757 structural location of the evolution scheme). (a) During the early deformation stage, veins
758 perpendicular to bedding develop within the clastic deposits in response to far field tectonic
759 stress. (b) Initial shortening affect the clastic deposits generating a weak scaly foliation
760 parallel respect to bedding (see Fig. 3a,b). (c) Progressive shortening generated S-C fabric and
761 boudinage of competent bedding (limestones and sandstones). (d) During the late stage of
762 deformation, the strongly deformed tectonic mélangé develop. In particular, pervasive S-C
763 tectonites develop within the weak (marls and shale) matrix and relicts of competent strata are
764 deformed generating scattered clasts with sigmoidal shape. Notice that hemipelagic marls are
765 scraped off and mixed within the tectonic mélangé, while the underlying Meso-Cenozoic
766 limestones are not deformed. The inset shows the different type of veins within the mélangé
767 (blocky and fibrous) and their structural position respect to stylolites.

768

769 **Figure S1.** Schematic evolutionary model for mélangé-related veins evolution through time. Notice
770 alternate cycles of mutually overprinting brittle (fracturing/veining) and ductile (pressure-
771 solutional and stylolites generation) processes.

772

Figure 1
[Click here to download high resolution image](#)

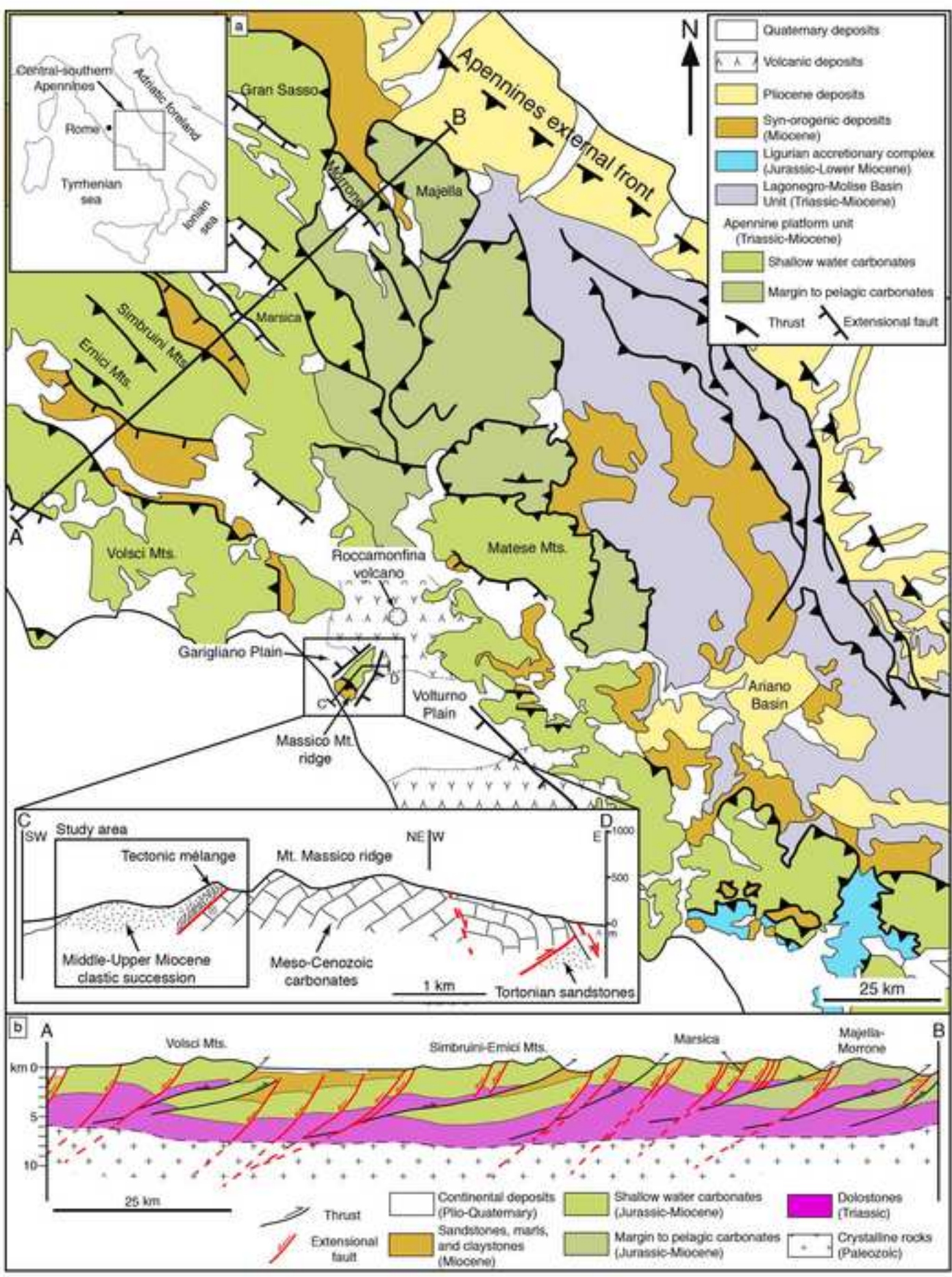


Figure 2
[Click here to download high resolution image](#)

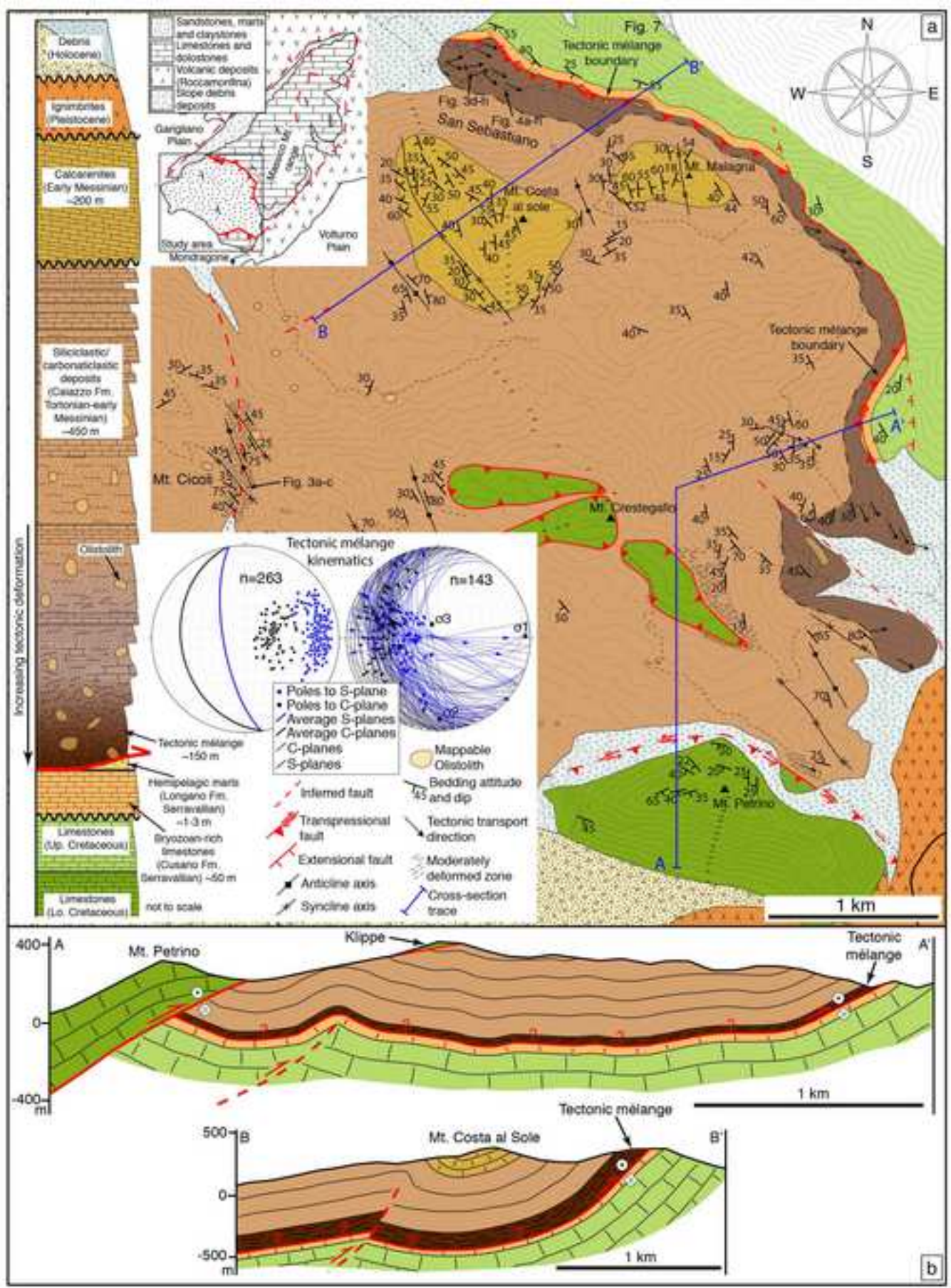


Figure 3
[Click here to download high resolution image](#)

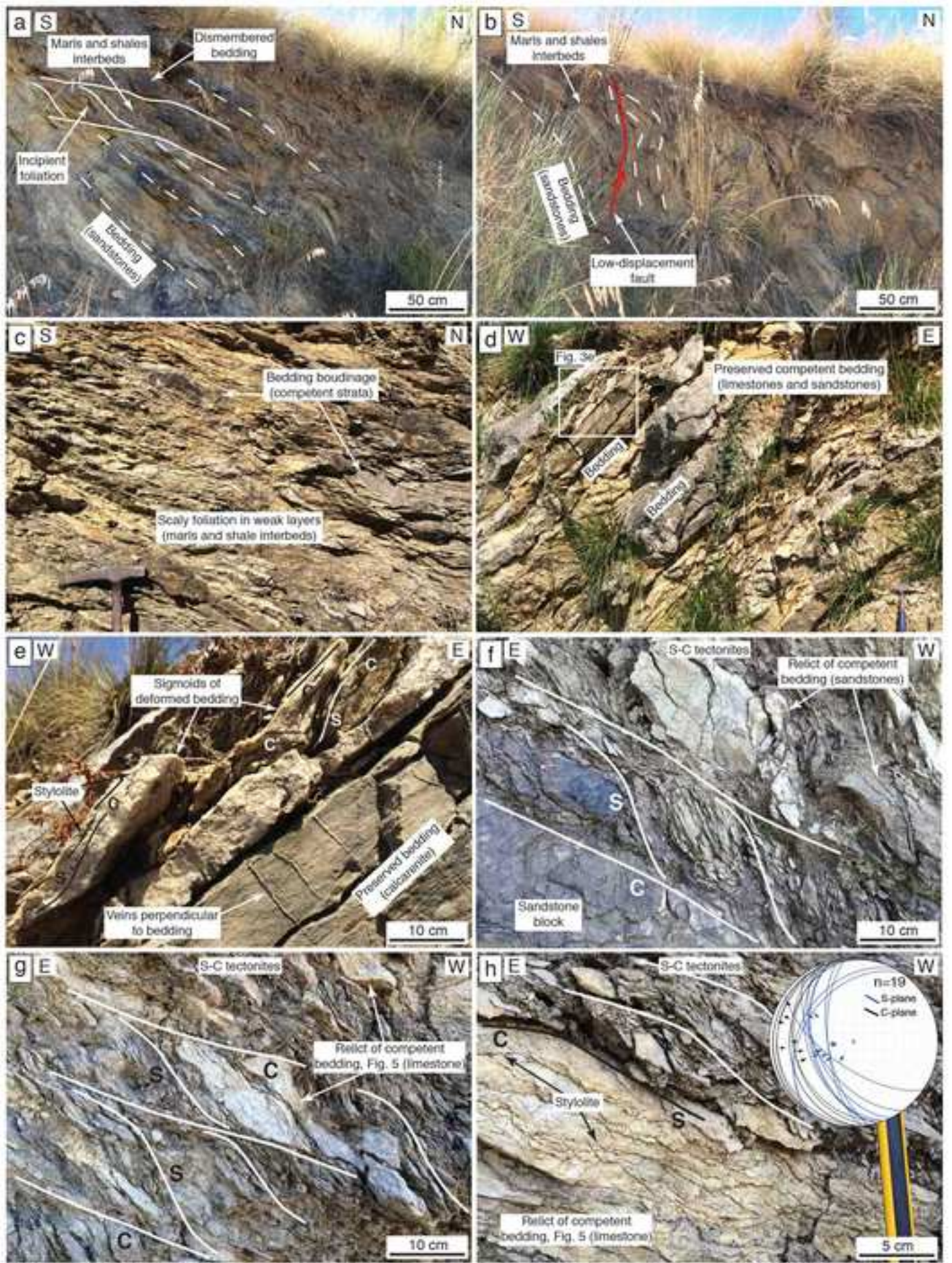


Figure 4
[Click here to download high resolution image](#)

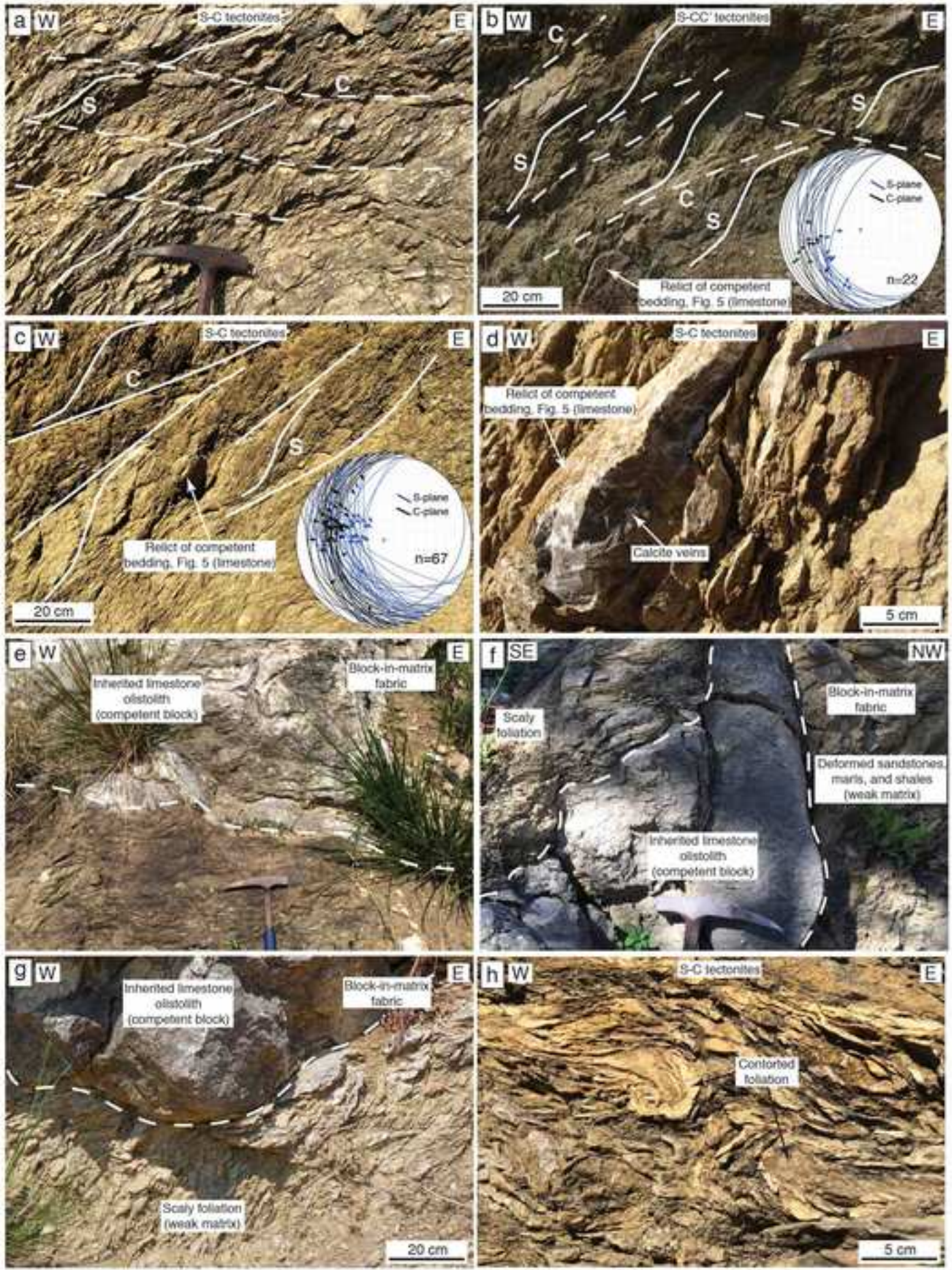


Figure 5
[Click here to download high resolution image](#)

Relicts of competent bedding

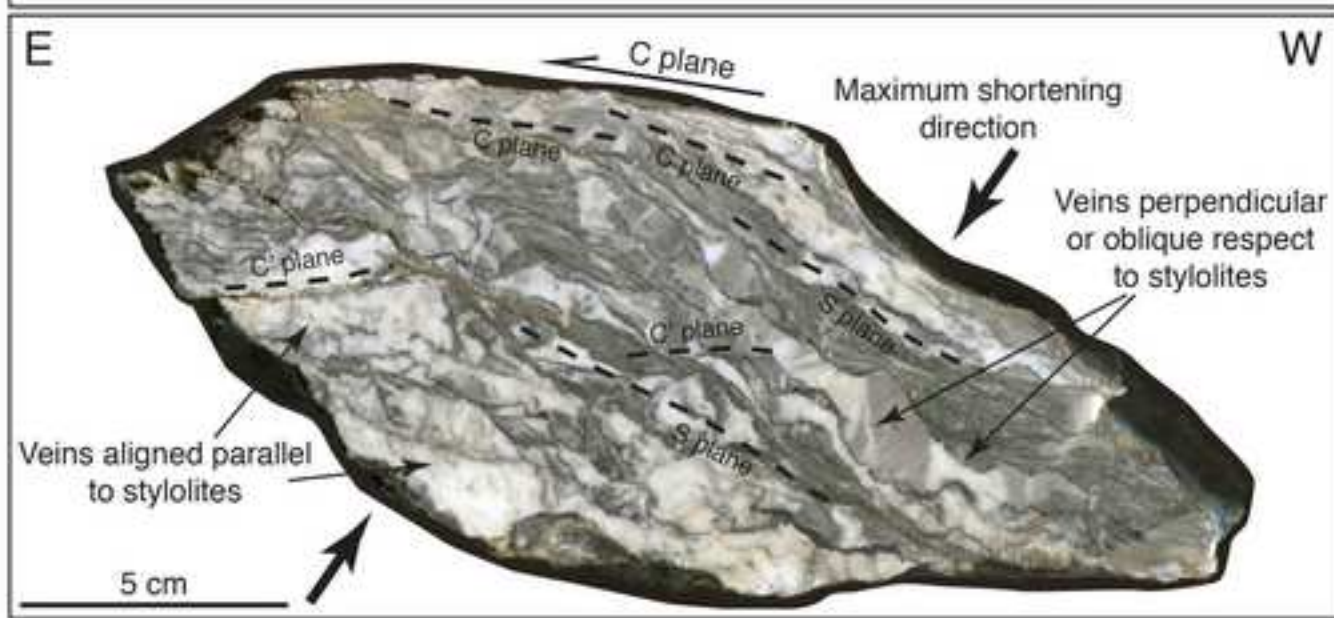
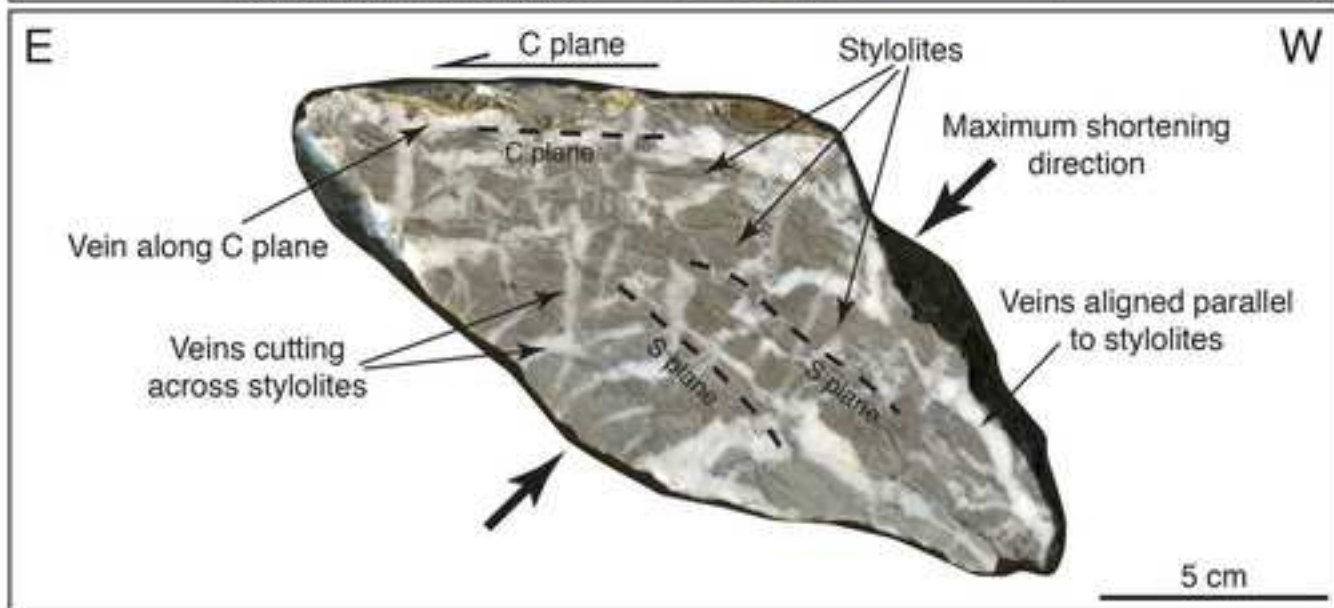
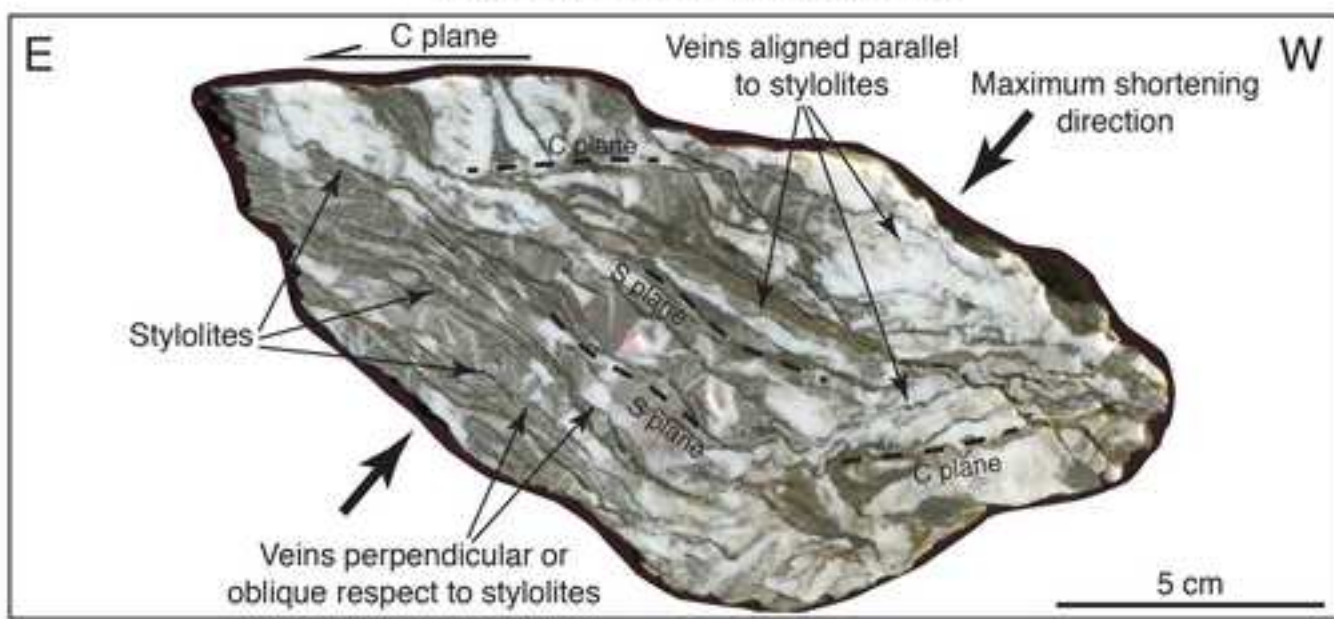


Figure 6
[Click here to download high resolution image](#)

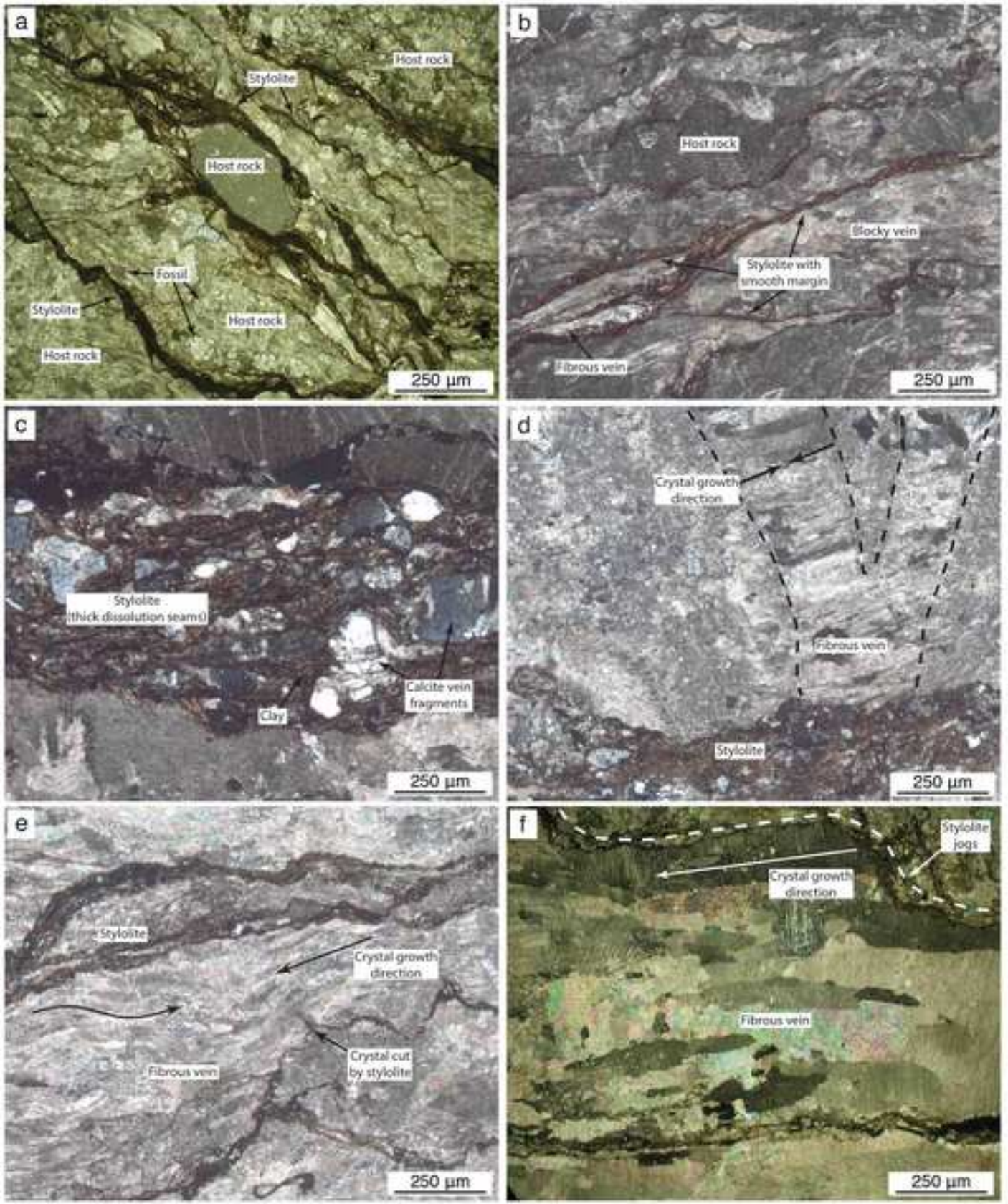


Figure 7
[Click here to download high resolution image](#)

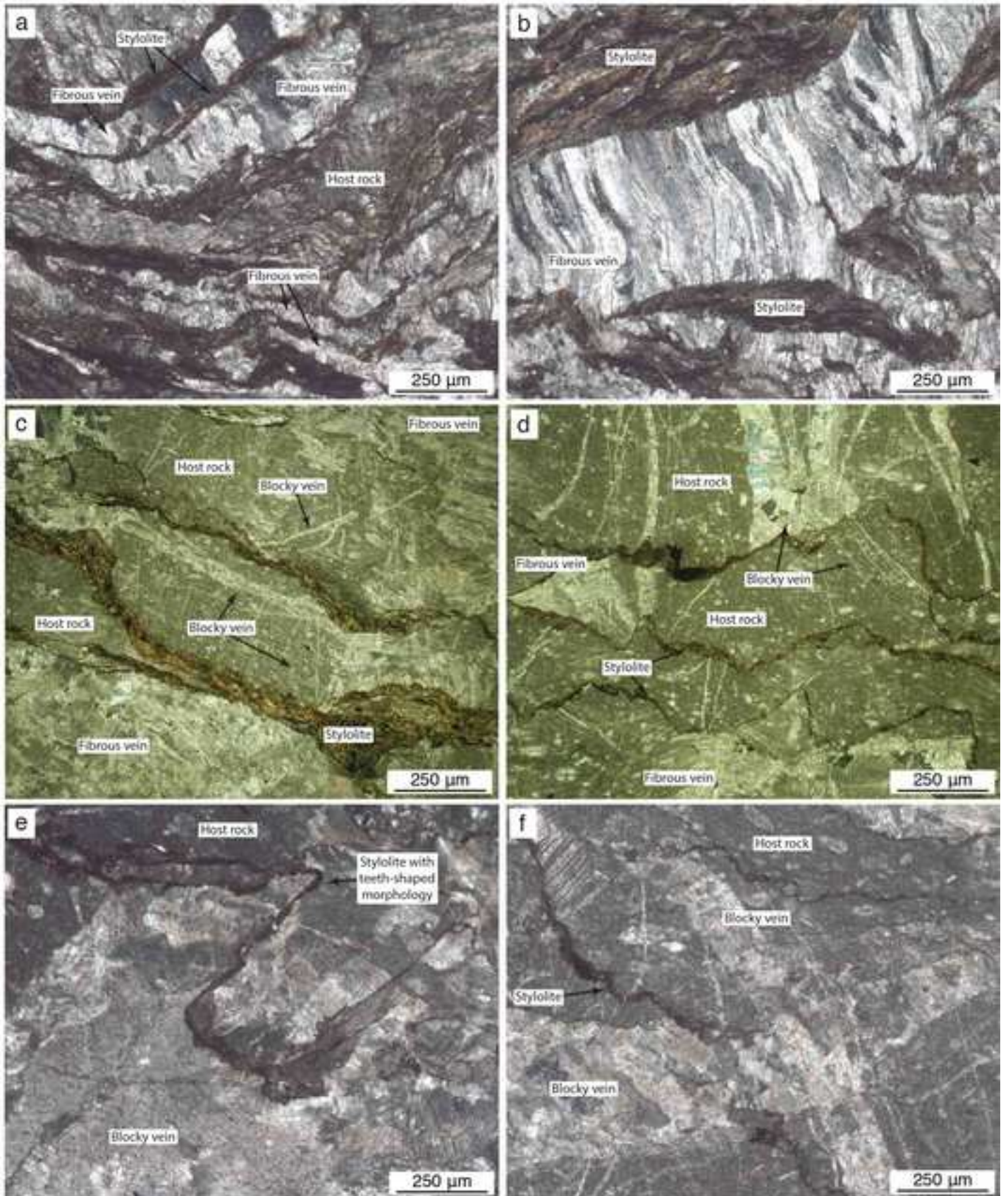


Figure 8

[Click here to download high resolution image](#)

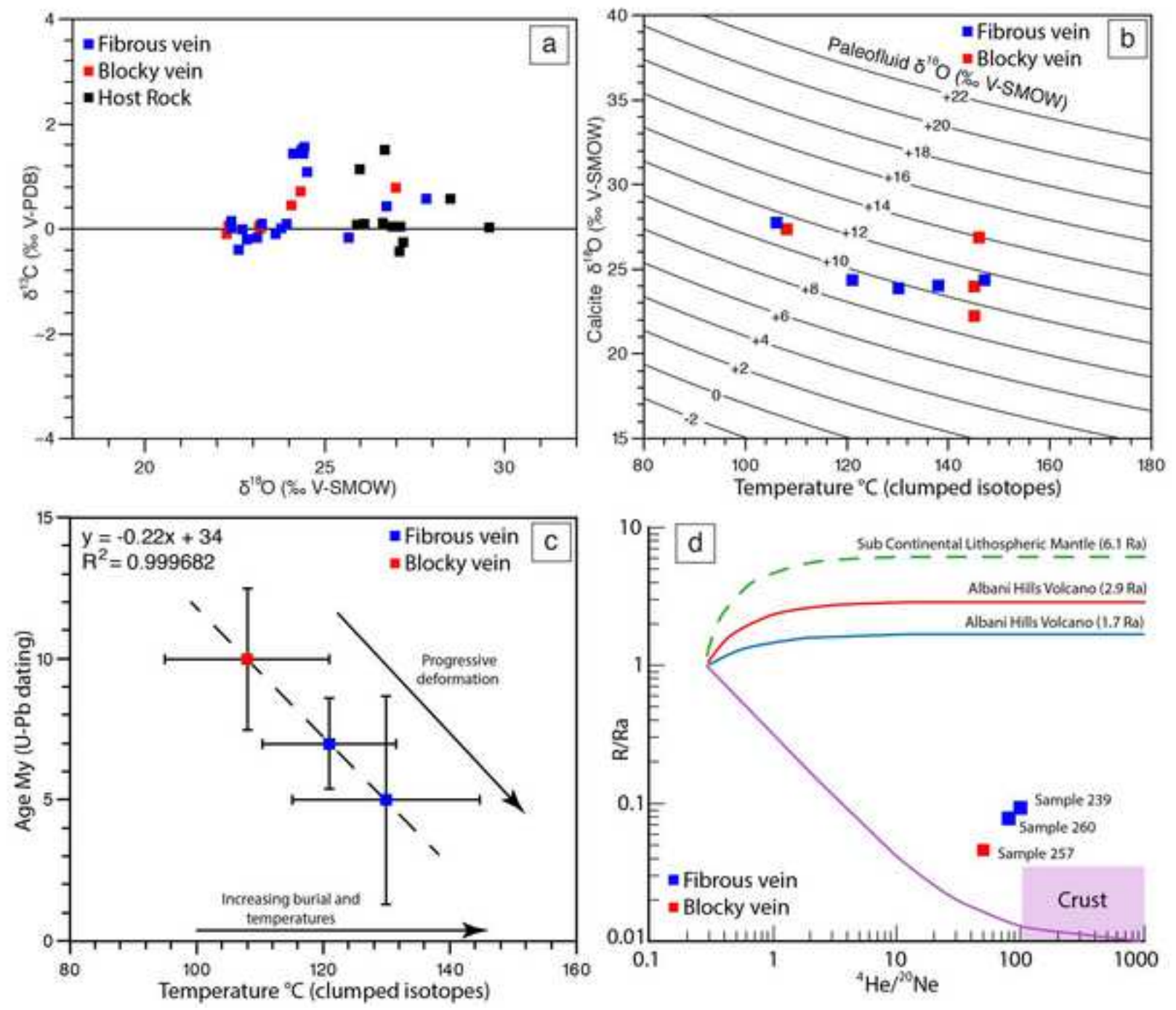


Figure 9
[Click here to download high resolution image](#)

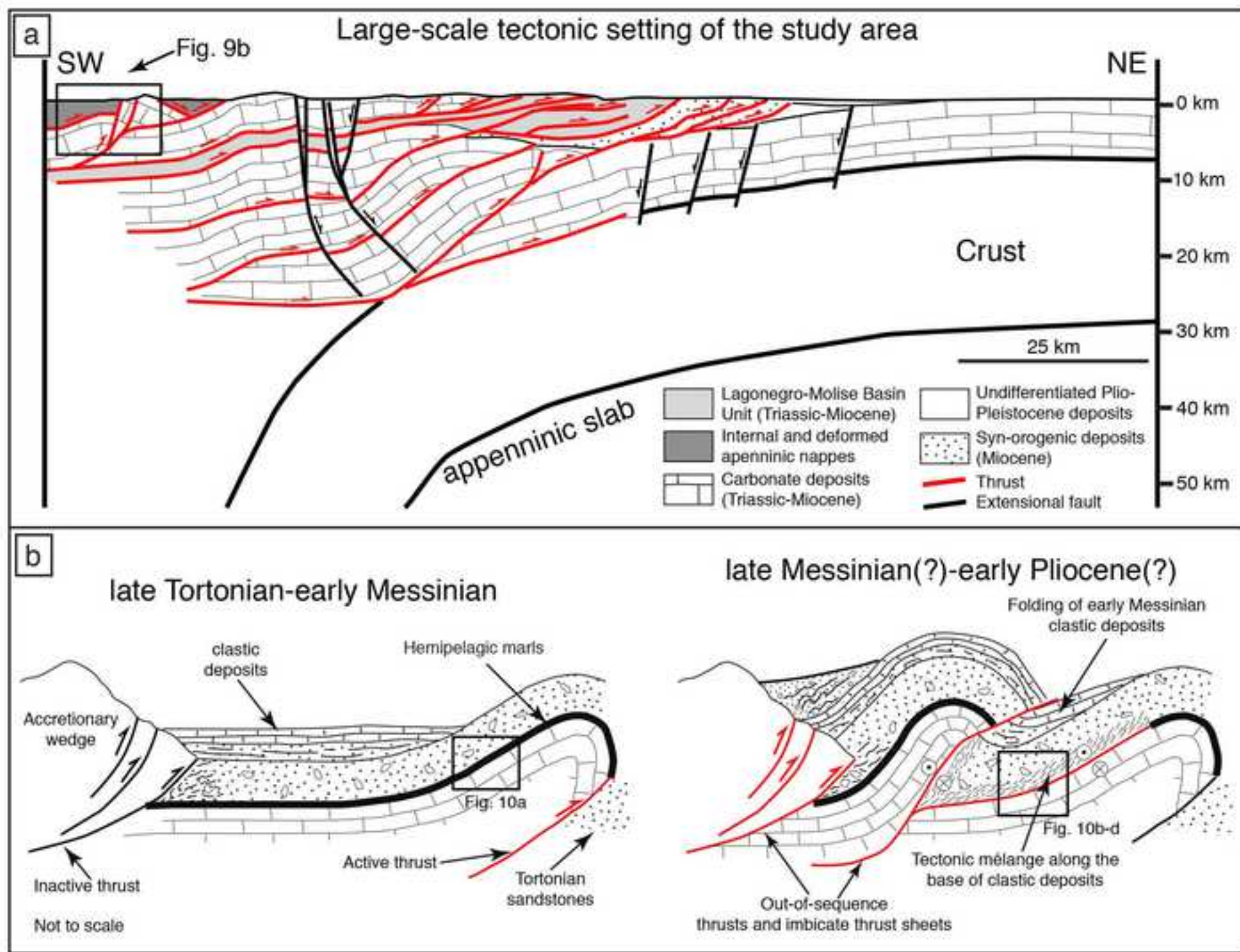
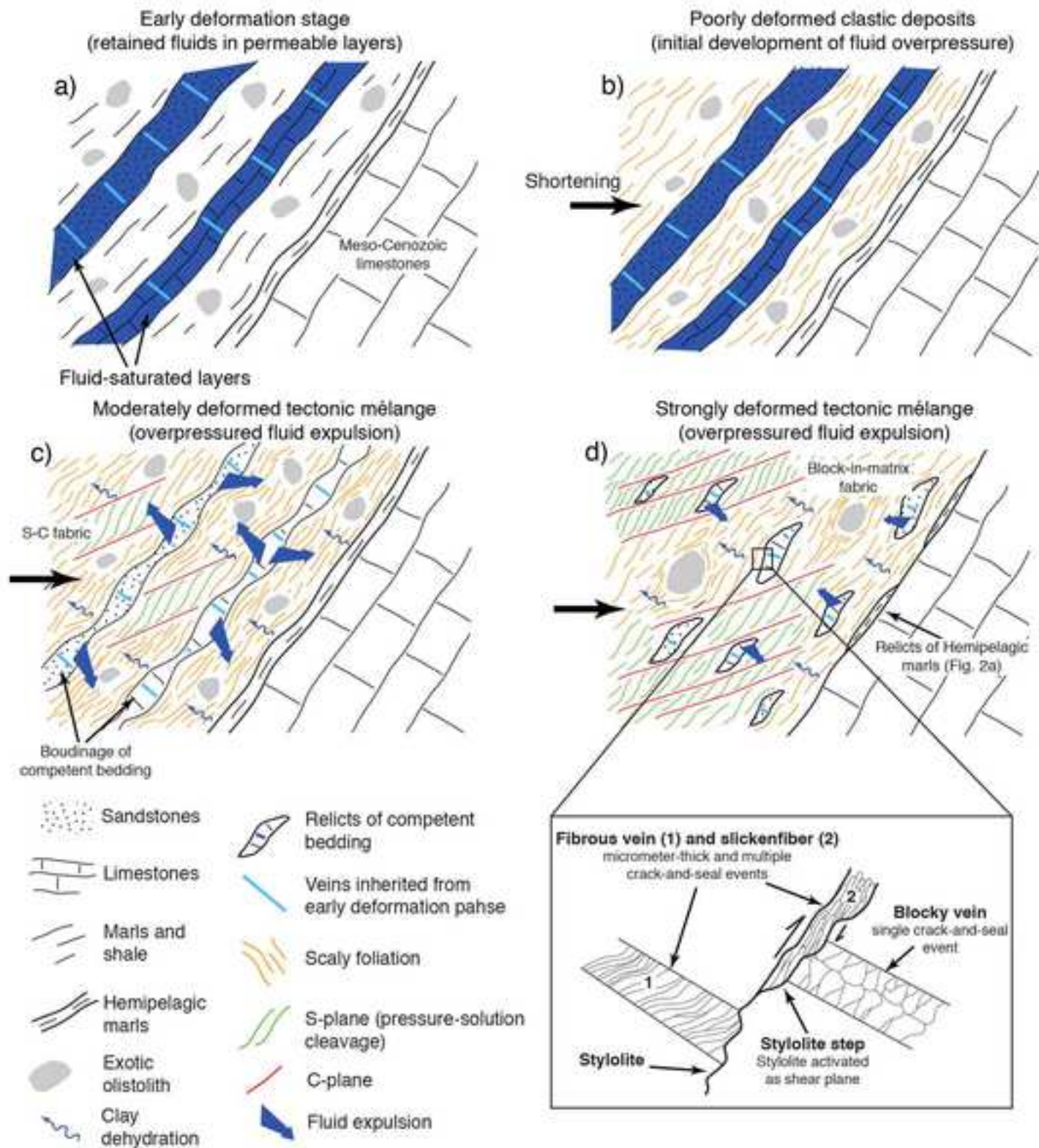


Figure 10
[Click here to download high resolution image](#)



Supplementary material for online publication only

[Click here to download Supplementary material for online publication only: Table S1.docx](#)

Supplementary material for online publication only

[Click here to download Supplementary material for online publication only: Table S2.docx](#)

Supplementary material for online publication only

[Click here to download Supplementary material for online publication only: Table S3.docx](#)

Supplementary material for online publication only

[Click here to download Supplementary material for online publication only: Table S4.docx](#)

Supplementary material for online publication only

[Click here to download Supplementary material for online publication only: Smeraglia Fig. S1.jpg](#)

Supplementary material for online publication only

[Click here to download Supplementary material for online publication only: Smeraglia Fig. S2.jpg](#)

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: