#### Accepted Manuscript

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9)30142-X
10.1016/j.gr.2019.04.011
rearch
2018

Please cite this article as: M. Lustrino, H. Abbas, S. Agostini, et al., Origin of Triassic magmatism of the Southern Alps (Italy): Constraints from geochemistry and Sr-Nd-Pb isotopic ratios, Gondwana Research, https://doi.org/10.1016/j.gr.2019.04.011

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# Origin of Triassic magmatism of the Southern Alps (Italy): constraints from geochemistry and Sr-Nd-Pb isotopic ratios

Michele Lustrino<sup>1,2\*</sup>, Hassan Abbas<sup>1</sup>, Samuele Agostini<sup>3</sup>, Marcello Caggiati<sup>4</sup>, Eugenio Carminati<sup>1</sup>, Piero Gianolla<sup>4</sup>

1 = Dipartimento di Scienze della Terra, Sapienza Università di Roma, P.le A. Moro 5, 00185, Roma, Italy

2 = Istituto di Geologia Ambientale e Geoingegneria (CNR – IGAG) c/o Dipartimento di Scienze della Terra, Sapienza Università di Roma, P.le A. Moro, 5, 00185 Roma, Italy

3 = Istituto di Geoscienze e Georisorse (CNR – IGG), Via Moruzzi 1, 56124, Pisa, Italy 4 = Dipartimento di Fisica e Scienze della Terra, Università degli studi di Ferrara, Via Saragat 1, 44122, Ferrara, Italy

\* = Corresponding author. E-mail: michele.lustrino@uniroma1.it

**Key-words:** Dolomites, Ladinian magmatism, Petrogenesis, Geochemistry, Geodynamics

#### Abstract

During Middle-early Late Triassic (~243-235 Ma) a diffuse igneous activity developed in the Southern Alps (Italy). Sparse lava flow and pyroclastic succession remnants of such Southern Alps Triassic Igneous Rocks (SATIR) crop out in the Brescian pre-Alps, the Vicentinian Alps (Recoaro-Schio-Posina), Non Valley, Dolomites and Julian Alps. Plutonic rocks are found in two main plutonic complexes (Monzoni and Predazzo) and a small stock (Cima di Pape). Coeval igneous products can be traced eastward to Austria and Dinarides, for a total length of ~450 km.

The coeval formation of major late Anisian-late Ladinian carbonate platforms in the subsiding eastern Dolomites, and significant uplift and subaerial erosion in the western Dolomites suggest, for these areas, the occurrence of large-scale strike-slip and extensional tectonics with the development of horst-and-graben structures.

This study reports the first complete review of the SATIR activity, including new mineral chemical data on 14 samples, 61 major and trace element whole rock analyses and 7 Sr-Nd-Pb isotopic ratios for volcanic and plutonic samples from Dolomites (lavas plus Monzoni and Predazzo plutonic rocks) and Vicentinian Alps lavas. Despite the variable post-magmatic modifications, the large areal distribution of the products and their wide spectrum of chemical compositions, these samples show rather common geochemical and mineralogical characteristics and define major and trace element trends that can be associated with nearly close-system

magmatic evolution. Minor upper crustal contaminations can be observed in specific cases, mostly in the most differentiated products ( $SiO_2 > 70$  wt%).

A specific characteristic of SATIR is their calcalkaline to shoshonitic affinity, resembling the derivation from subduction-modified mantle sources, a feature at odds with the coeval strike-slip and extensional tectonics. Geochemical modelling, petrological considerations and geological constraints allow us to propose a model in which the SATIR mantle sources reflect previous subduction metasomatism (likely occurred during Variscan times). These metasomatised mantle sources were reactivated ~90-100 Myr after the end of the subduction, when continental rifting caused a raise of the geotherms and passive upwelling of asthenospheric mantle.

Keywords: Dolomites, Triassic, Gondwana, Continental rifting, Petrology

#### 1. Introduction

Magmas generated in active subduction settings usually show peculiar volcanological, petrographic, mineral chemical, geochemical and isotopic characteristics, commonly very different from those emplaced in intra-plate settings and along passive plate margins (e.g., Lustrino et al., 2011; Turner and Langmuir, 2015; Di Giuseppe et al., 2017; Kimura, 2017; Schmidt and Jagoutz, 2017; Zheng and Zhao, 2017). However, the use geochemical data and petrological arguments to infer a given tectonic setting does not always guarantee correct conclusions. Indeed, compositions found along active plate margins, falling in the calcalkaline, high-K calcalkaline and potassic-ultrapotassic series are also recorded in intra-plate settings and in extensional areas post-dating subduction processes (Davidson, 1996; Turner et al., 1996; Liegeois et al., 1998; Fan et al., 2003; Moghazi, 2003; Lan et al., 2012; Lustrino et al., 2016).

If geological and geophysical data (e.g., earthquake distribution, focal mechanisms, mantle tomography) can help unravelling the geodynamic setting of active to recent magmatism, similar constraints are hard to obtain for the geological past. Thus, when dealing with remnants of past igneous activity, Earth scientists work mostly with geochemical data, using petrographic evidences and inferring petrological reasoning, helped by geological and structural constraints. The multidisciplinary approach could drive to non-unique definitions of the geodynamic processes responsible for magmatism in the past, because geological s.l. (i.e., stratigraphy, structural geology) and geochemical-petrological interpretations do not always match.

A case study is represented by the Middle-Late Triassic igneous activity occurred coeval to strike-slip and extensional tectonics in the Southern Alps (northern Italy; e.g., Doglioni, 1992; Bertotti et al. 1993; Gianolla et al., 1998; Brandner et al., 2016; Abbas et al., 2018) and adjoining regions (Carinthia, Po Plain, Adriatic Sea and Dinarides), for a total width of ~450 km (Fig. 1). The Italian products of this phase

investigated in this study are hereafter abbreviated into SATIR (Southern Alps Triassic Igneous Rocks). SATIR show calcalkaline to shoshonitic affinities, at odds with geological evidence, which indicates coeval strike-slip and extensional tectonics. This renders the geodynamic framework in which SATIR originated still a matter of discussion (e.g., Sloman, 1989).

A long list of geodynamic and tectonic scenarios to explain the middle Triassic tectonic and magmatic activity in the Dolomites and whole Southern Alps was proposed in the literature. These can be grouped as follows (Abbas et al., 2018): 1) aborted continental rifting – based on the association of extensional structures and mafic volcanism (Bechstadt et al., 1977); 2) Northward subduction of lower continental crust in the upper mantle (Castellarin et al., 1988) - based on the calcalkaline and shoshonitic magmatic association; 3) Sinistral strike-slip tectonics based on the association of compressional and extensional structures with volcanic and plutonic intrusions (Blendinger, 1985; Doglioni, 1987, 1988); 4) Heritage of ancient subduction events of Variscan age, coupled with assimilation of upper crustal rocks (Crisci et al., 1984; Sloman, 1989; Bonadiman et al., 1994; Beccaluva et al., 2005); 5) Development of a marginal back-arc basin associated with the post-Variscan evolution of the Alpine sector (Marinelli et al. 1980; Viel, 1982); 6) Intra-Pangea dextral mega-shear system with lithosphere-scale extension enabling hybridization between mantle melts and lower crust lithologies (Brandner and Keim, 2011); 7) Active upwelling of hot asthenospheric mantle (Stahle et al., 2001); 8) Subduction of small Permian back-arc oceanic basins (Garzanti 1985; Zanetti et al. 2013); 9) Extension-related magmatism during the Middle Triassic in the Southern and Eastern Alps following the opening of Meliata Ocean (Brandner et al., 2016; Beltrán-Trivinõ et al., 2016); 10) Active arc/back-arc development following the NNW-directed subduction of the Paleotethys oceanic lithosphere beneath the southeastern European paleo-margin (Cassinis et al., 2008); 11) closure, by a subduction dipping beneath the Southalpine, of a Paleozoic rifted continental basin or a narrow oceanic basin, located between the Southalpine and Austroalpine continental blocks, (Bianchini et al., 2018).

In this work we provide new petrographic, mineral chemical, whole-rock chemical and Sr-Nd-Pb isotope data of Ladinian lava flows, dykes and plutonic rocks from the Dolomites and Vicentinian Alps (Recoaro-Schio-Posina area). The aim is their characterisation from a petrological point of view for a better comprehension of the geodynamic framework in which they were emplaced. These data are discussed in the framework of a general review of the entire Triassic igneous activity of the Southern Alps and adjoining regions, based on a comprehensive dataset containing more than 1000 whole-rock data (provided as electronic appendix). Such a regional approach allows us to better constrain the mantle sources and discuss the geodynamic origin of Middle-Late Triassic igneous activity.

#### 2. Geological setting

The Southern Alps (Fig. 1) are located south of the Neogene Periadriatic Line, a Sshaped NE-SW-trending dextral mylonitic shear zone separating Europe-verging thrusts to the north from Adria-verging thrusts to the south (Handy et al., 2010). The Southern Alps (i.e., the part of the Alps located south of the Periadriatic line) are considered in the literature as the retro-wedge of the double-verging Alpine Chain. They consist of a well-preserved Mesozoic passive continental margin (e.g., Bertotti et al., 1993), inverted during the Alpine Orogenesis (Doglioni, 1987; Handy et al., 2010). Their structuration initiated during the Cretaceous-Paleogene subduction of an eastern branch of the Alpine Tethys. This belt widened as a consequence of the Eocene Europe-Adria collision (Handy et al., 2010; Carminati et al., 2012; Carminati and Doglioni, 2012).

The Dolomites (Figs. 1 and 2) consist of a large-scale Neogene pop-up structure bounded by two main tectonic lineaments belonging to the Periadriatic Line: the dextrally transpressive Pusteria Line to the north, and the SSE-verging thrust of the Valsugana Line to the south. The Recoaro area lies in a more external wedge of the Southern Alps (Figs. 1 and 2), separated from the Cenozoic Veneto magmatic province to the south by the Cima Marana thrust, and affected to the east by the post-Miocene Schio-Vicenza and Val d'Astico sinistral strike-slip fault system (Castellarin et al., 2006, Fondriest et al., 2012).

#### 3. Permian to Middle Triassic stratigraphy of the Dolomites

During Carboniferous time, the agglutination of Gondwana and Laurussia led to the formation of the Appalachian-Variscan Belt (e.g., Bell and Newman, 2006; Franke et al., 2017). The subduction of the Rheic Ocean, once separating northern Gondwana from southern Laurussia, led to the development of abundant Permian magmatism peaking during Early Permian (~300  $\pm$  20 Ma).

The Dolomites sedimentary succession unconformably overlies these Permian volcanic rocks or directly older basement rocks (Massari and Neri, 1997; Brandner and Keim, 2011). Late Permian red-beds (Val Gardena Fm.) and evaporites/carbonates (Bellerophon Fm.; Bosellini and Hardie, 1973; Massari and Neri, 1997; Kustatscher et al., 2017) were followed by Early Triassic shallow-water carbonate and siliciclastic deposits (Werfen Fm. and Lower Serla Dolomite).

Late Anisian tectonics disrupted the Contrin carbonate platform and was followed by a strong regional subsidence. Isolated carbonate platforms nucleated and survived from the Late Anisian to Late Ladinian, facing deep water basins (Sciliar and Buchenstein Fm.; Maurer and Schlager, 2000; Preto et al., 2005; Brack et al., 2007; Stefani et al., 2010). Starting from the early Ladinian, but with a climax in late Ladinian, widespread magmatism occurred in the Southern Alps, now preserved as lava flows, pyroclastitic (including epiclastitic) and plutonic rocks. Local magma intrusions (Predazzo, Monzoni and Cima Pape; Lucchini et al., 1982; Bonadiman et

al., 1994; Visonà, 1997; Casetta et al., 2018a, 2018b; Abbas et al., 2018) occurring in the Dolomites were possibly related to subaerial volcanoes (Calanchi et al., 1978; Castellarin et al., 1982).

Ladinian volcanic rocks accumulated mostly in basinal depressions and onlapped the carbonate platform slopes (e.g., Sacerdoti and Sommavilla, 1962; Neri et al., 2007), while magmatic dykes intruded carbonate platform deposits (Vardabasso, 1930; Bosellini et al., 1982; Doglioni, 1983; Brandner and Keim, 2011). While close to the magmatic centers (e.g., Latemar and Marmolada areas) the carbonate platforms were buried beneath the volcanic products and demised, in other areas, still not far from magmatic centers (e.g., Sciliar Massif), carbonate production continued (De Zanche et al., 1993; Brandner and Keim, 2011). The erosion of volcanics led to deposition of coarse (e.g., Marmolada Conglomerate) to fine (Wengen Fm.) clastic deposits (Gianolla and Neri, 2007).

As widely discussed in the following sections, roughly coeval magmatism is recorded also in the Julian Alps (e.g., Spadea, 1970; Lucchini et al., 1980; Gianolla et al., 1992), Vicentinian Alps (e.g., Barbieri et al., 1982; De Vecchi and Sedea, 1983) and Brescian Prealps (e.g., Cassinis and Zezza, 1982; Armienti et al., 2003; Cassinis et al., 2008, 2011). At the end of the magmatic pulse, carbonate deposition fully reestablished and several carbonate platforms (Cassian Dolomite) developed, prograding onto coeval basinal deposits (San Cassiano Fm.; Gianolla et al., 1998; Neri et al., 2007; Keim et al., 2001).

#### 4. Pre-Cenozoic magmatism in the Southern Alps and adjoining areas

#### 4.1. Permian magmatism

In the central-eastern Southern Alps, the Permian medium to high-K calcalkaline magmatism consists of volcanic rock piles (Athesian volcanism) and plutons (Cima d'Asta, Bressanone, Ivigna, Monte Croce and Monte Sabion; e.g., Macera et al., 1994; Rottura et al., 1997, 1998; Marocchi et al., 2008; Schaltegger and Brack, 2007; Bellieni et al., 2010). In the western and central Southern Alps, the Permian magmatism is represented by Ivrea Mafic Complex, the "Graniti dei Laghi" and the Lugano volcanics (e.g., Boriani et al., 1992; Pinarelli et al., 2002; Quick et al., 2009). This activity is mostly represented by bimodal calcalkaline to high-K calcalkaline products (e.g., Cocherie et al., 1994; Cortesogno et al., 1998; Romer et al., 2001; Perini et al., 2004; Kroner and Romer, 2013; Casini et al., 2015; Willcock et al., 2015; Gaggero et al., 2017; Braid et al., 2018), albeit sodic alkaline basic compositions are also present, principally in the last stages (e.g., Neumann et al., 2004).

#### 4.2. Triassic magmatism

Scattered Middle Triassic magmatic rocks crop out in several areas along the Alps and the Dinarides. The following discussion will be restricted to the Southern Alps,

where Middle Triassic igneous rocks are widely recorded (Fig. 1). Magmatic activity started with Anisian acid volcanic rocks restricted to small outcrops in eastern Carnia (Rio Turriea and Gartnerkofel; e.g., Obenholzner and Pfeiffer, 1991; Venturini, 2006) and in southern Karawanken (Loibl pass; Buser, 1980). Upper Anisian to lower Ladinian porphyritic and plutonic rocks are more common in the eastern Southern Alps. The volume of these volcanic products increases eastward from the western Julian Alps (Rio Freddo, Prisjonik; Lucchini et al., 1980; Gianolla, 1992; Celarc et al., 2013) to the southern Karawanken, Tolmin Basin and to the Kamnik-Savinja Alps (Buser, 1980, 1986; Pamic, 1984; Visonà and Zanferrari, 2000; Dozet and Buser, 2009). Acid pyroclastic rocks are however frequent in the whole Southern Alps and occur as "Pietra Verde" tuff layers or ash interbeds in basinal limestones of Buchenstein Fm. (Viel, 1979; Cros, 1980; Brack and Rieber, 1993; Maurer, 2003; Wotzlaw et al., 2017).

Upper Ladinian volcanic rocks are very common (both in basinal and shelf settings) in the western and central Dolomites (Figs. 1, 2; Pisa et al., 1980; Bosellini et al., 1982; Sloman, 1989), along the western side of the Adige Valley (Mendola massif and Non Valley; Rossi et al., 1980; Avanzini et al., 2007), and in the Vicentinian Prealps (Recoaro-Schio-Posina; Barbieri et al., 1982; De Vecchi et al., 1986). Small outcrops occur also in western Carnia (Forni di Sopra; Castellarin and Pisa, 1973) and in the Brescian Prealps (Monte Guglielmo group; Cassinis et al., 2008, 2011). In addition, Middle Triassic (mainly Ladinian) magmatism has been recognised in boreholes drilled in the Po Plain and in the Adriatic Sea (Fig. 1; Brusca et al., 1982; Castellarin et al., 1988).

In the Dolomites, the age of late Ladinian volcanic rocks can be constrained by a well-defined bio-chronostratigraphic framework (Gianolla et al., 1998; Brack and Muttoni, 2000; Wotzlaw et al., 2017; Abbas et al., 2018; Maron et al., 2019; Storck et al., 2019) and by geochronological U-Pb-dating. Zircons from volcanic ash beds interbedded in the underlying Buchenstein Fm., in syn-volcanic clastics (Fernazza Fm.) and in the mainly post-volcanic Wengen Fm. (Mundil et al., 1996; Brack et al., 1997, 2007; Mietto et al., 2012; Wotzlaw et al., 2017; Storck et al., 2019) allows us to bracket the time interval of basaltic volcanism in the Dolomites between 239.044  $\pm$  0.038 Ma (Wotzlaw et al., 2017) and 237.773  $\pm$  0.052 Ma (Seiser Alm in Mietto et al., 2012). According to Storck et al. (2019) the duration of the paroxysmal phase of Ladinian volcanism in the Dolomites lasted less than 0.87  $\pm$  0.06 Myr, in agreement with a short-lived Late Ladinian magmatic Event (Brandner et al., 2016; Abbas et al., 2018).

The ages of intrusive rocks have been recently updated by Storck et al. (2019) through high-quality Zircon U-Pb datings of the monzonitic intrusions and the syenitic dykes from Predazzo and Monzoni (ages between 238.190  $\pm$  0.050 and 238.075  $\pm$  0.087 Ma). These ages, together with the data of the Predazzo granite

 $(237.3 \pm 1.0 \text{ Ma from mechanically abraded zircon; Brack et al., 1997 and 2005})$  indicate an equivalent age for intrusive and effusive products.

Lower Carnian magmatism is recorded also in the western Southern Alps (Brescian Prealps), with both effusive and intrusive products (Cassinis et al., 2008). A possible occurrence of coeval volcanic edifices more to the south is suggested by the occurrence of very common Lower Carnian volcaniclastic sandstones (Val Sabbia Ss., Garzanti, 1985; Jadoul et al., 2004; Cassinis et al., 2011).

#### 5. Tectonic evolution of the Dolomites

The main tectonic events recorded in the Dolomites area can be resumed as follows: 1) Permian-Triassic strike-slip and extensional tectonics (details below); 2) nearly amagmatic Jurassic rifting associated with the opening of the Alpine Tethys Ocean; 3) Paleogene ENE-WSW thin-skinned shortening related to the Europe-Adria plates convergence, which generated WSW-verging thrusts, N-S or NNW-SSE trending folds and conjugate strike-slip faults (Doglioni, 1987); 4) Late Oligocene to Recent NNW-SSE thick-skinned shortening, which produced SSE-verging thrusting (Caputo et al., 2010).

Evidence for Middle Triassic tectonics in the Dolomites is provided by sinistral strike-slip faults oriented N70-90 (Stava, Trodena and Cavalase Lines; Abbas et al., 2018) associated with positive flower structures (Cima Bocche Anticline; Doglioni, 1983) and diapirs involving Late Permian evaporites (Bellerophon Fm.; Bechstadt et al., 1977; Pisa et al., 1980; Bosellini et al., 1982; Doglioni 1984, 1987; Castellarin et al., 1998; Doglioni and Carminati, 2008). These structures displace both basement and sedimentary successions up to the lower-middle Ladinian (Doglioni 1984, 1987; Doglioni and Carminati, 2008). Middle Triassic tectonics and coeval subsidence were ascribed to sinistral movements between Adria and Europe (Doglioni 1984, 1987).

Well-dated volcanic dykes, lava flows and plutonic bodies crosscut Triassic structures (thrusts, folds and diapirs) confirming their middle Triassic (late Ladinian) age (Doglioni 1984, 1987; Castellarin et al., 1998; Stefani and Caputo, 1998). Domal uplift associated with magmatism is reflected by the radial pattern of the Ladinian dykes in the central-western part of the Dolomites (Doglioni, 1983). The orientation of the major axis of the dome (N70E, Stava Line, Cima Bocche anticline, Selle Line) was possibly controlled by a zone of weakness, inherited from previous sinistral transcurrent faults.

#### 6. Analytical methods

More than two hundred rocks have been collected during three fieldwork campaigns from 2015 to 2017. All the samples were cut to produce thin sections and, after a detailed petrographic check, 61 of them were selected for whole-rock chemical analyses (28 lavas from the Dolomites, 19 plutonic and volcanic rocks from Predazzo, 8 plutonic rocks from Monzoni and 6 lavas from the Vicentinian Alps; Fig.

2). Representative samples were cut with a diamond-disc saw to small chips to completely remove weathered parts. These were first crushed in a steel mill to about mm-scale fragments, then washed with distilled water and dried at 110 °C overnight. The dried and clean chips were powdered in a low-blank agate mortar to a size passing 200-mesh sieve.

Whole-rock major and trace element analyses were performed at Activation laboratories (Ontario, Canada) using Code 4LITHO Major Elements Fusion ICPAES and trace Elements Fusion ICPMS. The detection limit ranges from 0.001 to 0.01 % for major elements, 0.1 to 30 ppm for trace element and 0.004 to 0.1 ppm for REE.

Mineral chemistry analyses were performed at the *Istituto di Geologia Ambientale e Geoingegneria* (CNR-IGAG) laboratory, *Dipartimento di Scienze della Terra* of Sapienza University of Rome, with a CAMECA SX50 electron microprobe. The analyses were carried out at 15 kV accelerating voltage, 15 nA beam current, 10  $\mu$ m beam diameter for feldspar and 1  $\mu$ m for pyroxene and opaque minerals. Counting times were 20 s at the peak position and 10 s for background for all elements. Calibration was made on synthetic and natural minerals.

Seven representative samples from the volcanic rocks of the Dolomites area have been analysed for Sr-Nd-Pb isotope ratios at the *Istituto di Geoscienze e Georisorse*, (CNR-IGG) in Pisa. Rocks powders i were dissolved in HF+HNO<sub>3</sub> and then completely dried. Sr and Nd were extracted by ion exchange chromatography. Lead was extracted from the matrix after eluting with HBr and HCl. The separated Sr, Nd and Pb aliquots were loaded on Re filaments and then loaded into a Finnigan Mat 262 multi-collector Thermal Ionization Mass Spectrometer (TIMS). A complete description of the analytical techniques is reported in Di Giuseppe et al. (2017).

#### 7. Results

#### 7.1. Petrographic description and mineral chemical composition

The investigated samples are essentially massive rocks (44 samples; dykes, sills and lava flows) plus rarer pyroclastic facies rocks (4 samples) from the Dolomites. Seven volcanic rocks from Vicentinian Alps (hereafter referred to as Recoaro), 8 plutonic rocks from Monzoni and 16 plutonic rocks from Predazzo complete the dataset. This research focusses on the massive volcanic rocks of the Dolomites and consequentially only minor comments will be devoted to the other volcanic and plutonic rocks presented here, the readers being referred to the recent articles of Casetta et al. (2018a, 2018b) and to Bonadiman et al. (1994) for Predazzo and Monzoni plutonic rocks description, respectively. A detailed petrographic description of the two types of Dolomite volcanic rocks and their mineral chemical compositions is reported in the electronic appendix 1.

#### 7.2. Whole-rock chemistry

Thirty-one representative samples of Dolomites volcanic rocks were analysed for whole-rock chemistry. The results of these chemical analyses and CIPW normative minerals are reported in Table 1. In the same table, new whole-rock analyses of Recoaro volcanic rocks as well as the Monzoni and Predazzo plutonic rocks are reported too. Selected major oxides and trace elements of the new and literature data (a total of 1120 whole-rock analyses, available as Electronic Appendix 3) are reported in Figs. 6 and 7. For sake of clarity, the same diagrams, with each single district shown at the time, are reported in the Electronic Appendix 4.

In terms of silica content, the massive volcanic rocks of the Dolomites are basic to intermediate (SiO<sub>2</sub> = 49.2-58.1 wt%, LOI-free basis) with alkali content (Na<sub>2</sub>O+K<sub>2</sub>O) ranging from 4.0 to 7.9 wt%. The Loss-on-ignition (LOI) value is generally <3 wt%, although few samples record higher values (up to 7.3 wt%). Based on TAS classification scheme (Le Maitre, 2002), the analysed samples are classified mostly as trachybasalts and basaltic trachyandesites, with minor alkali basalts, basaltic andesites and one trachyandesite (Fig. 3a). The Alpe di Siusi hyaloclastite tuff (sample AS6) is characterised by fresh glassy shards. These show peculiar compositions, being characterised by higher SiO<sub>2</sub> (55.1-64.0 wt%) and alkalis (Na<sub>2</sub>O+K<sub>2</sub>O = 10.4-13.1 wt%) than the massive rocks. The glassy shard compositions mostly fall in the trachyte field with rarer tephri-phonolite and one trachyandesite (Fig. 3a). Only the altered tuff sample shows a sodic alkaline affinity, falling in the mugearite field, possibly indicating K<sub>2</sub>O depletion.

The Monzoni plutonic rocks range from ultrabasic to intermediate compositions  $(SiO_2 = 41.7-57.2 \text{ wt\%})$ , aligned along a rather sharp trend with mild enrichment of alkalis (Na<sub>2</sub>O + K<sub>2</sub>O = 1.6-7.6 wt%). The Predazzo plutonic rocks spread over a much larger range of SiO<sub>2</sub> (44.0-75.9 wt%) and alkalis (Na<sub>2</sub>O+K<sub>2</sub>O = 1.5-9.6 wt%), completely overlapping the Monzoni rocks, straddling the subalkaline-alkaline division in the TAS diagram, reaching rhyolitic compositions, with a gap in the trachyte field. The Recoaro volcanic rocks mostly fill the Predazzo rock gap, plotting in the 59.3-69.6 wt% SiO<sub>2</sub> range. As already discussed in the literature (De Vecchi and Sedea, 1983), and confirmed in this study, the Recoaro rocks are characterised by strong alkali mobility, rendering handling of geochemical data of these samples at least dubious (see the discussion section).

In the K<sub>2</sub>O vs. Na<sub>2</sub>O diagram (Fig. 3b), all the Dolomites samples fall into the field of the transitional and potassic series fields, with the exception of two outliers characterised by high LOI. The two outliers are the Lago di Alleghe mugearitic tuff (LOI = 5.8 wt%), characterised by anomalously high Na<sub>2</sub>O (6.3 wt% on LOI-free basis) and very high Na<sub>2</sub>O/K<sub>2</sub>O (3.93), and the Alpe di Siusi shoshonite (LOI = 6.2 wt), which is characterised by high K<sub>2</sub>O (5.7 wt%) and low Na<sub>2</sub>O/K<sub>2</sub>O (0.38). Also in this case, the EMP compositions of sample AS6 glassy shards fall into the potassic and ultrapotassic series fields (Fig. 3b). The new samples from Predazzo, Monzoni and Recoaro districts completely overlap the Dolomites rock field.

According to the K<sub>2</sub>O vs. SiO<sub>2</sub> diagram (Peccerillo and Taylor, 1976), most of the investigated rocks belong to the high-K calcalkaline and shoshonitic series, (Fig. 3c), as most of the samples reported in literature. Only moderately to strongly altered SiO<sub>2</sub>-rich samples from Vicentinian and Brescian areas tend to plot in the calcalkaline or arc-tholeiite fields, due to K<sub>2</sub>O depletion. On the AFM Diagram (Kuno, 1968), all the studied samples and the literature analyses plot in the calcalkaline field, lacking substantial iron enrichment during the evolutionary trend (Fig. 3d).

More than half of the Dolomites samples are SiO<sub>2</sub>-saturated with CIPW normative orthopyroxene and olivine. Six are characterised by slight normative quartz content (0.62-4.98%), and eight of them are SiO<sub>2</sub>-undersaturated with normative nepheline ranging from 1.92 to 7.42%. The glassy shards in the hyaloclastite sample range from slightly SiO<sub>2</sub>-oversaturated (with CIPW normative quartz = 1.7-3.3%) to slightly SiO<sub>2</sub>-undersaturated (normative nepheline = 1.1-3.4%). More than 37% of Monzoni samples, more than 60% of the Predazzo samples and all the Recoaro rocks are quartz-normative.

The major oxides of the analysed samples were plotted vs. the Differentiation Index parameter (D.I.= sum of CIPW normative Q, Or, Ab, Ne, Lc and Kp; Thornton and Tuttle, 1960) in Fig. 4. When considering the entire dataset, MgO, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3tot</sub> and CaO exhibit well defined negative correlation with D.I (Fig. 4). Al<sub>2</sub>O<sub>3</sub> and P<sub>2</sub>O<sub>5</sub> define bell-shaped patterns, with maximum at ~60 and ~40, respectively, whereas a correlation is observed for SiO<sub>2</sub>, K<sub>2</sub>O (well-defined) and Na<sub>2</sub>O (more scattered) vs. D.I.. The glassy shards usually overlap whole-rock data of the other Triassic igneous rocks from the Alps and Dinarides.

Predazzo plutonic rocks define a large and quite continuous spread of major oxides, showing always a good correlation with D.I., in nearly all the cases with  $R^2 > 0.85$  (up to >0.96 for CaO and Fe<sub>2</sub>O<sub>3tot</sub>). Monzoni and Recoaro rocks exhibit straight correlations with D.I. too, overlapping the trend of the previous two areas.

All the Dolomites samples are metaluminous with ASI [ASI = Alumina Saturation Index = Al/(Na+K+Ca)] ranging from 0.52 to 1.00, similarly to what observed for the Alpe di Siusi glassy shards (ASI = 0.75-0.95) and the other investigated Southern Alps igneous rocks. A good correlation exists between ASI and D.I., with ASI values increasing from 0.47 to 1.00 in the 19.2-66.8 D.I. range. Only the most evolved compositions (D.I. >78; SiO<sub>2</sub> >66.5 wt%) have peraluminous compositions with ASI as high as 1.49. Mg number [Mg# = 100\*Mg/(Mg+Fe<sup>2+</sup>), assuming Fe<sup>3+</sup> = 0.15%  $\Sigma$ Fe] of Dolomites rocks ranges from 35 to 63, with no correlation with D.I. and a poor correlation with SiO<sub>2</sub> (R<sup>2</sup> = 0.39, excluding the two SiO<sub>2</sub>-richest samples). On the contrary, the Predazzo and Recoaro rocks show good negative correlations of Mg# with SiO<sub>2</sub> (R<sup>2</sup> = 0.96 and 0.86, respectively). The low Mg# value, coupled with relatively low Cr (30-330 ppm) and Ni (20-80 ppm) indicate that the investigated rocks cannot be considered primary melts in equilibrium with mantle rocks and that they experienced fractionation during their ascent to the surface (see below).

Selected trace elements are plotted vs. D.I. in Fig. 5. Dolomites rocks show no correlation between compatible/incompatible elements and D.I.. Light-REE (LREE; La, Ce, Pr, Nd and Sm) are roughly correlated with SiO<sub>2</sub>, except for sample PR23 (highly altered basaltic andesite). Middle-REE (MREE: Eu, Gd, Tb, Dy, and Ho) and heavy-REE (HREE; Er, Tm, Yb and Lu) do not show any correlation with D.I..

The other three investigated SATIR districts show recognizable and rather coherent trends. Among LILE, only Rb behaves as an incompatible element, showing enrichment with increasing D.I. (Fig. 5). Strontium and Ba reach a peak at D.I. ~50 and then decrease. Transition elements show well-defined negative trends with D.I., particularly evident for Sc, V and Co (Fig. 5). HFSE + Y behave as a coherent group, aligning along straight correlation with D.I., with the only exception of the most differentiated compositions of Predazzo (D.I. >87). What described for the HFSE is mimicked by the REE, with the exception of Eu, which is strongly depleted in the most differentiated Predazzo samples (Fig. 5). Thorium and U behave as strongly incompatible elements, and the most differentiated Predazzo samples are characterised by high Th (up to 70 ppm) and U (up to 14 ppm). Lead distribution is less defined for all the districts.

Primitive mantle (PM)-normalised multi-elemental patterns (Fig. 6) are similar with limited inter-elemental fractionation for the different analysed rock types. Key features of the patterns are medium to high enrichment of LILE (Rb ~39-315, Ba ~39-143, Th ~38-181, U ~40-168, K ~46-235 and Pb ~42-257 times PM), deep Nb-Ta troughs (~13-26 times PM), strong trough at Ti (~3-8 times PM) and very flat HREE (Ho<sub>N</sub>/Lu<sub>N</sub> = 1.02-1.29). The Dolomite rocks define a pattern that, with the only exception of P, perfectly overlaps the Global Subducting Sediment (GloSS) composition (Plank, 2014). When compared to a classical within-plate oceanic locality such as the St. Helena basalts in central Atlantic Ocean (the type locality of HiMu-OIB), the Dolomite rocks show remarkable differences, in particular much higher LILE, negative anomalies at Nb-Ta-Ti and strong positive peaks at K and Pb (Fig. 6a).

The rocks from the other three investigated districts (Predazzo and Monzoni plutons and Recoaro) show inter-elemental fractionation patterns similar to those of Dolomites volcanic rocks. The Predazzo plutonic rocks nearly overlap the incompatible elements of Dolomites, showing slightly higher Rb, peaking at U-Th. Predazzo clinopyroxenites show the lowest incompatible element content, but overall they have the same pattern of the bulk plutonic rocks. The only syenitic sample analysed here (PR25) is characterised by the highest enrichment in nearly all the elements (Fig. 6b). Predazzo granites have an even more spiked pattern, with deep troughs at Ba, Sr, P, Eu and Ti and the highest concentration for the other elements, as well as flat HREE clustering around 13-16 PM times (Fig. 6c). Monzoni plutonic rocks closely resemble the Dolomites lava pattern too, sharing strong similarities with the GloSS composition, albeit incompatible elements content is

generally displaced towards lower abundances (Fig. 6d). Also in this case the cumulitic rocks (gabbros) show very low elemental content, overlapping the Predazzo pyroxenites.

The Recoaro samples are usually displaced towards higher incompatible element contents, with the exceptions of deeper troughs at Sr, P and Ti. The sample with the highest LOI (HA9; LOI = 4.19 wt%) slightly depart from the main pattern; in particular it displays the lowest Sr and P and a high MREE-HREE content (Fig. 6e).

#### 7.3. Sr-Nd-Pb isotopic ratios

Based on petrographic characteristics, geochemical signatures and geographic position, seven Dolomites volcanic rock samples were selected for Sr-Nd-Pb isotopic determination. These analyses are reported in Table 2 and shown in Fig. 7, with the isotopic ratios corrected to 238 Ma. The Dolomites samples have relatively high  ${}^{87}$ Sr/ ${}^{86}$ Sr<sub>(i)</sub> (0.7043-0.7051) with  $\epsilon$ Sr<sub>(i)</sub> ranging from 1.8 to 12.7, with the exception of a Latemar basaltic dyke (LAT2) that shows slightly more radiogenic  ${}^{87}$ Sr/ ${}^{86}$ Sr (0.7058) with  $\epsilon$ Sr<sub>(i)</sub> 22.5. The  ${}^{143}$ Nd/ ${}^{144}$ Nd<sub>(i)</sub> ranges from 0.51227 to 0.51237, with  $\epsilon$ Nd<sub>(i)</sub> values slightly lower to slightly higher than ChUR<sub>(238 Ma)</sub> (from -1.4 to +0.5). The Pb isotopic compositions are homogeneous, with  ${}^{206}$ Pb/ ${}^{204}$ Pb clustered around 18.26 and 18.41,  ${}^{207}$ Pb/ ${}^{204}$ Pb from 15.62 to 15.67 and  ${}^{208}$ Pb/ ${}^{204}$ Pb from 38.36 to 38.48, with the exception of sample LAT2 showing  ${}^{208}$ Pb/ ${}^{204}$ Pb=38.89, slightly higher than in the other samples.

The Dolomites lavas mostly plot in the enriched Sr-Nd isotopic quadrant (Fig. 7a), partially overlapping the plutonic rock compositions of Predazzo plutonic rocks (Casetta et al., 2018b), but being displaced towards slightly more radiogenic Nd compared to Monzoni plutonic rocks (Bonadiman et al., 1994) for a given <sup>87</sup>Sr/<sup>86</sup>Sr. Recent data from Valsugana dykes (poorly age constrained at 227-260 Ma with K/Ar datings; Bianchini et al., 2018), sampled between Dolomites and Vicentinian Alps, ~10-15 km E of Trento city, are characterised by a much larger content of radiogenic Sr (<sup>87</sup>Sr/<sup>86</sup>Sr = 0.7082-0.7172) and much lower content of radiogenic Nd (<sup>143</sup>Nd/<sup>144</sup>Nd = 0.51197-0.51209; Fig. 7a).

To the best of the authors' knowledge, the only Pb isotopic data on SATIR are those reported for the sulphides in Maso Furli, Val di Non, Doss de la Grave and Sasso Negro areas (Nimis et al., 2012) and for Valsugana dykes (Bianchini et al., 2018). The new data presented here show a partial overlap with these literature data, being the Valsugana dykes characterised by sensibly higher content of radiogenic <sup>206</sup>Pb/<sup>204</sup>Pb (18.57-19.12) and <sup>207</sup>Pb/<sup>204</sup>Pb (15.68-15.72; Fig. 7b,c). No direct comparison with <sup>208</sup>Pb/<sup>204</sup>Pb can be made, because Th elemental content to recalculate the initial values is not reported in Bianchini et al. (2018). Assuming a reasonable Th/Pb ratio ~0.5 for the Valsugana dykes, the <sup>208</sup>Pb/<sup>204</sup>Pb(<sub>238 Ma</sub>) ratios of these samples ranges from 38.87 to 40.19, values much more radiogenic than those for Dolomites massive rocks presented here.

The Dolomites samples analysed in this study completely overlap the Predazzo and Monzoni plutonic rocks in terms of <sup>87</sup>Sr/<sup>86</sup>Sr and do not show any appreciable variation with SiO<sub>2</sub> or MgO, similarly to what recorded by Predazzo and Monzoni plutonic samples (Fig. 7a,b). The Valsugana dykes are displaced towards very high radiogenic values, but again without any correlation with differentiation parameters. On the other hand, the Northern Karawanken (Austria) Triassic igneous rocks mimic increase of <sup>87</sup>Sr/<sup>86</sup>Sr with increase of magma evolution. With the exception of the most evolved sample analysed here, no correlation between <sup>143</sup>Nd/<sup>144</sup>Nd and SiO<sub>2</sub> or MgO is observed (Fig. 7c,d). The samples analysed here are the most radiogenic among the SATIR in terms of <sup>143</sup>Nd/<sup>144</sup>Nd, with higher ratios recorded in the Karawanken pluton only (Miller et al., 2011). As Pb isotopes are concerned, the bulk of the Dolomites samples does not show any correlation with SiO<sub>2</sub> or MgO, even if the most evolved sample (PR3 latite; 1.8 wt% MgO) is characterised by the lowest <sup>207</sup>Pb/<sup>204</sup>Pb (Fig. 7e,f).

#### 8. Discussion

New and literature data on SATIR are discussed with three approaches, the first focussing on the origin of the inter- and intra-district geochemical variations, the second trying to constrain the composition of mantle source(s) and the third aiming to define a geotectonic model in a large scale geological framework.

#### 8.1. Inter- and intra-district geochemical variations.

As a whole, our data define relatively coherent trends in Harker-type diagrams for SATIR. This is particularly surprising, considering their subaqueous emplacement, with associated variable degrees of element mobility, the large width of the study area (>4000 km<sup>2</sup>; Figs. 1 and 2) and the thick and compositionally heterogeneous crust pierced by the various magma batches.

When major elements are plotted against differentiation parameters such as  $SiO_2$ , MgO or D.I., some important considerations can be made:

1) Figures 6 and 7 show the major oxide and trace element variation against D.I. for the four investigated districts (Dolomites volcanic rocks, Predazzo and Monzoni plutonic rocks and Recoaro volcanic rocks). With a few exceptions, the investigated rocks define positive (SiO<sub>2</sub>, Na<sub>2</sub>O+K<sub>2</sub>O) and negative correlation (TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3tot</sub>, MnO, MgO, CaO, CaO/Al<sub>2</sub>O<sub>3</sub>) with D.I. (Fig. 4). Only Al<sub>2</sub>O<sub>3</sub> does not show any clear trend with this index, with a rough bell-shaped pattern, being mostly confined in the 14.5-19 wt% range with D.I. ranging from ~5 to ~60.

2) The samples with the lowest and highest D.I. values are plutonic rocks. Among these, the Monzoni samples mostly show poor- to medium-evolved compositions. Predazzo rocks span the largest chemical variation for all the major oxides (e.g.,  $SiO_2$  = 40.2-78.3 wt%; MgO = 0.0-11.9 wt%; Alkalis = 0.7-12.0 wt%). The Dolomites

volcanic rocks show a rather restricted compositional range compared to the other SATIR districts.

3) The Monzoni and Predazzo samples with the lowest D.I. show similar compositions, resembling accumulation/fractionation of clinopyroxene (CaO = 15.6-16.2 wt%; Na<sub>2</sub>O+K<sub>2</sub>O = 1.5-1.6 wt%) and variable accumulation of Fe-Ti oxides (Fe<sub>2</sub>O<sub>3tot</sub> = 14.7-22.9 wt%; TiO<sub>2</sub> = 1.3-1.5 wt%) and minor amounts of intercumulus plagioclase (CaO/Al<sub>2</sub>O<sub>3</sub> = 0.9-3.0; Fig. 4), coherently with the interpretation provided in the literature (Bonadiman et al., 1994; Casetta et al., 2018a).

4) In the literature, the Predazzo plutonic rocks have been divided into four (SiO<sub>2</sub>-saturated and SiO<sub>2</sub>-oversaturated shoshonite, potassic and calcalkaline; Visonà, 1997) or three (SiO<sub>2</sub>-saturated shoshonite, SiO<sub>2</sub>-undersaturated shoshonite and granitic; Casetta et al., 2018a) groups. However, in the diagrams reported in Electronic Appendix 4 no substantial intra-district differences can be evidenced. With the exception of a small Na<sub>2</sub>O enrichment of a restricted sub-group (Casetta et al., 2018a), the remaining Predazzo rocks follow a rather continuous liquid line of descent, with most evolved samples displaying strong SiO<sub>2</sub> and K<sub>2</sub>O enrichment, and Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O decrease, questioning the actual existence of different serial affinities in this plutonic complex. Our new data are qualitatively consistent with a gabbroic fractionation to explain the gabbro-to-syenite transition (Casetta et al., 2018a). Worth noting, however, none of the hypothetical fractionating assemblages proposed by Casetta et al. (2018a) reflects the composition of the cumulitic clinopyroxenites, characterised by <10% plagioclase.

5) The most differentiated syenogranitic samples of Predazzo are not considered cogenetic with the rest of the plutonic rocks because of the impossibility to model fractional crystallization processes (Casetta et al., 2018a). Consequently, the existence of three distinct magma batches has been proposed in literature (Visonà, 1997; Casetta et al., 2018a). Given the large volume of granitic magma (~1 km<sup>3</sup>), its derivation from less differentiated melts via prolonged fractional crystallization is quite improbable. Similar mechanisms perhaps operated during the Permian rift stages in the Oslo rift, where small differences in silica activity of mafic to intermediate melts evolving in variable conditions (pressure,  $P_{H2O/CO2}$ ,  $fO_2$ ) generated a series of magma chambers at various levels in the thinned continental crust. Relatively hot magma ponding may have caused local crust partial melting generating evolved liquids with D.I. up to 94, with limited genetic link with mafic and intermediate magmas (Neumann, 1980).

6) The Mg# and major oxide variation of Dolomites volcanic rocks suggest fractional crystallization of Mg-bearing phases such as olivine and pyroxene. No quantitative assessment can be made because of the absence of clear correlations of major oxides and trace elements with D.I. The rough correlation of  $Al_2O_3$  vs. D.I. and the strong negative correlation of  $CaO/Al_2O_3$  vs. D.I. of Ladinian volcanic rocks indicate

only a minor role of plagioclase in the fractionating assemblage, despite its common presence among the phenocryst phases and the  $Eu/Eu^* < 1$  (1.01-0.75).

7) The definition of the serial affinity of SATIR is not as straightforward as it could be assumed. Essentially, all the SATIR plot in the calcalkaline field in the AFM diagram (Fig. 3d). On the other hand, in the Miyashiro (1974) FeO<sub>tot</sub>/MgO vs. SiO<sub>2</sub> diagram, modified by Arculus (2003), more than two thirds of the SATIR (with <70 wt% SiO<sub>2</sub>) show relatively high FeO<sub>tot</sub>/MgO, clustering in the tholeiitic field (mostly "Medium-Fe field" of Arculus, 2003).

The mildly alkaline composition of most of the SATIR (Fig. 3a), coupled with variable  $K_2O/Na_2O$  ratios (mostly in the 0.3-1.6 range; average 1.16 ± 0.58) and the common mobility of alkalis, with widespread leakage of  $Na_2O$  and enrichment of  $K_2O$  (e.g., De Vecchi and Sedea, 1983), render the definition of the magmatic affinity a difficult task. Despite these caveats, we agree with the common use of "shoshonitic affinity" for the SATIR, whose least differentiated compositions have ~1.2-3.9 wt%  $K_2O$  in the MgO 6-8 wt% and SiO<sub>2</sub> 49.2-51.2 wt% interval.

7) A limited to moderate amount (2-10 wt%) of assimilation of Permian micaschist/dioritic/rhyolitic/carbonate country rocks can explain the inter-group Sr and Nd isotopic variation of Predazzo plutonic rocks (Casetta et al., 2018a). The <sup>143</sup>Nd/<sup>144</sup>Nd-<sup>87</sup>Sr/<sup>86</sup>Sr correlation of silica-undersaturated shoshonitic group of Predazzo (albeit defined by three samples only) is at odd with a crustal contamination process, but Casetta et al. (2018a) interpreted the spread of Sr isotopic ratios with local fluid mobilization along the intrusion borders.

8) The high Rb/Sr of the most differentiated plutonic rocks of Predazzo does not allow precise recalculation of the initial <sup>87</sup>Sr/<sup>86</sup>Sr isotopic ratios (Casetta et al., 2018b). Initial Nd isotopic ratios of Predazzo granites (143Nd/144Nd = 0.51222-0.51230) overlap with those of the less differentiated compositions (0.51219-0.51229). More in detail, on the basis of the differences in Nd isotopes, Casetta et al. (2018b) confirm an earlier hypothesis of the existence of two independent magma batches for the least differentiated rocks with silica-undersaturated  $(^{143}Nd)^{144}Nd_i =$ 0.51226-0.51229) and silica-saturated shoshonitic groups (0.51219-0.51225. Our Predazzo granitic rocks have not been analysed for isotopic ratios, but they could be qualitatively interpreted as the most extreme differentiation products of the basic compositions (gabbros). The major oxide variation seen in Fig. 4 indicates the possible involvement of feldspars in the latest crystallization phases, causing an abrupt change in the pattern of Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O and, less evident, K<sub>2</sub>O. The strong depletion of Sr and Ba in the most differentiated samples of Predazzo is compatible with such a process, as well as the strong depletion of Hf and Zr could involve zircon fractionation. In any case, volumetric considerations on the evolved and least differentiated igneous compositions speak against simple direct derivation via fractional crystallization processes.

9) Only a few SATIR samples have been analysed in literature for both Sr-Nd isotopes and whole-rock analyses (5 from Monzoni, 8 from Predazzo, 8 from Karawanken, and 8 from Valsugana). Our seven samples are the first covering the entire Dolomites area. The situation for Pb isotopes is even worst, being the data presented here the first for the entire SATIR, with the exception of the recent work of Bianchini et al. (2018) on Valsugana dykes. Excluding the few Monzoni data (Bonadiman et al., 1994) and two basaltic and andesitic 218 Myr-old lavas from Brescian Alps (Cassinis et al., 2008), all the SATIR plot along a classical hyperbolic trend in <sup>143</sup>Nd/<sup>144</sup>Nd vs. <sup>87</sup>Sr/<sup>86</sup>Sr diagram (Fig. 8a). This is classically interpreted as the result of interaction of mantle melts with ancient continental crust or the derivation from ancient mantle sources that have experienced variable degrees of melt extractions and/or modifications in the form of digestion of subducted material (e.g., Lustrino et al., 2011; Lustrino and Anderson, 2015, and references therein). In the first case, the isotopic ratios are expected not to vary or to vary without any correlation with evolutionary degrees, while in the case of continental crust clear contamination trends should emerge with major oxides.

<sup>87</sup>Sr/<sup>86</sup>Sr ratios of the Dolomites volcanic rocks presented in this study (0.70432-0.70577) do not show any correlation with D.I. ( $R^2 = 0.03$ ), with SiO<sub>2</sub> ( $R^2 = 0.001$ ) or MgO ( $R^2 = 0.14$ ). The spread of isotopic data can be interpreted, therefore, as characteristic of the mantle sources, only little modified by interaction with local crust. Interestingly, Predazzo and Monzoni rocks (with the exception of the SiO<sub>2</sub>richest sample) do not show any correlation with D.I. too ( $R^2 = 0.02$  and 0.0004, respectively). The same conclusions can be obtained for the (fewer) <sup>143</sup>Nd/<sup>144</sup>Nd vs. D.I. trends. In conclusion, most of the isotopic variation seen in the SATIR is here related do mantle source heterogeneities rather than to post-melting interaction with upper crustal lithologies. It is also worth of noting, however, that interaction of basaltic melt with distinct crustal rock types (e.g., metapelite-metagreywackemetacarbonate successions, meta-igneous rocks) can lead to the absence of correlation between isotopic ratios and major oxides.

#### 8.2. Constraints on the mantle source(s)

Magmas generated by subduction-modified mantle sources are usually characterised by strongly fractionated incompatible element concentrations, manifested as peaks at U, K and Pb, troughs at Nb, Ta, Ti and, less marked, at Hf and Zr. Other key features are a general LILE enrichment relative to HFSE in primitive mantle-normalised diagrams (Fig. 6a). The Dolomites lava shows high Ba/Nb (32.8-93.9), low Ce/Pb (1.8-10.4) and low U/Nb (0.11-0.33) coupled with low HFSE (e.g., Nb = 6-12 ppm) with negative Nb/Nb\* ratio (0.1-0.35), resembling the typical characteristics of magmas generated by subduction-modified mantle sources (Turner and Langmuir, 2015; Kimura, 2017; Schmidt and Jagoutz, 2017; Zheng and Zhao, 2017).

Several are the geochemical tools to infer derivation from a subduction-modified mantle source, and the Th/Yb vs. Ta/Yb diagram is one of the most widely used. It is based on the behaviour of Ta, which is substantially immobile in the restite during the metamorphic reactions in a titanate-bearing sinking slab, while Th is strongly partitioned into the fluid phase (e.g., Brenan et al., 1994) in focused fluid transfer through mantle wedges (Pirard and Hermann, 2015). Moreover, Ta and other HFSE are forced to remain in the subducting slab where titanates with very high  $K_d^{HFSE}$  are easily stabilised (e.g., Foley et al., 2000; Kimura, 2017). The Yb at the denominator is used to buffer the absolute Th and Ta values to the same degree of evolution. In Fig. 9a, the Dolomites samples plot outside of the mantle array, displaced towards high Th/Yb ratios (1.3-4.9) for given Ta/Yb values (0.22-0.45). This can be interpreted as additional evidence for the derivation from subduction-modified mantle sources.

The Dolomites lavas are characterised by  $Eu/Eu^* < 1$  also in the least differentiated terms. The absence of correlation of this parameter with SiO<sub>2</sub>, MgO or D.I. indicates source characteristics that could be ultimately related to the digestion of subduction-related recycling of continental crust material ( $Eu/Eu^* = 0.70$ ; Rudnick and Gao, 2003) in their mantle sources, confirming the previous hypothesis.

A quantitative approach to define the intensive and extensive variables that had a role in the genesis of the middle Triassic volcanic rocks of the Dolomites (and in arc magmas in general) is not possible. Only qualitative or semi-quantitative geochemical modelling can be drafted, hypothesizing fundamental parameters responsible for the chemical composition of mantle wedge partial melts.

The latest release of the Arc Basalt Simulator software (ABS5; Kimura, 2017) was used to infer the conditions of magma genesis, assuming for the Dolomites lava the derivation from a supra-subduction mantle wedge. As input parameters, we hypothesized an original mantle source (pristine mantle wedge) with a depleted mantle composition (Salters et al., 2011), with an additional 0.8% MORB extraction from DMM. Additional assumed paremeters are the P-T path of Solomon subduction zone (#32 in Kimura, 2017), slab-derived flux originating at P = 3 GPa, and a slab surface temperature = 792 °C (calculated by ABS5 on the basis of the selected P and P-T path of subduction zone). The slab liquid is assumed to derive 20% from the 0.3 km thick sedimentary cover, and 80% from 0.3 km thick altered oceanic crust in a reactive porous flow regime (%R slab = 90; Kimura 2017). Without the involvement of zone refining processes, open system partial melting is assumed at P = 2.1 GPa and T = 1280 °C, with 2% slab melting and 1.1% peridotite wedge melting. The calculated slab melt contains 1.9 wt% H<sub>2</sub>O and the basaltic melt contains 2.1 wt% H<sub>2</sub>O. All these parameters represent reasonable values acting in a subduction system.

The composition of the hypothetical liquid produced, together with the hypothetical DMM source and LAT5 potassic basalt are shown in Fig. 9b. Bearing in mind the highly speculative approach, the model results in a close match between

calculated and target (LAT5) melts The calculated degree of melting of the mantle wedge is low, likely due to the effect of non-primary composition of the target melt (LAT5). Indeed, during fractional crystallization, incompatible elements tend to be concentrated in the residual melts, and this process is modelled by ABS5 reducing the degree of melting. The overlap between the calculated melt and LAT5 sample is nearly total in terms of incompatible element budget, with slight differences only in very mobile elements such as Rb, Th and K. In conclusion, the results obtained with ABS5 software indicate, with the necessary caveats, that it is possible to obtain a basaltic liquid with incompatible element fractionation and absolute content closely resembling that of basalt sample LAT5 assuming typical subduction settings from a peridotitic mantle wedge source.

#### 8.3. Geodynamic and tectonic setting.

Although paleotectonic environments are usually inferred interpreting geochemical characters of igneous rocks (e.g., Pearce and Cann, 1973; Meschede, 1986; Saccani, 2015), a warm caveat seems to emerge in recent literature in using tectonic discrimination diagrams (e.g., Li et al., 2015). In particular, it has been suggested that the geochemical signature needs always to be checked against y geological/geophysical data (e.g., Lustrino et al., 2011, 2016). When misfits arise between geochemical data and geological/geophysical evidence, a solution needs to be looked for. Several authors invoked ancient (i.e., not directly related with the coeval tectonic setting) subduction-related modifications of mantle sources to reconcile such misfits (e.g., Lustrino et al., 2011; Mazzeo et al., 2014; Gaeta et al., 2016; Di Giuseppe et al., 2018). In other cases, the geochemical message of igneous rocks has been explained with shallow rather than deep geological processes (i.e., contamination of mantle melts with upper crustal lithologies instead of subductionmodified mantle sources; e.g., Esperança et al., 1992).

The SATIR were emplaced during Pangea rifting in a mainly transtensional tectonic setting, as testified by Triassic tectonic structures widespread in the Southern Alps (Doglioni 1984, 1987; Brandner et al., 2016a, Abbas et al., 2018). However, the geodynamic scenario that originated these tectonic structures is still matter of debate. Indeed, the recorded stratigraphic successions and extensional tectonic structures have been alternatively related to rifting processes of the Meliata-Maliac Ocean (Gawlick et al., 2012; Sudar et al., 2012; Brandner et al., 2016b; Ferriere et al., 2016). Conversely, other paleogeographic settings have been proposed for the Middle Triassic western Tethys, invoking active subduction processes located west (Brack et al., 1999) or south (Stampfli et al., 2013) of Adria, Dinarides and Southern Alps nappes.

In this study we advocate, for the SATIR, an origin from subduction-modified (not directly subduction-related) mantle sources. The existence of a direct volcanic arc settings, as instead proposed by several authors (a.o., Castellarin et al., 1988;

Garzanti 1985; Zanetti et al. 2013; Bianchini et al., 2018) can be excluded because the Rheic Ocean was already completely exhausted in the Alpine realm during Middle Triassic times. A back-arc setting for the SATIR (e.g., Marinelli et al. 1980; Viel, 1982; Brack et al., 1999; Cassinis et al., 2008) can be similarly excluded, because of geochemical considerations on Eisenkappel magmatism (Northern Karawanken, eastern Alps), pointing to anorogenic magmatism in an extensional setting (e.g., Visonà and Zanferrari, 2000; Miller et al., 2011).

Back-arc basins are characterised by progressive migration of extensional tectonics and magmatism. Typical examples of migrating magmatism are described for the Tyrrhenian Sea, associated with the Apennine subduction (Carminati et al., 2012), for the Lau Basin, associated with the Tonga subduction (e.g., Hawkins, 1995) and for the Parece Vela Basin, associated with the Marianas subduction (Ishizuka et al., 2010). The existence of a Middle Triassic back-arc basin setting is in our view unlikely because of two major observations: 1) the SATIR activity does not show any agespace migration trend of magmatism, differently from what observed in present-day back-arc basins. Indeed, the oldest SATIR occurred in the central-eastern part of the 450 km wide volcanic area, and subsequent activity occurred to the east and to the west with no clear trends (Fig. 1); 2) Magmas generated in back-arc basins have both MORB and subduction affinities, differently from the SATIR case (Taylor and Martinez, 2003).

The disagreement between the geochemical message of the igneous rocks (i.e., derivation from mantle sources modified by subduction) and the geological evidence (i.e., development of continental rift with horst-and-graben structures) requires a specific solution. The most likely model in this case is the derivation of partial melts by mantle sources previously modified by the north-directed subduction of the Rheic oceanic lithosphere before the late Carboniferous Gondwana-Laurussia collision.

#### 9. Conclusions

During Middle-Late Triassic time, a large area in the Southern Alps experienced an intense and diffuse igneous activity. This magmatism (here referred to as SATIR = Southern Alps Triassic Igneous Rocks) followed the Devonian-Carboniferous subduction of the Rheic Ocean and the Carboniferous collision between the northern margin of Gondwana and the southern sectors of Laurussia with the development of Pangea. The last subduction stages and the collisional events were associated with abundant Permian calcalkaline to potassic magmatism in large sectors of the Variscan/Hercynian Chain.

During early Mesozoic, the Southern Alps portion of Pangea was affected by extensional tectonics with formation of intra-montane rifts and the development of horst-and-graben structures. This extensional tectonic phase ultimately evolved into the development, in Middle Triassic time, of huge carbonate platforms along subsiding area. During a narrow (<1 Myr) eruptive interval (Storck et al., 2019) huge

amounts of magmas reached the surface in Southern Alps, now represented by volcaniclastic and epiclastic deposits up to 150 m thick, massive lava flows, dyke swarms and rare plutonic complexes.

The igneous products are characterised by a wide compositional spectrum with compositions ranging from metaluminous basalt/gabbros to peraluminous rhyolites/leucogranites, including also cumulitic lithologies such as ultrabasic clinopyroxenites. The petrography, mineral chemistry, whole-rock chemistry and Sr-Nd-Pb isotopic ratios point to the derivation of the least differentiated melts from a subduction-modified mantle source. The shoshonitic affinities defined in terms of K<sub>2</sub>O vs. SiO<sub>2</sub> are the most abundant, followed by high-K calcalkaline types. The mildly to strongly evolved compositions are generically linked with the least differentiated terms by closed system fractional crystallization of gabbroic to monzonitic assemblages, even if the SiO<sub>2</sub>-richest magmas likely require a separate origin.

At a large scale, no substantial differences can be recorded in the four districts investigated in this study (Dolomites lavas, Predazzo, Monzoni and Vicentinian Alps), all sharing similar geochemical affinity and likely similar mantle sources, identified in a depleted mantle metasomatised by subduction event(s). A close geochemical modelling and quantification of evolutionary processes is hindered by the bad preservation state of some of the samples (e.g., the Vicentinian Alps) and, in general, by the absence of true primitive magmas and the abundance of mildly to strongly evolved compositions.

The geochemical message of these products, that is derivation from a subductionmodified mantle source, is at odds with the geological, sedimentological and structural evidence indicating that magmatism occurred in association with tectonic and geodynamic processes (rifting and/or wrench tectonics) that will eventually lead to the development of the Adria passive margins. The apparent paradox can be solved requiring the activation of upper mantle sources, contaminated during the previous Variscan subduction, when local geotherms were raised due to the passive upwelling of asthenospheric mantle along the rifted margins.

#### **10. Acknowledgements**

H.A. thanks the Erasmus Mundus European Commission for providing financial support for 33 months in framework of EU METALIC II project (Erasmus Mundus Action 2) during his PhD program. This article benefitted of thorough and detailed reviews of Tom Andersen (Oslo, Norway), Stefan Jung (Hamburg, Germany), Jörn-Frederik Wotzlaw (Zurich, Switzerland) and an anonymous reviewer. To all of them our thanks for the work that helped to clarify many aspects of the article. We thank also the Editor Sebastian Tappe (Johannesburg, South Africa) for coordinating the review process and for precious hints to improve the text readability. Special thanks to Marcello Serracino (CNR-IGAG, Rome) for his assistance during the electron microprobe analyses, to Domenico Mannetta for his help during the thin section

production and to Paolo Di Giuseppe for his assistance during the isotope analyses. Funding by FAR 2016-2017 (M. Caggiati and P. Gianolla) and Progetti di Ateneo 2016 and 2017 (E. Carminati and M. Lustrino) is acknowledged. M.L. indifferently thanks Sergio Bruni.

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#### **Figure captions:**

Fig. 1. Geographic (A) and geological (B) setting of the investigated area, with the distribution of volcanic products and possible extension of relative magmatic areas. Numbers in the circles indicate different regions of the Southern Alps: 1) Brescian Prealps; 2) Non Valley and Western Adige Valley; 3) Vicentinian Prealps; 4) Dolomites and Western Carnia; 5) Eastern Carnia and Western Julian Alps; 6) Eastern Julian Alps and Slovenian (Tolmin) Basin; 7) Southern Karawanken and Kamnik-Savinja Alps. PAL: Periadriatic Line; VS: Valsugana Fault System.

Fig. 2. Sampling sites (yellow stars) collected from volcanic (purple) and plutonic (red) outcrops in the Dolomites (a) and in the Vicentinian Alps (b). The regional position of the two regions is reported in Fig. 1. Samples outside the coloured areas are from not mappable outcrops (mainly dykes). Detailed geographic sample locations are reported in Table 1.

Fig. 3. a) Total alkali vs. SiO<sub>2</sub> (TAS) diagram (Le Maitre, 2002) for the studied rocks and literature SATIR (Southern Alps Triassic Igneous Rocks). b)  $K_2O$  vs. Na<sub>2</sub>O diagram defining the limit between the sodic series and the potassic series among the alkaline rocks. c)  $K_2O$  vs. SiO<sub>2</sub> classification (Peccerillo and Taylor, 1976) d) AFM (A = Na<sub>2</sub>O+K<sub>2</sub>O; F = FeO<sub>tot</sub>; M = MgO) ternary diagram with boundary curves dividing calcalkaline and tholeiitic fields (Kuno, 1968). The full list of sources for SATIR is reported in the Electronic Appendix 3.

Fig. 4. Major oxides vs. D.I. for the studied samples and literature SATIR. The full list of sources for SATIR is reported in the Electronic Appendix 3.

Fig. 5. Trace elements vs. D.I. for the studied samples and literature SATIR. The full list of sources for SATIR is reported in the Electronic Appendix 3.

Fig. 6. Primitive mantle-normalised diagrams (normalizing factor after Lyubetskaya and Korenaga, 2007) for the studied rocks. (a) = Dolomites lava; (b) = Predazzo plutonic rocks; (c) = Predazzo granite; (d) Monzoni plutonic rocks. Dotted lines: cumulitic gabbro; (e) = Vicentinian Alps (Schio-Recoaro area). Light blue field in (a) = St. Helena Island basalts (Southern Atlantic Ocean), considered the classical HiMu-OIB composition. Black line = GloSS composition (Global Subducting Sediments; Plank 2014).

Fig. 7. (a)  ${}^{87}$ Sr/ ${}^{86}$ Sr vs. SiO<sub>2</sub>; (b)  ${}^{87}$ Sr/ ${}^{86}$ Sr vs. MgO; (c)  ${}^{143}$ Nd/ ${}^{144}$ Nd vs. SiO<sub>2</sub>; (d)  ${}^{143}$ Nd/ ${}^{144}$ Nd vs. MgO; (e)  ${}^{207}$ Pb/ ${}^{204}$ Pb vs. SiO<sub>2</sub>; (f)  ${}^{207}$ Pb/ ${}^{204}$ Pb vs. MgO of the investigated samples and literature SATIR. The full list of sources for SATIR is reported in the Electronic Appendix 3.

Fig. 8. (a) <sup>143</sup>Nd/<sup>144</sup>Nd vs.<sup>87</sup>Sr/<sup>86</sup>Sr diagram. (b) <sup>208</sup>Pb/<sup>204</sup>Pb vs. <sup>206</sup>Pb/<sup>204</sup>Pb diagram. (c) <sup>207</sup>Pb/<sup>204</sup>Pb vs. <sup>206</sup>Pb/<sup>204</sup>Pb diagram. BSE = Bulk Silicate Earth at 230 Ma; ChUR = Chondritic Uniform Reservoir at 230 Ma. Empty circles and rectangles indicate the

isotopic signatures of the principal mantle sources. DMM, Depleted MORB Mantle; EM-I, Enriched Mantle I; EM-II, Enriched Mantle II; EAR, European Asthenospheric Reservoir; PreMa, Prevalent Mantle. NHRL = Northern Hemisphere Reference Line (Hart, 1984).

Fig. 9. a) Th/Yb vs. Ta/Yb (Pearce, 1982; Pearce and Peate, 1995) diagram for the studied rocks. N-MORB (normal MORB), E-MORB (enriched MORB) and OIB fields are from Sun and McDonough (1989). GloSS, Global Subducted Sediments (Plank, 2014); UCC, Upper Continental Crust. (b) Primitive mantle-normalised diagrams for three compositions: LAT5 represents the most primitive basalt from Dolomites (this study); ABS5 represents the best-fit composition obtained using Arc Basalt Simulator 5 (Kimura, 2017); PERID = Composition of the pre-metasomatism mantle wedge calculated by Arc Basalt Simulator software. The close match between sample LAT5 and the hypothetical melt composition (ABS5) indicates the possibility of derivation of Dolomites magmas from a subduction-modified mantle source. Full details reported in the manuscript.

#### Table captions:

Table 1. Major and trace-element contents of the studied samples from Dolomitesand Vicentinian Alps.

Table 2. Sr-Nd-Pb radiogenic isotope values of representative samples.

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1 s i N E e 7 9 4 4 9 6 3 4 9 0 7 0 5 7 1 5 8 9 1 0 8 0 0 0 1 1 6 2 3 6 6 3 7 8 5 2 1 6 1 2 5 3 9 0 2 3
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Т Vr i a c il e t 1 ANUSCRIF n o 4 1 5° t i B°2 nu 41 is 5' ai'5 n, 90 H S. . L 5 1 9 A A c 5 4 a 8 0 5 6 0 3 3 3 4 0 3 9 0 4 8 1 4 0 0 1 2 lh 23 ti. 1 5 1 7 3 0 0 8 . 7 1 5 1 3 . 2 . 3 3 1 2 6 3 1 p i " " t 0 8 8 7 1 6 4 1 1 2 2 4 583.1661 4 8 3 9 1 . . . . . . 0 . . . . 4 . 4 1 . . 5 3 3 6 1 9 3 0 6 9 s o N E e 4 3 7 8 0 3 1 7 3 2 6 5 0 0 5 8 4 1 2 5 3 1 3 3 4 9 1 9 2 2 4 8 2 5 2 2 5 V C i o 4 1 c n 5 1 e t 0 nr 4 2 tà 52 1 i n L 2 1 6 Hio9 0 D 6 Aav. 4 а 3 0 5 4 0 1 4 2 3 0 3 0 5913 1 1 0 0 108087.6 513.30 43 1485 n a 5 5 c 2 1 t 7 " it 8 5 6 9 0 2 2 2 9 2 1 1 3 5 0 2 . 1 7 8 3 0 1 . . . . . 7 . . . . 5 . . 2 . . 7 A i " E e 1 5 6 5 9 4 7 3 3 1 5 0 6 9 2 5 7 2 0 8 0 2 0 3 5 4 8 2 6 9 9 6 9 1 9 1 5 1 4 5 5 9 6





0 8 n s 9 8 п п n a N E р s

Table 1. Major and trace-element contents of the studied samples from Dolomites and Vicentinian Alps.

Individual of the second of th

												Age	e-corr	ected	(230	Ma)
				Mea	sured	d data	(wit	h erro	ors)					value	S	
				143		206		207		208		87	143	206	207	208
		87		Nd		Pb		Pb		Pb		Sr	Nd	Pb	Pb	Pb
		Sr		/14		/20		/20		/20		/ <sup>8</sup>	/14	/ <sup>20</sup>	/ <sup>20</sup>	/ <sup>20</sup>
	Rock	/ <sup>86</sup>		<sup>4</sup> N		<sup>4</sup> P		<sup>4</sup> P		<sup>4</sup> P		<sup>6</sup> S	<sup>4</sup> N	<sup>4</sup> P	<sup>4</sup> P	<sup>4</sup> P
	Туре	Sr	±	d	±	b	±	b	±	b	±	r	d	b	b	b
							0		0		0	0.				
G		0	0	Ο	0	18	0.	15	0.	28	0.	7				
^	Subal	70	0.	51	0.	5	0	6	0	7	0	0		4.0	4 -	20
A D	kali	70 E2	00	24	00	.J 20	2	.0	2	./ 76	С Г	5	0.5	18	15	38
л Э	Basai	55	10	24	00	29 F	2	01	2	70 6	1	0	12	.2	.0	.4
3	ι	64	13	90	09	Э	4	ð	T	0		8	29	63	48	06
							0.		0.		0.	0.	*			
В	Subal	0.	0.	0.	0.	18	0	15	0	38	0	/				
U	kali	70	00	51	00	.5	0	.6	0	.7	0	1	05	18	15	28
F	Basal	53	00	25	00	86	1	53	1	46	2	9	12	2	6	3
2	t	21	09	05	08	6	2	4	0.	8	4	2	30	96	39	.5 56
-	L.		00	00	00	Ũ	-	•	Ū			0.	00	50	00	50
							0.		0.		0.	7				
L	K-	0.	0.	0.	0.	19	0	15	0	39	0	0				
А	Alkali	70	00	51	00	.4	1	.6	1	.0	2	5	0.5	18	15	38
Т	Basal	63	00	25	00	95	3	81	0	52	6	7	12	.3	.6	.8
2	t	44	07	33	09	6	7	0	7	6	3	7	34	53	74	94
							0	7	0		0	0.				
	Potas	0	0	0	0	10	0.	4 5	0.	20	0.	7				
в	sic	0.	0.	0.	0.	18	0	15	0	38	0	0				
-	Trach	/0	00	51	00	.5	0	.6	0	.6	0	4	0.5	18	15	38
F	ybasa	45	00	25	00	32	1	52	0	29	2	3	12	.3	.6	.4
4	lt	83	10	61	08	9	2	2	9	2	3	2	37	93	45	50
							0.		0.		0.	0.				
м	Potas	0.	0.	0.	0.	18	0	15	0	38	0	/				
Δ	SIC Tura ala	70	00	51	00	5	0	6	0 0	7	0	0	0 F	10	4 5	20
R	rach	18	00	25	00	01	2	.0 /11	2	04	8	4 F	12	2 78	15	38 1
1	yuasa It	20	00	50	10	2	0	41	5	2	1	2 1	26	.5 27	ס. ככ	.4 02
Т	IL	59	09	50	10	5	9	4	5	5	4	1	50	57	22	00
			)				0.		0.		0.	0. 7				
D	7	0.	0.	0.	0.	18	0	15	0	38	0	, 0				
U	Shos	70	00	51	00	.4	0	.6	0	.5	0	4	05	18	15	38
R	honit	55	00	25	00	93	1	44	0	62	2	8	12	.4	.6	.4
4	e	48	08	35	06	7	2	0	9	7	4	0	34	06	40	55
-	C					-	_	-	-	-	-	0.	0.			
							0.		0.		0.	7				
		0.	0.	0.	0.	18	0	15	0	38	0	0				
Ρ		70	00	51	00	.4	0	.6	0	.5	0	4	0.5	18	15	38
R		64	00	24	00	92	0	21	0	52	1	9	12	.3	.6	.4
3	Latite	58	07	49	09	3	5	0	4	6	1	1	27	98	16	34
Tabl	e 2. Sr-N	d-Pb	radio	genic	isoto	pe val	ues d	of rep	reser	ntativ	e samp	oles				

Highlights

The first complete review of the Middle Triassic magmatism of Southern Alps is presented

The composition of the igneous rocks indicates subduction-modified mantle sources The geochemical message is at odds with the geological evidences of continental rifting stages.

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Figure 5





Figure 7





Figure 9