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


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 carbonatites 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 $187 \pm 2.4$ and $192 \pm 2.5$ 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 CO$_2$-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 breakup (Decarlis 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 CO$_2$-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 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 hornblende dites (Stühle et al., 2001),
alkali gabbros, and diorites to plagioclase and nepheline syenites (Schaltegger et al., 2015), occurs associated in space with amphibole peridots. 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 peridots 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-amphibole gabbro-norites, whereas VF intrudes paragneisses and an ultramafic-mafic body composed of plagiogopite-amphibole-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-amphibole–carbonate zone. VM encloses plagioclase xenoliths from the host rocks and plagiogopite–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, 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, P, Hf, Zr, and Ti, as typically reported for carbonatites (Fig. 2; Item DR3). Absolute trace-element concentrations are lower than average carbonatite (Woolley and Kempe, 1989; Le Bas, 1999) 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 homogeneus 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 isotopic data), Item DR7 (zircon Hf-La-Yb isotopic data), Item DR8 (zircon trace element composition), Item DR9 (major element bulk rock composition of alkaline 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 REE, U, Th contents (Item DR8) and relatively high Th/U (0.2–1.4; Fig. 3F) and Zr/Hf (44–145). Chondrite-normalized REE patterns (Fig. 3G; Item DR5) show 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(195 Ma) of 0.8 to −5.2 (average value −1.2 ± 0.8, MSWD = 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(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(195 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 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 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...
with the collapse of the Variscan belt in the late Carboniferous and, after
the Permian carbonatite-related rifting on the nascent margin of Adria,
but rather wall cumulates formed during the early stages of carbonatite
melting of various mantle volumes yields slightly differing primitive
melts and most intrusions are slightly cumulative, thus fractionation
paths are approximate. Bulk-rock compositions and references are
available in Schmidt and Weidendorfer (2018). Note that melting of various mantle volumes yields slightly differing primitive melts and most intrusions are slightly cumulative, thus fractionation paths are approximate. Bulk-rock compositions and references are available in Schmidt and Weidendorfer (2018).

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-phlogopite 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 phlogopite peridotites related to crustal metasomatism (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/clinopyroxene ratios in the source control the amount of highly incompatible elements (Pilet et al., 2008). Fractionation of olivine, clinopyroxene, amphibole, and Ti-oxides then further increases Al and alkalai 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 alkalai enrichment, producing residual melts sufficiently rich in alkalai to hit the carbonate-
silicate miscibility gap. In the total alkalai–silica (TAS) diagram (Fig. 4), alkalai gabbros, alkalai diorites, plagioclases, and syenites follow differentiation trends that lead through alkalai enrichment to immiscibility with carbonate 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 alkalai silicate melts just before or at immiscibility.

LINK TO ALKALINE MAGMATISM

Nearly 95% of the Late Triassic–Early Jurassic alkaline intrusions in
the Ivrea zone are sodic (on average Na2O + K2O ~8; Item DR9). Horn-blendites and alkalai gabbros are rich in Ti and Nb, and show variable Th and U contents and an enrichment of LREEs over HREEs. More-evolved alkalai diorites, plagioclases, and syenites are rich in Al, poor in Ti, display steep LREE patterns, but flat to spoon-shaped middle RIEE (MREE)–HREE patterns and one order of magnitude less enrichment than typical

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**Figure 3. Data from sampled zircons, Ivrea zone, European Southern Alps.** A: Cathodoluminescence image of faintly zoned zircon (sample VM1). B: Calcite inclusion within zircon (sample VF33). C: Concordia diagrams of carbonate zircons. Ages are calculated as weighted mean and errors at 95% confidence level. Values along the Concordia are in Ma. Ellipses are plotted with 2σ error; colored ellipses are calculated average ages. MSWD—mean square of weighted deviates. E,F: Trace-element composition of zircons. Red is sample VM1; blue, homogeneous grains in sample VF33; yellow, mixed core and rim in VF33; black, Permian core in VF33. G: εHf versus age in zircon (g1, g2—zircon groups 1 and 2). Ivrea metapelite zircons are from Ewing et al. (2014); zircons from Ivrea chromitite layers within mantle peridotite are after Zanetti et al. (2016) and Malitch et al. (2017).

**Figure 4. Total alkalai–silica (TAS) diagram with composition of alkaline rocks from Ivrea zone, European Southern Alps.** Gray arrow shows fractionation path following Schmidt and Weidendorfer (2018). Note that melting of various mantle volumes yields slightly differing primitive melts and most intrusions are slightly cumulative, thus fractionation paths are approximate. Bulk-rock compositions and references are in Item DR9 (see footnote 1). VF—Val Fiorina; VM—Val Mastallone.
but their local involvement would contribute to the variable Na2O/K2O ratios (40–0.4) and isotopic signature of the alkali 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 Pangea 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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