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# Petrology of the Eocene alkaline volcanism from the western Rio Grande Rise, South Atlantic Ocean

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The origin and evolution of the Rio Grande Rise is deeply related to the opening of the South Atlantic Ocean. The geology of the plateau records the transition from divergent plate margins at the Mid-Atlantic Ridge to an intraplate tectonic setting. Despite the potential to bring insights into the complex tectono-magmatic processes involved in the development of the Rio Grande Rise, there is an overall lack of integrated petrological studies regarding its intraplate Eocene alkaline magmatism. We have investigated trachytes, trachyandesites, alkali basalts, a trachybasalt and a basanite dredged from the western Rio Grande Rise to characterize its magmatic system. Integrated petrography, mineral chemistry and whole-rock geochemistry suggests that these rocks have evolved in a complex transcristal polybaric magmatic system, where crystals were remobilized by host liquids with different composition at distinct depths. Disequilibrium between crystals and host magmas is evidenced by abundant clinopyroxene macrocrysts with resorbed or corroded cores and rims with contrasting composition, as well as by resorbed feldspar macrocrysts. Clinopyroxene crystals also record cyclic compositional variations in magmatic chambers submitted to multiple magma recharge episodes and a strong control by fractional crystallization. U-Pb dating of zircons from a trachyte yielded an age of  $46.9 \pm 0.3$  Ma, which reinforces the importance of the Eocene volcanism from the western Rio Grande Rise. Moreover, results from Pb, Sr and Nd isotope analysis reveal that Eocene alkaline volcanic rocks from the Western Rio Grande Rise have EMI-flavored Tristan-type signatures. This suggests that the mantle sources from the western Rio Grande Rise and from the Walvis Ridge and Guyot Province magmatism still shared common characteristics long after its separation from the Walvis Ridge.

## KEYWORDS

Rio Grande Rise, alkaline volcanism, igneous petrology, mineral chemistry, South Atlantic Ocean, Enriched Mantle I, Tristan-Gough mantle plume

# 1 Introduction

The Rio Grande Rise (RGR; [Figure 1](#)) is a plateau with noteworthy bathymetry in the South Atlantic Ocean. Its morphology results from a combination of complex processes which shaped it along its evolution in the context of the South Atlantic opening, and volcanism has played a major role. Extensive magmatism on a spreading center under influence of a mantle plume is frequently evoked to explain its anomalous crustal thickness ([Gamboa and Rabinowitz, 1984](#); [O'Connor and Duncan, 1990](#); [Rohde et al., 2013b](#); [Hoyer et al., 2022a](#); [Hoyer et al., 2022b](#)) with estimated values of 17 to up to 30 km ([Ussami et al., 2013](#); [Constantino et al., 2017](#); [Graça et al., 2019](#)). This is also supported by the enriched geochemical and isotope composition of its tholeiitic basalt basement ([Thompson et al., 1983](#); [Weaver et al., 1983](#); [Gibson et al., 2005](#); [Hoernle et al., 2015](#); [Hoyer et al., 2022a](#); [Hoyer et al., 2022b](#)).

The RGR was formed together with the Walvis Ridge (WR), as supported by paleogeographic reconstructions and the similar ages, geochemical and geophysical characteristics from their tholeiitic basaltic basements ([Gamboa and Rabinowitz, 1984](#); [Graça et al., 2019](#); [Musset and Barker, 1983](#); [O'Connor and Duncan, 1990](#); [Rohde et al., 2013b](#); [Ussami et al., 2013](#)). They were later separated due to a combination of seafloor spreading and rift jumps (e.g., [Gamboa and Rabinowitz, 1984](#); [Graça et al., 2019](#); [O'Connor and Duncan, 1990](#); [Praxedes et al., 2019](#); [Rohde et al., 2013b](#)), possibly involving reorganization of the Mid-Atlantic Ridge and the formation of a microplate ([Sager et al., 2021](#)). Consequently, their tectonic setting changed from divergent plate margins to oceanic intraplate, a transition marked by the change from on-axis to intraplate volcanism ([O'Connor and Duncan, 1990](#); [Rohde et al., 2013b](#)). In the case of the RGR, the ~80–88 Ma tholeiitic basaltic basement drilled by the Deep Sea Drilling Project (DSDP) at Site 516F, as well as the tholeiitic lavas from the ERGR, represent on-axis volcanism ([Musset and Barker, 1983](#); [O'Connor and Duncan, 1990](#); [Rohde et al., 2013b](#); [Thompson et al., 1983](#); [Hoyer et al., 2022a](#)), whilst its guyots and seamounts were formed by alkaline intraplate volcanism during the Eocene ([Bryan and Duncan, 1983](#); [Fodor et al., 1977](#); [Fodor and Thiede, 1977](#); [Gamboa and Rabinowitz, 1984](#); [Hoyer et al., 2022a](#); [Rohde et al., 2013b](#)). In the case of the Walvis Ridge, this change in the tectonic setting is reflected by the transition of magmatism in the main ridge to the Guyot Province, the latter formed by intraplate volcanism associated with the Tristan-Gough mantle plume ([O'Connor and Duncan, 1990](#); [Rohde et al., 2013b](#)).

While lavas from the Walvis Ridge and Guyot Province have been subject to multiple investigations (e.g., [Richardson et al., 1982](#); [1984](#); [Thompson and Humphris, 1984](#); [Gibson et al., 2005](#); [Rohde et al., 2013b](#); [O'Connor and Jokat, 2015](#); [Homrighausen et al., 2018](#); [Homrighausen et al., 2019](#)), only a few petrological and geochemical studies were carried out on the Rio Grande Rise, despite its potential to contribute to a better understanding of the complex tectono-magmatic processes related to their origin and evolution. Moreover, there was considerably limited knowledge about the petrology of the RGR alkaline volcanism until very recently, when the works by [Fodor and Thiede \(1977\)](#), and [Fodor et al. \(1977\)](#) were complemented by the contributions by [Hoyer et al. \(2022a\)](#), [Hoyer et al. \(2022b\)](#) and [Homrighausen et al. \(2023\)](#), which shed light on the Pb, Sr, Nd and Hf isotope signatures and differences between and the whole-rock compositions of volcanic

rocks dredged from the western and eastern RGR. The lack of knowledge regarding this alkaline magmatism is one of the main obstacles to the understanding of the evolution of the RGR, as highlighted by [O'Connor and Duncan \(1990\)](#).

This study aimed to investigate the petrology of alkaline volcanic rocks dredged from the Western Rio Grande Rise (WRGR) through their detailed characterization, aiming to contribute to a better understanding of their magmatic evolution, integrating petrography, mineral chemistry, whole rock geochemistry, Sr, Nd and Pb isotopes and U-Pb dating.

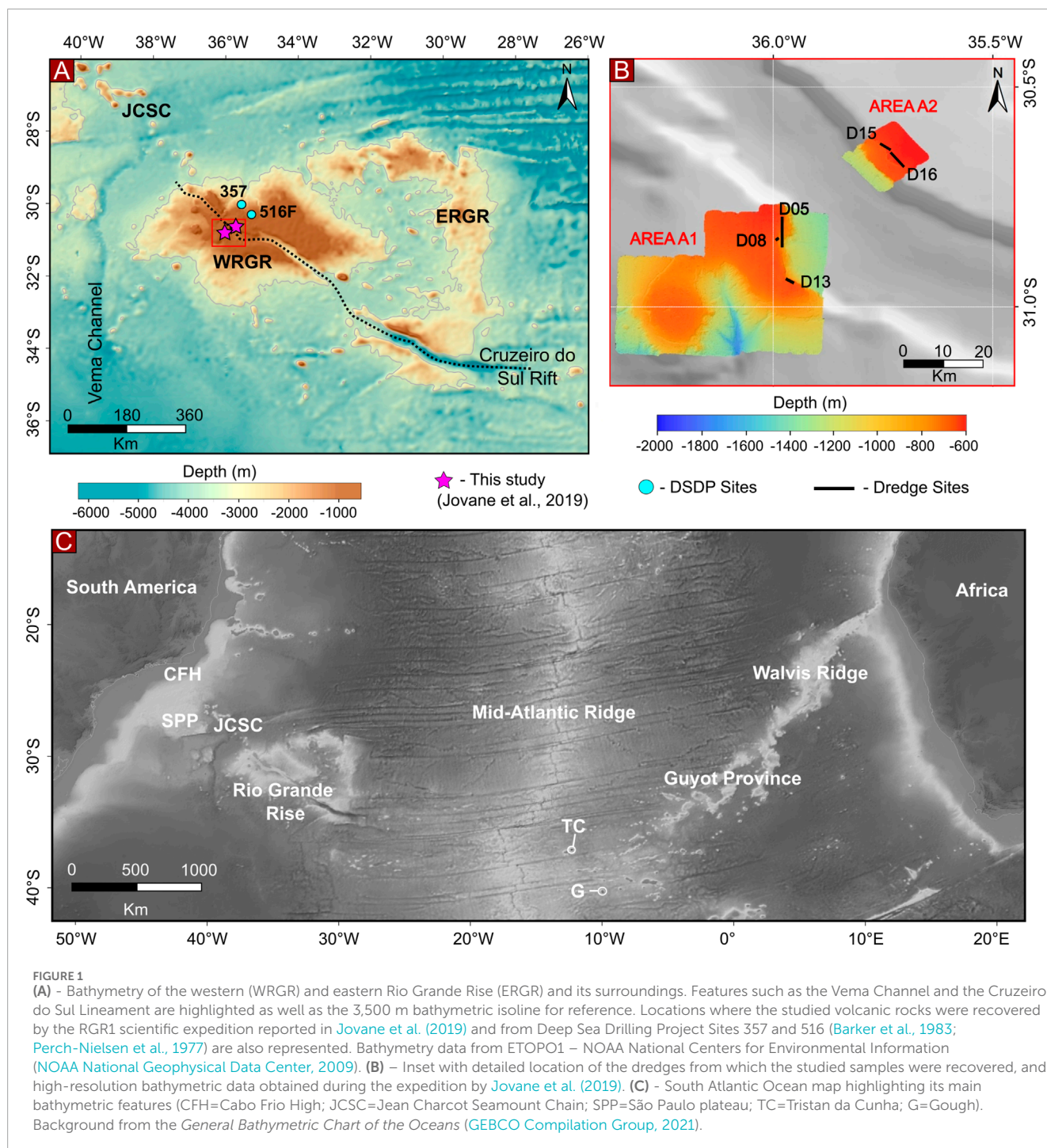
## 2 Eocene alkaline volcanism from the western Rio Grande Rise

Evidence of the younger RGR alkaline volcanism was first reported as a 4 m interval of volcanic breccia between middle-Eocene calcareous sediments recovered at DSDP Site 357 ([Fodor and Thiede, 1977](#)). Following this, [Fodor et al. \(1977\)](#) investigated a few samples dredged from the WRGR, showing that magmatic differentiation occurred from alkali-basalt to at least trachyandesite. The authors reported the presence of disequilibrium, resorption, and reaction textures such as embayments in clinopyroxene and olivine macrocrysts and nodules found in an alkali basalt. These were interpreted as indicative of incipient equilibration of the macrocrysts with the host basaltic magma at lower pressure conditions ([Fodor et al., 1977](#)). The authors suggested that the clinopyroxene and feldspar megacrysts with contrasting composition relative to their host liquids are early formed phenocrysts crystallized at depth.

Recently, [Hoyer et al. \(2022a\)](#) analyzed a larger set of samples, confirming that the alkaline volcanic rocks from the WRGR and Jean Charcot Seamount Chain (JCSC) have OIB signatures and are chemically similar to those from Tristan da Cunha and Gough Islands. They are also more variable in composition (alkali basalts, foidites, trachyandesites and tephriphonolites), enriched in light rare-earth elements (REE) and high field strength elements (HFSE), and depleted in heavy REE compared to ERGR, DSDP Site 516F and Walvis Ridge lavas.

The limited geochronology data available for the RGR is one of the main obstacles in the debate over the origin of its alkaline magmatism. While preliminary geochronological data from [Davidson et al. \(2021\)](#) suggests that the plateau could have been formed over a prolonged period of time with significant contribution from off-axis volcanism in the northeastern RGR, geochemical data is not yet available for the samples dated, limiting the interpretation in terms of the duration and volume of tholeiitic *versus* alkaline intraplate magmatism in the plateau. Until now, alkaline rocks have been sampled only in the WRGR and only two ages were reported for them. [Bryan and Duncan \(1983\)](#) dated a euhedral detrital biotite using the K-Ar method and obtained an age of  $46.3 \pm 0.7$  Ma, and [Rohde et al. \(2013b\)](#) dated a biotite crystal from a dredged phonotephrite by step-heating  $^{40}\text{Ar}/^{39}\text{Ar}$  and reported an age of  $46.0 \pm 0.1$  Ma. [Rohde et al. \(2013b\)](#) suggested that the alkalic composition of the RGR seamounts and guyots might be related to a late-stage volcanic event, as commonly observed in other hotspot systems. However, tholeiitic and alkaline volcanism in the WRGR seem to be separated by a period of tens of Ma, longer than what would be expected between shield stage and late-stage volcanism ([Hoyer et al.,](#)





2022a). Considering this, [Hoyer et al. \(2022a\)](#) proposed that the WRGR alkaline volcanism could be related to lithospheric rifting along the Cruzeiro do Sul lineament instead.

### 3 The significance of Enriched Mantle I signatures from the Rio Grande Rise and South Atlantic lavas

The debate on the origin of the EMI component in the South Atlantic Ocean is extensive and involves multiple proposed

models. Many authors argue exclusively in favor of a deep origin, attributing EMI signatures to mantle plumes, often suggesting remobilization of deep-recycled continental material by these plumes (e.g., [Class and le Roex, 2011](#); [Homrighausen et al., 2023](#); [Rohde et al., 2013a](#); [Schwindrofska et al., 2016](#)). On the other hand, a few studies advocate for a shallow and more recent origin, which would be related to thermal erosion or delamination of the subcontinental lithospheric mantle and/or lower continental crust and incorporation of enriched material into the underlying asthenosphere during rifting and breakup of Gondwana (e.g., [Hawkesworth et al., 1986](#); [Richardson et al.,](#)

1982; Ussami et al., 2013). There are also authors who consider a contribution from both the Tristan-Gough plume and possibly metasomatized shallow material incorporated by the mantle during the continental break-up (e.g., Gibson et al., 2005; Peate et al., 1999). Willbold and Stracke (2006), Willbold and Stracke (2010) and Stracke (2012) attribute mantle compositional heterogeneities to recycling of different proportions of lower and upper continental crust and oceanic lithosphere, proposing that sampling and mixing of a specific reservoir correspondent to an enriched mantle component is not needed to explain such enriched signatures.

In the case of the Rio Grande Rise and Walvis Ridge, most of the recent studies point towards a relationship between Enriched Mantle I signatures and the Tristan-Gough plume, which was probably close to the spreading center where they originated together (e.g., Gibson et al., 2005; Hoyer et al., 2022a; Homrighausen et al., 2023; O'Connor and Duncan, 1990; Rohde et al., 2013a; Rohde et al., 2013b). This plume model is strongly supported by numerous investigations of isotope signatures from the Walvis Ridge, Guyot Province, Tristan da Cunha and Gough islands which evidence the age-progression along the plume track, the persistence of the plume chemical zonation with time, and the spatial relationship with the African Large Low Shear Velocity Province, (e.g., Class and le Roex, 2011; Hoernle et al., 2015; Homrighausen et al., 2019; O'Connor and Duncan, 1990; O'Connor et al., 2012; 2018; O'Connor and Jokat, 2015; Rohde et al., 2013a). This is manifested in the regular and parallel trails formed by the spatial distribution of Tristan-type and Gough-type isotope signatures in the Guyot Province on the African plate.

The discussion about the complex interplay of tectonics and magmatism during the evolution of the RGR and the nature of its mantle sources continues as further data become available. While the Enriched Mantle I (EMI) isotope signatures from the RGR tholeiitic basalts drilled at DSDP Site 516F have been discussed for decades (Hart, 1984; Zindler and Hart, 1986; Gibson et al., 2005; Class and le Roex, 2006; Class and le Roex, 2011; Hoernle et al., 2015), it was only recently that similar EMI signatures were reported for alkaline lavas from the WRGR (Hoernle et al., 2015; Homrighausen et al., 2023). More specifically, Homrighausen et al. (2023) show that both alkaline and tholeiitic rocks from the WRGR and ERGR have Tristan-type isotope signatures. However, Sr, Nd, Pb and Hf isotope ratios of RGR volcanic rocks trend towards more extreme EMI signatures compared to Tristan-type compositions from the Walvis Ridge and Guyot Province lavas, forming a continuous Tristan-type array in the uranogenic diagram (Homrighausen et al., 2023). To explain the spatial and temporal distribution of Tristan and Gough-type signatures in the South Atlantic, Homrighausen et al. (2023) proposed a plumelet model. However, Class et al. (2023) show that Gough-type lavas are also found in the ERGR, and that the spatial distribution of EMI-flavored signatures in the RGR seems to be much more complex than in the African plate, possibly because it was influenced by its complex tectonic evolution (Sager et al., 2021; Davidson et al., 2021; Class et al., 2023).

## 4 Materials and methods

The 17 studied samples were dredged from the WRGR along the flanks of the Cruzeiro do Sul Rift in water depths between 641 and 730 m (Figure 1) by the scientific cruise RGR1 reported in Jovane et al. (2019). They comprise alkali basalts, trachybasalts, trachyandesites, trachytes, a basanite, and a volcanic breccia. The adopted sample nomenclature is RGR1-DXX-YYY, where RGR1 refers to the expedition name, DXX is the dredge number and YYY the sample number. Petrographic descriptions of all rocks were made, and a subset of samples were submitted to additional analyses, including whole-rock geochemistry (XRF and ICP-MS) and Sr, Nd and Pb isotope analysis. Samples were selected for whole-rock geochemistry and isotope analysis based on their representativeness and relatively lower alteration grade. The focus of this work was mineral chemistry (EPMA and LA-ICP-MS analyses) because these rocks are mostly porphyritic, with up to 30% of macrocrysts, and the abundant, well-preserved clinopyroxene macrocrysts have textural and compositional features which offer important insights into the magmatic processes involved in their petrogenesis. A single trachyte was subject of U-Pb zircon dating by Sensitive High-Resolution Ion MicroProbe (SHRIMP). Three trachyte samples were analyzed by X-Ray powder diffraction to confirm the presence of sanidine (Supplementary File SA, Supplementary Figures S1–3). Details of preparation and analytical procedures are presented in Supplementary File SB. All data obtained from analysis of samples and standards is available in the Supplementary Files.

## 5 Results

### 5.1 Petrography

Trachytes have fine-grained groundmasses made of alkali feldspar laths and sparse diopside, Ti-magnetite, apatite  $\pm$  interstitial analcime, and up to  $\sim$ 25% macrocrysts of alkali feldspar, diopside  $\pm$  Ti-magnetite, titanite, biotite and very rare kaersutite and ilmenite. Euhedral to subhedral alkali feldspar are the most abundant and the largest macrocrystals (0.5–5 mm; Figure 2). Trachytic texture and agglomerates made of Ti-magnetite, diopside and apatite, or multiple feldspar laths are common. Samples recovered by dredge D16 have abundant round amygdales (0.2–4 mm) filled with calcite and/or analcime and rare apatite microphenocrysts (0.12–0.44 mm).

Dredge D05 trachyandesites have  $\sim$ 4%–7% macrocrysts of diopside, kaersutite and Ti-magnetite  $\pm$  plagioclase, rare titanite and biotite. Their fine-grained groundmass has alkali feldspar  $\pm$  plagioclase, Ti-magnetite, diopside, apatite, and interstitial analcime. Trachytic texture and sparse agglomerates formed by diopside and Ti-magnetite occur locally. Sample RGR1-D15-001 is strikingly different from others and has rare alkali feldspar, Ti-magnetite, and apatite microphenocrysts (0.05–0.25 mm), round amygdales (0.1–1.3 cm) filled with calcite, and a groundmass with alkali feldspar, apatite, acicular biotite and ilmenite.

Basalts from D05 and D08 are highly phyrlic (25%–30% macrocrysts) with fine-grained groundmass made of plagioclase,



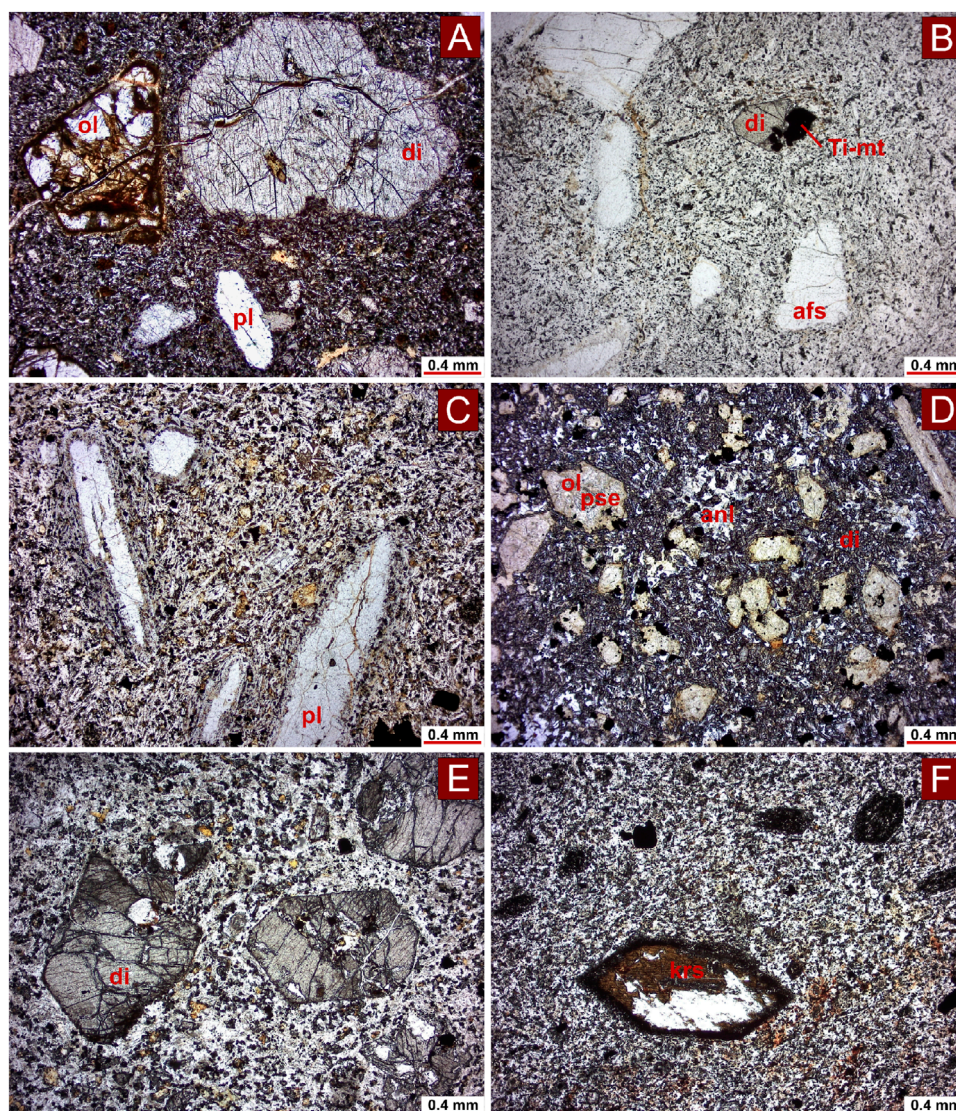


FIGURE 2

Photomicrographs under plane polarized light with examples of textural and mineralogical features observed in the studied samples. **(A)** – Olivine, diopside and plagioclase macrocrysts from picro-basalt RGR1-D08-004, which has a groundmass made of plagioclase, diopside, Ti-mt and interstitial analcime. **(B)** – Trachyte RGR1-D08-002 with alkali feldspar, diopside and Ti-magnetite macrocrysts in a groundmass with alkali feldspar laths, diopside, Ti-magnetite and apatite. **(C)** – Subhedral plagioclase macrocrysts with rounded borders rich in inclusions observed on trachybasalt RGR1-D13-002, which has plagioclase, diopside, opaque minerals and altered interstitial material in its groundmass. **(D)** – Basanite RGR1-D08-001 with abundant olivine pseudomorph macrocrysts altered to bowlingite associated with Ti-magnetite in a groundmass made mostly of prismatic diopside crystals, interstitial analcime (colorless) and rare alkali feldspar. **(E)** – Diopside macrocrysts from alkali basalt RGR1-D05-019, which has a groundmass made of plagioclase laths, diopside, olivine pseudomorphs, possibly interstitial altered glass and apatite. **(F)** – Kaersutite macrocrysts and smaller pseudomorphs rich in opaque minerals from trachyandesite RGR1-D05-009. Abbreviations: afs=alkali feldspar; anl=analcime; di=diopside; krs=kaersutite; ol=olivine; ol pse=olivine pseudomorph; pl=plagioclase; Ti-mt=Ti-magnetite.

diopside, Ti-magnetite, apatite  $\pm$  olivine pseudomorphs and interstitial analcime. The most abundant macrocrysts are of euhedral zoned diopside (0.25–8 mm) sometimes with colorless cores and brownish rims. A few relict olivine macrocrysts (0.5–4 mm) altered to iddingsite and/or bowlingite are observed, as well as smaller (0.13–0.8 mm) plagioclase and Ti-magnetite macrocrysts and microphenocrysts. Rare resorbed biotite macrocrysts are found in sample RGR1-D05-019, which also has sparse amygdaloids (0.4–0.8 mm) filled by zeolite.

The analyzed trachybasalt has plagioclase, diopside, Ti-magnetite, and rare olivine pseudomorph and apatite macrocrysts

in a fine-grained groundmass made of plagioclase, diopside, Ti-magnetite, interstitial analcime, apatite, and sparse altered crystals which resemble olivine pseudomorphs. Most macrocrysts are of subhedral plagioclase (0.3–2.5 mm) with rounded borders rich in inclusions (Figure 2C). Rare glomerocrysts made of plagioclase, Ti-magnetite and diopside are also observed.

The basanite (RGR1-D08-001, Figure 2D) has ~30% euhedral macrocrysts and microphenocrysts of olivine pseudomorphs replaced by bowlingite (0.13–2.5 mm) and zoned diopside (0.5–1 mm) in a fine-grained groundmass made mostly of prismatic

diopside and interstitial analcime, with smaller amounts of Ti-magnetite, rare interstitial feldspar, and apatite.

The autobreccia (RGR1-D15-013) has subrounded to angular clasts (0.025 mm to >2 cm) of porphyritic trachyte and groundmass made of carbonate, iron oxide/hydroxide and clays. Feldspar macrocryst fragments are also found amid the groundmass. Trachyte clasts have variable grain size, with 0.04–0.2 mm alkali feldspar laths and rare Ti-magnetite (0.01–0.05 mm).

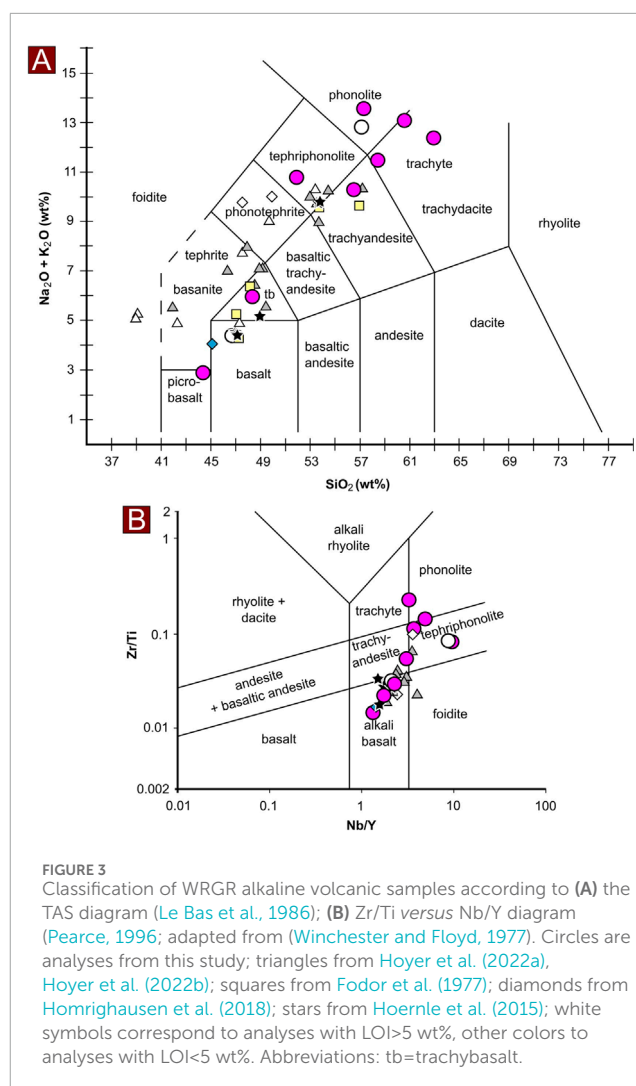
Weathering grade of the samples varies from relatively fresh to heavily altered and no fresh glass was found. However, the primary mineralogy of all studied samples is largely preserved. More detailed descriptions are available in [Supplementary File SC](#).

## 5.2 Whole-rock geochemistry

Despite careful sample selection and preparation for analysis, the obtained LOI values are significant (1.02–9.88 wt%). Sea-water alteration may modify the contents of some major elements such as Si, Mg, Ca and K, as well as large-ion lithophile elements like Rb, Cs, Ba and Sr, which are fluid-mobile (e.g., [Hart et al., 1974](#); [Verma, 1981](#); [Verma, 1992](#)). Therefore, this section is more focused on trace-elements which are not as mobile, while major oxide and additional trace element results are presented in [Supplementary File SD](#).

Detailed petrography and mineral chemistry analyses reveal a few differences between the chemical and QAPF modal classification of the studied samples. While the most evolved rocks are classified as phonolites according to diagrams such as the TAS ([Le Bas et al., 1986](#); [Figure 3A](#)) and Zr/Ti versus Nb/Y ([Pearce, 1996](#); [Figure 3B](#)), they would be classified as trachytes according to the QAPF modal classification of volcanic rocks recommended by the International Union of Geological Sciences (IUGS; [Le Maitre et al., 2002](#)), as they are essentially made of alkali feldspar, have less than 10% analcime and no other feldspathoids. A sample chemically classified as a tephriphonolite also has less than 10% feldspathoids and would be considered a trachyandesite according to the mineralogical classification. In the case of the TAS diagram, this is probably due to the higher K<sub>2</sub>O contents (8.57–10.34 wt%) of these samples, which were all recovered from dredges D15 and D16 (Area A2, [Figure 1B](#)). Also, sample RGR1-D05-001 is chemically classified as a basalt, but only alkali feldspar was found in its heavily altered groundmass and its mineralogy, with clinopyroxene and kaersutite macrocrysts, is suggestive of a composition closer to that of the studied trachyandesites than to the basalts.

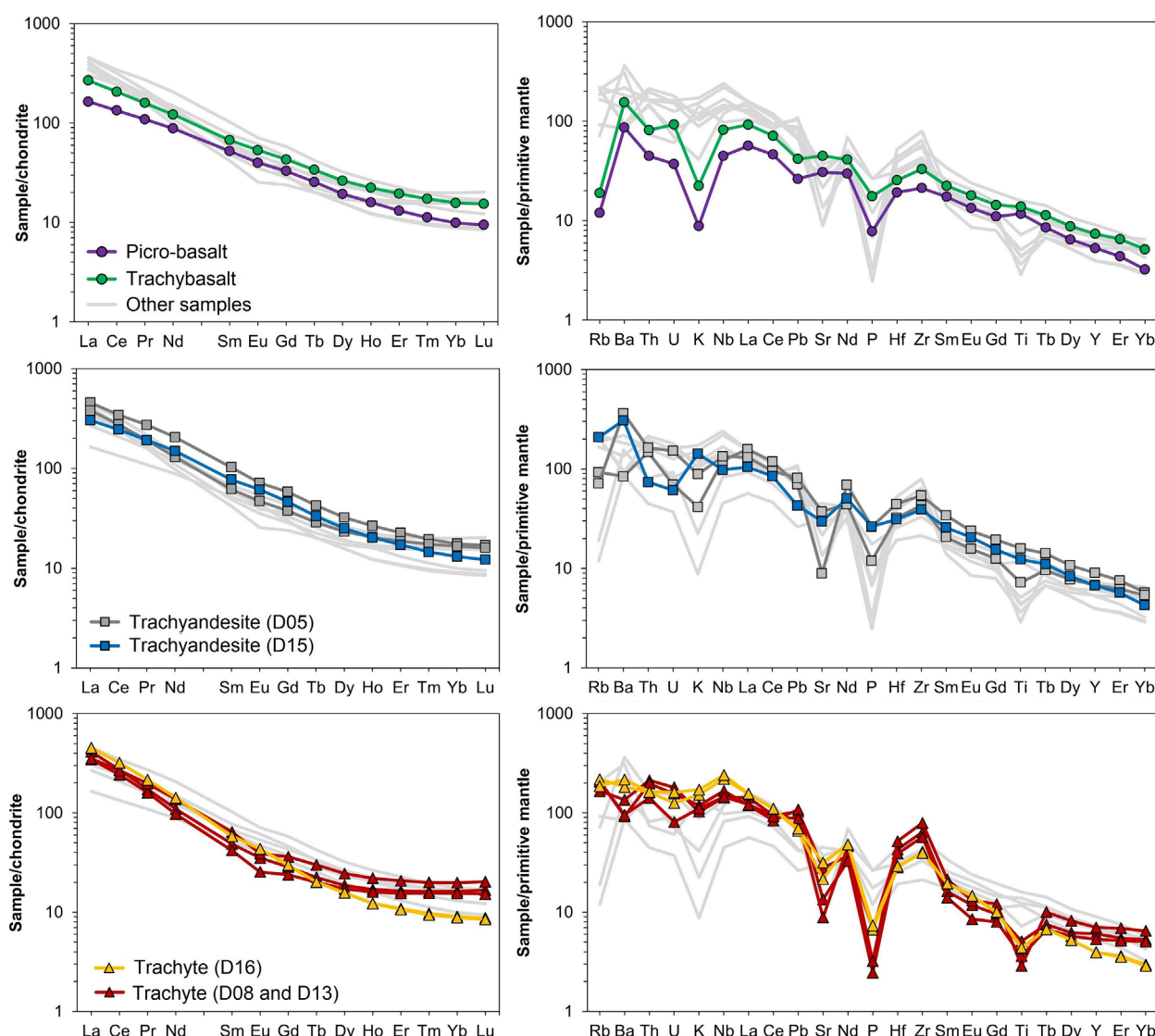
The distribution of alkaline volcanic samples from the WRGR ([Fodor et al., 1977](#); [Hoernle et al., 2015](#); [Homrighausen et al., 2018](#); [Hoyer et al., 2022a](#); this study) on the TAS diagram suggests the possible existence of two magmatic series ([Figure 3A](#)). One of them would evolve from picro-basalt to at least trachyte, and the other would be more undersaturated, evolving from basanite to phonolite. However, on the diagram by [Pearce \(1996\)](#), many samples classified as basanites, tephrites and phonotephrites in the TAS diagram are classified as alkali basalts and trachyandesites instead. Therefore, it is possible that at least part of the scatter towards more undersaturated fields in the TAS diagram is due to alteration and enrichment in Na and K.



On the chondrite-normalized rare-earth elements (REE) diagram ([Figure 4](#)), four main types of patterns, all concave-upwards, are observed. The first one corresponds to the picro-basalt and trachybasalt, which have relatively low (La/Sm)<sub>N</sub> (3.2–4.0) and (La/Yb)<sub>N</sub> (~17.0) compared to other samples. The second one corresponds to the trachyandesites, which are slightly more enriched in light REE, with (La/Sm)<sub>N</sub> = 4.0–6.1, (Tb/Yb)<sub>N</sub> = 1.7–2.5 and (La/Yb)<sub>N</sub> = 23–26. The third one corresponds to trachytes from dredges D08 and D13, which have the highest (La/Sm)<sub>N</sub> (5.5–8.5), lowest (Tb/Yb)<sub>N</sub> (1.3–1.5), and the most significant Eu anomalies (Eu/Eu\* = 0.80–0.94). The last one refers to the trachytes from dredge D16, which have the greatest (La/Yb)<sub>N</sub> (49 and 51). All patterns observed are smooth, and none of the samples show negative Ce anomalies, suggesting that REE contents of the magmas and their sources were not affected by seawater alteration (e.g., [Cotten et al., 1995](#); [Price et al., 1991](#)).

On the spidergrams ([Figure 4](#)), some differences between the rock groups can be observed. Trachytes generally have stronger Sr and Ti negative anomalies. The trachyandesite patterns are similar to that of the trachytes, but with lower normalized values for the more incompatible elements (with the exception of Ba in two samples),





**FIGURE 4**  
Chondrite (McDonough and Sun, 1995) normalized REE patterns and spidergrams with primitive mantle (Sun and McDonough, 1989) normalized trace element contents from the analyzed WRGR alkaline volcanic samples. "Other samples" correspond to the remaining samples from this study and are plotted as grey lines to facilitate comparison.

and less intense Sr, P and Ti negative anomalies, although one of them has a stronger Sr anomaly. The most mafic samples are poorer in incompatible elements and have positive Ti anomalies and negative K anomalies.

The results obtained are consistent with the incompatible element patterns, contents, and ratios (e.g., Nb/Zr, Nb/Th, Hf/Th, Nb/La) reported by Hoyer et al. (2022a); Hoyer et al. (2022b); Supplementary Files SD, A, Supplementary Figure S4.

## 5.3 Mineral chemistry

### 5.3.1 Clinopyroxene

Figure 5 shows the compositional variability of the analyzed clinopyroxene crystals, which are mostly chemically

classified as diopside using the Morimoto et al. (1988) diagram ( $Wo=43.3\text{--}57.1$ ;  $En=32.6\text{--}50.9$ ;  $Fs=2.32\text{--}18.7$ ; Supplementary File SA, Supplementary Figure S5). An initial trend of increasing Al and Ti with decreasing Mg# is observed, followed by an inflection towards lower Al and Ti. Compositions also tend to become more enriched in  $Na_2O$  and MnO and poorer in  $Cr_2O_3$  with decreasing Mg#.

Clinopyroxene from the mafic rocks have the highest Mg# and  $Cr_2O_3$  and the most variable compositions in terms of  $Al_2O_3$ ,  $TiO_2$ ,  $SiO_2$  and  $Cr_2O_3$ . Crystals from the trachytes are the most enriched in MnO and  $Na_2O$  and have lower Mg#, as well as lower  $Cr_2O_3$ ,  $Al_2O_3$  and  $TiO_2$  for a given Mg#. The composition of the clinopyroxene from the trachyandesites and trachybasalts is intermediate between that of crystals from the trachytes and mafic rocks.

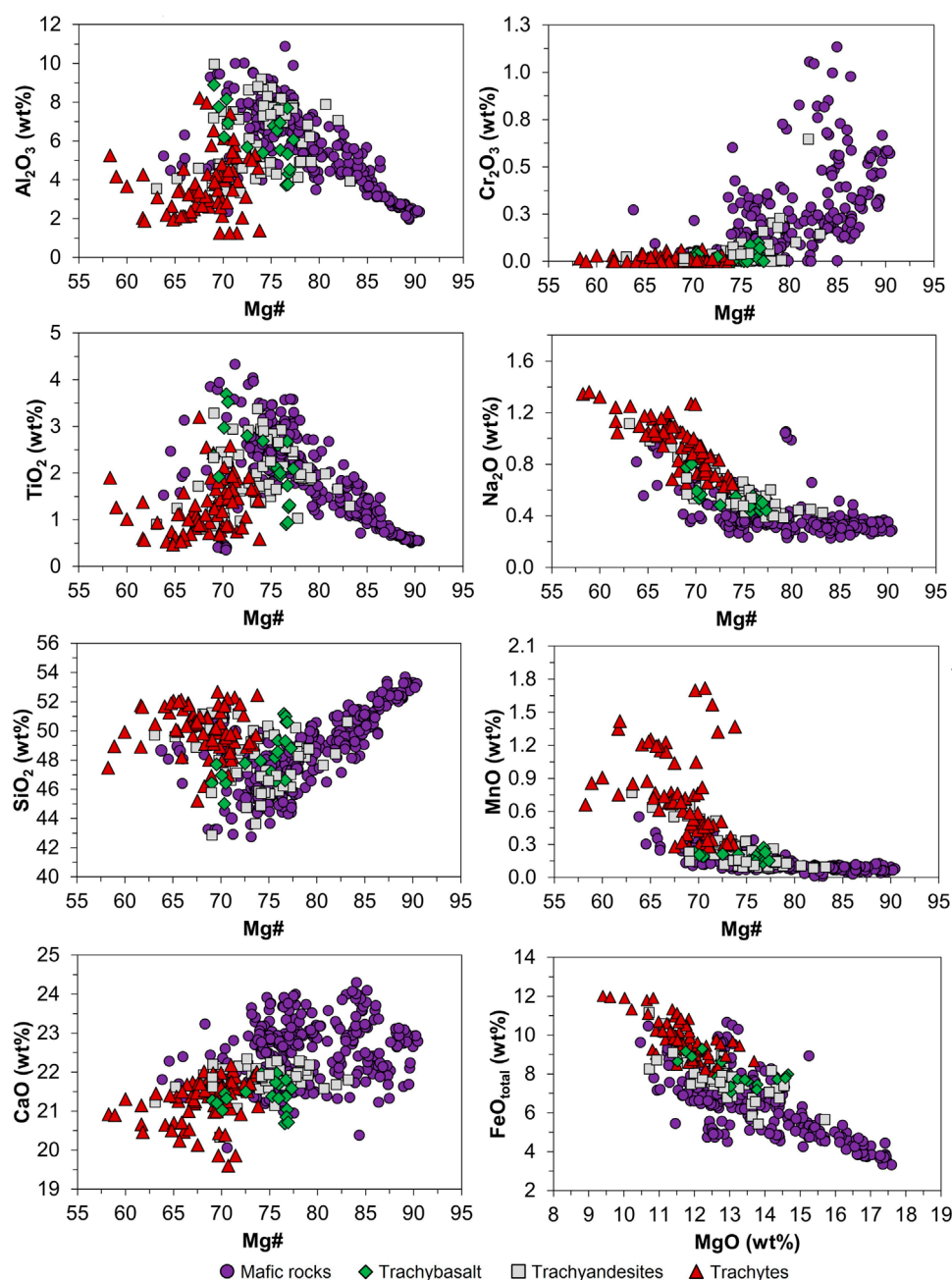


FIGURE 5

Variation diagrams showing results from clinopyroxene analyses by EPMA, highlighting differences between clinopyroxene from the most mafic rocks (alkali-basalt, picro-basalt and basanite), trachybasalt, trachyandesites and trachytes dredged from the western Rio Grande Rise. Mg# was calculated using  $\text{FeO}_{\text{total}}$ .

The strongest and most abrupt normal or oscillatory zoning patterns are observed in clinopyroxene from the basalts and basanite. Crystals with distinct textural and compositional characteristics occur in a single sample (Figure 6). Mafic samples also have sparse crystals with reverse zoning, and rare macrocrysts compositionally similar to the rims of zoned crystals, without any zoning. Additionally, infiltration textures in clinopyroxene like those observed in Figure 6D and in the central part of the primitive core in Figure 6A are more frequently observed in the

mafic rocks, and rarely found in crystals from the trachyandesites and trachytes.

Overall, the composition of groundmass crystals is similar to that of the rims of macrocrysts and microphenocrysts, but there are exceptions, like in the case of trachyte RGR1-D13-004, which has groundmass clinopyroxene with higher Ti/Al ratios (0.26–0.44), higher Mg# (70–74), and lower  $\text{Na}_2\text{O}$  (0.65–0.89 wt%) than its macrocrysts (Mg#=62–70,  $\text{Na}_2\text{O}$ =0.94–1.13 wt%, Ti/Al=0.15–0.20).



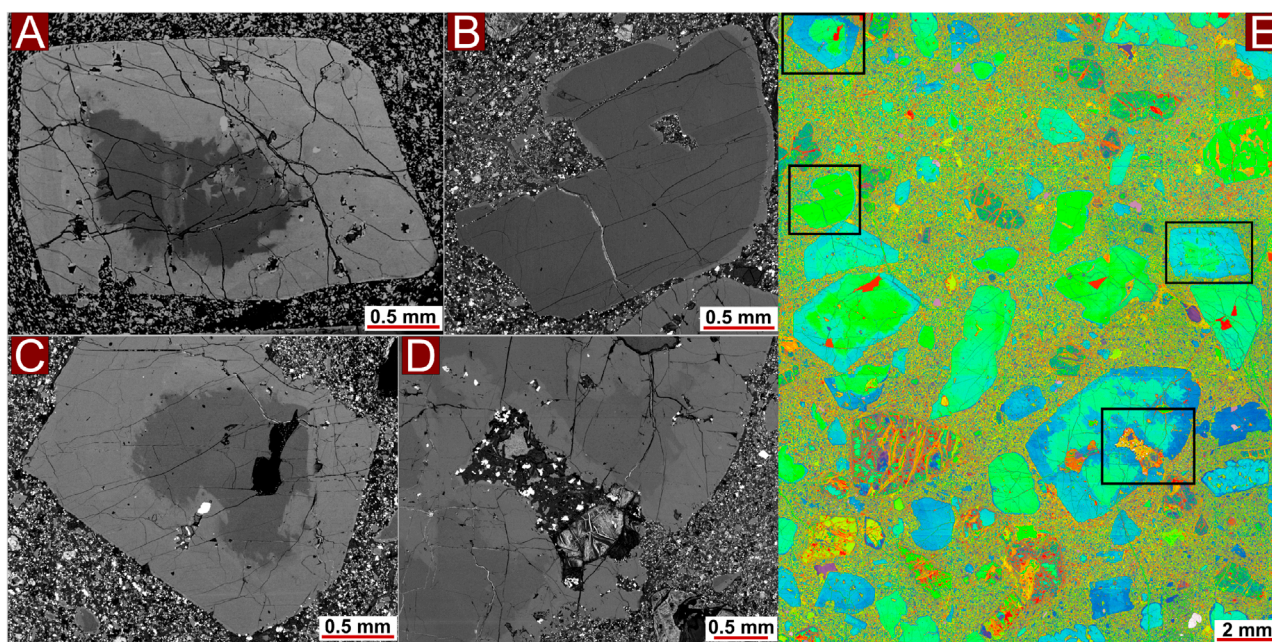


FIGURE 6

SEM backscatter images showing examples of common textures observed on diopside macrocrysts from picro-basalt RGR1-D08-004. (A) – Macrocryst with a euhedral rim and an irregular-shaped more primitive core with disequilibrium texture. The core is also affected by infiltrations with more evolved composition on its central part. (B) – Subhedral macrocryst with a resorbed relict primitive core rimmed by a thin layer of relatively more evolved clinopyroxene. (C) – Another euhedral macrocryst with a more primitive core with disequilibrium texture and a more evolved rim. (D) – Infiltrations (lighter portions) on a more primitive macrocryst along a fracture. (E) – false colored SEM backscatter image highlighting differences in grey level between diopside macrocrysts. The most evolved clinopyroxene compositions are observed in tones of blue while the most primitive are in tones of green.

Figures 7, 8 show compositional maps of a few clinopyroxene crystals. While primitive compositions with higher MgO and Cr<sub>2</sub>O<sub>3</sub> and lower Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> are usually observed in cores, two analyzed crystals from the basanite have more evolved cores, an intermediate zone with primitive composition, and an outer rim with evolved composition (Figures 7, 8C,D). A macrocryst from the alkali-basalt (RGR1-D05-019; Figures 7, 8F) also has an internal zone with higher MgO and Cr<sub>2</sub>O<sub>3</sub>. Cr<sub>2</sub>O<sub>3</sub> compositional maps highlight complex patterns in the primitive cores (Figures 7B,G,H) which are not obvious in MgO maps, as the diffusion rates of divalent cations is faster than that of trivalent cations (Van Orman et al., 2001; Morgan et al., 2004). The sector and oscillatory zoning patterns observed on more evolved crystals are highlighted by Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> maps (Figure 8), as well as the effect of infiltrations (e.g., Figures 8A,B). Moreover, TiO<sub>2</sub> highlights the unique composition of one of the clinopyroxene cores from the basanite (Figures 7, 8D), referred to as evolved core #1 in other diagrams, which has the lowest TiO<sub>2</sub> content (0.35–0.46 wt%) and Ti/Al ratio (0.06–0.08) of our whole dataset and is compositionally similar to with crystals from the trachytes and trachyandesites. The other evolved core found in the basanite is referred to as #2 and differs from core #1 for its higher Mg# and TiO<sub>2</sub> and lower MnO and has the highest Na<sub>2</sub>O contents of our dataset (1.0–1.1 wt%).

The contrasting composition of clinopyroxene cores and rims in the mafic rocks is evident in Figure 9. Infiltrated portions in cores are marked by an increase in Ti, Al and Na and a decrease in Mg# and Cr, and have intermediate compositions, forming a continuous compositional trend between primitive cores and

more evolved rims. Analyses made on macrocrysts with reverse zoning are also plotted, and their more primitive and more evolved compositions are generally similar to those of macrocrysts with normal zoning. Furthermore, there is a partial overlap between the most primitive clinopyroxene cores found in the picro-basalt and fields defined by clinopyroxene from mantle xenoliths compiled from literature (Figure 9).

The compositional range of the clinopyroxene from the mafic rocks is indicative of substitutions of diopside for the Ca-tschermak endmembers and for hedenbergite (Supplementary File SA; Supplementary Figure S6). A positive correlation between Ti+Al<sup>VI</sup> and Al<sup>IV</sup> evidences the progressive increase of the CaAl-tschermak and CaTi-tschermak components. Moreover, crystals from the basanite have variable Fe<sup>3+</sup>/Fe<sup>2+</sup> and achieve relatively higher values than those from other samples (Supplementary File SE).

Trace-element analyses by LA-ICP-MS were focused on the compositional difference between clinopyroxenes from the mafic rocks, trachyandesites and trachytes, since analysis of most of the rims from macrocrysts was not possible because of their relatively small size. Results were compared to Mg# calculated from MgO and FeO contents obtained by EPMA analysis. Therefore, these comparisons are not exact since the LA spot analyses correspond to sampling of a much larger mass than EPMA spot analyses. Despite this, the data shows an overall progressive increase in incompatible elements and decrease in compatible elements with decreasing Mg# (Figures 10, 11; Supplementary File SE).

Four main patterns are observed on the spidergram and normalized REE diagram for clinopyroxene (Figure 11). The most



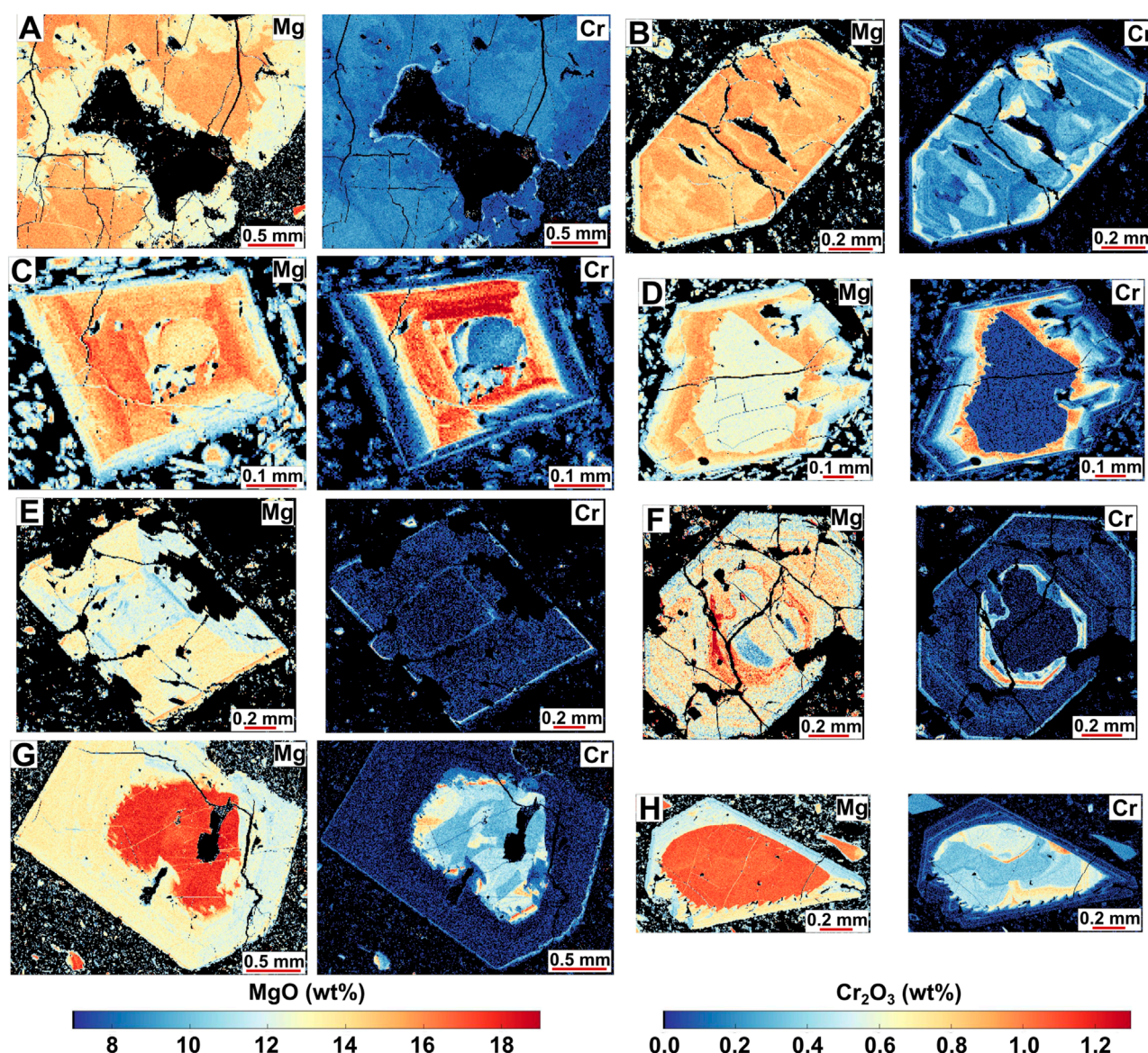


FIGURE 7

Compositional maps showing MgO (wt%) and Cr<sub>2</sub>O<sub>3</sub> (wt%) variations on diopside macrocrysts and groundmass crystals. (A) – Infiltrations along fracture on a macrocryst from picro-basalt RGR1-D08-004; (B) – Euhedral macrocryst with concentric primitive core and more evolved rim; (C, D) – Microphenocrysts from basanite RGR1-D08-001 showing more evolved cores with lower MgO and Cr<sub>2</sub>O<sub>3</sub> surrounded by intermediate primitive Cr<sub>2</sub>O<sub>3</sub> and MgO rich zones and more evolved outer rims; (E) – Sector and oscillatory zoning observed in a diopside from sample RGR1-D05-019; (F) – Macrocryst with oscillatory zoning and a more primitive intermediary layer; (G) – Diopside with disequilibrium textures in its primitive core with irregular borders and evolved rim with oscillatory zoning; (H) – Another example of macrocryst with a primitive core and a more evolved rim with oscillatory zoning.

depleted in incompatible elements is that of the most primitive analyzed cores from the picro-basalt (Mg# = 82–90). The patterns of clinopyroxene from the basanite and trachyandesite overlap with the remaining analyses of crystals from the picro-basalt, including a few made on larger, relatively evolved rims with oscillatory zoning. This overlap might be in part an analytical effect because only cores from the trachyandesite macrocrysts were analyzed, and it is possible that parts of rims have been sampled unintentionally together with cores from the basanite microphenocrysts due to their small size. Clinopyroxene from trachytes is the most enriched in incompatible elements and the patterns obtained have Eu and

Ti negative anomalies, as well as a more pronounced negative Sr anomaly than that observed in crystals from trachyandesites and mafic rocks.

### 5.3.2 Feldspar

Plagioclase is found on the mafic rocks except for the basanite, which only has rare interstitial anorthoclase on its groundmass (Supplementary File SF). Generally, plagioclase macrocrysts have weak normal zoning and groundmass laths have similar compositions to those of the rims. Strong abrupt zoning patterns are found only on macrocrysts from the picro-basalt (Figure 12),



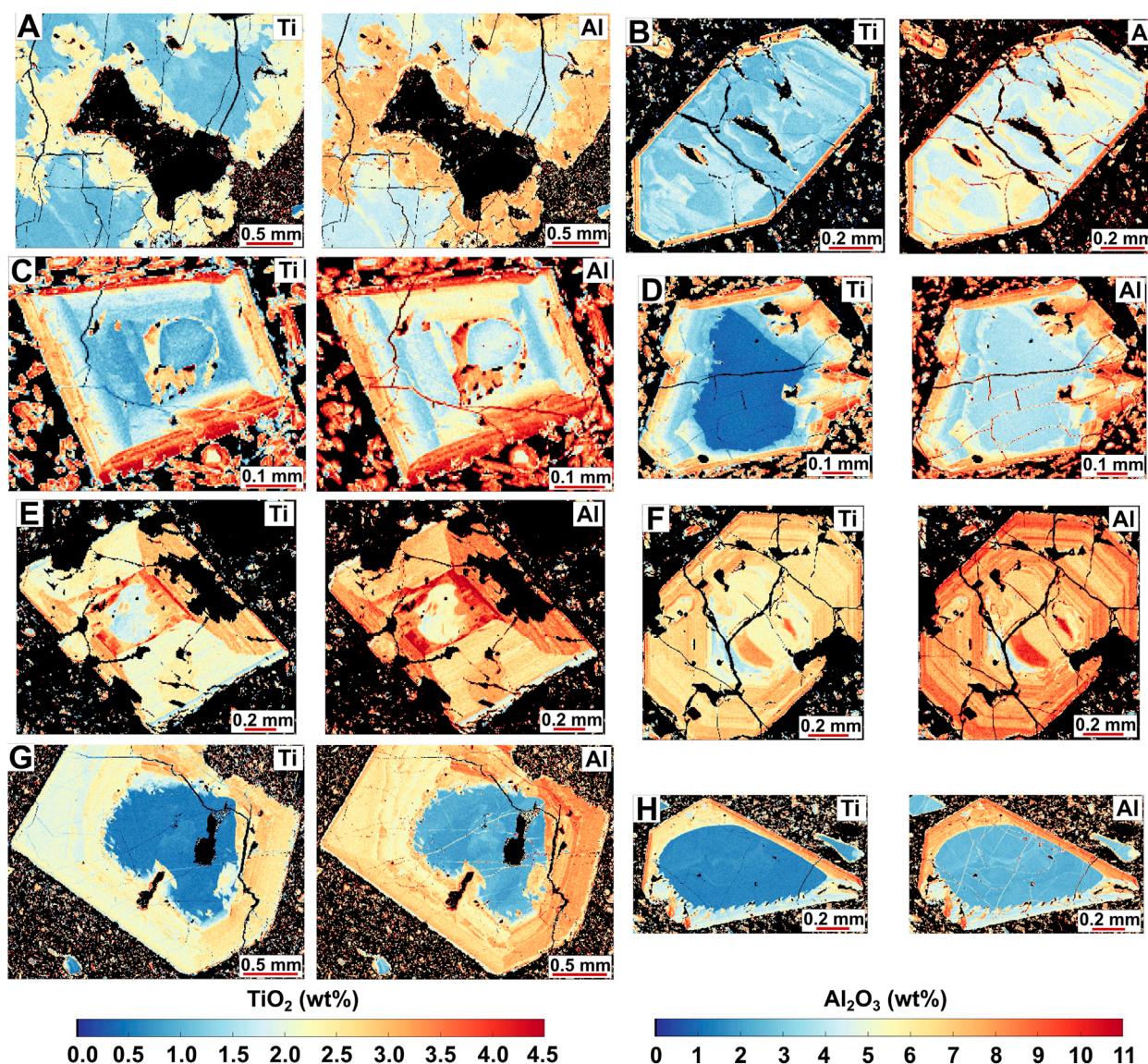


FIGURE 8

Compositional maps showing  $\text{TiO}_2$  (wt%) and  $\text{Al}_2\text{O}_3$  (wt%) variations in diopside macrocrysts and groundmass crystals. (A) – Infiltrations along fracture on a macrocryst from picro-basalt RGR1-D08-004; (B) – Euhedral macrocryst with concentric primitive core and more evolved rim with higher  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ ; (C, D) – Microphenocrysts from basanite RGR1-D08-001 with higher  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  contents in their outer rims relative to their inner areas, note lower  $\text{TiO}_2$  core in D; (E) – Sector and oscillatory zoning observed in a diopside from sample RGR1-D05-019; (F) – Macrocryst with oscillatory zoning and a more primitive intermediary layer with lower  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$ ; (G) – Diopside with disequilibrium textures in its primitive core with lower  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  and evolved rim with oscillatory zoning; (H) – Another example of macrocryst with a primitive core and a more evolved rim with oscillatory zoning.

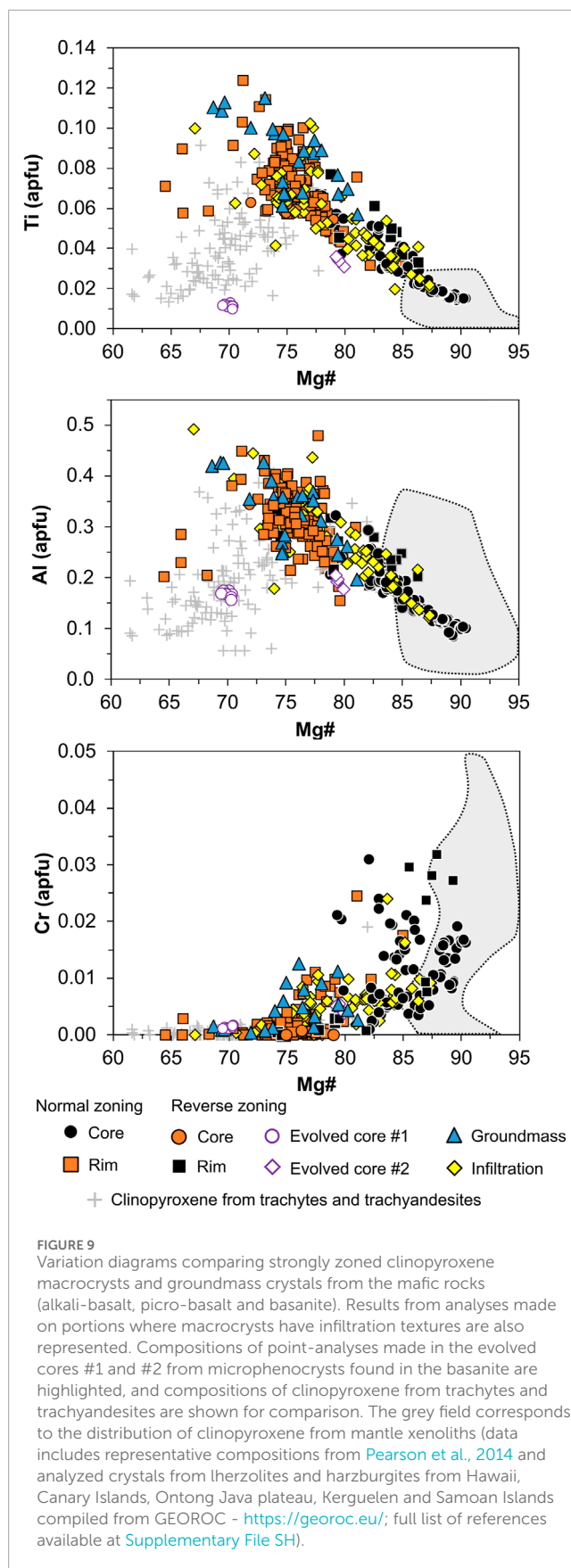
which have bytownite cores and labradorite rims. These cores and bytownite inclusions in diopside macrocrysts from the same sample correspond to the highest An values (73–87) observed among the studied rocks. One of the trachyandesites has only plagioclase (RGR1-D05-002), while the others have alkali feldspar.

Anorthoclase and sanidine occur in the trachytes and macrocrysts may have weak compositional variations, usually with an increase in Or towards their borders. Crystals with well-defined core/rim boundaries are sparse and a single trachyte (RGR1-D08-003) has rare macrocrysts with resorbed plagioclase cores and sanidine rims. In this sample, groundmass feldspar

has higher Or than macrocrysts, while in the others there is no significant compositional difference between groundmass feldspar and macrocrysts. A few crystals with irregular-shaped resorbed anorthoclase cores and sanidine rims are locally observed (Figure 12). Very rare, irregular-shaped infiltrated areas on feldspars are enriched in SrO (0.33–0.46 wt%) and BaO (1.1–1.6 wt%; Figure 12D).

Samples recovered by dredges D15 and D16 were not the focus of EPMA analyses because they are more altered but were investigated by SEM semi-quantitative EDS analyses because of their high  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratios. Their feldspars have considerably higher





K<sub>2</sub>O (up to 17 wt%) and BaO (up to 3.8 wt%) than those observed on samples from other dredges, which have K<sub>2</sub>O up to 10.0 wt% and BaO < 1.6 wt% ([Supplementary File SF](#)).

### 5.3.3 Other minerals

Other minerals were analyzed and detailed results are available at [Supplementary File SF](#). Olivine macrocryst relicts from the picro-basalt have Fo=80.0–86.5 and NiO=0.12–0.19 wt%. Analcime and kaersutite have relatively homogenous compositions independent of the sample. Rare biotite macrocrysts are enriched in TiO<sub>2</sub> (5.6–9.3 wt%), with variable SiO<sub>2</sub>, FeO<sub>T</sub>, K<sub>2</sub>O, BaO and F contents depending on the sample. Kaersutite and biotite macrocrysts are mostly resorbed and frequently associated with multiple fine-grained magnetite crystals. Only relatively coarser-grained apatite was analyzed, such as rare macrocrysts from the trachybasalt and crystals associated with clinopyroxene or biotite macrocrysts in trachytes, as well as acicular groundmass crystals from the basanite. It has variable La<sub>2</sub>O<sub>3</sub>, Ce<sub>2</sub>O<sub>3</sub>, SrO and MnO depending on the sample ([Supplementary File SF](#)).

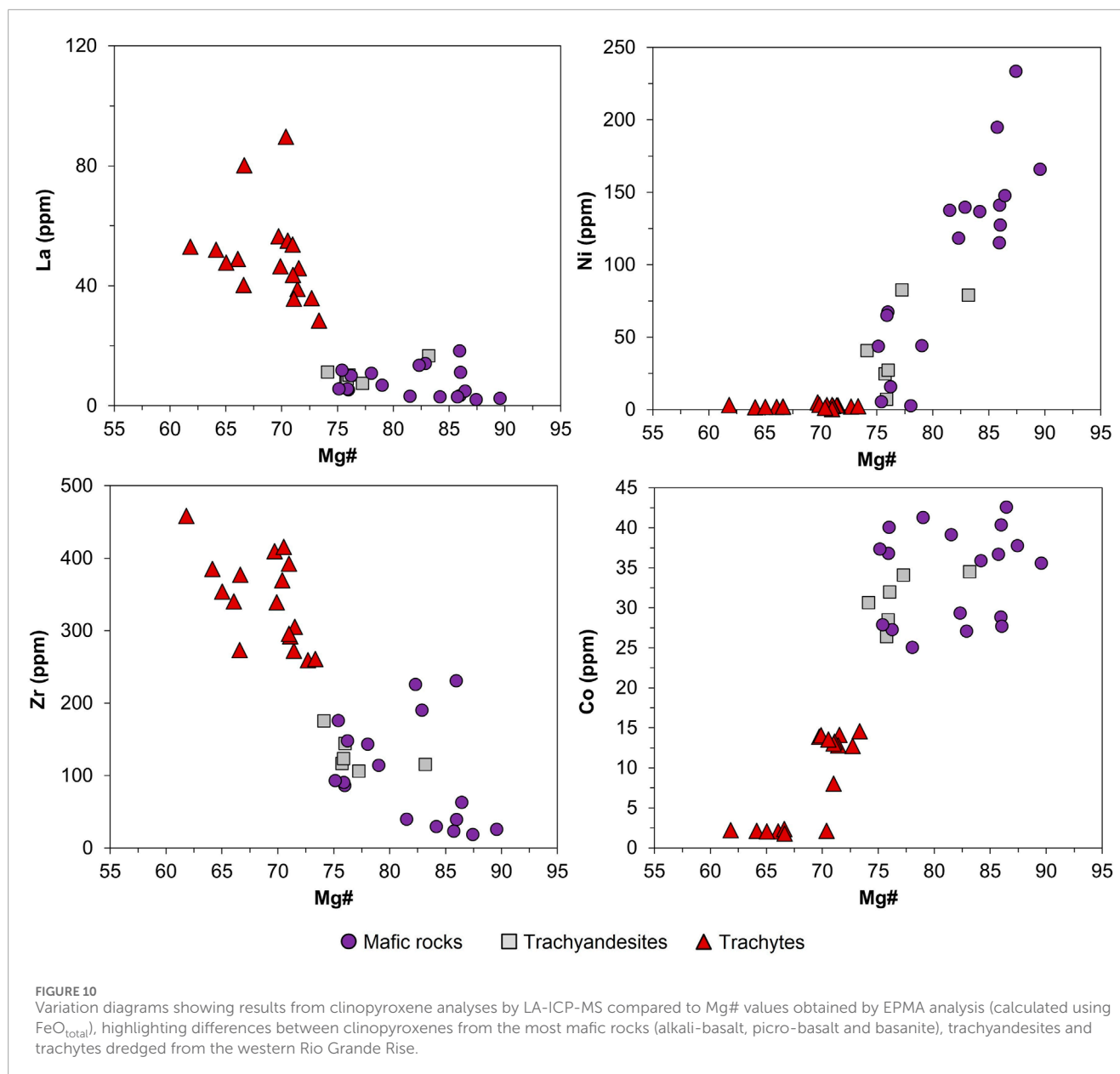
Ti-magnetite is the main oxide found in all samples and has variable composition as well. There seems to be a tendency of decreasing ulvöspinel proportions on the Ti-magnetite from the most primitive to the most evolved rocks (36–84 mol%). However, crystals from the trachybasalt have similar proportions to those from the trachyte from the same dredge (D13, [Supplementary File SF](#)). Additionally, crystals from the trachytes have lower Al<sub>2</sub>O<sub>3</sub>, MgO and Cr<sub>2</sub>O<sub>3</sub> and higher MnO contents than those found in more mafic rocks ([Supplementary File SF](#)). Lower Al<sub>2</sub>O<sub>3</sub> contents mark the main difference between groundmass crystals and macrocrysts in the same sample.

## 5.4 U-Pb dating

Zircons found in a single trachyte (RGR1-D13-004) were dated by Sensitive High-Resolution Ion MicroProbe (SHRIMP). A total of 22 spots were analyzed in mostly subhedral 130–240 µm long crystals with aspect ratios between 2:1 and 3:1 ([Supplementary File SA](#); [Supplementary Figure S7](#)). Sector zoning is observed in almost every crystal and oscillatory zoning is frequent. No inherited cores were observed. Average U and Th contents are 491 and 1,000 ppm respectively (U=168–1007 ppm; Th=187–2,629 ppm; [Supplementary File SG](#)). Results yielded a concordia age of  $46.9 \pm 0.3$  Ma (2σ; MSDW=0.00052; probability=0.98; n=22; [Figure 13](#)), the first U-Pb age obtained for any WRGR magmatic rock. The result obtained is close to the K-Ar age of  $46.3 \pm 0.7$  Ma ([Bryan and Duncan, 1983](#)) and the Ar-Ar age of  $46.0 \pm 0.1$  Ma ([Rohde et al., 2013b](#)) reported on the literature for WRGR rocks.

## 5.5 Pb, Sr and Nd isotopes

Pb, Sr and Nd isotope ratios of the studied alkaline volcanic rocks, including trachyte RGR1-D13-004, dated in



this work at  $46.9 \pm 0.3$  Ma, are similar to results available in the literature (Hoernle et al., 2015; Homrighausen et al., 2023), and differ only for the higher  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of three samples (Figure 14). The results lie along the Tristan compositional trend on the  $^{207}\text{Pb}/^{204}\text{Pb}$  versus  $^{206}\text{Pb}/^{204}\text{Pb}$  diagram like both WRGR and ERGR samples analyzed by Homrighausen et al. (2023), but WRGR alkaline rocks generally have less radiogenic signatures. The only analyzed sample dredged from the northern flank of the Cruzeiro do Sul Rift (trachyte RGR1-D16-003, Area A2, Figure 1), has more radiogenic Pb and Nd ratios than the rocks which were dredged from the southern flank (Area A1), and plots over Tristan-type samples from the Walvis Ridge and Guyot Province. This sample also differs from the others for its higher Nb/Zr and Nb/La ratios, even when compared to samples with similar MgO (Supplementary Figure S4).

The EMI-flavored signatures of the analyzed alkaline samples are similar to those from the tholeiitic basalt drilled at DSDP Site 516 in terms of Pb ratios but have lower  $^{144}\text{Nd}/^{143}\text{Nd}$  and higher  $^{87}\text{Sr}/^{86}\text{Sr}$ . In contrast, the alkali basalt analyzed by Homrighausen et al. (2018), which was recovered by the same dredge as the phonotephrite dated by Rohde et al. (2013b), has strikingly different Pb, Sr and Nd signatures compared to other samples from the RGR, and plots on the Prevalent Mantle (PREMA) field (Figure 14). It also has higher Nb/La and Nb/Th ratios for a given MgO (Supplementary Figure S4).

## 6 Discussion

Most alkaline WRGR samples have similar Nb/Zr and Nb/Th ratios, as well as similar isotope ratios (see discussion



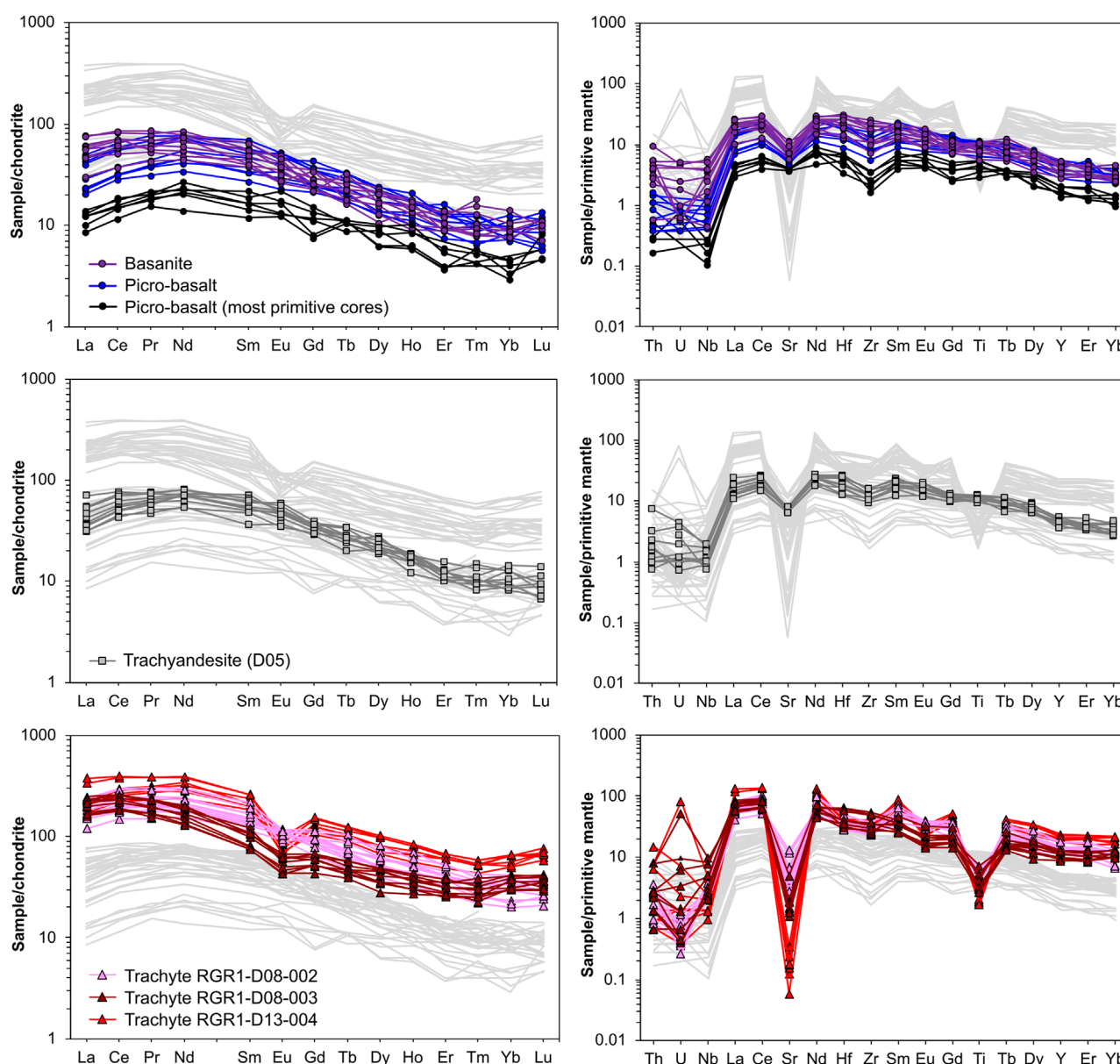


FIGURE 11 Chondrite (McDonough and Sun, 1995) normalized Rare-Earth Element patterns and primitive mantle (Sun and McDonough, 1989) normalized trace-element patterns from the analyzed clinopyroxene from the mafic rocks, trachyandesite and trachytes. Light grey lines in the background correspond to results from clinopyroxene from other samples for reference.

below), suggesting that they are genetically related. The trachytes recovered by dredge D16, however, differ for their significantly higher Nb/Zr ratio for a given MgO (Supplementary Figure S4), and their steeper, more fractionated pattern on the chondrite-normalized REE diagram when compared to trachytes recovered by other dredges (Figure 4). Additionally, trachyte RGR1-D16-003 has a distinct isotope signature compared to other samples (Figure 14), which suggests the existence of at least two different magmatic suites originated from distinct source magmas.

A few geochemical characteristics from the trachytes recovered by dredge D16 might reflect remobilization and partial melting of

alkali feldspar cumulate by mafic magma recharge. These samples differ from other studied trachytes for their enrichment in K and Ba, high K/Zr ratios (168–194), and normalized REE patterns with a slightly positive Eu anomaly ( $\text{Eu}/\text{Eu}^* = 1.04\text{--}1.05$ ; Figure 4), attributes which Wolff (2017) mentions as indicative of such a process. They were also investigated using SEM and have no clear signs of potassic or hydrothermal alteration. Moreover, the studied trachytes composition is neither significantly quartz-normative nor nepheline-normative. The persistence of such trachytic liquids, possibly marking an endpoint in the evolution of the alkaline volcanism from the WRGR instead of fractionation towards rhyolitic or phonolitic magmas, can be explained by an origin by melting of

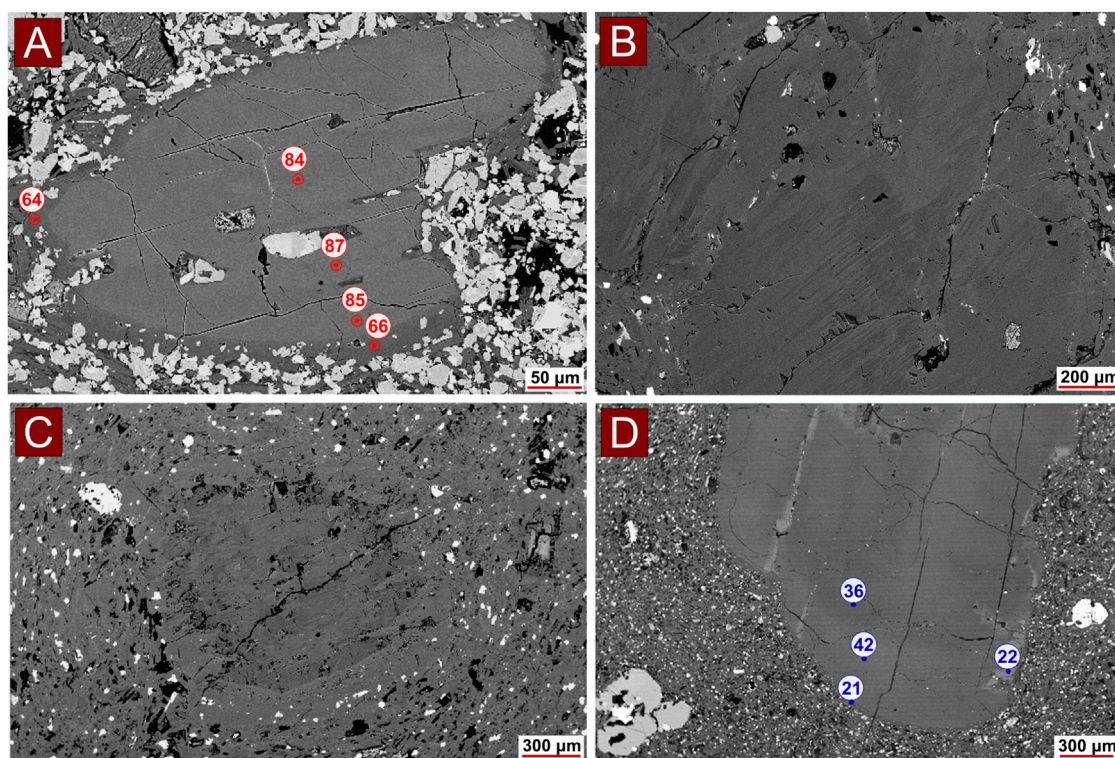


FIGURE 12

Backscatter images with examples of textural and compositional features of the feldspar macrocrysts from the analyzed samples. (A) – Plagioclase macrocryst with a bytownite core and labradorite rim found on the picro-basalt RGR1-D08-004. Values in red correspond to the anorthite (An) contents of the EPMA point analyses. (B) – Perthite observed on a sanidine macrocryst from trachyte sample RGR1-D13-004. (C) – Smaller alkali feldspar macrocryst from the same trachyte sample with sanidine rims and an anorthoclase core. (D) – Zoned alkali feldspar macrocryst from trachyte sample RGR1-D08-002 with varying Orthoclase (Or) contents represented by point analyses in blue. Note the presence of infiltrations (lighter) along a few borders and fractures on the macrocryst. The point analysis with Or=22 was made at an infiltrated area and has higher BaO (1.14 wt%) than the others (0.16–0.64 wt%).

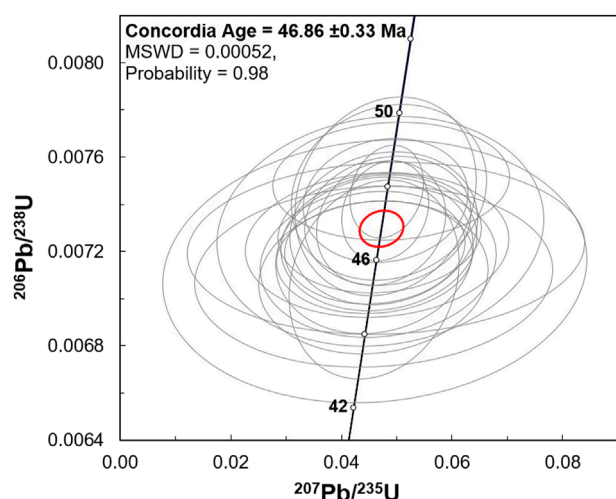


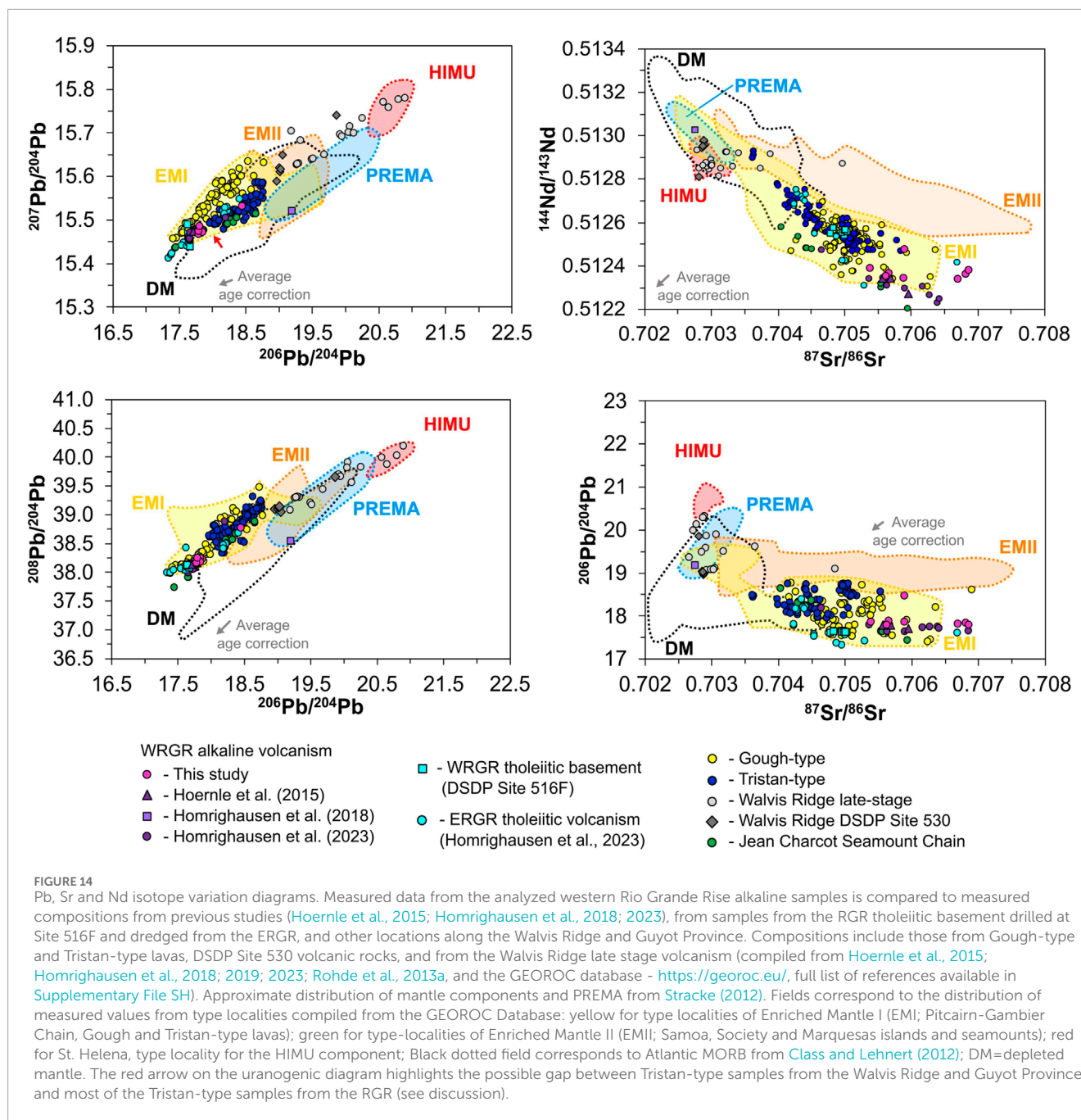
FIGURE 13

Concordia diagram showing U-Pb results and concordia age  $\pm 2\sigma$  (red) obtained for zircons from trachyte RGR1-D13-004. Data-point error ellipses (grey) are  $2\sigma$ .

alkali-feldspar cumulates as suggested by Wolff (2017). However, the limited number of samples does not allow better evaluation of this model in the case of the WRGR by comparing K/Zr and Ti/Zr trends like Wolff (2017) does for the Agua de Pau volcano in Azores.

Fractional crystallization has played a major role in the evolution of the magmatic system. This is supported by the presence of negative Ti, Sr and Eu anomalies with different intensities in the normalized trace element patterns from both whole-rock and clinopyroxene from the trachyandesites and trachytes, which record the influence of distinct amounts of previous feldspar and Fe-Ti oxide fractionation on the composition of the more evolved magmas from the system. Moreover, progressive enrichments in incompatible elements are also observed with decreasing Mg#. Previous fractionation of Fe-Ti oxides is also suggested by the trends observed on the variation diagrams for clinopyroxene compositions with decreasing Mg#. Firstly, compositions follow a trend of increasing  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  coupled with a decrease in  $\text{SiO}_2$  (Figure 5) due to the decrease in silica activity which results from the progressive  $\text{Al}^{3+}$  incorporation in the tetrahedral site as  $\text{Ti}^{4+}$  also increases (Wass, 1979). At  $\text{Mg}\# \sim 73$ , a shift towards lower  $\text{Al}_2\text{O}_3$  and





TiO<sub>2</sub> and higher SiO<sub>2</sub> with decreasing Mg# might reflect the onset of significant Fe-Ti oxide fractionation.

## 6.1 Textural evidence of a complex magmatic system

The variable textural and compositional features observed in clinopyroxene are suggestive of an open system, as evidenced by complex zoning patterns which include oscillatory zoning, normal abrupt zoning on macrocrysts with resorbed and corroded rounded or irregular-shaped cores, and less frequent reverse zoning, all indicative of disequilibrium between crystals and host

magmas (e.g., Cao et al., 2022; Jerram and Martin, 2008; Streck, 2008; Ubide et al., 2014a; 2014b). The normal abrupt zoning patterns observed probably result from reaction between more primitive crystals with host magmas in response to changes in temperature, pressure, and/or composition. The presence of crystals with reverse zoning is indicative that not only more primitive cores were remobilized by more evolved magmas, but also that more evolved crystals interacted with more primitive magmas. Moreover, frequent oscillatory zoning indicates that crystals recorded cyclic compositional variations while stored in magmatic chambers submitted to multiple episodes of more primitive magma recharge, also affected by magma differentiation by fractional crystallization. Crystals with sector zoning are found

only in the alkali-basalt and indicate dynamic crystallization conditions.

The disequilibrium textures observed on clinopyroxene primitive cores and their contrasting composition when compared to rims and groundmass crystals indicate that they are not *s.s.* phenocrysts, i.e., they are not early-formed crystals which grew larger than others crystallized from the same magma. Furthermore, the abrupt zoning patterns are not consistent with subsolidus diffusive processes. These cores are probably antecrysts crystallized from magmas which were more primitive than their host liquid, and it is possible that some correspond to mantle xenocrysts, considering the partial overlap between the cores with the highest Mg# (>85) and compositional fields of clinopyroxene from mantle xenoliths (Figure 9). Many feldspar macrocryst cores might also be antecrysts. This is probably the case of the plagioclase cores from macrocrysts with alkali feldspar rims from trachyte RGR1-D08-003, of the resorbed bytownite cores found in the strongly zoned picro-basalt macrocrysts with labradorite rims, and of the plagioclase macrocrysts found in the trachybasalt, which are strongly corroded and rounded.

The infiltration textures commonly observed in clinopyroxene evidence the effect of the cryptic metasomatic processes to which they were submitted along their evolution, possibly in multiple stages, as suggested by the complex patterns observed in the Cr<sub>2</sub>O<sub>3</sub> compositional maps of primitive cores (Figure 7). A few of the point-analyses made in these cores yielded the highest Cr contents of the dataset, what suggests that the superimposed cryptic metasomatism is partially masking the possible mantle-derived nature of xenocrystic cores.

Most of the groundmass clinopyroxene and feldspar, which represent quench low-pressure crystals, have similar composition to that of macrocryst rims from the host sample. This suggests that outer rims from macrocrysts frequently represent low-pressure overgrowths on host higher-pressure crystals. The only sample which has clinopyroxene groundmass crystals and macrocryst rims with significant compositional differences is trachyte RGR1-D13-004. The higher Mg# and Ti/Al and lower Na<sub>2</sub>O from the groundmass crystals suggest that the clinopyroxene macrocrysts from this sample are also antecrysts.

Despite the multiple evidence of disequilibrium between more primitive macrocryst cores and their respective host liquids, a few euhedral clinopyroxene crystals with concentric cores and rims of contrasting composition are observed. This is indicative that in some cases there was progressive equilibrium of the primitive crystals with the magma which generated the rims with lower Mg#.

## 6.2 Polybaric nature of the magmatic system

To further evaluate the equilibrium between crystals and host magmas from a compositional point of view, clinopyroxene from samples with lower proportions of macrocrysts were compared to the results of whole-rock geochemistry analyses using the Rhodes diagram (Rhodes et al., 1979) and predicted and observed clinopyroxene components (DiHd, EnFs, CaTs; Putirka et al., 1996; Putirka, 1999). Additionally, the composition of

the very fine-grained groundmass of the picro-basalt (RGR1-D08-004) was estimated using a semi-quantitative EDS area analysis to further investigate this sample, which has the clinopyroxene with the strongest abrupt zoning patterns and the most primitive cores.

Most of the analyzed clinopyroxene are in disequilibrium with their respective whole-rock composition, which is probably biased even by smaller proportions of macrocrysts (Supplementary File SA, Supplementary Figure S8). Trachyte RGR1-D08-002 is the only sample with a few clinopyroxene crystals in equilibrium with the whole-rock, but most of its crystals plot below the equilibrium curve in the Rhodes diagram, suggesting that they were crystallized from a host liquid with lower Mg#. For these clinopyroxene-melt pairs, temperatures of 1023°C–1040°C and pressures of 3.1–3.8 kbar were estimated using the thermobarometer from Masotta et al. (2013), which was calibrated for trachytic and phonolitic compositions and has standard errors of estimate (SEE) of 1.15 kbar and 18.2°C. A single ilmenite and Ti-magnetite pair found in the same trachyte was used to estimate temperature and oxygen fugacity using ILMAT (Lepage et al., 2003) and yielded temperatures of 826°C–839°C and log<sub>10</sub>fO<sub>2</sub> between −14.1 and −13.6 using the thermobarometer by Andersen and Lindsley (1985), indicating relatively high oxygen fugacity, close to the NiNiO redox buffer.

In the case of the picro-basalt, 24 clinopyroxene-melt pairs are in apparent equilibrium with the estimated groundmass composition. Among these, there are mostly point-analyses from evolved rims, one made on rare homogeneous macrocrysts with no zoning, a few analyses of infiltrated portions on the macrocrysts, and a single groundmass crystal. The remaining 4 point-analyses on groundmass crystals yielded K<sub>D</sub>Fe-Mg values which are suggestive of equilibrium with the melt estimative but did not satisfy the equilibrium criteria considering predicted and observed clinopyroxene components, probably due to the uncertainty associated with the estimated host liquid composition. The most primitive clinopyroxene cores would be in equilibrium with melts with significantly higher Mg# (>70).

Estimates for the picro-basalt clinopyroxene-melt pairs were made using the thermometer from Putirka et al. (2003) and Equation 32b barometer from Putirka (2008), which have SEEs of 59°C and 2.6 kbar. These were selected based on the work by Hammer et al. (2016), which evaluates the best models to estimate temperature and pressure of high-Al diopsides from Hawaiian ankaramites. The average temperature obtained is 1144°C. Results from the thermometer from Putirka et al. (2003) agree within error with estimates using Equation 33 from Putirka (2008) iteratively calculated with the barometer from Neave and Putirka (2017). Pressure estimates depend on the H<sub>2</sub>O content of the liquid in equilibrium with clinopyroxene, which is unknown; thus, they were made considering an anhydrous composition and H<sub>2</sub>O contents=0.5%, 1%, and 2%. The results are variable (averages between 2.2 and 3.1 kbar with increasing H<sub>2</sub>O) but agree within error (Supplementary File SE). Despite the limitations, the calculations constrain the pressure to an interval between 0 and 5.7 kbar, considering the SEE.

Even though it is not possible to use thermobarometers to estimate pressure conditions for the crystallization of other macrocrysts, qualitative aspects can be assessed based on clinopyroxene composition, especially in the case of the strongly zoned clinopyroxene from the mafic rocks. For instance, the Al/Ti ratio increases significantly with pressure (e.g., Dobosi and



Fodor, 1992; Thy, 1991). Trends towards higher  $Al^{VI}/Al^{IV}$  are also indicative of an increase in pressure crystallization conditions (e.g., Aoki and Kushiro, 1968; Dobosi and Fodor, 1992; Wass, 1979). The  $Al^{VI}/Al^{IV}$  value depends on the magma composition, but the trend of increasing  $Al^{VI}/Al^{IV}$  ratios with increasing pressure is observed independent of melt compositions and is not restricted to alkali basalts (Wass, 1979). Other trends observed in clinopyroxene composition with decreasing pressure are the increase in  $Ti+Al^{IV}$  with decreasing Si and increase in  $TiO_2$  with decreasing Mg# (Wass, 1979).

Clinopyroxene macrocrysts and groundmass crystals from the picro-basalt and alkali basalt have similar composition and  $Al/Ti$  and  $Al^{VI}/Al^{IV}$  trends (Figure 15). Cores generally follow a trend of higher  $Al/Ti$  and  $Al^{VI}/Al^{IV}$  ratios than most analyzed rims, except for analyses made on the inner parts of rims with oscillatory zoning. Such trends suggest that cores and part of the oscillatory-zoned rims were formed under higher pressure in deeper parts of the magmatic system. This is also supported by a general trend of increasing  $Al^{IV}/Al^{VI}$  and Ti and decreasing Si with decreasing Mg# from cores to groundmass and rims without oscillatory zoning (Wass, 1979). Furthermore, macrocrysts with reverse zoning and microphenocrysts have similar  $Al/Ti$  and  $Al^{VI}/Al^{IV}$  to those of rims from macrocrysts with normal zoning, which suggests that they were formed under similar pressure conditions, in shallower depths when compared to the most primitive cores.

In contrast, cores and rims of crystals with normal abrupt zoning from the basanite have more similar  $Al^{IV}/Al^{VI}$  ratios and  $Al/Ti$  ratios (Figure 15), which are also close to those from the primitive intermediate zones of the mapped microphenocrysts (Figures 7C, D), suggesting that they were crystallized at similar depths. Although  $Al/Ti$  ratios from cores are slightly higher when compared to rims, the trend observed suggests that the possible difference in pressure conditions is not as significant as in the case of the basalts. The more evolved cores from the mapped basanite microphenocrysts have higher  $Al^{VI}/Al^{IV}$  and core #1 has much higher  $Al/Ti$  ratios than any other crystal. This evolved core might have been formed under high pressure conditions before it was remobilized by a more primitive magma, which indicates that interaction between more evolved macrocrysts and primitive magmas occurred under variable pressure.

### 6.3 Pb, Sr and Nd isotopes and implications for the origin of the Rio Grande Rise alkaline volcanism

Recent investigations of the RGR provided new constraints on the isotope compositional variability of its volcanic rocks. Perhaps the most relevant finding of this study is that trachyte sample RGR1-D13-004, dated at  $46.9 \pm 0.3$  Ma, has a Tristan-type isotope signature like most other RGR alkaline lavas (this study; Hoernle et al., 2015; Homrighausen et al., 2023). Such signatures were previously found only in Eocene volcanic rocks on the African Plate (Rohde et al., 2013a; b; O'Connor and Jokat, 2015; Homrighausen et al., 2019). Sample RC11-2RD (analyzed by Homrighausen et al., 2018), which was recovered by the same dredge as the  $46.0 \pm 0.1$  Ma phonotephrite dated by Rohde et al. (2013b),

has contrasting isotope signatures and differs from other WRGR alkaline volcanics (Hoernle et al., 2015; Homrighausen et al., 2023; this work) for its considerably higher  $^{206}Pb/^{204}Pb$  and  $^{144}Nd/^{143}Nd$  and lower  $^{87}Sr/^{86}Sr$ . This observed variability might be due to small-scale source heterogeneities.

In the uranogenic diagram in Figure 14, there seems to be a gap in the middle of the Tristan-type trend between samples from the Walvis Ridge and Guyot Province and most samples from the RGR, which are less radiogenic. Only two WRGR alkaline samples overlap with lavas from the Walvis Ridge and Guyot Province in this diagram, and these samples have higher Nb/Zr ratios compared to the others. This might also be a result of source heterogeneity, but the gap itself could also reflect the limited sampling of the plateau.

Hoyer et al. (2022a) suggested that the Eocene alkaline volcanism from the Walvis Ridge/Guyot Province and the Rio Grande Rise was not originated by the same processes because by  $\sim 70$  Ma they were already separated from each other according to paleogeographic reconstructions (Graça et al., 2019). The authors also mention the different isotope signatures of the single WRGR sample analyzed by Homrighausen et al. (2018) and late-stage Walvis Ridge lavas (Homrighausen et al., 2019). The WRGR alkaline volcanism might actually be related to lithospheric rifting along the Cruzeiro do Sul Rift as suggested by Hoyer et al. (2022a) and Mohriak et al. (2010). However, the compositional similarity between Walvis Ridge, Guyot Province and RGR lavas supported by more recent data (Homrighausen et al., 2023; this study), strongly suggests that at least the enrichment of the sources from their magmatism is related to the same processes. Moreover, even after the separation of the RGR and the Walvis Ridge, these sources still shared common characteristics.

Homrighausen et al. (2023) point out that the EMI signatures with the lowest  $^{206}Pb/^{204}Pb$  ratios are found in the oldest Gough-type samples from the Walvis Ridge and the oldest Tristan-type samples from the Rio Grande Rise and conclude that both Gough and Tristan-type lavas follow an evolution trend towards PREMA compositions with time. However, until now, there is no evidence of alkaline volcanism in the plateau before the Eocene, and our work shows that signatures of Eocene alkaline rocks from the WRGR have low  $^{206}Pb/^{204}Pb$  values close to those of the 80–88 Ma tholeiitic basement drilled at DSDP Site 516F. More geochronology investigations are essential to better understand the temporal distribution of the plateau's enriched signatures, but it seems that in the case of the WRGR, there is no trend of evolution towards higher  $^{206}Pb/^{204}Pb$  ratios with time.

The origin of the EMI component and the Tristan/Gough chemical zonation remains unclear, and the results obtained are not supportive of a specific model, but they have important implications as any attempts to explain such signatures in South Atlantic lavas need to consider that during the Eocene they were still manifested in both South American and African plates. According to the model proposed by O'Connor et al. (2018), it is possible that supply of enriched material from the Tristan-Gough plume persisted through time because of lateral fast flows caused by the horizontal deflection of upwelling material from the African superplume in the asthenosphere beneath the RGR. However, more investigations are needed to understand the mechanisms behind the manifestation of Tristan and Gough-type signatures, and new studies of the RGR have significant potential to shed light on this matter. Not only the

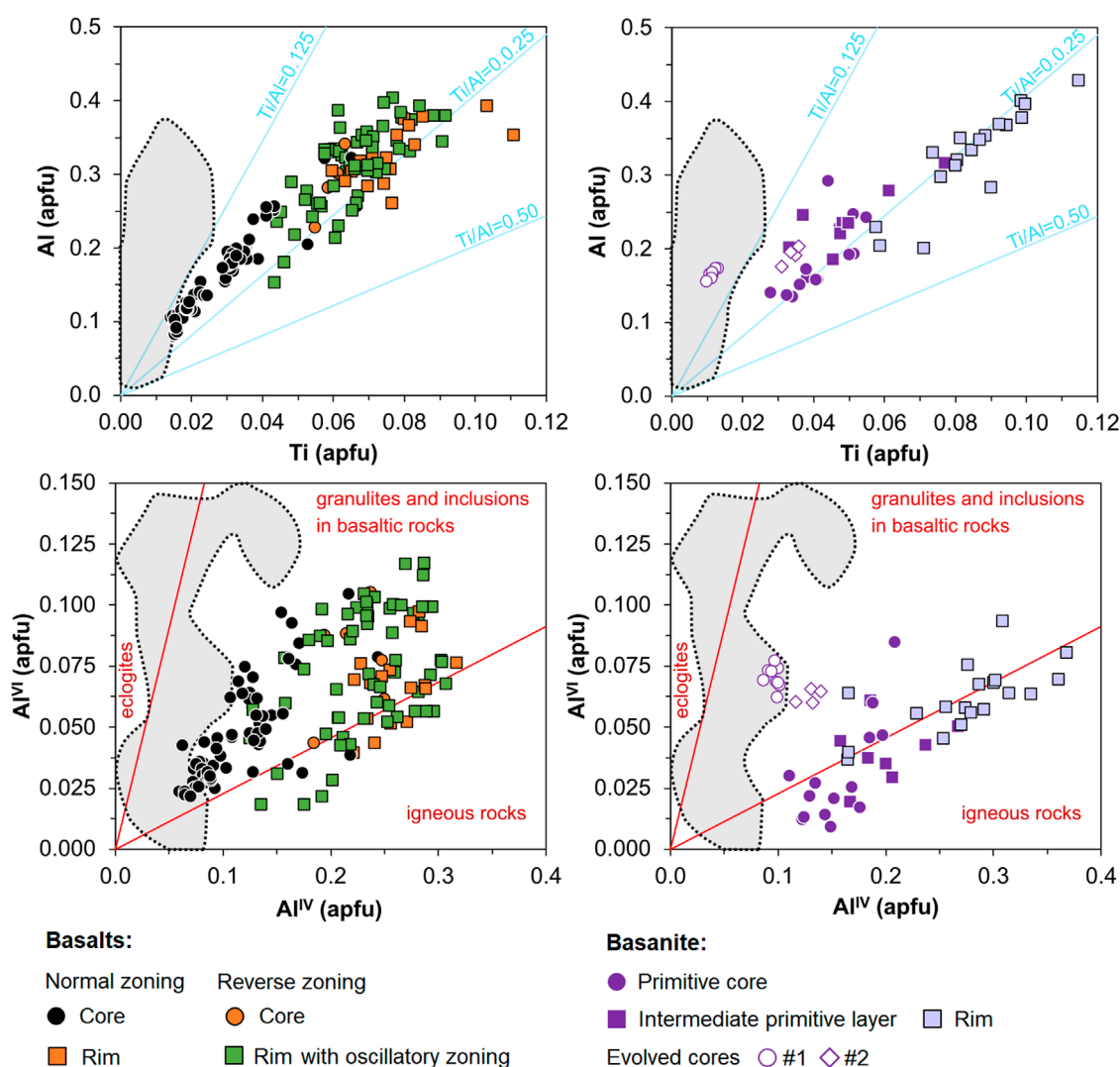


FIGURE 15

Distribution of the analyzed clinopyroxene from the basalts and the basanite on Al versus Ti and  $Al^{VI}$  versus  $Al^{IV}$  diagrams. Red lines are the limits of the fields for igneous rocks, granulites and inclusions in basaltic rocks and eclogite according to Aoki and Kushiro (1968). The grey field corresponds to the distribution of clinopyroxene from mantle xenoliths (data includes representative compositions from Pearson et al., 2014 and analyzed crystals from lherzolites and harzburgites from Hawaii, Canary Islands, Ontong Java plateau, Kerguelen and Samoan Islands compiled from GEOROC - <https://georoc.eu/>; full list of references available at Supplementary File SH). apfu=atoms per formula unit.

complex spatial and temporal distribution of EMI-flavored lavas on the plateau needs to be better constrained, but also the duration and volume of its alkaline versus tholeiitic magmatism, as well as the spatial relationship between their volcanic products.

## 7 Conclusion

This work investigated alkali basalts, a picro-basalt, a basanite, a trachybasalt, trachyandesites and trachytes dredged from the western Rio Grande Rise. These rocks were subject to detailed characterization integrating petrography, whole-rock geochemistry, mineral chemistry and whole-rock Sr, Nd and Pb isotope analysis. Moreover, U-Pb dating of zircons from a single trachyte was also performed.

The obtained U-Pb age of  $46.9 \pm 0.3$  Ma is coherent with previous ages reported in the literature and reinforces the importance of the Eocene alkaline volcanism in the WRGR.

The compositional and textural variability of clinopyroxene macrocrysts is key to better understand the complex magmatic system. The variable zoning patterns and disequilibrium textures suggest that crystals reacted with their host magmas due to changes in temperature, pressure, and/or composition. Several crystals record the influence of multiple stages of magma recharge and those with oscillatory zoning were formed under cyclic compositional variations in magma chambers or mush columns also influenced by fractionation processes, as evidenced by trace-element patterns from both clinopyroxene and whole-rock compositions. The difference between  $Al/Ti$  and  $Al^{VI}/Al^{IV}$  ratios of cores and rims of clinopyroxene from the mafic rocks suggests that crystals



were formed at variable depths in a polybaric transcrustal magmatic system. Both more evolved and more primitive antecrysts and a few xenocrysts were remobilized by host magmas with distinct composition and transported to shallower portions of the crust.

The studied alkaline volcanic rocks have Tristan-type EMI-flavored signatures, which suggests that the mantle sources from the WRGR Eocene alkaline volcanism still shared common characteristics with those from other locations along the Walvis Ridge and Guyot Province, even after a considerable period of time since the plateaus were separated from each other. This needs to be considered by any models used to explain EMI signatures in the South Atlantic Ocean and the Tristan/Gough plume chemical zonation.

## Data availability statement

All datasets presented in this study can be found online in the article [Supplementary Material](#).

## Author contributions

JT: Conceptualization, Data curation, Formal Analysis, Investigation, Methodology, Project administration, Writing—original draft, Writing—review and editing. VA: Conceptualization, Data curation, Formal Analysis, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Writing—original draft, Writing—review and editing. PS: Data curation, Formal Analysis, Investigation, Methodology, Writing—review and editing. MS: Data curation, Formal Analysis, Investigation, Methodology, Supervision, Writing—review and editing. GL: Writing—review and editing, Data curation, Formal Analysis, Investigation, Methodology. LJ: Conceptualization, Funding acquisition, Project administration, Supervision, Writing—review and editing.

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## Conflict of interest

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## Supplementary material

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/feart.2024.1527863/full#supplementary-material>

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