Jurassic carbonate and alkaline magmatism in the Ivrea zone (European Alps) related to the breakup of Pangea

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ABSTRACT
We report on pipe-like bodies and dikes of carbonate rocks related to sodic alkaline intrusions and amphibole mantle peridotites in the Ivrea zone (European Southern Alps). The carbonate rocks have bulk trace-element concentrations typical of low–rare earth element carbonatites interpreted as cumulates of carbonatite melts. Faintly zoned zircons from these carbonate rocks contain calcite inclusions and have trace-element compositions akin to those of carbonatite zircons. Laser ablation–inductively coupled plasma–mass spectrometry U–Pb zircon dating yields concordant ages of 187 ± 2.4 and 192 ± 2.5 Ma, coeval with sodic alkaline magmatism in the Ivrea zone. Cross-cutting relations, ages, as well as bulk and zircon geochemistry indicate that the carbonate rocks are carbonatites, the first ones reported from the Alps. Carbonatites and alkaline intrusions are comagmatic and were emplaced in the nascent passive margin of Adria during the Early Jurassic breakup of Pangea. Extension caused partial melting of amphibole-rich mantle domains, yielding sodic alkaline magmas whose fractionation led to carbonatite-silicate melt immiscibility. Similar occurrences in other rifts suggest that small-scale, sodic and CO₂-rich alkaline magmatism is a typical result of extension and decompression-driven reactivation of amphibole-bearing lithospheric mantle during passive continental breakup and the evolution of magma-poor rifts.

INTRODUCTION
The common occurrence of carbonatites, alkaline intrusions, and metasomatized mantle peridotites in passive continental margins (e.g., Bailey, 1974; Natarajana et al., 1994; Azer et al., 2010) suggests that (1) a metasomatized mantle source is a prerequisite to generate rift-related alkaline and carbonatite melts (Foley, 1992; Pilet et al., 2008), (2) reactivation of metasomatic mantle domains and magma production are tectonically controlled, and (3) alkaline and carbonate melts are cogenetic and share common mantle sources. In this regard, carbonate-silicate liquid immiscibility after strong fractionation of alkaline silicate melts has been invoked to produce carbonatites (Lee and Wyllie, 1997). We present field, petrological, geochemical, and geochronological data on intrusive carbonate rocks and alkaline intrusions spatially related to amphibole-rich mantle peridotites from the Ivrea zone (European Southern Alps). The Ivrea zone exposes a piece of lower crust that was located in the margin of Adria during Triassic–Jurassic Pangea breakup (Decaris et al., 2017) and offers the opportunity to study magmatic processes that acted in both the lithospheric mantle and the lower continental crust during passive rifting. This study aims to understand the origin and evolution of CO₂-rich alkaline intrusions in such a passive rift setting, where the reactivation of heterogeneously metasomatized amphibole-bearing mantle domains can be observed in the field.

GEOLOGICAL SETTING
The Ivrea zone and Serie dei Laghi (Fig. 1) show a complete continental crustal section. In the lower crust, Permian gabbros intruded paragneisses, marbles, and amphibolites; at shallower levels, Permian granitoids intruded gneisses, whereas acidic volcanic rocks extruded at the surface (Quick et al., 2009). Lenses of mantle peridotite occur within the gabbros. Peridotites exhibit amphibole-, apatite-, carbonate-, or phlogopite-rich domains, pyroxenites, hornblendites, and gabbro dikes, and dunite, wehrlite, and chromitite bands (e.g., Zanetti et al., 1999). Geochronological data (e.g., Grieco et al., 2001) and the spread in Sr and Nd bulk isotope data (Voshage et al., 1987) suggest that the mantle experienced a multistage history of melt and fluid percolation from the Devonian to the Early Jurassic, with the involvement of both mantle and crustal components (Grieco et al., 2001; Locmelis et al., 2016).

Alkaline ultramafic pipes (Garuti et al., 2001) intruded the lower crust in the Permian–Early Triassic (Locmelis et al., 2016; Fiorentini et al., 2018). Their origin is attributed to the melting of mantle domains metasomatized through the Variscan subduction and reactivated during the collapse of the Variscan belt (Locmelis et al., 2016). A suite of Late Triassic–Early Jurassic sodic and alumina-rich alkaline intrusions, ranging from calcite-clinopyroxene–bearing hornblendlites (Stühle et al., 2001),
alkali gabbros, and diorites to plagioclases and nepheline syenites (Schaltegger et al., 2015), occurs associated in space with amphibole peridotites. Their ages suggest a relation to the early Mesozoic breakup of Pangea (Schaltegger et al., 2015). Intrusive carbonate rocks of unknown age and origin are found with amphibole peridotites and alkaline intrusives (Fig. 1). In the field, these discordant intrusive carbonate rocks form pipe-like bodies and dikes (Items DR2A–DR2E in the GSA Data Repository1) structurally distinct from metasedimentary marbles, which are concordant with paragneisses. In this study, three intrusive carbonate rocks from Val Mastallone, Val Fiorina, and Bocchetta di Campo, Italy (referred to as VM, VF, and BC; locations in Fig. 1), and their associated alkaline intrusives were investigated by geochemical analyses. Zircons from VM and VF were U-Pb dated by laser ablation–inductively coupled plasma–mass spectrometry (analytical methods are provided in Item DR1).

**INTRUSIVE CARBONATE ROCKS: FIELD RELATIONS, MINERALOGY, AND WHOLE-ROCK GEOCHEMISTRY**

VM and VF are up to 40 × 70 m large, subcircular, steeply dipping pipe-like bodies with sharp discordant magmatic contacts to the host rocks (Items DR2A and DR2D). VM cuts across garnet-ampithe gabbro-norrites, whereas VF intrudes paragneisses and an ultramafic-mafic body composed of phlogopite-ampithe-carbonate–bearing peridotite surrounded by alkaline hornblende and gabbro. Plagioclase dikes are associated with both carbonate rocks. BC is a 250-m-long and 20-m-thick, steeply dipping dike (Item DR2E) intrusive into a garnet-ampithe-carbonate–bearing plagioclase. All carbonate rocks are composed of calcite with minor clinopyroxene, amphibole, apatite, plagioclase, and zircon (Item DR2F) and contain polymict xenoliths and enclaves. VM encloses clinopyroxenites (Item DR2B). VF and BC contain xenoliths from the host rocks and phlogopite-ampithe–bearing plagioclase.

Intrusive carbonate rocks have 0.01–0.94 wt% NaO, 278–4368 ppm Sr, and total rare-earth-element (REE) content of 83–211 ppm, are enriched in light REEs (LREEs) over heavy REEs (HREEs) (chondrite-normalized La/Yb ratio of 13.9–18.4) Ba, Th, U, and Sr, and total rare-earth-element (REE) content of 83–211 ppm, are enriched in light REEs (LREEs) over heavy REEs (HREEs) (chondrite-normalized La/Yb ratio of 13.9–18.4) Ba, Th, U, and Sr, and total rare-earth-element (REE) content of 83–211 ppm, are enriched in light REEs (LREEs) over heavy REEs (HREEs) (chondrite-normalized La/Yb ratio of 13.9–18.4). Ba, Th, U, and Sr, and total rare-earth-element (REE) content of 83–211 ppm, are enriched in light REEs (LREEs) over heavy REEs (HREEs) (chondrite-normalized La/Yb ratio of 13.9–18.4).

In the studied area, marbles within paragneisses display lower Sr contents of 189–546 ppm and REE contents one to two orders of magnitude lower than in intrusive carbonate rocks (Fig. 2).

**INTRUSIVE CARBONATE ROCK ZIRCONS**

Zircons from samples VM1 and VF33 are rounded to slightly elongated, 50–150 μm long, and homogeneous to faintly zoned in cathodoluminescence (Fig. 3A; Item DR4). A few grains in VF33 display oscillatory-zoned cores and homogeneous or faintly zoned rims (Item DR4). In the homogeneous zircons of both samples, calcite inclusions were identified by Raman spectroscopy (Fig. 3B; Item DR5), testifying for crystallization from a calcite-saturated environment. In sample VM1, 30 spots were analyzed by laser ablation–inductively coupled plasma–mass spectrometry on 30 homogeneous to faintly zoned grains. Nineteen (19) spots are concordant and give an age of 187 ± 2.4 Ma (Fig. 3C), interpreted as intrusion age.

In sample VF33, 20 points on 20 homogeneous to faintly zoned grains and seven points in the cores of grains with oscillatory-zoned cores and homogeneous rims were analyzed. On the homogeneous grains, 17 points are concordant; 15 of them yielded a concordant age of 192 ± 2.5 Ma (Fig. 3D), interpreted as intrusion age. Two points are slightly younger, probably due to the influence of inclusions, as suggested by their compositions (Item DR6). One point on the largest oscillatory-zoned core yielded a Permian age of 287 ± 6 Ma, and six points yielded mixed core-rim ages of 201–226 Ma.

Concordant homogeneous zircons from both samples have low REE, U, Th, Y contents (Item DR5) and relatively high Th/U (0.2–1.4; Fig. 3F) and Zr/Hf (44–145). Chondrite-normalized REE patterns (Fig. 3E) have no Eu and almost no Ce anomalies, and HREEs are only slightly fractionated over LREEs as is characteristic for zircons in carbonatites (Belousova et al., 2002). VM1 zircons have an εHf(187 Ma) of 0.8 to −5.2 (average value −1.2 ± 0.8, MSWD [mean square of weighted deviates] = 1.1, probability of fit = 0.35, 176Hf/177Hf = 0.28259–0.28268; Fig. 3G; Item DR7). VF33 zircons show two groups of distinct εHf composition. In group 1, εHf(195 Ma) is 3.5 to −0.8 (average value 1.3 ± 1.2, MSWD = 0.95, prob. = 0.489, 176Hf/177Hf = 0.28263–0.28275), whereas in group 2, εHf(195 Ma) is −5.3 to −9.5 (average value −7.7 ± 2.4, MSWD = 0.77, prob. = 0.46, 176Hf/177Hf = 0.28238–0.28250). The Permian oscillatory-zoned zircon in sample VF33 has lower Th/U and Zr/Hf ratios of 0.01 and 35, and is rich in Hf and poor in Th (Fig. 3F). Its εHf(227 Ma) of −15 (176Hf/177Hf = 0.28217) is similar to εHf in zircons from paragneisses of the Ivrea zone (Fig. 3G; Ewing et al., 2014).

**RIFT-RELATED JURASSIC CARBONATITITES**

The Early Jurassic ages of the intrusive carbonate rocks exclude that they formed through partial melting of crustal carbonates during the granulitic thermal peak, which occurred during the Permian (Ewing et al., 2015). Their bulk geochemistry, zircon composition, calcite inclusions, and ages suggest that these intrusive carbonate rocks are Jurassic carbonatites, the first ones reported so far in the Alps. The telltale association with alkaline intrusions supports this interpretation. The alkaline magmatism in the Ivrea zone is mostly Late Triassic to Early Jurassic (Schaltegger et al., 2015), but was already present in the late Permian (Fiorentini et al., 2018), testifying for a protracted period of extension. Extension started...
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In fact, the almost monomineralic alkali-poor calcite which contrasts with the shallow-crust or surface environment of most which strongly modified the geochemical and rheological structure of the with the collapse of the Variscan belt in the late Carboniferous and, after the opening of the Tethys Ocean and the formation of oceanic crust in the Late Jurassic (Rubatto et al., 1998). The Ivrea carbonatites present absolute bulk trace-element concentrations lower than those of typical carbonatites (Woolley and Kempe, 1989) but in the range of those of low-REE carbonatites interpreted as cumulates (Yang et al., 2011). In fact, the almost monomineralic alkali-poor calcite rocks do not represent true carbonatite melt compositions, which should contain 5–20 wt% bulk Na₂O + K₂O (Schmidt and Weidendorfer, 2018), but rather wall cumulates formed during the early stages of carbonatite crystallization stacked in the lower crust. During the Early Jurassic, the country rocks had a regional temperature <600 °C (Ewing et al., 2015), which contrasts with the shallow-crust or surface environment of most carbonatites and led to a comparatively slower cooling and more favorable conditions for cumulate formation.

**LINK TO ALKALINE MAGMATISM**

Nearly 95% of the Late Triassic–Early Jurassic alkaline intrusions in the Ivrea zone are sodic (on average Na₂O/O₂ -5; Item DR9). Hornblendites and alkali gabbros are rich in Ti and Nb, and show variable Th and U contents and an enrichment of LREEs over HREEs. More-evolved alkali diorites, plagioglasites, and syenites are rich in Al, poor in Ti, display steep LREE patterns, but flat to spoon-shaped middle REE (MREE)–HREE patterns and one order of magnitude less enrichment than typical oceanic island basalt series. We propose that melting of amphibole-rich mantle domains generates sodic magmas enriched in LREEs over HREEs and Nb but with variable Th and U contents, consistent with the results of melting experiments on amphibole-rich ultramafic sources (Pilet et al., 2008). The degree of melting and amphibole-clinopyroxene ratios in the source control the amount of highly incompatible elements (Pilet et al., 2008). Interactions of such melts with shallower mantle increases their Al content by dissolution of Al-rich orthopyroxene and precipitation of olivine (Pilet et al., 2008). Fractionation of olivine, clinopyroxene, amphibole, and Ti-oxides then further increases Al and alkalis but decreases Ti. Amphibole fractionation yields the flat to spoon-shaped MREE–HREE patterns of the more-evolved melts (Blundy and Wood, 2003). The late fractionation of plagioclase would favor a strong alkali enrichment, producing residual melts sufficiently rich in alkalis to hit the carbonatite-silicate miscibility gap. In the total alkali–silica (TAS) diagram (Fig. 4), alkali gabbros, alkali diorites, plagioglasites, and syenites follow differentiation trends that lead through alkali enrichment to immiscibility with carbonatite melts (Schmidt and Weidendorfer, 2018). Plagioglasite enclaves are similar in composition to plagioglasite dikes and fit the fractionation path of the syenites, which may represent the evolving alkali silicate melts just before or at immiscibility.

**MAGMA SOURCE**

In the studied carbonatites, the positive to slightly negative εHf(t) of the sample VM1 zircons and the sample VF33 group 1 zircons points to a metasomatic mantle source of the parent magma, whereas moderate incorporation of paragneiss during magma emplacement is suggested by the lower εHf(t) of group 2 zircons and Permian oscillatory-zoned core in sample VF33. Zircons with age and εHf(t) akin to those of the VM1 zircons and VF33 group 1 zircons occur in metasomatic chromitite layers within amphibole-plagiogpote mantle peridotites of the Ivrea zone (Fig. 3G; Zanetti et al., 2016; Malitch et al., 2017), indicating that the studied carbonatites isotopically match parts of the mantle. Available bulk Sr-Nd isotope data for the Ivrea alkaline intrusions present a large scatter (Stähle et al., 2001; Garuti et al., 2001) fitting the spread in mantle rocks (Voshage et al., 1987). This suggests that these magmas arise from heterogeneously metasomatized mantle domains. Their variable isotopic signatures reflect the complex compositional structure of the source, irrespective of the age(s) and mechanism(s) of metasomatism. The generation of sodic CO₂-bearing melts from isotopically variable amphibole-rich peridotites during passive rifting explains the relatively low trace-element concentrations and heterogeneous isotopic signature. The Ivrea zone is also famous for isotopically enriched plagiogpote peridotites related to crustal metasomatism (Voshage et al., 1987). These do not constitute a suitable source for the sodic melts,
but their local involvement would contribute to the variable Na/O,K,O ratios (40–0.4) and isotopic signature of the alkaline melts. Finally, the small-scale alkaline magmatism in the Ivrea zone occurs over a distance of ~80 km, hence cannot stem from a single mantle volume but from local mantle regions, in all likelihood the most enriched ones. Parent magmas are hence expected to be slightly heterogeneous in geochemical and isotopic compositions, rendering the entity of all intrusions not strictly magmatic and enabling some differences in the fractionation path.

CONCLUSIONS

The association of carbonatites, sodic alkaline intrusions, and amphibole peridotites is a common feature of magma-poor passive continental margins. We propose that low-degree partial melting of amphibole-bearing lithospheric mantle domains during extension generated small-scale sodic, CO₂-rich alkaline magmatism in the passive margin of Adria during Triassic–Jurassic Punagea breakup. Fractionation of these melts resulted in sodic alkaline and carbonate intrusions. This magmatism contrasts in style and volume with the deeply rooted, strongly enriched alkaline magmas typical of continental breakup driven by large-scale mantle convection (e.g., the East African Rift; Baker et al., 1972). This study suggests that strong fractionation of alkaline suites may be an efficient mechanism to produce carbonatites at relatively high lithospheric levels.

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