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3 **RSCM THERMOMETRY IN THE ALPI APUANE (NW TUSCANY, ITALY):**
4 **NEW CONSTRAINTS FOR THE METAMORPHIC AND TECTONIC**
5 **HISTORY OF THE INNER NORTHERN APENNINES**
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10 Molli G.^{1*}, Vitale Brovarone A.², Beyssac O.², Cinquini I.¹
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17 1) Dipartimento Scienze della Terra, Università di Pisa, Via S.Maria 53, 56126 Pisa, Italia

18 2) Sorbonne Université, Muséum National d'Histoire Naturelle, UMR CNRS 7590, IRD, Institut de
19 Minéralogie, de Physique des Matériaux et de Cosmochimie, IMPMC, 75005 Paris, Francee

20
21
22 * Corresponding author
23
24
25

26 **Keywords:**

27 RSCM Thermometry, Thermal structure, Tectonics, Alpi Apuane, Northern Apennines
28

29 **Highlight:**

30 - First RSCM data for the Northern Apennines

31 - Peak temperature in the Alpi Apuane metamorphic core and surroundings region

32 - New definition of the thermal structure and nappe architecture of the inner Northern Apennines
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ABSTRACT

In this study, Raman spectroscopy on carbonaceous material (RSCM) is applied, for the first time, in the Northern Apennines with particular focus on the Alpi Apuane (NW Tuscany, Italy) and surrounding areas in order to constrain peak metamorphic temperatures and their variability in the different continent-derived units of the nappe stack.

Peak temperatures in the range of ~ 530 - 320 °C were found in the Alpi Apuane, whereas in the nearby metamorphic core of the Monte Pisano and Punta Bianca lower peak temperatures of 305 - 315 °C and 350 °C were found, respectively. The Tuscan Nappe in La Spezia area (west of Alpi Apuane) shows temperatures in the range of 295 - 246 °C, whereas the same unit in the Lima Valley (east of the Alpi Apuane) shows temperatures lower than 230 °C.

The collected data allowed refining the thermal architecture of the belt and the relationships between deformation (early and late folds and low angle normal detachments) and the metamorphic architecture of the Alpi Apuane core. These results provide new constraints for the thermo-mechanical evolution and exhumation history of the inner Northern Apennine and its geodynamic setting. In particular our data support the interpretation of the Alpi Apuane as a cold metamorphic core complex in which the preserved paleothermal structure and part of the exhumation are related with crustal thickening while the final exhumation stages (depth ≤ 15 Km and at ambient crustal temperature ≤ 350 °C) are associated with crustal thinning still ongoing in the area.

72 **1. Introduction**

73

74 The thermal structure and the field metamorphic gradient in mountain belts may be first order
75 parameters directly related to the tectonic setting and the crustal-scale architecture of the orogens
76 (between others Chopin et al., 1991; Hervegh and Pfiffer, 2005, Brown, 2009, Vitale Brovarone et
77 al 2013, Agard and Vitale Brovarone, 2013 and references). Data on the thermal structure of
78 metamorphic units combined with those constraining kinematic history delineates the extent to
79 which heat and mass are transferred from mid to upper crust (e.g. Allemand, Lardeaux, 1997;
80 Selverstone, 1988; Platt et al., 1998; Jolivet et al., 1998; Ring et al., 1999; Berger et al., 2011; Chen
81 et al., 2011; Cottle et al. 2011; Bousquet et al., 2012). Therefore, the understanding of the thermal
82 structure of the internal part of mountain belts is a key element to unravel the tectonic and
83 kinematic frame of orogenic systems and the reconstruction of past geological boundary conditions
84 as inputs for large-scale thermokinematic and geodynamics simulations (Aygüll et al., 2015;
85 Beyssac et al., 2007; Simoes et al., 2007; Avouac et al., 2012; Scharf et al., 2013; Wiederkehr et al.,
86 2011, Rosenberg et al., 2015).

87 The thermal characters of the inner Northern Apennines and the evolution of its main units were
88 defined through a series of the classical methods including clay mineralogy, vitrinite reflectance,
89 fluid inclusions and illite cristallinity for the shallowest units of the nappe stack (Cerrina et al.,
90 1983; Carter and Dorwkin, 1990; Carosi et al., 2003; Reutter et al., 1978; Reutter et al., 1983;
91 Ellero et al., 2001; Montomoli et al., 2001; Montomoli et al., 2002; Botti al., 2004; Dellisanti et al.
92 2010, Caricchi et al., 2014; Ventura et al., 2001), and Al-silicates, chloritoid-chlorite thermometry,
93 calcite-dolomite, stable isotope geothermometers, and conodonts color in the lowermost
94 metamorphic units (Franceschelli et al., 1986; Franceschelli et al., 1997; Franceschelli and Memmi,
95 1999; Molli et al., 2000a,b; Molli et al., 2002; Cortecchi and Orlandi, 1975; Cortecchi et al., 1994;
96 Costagliola et al., 2002; Consani, 2002). More recently, thermodynamical modeling was also
97 applied in the Paleozoic basement terms of the Tuscan metamorphic units (Lo Po' and Braga, 2014;
98 Lo Po' et al., 2017).

99 Due to the patchy distribution of suitable rock types in the different units and within the nappe
100 stack, however, we still lack a precise definition of the regional thermal structure and of the
101 paleothermal field gradients. As a consequence the overall tectonic setting shaping the present day
102 nappe-architecture is still a matter of debate, with crustal contractional and crustal extensional
103 models being alternatively supported by different studies (Carmignani and Kligfield, 1990;
104 Carmignani et al., 1994; Storti, 1995; Jolivet et al., 1998; Boccaletti et al., 1999; Carosi et al., 2003,
105 2004; Bonini and Sani, 2002; Brogi and Liotta, 2008; Thomson et al., 2010; Sani et al., 2014;

106 Musumeci et al., 2015). This in turn leaves open some relevant questions, for instance the
107 relationships between exhumation processes and the mode of crustal deformation (thickening vs.
108 thinning) as well as the timing, thermal and structural record of crustal/litospheric stretching, which
109 shaped characteristic features of the inner Northern Apennine in Tuscany such as the present day
110 Moho depth and thermal anomaly (Carminati and Doglioni, 2012; Della Vedova et al., 2001; Di
111 Stefano et al., 2011; Spada et al., 2013 and references).

112 In this study, we present a regional-scale set of paleo-thermal estimates obtained by means of
113 Raman spectroscopy on carbonaceous material (RSCM), including a large range of lithologies from
114 the main units of the inner Northern Apennines, with special focus on the Alpi Apuane
115 metamorphic core and nearby areas. Thanks to the irreversible process of graphitization of
116 carbonaceous material (CM), this geothermometer can provide peak temperature (T) estimates for
117 CM-bearing metasedimentary rocks independently from their mineralogical assemblage, and is
118 therefore applicable to a wider range of rock types in the considered units compared to previous
119 studies.

120 Our data allow constraining the thermal structure and the exhumation-related paleogradients,
121 thereby improving our understanding of the orogenic processes recorded in the inner Northern
122 Apennines. Moreover, our data document the thermal architecture and metamorphic signature of a
123 mid-shallow orogenic wedge and its relationships with the regional structures, the nappe and thrust
124 stack styles and their internal deformation.

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126

127 **2. Regional Geology**

128

129 The Northern Apennines (Fig.1) are characterized by a pile of thrust-sheets and fold nappes derived
130 from the distal part of the Adria continental margin (the Tuscan Domain), which presently rests
131 below the remnants of a former intraoceanic accretionary wedge represented by the Ligurian and
132 sub-Ligurian units relicts of the former Mesozoic western alpine Tethys ocean (Elter, 1975;
133 Marroni and Pandolfi, 1996; Bortolotti et al. 2001, Bernoulli, 2001; Butler et al., 2006; Molli, 2008;
134 Malavieille et al., 2016; Schmid et al., 2017). The recent to active tectonic framework of the
135 Northern Apennines is characterized by crustal-scale extension in the inner-western (Tyrrhenian)
136 side of the orogen, and shortening in its external eastern side (Po Plain and Adriatic) (e.g. Elter et
137 al., 1975; Barchi et al., 1998; Doglioni et al., 1998; Liotta, 2002; Bennett et al., 2012; Cuffaro et al.,
138 2010; Eva et al., 2014; Faccenna et al., 2014; Molli et al., 2016; Le Breton et al., 2018).

139 In the NW of Tuscany, the Alpi Apuane complex forms the largest tectonic window in the inner

140 Northern Apennines and expose the deepest crustal units of the belt (Tuscan Metamorphic Units)
141 (Fig.1). Three major stratigraphic and tectono-metamorphic units are traditionally distinguished in
142 the region, the Tuscan Nappe, the Massa unit and the Apuane unit, all derived from the Adria
143 continental paleomargin (Fig.2). The Tuscan Nappe consists of Mesozoic carbonate rocks and
144 Tertiary deep water and turbiditic sequences mainly detached from their original basement along
145 the décollement level of the former Carnian and Norian evaporites (Ciarapica and Passeri, 2002
146 and references therein). These anhydrites and dolostones are transformed almost everywhere (with
147 some relevant exceptions) into cataclastic breccias called *Calcare Cavernoso* or “cellular” limestone
148 (Baldacci et al., 1967; Gandin et al., 2000). The post-Norian sequence continues with Rhaetian to
149 Hettangian shallow water limestones (*Rhaetavicula Contorta* and *Calcare Massiccio*), Lower Liassic
150 to Cretaceous pelagic limestones, radiolarites and shales (*Calcare selcifero*, *Marne a Posidonomya*,
151 *Diaspri*, *Maiolica*), grading to hemipelagic deposits of the *Scaglia* (Cretaceous-Oligocene), to end
152 with the siliciclastic foredeep turbidites of the *Macigno* (Late Oligocene-Early Miocene). The entire
153 sequence has a thickness between 2000 and 4000 m (Fazzuoli et al., 1986; Ciarapica and Passeri,
154 2002; Molli and Meccheri, 2012).

155 The Apuane Unit forming most of the Alpi Apuane tectonic window is made up of a Paleozoic
156 basement unconformably overlain by an Upper Triassic–Oligocene metasedimentary sequence. The
157 Paleozoic basement is represented by metasedimentary and metavolcanic rocks including Upper
158 Cambrian–Lower Ordovician phyllites and quartzites, Middle Ordovician metavolcanics and
159 metavolcanoclastics, Upper Ordovician quartzitic metasandstones and phyllites, Silurian black
160 phyllites and *Orthoceras*-bearing metadolostones (Gattiglio et al., 1989; Conti et al., 1993; Pandeli
161 et al., 1994; Paoli et al., 2017). The Paleozoic lithostratigraphic units were deformed and
162 metamorphosed under low-grade conditions, not well precisely defined, during the Variscan
163 orogeny (Conti et al., 1991, 1993). The Mesozoic cover-rocks, where complete, include thin
164 Triassic continental to shallow-water *Verrucano*-like deposits followed by Upper Triassic–Liassic
165 carbonate platform metasediments comprising dolostone (*Grezzoni Fm.*), dolomitic marble, and
166 marble (the *Carrara Marble*), in turn covered by Middle Liassic–Lower Cretaceous cherty
167 metalimestone, cherts, and calcschists, and Lower Cretaceous to Lower Oligocene sericitic phyllites
168 and calcschists with marble interlayers. Oligocene-early Miocene (?) metasediments related to
169 turbiditic systems (*Pseudomacigno Fm.*) complete the sedimentary succession (Patacca et al., 2011
170 and reference therein).

171 The Massa unit is exposed in the westernmost part of the Alpi Apuane complex and includes a
172 litho-stratigraphic sequence formed by a Paleozoic basement similar to that of the Apuane unit and
173 a characteristic and distinctive Upper Permian–Upper Triassic metasedimentary succession,

174 including a Mid Triassic continental (conglomerates and pelites) to marine (carbonate platform
175 derived deposits) succession associated with intraplate alkaline basalts (Martini et al, 1985).
176 Lithostratigraphic terms younger than late Mid Triassic are not described in the literature, although
177 (see below) they are be locally found as tectonic lenses and small-scale remnants within a
178 cataclastic fault zone below the contact with the overlaying Tuscan Nappe (Molli et al., 2002; Conti
179 et al., 2004). Based on the similarities in stratigraphic contents of the pre-Late Triassic sequences,
180 traditional literature correlated the P.Bianca and M.Pisano exposures to those of the Massa unit
181 (Baldacci et al., 1967; Elter, 1975), whereas more recent papers defined different peak metamorphic
182 conditions (Storti, 1995; Leoni and Pertusati, 2003; Carosi et al., 2004; Molli, 2008).

183 The deformation structures of the Tuscan metamorphic units of the Alpi Apuane and surroundings
184 metamorphic cores may be referred to two main tectono-metamorphic regional events (D1 and D2
185 phases of Carmignani and Kligfield, 1990), which are regarded (Molli et al., 2000, 2002) as
186 recording progressive deformation of the distal Adriatic continental margin during continental
187 subduction and the syn- to post-contractual exhumation (Carmignani et al., 1990; Jolivet et al.,
188 1998; Carmignani et al., 2001; Molli, 2008). The two main regional events D1 and D2 were related
189 to different fold generations as illustrated by Molli and Meccheri (2012). The same deformation
190 patterns may be also recognized in the Punta Bianca and Monte Pisano metamorphic cores (Storti,
191 1995; Montomoli, 2002; Carosi et al., 2007; Molli, 2008; Balestrieri et al., 2011).

192 Deformation event D1, which can be associated with underplating and antiformal stacking of the
193 metamorphic units, is defined by a main axial-plane foliation of isoclinal folds observable on a
194 micro- to kilometer-scale (Fig. 2) and is associated with a regionally NE-oriented stretching
195 lineation interpreted as recording the main transport direction of the inner Northern Apennines
196 (Carmignani et al., 1978; Molli, 2008; Molli and Meccheri, 2012).

197 During deformation D2, the previously formed structures were reworked by different generations of
198 folds and high-strain zones, related to exhumation of the metamorphic units within the inner portion
199 of the Northern Apenninic wedge (Molli, 2008). Characteristic structures of D2 event, are the late
200 folds with subhorizontal axial plane crenulation, later deformed by semibrittle and brittle structures,
201 represented by kink and open folds, and low-angle normal faults (Molli and Meccheri, 2000; Molli
202 et al., 2010). The final stages of deformation are recorded by systemes of high-angle normal to
203 oblique-normal and trascurrent faults related with the recent to active deformation regime affecting
204 the area (Corti et al., 2006; Bennett et al., 2012; Molli et al., 2016).

205 In the metamorphic units of the Alpi Apuane, peak conditions are roughly related to T between 450
206 and 350 °C and P of 0,8-0.4 GPa (Molli et al., 2002 and references therein). In particular, kyanite +
207 chloritoid + phengitic muscovite characterize the mineral assemblages in metapelites of the Massa

208 unit, with peak conditions estimated in the range of 0,6-0,8 GPa and 420- 500°C (Franceschelli et
209 al., 1986; Jolivet et al., 1998; Franceschelli and Memmi, 1999; Molli et al., 2000b). Instead,
210 pyrophyllite + chloritoid + chlorite + phengitic muscovite in metapelites are found in the Apuane
211 unit, with peak metamorphic conditions estimated in the range of 0.4-0.6 GPa and 350-450 °C
212 (Franceschelli et al., 1986; Jolivet et al., 1998; Molli et al., 2000b).

213 The early deformation D1 in the metamorphic units of the Alpi Apuane occurred during early
214 Miocene at 27–20 Ma (Kligfield et al., 1986), whereas the syn-metamorphic D2 structures
215 developed at T higher than 250 °C, predated 11 Ma according to zircon fission-track ages of Fellin
216 et al. (2007).

217 In contrast to the Tuscan metamorphic units, the Tuscan nappe was accreted at a shallow crustal
218 level within the Northern Apennines wedge beginning from early Miocene (Cerrina Feroni et al.,
219 1983; Molli, 2008). Burial occurred under a sequence of thrust sheets now preserved in the
220 overlying sub-Ligurian and Ligurian units (Figs. 1, 2). Early thrusting is documented by top-to-the
221 east small scale shear zones and an early generation of east vergent tight to isoclinal folds within
222 incompetent stratigraphic layers (Gianmarino and Giglia, 1990; Carter and Dworkin 1990; Molli et
223 al., 2011). The early structures in the Tuscan nappe were subsequently overprinted by small to large
224 (kilometer-scale) refolding associated with sub-horizontal crenulation cleavage observable in pelitic
225 rock units, low-angle normal faults and later upright folds (Carmignani et al., 1994; Storti, 1995;
226 Carosi et al., 2003). Metamorphism to anchizone grade (Cerrina Feroni et al., 1983; Carosi et al.,
227 2003; Molli et al., 2011) during burial and deformation is constrained by tectono-stratigraphic
228 features to a maximum depth of 7 km for the Macigno sandstones (Reutter et al., 1978; Montomoli
229 et al., 2001; Montomoli, 2002; Fellin et al., 2007).

230

231

232 **3. Raman Spectroscopy of Carbonaceous Material**

233

234 Raman spectra were obtained using a Renishaw InVIA Reflex microspectrometer (IMPMC Paris).
235 We used a 514 nm Laser Physics argon laser with circular polarization. The laser was focused on
236 the sample by a Leica microscope with a 100× objective (NA = 0.85), and the laser power at the
237 sample surface was set around 1 mW. The Rayleigh diffusion was eliminated by edge filters, and to
238 achieve nearly confocal configuration the entrance slit was closed down to 15 µm. The signal was
239 finally dispersed using a 1800 gr/mm grating and analyzed by a Peltier cooled RENCAM CCD
240 detector. Before each session, the spectrometer was calibrated with a silicon standard. Because
241 Raman spectroscopy of CM can be affected by several analytical mismatches, we closely followed

242 the analytical and fitting procedures described by Beyssac et al. (2002, 2003). Measurements were
243 done on polished thin sections cut perpendicularly to the main fabrics and CM was systematically
244 analyzed below a transparent adjacent mineral, generally quartz. Between 10–20 spectra were
245 recorded for each sample in the extended scanning mode (1000–2000 cm⁻¹) with acquisition times
246 from 30 to 60 s. Spectra were then processed using the software Peakfit (following Beyssac et al.,
247 2002). Based on the obtained spectra, T from samples characterized by lower-T metamorphism (i.e.
248 $\sim 200 \leq T \leq 350$ °C) were estimated.

249 Both low-grade (<350°C) and high-grade (>350 °C) were considered. In the former case, RSCM T
250 was estimated using the correlation proposed by Lahfid et al. (2010) for the T range of $\sim 200 \leq T \leq$
251 350 °C. In the latter case, the T was calculated using the calibration of Beyssac et al. (2002) for a T
252 range of $\sim 350 \leq T \leq 650$ °C. Both calibrations have an attached accuracy of ± 50 °C due to
253 uncertainties on petrologic data used for the calibration. Relative uncertainties on T are, however,
254 much smaller, around 10–15 °C (Beyssac et al., 2004).

255 For each sample, several spectra were acquired to assess the potential within-sample structural
256 heterogeneity, with the exception of a few samples containing very little CM amount (Table 1). The
257 latter samples have therefore higher uncertainty compared to the others, and were not considered for
258 tectonic interpretations even though the obtained T is in the range of the neighbouring ones. In a
259 few samples, isolated spectra of crystalline graphite (no defect bands) were interpreted as detrital
260 CM incorporated in the sedimentary rocks prior to metamorphism, and not considered for
261 thermometric estimates. Some structural heterogeneity was found in the samples, with a maximum
262 standard error (standard deviation divided by \sqrt{n}) < 8 for most samples (Table 1).

263 The Raman spectra obtained from the selected samples set show a large between-sample variation
264 in structural organization ranging from poorly organized CM (lower-T) to well cristallized graphite
265 (higher-T) (Table 1). The collected data allow distinguishing samples characterized by T gaps in
266 the order of about 20 °C (Fig. 3), as already observed for this method along continuous
267 metamorphic gradients in Alpine settings (Beyssac et al., 2004; Gabalda et al., 2009; Vitale
268 Brovarone et al., 2014)

269 270 271 **4. RSCM Temperature record in the Alpi Apuane and surroundings**

272
273 Seventyfour samples were selected for RSCM analysis among 120 collected in various stratigraphic
274 and structural positions within the different tectonic units (Table 1). The samples were collected
275 along a regional SW-NE oriented section across the inner Northern Apennines (Fig. 1). The

276 uppermost continental unit of the nappe pile was sampled west of the Alpi Apuane in the La Spezia
277 area (Fig. 1,2), where the stratigraphic sequence of the Tuscan Nappe is exposed in different
278 localities, from Portovenere (southern tip of western promontory of La Spezia) northward to the 5
279 Terre area as part of a regional-scale fold called La Spezia fold (e.g. Gianmarino and Giglia, 1991;
280 Carter, 1992; Carosi et al., 2002; Molli et al., 2011 and references therein), in the eastern
281 promontory of La Spezia (between Lerici and Punta Bianca) (Storti, 1995; Clemenzi et al., 2015
282 and references), north and east of the Alpi Apuane in the Lunigiana and Lima Valley (Molli et al.,
283 2015; Clemenzi et al., 2014 and references).

284 A more systematic sampling was performed across the Alpi Apuane in order to enlighten the
285 thermal structure of the metamorphic core that was poorly documented so far (Figs. 2,4 and Table
286 1). Some samples of the metamorphic units were also collected in the eastern promontory of La
287 Spezia as well as southeastward of the Alpi Apuane in the Monte Pisano (Fig. 2).

288 The stratigraphic units sampled in our study are mainly from the Mesozoic to Tertiary cover
289 sequence and in particular from siliciclastic sandstones of Macigno fm. (Late Oligocene-Early
290 Miocene in age) and impure Triassic limestones for the Tuscan Nappe. The metamorphic
291 equivalent (metasandstones, slates, schists, calcschists and impure marbles) were sampled in the
292 Apuane and Massa units, together with some samples from the Paleozoic basement units (mainly
293 phyllites and schists) (Fig. 2). The samples collected in the eastern promontory of La Spezia come
294 from the Triassic impure limestone at the base of the Tuscan Nappe and from the underlying pre-
295 Mesozoic terms (black phyllites supposed to be Permian age) of the metamorphic Punta Bianca unit
296 i.e. respectively in the hanging-wall and footwall of the former major thrust reworked as a low
297 angle normal fault (Storti, 1995; Carosi et al., 1998, Clemenzi et al., 2015). Moreover, the two
298 analyzed samples in the Santa Maria del Giudice unit are part of the Monte Pisano metamorphic
299 core (Rau and Tongiorgi, 1974; Carosi et al., 1993; Montomoli, 2002; Leoni et al., 2009) and are
300 derived from its Tertiary cover sequence (Pseudomacigno Fm.).

301 Results are presented in maps and projected along the SW-NE structure-orthogonal regional and
302 local cross sections (Figs. 4, 5, 6). For the sake of comparison, results of previous studies including
303 illite-crystallinity (Cerrina Feroni et al., 1983; Carosi et al., 2003; Leoni et al. 2003) and
304 Calcite/Dolomite thermometer (quoted references) are also shown (Fig. 2, 4).

305

306 The sampling strategy allowed constraining RSCM T within the classically defined continent-
307 derived units of the inner Northern Apennines (Elter, 1975; Carmignani et al., 1978; Carmignani
308 and Kligfield, 1990; Carmignani et al., 2001 between the others) which are in the current view (see
309 above) subdivided into three major slices referred, from top to bottom, to as Tuscan nappe, Massa

310 and Apuane (also called “Authochthonous”) units (Fig. 1). In the La Spezia area, the Punta Bianca
311 metamorphic occurrences are associated with a pristine lithostratigraphic assemblage similar to that
312 of the Massa unit but affected by a lower grade peak metamorphic imprint (Storti, 1996; Leoni and
313 Pertusati, 2003; Lo Po’ et al., 2017), whereas the Monte Pisano metamorphic core is similarly
314 considered part of the Massa unit for the presence of widespread continental “Verrucano” deposits
315 (Rau and Tongiorgi, 1974; Carosi et al., 2004; Balestrieri et al. 2011).

316

317 The overall data sets, summarized in Fig. 7 and Table 1, show significant difference in mean peak T
318 among the major tectonic units so far defined. RSCM peak T are in the range of 246-284 °C (mean
319 260 ± 26 °C) for the Tuscan Nappe; 306-537 °C (mean 397 ± 64 °C, n=63) for for the Apuane and
320 454-509 °C (485 ± 28 °C, n=3) for the Massa unit.

321 In the Tuscan Nappe exposed in the La Spezia area (Figs. 1,2), a simple relationship between
322 stratigraphic positions of the samples and peak T appears (Fig. 6). The youngest terms of the
323 succession represented by the Macigno fm. show a mean T of 253 °C, whereas in the lowermost
324 measured Triassic term of the Calcari a Rhaetavicula Contorta fm. (Rhaetian in age) a mean T of
325 289 °C was obtained.

326 In the eastern Promontory of La Spezia in the same stratigraphic unit i.e. the Calcari a Rhaetavicula
327 Contorta (Rhaetian in age), a mean T of ~ 284 °C well confirmed the T obtained in the same
328 stratigraphic unit in the western promontory.

329 Samples from the Tuscan Nappe in the Lima Valley (Baldacci et al., 1967; Fazzuoli et al. 1994;
330 Botti et al., 2009; Clemenzi et al., 2014) east of the Alpi Apuane show instead lower mean
331 temperature of 227 °C obtained for Jurassic and Cretaceous pelites and marls (Table 1, Fig. 6).

332

333 In the Alpi Apuane, although the highest T were measured in samples of the Paleozoic basement
334 (364 - 537 °C, mean 445 ± 66 °C, n=9) and the lowest in the youngest stratigraphic terms of the cover
335 sequence (PseudoMacigno fm.) (306 - 511 °C, mean 368 ± 50 °C, n=22), no simple relationships
336 between stratigraphy and T appear at the scale of the whole metamorphic core (Figs. 4,5,8).

337 The mean T in the north-western part of the metamorphic complex (north of the Seravezza-Monte
338 Corchia, Turrite valley alignment) is basically the same as those defined in the south-eastern
339 segment (south of the Seravezza-Monte Corchia, Turrite valley alignment), around ~ 380 °C. The T
340 data plotted on composite vertical cross-sections (Figs. 5,9) show, however, a well defined, yet
341 different thermal structure and overall thermal architecture between the northern and southern Alpi
342 Apuane.

343 The north-western part of the Alpi Apuane, as previously defined, (cross-sections A,B,C,D,E,F,G)
344 shows an inverted field metamorphic gradient. Within the Apuane unit, higher T (483-507 °C,
345 mean 465 °C) are found to the west, within a structural distance of ~500 m from the basal contact
346 of the Massa unit (Figs. 5,9). The T decrease eastward and structurally downward to ~ 345 °C in
347 the Orto di Donna syncline and in the Arni-Boana structural culmination, i.e. in the geometrically
348 deepest parts of the Alpi Apuane metamorphic core (Kligfield et al., 1981; Carmignani and
349 Kligfield, 1990; Carmignani et al., 2001; Molli and Vaselli, 2006).

350 The south-eastern parts of the Alpi Apuane (cross-sections H,I,L,M) are instead characterized by a
351 normal-type metamorphic field gradient with overall upward decreasing T from 510 °C to 320 °C in
352 a vertical structural distance of 3000 m.

353 Samples with the highest RSCM T are found in the south-eastern part of the Alpi Apuane, an area
354 known in the local geological literature as “Zona dello Stazzemese” or “Stazzemese Shear Zone”
355 (Stazzema is village included in it). The area is characterized and recognized for a long time for its
356 distinctive structural style (see Massa 2007 for an historical overview) with kilometer scale
357 recumbent D2 isoclinal folds with highly sheared and mylonitized limbs (see Carmignani et al.
358 1996, Conti et al., 2009; Cinquini, 2014). Samples characterized by the highest RSCM T are
359 intimately related to mineralized bodies (Pb-Zn±Au Hg, Fe-Cu and Barite-Iron Oxide-Pyrite
360 deposits), characteristic of this area with respect to the whole Alpi Apuane and studied and
361 exploited since the mid of last century (Carmignani et al., 1972; Carmignani et al., 1976; Orberger,
362 1985; Costagliola et al., 1990; Dini et al., 1995; Costagliola et al., 1998; Biagioni et al., 2016). This
363 was observed in samples of different age (Palaeozoic, Mesozoic and Cenozoic). Other samples from
364 the Stazzemese Shear Zone but far away from these ore bodies show lower RSCM T. The RSCM T
365 for these samples exceed of about 180-200 °C the values obtained for the enclosing host rocks. As
366 an example, in the Fornovolasco area (the easternmost extension of the “Zona dello Stazzemese”),
367 Tertiary metasandstones (Pseudomacigno Fm.) show RSCM T >500°C (sample 70) if close to
368 mineralized levels (Trimpello ore bodies), whereas the same rock type far from mineralized bodies
369 shows T <360 °C (samples 68,69,71) (Fig. 5 and Table1). This feature suggests that the origin
370 higher T recorded by CM is related to the hydrothermal activity responsible for the ore
371 mineralization.

372

373 **5. Comparison with previous data**

374

375 Our new RSCM data find good agreement with previous available data, in particular those derived
376 from calcite/dolomite (Ca/Do) geothermometer/analysis (Fig.4) (Di Pisa et al., 1985; Molli et al.,

377 2000; Oesterling et al., 2007). Although different in absolute value, the RSCM and Ca/Do data well
378 document the presence of inverted metamorphism in the north-west part of the Alpi Apuane, with
379 higher T in the westernmost and uppermost structural positions, decreasing eastward and downward
380 within the structural building.

381 To the West (where the T are highest), Ca/Do shows lower values with respect to RSCM, whereas
382 this is not always the case or is the opposite in the central and easternmost part of the Apuane
383 (Fig.4).

384 The comparison between Ca/Do and RSCM cannot be drawn for the lack of data in the south-
385 eastern part of the Alpi Apuane (“Zona dello Stazzemese”) where suitable rock-types for Ca/Do
386 analyses are less common and therefore not deeply investigated in the literature. In this area,
387 however, studies based on various techniques including stable isotope compositions and
388 geothermometry, fluid inclusions and phase relationships between sulfosalts in ore bodies give host
389 rock T around 350-400 °C and T for mineralizing fluids and ore bodies higher than 450 °C
390 (Cortecci et al., 1989; Cortecci et al., 1994; Costagliola et al., 1997; Costagliola et al., 1998;
391 Biagioni et al., 2013, 2016) which are similar to our RSCM results.

392 For the Massa unit, owing to intense weathering and oxidation, only 3 out of 25 samples from
393 Verrucano continental metasediments were analyzed. Our mean RSCM T is in agreement with the
394 estimates based on Fe-Mg exchanges in coexisting chloritoid and chlorite (450-500 °C;
395 Franceschelli and Memmi, 1999). Similar T ranges were also constrained by the stability field of
396 the kyanite+quartz pair and chlorite+chloritoid+quartz assemblages in the FeO-Al₂O₃-SiO₂-H₂O
397 (Franceschelli et al., 1998). Using similar methods chloritoid±chlorite Mg±Fe-exchange
398 thermometer a peak temperature of 455 °C was found by Molli et al. (2000). Ca-Do data in the
399 Mid-Triassic marble of the Massa unit also give a similar T in the range of 430-520 °C (Cardaci,
400 1987).

401

402

403 **6. Summary and discussion**

404

405 The RSCM data presented in this study allowed us to better constrain the relationships between the
406 nappe architecture and the thermal structure in the Alpi Apuane and their surroundings. This
407 highlighting new subjects for a better and more complete understanding of the thermo-mechanical
408 evolution and exhumation history of the inner Northern Apennines in the general frame of the
409 evolution of the Apennines orogen. Hereafter the results and the first order points of our
410 contribution are summarized and discussed.

411

412 6.1 *Peak temperature and tectonic units*

413 A first point to be remarked is the difference in the mean peak T among the
414 structurally/stratigraphically defined tectonic units (Fig. 7). The classically accepted subdivision
415 (Elter, 1975, Carmignani and Kligfield, 1990; Decandia et al., 1996, Vai and Martini, 2001) into
416 three major continental units forming the backbone of the inner Northern Apennines – from top to
417 bottom: the Tuscan nappe, the Massa and the Apuane units – appears to be fully supported by the
418 new measured RSCM T (Fig.7) which show a mean peak T of ~ 260 °C for the Tuscan Nappe, ~
419 485 °C for the Massa unit and ~ 385 °C for the Apuane unit.

420 Moreover, our data allow defining new tectonic units that were not clearly identified and considered
421 in the previous models. In such group of units may be included the Punta Bianca Unit in the west
422 and the Monte Pisano Unit in the south. Moreover, in the southern-eastern Alpi Apuane the Panie
423 may be inserted within this group, since they are here characterized by a RSCM T of 320 °C, an
424 intermediate value between those of the Apuane Unit and those of the Tuscan Nappe. Other
425 evidence of missing units, inside the Alpi Apuane, may be searched for between the Massa unit and
426 the overlying Tuscan Nappe (Fig.5 cross section E), where remnants of a post mid-Triassic cover
427 (cherty metalimestones, marbles, phyllites) with a peak RSCM T of ~350 °C were sampled (sample
428 16). Those remnants are also observable as structural relicts exposed as hectometer to
429 pluridecameter thick slices and lenses (see Molli et al., 2000) and widely recognizable as clasts
430 (meter, decimeter to centimeter in scale) within the carbonate tectonic breccia at the base of the
431 Tuscan Nappe in the southern Alpi Apuane (Conti et al., 2009; CARG F.260; Cinquini and Molli,
432 2015). These data and occurrences may be interpreted as related to the former existence of a
433 metasedimentary unit (“X unit”, “missing section” in Fellin et al. 2007) originally including the
434 post Mid-Triassic cover sequence now only scatterly observable on top of the Massa Unit.

435 The rank of individual tectonic unit for the Panie (Maxwell, 1956; Nardi, 1961; Giglia 1967;
436 Carmignani et al., 2001) as well as the importance of the “X unit” to fill the gap between the base of
437 the Tuscan Nappe and the top of the Massa unit during the syn-peak metamorphism nappe stacking
438 are in line with what anticipated and discussed in the frame of the tectonic history of the
439 metamorphic units by Molli et al., (2000); Molli et al., (2002); Fellin et al. (2007). Thanks to the
440 newly defined RSCM data, and considering the mean T as an estimate for the “whole unit” thermal
441 peak, we may emphasize that the classical subdivision into three major Tuscan units across the Alpi
442 Apuane and surrounding introduced in literature since Elter (1975) as related to the original thrust
443 stacking, is due instead to tectonic excision during exhumation. In other words, the present day
444 tectonic units have to be considered as remnants of a former thicker, more complete and now only
445 partially preserved contractional nappe stack (Coli, 1989; Van den Berg, 1989; Carmignani et al.,

446 1990; Carmignani et al. 1995; Jolivet et al., 1998; Molli et al., 2002).

447

448 *6.2 Metamorphic field gradients and thermal architecture*

449 For the Tuscan Nappe, the dataset in the La Spezia area (Fig.2, 6) indicates a base (Triassic
450 Rhaetian limestone) to top (Oligocene-early Miocene Macigno sandstone) difference of ~40 °C
451 which occurs within a structural distance of 2000 m. Thus, assuming that the peak T are: (i) coeval
452 in age and (ii) related with the pre-folding thermal architecture of the unit within the orogenic
453 prism, a peak T normal-type field gradient of 20 °C/Km may be defined (Fig.10).

454 At regional scale, the collected data from the Tuscan Nappe suggest for its westernmost exposure
455 (La Spezia area) a mean RSCM T of 271° C and a lower mean T of 227°C in the easternmost
456 position in the Lima Valley, east of the Alpi Apuane (Fig.1,2,10). This west to east decrease of peak
457 T, in line with previously recorded illite crystallinity and organic matter data (Reutter et al., 1978,
458 1983; Cerrina Feroni et al., 1983), may be referred to an original thickness of the orogenic wedge
459 stack above the Tuscan Nappe. Moreover, assuming that the field gradient defined in the La Spezia
460 area was constant at regional scale, this results in a variation of the wedge thickness above the
461 Tuscan Nappe of ~2 Km from west (La Spezia) to east (Val di Lima) (Fig.10).

462

463 For the Alpi Apuane, taking into account the whole data set in the Apuane unit, a difference in T
464 between the pre-Mesozoic samples and the Mesozoic to Tertiary ones may be underlined (Figs. 4,
465 5, 8, 9). The pre-Mesozoic basement rocks show a mean peak RSCM T of 445 °C whereas a mean
466 of 386°C is found in the metasedimentary Mesozoic to Tertiary cover.

467 These data may be explained considering the higher peak T in the basement rock as a relict
468 metamorphism of the Variscan age (Conti et al., 1993, Pandeli et al., 2003) or as a relict of a Late
469 Variscan (Permian) thermal event in line with recently acquired data (Vezzoni et al., 2017;
470 Pieruccioni et al., 2017).

471 Nevertheless, since similar higher T (Fig.8) were also found in samples with Mesozoic to Tertiary
472 protoliths, an alternative hypothesis may also be taken into account. In this alternative frame, an
473 Apenninic-age heating possibly related to a fluid flow infiltration in the basement rocks (and locally
474 in the Mesozoic cover) during its detachment from the underlying subducted middle to lower crust
475 may be envisaged (Fig. 10d). The higher peak T found in association with mineralized horizons in
476 the southern Alpi Apuane (“Zona dello Stazzemese” or “Stazzemese Shear Zone” Figs. 9, 10) may
477 thus be interpreted as an evidence of Apenninic-age infiltration and hot fluid flow along high-strain
478 localized zones of deformation, which were reworked during exhumation.

479

480 Finally, the distribution of peak T at the scale of the whole Alpi Apuane (Fig.9) indicates a different
481 and systematic arrangement with respect to the overall architecture of the structures in the north-
482 west as opposed to the south-easternmost part. The north-west part of the Alpi Apuane (Figs. 5,9) is
483 characterized by a SW to NE decrease of peak temperature from 495 °C in the west to 357 °C in the
484 central and 336 °C in the easternmost position. A difference of 125° C is observed with a structural
485 distance of ~8 Km, thus an inverted field metamorphism with a T gradient of ~20 °/Km could be
486 defined.

487 Furthermore, the distribution of the peak temperatures and the resulting thermal architecture are
488 different in the south-east part of the Alpi Apuane (Fig. 9) where an apparent normal-type gradient
489 is observed with transition from temperatures higher than 500 °C to less than 300 °C (projected
490 base of the Tuscan Nappe) in less than 1,5 Km (e.g. cross-section L) with an apparent field gradient
491 in excess of 90 °C / Km.

492 This clearly points out the complexity of the thermal vs. structural architecture in the Alpi Apuane
493 which well fits an overall “contractional” model of antiformal stacking (i.e. an orogenic wedge
494 dominated by material advection) in the northern part and an opposite “extensional” core complex
495 model with condensed isograds (i.e. an orogenic wedge dominated by temperature advection) for
496 its southernmost part.

497 This variability in the thermal structure between the two sectors of the Alpi Apuane, however, may
498 be only apparent since the exposed geometrically deepest and cooler levels of the eastern Alpi
499 Apuane are not exposed in the central-southeasternmost segment of the dome in relationship with
500 its 3D structure, see below (Fig.9).

501

502 *6.3 Regional structures of the Alpi Apuane, kinematic and paleothermal evolution*

503

504 *6.3.1 Internal deformation of the Alpi Apuane metamorphic core*

505 The regional structure of the Alpi Apuane metamorphic core is that of an asymmetric antiform
506 dome-like structure defined by the attitude of the main foliation D1 dipping west along the western
507 side of the dome and to the east along the eastern side (Carmignani and Giglia, 1979; Kligfield et
508 al., 1979; Kligfield et al., 1981; Carmignani and Kligfield, 1990; Carmignani et al., 1995; Molli and
509 Vaselli, 2007; Molli and Meccheri, 2012). This regional scale antiform (Figs. 4,5,9) shows internal
510 complexities due to the presence of two minor culminations, respectively centered in the south west
511 and north east part of the dome (Figs. 4,9). The paleoisotherms defined by our RSCM data are
512 deformed by the later (i.e. post-D1) dome-shaped regional structures of the core, resulting in an
513 apparently inverted type field gradient in the north-west, where the main phase (D1) isoclinal

514 regional fold structures (Bergiola Anticline in the Massa unit, Carrara Syncline, Vinca-Forno
515 anticline and Orto di Donna syncline, Figs. 4,5) and related axial planar foliation D1 are west-
516 dipping, and in a normal type field gradient in the east and southeast part of the Alpi Apuane, where
517 the main phase (D1) isoclinal regional fold structures, e.g. the M.Corchia syncline (southern
518 prolongation of the Orto di Donna-Altissimo syncline), and related axial planar foliation D1 are
519 east- or south/east-dipping.

520 These relationships between the paleothermal architecture and regional deformation features within
521 the Alpi Apuane and surroundings area may be inserted in the conceptual model suggested in
522 Figure 10, which takes into account all available structural and geo-thermochronological data
523 together with presented RSCM results.

524 The proposed evolutionary model envisages: i) crustal underplating of the Tuscan continental units
525 (Fig. 10a,b) with an early stage of underthrusting and stacking below the Ligurian/subligurian lid
526 (former Ligurian Tethys-derived accretionary wedge). Assuming a constant thermal gradient of 20
527 °C/Km as defined in the upper continental unit (Tuscan Nappe), a $T > 400$ °C was reached at crustal
528 depth major than 20 Km, thus fitting available petrological data (Franceschelli et al., 1986; Molli et
529 al, 2000) and our RSCM data. The Massa unit, originally derived from the westernmost position,
530 records higher T (and P) peaks, with respect to the Apuane unit (see also Jolivet et al., 1998; Molli
531 et al., 2000a,b); ii) a successive duplexing stage (Fig. 10c,d) may be responsible for the formation
532 of the internal stacking and regional fold development including the overthrusting of the Massa
533 (higher grade) unit above the Apuane unit (lower grade). During this deformation stage (late D1 in
534 Molli et al., 2000), and following the thermo-kinematic model proposed by Dunlop et al. (1997) and
535 Bollinger et al. (2004) a folding of previous paleoisotherms is suggested to produce the
536 paleothermal and structural features in the western side of the Alpi Apuane across the contact
537 between the Massa and the Apuane units and downward (Figs. 4,5).

538 During the crustal duplexing and antiformal stacking (Fig. 10d,e,f) a possible pathway for hot fluids
539 coming from middle to lower crust may be suggested along some major tectonic contact and along
540 the decollement level at the base of detached Paleozoic terms. This hot fluid channelling associated
541 with ore mineralization was localized with the ongoing deformation and after the refolding of
542 previous D1 structures in the eastern limb of the regional antiformal stack within the “Stazzemese
543 Shear Zone” (Figs. 9,10e,f).

544 The successive stages of deformation in the Alpi Apuane metamorphic core recorded the switching
545 in the deformation mode from crustal thickening to crustal thinning in the wake of eastward
546 migration of contraction/extensional fronts which characterize the Northern Apennines
547 development (Elter et al., 1975; Patacca et al., 1990; Carmignani, Kligfield, 1990; Carmignani et

548 al., 1995; Doglioni, 1991; Piali et al., 1998; Liotta and Ranalli, 1999; Le Breton et al., 2017 and
549 references therein). During the vertical shortening of the previously developed antiformal stack the
550 “Stazzemese Shear Zone” as well as the later flat lying regional D2 foliation and structures were
551 formed (Fig.10g, h).

552

553 *6.3.2 The Alpi Apuane metamorphic core and its boundary faults*

554 As previously illustrated, the Alpi Apuane metamorphic core forms a regional scale northwest-
555 southeast trending elliptical dome, which is separated by the overlying Tuscan Nappe by meter to
556 hundreds of meters thick levels of carbonatic breccias and cataclasites which have been considered
557 since Trevisan (1965) as derived from the former basal layer of the Tuscan Nappe, i.e. by an
558 original alternation of dolomites and evaporites of Triassic age (“Calcare Cavernoso” Auct.).
559 Carmignani and Kligfield (1990) first interpreted this breccia-layer (“window fault” in Hodgkins
560 and Stewart, 1994; Casale, 2012) as the detachment horizon that separates low-grade to
561 unmetamorphic upper-plate units (our RSCM $T < 300$ °C) from the underlying metamorphic lower
562 plate units (401 ± 65 °C mean of all our data set of RSCM T).

563 From the kinematic point of view the “window fault” cuts down-section the footwall regional
564 structures along a south-west to north-east transport direction (Molli, 2012) as shown in map and
565 cross section in Figs. 4,5,9. The low angle detachment fault is therefore in contact with the
566 uppermost structures of the western Alpi Apuane (Massa unit, Carrara Syncline, Vinca-Forno
567 Anticline) and with progressively deeper and lower regional structures (Orto di Donna Syncline,
568 Tambura Anticline and easternmost Apuane).

569 This structural cut-down section corresponds to a paleothermal architecture which shows, across the
570 “window fault” and along the transport direction, an eastward decrease in the T gap between
571 hangingwall and footwall from $\Delta T > 200$ °C in the west to $\Delta T < 50$ °C in the east (Fig.9). This is
572 mainly due to the cross-cut relationship and kinematic interaction between the window fault and the
573 footwall antiformal stack of the metamorphic core as figured in the conceptual model of Figure
574 10e,h. Note that the window fault mainly formed by breccias and cataclasites derived from the basal
575 layers of the Tuscan Nappe locally includes (for instance in the southern Alpi Apuane) crushed and
576 brittely deformed relicts of X/“missing unit” originally on top of the Massa and Apuane units.

577 Furthermore, using the thermochronological data in Fellin et al. (2007), we may date some steps of
578 the proposed kinematic history with the end of distributed deformation in the footwall metamorphic
579 core, the antiformal stack development and the later Stazzemese Shear zone and D2 folding as
580 occurred before 11 Ma, a time at which the Alpi Apuane metamorphic core reached a temperature of
581 c. 250 °C as constrained by Zr FT age (Fellin et al., 2007). Localized brittle deformation along low

582 angle normal faults and the end of the activity of the “window fault” occurred at a crustal depth as
583 low as ~ 180 °C in a time interval between 7 to 4–5 Ma based on data collected along the western
584 and in the eastern side of the Alpi Apuane by Fellin et al. (2007). After that time crustal extension
585 was accommodated by the high angle (mainly) normal faults which shaped the present day tectonic
586 setting, the regional morphostructure and the deep crustal structure (Fig., 4,5,9, 10i,l). The high
587 angle faults cross-cut the former synmetamorphic structures as well as the “window fault” (Molli et
588 al., 2016 and references therein).

589

590 **7. Conclusions**

591

592 RSCM T estimates have proven an efficient mean to put extensive T constraints on the thermal
593 structure of coherent units and on tectonic contacts even within very narrow T ranges (Beysac et
594 al., 2002; Rahl et al., 2005; Chen et al., 2011; Vitale Brovarone et al., 2013, 2014; Bellanger et al.,
595 2014; Scharf et al., 2013; Wiederkehr et al., 2011).

596 Our data in the Alpi Apuane metamorphic core well illustrate how RSCM T distribution are
597 related/controlled in different ways by regional and local deformation structures and in turn that the
598 observed style of deformation and type of structures are controlled/related with local
599 paleotemperatures.

600 Since the seminal paper of Carmignani and Kligfield (1990), the Alpi Apuane have been world-
601 wide recognized as a metamorphic core complex (Withney et al., 2013), recording mid-crustal
602 distributed post-orogenic “ductile” extensional deformation. This view, however, has been
603 questioned by different authors who have suggested that extensional denudation of the Alpi Apuane
604 was instead related with underplating and thickening of the internal Northern Apennines (among
605 others Cello and Mazzoli, 1996; Jolivet et al., 1998, Fellin et al., 2007).

606 Beside localized fluid-mediated thermal effects (see Section 4), our RSCM data document that the
607 paleothermal architecture of the Alpi Apuane metamorphic core better fits a tectonic scenario of
608 syn-orogenic contractional exhumation associated with a cool paleothermal gradient, which allowed
609 the preservation of inverted metamorphism across the Alpi Apuane metamorphic core and its
610 overall paleothermal architecture.

611 Nevertheless, post-antiformal stack structures (regional flat-lying D2 foliation and the Stazzemese
612 Shear zone) may be related to the switching and transition from crustal thickening to crustal
613 thinning, when the metamorphic core was already at mid crustal depth (c.15 Km and temperature of
614 ≤ 350 °C). Our major conclusions put new constraints for the thermo-mechanical evolution and
615 exhumation history of the Northern Apennine in its inner (western) side; moreover, they may be of

616 general and widespread interest for other orogens, showing anchimetamorphic to metamorphic mid
617 to shallow crustal terrains and metamorphic cores. Our data clearly illustrate how the thermal and
618 metamorphic signature may have different characters and different field gradients at tens of
619 kilometer scale, calling for a careful analysis of thermal data in correlation with the associated
620 structural architecture for a firm interpretation of the tectonic frame at the orogen-scale.

621

622

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624

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1175 **Figures caption**

1176

1177 Fig.01. Geological setting of the Northern Apennines and regional cross sections (mod. by Molli,
1178 2008) with indicated the studied areas.

1179 Fig.02. Tectonic map of the inner Northern Apennines with locations of analyzed samples. In the
1180 figure are also reported previous Temperature data sets and related references. For illite cristallinity
1181 data grey and black values are related respectively to the Scaglia fm. (Late Cretaceous-Oligocene)
1182 and Calcari a Rhaetavicula Contorta Fm. (Late Trias).

1183 Fig.03 Examples of spectra RSCM of selected analyzed samples. To be noticed as significant
1184 differences in the spectra correspond to slight differences in peak temperatures.

1185 Fig.04 Geological map of the Alpi Apuane with measured RSCM temperatures and other data
1186 available from literatures: (1) Ca/Do from in Molli et al. 2000; (2) Di Pisa et al. 1985.

1187 Fig.05 Cross-sections across the Alpi Apuane with RSCM temperatures

1188 Fig.06. a) Cross section of La Spezia area and measured RSCM temperatures; b) Stratigraphy and
1189 RSCM temperatures in the Tuscan Nappe.

1190 Fig.07 RSCM temperatures in the different tectonic units of the Alpi Apuane and nearby
1191 metamorphic core of Punta Bianca and Monte Pisano. The vertical position of the samples
1192 correspond to the distance from the reference surface represented by the basal contact of Tuscan
1193 Nappe (see scal bar in meters).

1194 Fig.08 Stratigraphy and RSCM temperatures in the Apuane unit.

1195 Fig.09. Paleothermal and structural architecture of the Alpi Apuane metamorphic core complex. a)
1196 structural architecture of the Alpi Apuane metamorphic core; b) window-scale paleothermal
1197 architecture; c) paleothermal architecture in cross-sections view.

1198 Fig.10. Evolutionary model for the Alpi Apuane within the different stages of Apenninic wedge
1199 growth from crustal thickening to crustal thinning stages (* Kligfield et al., 1986; ** Giglia,
1200 Radicati di Brozolo, 1974; *** Fellin et al., 2007 and references): a) early stage of nappe stacking
1201 below the Ligurian/subligurian lid (former accretionary wedge); b) the same as in a) with in red
1202 dashed lines the 400°, 350° and 300 °C paleoisotherms; c,d) successive duplexing stage with
1203 formation of internal stacking and overthrusting of Massa (higher grade) above the Apuane unit
1204 (lower grade). During this deformation path, a folding of previous paleoisotherms is envisaged to
1205 produce the thermal features described at pages 10-11 (see cross sections E,F,I of Figs. 4,5 and
1206 Fig.9). In blue the possible path way of hot fluids coming from subducted middle to lower crust
1207 which may be associated with ore bodies, reworked within the Stazzemese Shear zone during

1208 following deformation stages; e) antiformal stacking phase with development of: 1) finite geometry
1209 of regional deformation structures (dome shape of main foliation and related regional D1 structures)
1210 and 2) the finite thermal structure with the regional folding of previous isotherms (f); g), h)
1211 switching from crustal thickening to crustal thinning with development of D2 structures related to a
1212 vertical shortening accounting for a minimum of 20% of distributed ductile thinning (see Molli and
1213 Vaselli, 2007), as well as the “Stazzemese Shear Zone”, which is the possible deeper expression of
1214 a linked extensional detachment system including the brittle “window fault”. The activity of the
1215 “window fault” continued up to crustal depth corresponding to an ambient temperature of 180 °C
1216 (see thermochronological data in Fellin et al., 2007; i) and l) final stages of exhumation (4-5 Km of
1217 vertical displacement) of the Alpi Apuane metamorphic core in a crustal thinning stage starting
1218 from 7-5 Ma (Ap Ft Fellin et al., 2007 and references) and continuing up to now (Bennett et al.,
1219 2012; Molli et al., 2016). During this stage, deformation is accommodated by high angle normal to
1220 transtensive faults cross cutting the “window fault” as well as the syn-metamorphic templates. In l)
1221 isotherms are drawn according to thermal data and modeling in Verdoya et al., 2005; Pauselli et al.,
1222 2006; Faccenda et al., 2009.

1223
1224 Table 1. Selected samples for RSCM thermometry. GPS coordinates in WGS84 system, number of
1225 spectra (n), mean R2ratio (Beysac et al., 2002a) or RA1 ratio (Lahfid et al., 2010) for n spectra
1226 with corresponding standard deviation (sdv), and calculated temperature with standard error (SE).
1227 Standard error is the standard deviation divided by \sqrt{n} . The absolute error on temperature is ± 50
1228 C (Beysac et al., 2002a). *low-T samples processed with RA1 ratio. ** Samples for which the
1229 degree of graphitization of CM might reflect hydrothermal processes rather than regional
1230 metamorphism.

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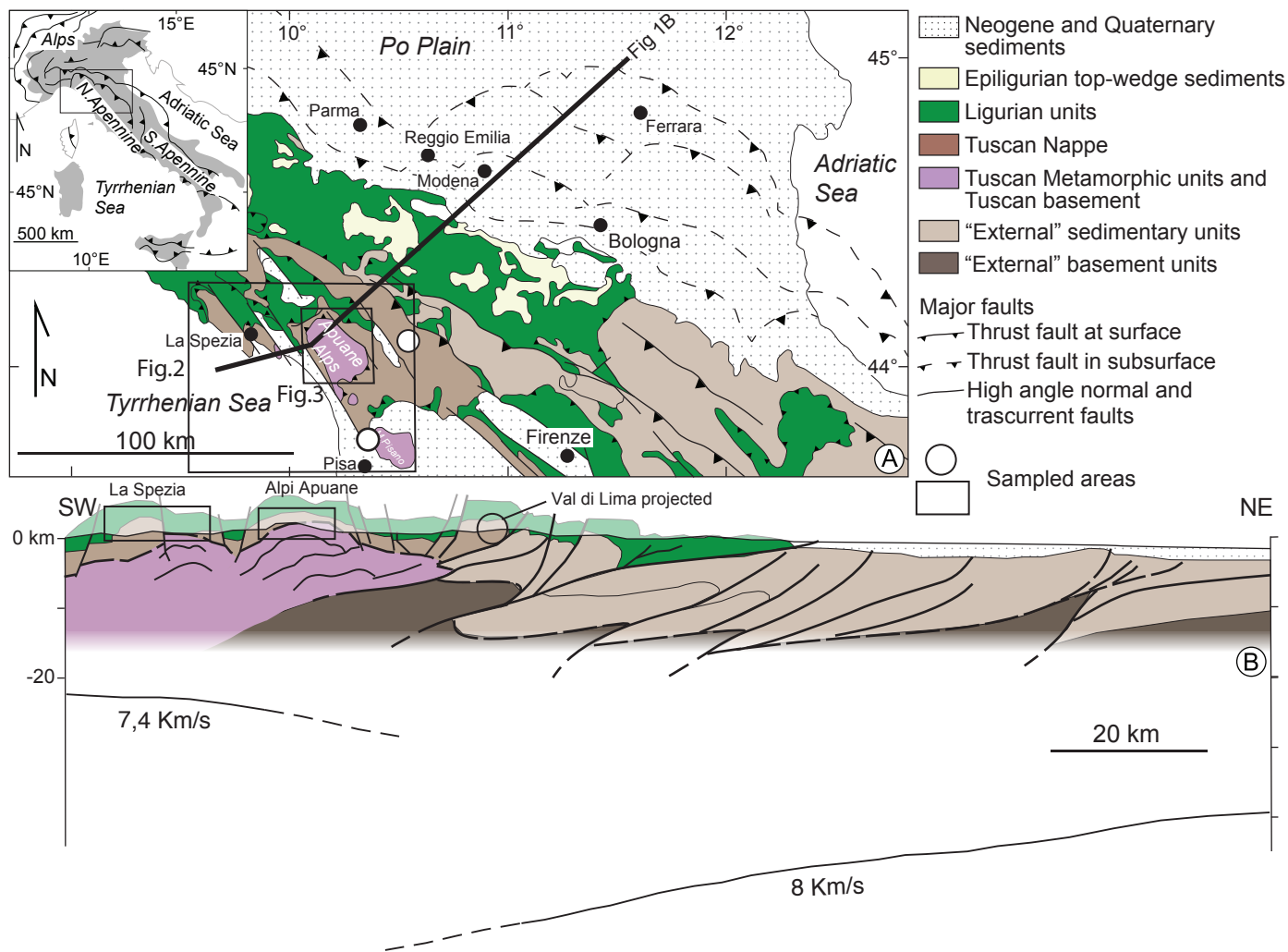


Fig.01 Molli et al., JSG

Fig.01. Geological setting of the northern Apennines and regional cross sections (mod. by Molli, 2008) with indicated the studied areas.

Fig.02 Molli et al., JSG

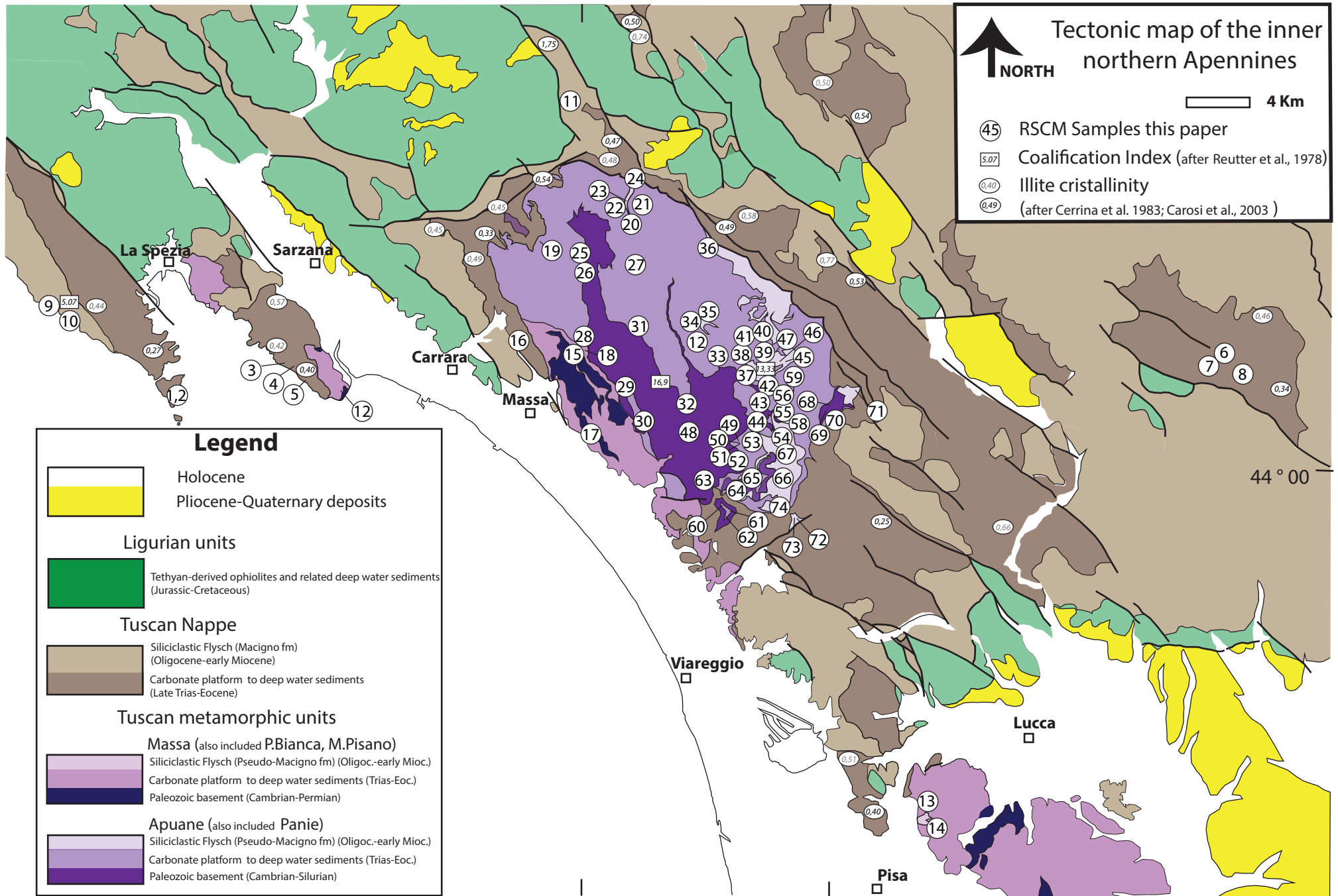


Fig.02. Tectonic map of the inner northern Apennines with locations of analyzed samples. In the figure are also reported previous Temperature data sets and related references. For illite cristallinity data grey and black values are related respectively to the Scaglia fm. (Late Cretaceous-Oligocene) and Calcarei Rhaeticus Contorta Fm. (Late Trias).

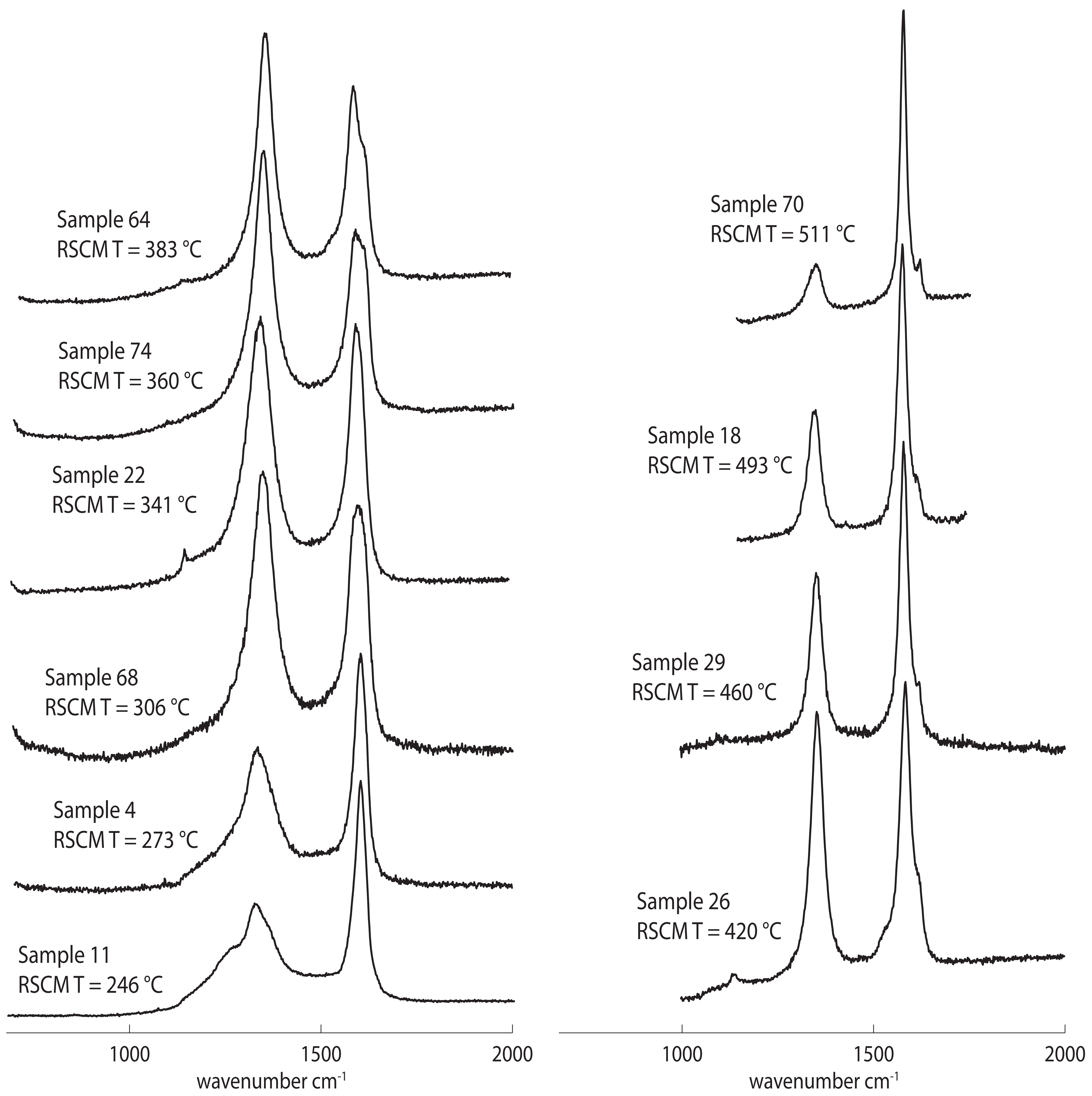


Fig.03 Examples of spectra RSCM of selected analyzed samples. To be noticed as significant differences in the spectra correspond to slight differences in peak temperatures.

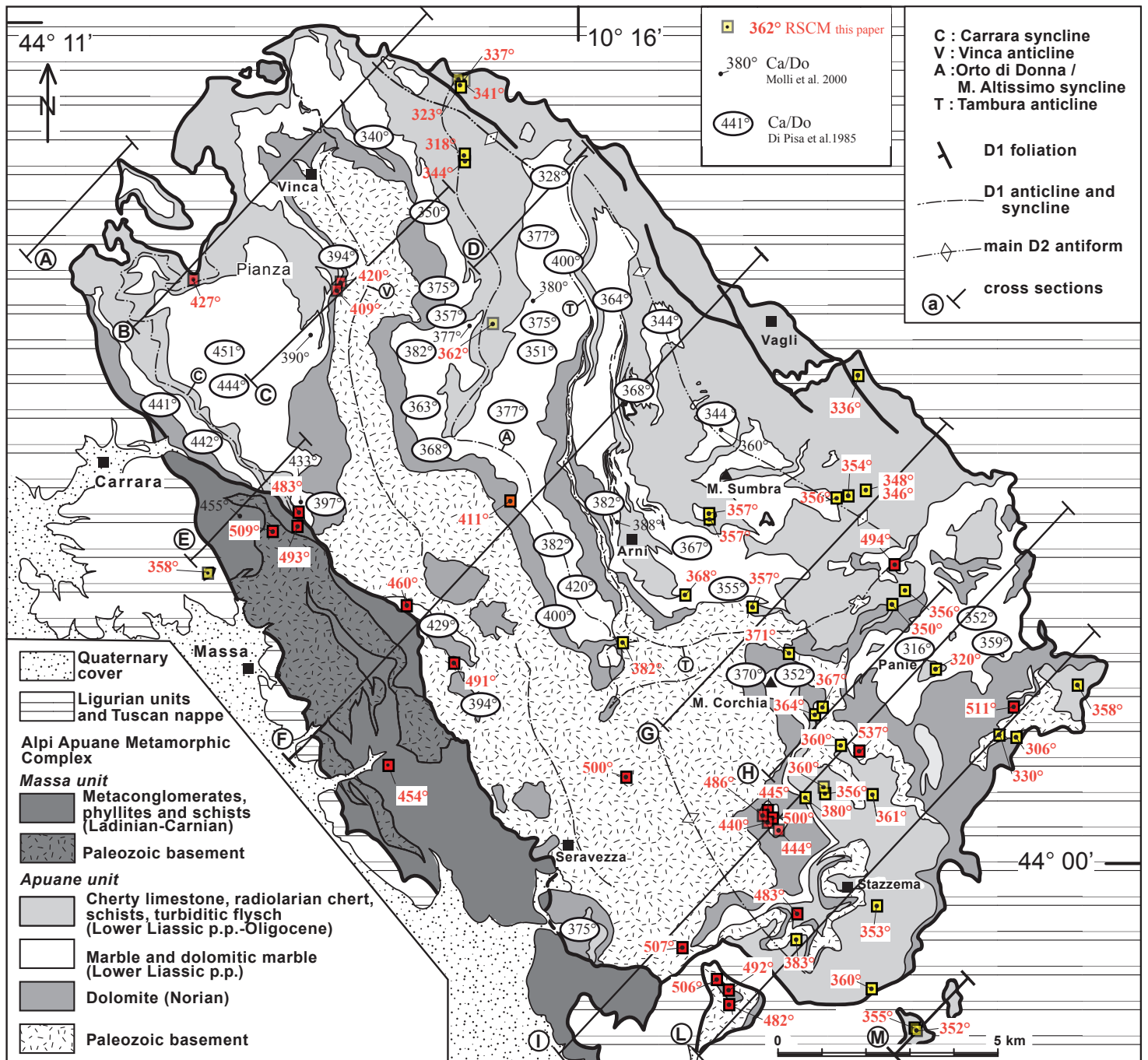
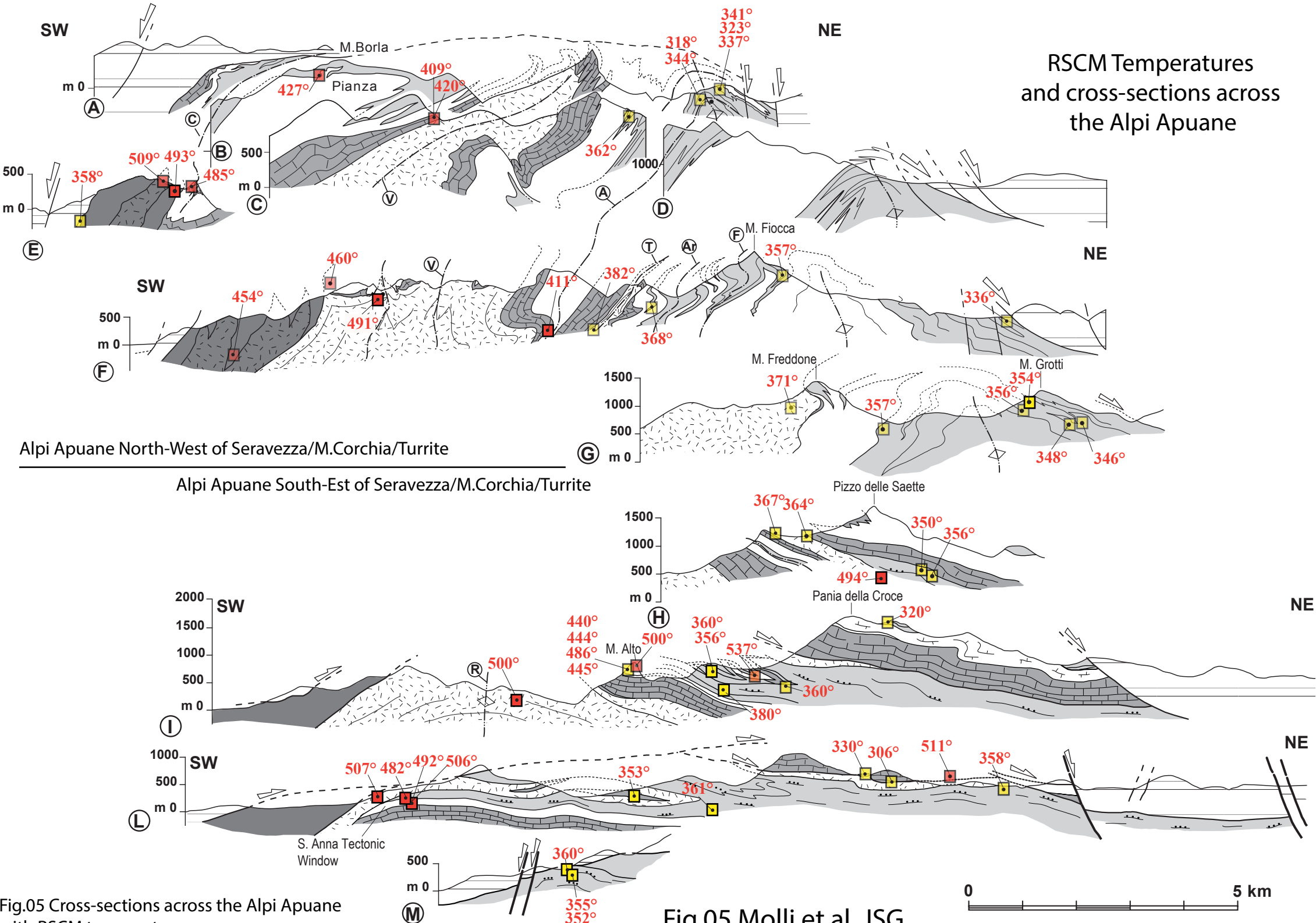


Fig.04 Molli et al. JSG

Fig.04 Geological map of the Alpi Apuane with measured RSCM temperatures and other data available from literatures: Ca/Do from in Molli et al. 2000; Di Pisa et al. 1985.

RSCM Temperatures
and cross-sections across
the Alpi Apuane



Alpi Apuane North-West of Seravezza/M. Corchia/Turrite

Alpi Apuane South-Est of Seravezza/M. Corchia/Turrite

Fig.05 Molli et al. JSG

Fig.05 Cross-sections across the Alpi Apuane with RSCM temperatures

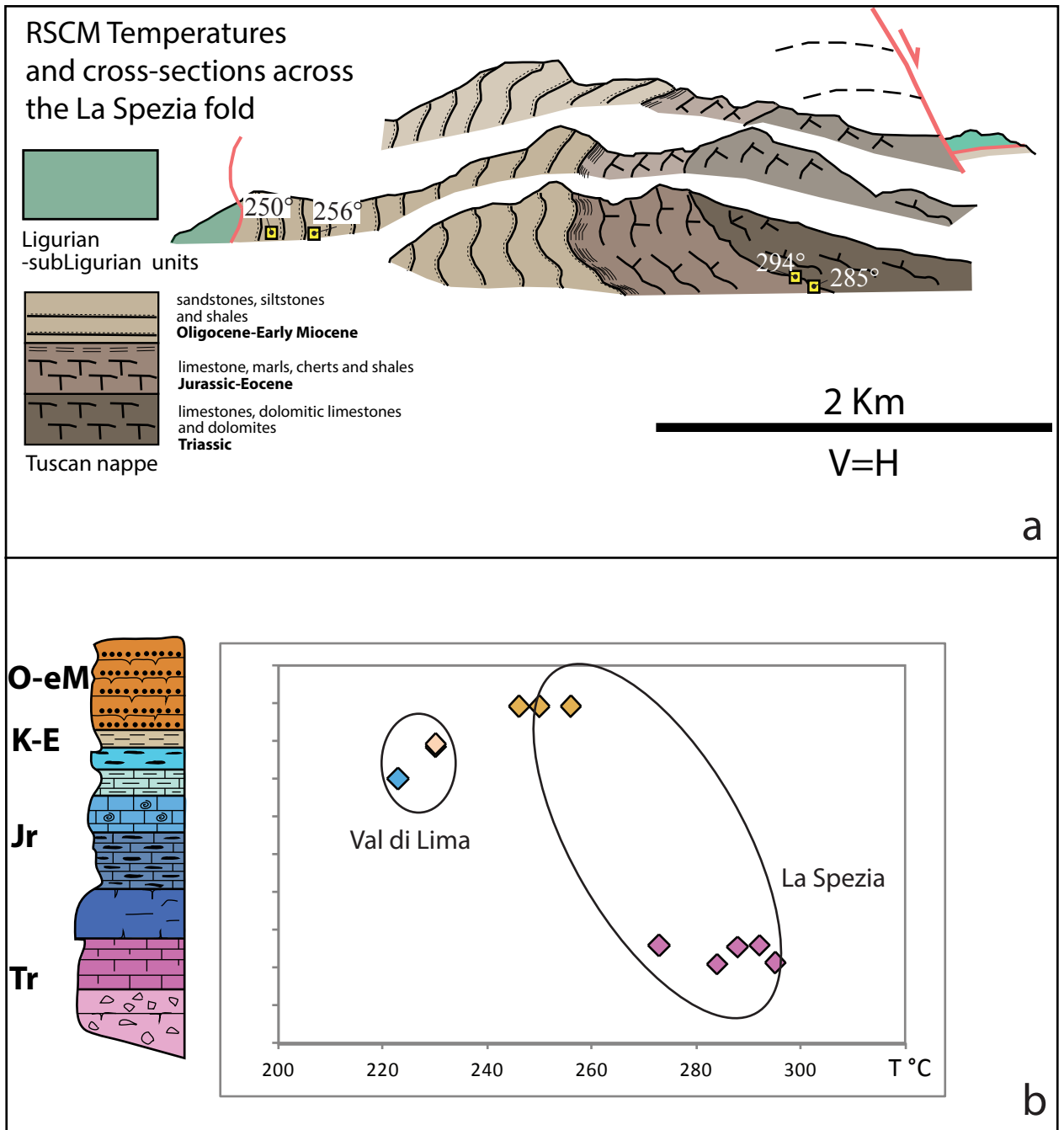


Fig. 06 Molli et al JSG

Fig.06. a) Cross section of La Spezia area and measured RSCM temperatures;
b) Stratigraphy and RSCM temperatures in the Tuscan Nappe.

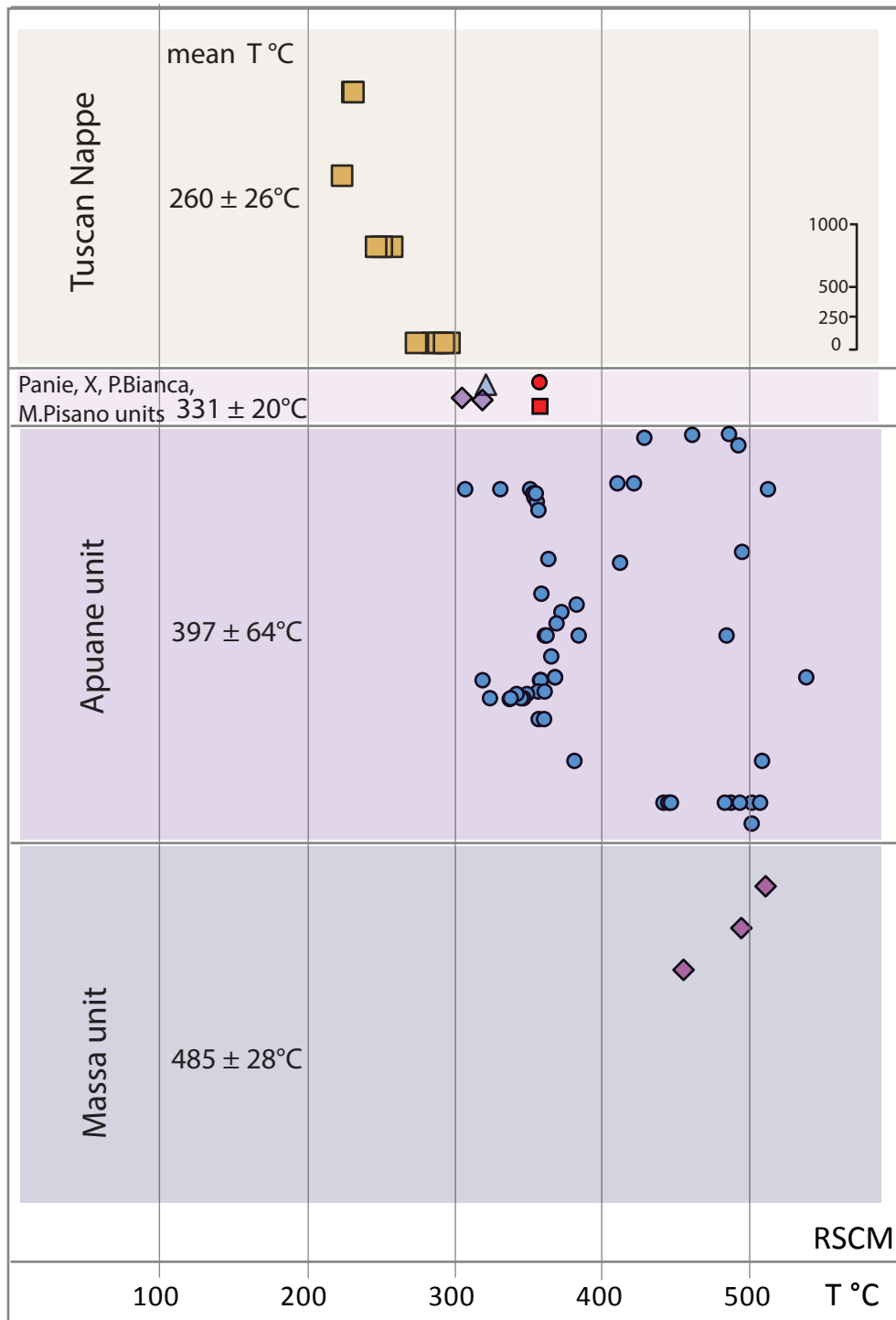


Fig07 Molli et al., JSG

Fig.07 RSCM temperatures in the different tectonic units of the Alpi Apuane and nearby metamorphic core of Punta Bianca and Monte Pisano. The vertical position of the samples correspond to the distance from the reference surface represented by the basal contact of Tuscan Nappe (see scal bar in meters).

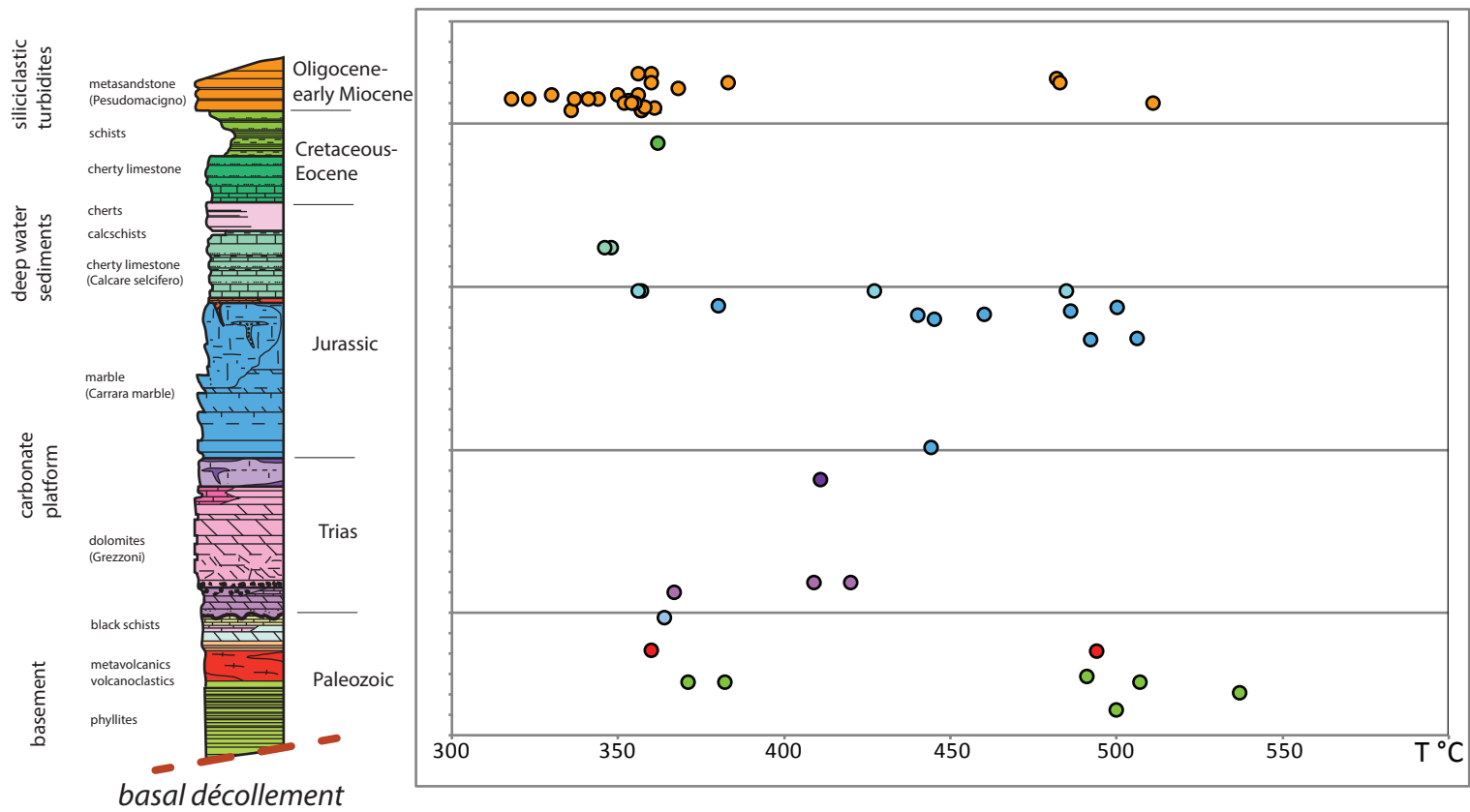


Fig08 Molli et al., JSG

Fig.08 Stratigraphy and RSCM temperatures in the Apuane unit.

Paleothermal and structural architecture of the Alpi Apuane metamorphic core

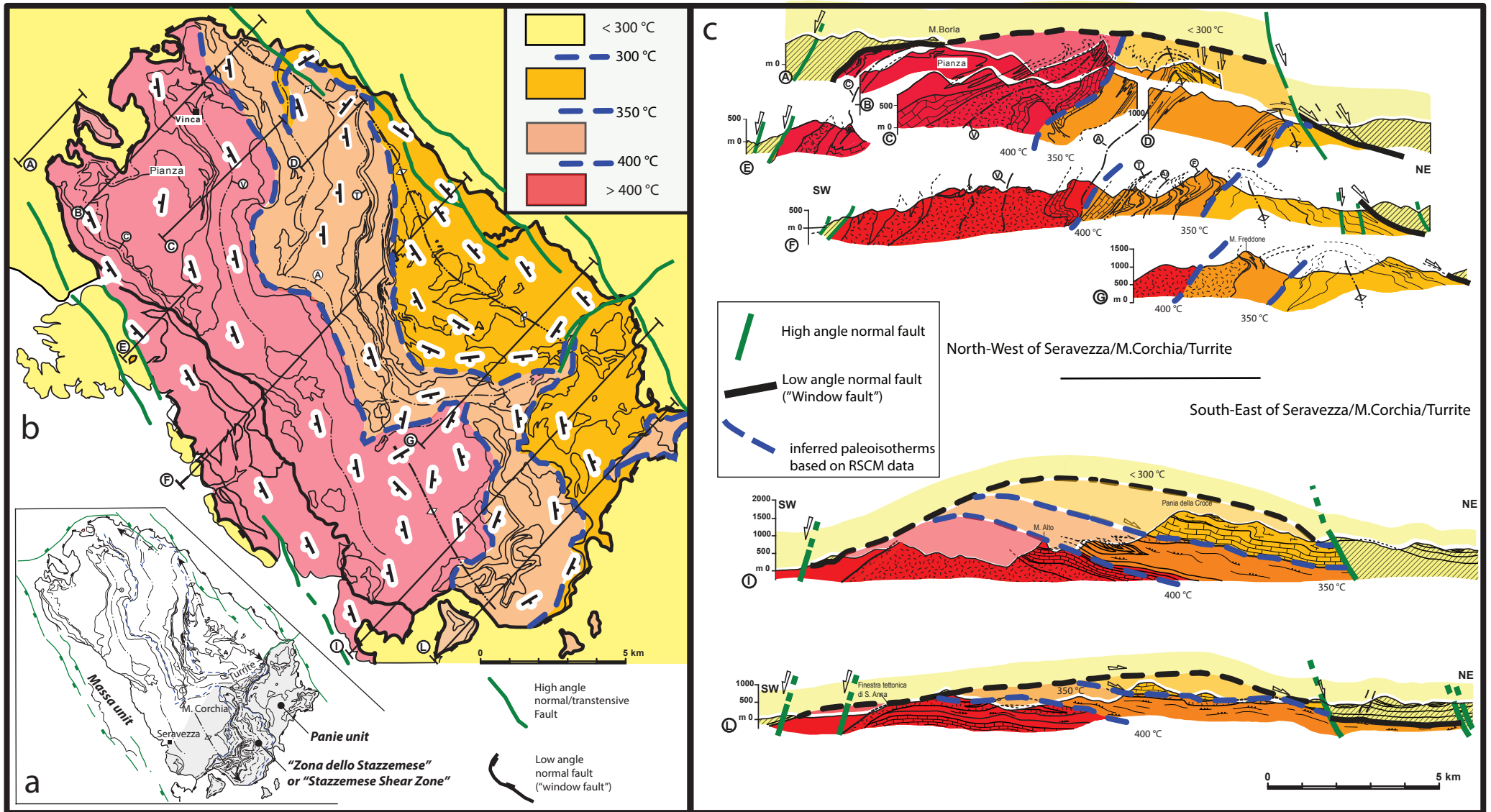


Fig. 09 Molli et al JSG

Fig.09. Paleothermal and structural architecture of the Alpi Apuane metamorphic core complex. a) structural architecture of the Alpi Apuane metamorphic core; b) window-scale paleothermal architecture; c) paleothermal architecture in cross-sections view.

Tectonic and paleothermal evolution of the Alpi Apuane metamorphic core

time constraints and setting

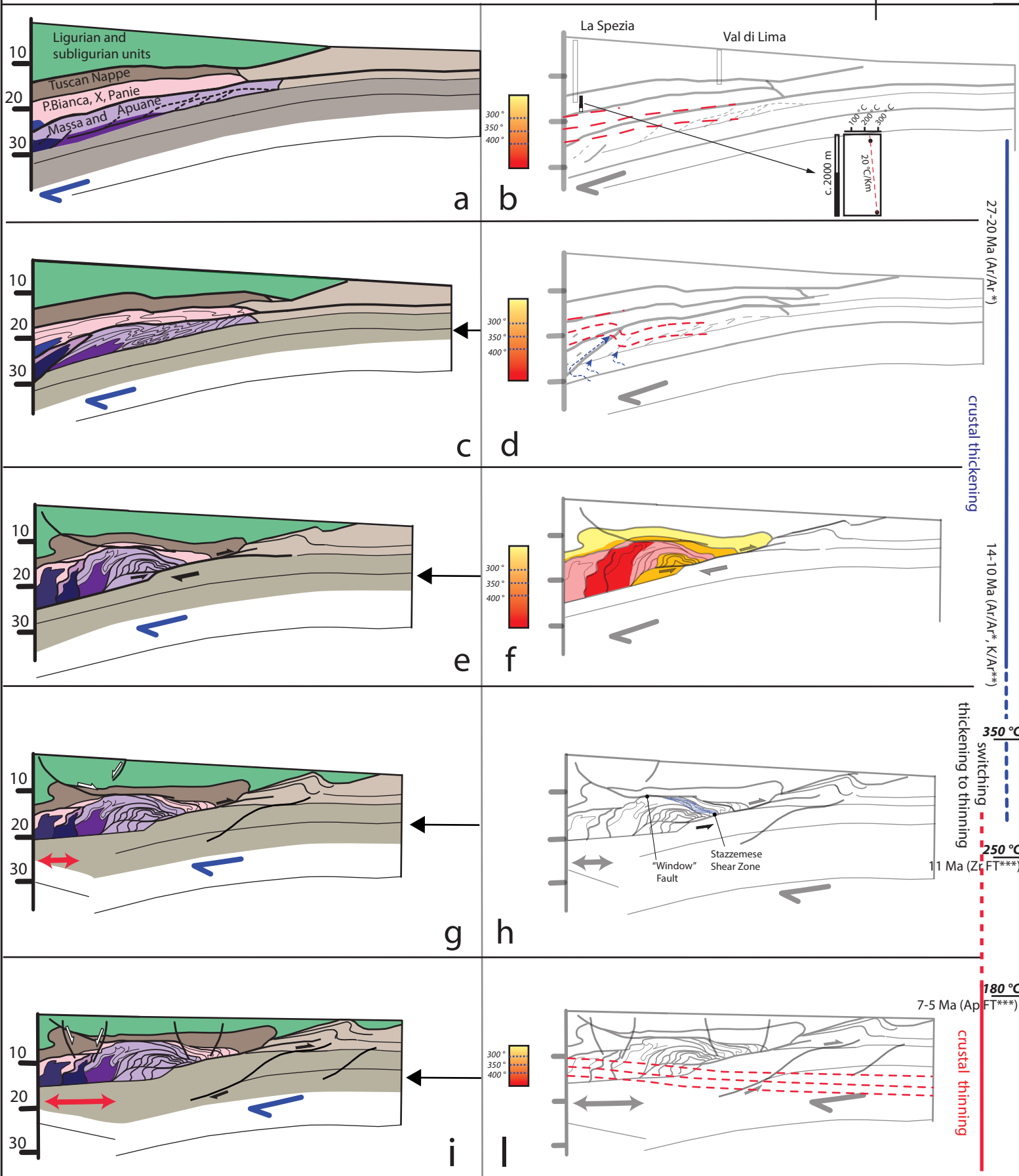


Fig.10. Evolutionary model for the Alpi Apuane within the different stages of Apenninic wedge growth from crustal thickening to crustal thinning (* Kligfield et al., 1986; ** Giglia, Radicati di Brozolo, 1974; *** Fellin et al., 2007 and references): a) early stage of nappe stacking; b) the same as in a) with in red dashed lines the 400°, 350° and 300 °C paleoisotherms. c,d) successive duplexing stage with formation of internal stacking and overthrusting of Massa (higher grade) above the Apuane unit (lower grade). During this stage, a folding of previous paleoisotherms is envisaged to produce the thermal features described at pages 10-11 (see cross sections E,F,I of Figs. 4,5 and Fig.9). In blue the possible path ways of hot fluids associated with ore bodies, reworked within the Stazzemese Shear Zone during later deformation stages; e), f) antiformal stack phase with development of: 1) finite geometry of regional D 1 deformation structures and 2) the finite thermal structure with the regional folding of previous isotherms by the structures of the antiformal stack-related dome; g), h) switching from crustal thickening to crustal thinning with development of D2 structures related to a vertical shortening as well as the "Stazzemese Shear Zone", which is the possible deeper expression of a linked extensional detachment system including the brittle "window fault". The activity of the "window fault" continued up to crustal depth corresponding to an ambient temperature of 180 °C (see thermochronological data in Fellin et al., 2007; i) and l) final stages of exhumation (4-5 Km of vertical displacement) of the Alpi Apuane metamorphic core in the crustal thinning stage continuing up to now. During this stage, deformation is accommodated by high angle normal to transpressive faults cross cutting the "window fault" as well as the syn-metamorphic templates. In l) isotherms are drawn according to thermal data and modeling in Verdoya et al., 2005; Pauselli et al., 2006; Faccenda et al., 2009.

| Sample | Tectonic unit | | coordinates | | n | R2/RA1* | SD | T(°C) | SE | | | |
|--------------------------------|----------------------|--------------------|--------------|---------------|----|---------|-------|-------|------|--|--|--|
| | Rock-type | stratigraphic age | latitude (N) | longitude (E) | | | | | | | | |
| Tuscan Nappe | | | | | | | | | | | | |
| 1 | impure limestone | Trias | 44°02'01.25" | 9°50'49.26" | 15 | 0.60* | 0,004 | 284 | 1,49 | | | |
| 2 | impure limestone | Trias | 44°02'29.79" | 9°51'05.45" | 15 | 0.61* | 0,006 | 295 | 2,24 | | | |
| 3 | impure limestone | Trias | 44°02'52.21" | 9°56'55.08" | 13 | 0.61* | 0,01 | 288 | 4 | | | |
| 4 | impure limestone | Trias | 44°02'43.99" | 9°57'05.56" | 12 | 0.59* | 0,01 | 273 | 3 | | | |
| 5 | impure limestone | Trias | 44°03'30.46" | 9°55'44.00" | 12 | 0,61 | 0,01 | 292 | 1 | | | |
| 6 | marls | Jurassic | 44°02'39.81" | 10°40'03.68" | 11 | 0.55* | 0,01 | 223 | 4,5 | | | |
| 7 | slate | Cretaceous | 44°01'05.25" | 10°42'31.67" | 3 | 0.55* | 0,001 | 230 | 1,71 | | | |
| 8 | marls | Jurassic | 44°02'40.39" | 10°40'05.18" | 15 | 0.56* | 0,01 | 230 | 4,64 | | | |
| 9 | sandstone (MG) | Oligocene-Miocene | 44°06'02.11" | 9°44'04.24" | 15 | 0.58* | 0,01 | 256 | 3,77 | | | |
| 10 | sandstone (MG) | Oligocene-Miocene | 44°06'02.75" | 9°44'00.92" | 14 | 0.58* | 0,02 | 250 | 6,13 | | | |
| 11 | sandstone (MG) | Oligocene-Miocene | 44°10'21.06" | 10°12'31.58" | 12 | 0,57 | 0,00 | 246 | 1 | | | |
| P.Bianca Unit | | | | | | | | | | | | |
| 12 | black schist | Permian? | 44°02'13.30" | 9°58'33.29" | 10 | 0,64 | 0,001 | 358 | 1,00 | | | |
| M.Pisano Unit | | | | | | | | | | | | |
| 13 | metasandstone (PMG) | Oligocene-Miocene | 43°46'49.15" | 10°26'03.93" | 12 | 0,62 | 0,01 | 305 | 4,00 | | | |
| 14 | metasandstone (PMG) | Oligocene-Miocene | 43°46'48.75" | 10°26'03.00" | 11 | 0,62 | 0,01 | 318 | 7,00 | | | |
| Massa Unit plus XX Unit | | | | | | | | | | | | |
| 15 | phyllite | Paleoz | 44°04'16.70" | 10°08'5046" | 17 | 0,3 | 0,07 | 509 | 8,12 | | | |
| 16 | impure metalimestone | Jurassic | 44°03'15.84" | 10°07'33.32" | 16 | 0,64 | 0,02 | 358 | 2,72 | | | |
| 17 | black schist | Permian?-Mid-Trias | 44°01'17.23" | 10°11'05.70" | 20 | 0,42 | 0,04 | 454 | 4,54 | | | |
| 18 | black schist | Permian?-Mid-Trias | 44°04'23.22" | 10°08'59.77" | 14 | 0,33 | 0,04 | 493 | 5 | | | |
| Apuane unit | | | | | | | | | | | | |
| 19 | impure metalimestone | Jurassic | 44°6'52.94" | 10°07'41.80" | 25 | 0,48 | 0,04 | 427 | 3,64 | | | |
| 20 | metasandstone (PMG) | Oligocene-Miocene | 44°8'16.54" | 10°11'48.83" | 13 | 0,73 | 0,03 | 318 | 3 | | | |
| 21 | metasandstone (PMG) | Oligocene-Miocene | 44°8'16.42" | 10°11'48.87" | 13 | 0,67 | 0,04 | 344 | 5 | | | |
| 22 | metasandstone (PMG) | Oligocene-Miocene | 44°9'31.65" | 10°12'00.87" | 14 | 0.65* | 0,01 | 341 | 3 | | | |
| 23 | metasandstone (PMG) | Oligocene-Miocene | 44°9'31.77" | 10°12'00.83" | 14 | 0.63* | 0,01 | 323 | 3 | | | |
| 24 | metasandstone (PMG) | Oligocene-Miocene | 44°9'32.19" | 10°12'00.84" | 13 | 0.65* | 0,01 | 337 | 4 | | | |
| 25 | black schist | Permian?-Mid-Trias | 44°6'34.10" | 10°09'53.45" | 15 | 0,52 | 0,01 | 409 | 1,29 | | | |
| 26 | black schist | Permian?-Mid-Trias | 44°6'33.45" | 10°09'53.23" | 15 | 0,50 | 0,02 | 420 | 2,37 | | | |
| 27 | impure metalimestone | Jurassic | 44°7'12.73" | 10°12'42.85" | 15 | 0,62 | 0,02 | 362 | 2,51 | | | |
| 28 | impure metalimestone | Jurassic | 44°04'21.33" | 10°09'03.79" | 19 | 0,35 | 0,04 | 485 | 3,93 | | | |
| 29 | impure marble | Jurassic | 44°11'37.34" | 10°11'37.13" | 13 | 0,41 | 0,04 | 460 | 5,62 | | | |
| 30 | phyllite | Paleoz | 44°02'20.74" | 10°12'04.74" | 16 | 0,34 | 0,06 | 491 | 7,23 | | | |
| 31 | schist | Late Trias | 44°04'30.71" | 10°12'56.02" | 1 | 0,51 | | 411 | | | | |
| 32 | phyllite | Paleozoic | 44°02'23.67" | 10°14'56.62" | 15 | 0,58 | 0,02 | 382 | 2,4 | | | |
| 33 | metasandstone (PMG) | Oligocene-Miocene | 44°03'29.81" | 10°15'39.26" | 10 | 0,6 | 0,05 | 368 | 6,79 | | | |