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# Middle Pleistocene fluid infiltration with 10-15 ka recurrence 1 within the seismic cycle of the active Monte Morrone Fault 2 System (central Apennines, Italy) 3 4 Gianluca Vignaroli<sup>1,\*</sup>, Federico Rossetti<sup>2</sup>, Lorenzo Petracchini<sup>3</sup>, Valentina 5 Argante<sup>2,4</sup>, Stefano M. Bernasconi<sup>5</sup>, Mauro Brilli<sup>3</sup>, Francesca Giustini<sup>3</sup>, Tsai-6 Luen Yu<sup>6</sup>, Chuan-Chou Shen<sup>7,8</sup>, Michele Soligo<sup>2</sup> 7 8 1 Dipartimento di Scienze Biologiche, Geologiche e Ambientali - Università degli Studi di Bologna, 9 Bologna, Italy (gianluca.vignaroli@unibo.it) 10 11 2 Dipartimento di Scienze - Università degli Studi di Roma Tre, Roma, Italy 3 Istituto di Geologia Ambientale e Geoingegneria - Consiglio Nazionale delle Ricerche, Roma, Italy 12 4 Leibniz Institute for Applied Geophysics, Stilleweg 2, 30655 Hannover, Germany 13 5 ETH Zürich, Geological Institute, 8092 Zürich, Switzerland 14 15 6 Marine Industry and Engineering Research Center, National Academy of Marine Research, Kaohsiung 16 80661, Taiwan, ROC 17 7 High-Precision Mass Spectrometry and Environment Change Laboratory (HISPEC), Department of 18 Geosciences, National Taiwan University, Taipei 10617, Taiwan, ROC 8 Research Center for Future Earth, National Taiwan University, Taipei 10617, Taiwan, ROC 19 20 21 22 23 24

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### 32 Abstract

This study integrates field, geochronological and geochemical data to constrain fluid 33 circulation in the damage and core zone of the seismogenic Monte Morrone Fault System (MMFS), 34 central Apennines (Italy). Faulting along the MMFS evolved from a diffuse deformation at the 35 36 damage zone towards progressive localisation of a narrower fault core and, finally, to (re)activation of discrete slip surfaces at shallower crustal conditions. Multiple generations of carbonate 37 mineralisations, including veins and slickfibers, occur along the main fault surfaces. Carbonate 38 mineralisations are locally fractured and incorporated in the surrounding cataclasites, documenting 39 40 repetitive structurally-controlled fluid infiltration during transient episodes of permeability creation and destruction. Stable carbon and oxygen isotopes of the carbonate mineralisations document a 41 42 dominant meteoric water source probably mixed with deeper circulating waters having longer residence time. Clumped-isotope yield formation temperatures of vein and slickenfibers in the range 43 44 between 23 and 40 °C. U-Th dating of carbonate mineralisations yield Middle Pleistocene ages (from 45 268 to 189 ka BP), with a 10-15-ka cyclicity that we link to the coseismic rejuvenation of the structural permeability in the fault zone. We propose that fault-related mineralisations recorded the 46 interactions among tectonic deformation and climate during the Quaternary. Our study is the first 47 documentation of fault-controlled recurrence intervals in fluid infiltration in a seismically active fault 48 of central Apennines. 49

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- 51 **Keywords:** Normal faulting, Mineralising fluid, Seismic cycle, U-Th carbonate dating, Monte
- 52 Morrone Fault, central Apennines.

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### 54 **1. Introduction**

In the upper seismogenic crust, the growth of major faults includes creation/destruction of 55 secondary permeability involving deformation and fluid pressure fluctuations in response to a 56 continuous stress accumulation throughout the entire seismic cycle (e.g., Sibson, 1992; 2014; 57 58 Hickman et al., 1995; Miller et al., 2004; Smeraglia et al., 2016; Fig. 1). The relationship between creation/destruction of secondary permeability in fault rocks and pulses of fluid ingress are sensitive 59 gauges of crustal deformation, with implication on location and recurrence intervals of earthquakes. 60 During the coseismic rupture, cataclastic processes and fracturing rejuvenate the internal 61 architecture of the fault in response to heterogeneous strain localisation during fault growth and 62 propagation (Sibson, 1992; Tesei et al., 2013; Delle Piane et al., 2017 and references therein). 63 64 Structural permeability increases depending on fracture persistency, interconnectivity, and geometry, allowing enhanced fluid ingress in fault rocks (e.g., Caine et al., 1996; Rowland and 65 66 Sibson, 2004; Cox, 2010; Sibson, 2014; Williams et al., 2015). Fluids migrate through the secondary permeability in hydrostatic condition if fault permeability is maintained by cycles of 67 coseismic failures (e.g., Sibson and Rowland, 2003). In the interseismic/postseismic stage, mineral 68 precipitation from circulating fluids progressively seals the fault zone permeability (e.g., Cox, 69 2010). This mechanism of permeability destruction sets the ground for the subsequent 70 suprahydrostatic pressure build up, which may enhance coseismic failure at seismogenic depths and 71 activation/reactivation of slip surfaces at shallower depths (e.g., Cox et al., 2001; Sibson, 2014; 72 Smeraglia et al., 2016). Consequently, cycles of permeability creation and destruction characterise 73 74 the fault zone evolution during the different stages of a seismic cycle, and the study of fluid 75 circulation is, therefore, key to reconstruct the space-time distribution and evolution of fault permeability (Caine et al., 1996; Sibson and Rowland, 2003). In particular, the geochemical 76 77 properties of the fluids infiltrating along structurally controlled pathway (faults and fractures) 78 provide constraints on the scale and types of fluid circulation. The absolute ages of different 79 generations of sealing mineralisations provide the timing of the fault activation/reactivation episodes. Reconstructing fault/host rock fluid interactions contributes to refine the recurrence model 80 81 of seismic failure during the geological history of major fault systems.

The seismotectonic framework of the central Apennines is controlled by distributed
extensional faulting (e.g., Cello et al., 1997; Galli et al., 2008; Faure Walker et al., 2010; Iezzi et al.,
2019). Fault activity is typified by a continuous interaction and feedback between fault
(re)activation and fluid migration during the complete seismic cycle (e.g., Smith et al., 2011;
Collettini et al., 2013; Doglioni et al., 2014; Smeraglia et al., 2016; 2018; Barberio et al., 2017).
Presently, instrumental (ISIDe database; http://terremoti.ingv.it/en/iside), historical (Rovida et al.,

2020; https://emidius.mi.ingv.it/CPTI15-DBMI15/index\_en.htm) and paleoseismological (e.g.,
Galli et al., 2008 and references therein) datasets can help reconstruct activity and recurrence
intervals of seismogenic faults through the entire Holocene. Very few studies, however, provide
geological and geochronological constraints on the long-term tectonic activity of seismically active
normal faults. In this view, the occurrence of distinctive fabrics and mineralisations in faults has
been used to identify the relative chronological sequence of Quaternary deformation events during
the interseismic and the coseismic stages (Smeraglia et al., 2018; Vignaroli et al., 2020a).

95 In this study, we describe the structural relationships between tectonic structures and fluid 96 infiltration within the Monte Morrone Fault System (MMFS), an outstanding example of active extensional faulting in the central Apennines (Fig. 2a,b). The MMFS consists of NW-SE-striking 97 98 normal fault strands, cutting across Pleistocene-to-Holocene continental deposits (Miccadei et al., 99 1998; Galadini and Galli, 2000; Gori et al., 2011). The trace of the MMFS corresponds to a regional-scale seismic gap with respect to the 2009 Mw 6.1 L'Aquila and the 2016-2017 Mw 6.0-100 101 6.5 Amatrice-Norcia earthquakes, the last destructive seismic sequences in central Italy (e.g., Chiarabba et al., 2009; Chiaraluce et al., 2017). We document multiple generations of syn-tectonic 102 carbonate mineralisations within the damage and core zone of the MMFS. We constrained the 103 meso- and micro-scale structural properties, the  $\delta^{13}$ C and  $\delta^{18}$ O and clumped isotope signature, and 104 the U-Th ages of these carbonate mineralisations to reconstruct the fault-fluid interplay and its 105 spatio-temporal evolution during the different stages of the seismic cycle. In particular, by dating 106 the fault-related mineralisations, we fixed the absolute ages of the MMFS activation episodes. 107 Finally, we propose a conceptual model of recurrence intervals of Middle Pleistocene fluid 108 109 infiltration and fault interaction during the seismic cycle of the MMFS. This study could set the ground for establishing a seismic recurrence model on regional-scale faults within the seismically 110 111 active tectonic setting of the central Apennines.

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# 114 **2.** Geological Setting

### 115 **2.1.** The central Apennines

The central Apennines (Fig. 2a,b) is a roughly NW-SE-trending orogenic segment originated
from the Cenozoic oceanic subduction and subsequent continental collision between the European
and the Adria plates (e.g., Dewey et al., 1989; Boccaletti et al., 1990; Faccenna et al., 2001;
Carminati et al., 2010). The resulting fold-and-thrust belt (Fig. 2b) deformed rocks belonging to

120 different paleogeographic domains, including (a) limestones and dolostones of Mesozoic platforms-

- 121 to-basin environments, and (b) flysch sediments of Tortonian-to-Pliocene foredeep basins (e.g.,
- 122 Vezzani et al., 2010; Cosentino et al., 2010). Crustal shortening operated through the activation of
- 123 west-dipping, regional-scale thrusts in a general eastward migration of compressive fronts toward
- the Adriatic foreland (e.g., Barchi et al., 1998; Patacca et al., 2008).

The present-day structural setting of the central Apennines results from the progressive 125 uplift of the early stacked units followed by extensional tectonics since the Pliocene. This post-126 orogenic phase has started from the hinterland (Tyrrhenian) side of the belt and migrated towards 127 the foreland, generating mainly NW-SE-striking normal faults and the formation of large 128 intermountain basins filled by transitional-to-continental Plio-Quaternary deposits (e.g., Malinverno 129 and Ryan, 1986; Dewey, 1988; Martini and Sagri, 1993; Faccenna et al., 1997; Cavinato and 130 DeCelles, 1999; Cavinato et al., 2002; Cosentino et al., 2017). Crustal thinning generated a complex 131 132 network of major extensional faults arranged in both en-echelon and collinear geometry (e.g., Ghisetti and Vezzani, 2002; Galadini and Messina, 2004; Roberts and Michetti, 2004; Pizzi et al., 133 134 2017; Galli et al., 2019; Fig. 2b). The major normal faults extend to a depth of 10–15 km, with dip  $\geq$  45°. Intermountain basins, mostly filled by continental deposits, often develop at the hanging wall 135 of the master faults, whereas Mesozoic carbonates are exposed at their footwall, indicating 136 kilometre-scale down-section stratigraphic displacements (e.g., Boncio et al., 2004; Roberts and 137 Michetti, 2004; Galli et al., 2008; Lanari et al., 2021). The estimated Holocene throw rate for the 138 major normal faults ranges from 0.3 to ~2 mm/yr (Roberts and Michetti, 2004; Cowie et al., 2017). 139

NW-SE-striking normal faults control the intense seismicity in the axial part of the central 140 Apennines, as testified by both the historical (Rovida et al., 2020) and the recent and destructive 141 events (the 1997 Colfiorito event, Mw 6.0; the 2009 L'Aquila event, Mw 6.1; the 2016-2017 142 Amatrice-Norcia sequence, Mw up to 6.5; Fig. 2b). Seismicity remains confined in the uppermost 143 10-12 km crustal section (Amato et al., 1998; Chiaraluce et al., 2017). Studies on fault slip rates 144 145 (Roberts and Michetti, 2004; Faure Walker et al., 2010), paleoseismology (Galli et al., 2008; Galli et al., 2018; 2019) and global-positioning system (D'Agostino et al., 2011) confirm that the major 146 normal faults are the locus of active deformation localisation at short- and long-term scales (up to 147  $10^4$  years). For the active normal faults, a 1-2 ka recurrence time for Mw > 6.5 earthquakes has been 148 149 estimated based on paleoseimological constraints (Galli et al., 2008). Recent U-series ages for syn-150 tectonic mineralisations constrained the long-term activity in potentially-seismogenic structures of the central Apennines in the ~350-108 ka time interval (Smeraglia et al., 2018; Vignaroli et al., 151 2020a). 152

The fluid-assisted deformation in the central Apennines has been documented in faulted 153 carbonate and siliciclastic units through the analysis of syn-tectonic mineralisations (e.g., Maiorani 154 et al., 1992; Conti et al., 2001; Ghisetti et al., 2001; Agosta et al., 2008; Smeraglia et al., 2016; 155 2018; Vignaroli et al., 2020a; Curzi et al., 2021; Coppola et al., 2021). Most syn-tectonic 156 mineralisations preserve the geochemical signature of cold-water circulation at shallow depths, 157 suggesting a dominant meteoric/groundwater fluid circulation. It is noteworthy, that earthquake-158 related fluid circulation is characterised by the interplay between transient permeability at the fault 159 damage zones and mixing of fluids from different reservoirs, in part also of deeper origin 160 161 (Smeraglia et al., 2018).

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# 3 2.2. The Monte Morrone Fault System

164 The MMFS consists of NW-SE-striking fault segments with an along-strike cumulative length of ~25 km (e.g., Miccadei et al., 2002; Gori et al., 2011; Fig. 2c). The MMFS runs sub-165 166 parallel and cuts across the SW-dipping, back-limb of the NW-SE-trending Monte Morrone anticline, developed at the hanging wall of E-verging thrust sheets (e.g., Vezzani et al., 2010). 167 168 Thrusting involved a Mesozoic-Cenozoic basinal succession of limestones and marls evolving to platform carbonates. Seismic profiles suggest that the MMFS penetrates the crust to a depth of 10-169 170 12 km, accommodating more than 2 km of cumulative movement during the Pleistocene-Holocene 171 (Patacca et al., 2008). Subsidence at the hanging wall of the MMFS provided the space for sedimentation of several hundred metres of alluvial-fluvial-lacustrine sediments that fill the 172 intermountain Sulmona Basin (e.g., Miccadei et al., 1998; Giaccio et al., 2009; Fig. 2d). In the 173 Sulmona Basin, the eastward dip and the fan geometry of the strata attest for syn-tectonic deposition 174 during normal-sense movement of the MMFS (e.g., Miccadei et al., 1998; Gori et al., 2011). Based 175 on geomorphic expressions and geological correlations, the Holocene slip rate of the MMFS has 176 been estimated to be between 0.4 and 1.1 mm/yr (Roberts and Michetti, 2004; Gori et al., 2011). 177

The MMFS developed through propagation and interaction of two parallel west-dipping 178 179 fault strands: the western fault system (WFS) and the eastern fault system (EFS) (Galadini and Messina, 2004; Boncio et al., 2012; Gori et al., 2014). The WFS runs through the Roccacasale 180 181 village and extends from the Popoli village in the NW to the Pacentro village in the SE (Fig. 2c). 182 This strand consists of a complex network of NW-SE-striking (SW-dipping) fault segments 183 arranged in collinear and, subordinate, right-stepping en-echelon geometry. The exposure of the 184 WFS fault scarps near Roccacasale reveals almost planar and striated surfaces (Boncio et al., 2012) 185 covering an up to half a metre-thick fault core developed through multiple events of fabric

186 formation and rejuvenation in response to cyclic stress accumulation and dissipation (Ferraro et al.,

- 187 2018; 2019; Coppola et al., 2021). Occurrence of different cemented fault rocks, from matrix-
- supported to grain-supported (Ferraro et al., 2018), and multiple microcrystalline calcite cement in
- 189 cataclastic-to-ultracataclastic layers (Ferraro et al., 2019; Coppola et al., 2021) suggests a co-
- seismic fabric reworking during fluid-assisted deformation.
- No major (i.e. Mw > 4) historical earthquakes are associated with the MMFS (Rovida et al., 191 2020). The seismic source of the catastrophic 1706 event that hit the Sulmona Basin is still debated 192 (Galli et al., 2015) and possibly located around the adjacent Majella ridge (Fig. 2b). However, 193 archaeoseismic and paleoseismic constraints set the elapsed time for the MMFS since the last event 194 at  $\sim$ 1850 yr ago, which is compatible with the average recurrence time of the Apennine 195 seismogenic faults (Galadini and Galli, 2001; Galli et al., 2015). Barberio et al. (2017) monitored 196 197 several springs located within the Sulmona Basin and associated their hydrochemical variation to the mainshocks of the 2016-2017 Amatrice-Norcia sequence. This hydrogeological setting suggests 198 199 an active structural permeability in the Monte Morrone area, potentially sensitive to seismic inputs.
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### **3. Materials and Methods**

Through the study of fault strands exposed near the Roccacasale village, we focused on the structural permeability of the WFS by characterising its brittle structural architecture and the associated fault-related carbonate mineralisations (see structural stops in Fig. 2e). Field criteria for fault rock classification (e.g., Sibson, 1977; Braathen et al., 2004) have been used to identify and characterise the fault structural fabrics, whereas classic kinematic criteria have been used to determine the sense of shear (e.g., Petit, 1987).

We collected hand samples of fault rocks and carbonate mineralisation (Table 1). Optical 209 and back-scattered electron (BSE) microscopy was performed on oriented thin sections to 210 characterise the overprinting relationships among different generations of structures and carbonate 211 mineralisations that took place during faulting. Cold cathodoluminescence (CL) imaging were 212 performed using a Cambridge Image Technology Limited luminoscope Leica DM2700P optical 213 microscope (model Mk5-2; operating system at 9.9 kV with a beam current of 256 µA) at the 214 Department of Chemistry, Life Sciences, and Environmental Sustainability of the University of 215 Parma. 216

U-Th dating was carried out on (1) a Thermo Electron Neptune multi-collector inductively 217 coupled mass spectrometer (MC-ICP-MS) (Shen et al., 2012) at the High-Precision Mass 218 Spectrometry and Environment Change Laboratory (HISPEC), National Taiwan University, and (2) 219 on α-spectrometer at the Laboratory of Environmental and Isotopic Geochemistry, Department of 220 221 Sciences, Roma Tre University, Italy. For MC-ICP-MS dating, we covered about 0.05 g of each sample with H<sub>2</sub>O and dissolved it gradually with double distilled 14 N HNO<sub>3</sub>. After dissolution, we 222 added a  $^{229}$ Th $^{-233}$ U $^{-236}$ U spike (Shen et al., 2003) to the sample, followed by 10 drops of HClO<sub>4</sub> to 223 decompose organic matter. We followed the chemical procedure described in Shen et al. (2003) for 224 225 the separation of uranium and thorium. Detailed instrumental analysis is given in Shen et al. (2012). Age correction was calculated using an estimated atomic  ${}^{230}$ Th/ ${}^{232}$ Th ratio of 4±2 x 10<sup>-6</sup>. The value 226 is the one typical for a material at secular equilibrium with the crustal <sup>232</sup>Th/<sup>238</sup>U value of 3.8 and an 227 arbitrarily assumed 50% error. Half-lives of U-Th nuclides used for age calculation with 2-sigma 228 229 uncertainty are from Cheng et al. (2013). For  $\alpha$ -spectrometry dating, samples were cut with a diamond saw and ultrasonically washed in deionized water. About 60 g of each prepared sample 230 231 were thus dissolved in 7 N HNO<sub>3</sub> and filtered to separate leachates from insoluble residue. The leachates were heated to 200 °C after adding a few millilitres of hydrogen peroxide to annihilate 232 organic matter, then spiked with a <sup>228</sup>Th/<sup>232</sup>U tracer. U and Th were extracted according to Edwards 233 et al. (1987), then analysed through alpha-counting using high-resolution ion-implanted Ortec 234 silicon-surface barrier detectors. For samples with a <sup>230</sup>Th/<sup>232</sup>Th activity ratio higher than 80 (with 235 insignificant non-radiogenic <sup>230</sup>Th), ages were determined using the measured <sup>230</sup>Th/<sup>234</sup>U and 236 <sup>234</sup>U/<sup>238</sup>U activity ratio. Sample ages characterized by a <sup>230</sup>Th/<sup>232</sup>Th activity ratio less than or equal 237 to 80 indicating the presence of non-radiogenic (detrital)<sup>230</sup>Th required a correction based on the 238 assumption of an average  $^{230}$ Th/ $^{232}$ Th activity ratio of 0.85 ± 0.36 for all detrital Th (Wedepohl, 239 240 1995). All ages were finally calculated using ISOPLOT (Ludwig, 2003) with errors expressed as ±1σ. 241

242 Samples for geochemical analysis were obtained by micro-drilling. Carbon and oxygen isotope analyses of 50 samples from the WFS (Table A1) were carried out at the Istituto di Geologia 243 244 Ambientale e Geoingegneria of the Consiglio Nazionale delle Ricerche (Rome, Italy), by acid digestion at 72°C using a Thermo Fisher Scientific Gasbench II coupled to a Delta+ mass 245 spectrometer. Approximately 120 µg of powder was weighted in duplicate. Standardisation to the 246 V-PDB scale was accomplished with three internal standards MC-200, CaCO<sub>3</sub> (Merck CCM) and 247 Solnhofen limestone (SLNF) calibrated against the international references NBS18 and NBS19. 248 Oxygen and carbon isotopes are reported with respect to the Vienna Pee Dee Belemnite standard 249 (V-PDB). 250

The clumped isotope compositions of the carbonates were determined at ETH Zürich using a 251 252 Thermo Fisher Scientific 253Plus mass spectrometer coupled to a Kiel IV carbonate preparation device, following the method described in Schmid and Bernasconi (2010), Meckler et al. (2014), 253 and Müller et al. (2017). The Kiel IV device included a PoraPakQ trap kept at - 40°C to eliminate 254 potential organic contaminants. Prior to each sample run, the pressure-dependent backgrounds were 255 determined on all beams to correct for non-linearity effects in the mass spectrometer according to 256 Bernasconi et al. (2013). During each run, 20 replicates of 100-120 µg of different samples and 5 257 replicates of each of the two carbonate standards ETH-1, ETH-2, and 10 of ETH-3 were analysed in 258 259 LIDI mode. Data processing was carried out with the software Easotope (John and Bowen, 2016) using the IUPAC parameters for 17O correction as suggested by Daeron et al. (2016). The data are 260 261 reported in the Intercarb Carbon dioxide equilibration scale (I-CDES) (Bernasconi et al. 2021) and the temperatures of formation were calculated with the Anderson et al. (2021) calibration. The 262 oxygen isotopic composition ( $\delta^{18}O_{\text{fluid}}$ ) of the fluids was calculated using the calibration of Kim and 263 O'Neil (1997). 264

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### 267 **4. Results**

# 268 *4.1. Outcrop scale structures*

269 Near Roccacasale (Fig. 2e), the WFS cuts through a sequence of Sinemurian dolomitised limestones. There, the WFS consists of multiple NW-SE-striking fault strands dipping moderately 270 (30°-50°) to SW, typically associated with dm-to-m-thick damage zones (Fig. 3a). The main slip 271 surface, which accommodates the most important offset, commonly show a planar morphology and 272 hosts slickenlines, provided by abrasion striae and rare calcite fibres (Fig. 3b). Slickenlines show 273 274 pitch values generally around 80° and 100° (Fig. 3b), indicative of nearly pure dip-slip kinematics. Stratigraphic offset, synthetic shears, dragging of the bedding at the fault surfaces, and calcite 275 fibres indicate normal-sense movement. 276

The main slip surface is associated with a metre-thick damage zone and dm-thick fault core at the footwall (Fig. 3c,d; see also Ferraro et al., 2018). The damage zone is characterised by dmthick lenses of either massive or foliated cataclasite (Fig. 3e). Cataclasites wrap around dm-to-half metre-thick lithons of almost undeformed limestone. The boundaries between the cataclasite lenses are commonly marked by mm-thick, subsidiary fault zones, synthetic to the main slip surface (Fig. 3e). Massive cataclasites are characterised by matrix-clast proportion >50% and clasts are subangular to sub-rounded and up to 1 cm-wide. Foliated cataclasites are characterised by faint layers with different grain size. Approaching the main slip surfaces, matrix becomes extremely dominant
and defines centimetre-thick layers of ultra-cataclasite (Fig. 3e; see also Coppola et al., 2021).

High angle (dip > 55°; insert in Fig. 3a) faults have been mostly observed at the hanging
wall of the main slip surface (Fig. 4a-c). These fault strands are characterised by roughly planar slip
surfaces (in section view) dipping to the W-WSW (Fig. 4a,b). The high-angle faults systematically
cut and displace the main slip surface, producing centimetre-to-decimetre down-dip offsets and
incipient rigid fault block rotation (Fig. 4b,c). They are commonly accompanied by sets of faultparallel joints and lenses of proto-cataclasites, defining centimetre-thick damage zones.

292 Carbonate mineralisations occur on the main slip surfaces and on the high-angle normal faults (Fig. 4d-h). The main mineralisation is up to 10 cm-thick and consists of a layered calcite, 293 294 found in the immediate hanging wall of the main slip surface (Fig. 4c,d). In section view, layering is 295 dominantly plane-parallel, although thickness variations from few centimetres up to 15 cm, and pinch-out geometry on older strata can be locally recognised (Fig. 4e,f). When associated with high-296 angle faults, carbonate mineralisations consist of up to one cm-thick layers of fine grained calcite 297 lying atop striated surfaces (Fig. 4g,h). Layering in these mineralisations is mm-thick, dominantly 298 plane and parallel to the fault surfaces. 299

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### 301 4.2. Meso- to micro-scale structures

The mineralisations consist of the rhythmic layering of mm-thick laminae and sparitic veins 302 (Figs. 5a,b and SM1a-e). The laminae, which often appears as alabaster-like translucent deposit of 303 fine-grained and massive calcite, are fault-parallel and often characterised by variation in thickness 304 and marked by change in colour from whitish to light brown (Figs. 5a and SM1a,d). Layers of fine-305 306 grained calcite are locally intercalated by mm-to-cm-thick pockets of sedimentary breccias, 307 probably filling voids of karst origin. The fabric of the breccia consists of a chaotic distribution of up to 1-cm large limestone clasts (i.e., protolith) mixed with other carbonate fragments deriving 308 from the previous cataclasite (Fig. 5a). The sparitic veins are up to one cm-thick, poorly- to non-309 310 porous and are disposed parallel to the fault surface (Figs. 5a,b; SM1a,b,e). Macroscopically, veins show fan-shaped morphology of elongated crystals, which provides unequivocal evidence on the 311 312 growth direction.

At the microscale, cataclasites show sub-rounded clasts, with increasing roundness associated with decreasing particle size (Figs. 5d-f and 6a). The main structural characteristics are: (i) sub-angular clasts fragmented at their edges and clasts showing internal set of polygonal fractures (Fig. 5e,f, 6a,b,d, SM2a-c,g); (ii) truncated clasts by sharp slip surfaces (Fig. 6c); (iii)

- traces of permeating fluid within the fine-grained matrix and mantling the carbonate clasts (Fig.
- 6d); (iv) sigmoidal foliation in proximity of the main slip surfaces (Figs. 5d; SM2d; SM3l,m).
- 319 Cathodoluminescence analysis reveals that the convolute structures are characterised by an overall
- bright-purple colour, distinctively brighter than the calcite of both the fine-grained matrix and the
- 321 clasts (Fig. 6e).

Carbonate laminae and sparitic veins grew from a slip surface that truncates the cataclasite 322 (Figs. 6f, SM2a-f, SM3). While the laminae are characterised by fine-grained, dirty calcite mixed 323 324 with clay particles (Fig. 6j), the sparitic veins show an internal fibrous texture with crystal growth direction roughly perpendicular to the vein wall (Fig. 6f). The calcite crystal tends to form vein-325 326 normal elongated fan-shaped patterns, which are indicative of the vein growth direction and sense. We observed both downward and upward growth patterns, with crystal that converge toward the 327 328 medial line of the veins, documenting a general syntaxial grow mechanism (Fig. 6f,k; SM3d,g). 329 Cathodoluminescence shows that this calcite is characterised by dull brown/black colour, 330 particularly darker than the calcite occurring within the cataclasite (Fig. 6g).

The mineralisations are locally reworked by fracturing and cataclasis to form new clasts 331 (Figs. 6h,i; SM2c-e; SM3h-m). They are affected by micro-joints producing micrometer 332 333 displacements or display deformation including sigmoidal foliation-like structure embedded in minor slip surfaces (Fig. SM2d; SM31,m). Reworked mineralisations are often surrounded by 334 secondary micro-crystalline calcite cements with a purple cathodoluminescence like the calcite in 335 the fine-grained matrix. Strips of protocataclasites are locally preserved or bracketed within 336 multiple generations of mineralisations (Fig. 6j,k). Bands parallel to the slip surface and formed by 337 cataclasites alternating with highly fractured mineralisations are observed within veins and laminae 338 339 (Fig. SM3). The boundaries between cataclasites and mineralisation are often represented by slip surfaces or extensional fractures (Figs. 5a,c; SM2c-f) and some mineralisations are flattened and 340 341 truncated along the slip surface (Fig. SM3f,g).

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### 343 4.3. U-Th geochronology

We dated calcites from nine mineralisations (Table 2). Dated samples are characterised by a roughly homogeneous  $^{230}$ Th/ $^{238}$ U activity ratio (between 0.87 and 0.93) and a highly variable  $^{230}$ Th/ $^{232}$ Th activity ratio (between 243.2 ± 2.5 and 18969 ± 315) (Table 2). Collectively, samples dated by the MC-ICP-MS method (samples M4G, M4H, M4H2, M4HW, M4F1, M4i) show ages between 190 and 270 ka, with  $2\sigma$  errors < 7 ka. The sample dated by α-spectrometry (sample M4e) shows a mean age of 178 ka and larger  $1\sigma$  error of +39 and -30 ka.

In the following, we detail the obtained ages with respect to the structural site of the 350 selected sample at the studied outcrop (Figs. 5, 7 and SM1). The oldest age  $(267.9 \pm 6.1 \text{ ka})$  has 351 352 been obtained from sample M4H, which is a carbonate mineralisation collected from the main slip surface. Three progressively younger ages ( $257.4 \pm 4.3$  ka;  $246.6 \pm 2.5$  ka;  $230.3 \pm 2.0$  ka) have 353 354 been obtained from three generations of calcite of sample M4G (bottom-to-top: M4G3, M4G2, M4G1, respectively), a dm-thick mineralisation collected along the main slip surface (Fig. 5a). 355 356 Sample M4e (178 +39/-30 ka) has been also collected from the same main slip surface of M4G. A cluster of similar ages have been obtained from samples M4H2 (218.3  $\pm$  3.7 ka), M4HW (215.8  $\pm$ 357 358 6.7 ka), and M4F1 (214.9  $\pm$  2.1 ka). Sample M4H2 is from the lower part of the M4H mineralisation; sample M4F1 are from the upward portion of the M4G mineralisation; sample 359 360 M4HW is from the top of the sample M4e. Finally, the youngest age (189.4  $\pm$  2.5 ka) has been 361 obtained from sample M4i, from a high angle normal fault crosscutting the main fault plane (Fig. 7). 362

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# 4.4. Stable carbon and oxygen and clumped isotopes

365 The analysed samples (carbonate clast in cataclasite, fine-grained matrix in cataclasite, sedimentary breccias embedded within the mineralisation, and carbonate mineralisations deposited 366 on fault surfaces) can be grouped in different endmembers showing distinct isotope signatures (Fig. 367 8). The clasts in cataclasites are characterised by  $\delta^{13}$ C ranging from 1.40‰ and 2.38‰ and  $\delta^{18}$ O 368 between -0.43‰ and -1.32‰ typical of marine limestones. Three samples of the fine-grained 369 cataclasite matrix are characterised by  $\delta^{13}$ C between 0.61‰ and 0.19‰ and  $\delta^{18}$ O between -1.83‰ 370 and -2.08‰ whereas one has much more negative  $\delta^{18}$ O (-9.04‰) and  $\delta^{13}$ C (-8.67‰). Two samples 371 of sedimentary breccias are characterised by negative  $\delta^{18}$ O between -3.04‰ and -3.33‰ and  $\delta^{13}$ C 372 373 between -1.13‰ and -1.35‰. Finally, the samples of carbonate mineralisations are characterised by negative values of both  $\delta^{18}$ O (between -7.37‰ and -11.65‰) and  $\delta^{13}$ C (between -7.14‰ and -374 10.46‰). 375

Clumped-isotope data from 6 carbonate mineralisations yield  $\Delta 47$  values in a narrow range between 0.552‰ and 0.600‰ (I-CDES) (Table A2). These values correspond to temperatures between 40 ±7 °C and 23 ±4 °C. Calcite from M4G mineralisations dated between ~257 and ~230 ka (samples M4G\_1b; M4G\_1e; M4G\_2a; M4G\_2b; M4G\_3c) precipitated at ~24-28 °C (95% confidence level between ±3 and ±9 °C). Calcite from younger M4F1 mineralisation (dated at  $\sim 215$ ) precipitated at 40±11 °C (sample M4F1\_2). Finally, a cataclasite (samples M4G\_5N) and the host rock clast (M4HW\_1N) yielded temperatures of 41-45 °C (±7 °C, 95% confidence level).

The calculated  $\delta^{18}$ O of the fluids from the 6 mineralisation samples range from -9.3 to -3 ‰ (VSMOW) reflecting a dominant meteoric water signal. The calculated fluids for the cataclasite and host rock clast reflect a combination of the original marine carbonate components and the composition of the fluids during burial diagenesis, and are not relevant for the further discussion of the vein fluids.

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### 390 **5. Discussion**

### 391 *5.1. Structural interpretation*

Previous structural studies of the MMFS documented fault rock heterogeneities (inner fault 392 core, outer fault core, damage zones, principal slip surfaces) developed via multiple deformation 393 phases of the Meso-Cenozoic carbonate bedrocks (Ferraro et al., 2018; 2019). Intense shear strain 394 localisation occurred along fluid-assisted co-seismic ultracataclastic layers (Coppola et al., 2021). 395 By integrating the insights from these studies with our data, we refine our understanding of the 396 structural permeability along the MMFS (Fig. 9a), which is governed by a continuous interplay 397 between tectonic deformation, fluid circulation and mineralisation. Our meso-to-microscale 398 observation can guide to a scenario of polyphasic permeability evolution from deep to shallow 399 400 conditions (Fig. 9b).

401 The early structural permeability formed in conditions of confined pressure corresponding to 402 the depth from which the main slip surface exhumed (< 3 km; Ghisetti and Vezzani, 2000; Coppola 403 et al., 2021). The early structural permeability (t<sub>n</sub> in Fig. 9b) is controlled by the spatial distribution 404 of structures associated with formation of the damage zone and the fault core at the expense of 405 carbonate bedrock (Fig. 3c,d; Ferraro et al., 2018). The transition from the damage zone to the fault core is attested by a strong grain size reduction and the occurrence of foliated cataclasites, which 406 progressively replace the massive ones in the damage zone proximal to the fault core (Figs. 3e, 4f). 407 Cataclasis is the main deformation mechanism steering significant deformation in the damage zone 408 and the fault core (Fig. 3c-e). Rock comminution and clast roundness in cataclasites is assisted by 409 chipping at the edges of the sub-angular clasts, as well as intergranular fracturing contributes to 410 grain size reduction in larger clasts (Figs. 5, 6a,d, SM2f; Billi, 2010 and references therein). 411 412 Carbonate clasts are commonly truncated by subsidiary slip surfaces and the fine cataclasite matrix

is permeated by fluidised ultra-fine material (Fig. 6c,e). As already argued by Coppola et al. (2021),
we consider these microstructural features as evidence for coseismic rupturing, comparable to
potential seismic markers documented from faulted carbonates within tectonic domains (Hadizadeh,
1994; Smith et al., 2011; Fondriest et al., 2012; Tesei et al., 2013; Smeraglia et al., 2016; Delle

417 Piane et al., 2017).

The subsequent structural permeability ( $t_{n+nx}$  in Fig. 9b) formed at shallower crustal 418 conditions and was connected to the development of sharp, discrete slip surfaces cutting through the 419 420 cataclastic fabric in both the damage zone and the fault core. Ferraro et al. (2018) document matrix-421 supported textures for these slip surfaces, developed in the latest stages of fault exhumation. The main slip surface occurs within the fault core and corresponds to the striated one atop the proximal 422 423 slip zone (of co-seismic origin) of Coppola et al. (2021) (Fig. 9c). This suggests a mechanical scenario of progressive fault narrowing through multiple episodes of fabric reworking and shear 424 425 strain localisation (Smith et al., 2011; Smeraglia et al., 2018; Vignaroli et al., 2020b). The 426 mineralisations are exclusively localised along the main slip surfaces and on the slip surface of the 427 high-angle fault (Fig. 9a), not associated with a system of veins in the damage zone. We propose that the fault surfaces acted as localised, fault-parallel conduits (Caine et al., 1996) and the fluid 428 circulation channelised within the fault core during reactivation and dilatancy of the slip surfaces 429 (Fig. 9b). The combination between faulting and dilatancy during creation of the structural 430 permeability is attested by: (i) carbonate mineralisation within cataclasite in dilatant jog (Fig. 4d); 431 (ii) fan-shaped crystals growth in veins documenting a general syntaxial grow mechanism (Figs. 432 433 6f,k; SM3); (iii) reworked carbonate mineralisations often fractured and cut by slip surfaces (Figs. SM2a-f; SM3a); (iv) carbonate mineralisations incorporated within the underlying cataclasites or 434 embedded as pockets in protocataclasite or breccias (Figs. 5; 6; SM2; SM3); (v) bands parallel to the 435 436 slip surfaces made of protolith cataclasite alternating with highly fractured mineralisations (Fig. SM3); and (vi) sigmoidal foliation-like structure embedded in minor slip surfaces within the 437 438 mineralisations (Figs. SM2d; SM3l,m). The (re)activation of main slip surfaces occurred during the progressive exhumation of the fault core-damage zone formed at deeper structural levels. 439 440 Considering the U-Th age range (between 268 and 189 ka) and the Holocene slip rate estimated for 441 the MMFS (0.4-1.1 mm/yr Roberts and Michetti, 2004; Gori et al., 2011), we obtain depths between 442 60 and 300 m below the present-day outcrop elevation (~450 m a.s.l.) for the development of the shallow structural permeability. In this time-dependent conceptual evolution of the structural 443 444 permeability, the development of the high-angle normal faults crosscutting the main fault core represents the last increment of strain during fault growth and exhumation. 445

#### 447 **5.2.***Fluid circulation*

The structural interpretation can be integrated with the isotope data (Fig. 8; Table A1) to 448 propose a comprehensive time-dependent scenario for fluid circulation during the progressive 449 exhumation of the MMFS and concomitant subsidence of the Sulmona Basin at its hanging wall 450 (e.g., Miccadei et al., 2002; Gori et al., 2011; Galli et al., 2015; Fig. 9d). The protolith carbonate 451 clasts embedded in cataclasites have the highest isotope values, in the range of unaltered Mesozoic 452 marine carbonates from the central Apennines (e.g., Ghisetti et al. 2001; Agosta and Kirschner 453 2003; Smeraglia et al., 2016). The cataclasite matrix, representing the early structural permeability, 454 455 shows more negative isotope values consistent with mixing of marine carbonate particles with calcite precipitated from meteoric waters. As observed in Figure 8, the cataclasites plot on a mixing 456 457 line between the host rock and the mineralisation.

The mineralisations formed within the shallowest structural permeability show typical 458 459 carbon and oxygen isotope signatures of calcite precipitated from meteoric waters that gained a significant contribution of respired organic carbon in the soils. The calculated  $\delta^{18}$ O of the fluids 460 ranges between -3 and -9‰ (VSMOW) and is like the average composition of rainfall (-7 and -9‰) 461 and slightly enriched with respect to the spring water (-8 and -11‰) in the central Apennines 462 (Minissale, 2004). Fluid temperatures (Table A2) range between 23 and 26° C. These temperatures 463 are, except for a mineralisation dated at 215 ka (Fig. SM1d), warmer than those of spring waters 464 found in the Sulmona Basin (6-15 °C; Barberio et al., 2017) and, in general, for cold springs 465 emerging in central Apennines (e.g., Minissale, 2004). Also, the calculated  $\delta^{18}$ O of the fluids are 466 enriched in <sup>18</sup>O with respect to the spring waters in the Sulmona Basin (-10 to -11‰; Barberio et 467 al., 2017). We, therefore, infer that syn-tectonic mineralisations occurring along the MMFS could 468 preserve a minimal component of deeper flow, probably from the deeper circulating waters with 469 470 longer residence time, mixed with the dominant shallow meteoric water circulation. It is noteworthy that the hottest sample at 40° C (M4F1-2; Table A2) yields the least negative calculated  $\delta^{18}$ O of the 471 472 fluids, suggesting a contribution of warmer fluid with a higher oxygen isotope composition resulting from more intense water-rock interaction as observe by Smeraglia et al. (2018) in the Val 473 474 Roveto Fault (see location in Fig. 2a). These temperatures are comparable with the coldest fluid temperatures (between 32 and 75 °C) estimated for syn-tectonic mineralisations in potentially-475 476 seismogenic structures (Smeraglia et al., 2016; 2018) and for tectonically controlled veins in thermogene travertines in central Apennines (e.g., Berardi et al., 2016). 477

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# 479 5.3.Implications for long-term fault history

The results from this and other studies (e.g., Ferrero et al., 2018; Coppola et al., 2021; Fig. 9c) confirm active coseismic rupturing during growing of the MMFS, creating secondary permeability through major fracturing and cataclastic flow, which produced viable structural network for fluid ingress. The U-Th ages spanning the Middle Pleistocene (between 268 and 189 ka) represent the first geochronological documentation of the long-term deformation history of the MMFS, constraining the timing of cycles of permeability creation and destruction in response to continuous interplay between brittle deformation and fluid ingress.

Our seismic scenario for the MMFS (Fig. 9e) proposes episodes of coseismic failure at 487 depth with faulting and tensile fracturing at shallower crustal levels, where the carbonate 488 mineralisations formed. Coseismic failure at seismogenic depths led to rejuvenation of the fault 489 490 permeability through the activation/reactivation of slip surfaces at shallower depths, favouring channelised mineralising flow (e.g., Caine et al., 1996; Cox et al., 2001; Rowland and Sibson, 2004; 491 492 Sibson, 2014). Between successive failure events (interseismic/postseismic stage), shallow fault 493 permeability decreased ever more by carbonate precipitation and progressive sealing of the fault-494 related structures. We propose that the syn-tectonic mineralisations within the MMFS constitute a record of fault (re)activation and tensile episodes in response to the cyclic stress accumulation that 495 can be used to constrain the age of fluid ingress in response to the seismic failure. U-Th data 496 document activation of faulting/tensile failure in the periods 267, 257, 246, 230, and 215 ka. This 497 suggests a time recurrence in the range of 10-15 ka (Fig. 9e). 498

Our integrated geological model can help to reconstruct the activity of seismogenic master 499 faults of central Apennines, currently primarily constrained by seismic catalogues (e.g., Rovida et 500 501 al., 2020) and paleoseismological datasets (e.g., Galli et al., 2008), to much longer temporal and spatial scales. Very few studies provided geochronological constraints on neotectonics by dating 502 503 syn-tectonic mineralisation related to major faults (Fig. 10). Smeraglia et al. (2018) dated four fault-504 related mineralisations along the Val Roveto Fault (see location in Fig. 2a), which the authors used 505 to constrain fluid migration and mixing during Late Pleistocene multiple displacement episodes and seismic slip along the fault. Vignaroli et al. (2020a) dated fault-related mineralisations along the 506 507 Amatrice Fault System (see location in Fig. 2a), used to constrain surface rupture and hydrodynamic interconnection with the vadose zone during Middle-Late Pleistocene faulting. While 508 509 a cyclical reactivation of the MMFS occurred within the Middle Pleistocene between 268 and 189 510 ka, both the Val Roveto Fault and the Amatrice Fault System activated before 290 ka, followed by 511 reactivation in the Late Pleistocene-Early Holocene (Fig. 10).

All together, these fault-related mineralisations typify the time of multiple rupture events 512 513 along major NW-SE-striking normal faults, their reactivation and the recurrence interval connected with their seismic cycle. Such an integrated geological model for seismogenic faults could play a 514 key role in seismic hazard assessment in those areas characterised by the absence of historical 515 seismicity and/or evidence of Mw < 6 paleoearthquakes. Additional studies on similar syn-tectonic 516 mineralisations could make possible to identify cyclical variations in the fluctuation of fluid ingress 517 at greater frequency and, therefore, to provide a viable contribution to the definition of a recurrence 518 519 pattern on a regional scale.

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# 521 *5.4.The paleoclimate influence*

To understand possible feedback relationships between paleoclimate changes and fault-522 523 controlled circulation of mineralising fluids, we compared our ages for the MMFS carbonate mineralisations with U-Th ages obtained for some Quaternary travertines and calcite veins located 524 on the Tyrrhenian margin of the Apennines (Semproniano-Saturnia travertines: Berardi et al., 2016; 525 Vignaroli et al., 2016; Radicofani and Val di Chiana travertines: Brogi et al., 2010; 2012; 2017; Fig. 526 10). We considered major Quaternary paleoclimate indicators determined at both local and regional 527 scale (Fig. 10), the pollen data set from Valle di Castiglione (Tzedakis et al., 2001) located ~100 528 529 km to the west of the MMFS and the atmospheric CO<sub>2</sub> concentration (Past Interglacial Working 530 Group of PAGES, 2016). We also considered the climate anomalies generated by periodic oscillations of Earth's orbital parameters over the Cenozoic (Zachos et al., 2001; Past Interglacials 531 Working Group of PAGES, 2016). 532

The available U-Th data cover the time spanning from MIS 10 to MIS 5 (MIS: Marine 533 Isotope Stage; Fig. 10). There is a consensus in considering warm and wet (interglacial) conditions 534 as the most favourable for thermogene travertine deposition during late Quaternary time (e.g., 535 Sturchio et al., 1994; Rihs et al., 2002; Faccenna et al., 2008; Uysal et al., 2009; De Filippis et al., 536 2013; Priewisch et al., 2014). In this view, the ages obtained for the Semproniano-Saturnia 537 538 travertines fall within warm and humid climate periods that have been considered as triggers for 539 tectonically controlled fluid discharge along faults (Berardi et al., 2016; Vignaroli et al., 2016). On 540 the other hand, a different pattern has been proposed for the travertines in Radicofani Basin, Val di Chiana Basin and Tiber Valley (Brogi et al., 2010; 2012; 2017; Giustini et al., 2018), suggesting the 541 importance of tectonic activity, rather than climate, to control travertine precipitation during low 542 stand conditions of the water table in dry glacial periods (e.g., Uysal et al., 2009; Özkul et al., 543 2013). Moreover, some studies documented a correlation between growth phases of surficial 544

carbonate mineralisation (travertines and veins) and times of cyclical variations of the Earth's
orbital characteristics, including the c. 25 ka precessional component that controls high insolation
(e.g., Wang et al., 2004; Kampman et al., 2012; De Filippis et al., 2013).

Discarding the sample M4e, due to its rather large error bars, we note that five of MMFS U-548 549 Th ages fall within the interglacial period, at 180-245 ka (MIS7 in Fig. 10), while three fall within the glacial period MIS8. Noteworthy, ages within the MIS7 and MIS8 show a preferential 550 551 correlation with the interstadial events (humid times suggested by the high values of the pollen data set from Valle di Castiglione). This correlation matches with paleoclimate conditions supplying the 552 553 deposition of the Semproniano-Saturnia thermogene travertines (Berardi et al., 2016; Vignaroli et al., 2016). In addition, over the periods 100-150 and 300-350 ka there is a good correlation between 554 the mean ages of mineralisations from the Val Roveto Fault (s61, s129, s132, s149 in Fig. 10), the 555 Amatrice Fault System (Fven1/2, Fin8 in Fig. 10), and travertines with the rhythmical negative 556 557 peaks of precession (i.e., conditions of high insolation). Overall, this might suggest that carbonate precipitation in active faults and travertines is sensitive to climate variation, being preferentially 558 559 facilitated by warm and humid climate conditions characterised by high-stands of the water table. In dryer times, scarce meteoric water supply might not allow the formation of carbonate 560 mineralisations in active tectonic structures. Therefore, the variations in climate-controlled water 561 availability could bias the recorded periodicity of fault activity, as cycles of permeability creation 562 and destruction under dry conditions would not lead to significant mineral precipitation. 563

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### 566 **6.** Conclusions

The structural evolution of the MMFS supports the general scenario of focussed,
structurally-controlled fluid flow and mineralisation at shallow depths during fault reactivation. We
document multiple events of permeability creation and destruction recording the long-term
evolution of the MMFS:

(i) The development of the secondary permeability in the MMFS evolved in space in
time from diffuse deformation (at the fault footwall) towards localisation of a
narrower fault core and to final (re)activation of discrete slip surfaces in the
shallower crustal levels. The latter correspond to a combination of faulting and
tensile fracturing, in response to the stress accumulation during its seismic cycle.

- 576 (ii) The hydrodynamic regime permeating the secondary permeability mineralising fluid
  577 was dominated by meteoric water circulation at the shallower conditions, where
  578 discrete slip surfaces (re)activated.
- 579 (iii) The polyphasic and syn-tectonic mineralisations on the fault surfaces reflect the
  580 interaction and feedback among seismically active tectonics and transient circulation
  581 of mineralising fluids, likely influenced by paleoclimate oscillations.
- (iv) U-Th dating of the carbonate mineralisations defined the time lapse encompassed in
  the fault permeability creation/destruction cycles, providing a pilot study to
  reconstruct the seismic recurrence model at a regional scale.
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# 937 Captions to Figures

Figure 1. Structural scenario of the fault-valve mechanism framed within the seismic cycle. The creation of
fault permeability is here correlated to the tectonics, mineralisation, and fluid pressure cycling. EQ:
earthquake.

941 Figure 2. a) Schematic tectonic framework of the Apennines within the western Mediterranean region; b) geological setting of the central Apennines, where the distribution of both the main thrust fronts and the 942 943 active normal faults is reported (modified and readapted after Cosentino et al., 2010). The map also shows the localisation of both the main recent earthquakes (including their focal mechanisms) and the historical 944 945 earthquakes in the area surrounding the Monte Morrone. The seismic data are after Amato et al. (1998), Chiarabba et al. (2009), Chiaraluce et al. (2017), and the Parametric Catalogue of Italian Earthquakes 946 (CPTI15 available at https://emidius.mi.ingv.it/CPTI15-DBMI15/index\_en.htm). The location of two dated 947 948 faults (Val Roveto Fault: Smeraglia et al., 2018; Amatrice Fault System: Vignaroli et al., 2020a) and dated Ouaternary travertines (Semproniano-Saturnia travertines: Berardi et al., 2016; Vignaroli et al., 2016; 949 Radicofani and Val di Chiana travertines; Brogi et al., 2010; 2012; 2017) is also shown; c) geological setting 950 of the Monte Morrone area showing the orientation and distribution of the western (WFS) and eastern (EFS) 951 strands of the Monte Morrone Fault System (modified after Pizzi et al., 2015); d) schematic cross section 952 953 illustrating the main stratigraphic/structural setting of the Monte Morrone-Sulmona Basin system (modified 954 after Miccadei et al., 2002). The Monte Morrone Fault System cuts through the Meso-Cenozoic carbonate 955 bedrock and accommodates more than 400 m-thick Quaternary continental deposits filling the Sulmona Basin; e) Google Earth © view of the study area around the Roccacasale village, showing the localisation of 956 957 structural sites along the western strand of the Monte Morrone Fault System. AFS: Amatrice fault System; 958 SeSa: Semproniano-Saturnia travertines; VRF: Val Roveto Fault.

959 Figure 3. Structural features of the western strand of the Monte Morrone Fault System observed at the 960 studied outcrops. a) Panoramic view of the main fault surface exposed southeast to the Roccacasale village (structural stop M3.1 in Fig. 2e). In the insert: stereographic projection (Schmidt net, lower hemisphere) of 961 962 the measured main slip surfaces; b) dip-slip slickenlines (rock abrasion) exposed on the fault surface; c) 963 metre-thick damage zone, produced at the expense of Meso-Cenozoic carbonate bedrock, occurring at the footwall of the main slip surface (structural stop M3.2 in Fig. 2e; compare with Fig. 4b of Ferraro et al., 964 2018); d) outcrop view of the fault damage zone exposed northwest to the Roccacasale village (structural 965 stop M4.1 in Fig. 2e) where the carbonate mineralisations were collected; e) the damage zone is 966 967 characterised by lenses of foliated or massive cataclasites produced at the expense of the Mesozoic limestone. 968

969 Figure 4. Mesoscopic properties of the WFS at the structural stop M4.1 (see Fig. 2e and Table 1 for location). a) Damage zone around the main slip surface that is, in turn, cross cut by a set of high-angle 970 normal faults; b) detail of the crosscutting relationships between the main slip surface and the high-angle 971 972 normal faults, the latter producing decimetre-to-half metre offset; c) high-angle normal fault crosscutting the main slip surface, the latter decorated by cm-thick carbonate mineralisation; d) detail of two separated cm-973 thick carbonate mineralisation occurring atop the main slip surface; e) detail of the main slip surface 974 975 intervening between a massive cataclasite (at the footwall) and a dm-to-cm-thick mineralisation (at the hanging wall); f) enlargement of the previous image (the broken mineralisation is here exposed) showing the 976 977 internal fabric of the carbonate mineralisation; g) and h) structural and petrographical details of high-angle 978 faults, where thin (a few mm) patina of carbonate mineralisation occurs on the slickensided surface. Samples used for microstructural investigation and geochemical/geochronological purposes are indicated by red 979 980 labels.

Figure 5. Example of rock slab (sample M4G; Table 1) used for defining the main observed structural
fabrics. (a) Polished rock slab of sample M4G with the indication of micro-drilling sites for geochemical and
geochronological purposes. U-Th ages and temperatures deriving from clumped isotopes analysis are also
indicated; (b) scanned thin section of sample M4G showing, from bottom to top, the cataclasite, the main slip
surface, the sedimentary breccias (probably filling voids of karst origin) and three main mineralisations

characterised by a layering of thin laminae and sparitic veins; (c) line drawing of the main features observed
in the scanned thin section of sample M4G; (d) and (e) BSE images (see Fig. 5b for location) showing the
main slip surface, sub-rounded small clasts in the ultracataclasite, sub-angular clasts and clasts with
polygonal fractures; (f) enlargement of Fig 5e.

990 Figure 6. Microscale properties of the collected samples. a) Petrographic image (crossed polarised light) of 991 massive cataclasite consisting of a fine- to very fine-grained matrix embedding a few large clasts (up to 1.5 992 mm in width); (b) back-scattered electron (BSE) image showing the occurrence of polygonal fractures within 993 the cataclasite; c) BSE image showing the occurrence of a slip surface that sharply truncate the carbonate 994 clasts; d) petrographic image (plane polarised light) and e) cathodoluminescence image showing traces of permeating fluid (bright colour in cathodoluminescence) within the fine-grained cataclasite matrix; f) 995 996 petrographic image (plane polarised light) and g) cathodoluminescence image showing layered (and partly 997 folded) carbonate mineralisation atop a very fine-grained cataclasite. Note the general upward-convex fanshaped crystals grown during incremental layering. Cathodoluminescence imaging reveals that calcite 998 999 making the mineralisation is characterised by a dark violet colour, darker than the colour of the adjacent 1000 cataclasite; h) petrographic image (plane polarised light) and i) BSE image showing fractured mineralisation 1001 embedded within the fine-grained cataclasite; j) petrographic image (crossed polarised light) showing 1002 polyphasic growth of mineralisation embedding lenses of protocataclasite. Note the different style of growing (including bedding-parallel layers, undulate layers, elongated crystals); k) upward-convex fan-1003 shaped crystals grown and downward-convex fan-shaped crystals grown in mineralisations separated by a 1004 1005 thin layer of cataclasite.

Figure 7. Line drawing of the studied outcrop (Fig. 3d) with indication of the selected mineralisation
samples for U-Th ages. The insets indicate the mineralisation slabs, as well as the selected portion for U-Th
analysis and the obtained results.

**Figure 8.** Combined plot of  $\delta^{13}$ C (‰V-PDB) and  $\delta^{18}$ O (‰V-PDB) isotope values derived from the collected samples. V-PDB: Vienna Peedee Belemnite standard.

1011 Figure 9. a) simplified structural architecture of the MMFS as deduced from observation at the studied 1012 outcrops; b) schematic scenario of fault permeability development during the progressive exhumation of the 1013 of the fault core-damage zone formed at depth (at  $t_n$ ) and reactivation of slip surfaces at shallower crustal 1014 conditions (at  $t_{n+nx}$ ); c) structural relationships between the analysed carbonate mineralisations and the fault domains as documented by previous work on the same fault strands (Ferraro et al., 2018; Coppola et al., 1015 1016 2021); d) two-stage structural evolution for the MMFS according to fault cross-cutting relationships, pattern of fluid circulation during faulting as deduced from the isotopic analysis, and absolute ages provided by U-1017 Th dating on carbonate mineralisations; e) proposed scenario of cyclical fault-fluid interactions in the MMFS 1018 1019 within a recurrence time of 10-15 ka between coseismic events as deduced from this study. fc: fault core; dz: 1020 damage zone. EFS and WFS are the eastern and western strands of the Monte Morrone Fault System, 1021 respectively.

1022 Figure 10. Comparison between U-Th ages of fault-related mineralisations from the MMFS (this study), the Amatrice fault System (AFS; Vignaroli et al., 2020a), the Val Roveto Fault (Smeraglia et al., 2018) and 1023 CaCO<sub>3</sub> samples (bedded and banded travertines, calcite-filled veins) from the northern part of the central 1024 1025 Apennines (Sem-Sat: Semproniano-Saturnia travertines: Berardi et al., 2016; Vignaroli et al., 2016; Ra-VdC: travertines from the Radicofani and Val di Chiana basins: Brogi et al., 2010; 2012; 2017; see location in Fig. 1026 1027 2b). Major paleoclimate indicators are represented by the deep-sea oxygen isotope trend (Zachos et al., 2001), the pollen data set from Valle di Castiglione (Tzedakis et al., 2001), and the atmospheric CO<sub>2</sub> 1028 1029 degassing (Past Interglacial Working Group of PAGES, 2016). Glacial-interglacial periods are redrawn and modified after Priewisch et al. (2014). Valle di Castiglione is located in central Italy (see location in Fig. 2b) 1030 1031 only ~100 km west to the MMFS. MIS: Marine Isotope Stages. AP: arboreal pollen; NAP: non-arboreal 1032 pollen. Eccentricity/precession are redrawn and modified after Past Interglacial Working Group of PAGES 1033 (2016).

**Table 1.** Summary of observed structures and collected samples during the structural survey along the
 western strand of the Monte Morrone Fault System (see Fig. 2e).

**Table 2.** U-Th ages of the carbonate mineralisations from the Monte Morrone Fault System collected at the studied outcrop near Roccacasale village (site M4.1; long.:  $13.883^{\circ}$ ; lat.:  $42.125^{\circ}$ ). Sample indicated with \* was analysed through MC-ICP-MS at the HISPEC of the National Taiwan University (errors quoted as  $2\sigma$ ), whereas sample indicated with \*\* was analysed through  $\alpha$  spectrometry done at the at the Laboratory of Environmental and Isotopic Geochemistry (Department of Sciences, Roma Tre University, Italy) (errors quoted as  $1\sigma$ ).

Table A1. Stable oxygen and carbon isotope composition of the selected samples from the Monte Morrone
Fault System collected at the studied outcrop near Roccacasale village (long.: 13.883°; lat.: 42.125°). Isotope
compositions are expressed in ‰ against Vienna Pee Dee Belemnite standard (VPDB).

**Table A2.** Clumped isotopes analyses on the selected samples from the Monte Morrone Fault System.

Figure SM1. Polished rock slabs of the analysed samples (sample M4G is reported in Fig. 5; Tables 1 and 2)
 with the indication of micro-drilling sites for geochemical (stable isotopes in black and clumped isotopes in
 red) and geochronological analysis (red-white circles). U-Th ages and temperatures deriving from clumped
 isotopes analysis are also indicated.

Figure SM2. Polished slab, high-resolution scanned thin section, detailed petrographic and back-scattered 1050 1051 electron (BSE) images showing the main observed structural fabrics of sample M4HW. a) Oriented polished rock slab showing the contact between the slip surface (here developed at the top of the carbonate 1052 1053 mineralisation) and the hanging wall of the massive cataclasite; b) high-resolution scanned thin section of 1054 sample M4HW showing the carbonate mineralisations (at the bottom) and cataclasite (at the top); c) 1055 petrographic image (crossed polarised light) showing brecciated mineralisations partially embedded within the fine-grained cataclasite. Secondary cement made by calcite crystals occurs within the reworked carbonate 1056 1057 mineralisations; d) petrographic image (plane polarized light) showing sigmoidal foliation within the 1058 carbonate mineralisations embedded in two minor slip surfaces; e) petrographic image (plane polarised light) showing fractured and brecciated carbonate mineralisations with several minor slip surfaces and embedding 1059 pockets of protocataclasites; f) BSE image showing the main slip surface at the top of the carbonate 1060 1061 mineralisations and the fractured mineralisations partially embedded in the cataclasite. Note the two extensional fractures developed along the main slip surface; g) BSE image showing structures high angle to 1062 1063 vertical slip surface, generally with undulating boundaries and characterised by tight cataclasite and calcite 1064 vein.

1065 Figure SM3. Petrographic images showing the microscale properties of M4H2 sample at different scale of 1066 observation. (a) Petrographic photomosaic (plane polarised light) of the lower part of M4H2 thin section showing (at the bottom) multiple generation of mineralisations (formed both by laminae and veins) and 1067 1068 breccia (at the top). The upper edge of the mineralisation is characterized by a thin layer of ultracataclasite. 1069 At least one slip surface is observed within the mineralisation. (b) Petrographic image (plane polarised light) 1070 showing within the breccia clasts of former mineralisations mixed with other carbonate fragments deriving 1071 from previous cataclasite and calcite cement. (c-d) Petrographic images (plane and crossed polarised light, respectively) showing a series of bands of cataclasite and ultracataclasite within the mineralisation. (e) 1072 1073 Petrographic image (plane polarised light) showing the upper edge of the mineralisation covered by a thin layer of ultracataclasite. (f-g) Petrographic images (plane and crossed polarised light, respectively) showing a 1074 series of bands parallel to the slip surface and formed by cataclasites alternating with highly fractured 1075 1076 mineralisations. The upper portion of the mineralisation is flattened and truncated along the slip surface and some fragments of the mineralisation are partially embedded within the thin layer of ultracataclasite. (h-i) 1077 1078 Petrographic images (plane and crossed polarised light, respectively) showing in detail a series of bands parallel to the slip surface and formed by cataclasites alternating with highly fractured mineralisations. 1079 1080 Interposed between two bands of cataclasite, a thin level of mineralisation is highly fractured, and some 1081 carbonate clasts are partially dispersed in the cataclasite. (1-m) Petrographic images (plane and crossed

1082 polarised light, respectively) showing a highly fractured portion of the mineralisation with a shape miming a

- sigmoidal foliation. (n-o) Petrographic images (plane and crossed polarised light, respectively) showing in
- 1084 detail the upper portion of the mineralisation. A thin layer of ultracataclasite, with some synthetic shear zone,
- 1085 covers the edge of the mineralisation.

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Structural stop	Lat.	Long.	Structural fabric	Sample for geochronology (Table 2)	Sample for isotope data (Table A1)
M1	42.124°	13.888°	• Damage zone (synthetic faults and extensional or hybrid fractures)		
M3.1	42.121°	13.893°	<ul> <li>Fault core (main slip surface and cataclasite)</li> <li>High-angle normal faults cutting the main slip surface</li> </ul>		
M3.2	42.121°	13.894°	• Fault core (main slip surface and cataclasite)		
M4.1	42.125°	13.883°	<ul> <li>Fault core (main slip surface, cataclasite, fault breccias and veins made by calcite precipitation)</li> <li>Damage zone (synthetic faults and extensional or hybrid fractures)</li> <li>High-angle normal faults cutting the main slip surface</li> </ul>	M4G/1, M4G/2, M4G/3, M4H, M4H2, M4HW, M4F1, M4i, M4e	M4G/1, M4G/2, M4G/3, M4H, M4H2, M4HW, M4F1, M4i, M4e
M4.2	42.127°	13.882°	<ul> <li>Fault core (main slip surface and cataclasite)</li> <li>High-angle normal faults cutting the main slip surface</li> </ul>		
M4.3	42.128°	13.881°	<ul><li>Fault core (main slip surface and cataclasite)</li><li>High-angle normal faults cutting the main slip surface</li></ul>		
M4.4	42.129°	13.879°	• Damage zone (synthetic faults and extensional or hybrid fractures)		

**TABLE 1.** Summary of observed structures and collected samples during the structural survey along the western strand of the Monte Morrone Fault System (see Fig. 2e).

**Table 2.** U-Th ages of the carbonate mineralisations from the Monte Morrone Fault System collected at the studied outcrop near Roccacasale village (site M4.1; lat.: 42.125° N; long.: 13.883° E). Sample indicated with \* was analysed through MC-ICP-MS at the HISPEC of the National Taiwan University (errors quoted as  $2\sigma$ ), whereas sample indicated with \*\* was analysed through  $\alpha$  spectrometry done at the the Laboratory of Environmental and Isotopic Geochemistry (Department of Sciences, Roma Tre University, Italy) (errors quoted as  $1\sigma$ ).

Sample ID	Weight g	<sup>238</sup> U Ppb (a)	<sup>232</sup> Th ppb	$\delta^{234}$ U measured (a)	[ <sup>230</sup> Th/ <sup>238</sup> U] activity (c)	<sup>230</sup> Th/ <sup>232</sup> Th atomic (x 10 <sup>-6</sup> )	Age (ka ago) uncorrected	Age (ka ago) corrected (c,d)	$\begin{array}{c} \delta^{234}U_{initial} \\ corrected (b) \end{array}$
M4G/1*	0.2311	$154.95\pm0.16$	$0.1216 \pm 0.0020$	$21.6 \pm 1.4$	$0.9030 \pm 0.0018$	18969 ± 315	$230.3\pm2.0$	$230.3\pm2.0$	$41.5\pm2.6$
M4G/2*	0.21021	$244.15\pm0.28$	$0.4809 \pm 0.0023$	$6.0 \pm 1.4$	$0.9027 \pm 0.0018$	$7556\pm38$	$246.6\pm2.5$	$246.6\pm2.5$	$12.1\pm2.8$
M4G/3*	0.19458	$198.01\pm0.27$	$2.5449 \pm 0.0055$	$7.7\pm1.6$	$0.9149 \pm 0.0033$	$1173.6\pm4.6$	$257.8\pm4.3$	$257.4\pm4.3$	$15.8\pm3.3$
M4H*	0.20549	$419.68\pm0.51$	$10.833\pm0.033$	$9.8 \pm 1.5$	$0.9264 \pm 0.0046$	$591.7\pm3.4$	$268.6\pm6.2$	$267.9\pm6.1$	$20.9\pm3.2$
M4H2*	0.22826	$429.58\pm0.55$	$11.059\pm0.036$	$17.6\pm1.8$	$0.8848 \pm 0.0043$	$566.7\pm3.3$	$219.0\pm3.7$	$218.3\pm3.7$	$32.6\pm3.3$
M4HW*	0.21036	$255.88\pm0.38$	$15.445\pm0.067$	$24.5\pm1.8$	$0.8902 \pm 0.0086$	$243.2\pm2.5$	$217.3\pm6.7$	$215.8\pm6.7$	$45.1\pm3.3$
M4F1*	0.20277	$323.87\pm0.38$	$0.2808 \pm 0.0023$	$8.9\pm1.7$	$0.8703 \pm 0.0020$	$16552 \pm 141$	$214.9\pm2.1$	$214.9\pm2.1$	$16.4\pm3.2$
M4i*	0.2008	$138.40\pm0.15$	$2.0115 \pm 0.0033$	$23.6 \pm 1.3$	$0.8483 \pm 0.0039$	$962.4\pm4.6$	$189.7\pm2.5$	$189.4\pm2.5$	$40.3\pm2.3$

Sample ID	U (ppm)	<sup>230</sup> Th/ <sup>232</sup> Th	<sup>234</sup> U/ <sup>238</sup> U	<sup>230</sup> Th/ <sup>234</sup> U	( <sup>234</sup> U/ <sup>238</sup> U) initial	Age (ka)
M4e**	$0.137 \pm 0.005$	83.105±10.401	1.030±0.037	0.809±0.036	1.050±0.061	178 +39/-30

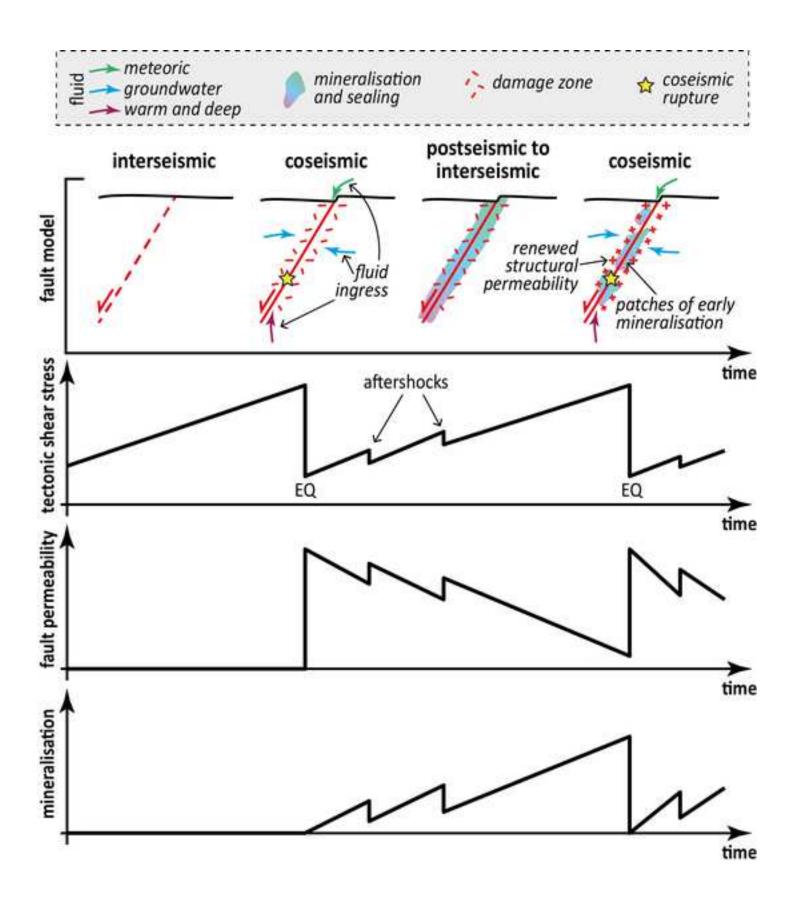
(a)  $[^{238}U] = [^{235}U] \times 137.818 (\pm 0.65\%)$  (Hiess et al., 2012);  $\delta^{234}U = ([^{234}U/^{238}U]_{activity} - 1) \times 1000$ .

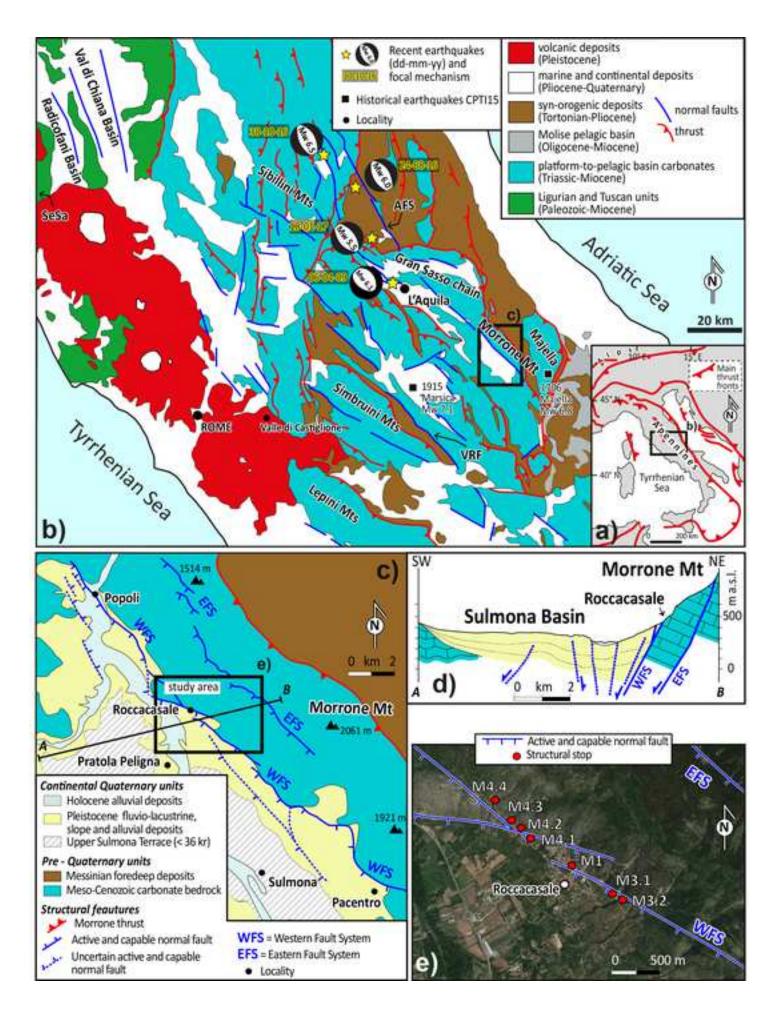
(b)  $\delta^{234}$ U<sub>initial</sub> corrected was calculated based on <sup>230</sup>Th age (*T*), i.e.,  $\delta^{234}$ U<sub>initial</sub> =  $\delta^{234}$ U<sub>measured</sub> *X* e<sup> $\lambda_{234*T}$ </sup>, and *T* is corrected age.

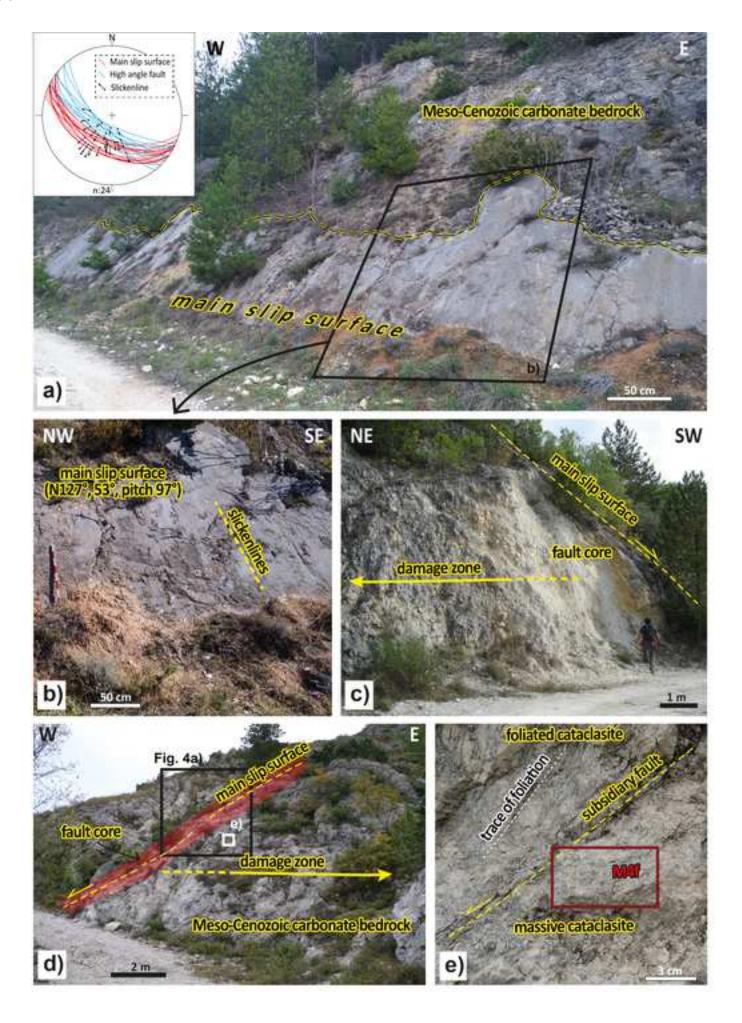
(c)  $[^{230}\text{Th}/^{238}\text{U}]_{\text{activity}} = 1 - e^{-\lambda_{230}T} + (\delta^{234}\text{U}_{\text{measured}}/1000)[\lambda_{230}/(\lambda_{230} - \lambda_{234})](1 - e^{-(\lambda_{230} - \lambda_{234})T})$ , where *T* is the age. Decay constants are 9.1705 x 10<sup>-6</sup> yr<sup>-1</sup> for <sup>230</sup>Th, 2.8221 x 10<sup>-6</sup> yr<sup>-1</sup> for <sup>234</sup>U (Cheng et al., 2013), and 1.55125 x 10<sup>-10</sup> yr<sup>-1</sup> for <sup>238</sup>U (Jaffey et al., 1971).

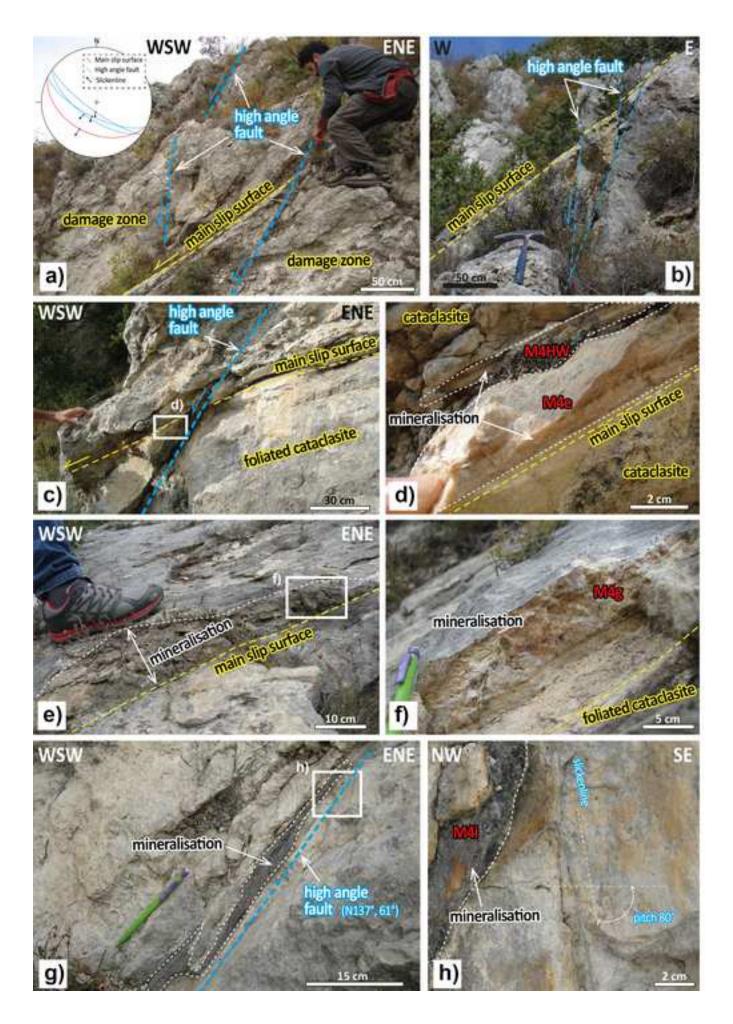
(d) Age corrections, relative to chemistry date on March 19th, 2019, were calculated using an estimated atomic  $^{230}$ Th/ $^{232}$ Th ratio of 4 (± 2) x 10<sup>-6</sup>.

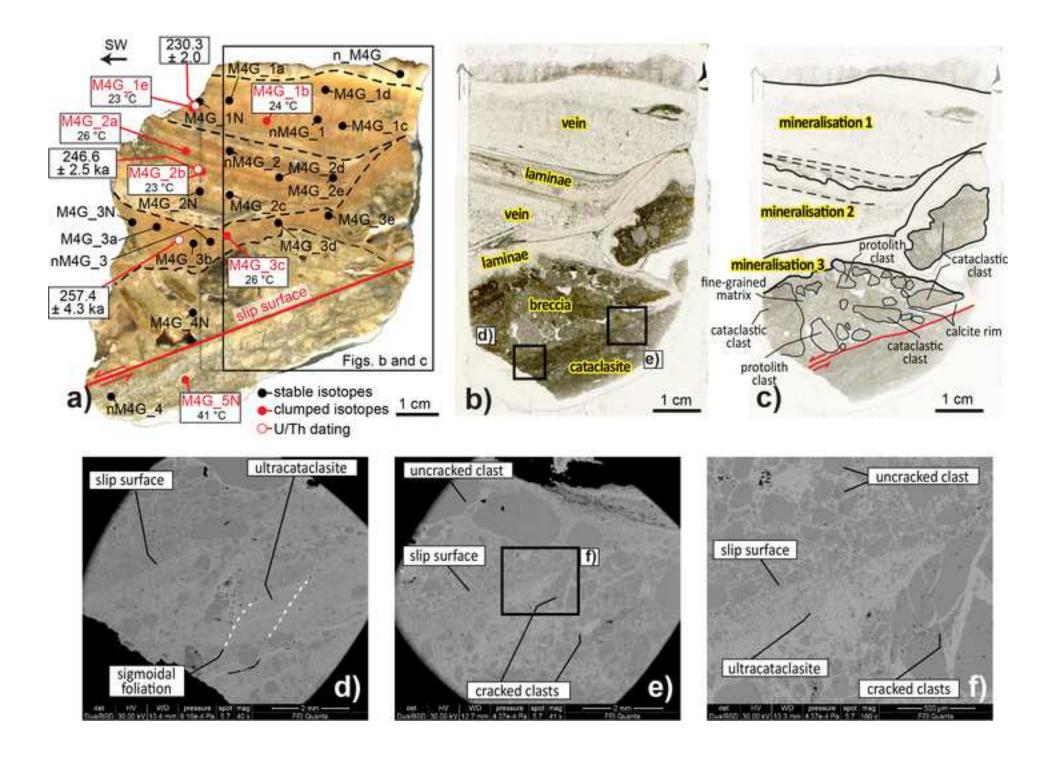
Those are the values for a material at secular equilibrium, with the crustal  $^{232}$ Th/ $^{238}$ U value of 3.8. The errors are arbitrarily assumed to be 50%.











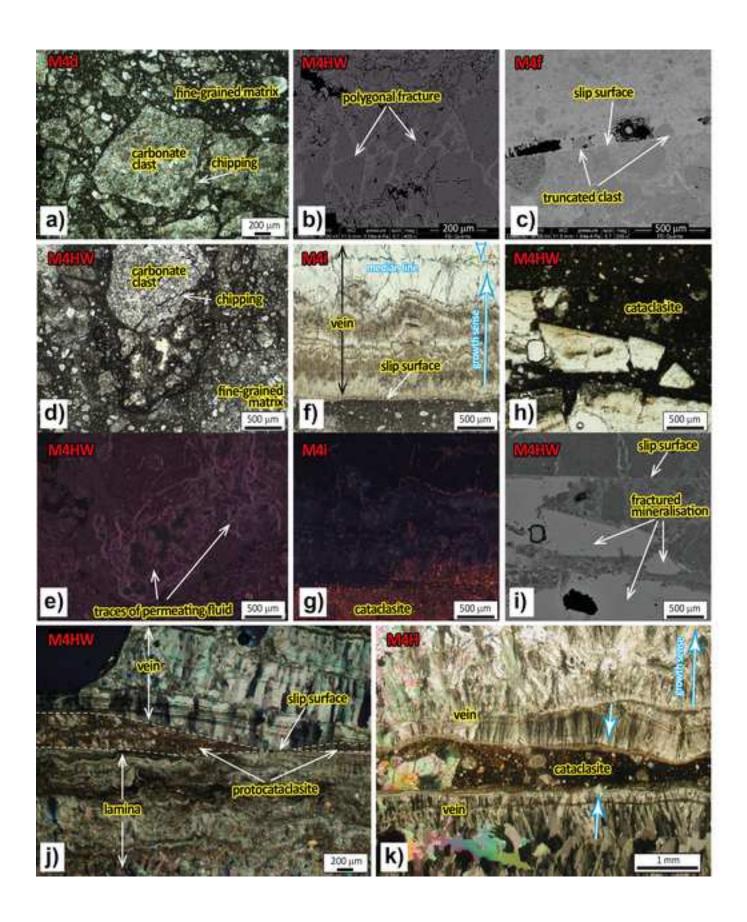
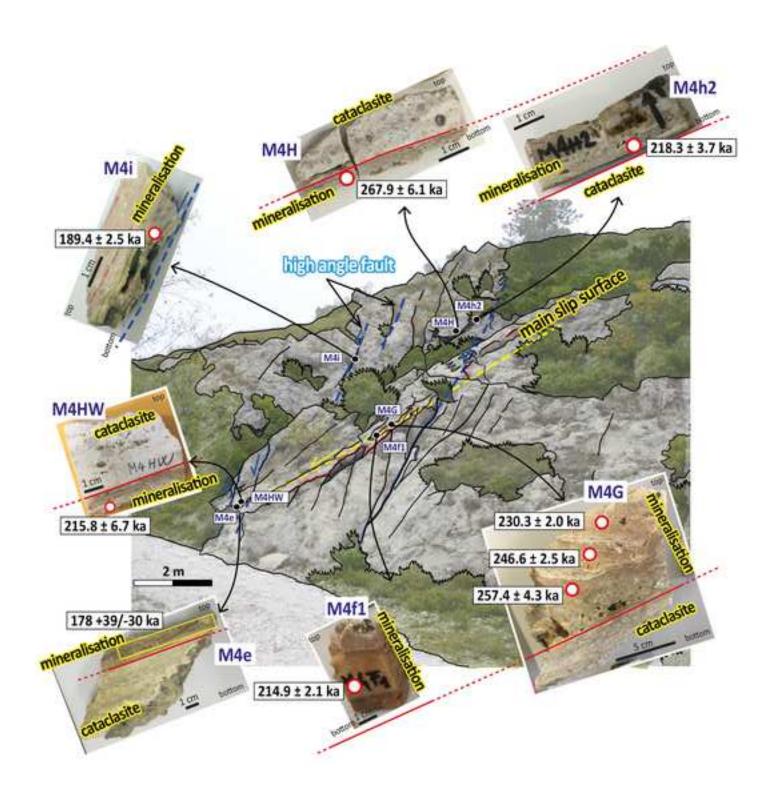
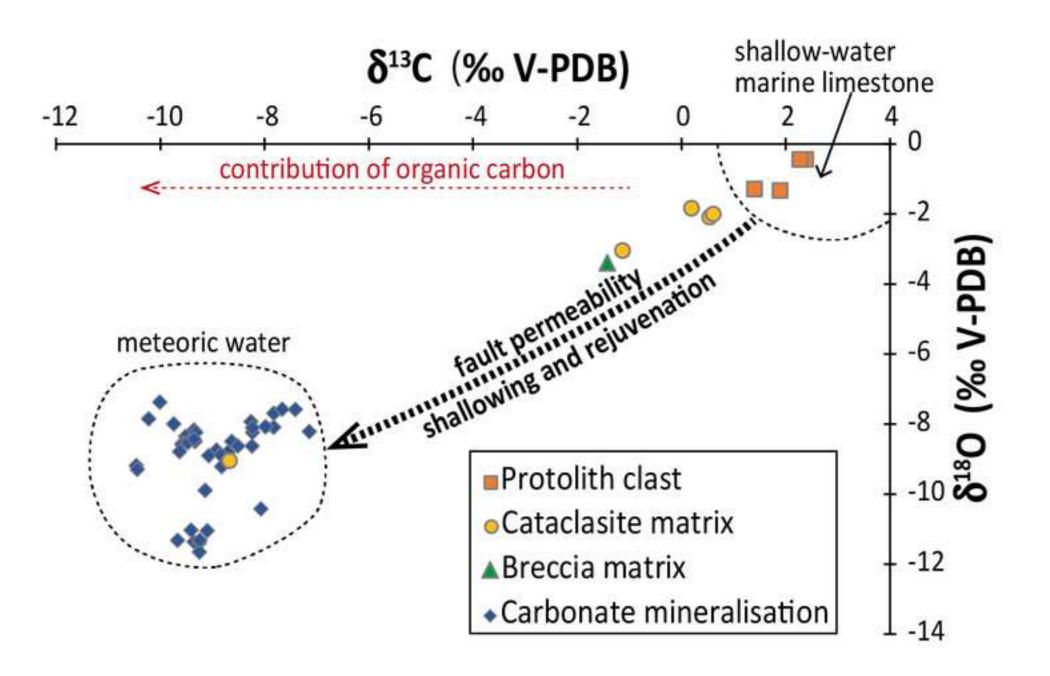
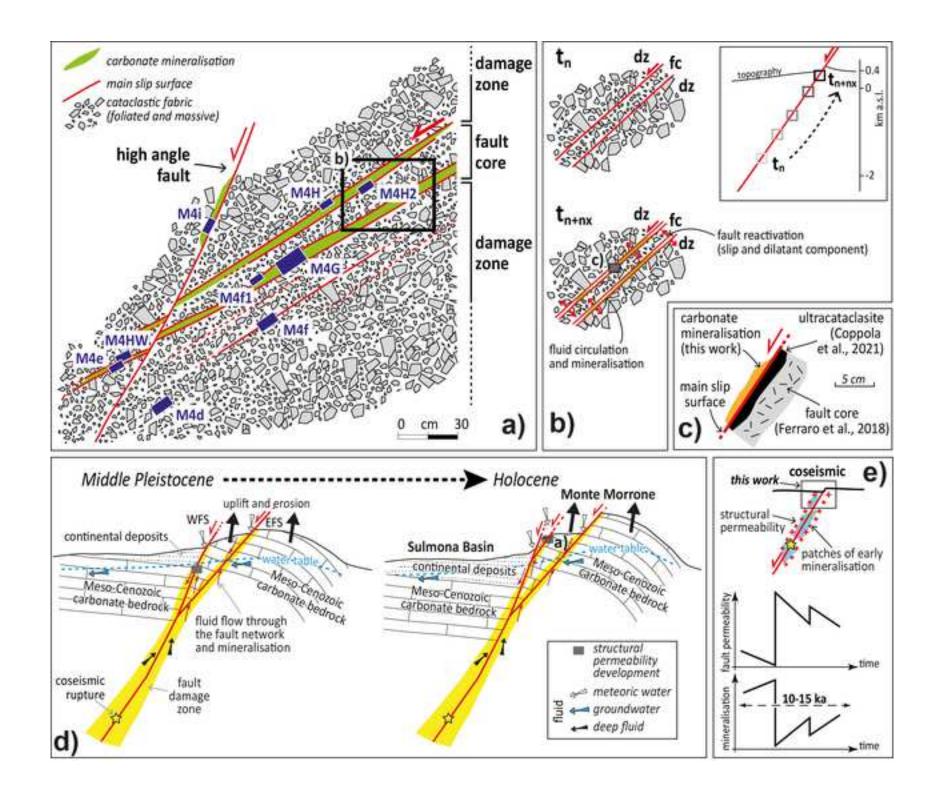
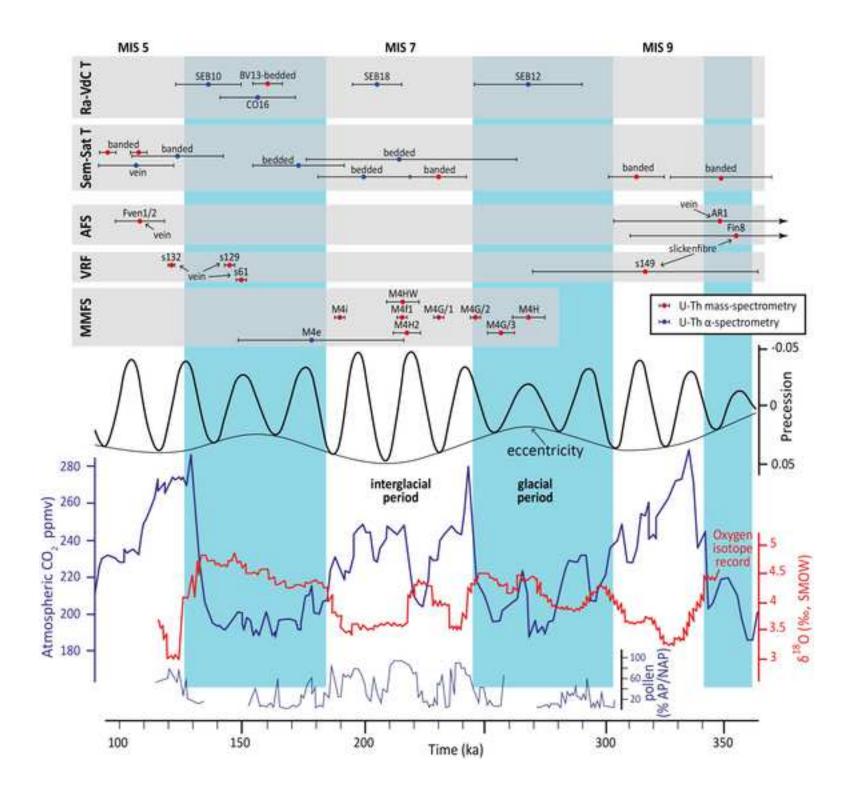


Figure 7









### **Credit author statement**

Gianluca Vignaroli: Methodology, Investigation, Data curation, Visualisation, Writing - original draft, review & editing

Federico Rossetti: Validation, Investigation, Resources, Writing - review & editing, Supervision Lorenzo Petracchini: Investigation, Data curation, Visualisation, Writing - review & editing Valentina Argante: Investigation, Data curation, Visualisation, Writing - original draft Stefano M. Bernasconi: Formal analysis, Investigation, Resources, Writing - review & editing Mauro Brilli: Validation, Formal analysis, Investigation, Writing - review & editing Francesca Giustini: Validation, Formal analysis, Investigation, Writing - review & editing Tsai-Luen Yu: Validation, Formal analysis, Investigation, Writing - review & editing Chuan-Chou Shen: Validation, Formal analysis, Investigation, Resources, Writing - review & editing Michele Soligo: Validation, Formal analysis, Investigation, Resources