Jurassic carbonatite 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.

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 plagiogrape-rich domains, pyroxenites, hornblendites, and gabbro dikes, and dunite, wehrlite, and chromite-rich bands (e.g., Zanetti et al., 1999). Geochemical 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 multi-stage 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 hornblenlites (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 Pangaea (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 Bobcetta 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-amphibole gabbro-norrites, whereas VF intrudes paragneisses and an ultramafic-mafic body composed of plagiopylite-amphibole-carbonate–bearing peridotite surrounded by alkaline hornblende 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-amphibole-carbonate–bearing gabbro-norite close to bodies of amphibole peridotites and dikes of alkali gabbro, alkali diorite, nepheline syenite, and plagioclase (10%–25% anorthite [An10–25]; item DR2C). All carbonate rocks are composed of calcite with minor clinopyroxene, amphibole, apatite, scheelite, and zircon (item DR2F) and contain polymict xenoliths and enclaves. VM encloses clinopyroxenites (item DR2B). VF and BC contain xenoliths of the host rocks and plagiopylite-amphibole–bearing plagioclase.

Intrusive carbonate rocks have 0.01–0.94 wt% Na2O + K2O, 278–436 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 are depleted in Rb, K, Ta, Nb, Hf, Zr, and Ti, as typically reported for carbonatites (e.g., Yang et al., 2011) but consistent with cumulative carbonatites (e.g., Yang et al., 2011; Fig. 2). 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 spectrometry (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.

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1GSA Data Repository item 2019068, Item DR1 (analytical methods), Item DR2 (photos of field area and samples), Item DR3 (bulk rock geochemistry), Item DR4 (cathodoluminescence images of carbonatite zircons), Item DR5 (inclusions in zircons), Item DR6 (zircon U-Pb-Th isotope data), Item DR7 (zircon Hf-Lu-Yb isotope data), Item DR8 (zircon trace element composition), Item DR9 (major element bulk rock composition of alkali intrusions from the Ivrea zone and Serie dei Laghi), and Item DR10 (LA-ICP-MS trace element bulk rock composition of alkaline intrusions from the Ivrea zone), is available online at http://www.geosociety.org/datarepository/2019/, or on request from editing@geosociety.org

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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 Rb, 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(t) 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 Hf composition. In group 1, εHf(t) 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(t) is −5.3 to −9.5 (average value −7.2 ± 4.8, 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(t) of −15 (176Hf/177Hf = 0.28217) is similar to εHf(t) in zircons from paragneisses of the Ivrea zone (Fig. 3G; Ewing et al., 2014).

### RIFT-RELATED JURASSIC CARBONATITES

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 tectilite 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...
Enclave in carbonatite VF on 17 March 2019 by guest

... which contrasts with the shallow-crust or surface environment of most... after Zanetti et al. (2016) and Malitch et al. (2017).

... are ages in Ma. Ellipses are plotted with 2σ mean and errors at 95% confidence level. Values along the Concordia... from Ivrea chromitite layers within mantle peridotite... are from Ewing et al. (2014); zircons from Ivrea metapelites are from Ewing et al. (2016) and Malitch et al. (2017).

... with the collapse of the Variscan belt in the late Carboniferous and, after... tions lower than those of typical carbonatites (Woolley and Kempe, 1989) and... carbonatitic zircons...carbonatites and led to a comparatively slower cooling and more favorable conditions for cumulate formation.

... nearly 95% of the Late Triassic–Early Jurassic alkaline intrusions in... and mechanism(s) of metasomatism. The generation of sodic CO2-bearing melts from isotopically variable amphibole-rich peridotites during passive... magma plume (Voshage et al., 1987). These do not constitute a suitable source for the sodic melts,... 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/chloropyroxene 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 alkali to hit the carbonatite-silicate miscibility gap. In the total alkalii–silica (TAS) diagram (Fig. 4), alkali gabbrros, alkali diorites, plagioclases, and syenites follow differentiation trends that lead through alkali enrichment to immiscibility with carbonatite melts (Schmidt and Weidendorfer, 2018). Plagioclase enclaves are similar in composition to plagioclase dikes and fit the fractionation path of the syenites, which may represent the evolving alkaline silicate melts just before or at immiscibility.

**MAGMA SOURCE**

In the studied carbonatites, the positive to slightly negative εNd values 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 of group 2 zircons and Permian oscillatory-zoned core in sample VF33. Zircons with age and εHf akin to those of the VM1 zircons and VF33 group 1 zircons occur in metasomatic chromitite layers within amphibole-plagiochlorite mafic 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 riftting explains the relatively low trace-element concentrations and heterogeneous isotopic signature. The Ivrea zone is also famous for isotopically enriched plagioclase 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 comagmatic 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, CO$_2$-rich alkaline magmatism in the passive margin of Adria during Triassic–Jurassic Pangea breakup. Fractionation of these melts resulted in sodic alkaline and carbonatite 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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