



# RSCM thermometry in the Alpi Apuane (NW Tuscany, Italy): New constraints for the metamorphic and tectonic history of the inner northern Apennines

G. Molli<sup>a,\*</sup>, A. Vitale Brovarone<sup>b</sup>, O. Beyssac<sup>b</sup>, I. Cinquini<sup>a</sup>

<sup>a</sup> Dipartimento Scienze della Terra, Università di Pisa, Via S.Maria 53, 56126 Pisa, Italy

<sup>b</sup> Sorbonne Université, Muséum National d'Histoire Naturelle, UMR CNRS 7590, IRD, Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, IMPMC, 75005 Paris, France

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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  $\sim 530$ – $320$  °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  $\leq 15$  km and at ambient crustal temperature  $\leq 350$  °C) are associated with crustal thinning still ongoing in the area.

## 1. Introduction

The thermal structure and the field metamorphic gradient in mountain belts may be first order parameters directly related to the tectonic setting and the crustal-scale architecture of the orogens (between others Chopin et al., 1991; Hervegh and Pfiffer, 2005; Brown, 2009; Vitale Brovarone et al., 2013; Agard and Vitale Brovarone, 2013 and references). Data on the thermal structure of metamorphic units combined with those constraining kinematic history delineates the extent to which heat and mass are transferred from mid to upper crust (e.g. Allemand and Lardeaux, 1997; Selverstone, 1988; Platt et al., 1998; Jolivet et al., 1998; Ring et al., 1999; Brown, 2008; Berger et al., 2011; Chen et al., 2011; Cottle et al., 2011; Bousquet et al., 2012). Therefore, the understanding of the thermal structure of the internal part of mountain belts is a key element to unravel the tectonic and kinematic frame of orogenic systems and the reconstruction of past

geological boundary conditions as inputs for large-scale thermokinematic and geodynamics simulations (Aygüll et al., 2015; Beyssac et al., 2007; Simoes et al., 2007; Scharf et al., 2013; Wiederkehr et al., 2011; Rosenberg et al., 2015).

The thermal characters of the inner Northern Apennines and the evolution of its main units were defined through a series of the classical methods including clay mineralogy, vitrinite reflectance, fluid inclusions and illite crystallinity for the shallowest units of the nappe stack (Cerrina Feroni et al., 1983; Carter and Dworkin, 1990; Carosi et al., 2003; Reutter et al., 1978, 1983; Ellero et al., 2001; Montomoli et al., 2001; Montomoli et al., 2002; Botti et al., 2004; Dellisanti et al., 2010; Carlini et al., 2013; Caricchi et al., 2014; Ventura et al., 2001), and Al-silicates, chloritoid-chlorite thermometry, calcite-dolomite, stable isotope geothermometers, and conodonts color in the lowermost metamorphic units (Franceschelli et al., 1986; Franceschelli et al., 1997; Franceschelli and Memmi, 1999; Molli et al., 2000a,b; Molli et al.,

\* Corresponding author.

E-mail address: [giancarlo.molli@unipi.it](mailto:giancarlo.molli@unipi.it) (G. Molli).

2002; Cortecchi and Orlandi, 1975; Cortecchi et al., 1994; Costagliola et al., 1998; Consani, 2003). More recently, thermodynamical modeling was also applied in the Paleozoic basement terms of the Tuscan metamorphic units (Lo Po' and Braga, 2016; Lo Po' et al., 2017).

Due to the patchy distribution of suitable rock types in the different units and within the nappe stack, however, we still lack a precise definition of the regional thermal structure and of the paleothermal field gradients. As a consequence the overall tectonic setting shaping the present day nappe-architecture is still a matter of debate, with crustal contractional and crustal extensional models being alternatively supported by different studies (Carmignani and Kligfield, 1990; Carmignani et al., 1994; Storti, 1995; Jolivet et al., 1998; Boccaletti et al., 1999; Carosi et al., 2003, 2004; Bonini and Sani, 2002; Brogi and Liotta, 2008; Thomson et al., 2010; Musumeci et al., 2015). This in turn leaves open some relevant questions, for instance the relationships between exhumation processes and the mode of crustal deformation (thickening vs. thinning) as well as the timing, thermal and structural record of crustal/lithospheric stretching, which shaped characteristic features of the inner Northern Apennine in Tuscany such as the present day Moho depth and thermal anomaly (Carminati and Doglioni, 2012; Della Vedova et al., 2001; Di Stefano et al., 2009; Spada et al., 2013 and references).

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

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

## 2. Regional geology

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

In the NW of Tuscany, the Alpi Apuane complex forms the largest tectonic window in the inner Northern Apennines and expose the deepest crustal units of the belt (Tuscan Metamorphic Units) (Fig. 1). Three major stratigraphic and tectono-metamorphic units are traditionally distinguished in the region, the Tuscan Nappe, the Massa unit and the Apuane unit, all derived from the Adria continental paleo-margin (Fig. 2). The Tuscan Nappe consists of Mesozoic carbonate rocks and Tertiary deep water and turbiditic sequences mainly detached from their original basement along the décollement level of the former Carnian and Norian evaporites (Ciarapica and Passeri, 2002 and

references therein). These anhydrites and dolostones are transformed almost everywhere (with some relevant exceptions) into cataclastic breccias called Calcare Cavernoso or “cellular” limestone (Baldacci et al., 1967; Gandin et al., 2000). The post-Norian sequence continues with Rhaetian to Hettangian shallow water limestones (Rhaeticavula Contorta and Calcare Massiccio), Lower Liassic to Cretaceous pelagic limestones, radiolarites and shales (Calcare selcifero, Marne a Posidonomya, Diaspri, Maiolica), grading to hemipelagic deposits of the Scaglia (Cretaceous-Oligocene), to end with the siliciclastic foredeep turbidites of the Macigno (Late Oligocene-Early Miocene). The entire sequence has a thickness between 2000 and 4000 m (Bernoulli et al., 1979; Fazzuoli et al., 1994; Ciarapica and Passeri, 2002; Molli and Meccheri, 2012).

The Apuane Unit forming most of the Alpi Apuane tectonic window is made up of a Paleozoic basement unconformably overlain by an Upper Triassic–Oligocene metasedimentary sequence. The Paleozoic basement is represented by metasedimentary and metavolcanic rocks including Upper Cambrian–Lower Ordovician phyllites and quartzites, Middle Ordovician metavolcanics and metavolcanoclastics, Upper Ordovician quartzitic metasandstones and phyllites, Silurian black phyllites and Orthoceras-bearing metadolostones (Gattiglio et al., 1989; Conti et al., 1993; Pandeli et al., 1994; Paoli et al., 2017). The Paleozoic lithostratigraphic units were deformed and metamorphosed under low-grade conditions, not well precisely defined, during the Variscan orogeny (Conti et al., 1991, 1993). The Mesozoic cover-rocks, where complete, include thin Triassic continental to shallow-water Verrucano-like deposits followed by Upper Triassic–Liassic carbonate platform metasediments comprising dolostone (Grezzoni Fm.), dolomitic marble, and marble (the Carrara Marble), in turn covered by Middle Liassic–Lower Cretaceous cherty metalimestone, cherts, and calcschists, and Lower Cretaceous to Lower Oligocene sericitic phyllites and calcschists with marble interlayers. Oligocene-early Miocene (?) metasediments related to turbiditic systems (Pseudomacigno Fm.) complete the sedimentary succession (Patacca et al., 2013 and reference therein).

The Massa unit is exposed in the westernmost part of the Alpi Apuane complex and includes a litho-stratigraphic sequence formed by a Paleozoic basement similar to that of the Apuane unit and a characteristic and distinctive Upper Permian–Upper Triassic metasedimentary succession, including a Mid Triassic continental (conglomerates and pelites) to marine (carbonate platform derived deposits) succession associated with intraplate alkaline basalts (Martini et al., 1986). Lithostratigraphic terms younger than late Mid Triassic are not described in the literature, although (see below) they are locally found as tectonic lenses and small-scale remnants within a cataclastic fault zone below the contact with the overlying Tuscan Nappe (Molli et al., 2002; Conti et al., 2004). Based on the similarities in stratigraphic contents of the pre-Late Triassic sequences, traditional literature correlated the P.Bianca and M.Pisano exposures to those of the Massa unit (Baldacci et al., 1967; Elter, 1975), whereas more recent papers defined different peak metamorphic conditions (Storti, 1995; Leoni and Pertusati, 2003; Carosi et al., 2004; Molli, 2008).

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

Deformation event D1, which can be associated with underplating and antiformal stacking of the metamorphic units, is defined by a main

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