LITHOS

New evidence for Late Cretaceous plume-related seamounts in the Middle East sector of the Neo-Tethys: Constraints from geochemistry, petrology, and mineral chemistry of the magmatic rocks from the western Durkan Complex (Makran Accretionary Prism, SE Iran)
--Manuscript Draft--

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Abstract:	The Durkan Complex in the Makran Accretionary Prism (SE Iran) has been interpreted either as a continental margin succession or a Late Cretaceous tectonically disrupted seamount chain. New whole rock and clinopyroxene chemical data for basaltic and metabasaltic rocks of the Durkan Complex allow us to distinguish two main rock groups: a) rocks showing transitional chemical affinity (Group 1) and compositions resembling those of plume-type mid-oceanic ridge basalts; b) rocks with within-plate oceanic island basalt (OIB) compositions showing a clear alkaline affinity (Group 2). Based on whole rock REE contents and clinopyroxene chemistry, alkaline rocks can be further subdivided in two sub-groups, namely, the Group 2a and 2b. Compared to Group 2a, Group 2b rocks show a more pronounced alkaline nature marked by higher whole rock La/Yb and Sm/Dy ratios and higher TiO_2 and Na_2O contents in clinopyroxenes. Trace element and REE petrogenetic models show that the Durkan basaltic rocks were generated from the partial melting of depleted sub-oceanic mantle source that was metasomatized by OIB-type chemical components in a within-plate oceanic setting. The chemical differences in the three rock groups are related to different combinations of partial melting degree, depths of melting, and various extent of enrichment of the mantle sources by OIB-type chemical components, which are related, in turn, to a Late Cretaceous mantle plume activity in the northern Neo-Tethys realm. We suggest that the Durkan Complex formed in a seamount setting and that its different volcano-sedimentary successions record different stages of seamount formation.

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Dear Editor,

    Thank you very much for your editorial help. We are very sorry for having left several silly grammatical issues in the revised text. We are submitting herein our revised manuscript. We have fixed all the issues you highlighted.

As usual, we upload two versions of the revised manuscript. One version is with changes marked (annotated) in which you can promptly see the changes we made. The other one is with no changes marked (only revised text).

We thank you again for your editorial help and consideration, and look forward to hearing from you soon.

Yours sincerely,

Emilio Saccani

On behalf of the co-authors

Abstract

The Durkan Complex in the Makran Accretionary Prism (SE Iran) has been interpreted either as a continental margin succession or a Late Cretaceous tectonically disrupted seamount chain. New whole rock and clinopyroxene chemical data for basaltic and metabasaltic rocks of the Durkan Complex allow us to distinguish two main rock groups: a) rocks showing transitional chemical affinity (Group 1) and compositions resembling those of plume-type mid-oceanic ridge basalts; b) rocks with within-plate oceanic island basalt (OIB) compositions showing a clear alkaline affinity (Group 2). Based on whole rock REE contents and clinopyroxene chemistry, alkaline rocks can be further subdivided in two sub-groups, namely, the Group 2a and 2b. Compared to Group 2a, Group 2b rocks show a more pronounced alkaline nature marked by higher whole rock La/Yb and Sm/Dy ratios and higher TiO_2 and Na_2O contents in clinopyroxenes. Trace element and REE petrogenetic models show that the Durkan basaltic rocks were generated from the partial melting of depleted sub-oceanic mantle source that was metasomatized by OIB-type chemical components in a within-plate oceanic setting. The chemical differences in the three rock groups are related to different combinations of partial melting degree, depths of melting, and various extent of enrichment of the mantle sources by OIB-type chemical components, which are related, in turn, to a Late Cretaceous mantle plume activity in the northern Neo-Tethys realm. We suggest that the Durkan Complex formed in a seamount setting and that its different volcano-sedimentary successions record different stages of seamount formation.

The Durkan Complex Plume-type ophiolites (Makran Prism, SE Iran): setting of formation
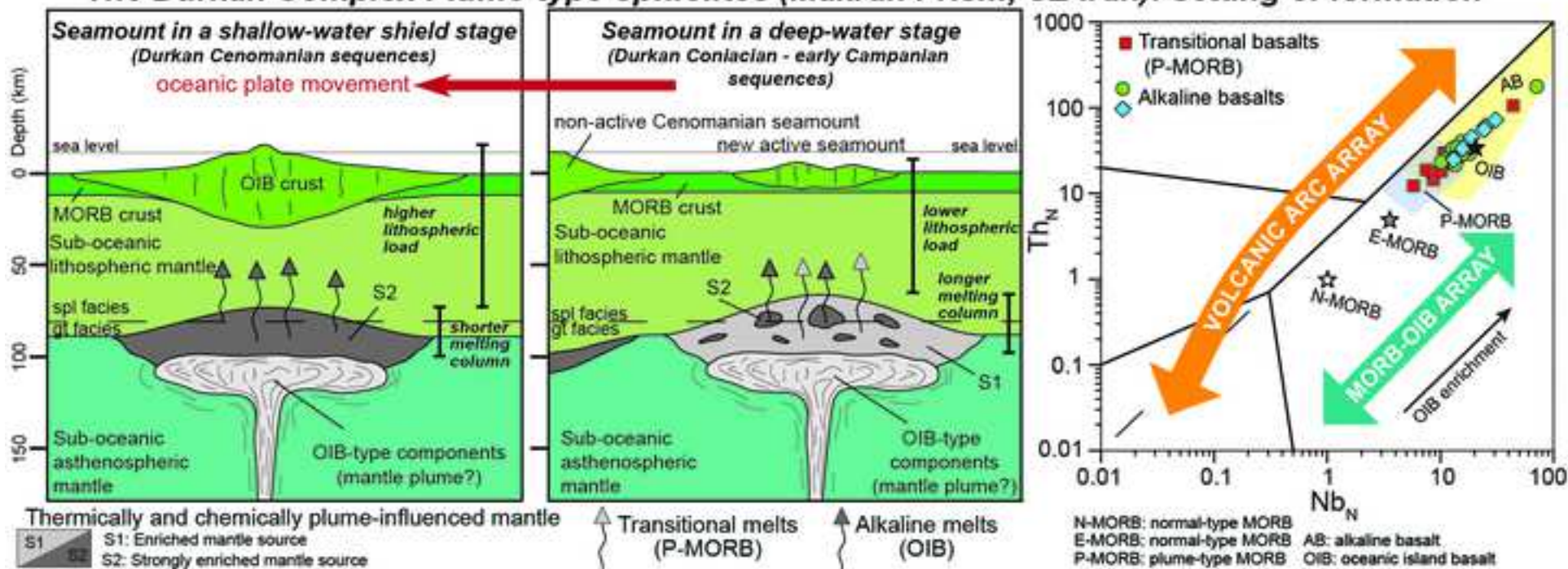
Research Highlights

- The western Durkan Complex consists of different volcano-sedimentary successions

- Basaltic rocks are largely prevailing though trachytes and rhyolites locally occur

- Volcanic rocks show transitional (P-MORB) and alkaline (OIB) geochemistry

- The Durkan volcanic rocks were erupted in different stages of seamounts life

- The Durkan Complex records the existence of seamounts in the Cretaceous Neo-Tethys

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2   of the Neo-Tethys: Constraints from geochemistry, petrology, and mineral chemistry of the

3   magmatic rocks from the western Durkan Complex (Makran Accretionary Prism, SE Iran)

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The Durkan Complex in the Makran Accretionary Prism (SE Iran) has been interpreted either as a continental margin succession or a Late Cretaceous tectonically disrupted seamount chain. New whole rock and clinopyroxene chemical data for basaltic and metabasaltic rocks of the Durkan Complex allow us to distinguish two main rock groups: a) rocks showing transitional chemical affinity (Group 1) and compositions resembling those of plume-type mid-oceanic ridge basalts; b) rocks with within-plate oceanic island basalt (OIB) compositions showing a clear alkaline affinity (Group 2). Based on whole rock REE contents and clinopyroxene chemistry, alkaline rocks can be further subdivided in two sub-groups, namely, the Group 2a and 2b. Compared to Group 2a, Group 2b rocks show a more pronounced alkaline nature marked by higher whole rock La/Yb and Sm/Dy ratios and higher TiO_2 and Na_2O contents in clinopyroxenes. Trace element and REE petrogenetic models show that the Durkan basaltic rocks were generated from the partial melting of depleted sub-oceanic mantle source that was metasomatized by OIB-type chemical components in a within-plate oceanic setting. The chemical differences in the three rock groups are related to different combinations of partial melting degree, depths of melting, and various extent of enrichment of the mantle sources by OIB-type chemical components, which are related, in turn, to a Late Cretaceous mantle plume activity in the northern Neo-Tethys realm. We suggest that the Durkan Complex formed in a seamount setting and that its different volcano-sedimentary successions record different stages of seamount formation.

1. Introduction

Ophiolitic basaltic and metabasaltic rocks are widespread within collisional-type and accretionary-type orogenic belts and are of particular importance, as their petrological features are sensitive to different geodynamic settings of formation. Different tectonic environments, such as mid-oceanic ridge, within-plate oceanic island, convergent and rifted margins, are indeed characterized by the occurrence of chemically distinctive types of basaltic rocks (Pearce, 1996; Dilek and Furnes, 2011; Saccani, 2015; Safonova et al., 2016). Among them, basaltic rocks with oceanic island basalt (OIB) chemical affinity are of particular interest as they may represent remnants of deformed oceanic seamounts (Yang et al., 2015, 2019; Wan et al., 2020). Seamounts are largely subducted and their remnants in the accretionary and collisional belts are represented only by blocks in ophiolitic mélanges (e.g., Yang et al., 2019; Safonova et al., 2016) or as coherent slices underplated at different depths (e.g., Isozaki et al., 1990; Bonnet et al., 2020). In addition, recognizing basalts with OIB affinity within accretionary and collisional belts is particularly important as they likely represent the only elements for reconstructing periods of mantle plume activity during Earth history (Safonova and Santosh, 2014; Wan et al., 2020). It follows that detailed petrological studies of basaltic rocks within the accretionary and collisional belts are fundamental for constraining their tectono-magmatic settings of formation and, consequently, for reconstructing the progressive geodynamic history of the paleo-oceanic basins and their related continental margins (Robertson, 2007; Hässig et al., 2013; Safonova, 2017; Saccani et al., 2018; Rolland et al., 2020).

The Makran Accretionary Prism (hereafter, simply Makran) in SE Iran and SW Pakistan (Figs. 1a, b) is related to the long-lived geodynamic evolution of the Neo-Tethys Ocean and its northern continental margin, represented by the Lut and Afghan blocks

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(McCall and Kidd, 1982; Burg et al., 2008; 2013; Burg, 2018; Saccani et al., 2018; Monsef et al., 2018; Barbero et al., 2020a). The Makran consists of several tectono-stratigraphic domains (Fig. 1b) that have been deformed and incorporated in the accretionary prism, starting from the Cretaceous (e.g., Platt et al., 1985; Dolati and Burg., 2013; Burg, 2018; Saccani et al., 2018; Barbero et al., 2020a, b). Among these, the North Makran domain records the pre-Eocene deformation history of the accretionary wedge. It consists of several tectonic units (Fig. 1c) that, in turn, represent distinct tectonic domains, including the Neo-Tethys oceanic lithosphere, seamounts and/or oceanic plateau, as well as arc-forearc-trench domains. The North Makran also includes tectonic units derived from an exotic microcontinental block and its sedimentary cover (McCall and Kidd, 1982; Dorani et al., 2017; Burg, 2018; Monsef et al., 2018; Saccani et al., 2018). The Durkan Complex is one of the major tectonic elements of the North Makran domain (Fig. 1c) and it was described as a highly deformed complex including Early Cretaceous – early Paleocene shallow water succession, abundant volcanic rocks, as well as subordinate tectonic slices of Carboniferous, Permian and Jurassic shallow water sedimentary rocks and Middle - Late Jurassic granitoids (McCall, 1985; Hunziker et al., 2015). It has been classically interpreted as the Permian – Cretaceous disrupted sedimentary cover of the passive margin of a continental basement as old as Paleozoic, whose remnants are now represented by the Bajgan Complex (McCall and Kidd, 1982; McCall, 2002). The Bajgan-Durkan Complexes are collectively thought to represent the remnants of a continental ribbon detached from the Eurasian margin by the Late Jurassic – Early Cretaceous rifting that led to the opening of the North Makran Ocean (McCall and Kidd, 1982; McCall, 2002; Hunziker et al., 2015; Burg, 2018). However, Barbero et al. (2021) showed that the western Durkan Complex consists of tectonic slices including volcano-sedimentary sequences, which represent remnants of a tectonically disrupted Late Cretaceous seamounts chain. This interpretation, which is radically different

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102 from the extant interpretation, is based on field investigations and detailed stratigraphic,

103 structural, and biochronological data, as well as preliminary petrographic and geochemical

104 data on volcanic rocks. However, a thorough geochemical and petrological investigations of

105 the volcanic rocks included in the Durkan volcano-sedimentary sequences is necessary for

106 better constraining the tectono-magmatic setting of formation of the Durkan Complex, as

107 well as its significance for the geodynamic evolution of the pre-Eocene Makran

108 Accretionary Prism. Therefore, in this paper, we present new whole-rock, as well as mineral

109 geochemical data on the volcanic and metavolcanics rocks from the Durkan Complex.

110 These data will be discussed in the context of the detailed tectono-stratigraphic results

111 presented by Barbero et al. (2021) with the purpose of adding the final touch to the

112 knowledge of tectono-magmatic setting of formation of this Complex. Finally, these

113 findings will then be discussed for the Late Cretaceous geodynamic evolution of the

114 northern Neo-Tethys realm.

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117   2. Geological setting

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119   *2.1. General geological setting of the Makran Accretionary Prism*

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121   The Makran Accretionary Prism is the result of a complex Cretaceous – Present day

122 geodynamic history, which is related to the subduction of the Neo-Tethys oceanic

123 lithosphere below the southern margin of Eurasia (McCall and Kidd, 1982; Dercourt et al.,

124 1986; Saccani et al., 2018; Burg, 2018; Monsef et al., 2018; Barrier et al., 2018; Barbero et

125 al., 2020a, b). The Makran is an E-W trending active subduction complex, which is laterally

126 separated from the Zagros and the Himalayan collisional systems by N-S trending strike-

slip fault zones (Figs. 1a, b) (e.g. Dercourt et al., 1986; Kopp et al., 2000; Burg et al., 2013; Mohammadi et al., 2016; Riaz et al., 2019). The present-day deformation front of the Makran is located offshore in the Oman Sea (Fig. 1a). The onshore Makran is characterized by the tectonic juxtaposition of several tectono-stratigraphic domains (Dolati, 2010; Burg et al., 2013). In the western part of the prism these domains are from the structural top to the bottom (i.e., from the north to the south): 1) the North Makran; 2) the Inner Makran; 3) the Outer Makran; 4) the Coastal Makran (Fig. 1c). The Inner, Outer and Coastal Makran domains represent the Eocene - present day accretionary complex and include Eocene – Pleistocene mainly terrigenous sedimentary successions (e.g., Dolati, 2010; Burg et al., 2013; Burg, 2018). The North Makran domain includes remnants of pre-Eocene accretionary stages and consists of a tectonic stack of oceanic and continental derived units, some of which showing variable degrees of metamorphic imprint (e.g., McCall and Kidd, 1982; Burg, 2018). These units include from north to south and from the higher to the lowermost structural position (Fig. 1c): 1) the Ganj Complex; 2) the Northern Ophiolites, 3) the Bajgan and Durkan Complexes, 4) the Sorkhband – Rudan tectonic slices 5) the Coloured Mélange Complex.

Recent studies have shown that the Ganj Complex represents fragments of a Late Cretaceous volcanic arc that was likely built up close to the southern margin of the Lut Block (Barbero et al., 2020a). The Northern Ophiolites (Fig. 1c) are Early to Late Cretaceous in age and include the Band-e-Zeyarat/Dar Anar (Ghazi et al., 2004; Barbero et al., 2020b), Remeshk-Mokhtarabad (McCall, 1985, 2002; Hunziker et al., 2015; Burg, 2018), and Fanuj-Maskutan (Moslempour et al., 2015) ophiolitic complexes. Their magmatic rocks mostly show enriched-type mid-ocean ridge basalts (E-MORB) chemical affinity for the Early Cretaceous ophiolites (Ghazi et al., 2004; Barbero et al. 2020b), whereas the Late Cretaceous ophiolites show supra-subduction zone chemical affinity

(Burg, 2018; Monsef et al., 2019, Sepidbar et al., 2020). These ophiolitic complexes were collectively interpreted as the remnants of the oceanic lithosphere of the North Makran Ocean, which is thought to represent an oceanic basin that existed during Late Jurassic – Early Cretaceous at the southern margin of the Central Iran continental plate. The Bajgan and Durkan Complexes (Figs.1c, 2) have classically been interpreted as remnants of a microcontinental block, which was separated from the Lut Block in the Late Jurassic - Early Cretaceous. The Bajgan Complex is made up of an assemblage of metamorphic rocks that include schists, paragneisses, amphibolites, marbles, as well as basic and acidic meta-intrusive rocks (McCall, 1985; McCall, 2002; Dorani et al., 2017). The P-T condition of the metamorphism and its age are poorly constrained. However, moderately high pressure and high temperature conditions have been suggested (McCall, 1985; Dorani et al., 2017). The Durkan Complex (Figs.1c, 2) consists of a highly deformed and locally slightly metamorphosed (i.e., up to sub-greenschist facies) complex including: 1) Late Cretaceous shallow-water limestones and thick sequences of alternating limestones, sandstones, shales, cherts and volcanic rocks (Barbero et al., 2021), 2) very minor tectonic slices of Carboniferous, Permian and Jurassic shelf carbonate rocks, as well as marbles and schists (McCall, 1985, 2002; Hunziker et al., 2015); 3) Early – Late Jurassic different types of granitoids intruded into Jurassic shelf limestones in the eastern part of the Makran (Hunziker et al., 2015; Burg, 2018). This Complex has been considered as the original sedimentary cover of the Bajgan metamorphic Complex (McCall, 1985, 2002). However, based on recent multidisciplinary investigation on its western part, Barbero et al. (2021) showed that this Complex represents a tectonically disrupted Late Cretaceous seamount chain incorporated as tectonic slices into the North Makran accretionary prism.

The Deyader Complex crops out in the eastern sector of the North Makran (Fig. 1c). It represents a meta-ophiolitic complex affected by high pressure-low temperature (HP-LT)

metamorphism (McCall, 1985; Hunziker et al., 2015: Omrani et al., 2017). The Sorkhband and Rudan ophiolites crop out in the western part of the North Makran within the shear zone between the Coloured Mélange and the Bajgan Complex (McCall, 2002; Delavari et al., 2016). The Coloured Mélange Complex is composed of metric- to decametric-thick tectonic slices and was formed in Cretaceous-Paleocene times (McCall and Kidd, 1982; McCall, 2002; Saccani et al., 2018; Burg, 2018; Esmaeili et al., 2019). Saccani et al. (2018) showed that the Coloured Mélange Complex incorporates a great variety of volcanic and meta-volcanic rock-types formed in both the subducting oceanic plate (i.e., oceanic plateau basalts, normal mid-ocean ridge basalts, and alkaline basalts) and the upper plate (i.e. Early - Late Cretaceous island arc tholeiites and calc-alkaline basalts).

2.2. Stratigraphic features of the western part of the Durkan Complex

Detailed fieldwork and stratigraphic, structural, and biostratigraphic investigations have recently been carried out on the western part of the Durkan Complex (Barbero et al., 2021). This works shows that this Complex (Fig. 2) consists of several tectonic slices, within which different stratigraphic successions can be recognized (Fig. 3). The different slices include both non-metamorphic and slightly metamorphosed successions, all characterized by abundant volcanic rocks (Fig 3a). These stratigraphic successions can be reconciled to three types of successions that are similar to those found at different depths of a seamount setting. The characteristics of these successions, as described by Barbero et al. (2021) are briefly summarized in the following sections.

2.2.1. Type I succession: deep-water stage of seamount growth

This succession type represents a Coniancian - Campanian pelagic sequence consisting of thin-bedded red cherts and cherty limestones alternated with shales and shaly marls, as well as minor volcaniclastic arenites and pillow breccias. Pillow basalts are frequently interbedded within this sequence (Fig. 3a), and are characterized by low vesicolarity (Fig. 3b). These features suggest eruption under a relatively thick water column pressure (Fig. 3b). This type of succession represents the remnants of a seamount in its deep-water stages of formation characterized by pelagic sedimentation and volcanic activity in a deep-water depositional environment.

2.2.2. Type II succession: seamount flank during shallow-water stage of a seamount growth

This succession is characterized by a volcanic sequence showing stratigraphic transition to a volcano-sedimentary sequence that, in turn, gradually passes upward to a pelagic and hemipelagic sedimentary sequence (Fig. 3a). The volcanic sequence is made up of alternating massive lava flows, pillow lavas, and volcaniclastic arenites and breccias (Fig. 3a). The volcano-sedimentary sequence consists of alternating volcaniclastic arenites and breccias, shales and siltstones, and Cenomanian limestone, as well as minor massive lava flows (Fig. 3a). Limestones show pelagic foraminifera assemblages suggesting a relatively deep-water depositional setting. Accordingly, the analysis of the volume percent of vesicles for the volcanic rocks suggest a relatively high eruption depth, which is however significantly lower than those of the Type I succession (Fig. 3b). The pelagic and hemipelagic sedimentary sequence consists of cherty limestones, shales, shaly marls, cherts, and minor carbonatic breccias and volcaniclastic arenites (Fig. 3a). The stratigraphic

226   features of Type-II succession indicates a depositional setting along and at the base of a

227   seamount flank during the relatively shallow-water shield stage of growth of a seamount.

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229   2.2.3. Type III: seamount summit during shallow-water stage of seamount growth

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231   This stratigraphic succession is characterized by a volcanic sequence passing laterally

232   and upward to a volcano-sedimentary sequence that is, in turn, followed by a Cenomanian

233   carbonatic platform sequence and ends upward with a pelagic and hemipelagic sequence

234   (Fig. 3a). The volcanic sequence is characterized by pillow and massive lava flows

235   alternating with volcaniclastic arenites. The volcano-sedimentary sequence is composed by

236   alternating volcanic rocks, volcaniclastic arenites and breccias, shales, as well as turbidites

237   showing mixed carbonatic - volcanic composition (Fig. 3a). In addition, minor platform-

238   derived massive limestones are interbedded in the sequences, suggesting a shallow-water

239   depositional setting, as also indicated by the particularly high vesicolarity of the pillow

240   lavas (Fig. 3b). The Cenomanian, shallow-water carbonatic platform sequence consists of

241   massive limestones alternating with subordinate volcaniclastic arenites but lacks of lava

242   flows (Fig. 3a). The uppermost hemipelagic and pelagic sequence marks the drowning of

243   the carbonatic platform. The stratigraphy of Type-III succession record shallow-water

244   volcanic activity associated with carbonatic platform sedimentation and it is comparable

245   with the stratigraphic successions formed in seamount summit setting during the shallow-

246   water shield stage of growth.

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248

249   3. Petrography

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251   The Durkan volcanic and volcano-sedimentary sequences include both volcanic

252   (prevailing) and metavolcanic (subordinate) rocks. The metavolcanic rocks underwent re-

253   crystallization under low-grade metamorphic conditions, though magmatic relicts are

254   commonly preserved in all samples. Volcanic rocks were affected by variable degrees of

255   alteration, which resulted in different extent of replacement of the primary magmatic

256   minerals. Nonetheless, their original magmatic texture is still recognizable. Fresh

257   plagioclase is very rare, and it is usually pseudomorphosed by a fine-grained assemblage of

258   albite, calcite and sericite. Similarly, olivine crystals are commonly replaced by iddingsite

259   and serpentine plus Fe-Ti oxides. Clinopyroxene crystals are present as both phenocrysts

260   and groundmass minerals. They occur either as fresh or altered crystals characterized by

261   pseudomorphic replacement by chlorite or actinolitic amphibole. Volcanic glass has been

262   generally replaced by an assemblage of chlorite and clay minerals. The studied volcanic

263   rocks are represented by basalts, ferrobasalts, and a couple of differentiated rocks (trachyte

264   and alkali-rhyolite). Four types of petrofacies have been distinguished according to

265   textures; they are: 1) aphyric type; 2) porphyritic type; 3) coarse-grained, doleritic type; 4)

266   metamorphic type. Representative microphotographs are given as Supplementary Figure

267   S1, whereas the texture of each sample is given in Table 1.

268   The aphyric type petrofacies includes basalts and ferrobasalts, as well as one trachyte

269   sample showing aphyric to slightly porphyritic ($PI < 10$) texture. In the slightly porphyritic

270   samples, the phenocrysts consist of plagioclase, clinopyroxene, and locally olivine. They

271   are set in a hypocrystalline groundmass showing intersertal to microcrystalline texture with

272   microlite of plagioclase, olivine, and clinopyroxene and less abundant Fe-Ti oxides,

273   surrounded by altered volcanic glass. In contrast, the trachyte sample is characterized by

274   aphyric texture, showing laths of plagioclase set in altered volcanic glass.

275   The porphyritic type petrofacies includes basalts and ferrobasalts showing porphyritic

276   and glomeroporphyritic texture with PI ranging from 15 to 60. The phenocrysts are up to 5-

277   6 mm in size and are mainly represented by clinopyroxene, minor plagioclase and Fe-Ti

278   oxides, and rare olivine. Clinopyroxene phenocrysts commonly show concentric zonation

279   and weak pleochroism from pale yellow to pale pink. The phenocrysts are set in a

280   hypohyaline groundmass showing intergranular to microcrystalline textures. Rarely,

281   intersertal texture can be observed in the groundmass. The groundmass consists of

282   clinopyroxene and plagioclase together with minor olivine and altered volcanic glass.

283   The coarse-grained doleritic type includes basalts and ferrobasalts showing

284   holocrystalline, inequigranular texture. They are characterized by euhedral plagioclase and

285   euhedral to subhedral clinopyroxene crystals, up to 5 mm in size. Locally, clinopyroxene

286   encloses plagioclase crystals, showing subophitic texture. These large clinopyroxene

287   crystals are surrounded by a fine-grained crystalline aggregate consisting of euhedral to

288   subhedral plagioclase, clinopyroxene as well as Fe-Ti oxides. In ferrobasalts, opaque

289   minerals show subhedral to anhedral morphology.

290   The slightly metamorphic type petrofacies includes metabasalts, and metaferrobasalts,

291   as well as one meta-alkali-rhyolite sample showing anastomosed foliation defined by a

292   fine-grained aggregate of chlorite, fibrous amphibole, Fe-Ti oxides, subordinate epidote, as

293   well as by the alignment of albite aggregates. In most samples, the foliation envelops

294   magmatic relicts consisting of clinopyroxene and minor plagioclase. In a few samples, the

295   metamorphic foliation is well developed and it is marked by the alternation of millimetre-

296   spaced and anastomosed domains with different mineralogical composition. In detail,

297   albite-rich domains alternate with domains showing chlorite, epidote and relicts of

298   magmatic clinopyroxene. The mineralogical paragenesis of these samples, as well as the

299   fine-grained size of the metamorphic minerals indicate very low-grade metamorphic

300   overprint, likely in the sub-greenschist-facies or the prehnite-pumpellyite metamorphic

301   conditions.

302

303

304   4. Analytical methods

305

306   Whole rock major and trace element compositions of a total of forty-three samples is

307   presented in this paper. Thirty-two samples were analysed for rock major and some trace

308   elements by X-ray fluorescence spectrometry (XRF) on pressed-powder pellets, using an

309   ARL Advant-XP automated X-ray spectrometer. The matrix correction method proposed

310   by Lachance and Trail (1966) was applied. Volatile contents were determined as loss on

311   ignition (L.O.I.) at 1000°C. In addition, XRF analyses of eleven samples are taken from

312   Barbero et al. (2021). For the discussion of the geochemical characteristics of the studied

313   rocks major element composition has been re-calculated on L.O.I.-free bases. The rare

314   earth elements (REE) and some trace elements (Rb, Sr, Zr, Y, Nb, Hf, Ta, Th, U) were

315   determined by inductively coupled plasma-mass spectrometry (ICP-MS) using a Thermo

316   Series X-I spectrometer on a total of thirty-nine selected samples. All whole-rock analyses

317   were performed at the Department of Physics and Earth Sciences of the Ferrara University;

318   results are shown in Table 1, where new data from this paper and XRF data from Barbero

319   et al. (2021) are identified. The accuracy of the XRF and ICP-MS data were evaluated

320   using results for international standard rocks run as unknown. The detection limits for XRF

321   and ICP-MS analyses were evaluated using results from several runs of twenty-nine

322   international standards. Results are presented in Supplementary Table S1.

323   The major element composition of clinopyroxene were obtained by electron

324   microprobe spectrometry using a Superprobe Jeol JXA 8200 (JEOL, Tokyo, Japan) at the

325   Eugen F. Stumpfl Laboratory at the University of Leoben, Austria, using both energy

326   dispersive spectrometry (EDS) and wave-length dispersive spectrometry (WDS) systems.

327   The electron microprobe was operated in the WDS mode during the quantitative analyses.

328   An accelerating voltage of 15 kV and beam current of 10 nA were used during the

329   analyses. The diameter of the beam was about 1 μm. Counting times were 20 s on the peak

330   and 10 s on both left and right backgrounds. Standards (element, emission line) were:

331   adularia (Al and Si, Kα), rutile (Ti, Kα), chromite (Cr, Kα), almandine (Fe, Kα), rhodonite

332   (Mn, Kα), olivine (Mg, Kα), wollastonite (Ca, Kα), albite (Na, Kα), and sanidine (K, Kα).

333   The following diffracting crystals were selected: TAP for Na, Mg, and Al; PETJ for K, Si,

334   and Ca; and LIFH for Ti, Cr, Mn and Fe. The detection limits were automatically

335   calculated by the Jeol microprobe software and they are listed in the following as ppm: Na,

336   Al, Mg, K, Ca (100), Si, Cr, Fe, Mn (150) and Ti (200). The results of microprobe analyses

337   are shown in Table 2.

338

339

340   5. Whole rock geochemistry

341

342   The petrographic analysis has shown that the studied rocks have undergone secondary

343   alteration (e.g., ocean-floor hydrothermal alteration) or sub-greenschist facies

344   metamorphism; therefore, some elements may have been remobilized during these

345   processes. In fact, it is well known that large ion lithophile elements and many major

346   elements are commonly affected by alteration-induced mobilization. In addition, light REE

347   (LREE) may also have been mobilized during secondary alteration processes (e.g., Pearce

348   and Norry, 1979). In contrast, many incompatible elements (e.g., Ti, P, Zr, Y, Sc, Nb, Ta,

349   Hf, Th), middle (M) and heavy (H) REE, as well as some transition metals (e.g., Ni, Co,

350   Cr, V) are considered to be immobile during low-temperature alteration and

351   metamorphism. For these reasons, the geochemical features of the Durkan Complex

352   magmatic rocks are described using those elements considered immobile during alteration

353   processes. Rb and Ba are generally considered as mobile elements. Nonetheless, these

354   elements did not demonstrate a high degree of mobility in most samples. In fact, in these

355   samples, their contents show good correlations with immobile element contents (e.g.,

356   correlation coefficient with Rb vs. Y = 0.71). Therefore, Rb and Ba will be used, though

357   with caution.

358   The volcanic rocks of the Durkan Complex largely consist of basalts, subordinate

359   ferrobasalts and rare basaltic andesites, trachytes, and alkali rhyolites. Metabasalts and

360   metaferrobasalts though subordinate in volume are also found in all the succession types

361   (Table 1). Metavolcanic rocks will be discussed together with volcanic rocks because this

362   paper is focused on the identification of the geochemical features of the original volcanic

363   protoliths and their tectono-magmatic setting of formation, regardless of the tectono-

364   metamorphic events that affected some tectonic slices of volcanic rocks during their late

365   incorporation in the accretionary wedge. For the sake of simplicity, the prefix "meta" will

366   be hereafter omitted. Basaltic rocks show variable major and trace elements compositions

367   (Table 1), which most likely suggest that they represent melts at different stages of

368   fractionation. Based on the Nb/Y ratios (Winchester and Floyd, 1977; Pearce, 1996), we

369   can distinguish two main groups of rocks (Fig. 4). Group 1 rocks show a transitional nature

370   with Nb/Y ratios in the range 0.8-1.00, whereas Group 2 rocks show a clear alkaline

371   affinity with Nb/Y ratios >1 (1.15-3.16).

372

373   *5.1. Group 1 rocks*

374

375   This group includes basaltic, basaltic andesitic, and ferrobasaltic rocks, as well as one

376   trachyte sample. These rocks are mainly found in the Type-I succession, whereas they are

377   less abundant in the Type-II succession and completely lacking in Type-III succession

378   (Table 1). Group 1 basalts show a wide range of composition in terms of SiO_2 (43.3 – 53.3

379   wt%), MgO (4.93 – 11.9 wt%), Al_2O_3 (12.2 – 17.2 wt%), and Mg# (47.8 – 75.4),

380   suggesting that they were likely formed from melts at different degrees of fractionation.

381   The basaltic rocks are characterized by relatively high TiO_2 (1.20 – 2.29 wt%), P_2O_5 (0.23

382   – 0.51 wt%), Zr (73 – 220 ppm), Nb (13.5 – 32.6 ppm), Th (1.49 – 3.66 ppm), and Ta (0.92

383   – 2.18 ppm) contents coupled with relatively low Y contents (16.9 - 33.5 ppm).

384   Compatible elements (Cr, V, Ni, and Co) contents are variable, but generally high, as

385   expected for basaltic rocks (Table 1). The Ti/V ratios are in the range 28 – 61, which are

386   values typically observed in MORB to alkaline transitional basalts (Shervais, 1982).

387   Normal type MORB (N-MORB) normalized incompatible elements spider-diagrams

388   display regularly decreasing patterns from Th to Yb, (Fig. 5a). Yb content in basaltic

389   samples is relatively low, ranging from 0.49 to 0.82 times N-MORB (Sun and

390   McDounough, 1989) abundance (Fig. 5a). Group 1 rocks show mild LREE enrichment

391   with respect to HREE, as well as moderate depletion of HREE if compared to MREE (Fig.

392   5b). This is testified by the $(La/Yb)_N$, $(Sm/Yb)_N$, and $(Dy/Yb)_N$ ratios, which are in the

393   range 4.44 – 7.86, 1.18 – 3.16, and 1.25 – 1.56, respectively (Figs. 6a, b). The Yb and La

394   contents are in the range 8.5 - 13.8 and 37.8 - 90.3, times chondrite abundance,

395   respectively (Figs. 5b, 6c). The overall chemical features of the Group 1 rocks are similar

396   to those of many plume-type MORB (P-MORB) in modern oceanic settings (e.g., Le Roex

397   et al., 1983; Sun and McDounough, 1989; Haase and Devey, 1996). Accordingly, in the

398   discrimination diagram in Fig. 7, these rocks plot in the fields for oceanic subduction-

399   unrelated setting, between the compositional fields of P-MORBs and Alkaline basalts.

16

These geochemical data collectively suggest a P-MORB affinity for Group 1 basaltic rocks. Compared to the basaltic samples, the trachyte MK795 shows higher SiO_2 and lower MgO contents (Table 1). As commonly observed in highly fractionated rocks, this sample shows very high Zr (701 ppm) and Y (58 ppm) contents and very low contents of compatible elements, TiO_2 and P_2O_5 (Table 1) as a consequence of early crystallization and removal of mafic minerals, Fe-Ti oxides, and apatite. In fact, this sample shows N-MORB normalized incompatible elements spider-diagrams with significant Ti and P negative anomalies (Fig. 5a). The chondrite-normalized REE pattern of this sample shows a marked Eu negative anomaly and depletion of middle REE (MREE) with respect to HREE (Fig. 5a), which suggest crystallization and removal of plagioclase and amphibole, respectively, prior to the formation of the trachytes melts.

5.2. Group 2 rocks

The Group 2 rocks include basaltic, and ferrobasaltic rocks, as well as one alkali rhyolitic sample. These rocks show a clear alkaline affinity, as indicated by Nb/Y ratios greater than 1 (Table 1, Fig. 4). Basaltic rocks are characterized by SiO_2 ranging from 41.94 to 53.52 wt% and Mg# ranging between 75 and 39 suggesting that these rocks represent melts at different stages of magmatic fractionation. Accordingly, these rocks show marked variation of MgO and Al_2O_3 contents (Table 1). The basaltic rock of the Group 2 show relatively high contents of TiO_2 (1.55 – 5.13 wt%), P_2O_5 (0.20 – 1.10 wt%), Zr (139 – 403 ppm), Nb (23.6 – 71.8 ppm), and Ta (1.42 – 5.13 ppm). Ti/V ratios (41 - 76) are in the range for alkaline basalts (Shervais, 1982). In contrast, Y abundance is rather low, ranging between 18.5 to 33.0 ppm. Compared to Group 1 basalts, the Ti/Y (526 – 1448) and Zr/Y (6.7 – 20.6) ratios in Group 2 basalts are higher. The N-MORB normalized

incompatible elements spiderdiagrams (Figs. 5c, e) display decreasing patterns from Th to Yb. Yb contents are ~0.6 times N-MORB abundance and are comparable with those of Group 1 rocks. In contrast, both Ta and Nb contents are slightly higher than those of Group 1 rocks (Figs. 5a, c, Table 1). The chondrite normalized REE patterns (Figs. 5d, f) show marked decrease from LREE to HREE (La_N/Yb_N = 9.26 – 28.07) with Yb and La contents ranging from ~6 - 13 to ~ 100 - 250 times chondrite abundance (Sun and McDonough, 1989), respectively. In addition, HREE show marked depletion with respect to MREE, as exemplified by the $(Sm/Yb)_N$ ratios (3.5 – 8.4), which are higher with respect to those of Group 1 (Figs. 6a, b; Table 1).

By contrast, alkali rhyolite sample MK339 shows higher contents of SiO_2 and lower MgO abundance with respect to the basaltic rocks (Table 1). This sample shows very high Zr (608 ppm) and Y (69.9 ppm) and very low contents of compatible elements, TiO_2 and P_2O_5 (Table 1). This sample shows N-MORB normalized incompatible elements spider-diagrams with significant Ti and P negative anomalies (Fig. 5c). The chondrite-normalized REE pattern of this sample shows a marked Eu negative anomaly and depletion of HREE with respect both LREE and MREE (Fig. 5d). The overall geochemical features of Group 2 rocks are very similar to those of the within-plate alkaline volcanic rocks typically forming oceanic islands (e.g., Yang et al., 2015; Safonova et al., 2016 and reference therein). In the discrimination diagram in Figure 7, the Group 2 rocks plot close to the composition of the ocean island basalt (OIB) (Sun and McDonough, 1989) and within the field for subduction unrelated alkaline basalts.

Although Group 2 basaltic rocks show similar major elements and most trace elements contents at comparable degree of fractionation (e.g., comparable Mg#), two different subgroups of samples (hereafter named as Group 2a and Group 2b) can be identified based on different REE patterns and REE ratios, as well as different ratios of some trace

18

450 elements. These differences are summarized by the REE ratios shown in Figure 6. Group

451 2a basaltic rocks show definitely lower $(La/Yb)_N$ and $(Sm/Dy)_N$ ratios compared to Group

452 2b equivalents (Figs. 6a, b). In contrast the $(Sm/Yb)_N$ ratios shown by Group 2a and Group

453 2b rocks are largely overlapping, though, as a general tendency, these ratios are

454 comparatively higher in Group 2b rocks (Figs. 6a, b). The variation of the REE ratios

455 shown in Figure 6 is totally independent from the degree of fractionation of the different

456 samples. It should also be noted that there is no correlation between the LREE/HREE (e.g.,

457 La_N /Yb_N) ratio and the absolute concentration of HREE (e.g., Yb_N) suggesting that the

458 enrichment in LREE with respect to HREE is totally independent on the absolute content

459 of HREE (Fig. 6c). In addition, Group 2b rocks show higher Nb/Y (Fig. 4), Nb/Yb, and

460 Th/Tb ratios compared to basaltic rocks of Group 2a

461

462

463   6. Clinopyroxene chemistry

464

465   No unaltered olivine or plagioclase was identified in the studied rocks, and

466 clinopyroxene underwent secondary alteration in many of the studied samples.

467 Nonetheless, a detailed petrographic study allowed us to recognize fresh clinopyroxene

468 crystals in basaltic samples of the different rock groups, as well as fresh magmatic

469 clinopyroxene relics in one metabasaltic sample. Representative chemical analyses of these

470 crystals are shown in Table 2, whereas their classification according to the quadrilateral

471 diagram is given in Supplementary Figure S2. In addition to crystal-chemical constraints,

472 the clinopyroxene composition is strongly influenced by the composition of the magmas

473 from which they crystallized. According to Leterrier et al. (1982) and Beccaluva et al.

474 (1989), clinopyroxene composition represents a petrogenetic indicator of the chemical

475 affinity of the magmatic melts from which they crystallized. Therefore, the mineral

476 chemistry of clinopyroxene can provide us robust constraints for understanding the

477 tectono-magmatic setting of formation of basaltic melts. The chemical features of

478 clinopyroxenes will be described according to the whole rock chemical groups.

479

480 *6.1. Group 1 rocks*

481

482 Clinopyroxenes in Group 1 basalts show augitic composition with the wollastonite

483 end-member ranging from ~38% to ~42% (Table 2). Clinopyroxenes of Group 1 rocks

484 show Mg# in the range 0.77 - 0.65, likely reflecting the crystallization from melts at

485 different fractionation stages. CaO, Al_2O_3, and Cr_2O_3 decrease with decreasing Mg#,

486 whereas FeO_{tot} and TiO_2 generally increase with the decreasing Mg# (Table 2). They

487 display relatively low contents of TiO_2 (0.91 – 1.45 wt%), Na_2O (0.28 – 0.46 wt%) and

488 CaO (19.26 – 21.11 wt%) compared to clinopyroxenes from Group 2a and Group 2b rocks

489 (Table 2, Fig. 8). Al_2O_3 (1.44 – 3.06 wt%) is lower than Group 2a and Group 2b

490 clinopyroxene at comparable value of Mg# (Table 2). The Cr_2O_3 content is relatively low

491 and shows positive correlation with Mg#. They are commonly unzoned; only three crystals

492 show little chemical variation from core to rim (Table 2). According to the discrimination

493 diagrams proposed by Leterrier et al. (1982), clinopyroxenes from Group 1 basalts plot in

494 the field for clinopyroxene from sub-alkaline tholeiitic and calc-alkaline rocks and are

495 clearly distinguished from clinopyroxene from Group 2a and Group 2b (Fig. 9a). In

496 addition, the (Ti + Cr) vs. Ca diagram shows that clinopyroxene from Group 1 rocks

497 display MORB affinity (Fig. 9b). Accordingly, in the discrimination diagram of Beccaluva

498 et al., (1989), they plot in the field for clinopyroxene from MOR and within-plate oceanic

499 settings (Fig. 10).

6.2. Group 2a rocks

Clinopyroxene from Group 2a were analysed in basalts and ferrobasalts. They mainly show augitic composition, though a few crystals display diopsidic composition. The wollastonite end-member range from ~43% to ~50% (Table 2). Mg# is generally high, ranging from 0.74 to 0.84. TiO_2 (1.01 – 2.1 wt%), Na_2O (0.33 – 0.5 wt%), CaO (21.02 – 22.3 wt%), and Al_2O_3 (2.66 – 4.39 wt%) contents are generally higher than in clinopyroxene from Group 1 rocks (Table 2; Fig. 8). Cr_2O_3 content is variable (0.12 – 0.67 wt%) and gradually decreases with decreasing Mg#. The crystals from sample MK479 are unzoned whereas those from sample MK491 commonly show zoning with Mg# in cores higher than the rims. This variation is coupled with an increase of TiO_2, Al_2O_3, and FeO_{tot} contents, and a decrease of Cr_2O_3, MgO, and CaO from core to rim (Table 2). These compositional variations likely reflect fractional crystallization processes during the growth of the crystals, as typically observed in clinopyroxene from ophiolitic sequence (Beccaluva et al., 1989). In the Ti – (Ca + Na) variation diagram, the clinopyroxenes from Group 2a rocks plot in the field for pyroxene from alkaline rocks and are clearly distinguished from the clinopyroxene of the Group 1 rocks (Fig. 9). Accordingly, in the discrimination diagram of Beccaluva et al. (1989), they plot in the field for clinopyroxenes typical of plume-influenced Iceland basalts and within-plate oceanic basalts (Fig. 10).

6.3. Group 2b rocks

Clinopyroxene from Group 2b rocks were analysed in basaltic, ferrobasaltic and metabasaltic samples (Table 2). They are mainly represented by diopsidic clinopyroxenes

525   and minor augite. The wollastonite end-member ranges from ~47% to ~49% (Table 2).

526   Mg#, though variable, is generally high (0.74 - 0.87). Clinopyroxenes in Group 2b rocks

527   show generally higher contents of TiO_2 (1.26 – 3.69 wt%), Na_2O (0.28 – 0.66 wt%), CaO

528   (21.7 – 24.3 wt%), and Al_2O_3 (2.88 – 7.08 wt%) compared to those from the other groups

529   of rocks (Fig. 8). Cr_2O_3 contents vary from 0.01 to 1.0 wt% and are positively correlated

530   with Mg# values. Concentric zoning and multiple zones of growth are frequently observed.

531   The zoning is associated to significant chemical variations of TiO_2, CaO, Al_2O_3, Na_2O,

532   MgO, FeO_{tot} and Cr_2O_3 contents from core to rim (Table 2). Generally, the core of the

533   crystals shows higher MgO, Cr_2O_3, and CaO contents coupled with lower TiO_2, Al_2O_3,

534   Na_2O, and FeO_{tot} contents with respect to the rim. However, reverse zoning is observed in

535   some crystals. In addition, some crystals show concentric, oscillatory zoning characterized

536   by different zones of growth, showing rhythmic variation of TiO_2, CaO, Al_2O_3, Na_2O,

537   MgO, FeO_{tot} and Cr_2O_3 contents (Table 2). This is particularly evident for the sample

538   MK859cr1, in which TiO_2, Na_2O, MgO, and Cr_2O_3 show oscillatory chemical variation

539   from the core to the rim of the crystal (Table 2). These features collectively indicate that

540   the growth of the crystals occurred either from a progressively differentiating melt or from

541   the equilibrium with different pulses of new batches of primitive melts at different

542   fractionation stages. The clinopyroxenes of the Group 2b rocks plot in the field for

543   clinopyroxene of alkaline rocks (Fig. 9). An alkaline affinity for the clinopyroxene of

544   Group 2b rocks is also suggested by the discrimination diagram in Figure 10, where they

545   plot within the field for plume-influenced Iceland and within-plate oceanic basalts.

546

547   *6.4. Correlation of clinopyroxene composition vs. whole rock geochemistry*

548

549   Our mineral chemistry data show that there is a close relationship between the

550   composition of clinopyroxenes and the compositions of their hosting rocks. The diagrams

551   in Figure 8 show that the variations of TiO_2, CaO, and Na_2O with respect to the variations

552   of Mg# in clinopyroxenes depict different trends depending on the different rock groups in

553   which these minerals are hosted. Clinopyroxenes from Group 1 transitional basaltic rocks

554   show relatively smooth increase in TiO_2 and Na_2O contents coupled with relatively sharp

555   decrease in CaO contents with decreasing Mg#. In contrast, in clinopyroxenes from the

556   alkaline basaltic rocks of Group 2a and Group 2b TiO_2 and Na_2O contents show sharp

557   increase with decreasing Mg#, whereas CaO contents decrease very smoothly with

558   decreasing Mg# (Fig. 8). In addition, clinopyroxenes from Group 2a and Group 2b show

559   distinct elemental behaviour with respect to the variation of Mg# values (Fig. 8). In

560   particular, clinopyroxenes from Group 2b show the relatively sharper increase of TiO_2 and

561   Na_2O contents with decreasing Mg# compared to clinopyroxenes from Group 2a (Figs. 8a,

562   c). Clinopyroxenes from Group 2a basaltic rocks are also characterized by higher (Ca +

563   Na) contents compared to those from Group 2b (Fig. 9). The variation in TiO_2 contents in

564   clinoyroxenes is commonly thought to reflect the degree of depletion or enrichment of the

565   mantle source (Pearce and Norry, 1979). High TiO_2 content in clinopyroxenes point out for

566   their crystallization from primary magmas generated from enriched mantle sources. The

567   diagrams in Figure 11 clearly show a positive correlation between the Nb/Y ratios of the

568   hosting rocks and the TiO_2, CaO, and Al_2O_3 contents of their clinopyroxenes. The increase

569   in Nb/Y ratios in basaltic rocks is commonly associated with the increase of enrichment of

570   the mantle sources from which they originated (Winchester and Floyd, 1979; Pearce, 1996,

571   2008). The contents in TiO_2, CaO, and Al_2O_3 in clinopyroxenes increase from transitional

572   Group 1 basalts to alkaline Group 2a and Group 2b basaltic rocks. Different compositions

573   and elemental co-variations can clearly be distinguished in the clinopyroxenes of the

23

574   different groups of rocks (Figs. 8, 9, 11). This evidence further supports the conclusions

575   obtained from whole rock chemistry that is, in the Durkan volcanic and metavolcanic rocks

576   three different groups of rocks can be identified (see section 5).

577

578

579   7. Discussion

580

581   *7.1. Melt petrogenesis of the volcanic and metavolcanic rocks*

582

583   The aim of this petrogenetic discussion is to identify the possible mantle sources for

584   the volcanic rocks and the magmatic protoliths of the metavolcanic rocks from the Durkan

585   Complex, as well as their melting conditions, in order to provide robust constraints for the

586   interpretation of the tectono-magmatic setting of formation of this Complex. Sections 5

587   and 6 have shown that the volcanic and metavolcanic rocks of the Durkan Complex exhibit

588   whole-rock and mineral chemistry with transitional (Group 1) and alkaline (Group 2a and

589   Group 2b) affinities. The different trace elements contents (e.g., Zr, Y, Nb) and REE

590   patterns (Fig. 5) observed in the rocks of these three groups, as well as their different

591   incompatible element (e.g., Zr/Y, Y/Nb, Nb/Yb) and REE ratios (i.e., La_N/Yb_N, Sm_N/Yb_N,

592   Sm_N/Dy_N,) (Table 2, Fig. 6) suggest that these rocks were derived from partial melting of

593   chemically distinct mantle sources and/or different melting conditions. Very similar HREE

594   (e.g., Yb) contents and no correlations between the LREE/HREE (i.e., La_N/Yb_N) ratios

595   observed in all rock groups (Table 2, Fig. 6c) suggest that the differences in the chemistry

596   of their possible mantle sources most likely consisted of different enrichments in LREE,

597   Zr, and Nb. A first idea about the petrogenesis of the Durkan volcanic and metavolcanic

598   rocks can be deduced from the Zr-Nb co-variation diagram in Figure 12a, which shows

24

599   that these rocks were generated by partial melting of an enriched and/or transitional mantle

600   source. The mineral chemistry of the clinopyroxenes, in particular their high TiO_2 contents,

601   also point out for the genesis of these rocks from a transitional to enriched mantle sources

602   (Fig. 10). The diagram in Figure 12b further supports this conclusion; in fact, the studied

603   rocks plot along the mixing curve between N-MORB and OIB with compositions

604   clustering toward the OIB end member. In addition, the enrichment of OIB-type chemical

605   components increases from Group 1 to Groups 2a and 2b (Fig. 12b). The Th-Nb co-

606   variation (Fig.7) further point out for a genesis of the studied rocks from the partial melting

607   of mantle sources that have been influenced by OIB-type chemical components prior to

608   melting without any contributions from subduction related chemical components and/or

609   continental crust contamination.

610   Given these considerations, we performed a semi-quantitative non-modal, batch partial

611   melting modelling in order to constrain the possible mantle peridotite compositions and

612   melting conditions that can reproduce the compositions of the most primitive basalts for

613   each geochemical group of rocks. An accurate definition and quantification of the

614   composition of mantle sources and degrees and depths of partial melting generating the

615   different rock-types is not possible, as these factors cannot be exactly constrained.

616   Therefore, we used different models based on incompatible trace elements ratios and REE

617   in order to better constrain the petrogenesis of the studied rocks (Figs. 13, 14). These

618   elements are used in the commonly accepted assumption that their content in basaltic rocks

619   basically depend on the composition of the mantle source and its degree of partial melting

620   and it is little influenced by moderate degrees of fractional crystallization of olivine,

621   clinopyroxene and plagioclase (e.g., Allègre and Minster, 1978).

622   The models in Fig. 13 have the advantage of combining information about the

623   increasing of enrichment of the mantle source (i.e., increasing of Nb/Yb with respect to

TiO$_2$/Yb in Fig. 13a and increasing of Th with respect to Nb/Yb in Fig. 13b) and the

presence of residual garnet in the source (i.e., TiO$_2$/Yb in Fig. 13a and Nb/Yb compared to

Th in Fig. 13b). Results from these binary models have been then compared with the REE

model (Fig. 14). We have previously shown that the composition of the Durkan volcanic

and metavolcanic rocks strongly point out for a genesis from partial melting of sub-oceanic

mantle sources that have been influenced by OIB-type chemical components. Therefore, in

our models we chose as a possible mantle source for the Durkan basaltic rocks a sub-

oceanic slightly depleted lherzolite residual after small volume of MORB melt extraction

metasomatized to various extents of enrichment by an OIB-type chemical component. In

our models, we used the lherzolite ZB2 from the Northern Apennines (Barbero et al.,

2020c) as representative of a slightly depleted sub-oceanic mantle and the enriched mantle

of Lustrino et al. (2002) as the metasomatizing chemical component. The modal

compositions of the assumed mantle sources, their chemical composition, the melting

proportions and the REE and trace elements distribution coefficients used in the models are

listed in Supplementary Table 2.

7.1.1. Group 1 rocks

The Nb/Yb vs. TiO$_2$/Yb model (Fig. 13a) shows that Group 1 rocks cannot be

generated from the partial melting of sources with depleted composition as the DMM

(Workman and Hart, 2005) or the lherzolite ZB2 (Barbero et al., 2020c). By contrast, the

geochemistry of Group 1 primitive basalts is compatible with the partial melting of a

calculated S1 mantle source that is significantly more enriched in Nb with respect to the

DMM and ZB2 mantle peridotites (Fig. 13a). The high TiO$_2$/Yb ratios characterizing the

Group 1 basalts can be explained by the presence of residual garnet in the mantle source

649 and, therefore, that partial melting started in the garnet-facies mantle (Fig. 13a).

650 Accordingly, the Nb/Yb vs. Th petrogenetic model suggest that the compositions of Group

651 1 primitive basalts can be explained by partial melting of the enriched mantle source S1

652 that starts partial melting in the garnet-facies mantle and continues to larger degrees in the

653 spinel-facies mantle. In detail, the model shows that partial melting degrees are ~2% and

654 ~7% in garnet- and spinel-facies, respectively with mixing of the different melts produced

655 in equal proportions (Fig. 13b).

656   The REE modelling well confirms these results clearly indicating that the REE

657 composition of Group 1 basalts can be explained by partial melting of the mantle source

658 S1, which is significantly enriched in LREE with respect to the DMM and the residual sub-

659 oceanic peridotite ZB2 by OIB-type chemical components (Fig. 14a). According to the

660 results from the models shown in Figure 13, the rather high $(Sm/Yb)_N$ ratios displayed by

661 Group 1 rocks suggest the involvement of residual garnet in their mantle source. In fact,

662 the composition of Group 1 primitive basalt MK282 fits well with the melt calculated for

663 2.5% and 7.5% of partial melting of the S1 mantle source at garnet- and spinel-facies,

664 respectively, with a mixing proportion between melts generated in the garnet and spinel

665 melts of 50:50 (Fig. 14a). Different melting degrees and mixing proportions of different

666 melts (Fig. 14a$_1$) fail to reproduce the REE composition of the Group 1 relatively primitive

667 basalt.

668   The fairly differentiated trachyte MK795 clearly display different geochemical

669 patterns compared to basaltic rocks of this Group (Figs. 5a, b). Shallow-level (i.e., magma

670 chamber) petrogenetic processes are beyond the scope of this work since the main goal of

671 this paper is to define the petrogenesis of primary melts in order to constrain their tectono-

672 magmatic setting of formation. In addition, as commonly seen in ophiolites, the

673 tectonically dismembered nature of the volcanic series does not allow basalt-differentiated

674 rocks comagmatic relationships to be reliably constrained. This is particularly true in the

675 Durkan Complex where differentiated samples are very rare. However, differentiated rocks

676 may have various origins and may eventually not be genetically related to the associated

677 mafic rocks. In fact, they may have been generated by fractional crystallization, partial

678 melting of lower crustal rocks (i.e., anatexis), mixing of different melts, etc. We therefore

679 performed Rayleigh fractionation model using REE. Results are shown in Supplementary

680 Figure S3 together with model parameters and constraints. This model clearly indicates

681 that the REE compositions of the trachyte MK795 is compatible with the composition of a

682 24% residual melt after various steps of crystal fractionation of olivine, plagioclase,

683 clinopyroxene, hornblende, magnetite, and ilmenite starting from the composition of the

684 near-primary basalt MK282 used in the mantle partial melting model shown above (see

685 also Figs. 13, 14). It follows that trachyte MK795 represent a differentiated product formed

686 by fractional crystallization.

687

688   7.1.2. Group 2a and Group 2b rocks

689

690   Group 2a and Group 2b alkaline rocks collectively show overall whole rock chemistry

691 (Table 1; Fig. 6) and mineral chemistry (Fig. 9) that are quite different from those of the

692 transitional Group 1 rocks. In particular, basaltic rocks from these groups show much

693 higher Nb, Ta, Th, LREE/HREE and MREE/HREE ratios with comparable Yb absolute

694 contents (Fig. 6; Table 1), which cannot be explained with partial melting of the S1 source.

695 These chemical features point out for a genesis from a mantle source more enriched

696 (source S2) in these elements and LREE compared to the theoretical S1 source. Similar to

697 Group 1 rocks, the high $(La/Yb)_N$, TiO_2/Yb, and Nb/Yb ratios of Group 2a and Group 2b

698 rocks suggest residual garnet in the mantle source (Figs. 6a, 13). Nonetheless, Group 2a

and Group 2b rocks, though very similar in composition for many elements, slightly differ

in their $(La/Yb)_N$ and $(Sm/Dy)_N$ ratios (Fig. 6). These differences can be explained either

with slightly different compositions of their mantle sources or different proportions of

partial melting in the garnet- and spinel-facies mantle. However, the chemical differences

between basalts of these two groups are limited to a few elemental ratios basically

involving HREE (e.g., TiO_2/Yb, Nb/Yb, Th/Tb, Sm/Dy). As a consequence, it is

reasonable to assume that the chemical differences between basalts of these two Groups

are most likely due to different proportions of partial melting in the garnet- and spinel-

facies mantle, rather than chemical differences of the mantle sources. Therefore, in the

models in Figures 13 and 14 we use the same theoretical mantle source S2 for both Group

2a and 2b basalts. In fact, the TiO_2/Yb vs. Nb/Yb model suggests that the genesis of

relatively primitive basalts from both rock groups is related to the partial melting of the

mantle source S2 that starts in the garnet-facies mantle. However, the composition of the

relatively primitive basalt of Group 2a is compatible with partial melting starting at a

higher pressure (4GPa) compared to Group 2b primitive basalt (3GPa) (Fig. 13a). The

Nb/Yb vs. Th model show that the composition of Group 2a relatively primitive basalt

MK340 is compatible with ~2% partial melting of the source S2 in the garnet-facies mantle

followed by 5% partial melting in the spinel-facies mantle, with mixing of the different

melts in the proportions 60% garnet melt - 40% spinel melt. (Fig. 13b). In contrast, the

composition of Group 2b relatively primitive basalt MK499 is compatible with 1% partial

melting of the source S2 in the garnet-facies mantle followed by ~3% partial melting in the

spinel-facies mantle, with mixing of the different melts in the proportions 65% garnet melt

- 35% spinel melt. (Fig. 13b).

Accordingly, REE model indicates that the REE composition of the relatively

primitive basalt MK340 (Group 2a) can be explained by ~2 % partial melting in the garnet-

facies and ~5% partial melting in the spinel-facies of the mantle source S2 with mixing of
the different melts in the proportions 60% garnet melt - 40% spinel melt (Fig. 14b).
Likewise, the REE model carried out for Group 2b rocks (Fig. 14c) is perfectly in
agreement with the models based on TiO_2, Nb, Th, and Yb contents (Fig. 13). The model
in Figure 14c shows indeed that the REE composition of the relatively primitive basalt
MK499 is compatible with 1.5% partial melting in the garnet-facies mantle followed by
4% partial melting in the spinel-facies mantle of the source S2, with mixing of the different
melts in the proportions 65% garnet melt - 35% spinel melt.

As already discussed in section 7.1.1 for the trachyte MK795, the different chemistry
of the alkali rhyolite MK339 compared to Group 2 basalts (Figs. 5c-f) may reflect the
effect of fractional crystallization, or anatexis, or other petrogenetic processes. Rayleigh
fractionation model using REE are shown in Supplementary Figure S3. This model clearly
shows that the REE compositions of the alkali rhyolite MK339 is compatible with the
composition of a 25% residual melt after various steps of crystal fractionation of olivine,
plagioclase, clinopyroxene, magnetite, and ilmenite starting from the composition of the
near-primary basalt MK340 used in the mantle partial melting model for Group 2a rocks
(see also Figs. 13, 14b).

7.2. Tectono-magmatic significance of the volcanic and metavolcanic rocks

Previous studies have suggested that the Durkan Complex represents remnants of the
Permian - Cretaceous continental margin of the Bajgan Complex microcontinental
basement (McCall, 1985; Hunziker et al., 2015). However, a recent multidisciplinary study
of the western part of the Durkan Complex has demonstrated that it consists of Late
Cretaceous volcano-sedimentary successions, which represent portions of a seamount or,

most likely, of a seamount chain (Barbero et al., 2021). The geochemical and mineral

chemistry data, as well as petrogenetic models presented in this paper collectively suggest

that the volcanic rocks in these sequences consist of an association of transitional P-

MORBs and alkaline OIBs, which were formed by partial melting of enriched mantle

sources with variable contribution of melts formed at both garnet- and spinel-facies. These

data strongly support the interpretation of the Barbero et al. (2021). In Figure 15 we

therefore propose a schematic tectono-magmatic model that can explain the petrogenetic

processes, which occurred during the formation of the Durkan seamount chain. According

to Barbero et al. (2021), the Type-II and Type-III volcano-sedimentary successions consist

of remnants of seamount flank and seamount summit depositional and eruptional settings,

respectively, and were formed during the Cenomanian in the shallow-water stage of

growth of a seamount (Fig. 15a). These types of successions are characterized by alkaline

volcanic rocks (Group 2a and Group 2b), whose geochemistry and melt petrogenesis (see

section 7.1) clearly indicate that they derived from low degree of partial melting at both

garnet- and facies-spinel of an enriched OIB-type (plume-type) mantle source (S2 in Fig.

15a). By contrast, the Type-I volcano-sedimentary succession represents the remnants of

Coniacian – early Campanian sedimentation and volcanism in a pelagic setting during the

deep-water stage of growth of a seamount (Fig. 15b; Barbero et al., 2021). This Type of

succession is mainly characterized by transitional P-MORB rocks (Group 1) and minor

Group 2a alkaline rocks, whereas Group 2b basalts were not found in this succession. The

petrogenetic model show that, compared to Group 2a basalts, Group 2b basalts are

characterized by higher proportions of melts formed at garnet-facies with respect to melts

formed at spinel-facies mantle and an overall smaller degree of partial melting (Fig. 14).

By contrast, the deep-water stage of formation of the seamounts was characterized by the

partial melting of an enriched mantle source bearing strongly enriched mantle patches

774 (sources S1 and S2, respectively in Fig. 15b). The lack of Group 2b rocks and the

775 prevalence of Group 1 rocks may also be explained by mantle partial melting at relatively

776 shallower depth and higher partial melting degree during the deep-water stage of the

777 seamount formation with respect to the shallow-water stage of the seamount growth (Figs.

778 15a, b). In addition, this implies a minor contribution of melts produced at garnet-facies

779 with respect to the shallow-water stage of the seamount growth. These features are

780 compatible with oceanic within-plate magmatism related to the rising of deep, enriched

781 mantle plume material (Figs. 15a, b). Indeed, mantle plumes are likely the most effective

782 mean for transferring anomalous heat flux and enriched chemical components from the

783 lower to the upper mantle (e.g., Regelous et al., 2003; Pearce, 2008; White, 2010; Kerr,

784 2014; Safonova and Santosh, 2014). The rising of mantle material that is more enriched

785 and hotter than the ambient sub-oceanic mantle facilitates the starting of the partial melting

786 at deeper level within the garnet stability field (Figs. 15a, b). This can well explain the

787 clear residual garnet geochemical signature shown by all the studied rocks. The processes

788 responsible for the geochemical variation of the erupted basalts during the different stage

789 of growth of the Durkan seamount chain are difficult to be constrained in detail, mainly

790 because of the disrupted tectonic nature of the different Durkan successions, which is, in

791 turn, related to multiple deformative events occurred during their incorporation into the

792 accretionary prism (Barbero et al., 2021). However, it is commonly accepted that during

793 the progressive growth of seamounts, from the early stage of formation to their emergence

794 above the sea level (i.e., shallow-water shield stage), the volcanic products progressively

795 change from tholeiitic rocks to progressively more enriched transitional and alkaline rocks

796 (e.g., Moore and Clague, 1992; Regelous et al., 2003). In this classical scenario the Durkan

797 Type I, II and III successions are associated with progressive chemical changes of magmas

798 from tholeiitic to alkaline signatures, which could be mainly derived from different degrees

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799 of partial melting of variably enriched mantle sources. The chemical composition of

800 analysed clinopyroxenes is also consistent with progressive chemical changes of magmas

801 from tholeiitic to alkaline nature. The chemical variation of seamount volcanic rocks may

802 be explained by the combination of several factors, such as: 1) the increasing contribution

803 from an enriched mantle source to the ambient sub-oceanic mantle; 2) the decreasing in

804 partial melting degrees; 3) the increase of the depth of partial melting; 4) the variation of

805 the thickness of the melting column (e.g., Regelous et al., 2003; Safonova, 2008; White,

806 2010; Safonova and Santosh, 2014). According to Safonova et al. (2016), the large

807 volumetric prevalence of alkaline rocks in the shallow-water shield stage of the Durkan

808 volcano-sedimentary sequences suggest relatively higher contributions of melting in the

809 garnet-facies of a strongly enriched mantle source during this stage coupled with the

810 decrease of the overall partial melting degree (Fig. 15a). These features are consistent with

811 the deepening of the partial melting region in response of the enhancing of the lithospheric

812 load (i.e., crust + lithospheric mantle) due to the thickening of the seamount edifice

813 coupled with an increasing of the mantle plume influence on the sub-oceanic ambient

814 mantle and a shortening of the melting mantle column (Fig. 15a). By contrast, during the

815 deep-water stage of the seamount life the crustal load is significantly lower. In this stage,

816 the sub-oceanic mantle is relatively less influenced by the metasomatizing effects of the

817 mantle plume (Fig. 15b). The combination of these effects likely produces partial melting

818 of a moderately enriched mantle source, though partial melting may also involve strongly

819 enriched portions of the mantle. In this stage, partial melting in the spinel-facies is

820 prevailing with respect that in the garnet-facies mantle as the melting mantle column is

821 rather wide (Fig. 15b). This hypothesis agrees with data from both modern and ancient

822 seamounts, which point out the importance of the lithospheric thickness in controlling the

823 melting processes associated with the rising of a mantle plume. In detail, a thin lithosphere

824 above a mantle plume causes the shallowing of partial melting combined with higher

825 degree of the partial melting, producing melts less enriched in LREE with respect to M-

826 and HREE. By contrast, higher thickness of lithosphere likely causes the deepening of the

827 partial melting region combined with the decrease of the partial melting degree and the

828 shortening of the melting column, thus, promoting the prevalence of partial melting at the

829 garnet-facies (e.g., Regelous et al., 2003; Safonova, 2008; White, 2010).

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832 *7.3. Geodynamic significance of the western Durkan Complex: A Late Cretaceous*

833 *seamount chain in the northern Neo-Tethys?*

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835 Cretaceous alkaline and OIB rocks comparable with those of the Durkan Complex are

836 widespread within the Neo-Tethys-related collisional belts from Caucasus to Himalaya.

837 They have commonly been interpreted as remnants of seamounts and/or oceanic plateau

838 associated with mantle-plume activity (e.g., Rolland et al., 2010, 2020; Saccani et al.,

839 2013, 2018; Yang and Dilek, 2015; Yang et al., 2015, 2019; Esmaeili et al 2019; Barbero

840 et al., 2020b, 2021). This evidence supports the hypothesis that the tectono-magmatic

841 evolution of different sectors of the Neo-Tethys Ocean was strongly influenced by the

842 wide occurrence of mantle plume activity at a regional-scale during the Late Cretaceous.

843 Our data well agree with this general scenario of the Cretaceous Neo-Tethys, as they point

844 out for the existence of a significant mantle plume activity in the Makran sector of this

845 Ocean during the same time. Our data allow us to depict two different stages of a seamount

846 growth at two different times. The Type-II and Type-III volcano-sedimentary successions

847 of the Durkan Complex include Cenomanian carbonatic platform and strongly enriched

848 alkaline basalts, thus recording the existence of one or more oceanic seamounts that

849 reached a shallow-water shield stage during the early Late Cretaceous (Fig. 15a). The

850 occurrence of "mature" seamount edifices implies that a vigorous mantle plume activity

851 was already existing in the oceanic basin at that time. By contrast, the Durkan Type-I

852 succession, which is characterized by pelagic sediments and prevailing transitional

853 volcanic rocks, records an early phase of growth of a seamount (i.e., deep-water stage) in

854 the late Late Cretaceous (Fig. 15b). A general fading away at the end of Cretaceous of

855 OIB-type volcanism is observed in the Neo-Tethyan related belts from Caucasus to

856 Himalaya and it is interpreted to reflect a progressively decreasing mantle plume activity in

857 the Neo-Tethys during these times (e.g., Rolland et al., 2010, 2020; Yang and Dilek, 2015;

858 Esmaeili et al 2019; Barbero et al., 2020b, 2021). We can speculate that the occurrence in

859 the Durkan Complex of a relatively older (Cenomanian) mature seamount and a relatively

860 younger (Coniancian – Campanian) immature seamount may eventually be related to the

861 Late Cretaceous progressive decreasing of plume activity observed at a regional scale. This

862 hypothesis needs, however, to be proved by further studies.

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866   8. Conclusion

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868   The Durkan Complex represents a tectonic element of the North Makran domain that

869 was classically interpreted as a continental margin succession though a recent study

870 suggested that it represents a tectonically disrupted portion of a Late Cretaceous seamount

871 chain. The petrographic and geochemical study presented in this paper allow the following

872 conclusion to be drawn:

1) The Durkan Complex is composed by tectonic slices showing successions similar to those found at different depths of a seamount environment. The successions are characterized by abundant volcanic rocks and are either non-metamorphic or slightly metamorphosed.

2) The volcanic and metavolcanics rocks are largely represented by basaltic rocks. Based on whole rock chemistry and clinopyroxene chemistry, basaltic rocks consist of both transitional basalts showing P-MORB composition (Group 1) and alkaline basalts showing OIB composition (Groups 2a and 2b).

3) The chemical composition of clinopyroxenes from the different rock groups is strictly depending on the whole rock composition of their hosting rocks. In particular, TiO_2, Al_2O_3, and Na_2O contents in minerals increase from transitional to alkaline basalts.

4) Petrogenetic models indicate that the Durkan volcanic rocks derived from partial melting of a sub-oceanic mantle metasomatized to various extents by an OIB-type chemical component. The chemical difference between different Groups of basalts are related to a combination of different extents of metasomatic enrichment and different melting conditions (i.e., partial melting degrees and melting depths).

Our new data compared to literature data allow us to conclude that the different volcano-sedimentary successions of the Durkan Complex record portions of seamounts of different ages formed during both shallow-water shield stage (Cenomanian) and deep-water stage (Coniacian-Campanian). The age, composition, and evolution of these distinct seamounts in the Makran sector of the Neo-Tethys is compatible with regional-scale evidence (from Caucasus to Himalaya), which suggest that abundant transitional and alkaline basalts were erupted as a consequence of the interaction between the sub-oceanic lithosphere and significant mantle plume activity.

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1183 **Table captions**

1184

1185 **Table 1**. Major (wt.%) and trace (ppm) element composition of representative volcanic

1186 and metavolcanic rocks from the western part of the Durkan Complex. Abbreviations: bas:

1187 basalt; bas and: basaltic andesite; tra: trachyte; a-rhy: alkali-rhyolite; XRF: X-ray

1188 fluorescence spectrometry; ICP-MS: inductively coupled plasma-mass spectrometry; n.d.:

1189 not detected. $Mg\# = 100 \times MgO / (MgO + FeO)$. $Fe_2O_3 = 0.15 \times FeO$. Normalizing values

1190 for REE ratios from Sun and McDonough (1989). Asterisks indicate samples whose XRF

1191 composition is taken from Barbero et al. (2021).

1192

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1193   **Table 2**. Representative analyses of clinopyroxene from basaltic and metabasaltic

1194   rocks from the western part of the Durkan Complex. Atoms per formula units (a.p.f.u.) are

1195   calculated on the bases of four cations. The compositions of Fe^{3+} and Fe^{2+} were calculated

1196   from the measured total FeO according to Droop (1987); Mg# = Mg / (Mg + Fe2+).

1197   Abbreviations, Wo: wollastonite; En: enstatite; Fs: ferrosilite; Acm: Acmite.

1198   Abbreviations, c: core; ec: external part of the core; r: rim.

1199

1200   **Figure caption**

1201

1202   **Figure 1**. a) Simplified tectonic sketch map of the Iranian-Afghan-Pakistani area

1203   (modified from Khan et al., 2007; Bagheri and Stampfli, 2008; Allahyari et al., 2014;

1204   Mohammadi et al., 2016; Pirnia et al., 2020; Barbero et al., 2020b); b) structural sketch

1205   map showing the different tectono-stratigraphic domains of the Makran Accretionary

1206   Wedge (modified from Burg et al., 2013); c) simplified geological-structural map of the

1207   North Makran Domain showing the different tectonic units (modified from Eftekhar-

1208   Nezhad et al. 1979; Burg, 2018; Samimi Namin, 1982, 1983; Barbero et al., 2020b).

1209

1210   **Figure 2**. Simplified geological map of the western part of the Durkan Complex

1211   (based on Samimi Namin, 1982 and modified according to our original fieldwork and

1212   photointerpretation with satellite images). The locations of the sampled areas are also

1213   shown.

1214

1215   **Figure 3**. a) Schematic stratigraphic column and ages for the three different types of

1216   successions in the western part of the Durkan Complex; b) vesicle volume % vs. depth of

1217   eruption for basalts from the different successions. The different curves indicate the depth-

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1218   vesicles percent for tholeiitic (solid line, from Moore and Schilling, 1973) and alkaline

1219   (dashed line, from Moore, 1970) volcanic rocks. Modified from Barbero et al., (2021).

1220

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1222   **Figure 4**. Nb/Y vs. Zr/Ti discrimination diagram of Winchester and Floyd (1977)

1223   modified by Pearce (1996) for volcanic and metavolcanic rocks from the western part of

1224   the Durkan Complex.

1225

1226   **Figure 5**. N-MORB normalized incompatible element patterns (left column) and

1227   Chondrite-normalized rare earth element patterns (right column) for volcanic and

1228   metavolcanic rocks from the part of the Durkan Complex. Normalizing values are from

1229   Sun and McDonough (1989). Compositions of average plume-influenced mid-ocean ridge

1230   basalt (P-MORB) from the Southwest Indian Ridge and typical alkaline oceanic within-

1231   plate basalt (OIB) are from Janney et al. (2005) and Sun and McDonough (1989),

1232   respectively.

1233

1234   **Figure 6**. Chondrite-normalized $(Sm/Yb)_N$ vs. $(La/Yb)_N$ (a), $(Sm/Yb)_N$ vs. $(Sm/Dy)_N$

1235   (b), and $(La/Yb)_N$ vs. Yb_N (c) diagrams for the volcanic and metavolcanic rocks of the

1236   western part of the Durkan Complex. Normalizing values are from Sun and McDonough

1237   (1989).

1238

1239   **Figure 7**. N-MORB normalized Th vs. Nb discrimination diagram of Saccani (2015)

1240   for volcanic and metavolcanic rocks from the western part of the Durkan Complex.

1241   Vectors indicate the trends of compositional variations due to the main petrogenetic

1242   processes. Abbreviations, AFC: assimilation-fractional crystallization; OIB-CE: ocean

island-type (plume-type) component enrichment; FC: fractional crystallization; MORB: mid-ocean ridge basalt; N-: normal type; E-: enriched type; P-: plume type; D-: depleted type; IAT: island arc tholeiite; CAB: calc-alkaline basalt; AB: alkaline oceanic within-plate basalt; MTB: medium titanium basalt. Normalizing values, as well as the composition of typical N-MORB (white star), E-MORB (grey star), and OIB (black star) are from Sun and McDonough (1989).

Figure 8. Diagram showing the variation of TiO_2, CaO, and Na_2O contents vs. Mg# for clinopyroxenes from the basaltic and metabasaltic rocks of the western part of the Durkan Complex. Arrows represent the average trends of variation for clinopyroxene from the different geochemical groups of rocks.

Figure 9. a) Ti vs. (Ca + Na) and b) (Ti + Cr) vs. Ca discrimination diagrams of Leterrier et al. (1982) showing the compositions of clinopyroxenes from the volcanic and metavolcanic rocks from the western the part of the Durkan Complex.

Figure 10. Compositions of clinopyroxenes from the basaltic and metabasaltic rocks from the western the part of the Durkan Complex plotted in the TiO_2–Na_2O–SiO_2/100 diagram for discriminating clinopyroxenes in basalts from different oceanic settings (Beccaluva et al., 1989). Abbreviations, E-MORB: enriched mid-ocean ridge basalt; N-MORB: normal mid-ocean ridge basalt; WOPB: within oceanic plate basalts; ICB: Iceland basalts; and SSZ: supra-subduction zone basalts.

Figure 11. Variation of TiO_2 (a), CaO (b), and Al_2O_3 (c) contents in clinopyroxenes from basaltic and metabasaltic rocks from the western the part of the Durkan Complex vs.

1268   the Nb/Y ratios of their hosting rocks. Only clinopyroxene with Mg# in the range 0.74 –

1269   0.80 are plotted to allow comparison between the different chemical groups.

1270

1271   **Figure 12**. a) Nb vs. Zr and b) Zr/Y vs. Zr/Nb diagrams for volcanic and metavolcanic

1272   rocks from the western part of the Durkan Complex. N-MORB, E-MORB and OIB end-

1273   members are from Sun and McDonough (1989). Fields showing the compositional

1274   variation of different types of basalts from subduction-unrelated ophiolites and modern

1275   oceanic setting are shown for comparison in Panel b) (data from Saccani et al., 2013, Le

1276   Roex et al., 1983; Hanan et al., 2000; Chauvet et al., 2011). The dashed line in b)

1277   represents the mixing curve calculated using OIB and N-MORB end-members (from Le

1278   Roex et al. 1983).

1279

1280   **Figure 13**. a) Nb/Yb vs. TiO_2/Yb diagram showing the isobaric melting curves for

1281   theoretical mantle sources S1 and S2 calculated for different pressures according to Pearce

1282   (2008); b) Nb/Yb vs. Th batch melting curve for the theoretical mantle source S1 and S2

1283   calculated for both spinel- and garnet-facies conditions. The dashed line represents the

1284   mixing line of various melt fractions from garnet- and spinel-facies mantle. S1 and S2

1285   represent theoretical mantle sources calculated by assuming different degrees of

1286   enrichment by an OIB-type chemical component (Lustrino et al., 2002) of a sub-oceanic

1287   slightly depleted lherzolite residual after small volume of MORB melt extraction

1288   (lherzolite ZB2, Barbero et al., 2020c). Depleted MORB mantle (DMM) and primitive

1289   mantle (PM) compositions are also shown in Figure 13a (data from Workman and Hart,

1290   2005 and Sun and McDonough, 1989, respectively). Input parameters (source modes,

1291   melting proportions, and partition coefficients, source compositions) for the model in

1292   Figure 13b are given in Supplementary Table S2. Volcanic and metavolcanic rocks from

1293 the western part of the Durkan Complex are plotted in both diagrams. The relatively less

1294 fractionated basalts of each rock type are shown with large symbols, whereas other

1295 samples are shown with small, grey symbols.

1296

1297 **Figure 14**. Calculated chondrite-normalized (Sun and McDonough, 1989) rare earth

1298 element (REE) liquid composition for parental melts derived from mantle sources S1 and

1299 S2, assuming various degrees of non-modal batch partial melting in the spinel- and garnet-

1300 facies mantle, as well as different proportions of melt fractions from garnet- and spinel-

1301 facies mantle. S1 and S2 represent theoretical mantle sources calculated by assuming

1302 different degrees of enrichment by an OIB-type chemical component (Lustrino et al., 2002)

1303 of a sub-oceanic slightly depleted lherzolite residual after small volume of MORB melt

1304 extraction (lherzolite ZB2, Barbero et al., 2020c). Abbreviations: EM: enriched mantle

1305 source (from Lustrino et al., 2002); DMM: depleted MORB mantle (Workman and Hart,

1306 2005). Input parameters for the REE models (source modes, melting proportions, and

1307 partition coefficients), as well as compositions of the different mantle sources are shown in

1308 Supplementary Table S2. The comparison between the composition of the relatively less

1309 fractionated basalts of Group 1, Group 2a, and Group 2b and the calculated melts are

1310 shown in panels a), b), c), respectively. Representative examples of the mixing of various

1311 melt fractions from garnet- and spinel-facies mantle are shown in a1).

1312

1313 **Figure 15**. Conceptual cartoon showing the petrogenetic processes operating during

1314 the shallow-water (a) and deep-water (b) stages of growth of the Durkan seamounts. The

1315 depositional positions of the different types of successions within the seamount chain is

1316 modified from Barbero et al. (2021). Abbreviations, MORB: mid-oceanic ridge basalt;

1317 OIB: ocean island basalt; S1 and S2: enriched mantle sources derived from different

1318   degrees of enrichment by an OIB-type chemical component of a sub-oceanic slightly

1319   depleted lherzolite residual after small volume of MORB melt extraction; spl: spinel; gt:

1320   garnet.

1   New evidence for Late Cretaceous plume-related seamounts in the Middle East sector

2   of the Neo-Tethys: Constraints from geochemistry, petrology, and mineral chemistry of the

3   magmatic rocks from the western Durkan Complex (Makran Accretionary Prism, SE Iran)

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25

26   Abstract

27   The Durkan Complex in the Makran Accretionary Prism (SE Iran) has been interpreted

28   either as a continental margin succession or a Late Cretaceous tectonically disrupted

29   seamount chain. New whole rock and clinopyroxene chemical data for basaltic and

30   metabasaltic rocks of the Durkan Complex allow us to distinguish two main rock groups:

31   a) rocks showing transitional chemical affinity (Group 1) and compositions resembling

32   those of plume-type mid-oceanic ridge basalts; b) rocks with within-plate oceanic island

33   basalt (OIB) compositions showing a clear alkaline affinity (Group 2). Based on whole

34   rock REE contents and clinopyroxene chemistry, alkaline rocks can be further subdivided

35   in two sub-groups, namely, the Group 2a and 2b. Compared to Group 2a, Group 2b rocks

36   show a more pronounced alkaline nature marked by higher whole rock La/Yb and Sm/Dy

37   ratios and higher TiO_2 and Na_2O contents in clinopyroxenes. Trace element and REE

38   petrogenetic models show that the Durkan basaltic rocks were generated from the partial

39   melting of depleted sub-oceanic mantle source that was metasomatized by OIB-type

40   chemical components in a within-plate oceanic setting. The chemical differences in the

41   three rock groups are related to different combinations of partial melting degree, depths of

42   melting, and various extent of enrichment of the mantle sources by OIB-type chemical

43   components, which are related, in turn, to a Late Cretaceous mantle plume activity in the

44   northern Neo-Tethys realm. We suggest that the Durkan Complex formed in a seamount

45   setting and that its different volcano-sedimentary successions record different stages of

46   seamount formation.

47

48   **Keywords**: Ophiolite, Geochemistry, Petrology, Clinopyroxene chemistry, Alkaline

49   basalt, Seamount, Makran Accretionary Prism, Iran

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1. Introduction

Ophiolitic basaltic and metabasaltic rocks are widespread within collisional-type and accretionary-type orogenic belts and are of particular importance, as their petrological features are sensitive to different geodynamic settings of formation. Different tectonic environments, such as mid-oceanic ridge, within-plate oceanic island, convergent and rifted margins, are indeed characterized by the occurrence of chemically distinctive types of basaltic rocks (Pearce, 1996; Dilek and Furnes, 2011; Saccani, 2015; Safonova et al., 2016). Among them, basaltic rocks with oceanic island basalt (OIB) chemical affinity are of particular interest as they may represent remnants of deformed oceanic seamounts (Yang et al., 2015, 2019; Wan et al., 2020). Seamounts are largely subducted and their remnants in the accretionary and collisional belts are represented only by blocks in ophiolitic mélanges (e.g., Yang et al., 2019; Safonova et al., 2016) or as coherent slices underplated at different depths (e.g., Isozaki et al., 1990; Bonnet et al., 2020). In addition, recognizing basalts with OIB affinity within accretionary and collisional belts is particularly important as they likely represent the only elements for reconstructing periods of mantle plume activity during Earth history (Safonova and Santosh, 2014; Wan et al., 2020). It follows that detailed petrological studies of basaltic rocks within the accretionary and collisional belts are fundamental for constraining their tectono-magmatic settings of formation and, consequently, for reconstructing the progressive geodynamic history of the paleo-oceanic basins and their related continental margins (Robertson, 2007; Hässig et al., 2013; Safonova, 2017; Saccani et al., 2018; Rolland et al., 2020).

The Makran Accretionary Prism (hereafter, simply Makran) in SE Iran and SW Pakistan (Figs. 1a, b) is related to the long-lived geodynamic evolution of the Neo-Tethys Ocean and its northern continental margin, represented by the Lut and Afghan blocks

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77 (McCall and Kidd, 1982; Burg et al., 2008; 2013; Burg, 2018; Saccani et al., 2018; Monsef

78 et al., 2018; Barbero et al., 2020a). The Makran consists of several tectono-stratigraphic

79 domains (Fig. 1b) that have been deformed and incorporated in the accretionary prism,

80 starting from the Cretaceous (e.g., Platt et al., 1985; Dolati and Burg., 2013; Burg, 2018;

81 Saccani et al., 2018; Barbero et al., 2020a, b). Among these, the North Makran domain

82 records the pre-Eocene deformation history of the accretionary wedge. It consists of several

83 tectonic units (Fig. 1c) that, in turn, represent distinct tectonic domains, including the Neo-

84 Tethys oceanic lithosphere, seamounts and/or oceanic plateau, as well as arc-forearc-trench

85 domains. The North Makran also includes tectonic units derived from an exotic

86 microcontinental block and its sedimentary cover (McCall and Kidd, 1982; Dorani et al.,

87 2017; Burg, 2018; Monsef et al., 2018; Saccani et al., 2018). The Durkan Complex is one of

88 the major tectonic elements of the North Makran domain (Fig. 1c) and it was described as a

89 highly deformed complex including Early Cretaceous – early Paleocene shallow water

90 succession, abundant volcanic rocks, as well as subordinate tectonic slices of Carboniferous,

91 Permian and Jurassic shallow water sedimentary rocks and Middle - Late Jurassic granitoids

92 (McCall, 1985; Hunziker et al., 2015). It has been classically interpreted as the Permian –

93 Cretaceous disrupted sedimentary cover of the passive margin of a continental basement as

94 old as Paleozoic, whose remnants are now represented by the Bajgan Complex (McCall and

95 Kidd, 1982; McCall, 2002). The Bajgan-Durkan Complexes are collectively thought to

96 represent the remnants of a continental ribbon detached from the Eurasian margin by the

97 Late Jurassic – Early Cretaceous rifting that led to the opening of the North Makran Ocean

98 (McCall and Kidd, 1982; McCall, 2002; Hunziker et al., 2015; Burg, 2018). However,

99 Barbero et al. (2021) showed that the western Durkan Complex consists of tectonic slices

100 including volcano-sedimentary sequences, which represent remnants of a tectonically

101 disrupted Late Cretaceous seamounts chain. This interpretation, which is radically different

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102   from the extant interpretation, is based on field investigations and detailed stratigraphic,

103   structural, and biochronological data, as well as preliminary petrographic and geochemical

104   data on volcanic rocks. However, a thorough geochemical and petrological investigations of

105   the volcanic rocks included in the Durkan volcano-sedimentary sequences is necessary for

106   better constraining the tectono-magmatic setting of formation of the Durkan Complex, as

107   well as its significance for the geodynamic evolution of the pre-Eocene Makran

108   Accretionary Prism. Therefore, in this paper, we present new whole-rock, as well as mineral

109   geochemical data on the volcanic and metavolcanics rocks from the Durkan Complex.

110   These data will be discussed in the context of the detailed tectono-stratigraphic results

111   presented by Barbero et al. (2021) with the purpose of adding the final touch to the

112   knowledge of tectono-magmatic setting of formation of this Complex. Finally, these

113   findings will then be discussed for the Late Cretaceous geodynamic evolution of the

114   northern Neo-Tethys realm.

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116

117   2. Geological setting

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119   *2.1. General geological setting of the Makran Accretionary Prism*

120

121   The Makran Accretionary Prism is the result of a complex Cretaceous – Present day

122   geodynamic history, which is related to the subduction of the Neo-Tethys oceanic

123   lithosphere below the southern margin of Eurasia (McCall and Kidd, 1982; Dercourt et al.,

124   1986; Saccani et al., 2018; Burg, 2018; Monsef et al., 2018; Barrier et al., 2018; Barbero et

125   al., 2020a, b). The Makran is an E-W trending active subduction complex, which is laterally

126   separated from the Zagros and the Himalayan collisional systems by N-S trending strike-

slip fault zones (Figs. 1a, b) (e.g. Dercourt et al., 1986; Kopp et al., 2000; Burg et al., 2013; Mohammadi et al., 2016; Riaz et al., 2019). The present-day deformation front of the Makran is located offshore in the Oman Sea (Fig. 1a). The onshore Makran is characterized by the tectonic juxtaposition of several tectono-stratigraphic domains (Dolati, 2010; Burg et al., 2013). In the western part of the prism these domains are from the structural top to the bottom (i.e., from the north to the south): 1) the North Makran; 2) the Inner Makran; 3) the Outer Makran; 4) the Coastal Makran (Fig. 1c). The Inner, Outer and Coastal Makran domains represent the Eocene - present day accretionary complex and include Eocene – Pleistocene mainly terrigenous sedimentary successions (e.g., Dolati, 2010; Burg et al., 2013; Burg, 2018). The North Makran domain includes remnants of pre-Eocene accretionary stages and consists of a tectonic stack of oceanic and continental derived units, some of which showing variable degrees of metamorphic imprint (e.g., McCall and Kidd, 1982; Burg, 2018). These units include from north to south and from the higher to the lowermost structural position (Fig. 1c): 1) the Ganj Complex; 2) the Northern Ophiolites, 3) the Bajgan and Durkan Complexes, 4) the Sorkhband – Rudan tectonic slices 5) the Coloured Mélange Complex.

Recent studies have shown that the Ganj Complex represents fragments of a Late Cretaceous volcanic arc that was likely built up close to the southern margin of the Lut Block (Barbero et al., 2020a). The Northern Ophiolites (Fig. 1c) are Early to Late Cretaceous in age and include the Band-e-Zeyarat/Dar Anar (Ghazi et al., 2004; Barbero et al., 2020b), Remeshk-Mokhtarabad (McCall, 1985, 2002; Hunziker et al., 2015; Burg, 2018), and Fanuj-Maskutan (Moslempour et al., 2015) ophiolitic complexes. Their magmatic rocks mostly show enriched-type mid-ocean ridge basalts (E-MORB) chemical affinity for the Early Cretaceous ophiolites (Ghazi et al., 2004; Barbero et al. 2020b), whereas the Late Cretaceous ophiolites show supra-subduction zone chemical affinity

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152 (Burg, 2018; Monsef et al., 2019, Sepidbar et al., 2020). These ophiolitic complexes were

153 collectively interpreted as the remnants of the oceanic lithosphere of the North Makran

154 Ocean, which is thought to represent an oceanic basin that existed during Late Jurassic –

155 Early Cretaceous at the southern margin of the Central Iran continental plate. The Bajgan

156 and Durkan Complexes (Figs.1c, 2) have classically been interpreted as remnants of a

157 microcontinental block, which was separated from the Lut Block in the Late Jurassic - Early

158 Cretaceous. The Bajgan Complex is made up of an assemblage of metamorphic rocks that

159 include schists, paragneisses, amphibolites, marbles, as well as basic and acidic meta-

160 intrusive rocks (McCall, 1985; McCall, 2002; Dorani et al., 2017). The P-T condition of the

161 metamorphism and its age are poorly constrained. However, moderately high pressure and

162 high temperature conditions have been suggested (McCall, 1985; Dorani et al., 2017). The

163 Durkan Complex (Figs.1c, 2) consists of a highly deformed and locally slightly

164 metamorphosed (i.e., up to sub-greenschist facies) complex including: 1) Late Cretaceous

165 shallow-water limestones and thick sequences of alternating limestones, sandstones, shales,

166 cherts and volcanic rocks (Barbero et al., 2021), 2) very minor tectonic slices of

167 Carboniferous, Permian and Jurassic shelf carbonate rocks, as well as marbles and schists

168 (McCall, 1985, 2002; Hunziker et al., 2015); 3) Early – Late Jurassic different types of

169 granitoids intruded into Jurassic shelf limestones in the eastern part of the Makran

170 (Hunziker et al., 2015; Burg, 2018). This Complex has been considered as the original

171 sedimentary cover of the Bajgan metamorphic Complex (McCall, 1985, 2002). However,

172 based on recent multidisciplinary investigation on its western part, Barbero et al. (2021)

173 showed that this Complex represents a tectonically disrupted Late Cretaceous seamounts

174 chain incorporated as tectonic slices into the North Makran accretionary prism.

175   The Deyader Complex crops out in the eastern sector of the North Makran (Fig. 1c). It

176 represents a meta-ophiolitic complex affected by high pressure-low temperature (HP-LT)

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metamorphism (McCall, 1985; Hunziker et al., 2015: Omrani et al., 2017). The Sorkhband and Rudan ophiolites crop out in the western part of the North Makran within the shear zone between the Coloured Mélange and the Bajgan Complex (McCall, 2002; Delavari et al., 2016). The Coloured Mélange Complex is composed of metric- to decametric-thick tectonic slices and was formed in Cretaceous-Paleocene times (McCall and Kidd, 1982; McCall, 2002; Saccani et al., 2018; Burg, 2018; Esmaeili et al., 2019). Saccani et al. (2018) showed that the Coloured Mélange Complex incorporates a great variety of volcanic and meta-volcanic rock-types formed in both the subducting oceanic plate (i.e., oceanic plateau basalts, normal mid-ocean ridge basalts, and alkaline basalts) and the upper plate (i.e. Early - Late Cretaceous island arc tholeiites and calc-alkaline basalts).

2.2. Stratigraphic features of the western part of the Durkan Complex

Detailed fieldwork and stratigraphic, structural, and biostratigraphic investigations have recently been carried out on the western part of the Durkan Complex (Barbero et al., (2021). This works showsed that this Complex (Fig. 2) consists of several tectonic slices, within which different stratigraphic successions can be recognized (Fig. 3). The different slices include both non-metamorphic and slightly metamorphosed successions, all characterized by abundant volcanic rocks (Fig 3a). These stratigraphic successions can be reconciled to three types of successions that are similar to those found at different depths of a seamount setting. The characteristics of these successions, as described by Barbero et al. (2021) are briefly summarized in the following sections.

2.2.1. Type I succession: deep-water stage of seamount growth

202 This succession type represents a Coniancian - Campanian pelagic sequence consisting

203 of thin-bedded red cherts and cherty limestones alternated with shales and shaly marls, as

204 well as minor volcaniclastic arenites and pillow breccias. Pillow basalts are frequently

205 interbedded within this sequence (Fig. 3a), and are characterized by low vesicolarity (Fig.

206 3b). These features suggest eruption under a relatively thick water column pressure (Fig.

207 3b). This type of succession represents the remnants of a seamount in its deep-water stages

208 of formation characterized by pelagic sedimentation and volcanic activity in a deep-water

209 depositional environment.

210

211 2.2.2. Type II succession: seamount flank during shallow-water stage of a seamount

212 growth

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214 This succession is characterized by a volcanic sequence showing stratigraphic transition

215 to a volcano-sedimentary sequence that, in turn, gradually passes upward to a pelagic and

216 hemipelagic sedimentary sequence (Fig. 3a). The volcanic sequence is made up ~~by~~ of

217 alternating massive lava flows, pillow lavas, and volcaniclastic arenites and breccias (Fig.

218 3a). The volcano-sedimentary sequence consists of alternating volcaniclastic arenites and

219 breccias, shales and siltstones, and Cenomanian limestone, as well as minor massive lava

220 flows (Fig. 3a). Limestones show pelagic foraminifera assemblages suggesting a relatively

221 deep-water depositional setting. Accordingly, the analysis of the volume percent of vesicles

222 for the volcanic rocks suggest a relatively high eruption depth, which is however

223 significantly lower than those of the Type I succession (Fig. 3b). The pelagic and

224 hemipelagic sedimentary sequence consists of cherty limestones, shales, shaly marls, cherts,

225 and minor carbonatic breccias and volcaniclastic arenites (Fig. 3a). The stratigraphic

226 features of Type-II succession ~~point out for~~indicates a deposition~~al setting~~ along and at the

9

227 base of a seamount flank during the relatively shallow-water shield stage of growth of a

228 seamount.

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230 2.2.3. Type III: seamount summit during shallow-water stage of seamount growth

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232 This stratigraphic succession is characterized by a volcanic sequence passing laterally

233 and upward to a volcano-sedimentary sequence that is, in turn, followed by a Cenomanian

234 carbonatic platform sequence and ends upward with a pelagic and hemipelagic sequence

235 (Fig. 3a). The volcanic sequence is characterized by pillow and massive lava flows

236 alternating with volcaniclastic arenites. The volcano-sedimentary sequence is composed by

237 alternating volcanic rocks, volcaniclastic arenites and breccias, shales, as well as turbidites

238 showing mixed carbonatic - volcanic composition (Fig. 3a). In addition, minor platform-

239 derived massive limestones are interbedded in the sequences, suggesting a shallow-water

240 depositional setting, as also indicated by the particularly high vesicolarity of the pillow

241 lavas (Fig. 3b). The Cenomanian, shallow-water carbonatic platform sequence consists of

242 massive limestones alternating with subordinate volcaniclastic arenites but lacks of lava

243 flows (Fig. 3a). The uppermost hemipelagic and pelagic sequence marks the drowning of

244 the carbonatic platform. The stratigraphy of Type-III succession record shallow-water

245 volcanic activity associated with carbonatic platform sedimentation and it is comparable

246 with the stratigraphic successions formed in seamount summit setting during the shallow-

247 water shield stage of growth.

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250 3. Petrography

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252   The Durkan volcanic and volcano-sedimentary sequences include both volcanic

253   (prevailing) and metavolcanic (subordinate) rocks. The metavolcanic rocks underwent re-

254   crystallization under low-grade metamorphic conditions, though magmatic relicts are

255   commonly preserved in all samples. Volcanic rocks were affected by variable degrees of

256   alteration, which resulted in different extent of replacement of the primary magmatic

257   minerals. Nonetheless, their original magmatic texture is still recognizable. Fresh

258   plagioclase is very rare, and it is usually pseudomorphosed by a fine-grained assemblage of

259   albite, calcite and sericite. Similarly, olivine crystals are commonly replaced by iddingsite

260   and serpentine plus Fe-Ti oxides. Clinopyroxene crystals are present as both phenocrysts

261   and groundmass minerals. They occur either as fresh or altered crystals characterized by

262   pseudomorphic replacement by chlorite or actinolitic amphibole. Volcanic glass has been

263   generally replaced by an assemblage of chlorite and clay minerals. The studied volcanic

264   rocks are represented by basalts, ferrobasalts, and a couple of differentiated rocks (trachyte

265   and alkali-rhyolite). Four types of petrofacies have been distinguished according to

266   textures; they are: 1) aphyric type; 2) porphyritic type; 3) coarse-grained, doleritic type; 4)

267   metamorphic type. Representative microphotographs are given as Supplementary Figure

268   S1, whereas the texture of each sample is given in Table 1.

269   The aphyric type petrofacies includes basalts and ferrobasalts, as well as one trachyte

270   sample showing aphyric to slightly porphyritic (PI < 10) texture. In the slightly porphyritic

271   samples, the phenocrysts consist of plagioclase, clinopyroxene, and locally olivine. They

272   are set in a hypocrystalline groundmass showing intersertal to microcrystalline texture with

273   microlite of plagioclase, olivine, and clinopyroxene and less abundant Fe-Ti oxides,

274   surrounded by altered volcanic glass. In contrast, the trachyte sample is characterized by

275   aphyric texture, showing laths of plagioclase set in altered volcanic glass.

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276   The porphyritic type petrofacies includes basalts and ferrobasalts showing porphyritic

277   and glomeroporphyritic texture with PI ranging from 15 to 60. The phenocrysts are up to 5-

278   6 mm in size and are mainly represented by clinopyroxene, minor plagioclase and Fe-Ti

279   oxides, and rare olivine. Clinopyroxene phenocrysts commonly show concentric zonation

280   and weak pleochroism from pale yellow to pale pink. The phenocrysts are set in a

281   hypohyaline groundmass showing intergranular to microcrystalline textures. Rarely,

282   intersertal texture can be observed in the groundmass. The groundmass consists of

283   clinopyroxene and plagioclase together with minor olivine and altered volcanic glass.

284   The coarse-grained doleritic type includes basalts and ferrobasalts showing

285   holocrystalline, inequigranular texture. They are characterized by euhedral plagioclase and

286   euhedral to subhedral clinopyroxene crystals, up to 5 mm in size. Locally, clinopyroxene

287   encloses plagioclase crystals, showing subophitic texture. These large clinopyroxene

288   crystals are surrounded by a fine-grained crystalline aggregate consisting of euhedral to

289   subhedral plagioclase, clinopyroxene as well as Fe-Ti oxides. In ferrobasalts, opaque

290   minerals show subhedral to anhedral morphology.

291   The slightly metamorphic type petrofacies includes metabasalts, and metaferrobasalts,

292   as well as one meta-alkali-rhyolite sample showing anastomosed foliation defined by a

293   fine-grained aggregate of chlorite, fibrous amphibole, Fe-Ti oxides, subordinate epidote, as

294   well as by the alignment of albite aggregates. In most samples, the foliation envelops

295   magmatic relicts consisting of clinopyroxene and minor plagioclase. In a few samples, the

296   metamorphic foliation is well developed and it is marked by the alternation of millimetre-

297   spaced and anastomosed domains with different mineralogical composition. In detail,

298   albite-rich domains alternate with domains showing chlorite, epidote and relicts of

299   magmatic clinopyroxene. The mineralogical paragenesis of these samples, as well as the

300   fine-grained size of the metamorphic minerals indicate very low-grade metamorphic

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301 overprint, likely in the sub-greenschist-facies or the prehnite-pumpellyite metamorphic

302 conditions.

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304

305   4. Analytical methods

306

307   Whole rock major and trace element compositions of a total of forty-three samples is

308 presented in this paper. Thirty-two samples were analysed for rock major and some trace

309 elements by X-ray fluorescence spectrometry (XRF) on pressed-powder pellets, using an

310 ARL Advant-XP automated X-ray spectrometer. The matrix correction method proposed

311 by Lachance and Trail (1966) was applied. Volatile contents were determined as loss on

312 ignition (L.O.I.) at 1000°C. In addition, XRF analyses of eleven samples are taken from

313 Barbero et al. (2021). For the discussion of the geochemical characteristics of the studied

314 rocks major element composition has been re-calculated on L.O.I.-free bases. The rare

315 earth elements (REE) and some trace elements (Rb, Sr, Zr, Y, Nb, Hf, Ta, Th, U) were

316 determined by inductively coupled plasma-mass spectrometry (ICP-MS) using a Thermo

317 Series X-I spectrometer on a total of thirty-nine selected samples. All whole-rock analyses

318 were performed at the Department of Physics and Earth Sciences of the Ferrara University;

319 results are shown in Table 1, where new data from this paper and XRF data from Barbero

320 et al. (2021) are identified. The accuracy of the XRF and ICP-MS data were evaluated

321 using results for international standard rocks run as unknown. The detection limits for XRF

322 and ICP-MS analyses were evaluated using results from several runs of twenty-nine

323 international standards. Results are presented in Supplementary Table S1.

324   The major element composition of clinopyroxene were obtained by electron

325 microprobe spectrometry using a Superprobe Jeol JXA 8200 (JEOL, Tokyo, Japan) at the

13

326 Eugen F. Stumpfl Laboratory at the University of Leoben, Austria, using both energy

327 dispersive spectrometry (EDS) and wave-length dispersive spectrometry (WDS) systems.

328 The electron microprobe was operated in the WDS mode during the quantitative analyses.

329 An accelerating voltage of 15 kV and beam current of 10 nA were used during the

330 analyses. The diameter of the beam was about 1 μm. Counting times were 20 s on the peak

331 and 10 s on both left and right backgrounds. Standards (element, emission line) were:

332 adularia (Al and Si, Kα), rutile (Ti, Kα), chromite (Cr, Kα), almandine (Fe, Kα), rhodonite

333 (Mn, Kα), olivine (Mg, Kα), wollastonite (Ca, Kα), albite (Na, Kα), and sanidine (K, Kα).

334 The following diffracting crystals were selected: TAP for Na, Mg, and Al; PETJ for K, Si,

335 and Ca; and LIFH for Ti, Cr, Mn and Fe. The detection limits were automatically

336 calculated by the Jeol microprobe software and they are listed in the following as ppm: Na,

337 Al, Mg, K, Ca (100), Si, Cr, Fe, Mn (150) and Ti (200). The results of microprobe analyses

338 are shown in Table 2.

339

340

341   5. Whole rock geochemistry

342

343   The petrographic analysis has shown that the studied rocks have undergone secondary

344 alteration (e.g., ocean-floor hydrothermal alteration) or sub-greenschist facies

345 metamorphism; therefore, some elements may have been remobilized during these

346 processes. In fact, it is well known that large ion lithophile elements and many major

347 elements are commonly affected by alteration-induced mobilization. In addition, light REE

348 (LREE) may also have been mobilized during secondary alteration processes (e.g., Pearce

349 and Norry, 1979). In contrast, many incompatible elements (e.g., Ti, P, Zr, Y, Sc, Nb, Ta,

350 Hf, Th), middle (M) and heavy (H) REE, as well as some transition metals (e.g., Ni, Co,

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351 Cr, V) are considered to be immobile during low-temperature alteration and

352 metamorphism. For these reasons, the geochemical features of the Durkan Complex

353 magmatic rocks are described using those elements considered immobile during alteration

354 processes. Rb and Ba are generally considered as mobile elements. Nonetheless, these

355 elements did not demonstrate a high degree of mobility resulted significantly mobilized

356 only in some most samples, whereas in many samples they were little mobilised. In fact, in

357 these samples, their contents show good correlations with immobile element contents (e.g.,

358 correlation coefficient with Rb vs. Y = 0.71). Therefore, Rb and Ba will be used, though

359 with caution.

360 The volcanic rocks of the Durkan Complex largely consist of basalts, subordinate

361 ferrobasalts and rare basaltic andesites, trachytes, and alkali rhyolites. Metabasalts and

362 metaferrobasalts though subordinate in volume are also found in all the succession types

363 (Table 1). Metavolcanic rocks will be discussed together with volcanic rocks because this

364 paper is focused on the identification of the geochemical features of the original volcanic

365 protoliths and their tectono-magmatic setting of formation, regardless of the tectono-

366 metamorphic events that affected some tectonic slices of volcanic rocks during their late

367 incorporation in the accretionary wedge. For the sake of simplicity, the prefix "meta" will

368 be hereafter omitted. Basaltic rocks show variable major and trace elements compositions

369 (Table 1), which most likely suggest that they represent melts at different stages of

370 fractionation. Based on the Nb/Y ratios (Winchester and Floyd, 1977; Pearce, 1996), we

371 can distinguish two main groups of rocks (Fig. 4). Group 1 rocks show a transitional nature

372 with Nb/Y ratios in the range 0.8-1.00, whereas Group 2 rocks show a clear alkaline

373 affinity with Nb/Y ratios >1 (1.15-3.16).

374

375 *5.1. Group 1 rocks*

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376

377　　　　This group includes basaltic, basaltic andesitic, and ferrobasaltic rocks, as well as one

378　　trachyte sample. These rocks are mainly found in the Type-I succession, whereas they are

379　　less abundant in the Type-II succession and completely lacking in Type-III succession

380　　(Table 1). Group 1 basalts show a wide range of composition in terms of SiO_2 (43.3 – 53.3

381　　wt%), MgO (4.93 – 11.9 wt%), Al_2O_3 (12.2 – 17.2 wt%), and Mg# (47.8 – 75.4),

382　　suggesting that they were likely formed from melts at different degrees of fractionation.

383　　The basaltic rocks are characterized by relatively high TiO_2 (1.20 – 2.29 wt%), P_2O_5 (0.23

384　　– 0.51 wt%), Zr (73 – 220 ppm), Nb (13.5 – 32.6 ppm), Th (1.49 – 3.66 ppm), and Ta (0.92

385　　– 2.18 ppm) contents coupled with relatively low Y contents (16.9 - 33.5 ppm).

386　　Compatible elements (Cr, V, Ni, and Co) contents are variable, but generally high, as

387　　expected for basaltic rocks (Table 1). The Ti/V ratios are in the range 28 – 61, which are

388　　values typically observed in MORB to alkaline transitional basalts (Shervais, 1982).

389　　Normal type MORB (N-MORB) normalized incompatible elements spider-diagrams

390　　display regularly decreasing patterns from Th to Yb, (Fig. 5a). Yb content in basaltic

391　　samples is relatively low, ranging from 0.49 to 0.82 times N-MORB (Sun and

392　　McDounough, 1989) abundance (Fig. 5a). Group 1 rocks show mild LREE enrichment

393　　with respect to HREE, as well as moderate depletion of HREE if compared to MREE (Fig.

394　　5b). This is testified by the $(La/Yb)_N$, $(Sm/Yb)_N$, and $(Dy/Yb)_N$ ratios, which are in the

395　　range 4.44 – 7.86, 1.18 – 3.16, and 1.25 – 1.56, respectively (Figs. 6a, b). The Yb and La

396　　contents are in the range 8.5 - 13.8 and 37.8 - 90.3, times chondrite abundance,

397　　respectively (Figs. 5b, 6c). The overall chemical features of the Group 1 rocks are similar

398　　to those of many plume-type MORB (P-MORB) in modern oceanic settings (e.g., Le Roex

399　　et al., 1983; Sun and McDounough, 1989; Haase and Devey, 1996). Accordingly, in the

400　　discrimination diagram in Fig. 7, these rocks plot in the fields for oceanic subduction-

16

401   unrelated setting, between the compositional fields of P-MORBs and Alkaline basalts.

402   These geochemical data collectively suggest a P-MORB affinity for Group 1 basaltic

403   rocks. Compared to the basaltic samples, the trachyte MK795 shows higher SiO_2 and lower

404   MgO contents (Table 1). As commonly observed in highly fractionated rocks, this sample

405   shows very high Zr (701 ppm) and Y (58 ppm) contents and very low contents of

406   compatible elements, TiO_2 and P_2O_5 (Table 1) as a consequence of early crystallization and

407   removal of mafic minerals, Fe-Ti oxides, and apatite. In fact, this sample shows N-MORB

408   normalized incompatible elements spider-diagrams with significant Ti and P negative

409   anomalies (Fig. 5a). The chondrite-normalized REE pattern of this sample shows a marked

410   Eu negative anomaly and depletion of middle REE (MREE) with respect to HREE (Fig.

411   5a), which suggest crystallization and removal of plagioclase and amphibole, respectively,

412   prior to the formation of the trachytes melts.

413

414   *5.2. Group 2 rocks*

415

416   The Group 2 rocks include basaltic, and ferrobasaltic rocks, as well as one alkali

417   rhyolitic sample. These rocks show a clear alkaline affinity, as indicated by Nb/Y ratios

418   greater than 1 (Table 1, Fig. 4). Basaltic rocks are characterized by SiO_2 ranging from

419   41.94 to 53.52 wt% and Mg# ranging between 75 and 39 suggesting that these rocks

420   represent melts at different stages of magmatic fractionation. Accordingly, these rocks

421   show marked variation of MgO and Al_2O_3 contents (Table 1). The basaltic rock of the

422   Group 2 show relatively high contents of TiO_2 (1.55 – 5.13 wt%), P_2O_5 (0.20 – 1.10 wt%),

423   Zr (139 – 403 ppm), Nb (23.6 – 71.8 ppm), and Ta (1.42 – 5.13 ppm). Ti/V ratios (41 - 76)

424   are in the range for alkaline basalts (Shervais, 1982). In contrast, Y abundance is rather

425   low, ranging between 18.5 to 33.0 ppm. Compared to Group 1 basalts, the Ti/Y (526 –

17

426   1448) and Zr/Y (6.7 – 20.6) ratios in Group 2 basalts are higher. The N-MORB normalized

427   incompatible elements spiderdiagrams (Figs. 5c, e) display decreasing patterns from Th to

428   Yb. Yb contents are ~0.6 times N-MORB abundance and are comparable with those of

429   Group 1 rocks. In contrast, both Ta and Nb contents are slightly higher than those of Group

430   1 rocks (Figs. 5a, c, Table 1). The chondrite normalized REE patterns (Figs. 5d, f) show

431   marked decrease from LREE to HREE ($La_N/Yb_N = 9.26 – 28.07$) with Yb and La contents

432   ranging from ~6 - 13 to ~ 100 - 250 times chondrite abundance (Sun and McDonough,

433   1989), respectively. In addition, HREE show marked depletion with respect to MREE, as

434   exemplified by the $(Sm/Yb)_N$ ratios (3.5 – 8.4), which are higher with respect to those of

435   Group 1 (Figs. 6a, b; Table 1).

436   By contrast, alkali rhyolite sample MK339 shows higher contents of SiO_2 and lower

437   MgO abundance with respect to the basaltic rocks (Table 1). This sample shows very high

438   Zr (608 ppm) and Y (69.9 ppm) and very low contents of compatible elements, TiO_2 and

439   P_2O_5 (Table 1). This sample shows N-MORB normalized incompatible elements spider-

440   diagrams with significant Ti and P negative anomalies (Fig. 5c). The chondrite-normalized

441   REE pattern of this sample shows a marked Eu negative anomaly and depletion of HREE

442   with respect both LREE and MREE (Fig. 5d). The overall geochemical features of Group 2

443   rocks are very similar to those of the within-plate alkaline volcanic rocks typically forming

444   oceanic islands (e.g., Yang et al., 2015; Safonova et al., 2016 and reference therein). In the

445   discrimination diagram in Figure 7, the Group 2 rocks plot close to the composition of the

446   ocean island basalt (OIB) (Sun and McDonough, 1989) and within the field for subduction

447   unrelated alkaline basalts.

448   Although Group 2 basaltic rocks show similar major elements and most trace elements

449   contents at comparable degree of fractionation (e.g., comparable Mg#), two different

450   subgroups of samples (hereafter named as Group 2a and Group 2b) can be identified based

18

451   on different REE patterns and REE ratios, as well as different ratios of some trace

452   elements. These differences are summarized by the REE ratios shown in Figure 6. Group

453   2a basaltic rocks show definitely lower $(La/Yb)_N$ and $(Sm/Dy)_N$ ratios compared to Group

454   2b equivalents (Figs. 6a, b). In contrast the $(Sm/Yb)_N$ ratios shown by Group 2a and Group

455   2b rocks are largely overlapping, though, as a general tendency, these ratios are

456   comparatively higher in Group 2b rocks (Figs. 6a, b). The variation of the REE ratios

457   shown in Figure 6 is totally independent from the degree of fractionation of the different

458   samples. It should also be noted that there is no correlation between the LREE/HREE (e.g.,

459   La_N /Yb_N) ratio and the absolute concentration of HREE (e.g., Yb_N) suggesting that the

460   enrichment in LREE with respect to HREE is totally independent on the absolute content

461   of HREE (Fig. 6c). In addition, Group 2b rocks show higher Nb/Y (Fig. 4), Nb/Yb, and

462   Th/Tb ratios compared to basaltic rocks of Group 2a

463

464

465   6. Clinopyroxene chemistry

466

467   No ~~fresh~~ unaltered olivine ~~and~~ or plagioclase ~~crystals were found~~was identified in the

468   studied rocks, and clinopyroxene underwent secondary alteration in many of the studied

469   samples. Nonetheless, a detailed petrographic study allowed us to recognize fresh

470   clinopyroxene crystals in basaltic samples of the different rock groups, as well as fresh

471   magmatic clinopyroxene relics in one metabasaltic sample. Representative chemical

472   analyses of these crystals are shown in Table 2, whereas their classification according to

473   the quadrilateral diagram is given in Supplementary Figure S2. ~~Beside~~ In addition to

474   crystal-chemical constraints, the clinopyroxene composition is strongly influenced by the

475   composition of the magmas from which they crystallized. According to Leterrier et al.

19

476   (1982) and Beccaluva et al. (1989), clinopyroxene composition represents a petrogenetic

477   indicator of the chemical affinity of the magmatic melts from which they crystallized.

478   Therefore, the mineral chemistry of clinopyroxene can provide us robust constraints for

479   understanding the tectono-magmatic setting of formation of basaltic melts. The chemical

480   features of clinopyroxenes will be described according to the whole rock chemical groups.

481

482   *6.1. Group 1 rocks*

483

484   Clinopyroxenes in Group 1 basalts show augitic composition with the wollastonite

485   end-member ranging from ~38% to ~42% (Table 2). Clinopyroxenes of Group 1 rocks

486   show Mg# in the range 0.77 - 0.65, likely reflecting the crystallization from melts at

487   different fractionation stages. CaO, Al_2O_3, and Cr_2O_3 decrease with decreasing Mg#,

488   whereas FeO_{tot} and TiO_2 generally increase with the decreasing Mg# (Table 2). They

489   display relatively low contents of TiO_2 (0.91 – 1.45 wt%), Na_2O (0.28 – 0.46 wt%) and

490   CaO (19.26 – 21.11 wt%) compared to clinopyroxenes from Group 2a and Group 2b rocks

491   (Table 2, Fig. 8). Al_2O_3 (1.44 – 3.06 wt%) is lower than Group 2a and Group 2b

492   clinopyroxene at comparable value of Mg# (Table 2). The Cr_2O_3 content is relatively low

493   and shows positive correlation with Mg#. They are commonly unzoned; only three crystals

494   show little chemical variation from core to rim (Table 2). According to the discrimination

495   diagrams proposed by Leterrier et al. (1982), clinopyroxenes from Group 1 basalts plot in

496   the field for clinopyroxene from sub-alkaline tholeiitic and calc-alkaline rocks and are

497   clearly distinguished from clinopyroxene from Group 2a and Group 2b (Fig. 9a). In

498   addition, the (Ti + Cr) vs. Ca diagram shows that clinopyroxene from Group 1 rocks

499   display MORB affinity (Fig. 9b). Accordingly, in the discrimination diagram of Beccaluva

20

500 et al., (1989), they plot in the field for clinopyroxene from MOR and within-plate oceanic

501 settings (Fig. 10).

502

503 *6.2. Group 2a rocks*

504

505 Clinopyroxene from Group 2a were analysed in basalts and ferrobasalts. They mainly

506 show augitic composition, though a few crystals display diopsidic composition. The

507 wollastonite end-member range from ~43% to ~50% (Table 2). Mg# is generally high,

508 ranging from 0.74 to 0.84. TiO_2 (1.01 – 2.1 wt%), Na_2O (0.33 – 0.5 wt%), CaO (21.02 –

509 22.3 wt%), and Al_2O_3 (2.66 – 4.39 wt%) contents are generally higher than in

510 clinopyroxene from Group 1 rocks (Table 2; Fig. 8). Cr_2O_3 content is variable (0.12 – 0.67

511 wt%) and gradually decreases with decreasing Mg#. The crystals from sample MK479 are

512 unzoned whereas those from sample MK491 commonly show zoning with Mg# in cores

513 higher than the rims. This variation is coupled with an increase of TiO_2, Al_2O_3, and FeO_{tot}

514 contents, and a decrease of Cr_2O_3, MgO, and CaO from core to rim (Table 2). These

515 compositional variations likely reflect fractional crystallization processes during the

516 growth of the crystals, as typically observed in clinopyroxene from ophiolitic sequence

517 (Beccaluva et al., 1989). In the Ti – (Ca + Na) variation diagram, the clinopyroxenes from

518 Group 2a rocks plot in the field for pyroxene from alkaline rocks and are clearly

519 distinguished from the clinopyroxene of the Group 1 rocks (Fig. 9). Accordingly, in the

520 discrimination diagram of Beccaluva et al. (1989), they plot in the field for clinopyroxenes

521 typical of plume-influenced Iceland basalts and within-plate oceanic basalts (Fig. 10).

522

523 *6.3. Group 2b rocks*

524

21

525   Clinopyroxene from Group 2b rocks were analysed in basaltic, ferrobasaltic and

526   metabasaltic samples (Table 2). They are mainly represented by diopsidic clinopyroxenes

527   and minor augite. The wollastonite end-member ranges from ~47% to ~49% (Table 2).

528   Mg#, though variable, is generally high (0.74 - 0.87). Clinopyroxenes in Group 2b rocks

529   show generally higher contents of TiO_2 (1.26 – 3.69 wt%), Na_2O (0.28 – 0.66 wt%), CaO

530   (21.7 – 24.3 wt%), and Al_2O_3 (2.88 – 7.08 wt%) compared to those from the other groups

531   of rocks (Fig. 8). Cr_2O_3 contents vary from 0.01 to 1.0 wt% and are positively correlated

532   with Mg# values. Concentric zoning and multiple zones of growth are frequently observed.

533   The zoning is associated to significant chemical variations of TiO_2, CaO, Al_2O_3, Na_2O,

534   MgO, FeO_{tot} and Cr_2O_3 contents from core to rim (Table 2). Generally, the core of the

535   crystals shows higher MgO, Cr_2O_3, and CaO contents coupled with lower TiO_2, Al_2O_3,

536   Na_2O, and FeO_{tot} contents with respect to the rim. However, reverse zoning is observed in

537   some crystals. In addition, some crystals show concentric, oscillatory zoning characterized

538   by different zones of growth, showing rhythmic variation of TiO_2, CaO, Al_2O_3, Na_2O,

539   MgO, FeO_{tot} and Cr_2O_3 contents (Table 2). This is particularly evident for the sample

540   MK859cr1, in which TiO_2, Na_2O, MgO, and Cr_2O_3 show oscillatory chemical variation

541   from the core to the rim of the crystal (Table 2). These features collectively indicate that

542   the growth of the crystals occurred either from a progressively differentiating melt or from

543   the equilibrium with different pulses of new batches of primitive melts at different

544   fractionation stages. The clinopyroxenes of the Group 2b rocks plot in the field for

545   clinopyroxene of alkaline rocks (Fig. 9). An alkaline affinity for the clinopyroxene of

546   Group 2b rocks is also suggested by the discrimination diagram in Figure 10, where they

547   plot within the field for plume-influenced Iceland and within-plate oceanic basalts.

548

549   *6.4. Correlation of clinopyroxene composition vs. whole rock geochemistry*

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550

Our mineral chemistry data show that there is a close relationship between the composition of clinopyroxenes and the compositions of their hosting rocks. The diagrams in Figure 8 show that the variations of TiO_2, CaO, and Na_2O with respect to the variations of Mg# in clinopyroxenes depict different trends depending on the different rock groups in which these minerals are hosted. Clinopyroxenes from Group 1 transitional basaltic rocks show relatively smooth increase in TiO_2 and Na_2O contents coupled with relatively sharp decrease in CaO contents with decreasing Mg#. In contrast, in clinopyroxenes from the alkaline basaltic rocks of Group 2a and Group 2b TiO_2 and Na_2O contents show sharp increase with decreasing Mg#, whereas CaO contents decrease very smoothly with decreasing Mg# (Fig. 8). In addition, clinopyroxenes from Group 2a and Group 2b show distinct elemental behaviour with respect to the variation of Mg# values (Fig. 8). In particular, clinopyroxenes from Group 2b show the relatively sharper increase of TiO_2 and Na_2O contents with decreasing Mg# compared to clinopyroxenes from Group 2a (Figs. 8a, c). Clinopyroxenes from Group 2a basaltic rocks are also characterized by higher (Ca + Na) contents compared to those from Group 2b (Fig. 9). The variation in TiO_2 contents in clinoyroxenes is commonly thought to reflect the degree of depletion or enrichment of the mantle source (Pearce and Norry, 1979). High TiO_2 content in clinopyroxenes point out for their crystallization from primary magmas generated from enriched mantle sources. The diagrams in Figure 11 clearly show a positive correlation between the Nb/Y ratios of the hosting rocks and the TiO_2, CaO, and Al_2O_3 contents of their clinopyroxenes. The increase in Nb/Y ratios in basaltic rocks is commonly associated with the increase of enrichment of the mantle sources from which they originated (Winchester and Floyd, 1979; Pearce, 1996, 2008). The contents in TiO_2, CaO, and Al_2O_3 in clinopyroxenes increase from transitional Group 1 basalts to alkaline Group 2a and Group 2b basaltic rocks. Different compositions

23

575   and elemental co-variations can clearly be distinguished in the clinopyroxenes of the

576   different groups of rocks (Figs. 8, 9, 11). This evidence further supports the conclusions

577   obtained from whole rock chemistry that is, in the Durkan volcanic and metavolcanic rocks

578   three different groups of rocks can be identified (see section 5).

579

580

581   7. Discussion

582

583   *7.1. Melt petrogenesis of the volcanic and metavolcanic rocks*

584

585   The aim of this petrogenetic discussion is to identify the possible mantle sources for

586   the volcanic rocks and the magmatic protoliths of the metavolcanic rocks from the Durkan

587   Complex, as well as their melting conditions, in order to provide robust constraints for the

588   interpretation of the tectono-magmatic setting of formation of this Complex. Sections 5

589   and 6 have shown that the volcanic and metavolcanic rocks of the Durkan Complex exhibit

590   whole-rock and mineral chemistry with transitional (Group 1) and alkaline (Group 2a and

591   Group 2b) affinities. The different trace elements contents (e.g., Zr, Y, Nb) and REE

592   patterns (Fig. 5) observed in the rocks of these three groups, as well as their different

593   incompatible element (e.g., Zr/Y, Y/Nb, Nb/Yb) and REE ratios (i.e., La_N/Yb_N, Sm_N/Yb_N,

594   Sm_N/Dy_N,) (Table 2, Fig. 6) suggest that these rocks were derived from partial melting of

595   chemically distinct mantle sources and/or different melting conditions. Very similar HREE

596   (e.g., Yb) contents and no correlations between the LREE/HREE (i.e., La_N/Yb_N) ratios

597   observed in all rock groups (Table 2, Fig. 6c) suggest that the differences in the chemistry

598   of their possible mantle sources most likely consisted ~~in~~ of different enrichments in LREE,

599   Zr, and Nb. A first idea about the petrogenesis of the Durkan volcanic and metavolcanic

24

600   rocks can be deduced from the Zr-Nb co-variation diagram in Figure 12a, which shows

601   that these rocks were generated by partial melting of an enriched and/or transitional mantle

602   source. The mineral chemistry of the clinopyroxenes, in particular their high TiO_2 contents,

603   also point out for the genesis of these rocks from a transitional to enriched mantle sources

604   (Fig. 10). The diagram in Figure 12b further supports this conclusion; in fact, the studied

605   rocks plot along the mixing curve between N-MORB and OIB with compositions

606   clustering toward the OIB end member. In addition, the enrichment of OIB-type chemical

607   components increases from Group 1 to Groups 2a and 2b (Fig. 12b). The Th-Nb co-

608   variation (Fig.7) further point out for a genesis of the studied rocks from the partial melting

609   of mantle sources that have been influenced by OIB-type chemical components prior to

610   melting without any contributions from subduction related chemical components and/or

611   continental crust contamination.

612   Given these considerations, we performed a semi-quantitative non-modal, batch partial

613   melting modelling in order to constrain the possible mantle peridotite compositions and

614   melting conditions that can reproduce the compositions of the most primitive basalts for

615   each geochemical group of rocks. An accurate definition and quantification of the

616   composition of mantle sources and degrees and depths of partial melting generating the

617   different rock-types is not possible, as these factors cannot be exactly constrained.

618   Therefore, we used different models based on incompatible trace elements ratios and REE

619   in order to better constrain the petrogenesis of the studied rocks (Figs. 13, 14). These

620   elements are used in the commonly accepted assumption that their content in basaltic rocks

621   basically depend on the composition of the mantle source and its degree of partial melting

622   and it is little influenced by moderate degrees of fractional crystallization of olivine,

623   clinopyroxene and plagioclase (e.g., Allègre and Minster, 1978).

25

624   The models in Fig. 13 have the advantage of combining information about the

625   increasing of enrichment of the mantle source (i.e., increasing of Nb/Yb with respect to

626   TiO_2/Yb in Fig. 13a and increasing of Th with respect to Nb/Yb in Fig. 13b) and the

627   presence of residual garnet in the source (i.e., TiO_2/Yb in Fig. 13a and Nb/Yb compared to

628   Th in Fig. 13b). Results from these binary models have been then compared with the REE

629   model (Fig. 14). We have previously shown that the composition of the Durkan volcanic

630   and metavolcanic rocks strongly point out for a genesis from partial melting of sub-oceanic

631   mantle sources that have been influenced by OIB-type chemical components. Therefore, in

632   our models we chose as a possible mantle source for the Durkan basaltic rocks a sub-

633   oceanic slightly depleted lherzolite residual after small volume of MORB melt extraction

634   metasomatized to various extents of enrichment by an OIB-type chemical component. In

635   our models, we used the lherzolite ZB2 from the Northern Apennines (Barbero et al.,

636   2020c) as representative of a slightly depleted sub-oceanic mantle and the enriched mantle

637   of Lustrino et al. (2002) as the metasomatizing chemical component. The modal

638   compositions of the assumed mantle sources, their chemical composition, the melting

639   proportions and the REE and trace elements distribution coefficients used in the models are

640   listed in Supplementary Table 2.

641

642   7.1.1. Group 1 rocks

643

644   The Nb/Yb vs. TiO_2/Yb model (Fig. 13a) shows that Group 1 rocks cannot be

645   generated from the partial melting of sources with depleted composition as the DMM

646   (Workman and Hart, 2005) or the lherzolite ZB2 (Barbero et al., 2020c). By contrast, the

647   geochemistry of Group 1 primitive basalts is compatible with the partial melting of a

648   calculated S1 mantle source that is significantly more enriched in Nb with respect to the

26

649 DMM and ZB2 mantle peridotites (Fig. 13a). The high TiO_2/Yb ratios characterizing the

650 Group 1 basalts can be explained by the presence of residual garnet in the mantle source

651 and, therefore, that partial melting started in the garnet-facies mantle (Fig. 13a).

652 Accordingly, the Nb/Yb vs. Th petrogenetic model suggest that the compositions of Group

653 1 primitive basalts can be explained by partial melting of the enriched mantle source S1

654 that starts partial melting in the garnet-facies mantle and continues to larger degrees in the

655 spinel-facies mantle. In detail, the model shows that partial melting degrees are ~2% and

656 ~7% in garnet- and spinel-facies, respectively with mixing of the different melts produced

657 in equal proportions (Fig. 13b).

658   The REE modelling well confirms these results clearly indicating that the REE

659 composition of Group 1 basalts can be explained by partial melting of the mantle source

660 S1, which is significantly enriched in LREE with respect to the DMM and the residual sub-

661 oceanic peridotite ZB2 by OIB-type chemical components (Fig. 14a). According to the

662 results from the models shown in Figure 13, the rather high $(Sm/Yb)_N$ ratios displayed by

663 Group 1 rocks suggest the involvement of residual garnet in their mantle source. In fact,

664 the composition of Group 1 primitive basalt MK282 fits well with the melt calculated for

665 2.5% and 7.5% of partial melting of the S1 mantle source at garnet- and spinel-facies,

666 respectively, with a mixing proportion between melts generated in the garnet and spinel

667 melts of 50:50 (Fig. 14a). Different melting degrees and mixing proportions of different

668 melts (Fig. 14a$_1$) fail to reproduce the REE composition of the Group 1 relatively primitive

669 basalt.

670   The fairly differentiated trachyte MK795 clearly display different geochemical

671 patterns compared to basaltic rocks of this Group (Figs. 5a, b). Shallow-level (i.e., magma

672 chamber) petrogenetic processes are beyond the scope of this work since the main goal of

673 this paper is to define the petrogenesis of primary melts in order to constrain their tectono-

27

674 magmatic setting of formation. In addition, as commonly seen in ophiolites, the

675 tectonically dismembered nature of the volcanic series does not allow basalt-differentiated

676 rocks comagmatic relationships to be reliably constrained. This is particularly true in the

677 Durkan Complex where differentiated samples are very rare. However, differentiated rocks

678 may have various origins and may eventually not be genetically related to the associated

679 mafic rocks. In fact, they may have been generated by fractional crystallization, partial

680 melting of lower crustal rocks (i.e., anatexis), mixing of different melts, etc. We therefore

681 performed Rayleigh fractionation model using REE. Results are shown in Supplementary

682 Figure S3 together with model parameters and constraints. This model clearly indicates

683 that the REE compositions of the trachyte MK795 is compatible with the composition of a

684 24% residual melt after various steps of crystal fractionation of olivine, plagioclase,

685 clinopyroxene, hornblende, magnetite, and ilmenite starting from the composition of the

686 near-primary basalt MK282 used in the mantle partial melting model shown above (see

687 also Figs. 13, 14). It follows that trachyte MK795 represent a differentiated product formed

688 by fractional crystallization.

689

690   7.1.2. Group 2a and Group 2b rocks

691

692   Group 2a and Group 2b alkaline rocks collectively show overall whole rock chemistry

693 (Table 1; Fig. 6) and mineral chemistry (Fig. 9) that are quite different from those of the

694 transitional Group 1 rocks. In particular, basaltic rocks from these groups show much

695 higher Nb, Ta, Th, LREE/HREE and MREE/HREE ratios with comparable Yb absolute

696 contents (Fig. 6; Table 1), which cannot be explained with partial melting of the S1 source.

697 These chemical features point out for a genesis from a mantle source more enriched

698 (source S2) in these elements and LREE compared to the theoretical S1 source. Similar to

28

699   Group 1 rocks, the high $(La/Yb)_N$, TiO_2/Yb, and Nb/Yb ratios of Group 2a and Group 2b

700   rocks suggest residual garnet in the mantle source (Figs. 6a, 13). Nonetheless, Group 2a

701   and Group 2b rocks, though very similar in composition for many elements, slightly differ

702   in their $(La/Yb)_N$ and $(Sm/Dy)_N$ ratios (Fig. 6). These differences can be explained either

703   with slightly different compositions of their mantle sources or different proportions of

704   partial melting in the garnet- and spinel-facies mantle. However, the chemical differences

705   between basalts of these two groups are limited to a few elemental ratios basically

706   involving HREE (e.g., TiO_2/Yb, Nb/Yb, Th/Tb, Sm/Dy). As a consequence, it is

707   reasonable to assume that the chemical differences between basalts of these two Groups

708   are most likely due to different proportions of partial melting in the garnet- and spinel-

709   facies mantle, rather than chemical differences of the mantle sources. Therefore, in the

710   models in Figures 13 and 14 we use the same theoretical mantle source S2 for both Group

711   2a and 2b basalts. In fact, the TiO_2/Yb vs. Nb/Yb model suggests that the genesis of

712   relatively primitive basalts from both rock groups is related to the partial melting of the

713   mantle source S2 that starts in the garnet-facies mantle. However, the composition of the

714   relatively primitive basalt of Group 2a is compatible with partial melting starting at a

715   higher pressure (4GPa) compared to Group 2b primitive basalt (3GPa) (Fig. 13a). The

716   Nb/Yb vs. Th model show that the composition of Group 2a relatively primitive basalt

717   MK340 is compatible with ~2% partial melting of the source S2 in the garnet-facies mantle

718   followed by 5% partial melting in the spinel-facies mantle, with mixing of the different

719   melts in the proportions 60% garnet melt - 40% spinel melt. (Fig. 13b). In contrast, the

720   composition of Group 2b relatively primitive basalt MK499 is compatible with 1% partial

721   melting of the source S2 in the garnet-facies mantle followed by ~3% partial melting in the

722   spinel-facies mantle, with mixing of the different melts in the proportions 65% garnet melt

723   - 35% spinel melt. (Fig. 13b).

29

724   Accordingly, REE model indicates that the REE composition of the relatively

725   primitive basalt MK340 (Group 2a) can be explained by ~2 % partial melting in the garnet-

726   facies and ~5% partial melting in the spinel-facies of the mantle source S2 with mixing of

727   the different melts in the proportions 60% garnet melt - 40% spinel melt (Fig. 14b).

728   Likewise, the REE model carried out for Group 2b rocks (Fig. 14c) is perfectly in

729   agreement with the models based on TiO_2, Nb, Th, and Yb contents (Fig. 13). The model

730   in Figure 14c shows indeed that the REE composition of the relatively primitive basalt

731   MK499 is compatible with 1.5% partial melting in the garnet-facies mantle followed by

732   4% partial melting in the spinel-facies mantle of the source S2, with mixing of the different

733   melts in the proportions 65% garnet melt - 35% spinel melt.

734   As already discussed in section 7.1.1 for the trachyte MK795, the different chemistry

735   of the alkali rhyolite MK339 compared to Group 2 basalts (Figs. 5c-f) may reflect the

736   effect of fractional crystallization, or anatexis, or other petrogenetic processes. Rayleigh

737   fractionation model using REE are shown in Supplementary Figure S3. This model clearly

738   shows that the REE compositions of the alkali rhyolite MK339 is compatible with the

739   composition of a 25% residual melt after various steps of crystal fractionation of olivine,

740   plagioclase, clinopyroxene, magnetite, and ilmenite starting from the composition of the

741   near-primary basalt MK340 used in the mantle partial melting model for Group 2a rocks

742   (see also Figs. 13, 14b).

743

744   *7.2. Tectono-magmatic significance of the volcanic and metavolcanic rocks*

745

746   Previous studies have suggested that the Durkan Complex represents remnants of the

747   Permian - Cretaceous continental margin of the Bajgan Complex microcontinental

748   basement (McCall, 1985; Hunziker et al., 2015). However, a recent multidisciplinary study

30

749　of the western part of the Durkan Complex has demonstrated that it consists of Late

750　Cretaceous volcano-sedimentary successions, which represent portions of a seamount or,

751　most likely, of a seamount chain (Barbero et al., 2021). The geochemical and mineral

752　chemistry data, as well as petrogenetic models presented in this paper collectively suggest

753　that the volcanic rocks in these sequences consist of an association of transitional P-

754　MORBs and alkaline OIBs, which were formed by partial melting of enriched mantle

755　sources with variable contribution of melts formed at both garnet- and spinel-facies. These

756　data strongly support the interpretation of the Barbero et al. (2021). In Figure 15 we

757　therefore propose a schematic tectono-magmatic model that can explain the petrogenetic

758　processes, which occurred during the formation of the Durkan seamount chain. According

759　to Barbero et al. (2021), the Type-II and Type-III volcano-sedimentary successions consist

760　of remnants of seamount flank and seamount summit depositional and eruptional settings,

761　respectively, and were formed during the Cenomanian in the shallow-water stage of

762　growth of a seamount (Fig. 15a). These types of successions are characterized by alkaline

763　volcanic rocks (Group 2a and Group 2b), whose geochemistry and melt petrogenesis (see

764　section 7.1) clearly indicate that they derived from low degree of partial melting at both

765　garnet- and facies-spinel of an enriched OIB-type (plume-type) mantle source (S2 in Fig.

766　15a). By contrast, the Type-I volcano-sedimentary succession represents the remnants of

767　Coniacian – early Campanian sedimentation and volcanism in a pelagic setting during the

768　deep-water stage of growth of a seamount (Fig. 15b; Barbero et al., 2021). This Type of

769　succession is mainly characterized by transitional P-MORB rocks (Group 1) and minor

770　Group 2a alkaline rocks, whereas Group 2b basalts were not found in this succession. The

771　petrogenetic model show that, compared to Group 2a basalts, Group 2b basalts are

772　characterized by higher proportions of melts formed at garnet-facies with respect to melts

773　formed at spinel-facies mantle and an overall smaller degree of partial melting (Fig. 14).

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774   By contrast, the deep-water stage of formation of the seamounts was characterized by the

775   partial melting of an enriched mantle source bearing strongly enriched mantle patches

776   (sources S1 and S2, respectively in Fig. 15b). The lack of Group 2b rocks and the

777   prevalence of Group 1 rocks may also be explained by mantle partial melting at relatively

778   shallower depth and higher partial melting degree during the deep-water stage of the

779   seamount formation with respect to the shallow-water stage of the seamount growth (Figs.

780   15a, b). In addition, this implies a minor contribution of melts produced at garnet-facies

781   with respect to the shallow-water stage of the seamount growth. These features are

782   compatible with oceanic within-plate magmatism related to the rising of deep, enriched

783   mantle plume material (Figs. 15a, b). Indeed, mantle plumes are likely the most effective

784   mean for transferring anomalous heat flux and enriched chemical components from the

785   lower to the upper mantle (e.g., Regelous et al., 2003; Pearce, 2008; White, 2010; Kerr,

786   2014; Safonova and Santosh, 2014). The rising of mantle material that is more enriched

787   and hotter than the ambient sub-oceanic mantle facilitates the starting of the partial melting

788   at deeper level within the garnet stability field (Figs. 15a, b). This can well explain the

789   clear residual garnet geochemical signature shown by all the studied rocks. The processes

790   responsible for the geochemical variation of the erupted basalts during the different stage

791   of growth of the Durkan seamount chain are difficult to be constrained in detail, mainly

792   because of the disrupted tectonic nature of the different Durkan successions, which is, in

793   turn, related to multiple deformative events occurred during their incorporation into the

794   accretionary prism (Barbero et al., 2021). However, it is commonly accepted that during

795   the progressive growth of seamounts, from the early stage of formation to their emergence

796   above the sea level (i.e., shallow-water shield stage), the volcanic products progressively

797   change from tholeiitic rocks to progressively more enriched transitional and alkaline rocks

798   (e.g., Moore and Clague, 1992; Regelous et al., 2003). In this classical scenario the Durkan

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799   Type I, II and III successions are associated with progressive chemical changes of magmas

800   from tholeiitic to alkaline signatures, which could be mainly derived from different degrees

801   of partial melting of variably enriched mantle sources. The chemical composition of

802   analysed clinopyroxenes is also consistent with progressive chemical changes of magmas

803   from tholeiitic to alkaline nature. The chemical variation of seamount volcanic rocks may

804   be explained by the combination of several factors, such as: 1) the increasing contribution

805   from an enriched mantle source to the ambient sub-oceanic mantle; 2) the decreasing in

806   partial melting degrees; 3) the increase of the depth of partial melting; 4) the variation of

807   the thickness of the melting column (e.g., Regelous et al., 2003; Safonova, 2008; White,

808   2010; Safonova and Santosh, 2014). According to Safonova et al. (2016), the large

809   volumetric prevalence of alkaline rocks in the shallow-water shield stage of the Durkan

810   volcano-sedimentary sequences suggest relatively higher contributions of melting in the

811   garnet-facies of a strongly enriched mantle source during this stage coupled with the

812   decrease of the overall partial melting degree (Fig. 15a). These features are consistent with

813   the deepening of the partial melting region in response of the enhancing of the lithospheric

814   load (i.e., crust + lithospheric mantle) due to the thickening of the seamount edifice

815   coupled with an increasing of the mantle plume influence on the sub-oceanic ambient

816   mantle and a shortening of the melting mantle column (Fig. 15a). By contrast, during the

817   deep-water stage of the seamount life the crustal load is significantly lower. In this stage,

818   the sub-oceanic mantle is relatively less influenced by the metasomatizing effects of the

819   mantle plume (Fig. 15b). The combination of these effects likely produces partial melting

820   of a moderately enriched mantle source, though partial melting may also involve strongly

821   enriched portions of the mantle. In this stage, partial melting in the spinel-facies is

822   prevailing with respect that in the garnet-facies mantle as the melting mantle column is

823   rather wide (Fig. 15b). This hypothesis agrees with data from both modern and ancient

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824 seamounts, which point out the importance of the lithospheric thickness in controlling the

825 melting processes associated with the rising of a mantle plume. In detail, a thin lithosphere

826 above a mantle plume causes the shallowing of partial melting combined with higher

827 degree of the partial melting, producing melts less enriched in LREE with respect to M-

828 and HREE. By contrast, higher thickness of lithosphere likely causes the deepening of the

829 partial melting region combined with the decrease of the partial melting degree and the

830 shortening of the melting column, thus, promoting the prevalence of partial melting at the

831 garnet-facies (e.g., Regelous et al., 2003; Safonova, 2008; White, 2010).

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834 *7.3. Geodynamic significance of the western Durkan Complex: A Late Cretaceous*

835 *seamount chain in the northern Neo-Tethys?*

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837 Cretaceous alkaline and OIB rocks comparable with those of the Durkan Complex are

838 widespread within the Neo-Tethys-related collisional belts from Caucasus to Himalaya.

839 They have commonly been interpreted as remnants of seamounts and/or oceanic plateau

840 associated with mantle-plume activity (e.g., Rolland et al., 2010, 2020; Saccani et al.,

841 2013, 2018; Yang and Dilek, 2015; Yang et al., 2015, 2019; Esmaeili et al 2019; Barbero

842 et al., 2020b, 2021). This evidence supports the hypothesis that the tectono-magmatic

843 evolution of different sectors of the Neo-Tethys Ocean was strongly influenced by the

844 wide occurrence of mantle plume activity at a regional-scale during the Late Cretaceous.

845 Our data well agree with this general scenario of the Cretaceous Neo-Tethys, as they point

846 out for the existence of a significant mantle plume activity in the Makran sector of this

847 Ocean during the same time. Our data allow us to depict two different stages of a seamount

848 growth at two different times. The Type-II and Type-III volcano-sedimentary successions

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849 of the Durkan Complex include Cenomanian carbonatic platform and strongly enriched

850 alkaline basalts, thus recording the existence of one or more oceanic seamounts that

851 reached a shallow-water shield stage during the early Late Cretaceous (Fig. 15a). The

852 occurrence of "mature" seamount edifices implies that a vigorous mantle plume activity

853 was already existing in the oceanic basin at that time. By contrast, the Durkan Type-I

854 succession, which is characterized by pelagic sediments and prevailing transitional

855 volcanic rocks, records an early phase of growth of a seamount (i.e., deep-water stage) in

856 the late Late Cretaceous (Fig. 15b). A general fading away at the end of Cretaceous of

857 OIB-type volcanism is observed in the Neo-Tethyan related belts from Caucasus to

858 Himalaya and it is interpreted to reflect a progressively decreasing mantle plume activity in

859 the Neo-Tethys during these times (e.g., Rolland et al., 2010, 2020; Yang and Dilek, 2015;

860 Esmaeili et al 2019; Barbero et al., 2020b, 2021). We can speculate that the occurrence in

861 the Durkan Complex of a relatively older (Cenomanian) mature seamount and a relatively

862 younger (Coniancian – Campanian) immature seamount may eventually be related to the

863 Late Cretaceous progressive decreasing of plume activity observed at a regional scale. This

864 hypothesis needs, however, to be proved by further studies.

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868 8. Conclusion

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870 The Durkan Complex represents a tectonic element of the North Makran domain that

871 was classically interpreted as a continental margin succession though a recent study

872 suggested that it represents a tectonically disrupted portion of a Late Cretaceous seamount

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chain. The petrographic and geochemical study presented in this paper allow the following conclusion to be drawn:

1) The Durkan Complex is composed by tectonic slices showing successions similar to those found at different depths of a seamount environment. The successions are characterized by abundant volcanic rocks and are either non-metamorphic or slightly metamorphosed.

2) The volcanic and metavolcanics rocks are largely represented by basaltic rocks. Based on whole rock chemistry and clinopyroxene chemistry, basaltic rocks consist of both transitional basalts showing P-MORB composition (Group 1) and alkaline basalts showing OIB composition (Groups 2a and 2b).

3) The chemical composition of clinopyroxenes from the different rock groups is strictly depending on the whole rock composition of their hosting rocks. In particular, TiO_2, Al_2O_3, and Na_2O contents in minerals increase from transitional to alkaline basalts.

4) Petrogenetic models indicate that the Durkan volcanic rocks derived from partial melting of a sub-oceanic mantle metasomatized to various extents by an OIB-type chemical component. The chemical difference between different Groups of basalts are related to a combination of different extents of metasomatic enrichment and different melting conditions (i.e., partial melting degrees and melting depths).

Our new data compared to literature data allow us to conclude that the different volcano-sedimentary successions of the Durkan Complex record portions of seamounts of different ages formed during both shallow-water shield stage (Cenomanian) and deep-water stage (Coniacian-Campanian). The age, composition, and evolution of these distinct seamounts in the Makran sector of the Neo-Tethys is compatible with regional-scale evidence (from Caucasus to Himalaya), which suggest that abundant transitional and

898   alkaline basalts were erupted as a consequence of the interaction between the sub-oceanic

899   lithosphere and significant mantle plume activity.

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1185   **Table captions**

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1187   **Table 1**. Major (wt.%) and trace (ppm) element composition of representative volcanic

1188   and metavolcanic rocks from the western part of the Durkan Complex. Abbreviations: bas:

1189   basalt; bas and: basaltic andesite; tra: trachyte; a-rhy: alkali-rhyolite; XRF: X-ray

1190   fluorescence spectrometry; ICP-MS: inductively coupled plasma-mass spectrometry; n.d.:

1191   not detected. Mg# = 100 x MgO / (MgO + FeO). Fe_2O_3 = 0.15 x FeO. Normalizing values

1192   for REE ratios from Sun and McDonough (1989). Asterisks indicate samples whose XRF

1193   composition is taken from Barbero et al. (2021).

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1195   **Table 2**. Representative analyses of clinopyroxene from basaltic and metabasaltic

1196   rocks from the western part of the Durkan Complex. Atoms per formula units (a.p.f.u.) are

1197   calculated on the bases of four cations. The compositions of Fe^{3+} and Fe^{2+} were calculated

1198   from the measured total FeO according to Droop (1987); Mg# = Mg / (Mg + Fe2+).

1199   Abbreviations, Wo: wollastonite; En: enstatite; Fs: ferrosilite; Acm: Acmite.

1200   Abbreviations, c: core; ec: external part of the core; r: rim.

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1202   **Figure caption**

1203

1204   **Figure 1**. a) Simplified tectonic sketch map of the Iranian-Afghan-Pakistani area

1205   (modified from Khan et al., 2007; Bagheri and Stampfli, 2008; Allahyari et al., 2014;

1206   Mohammadi et al., 2016; Pirnia et al., 2020; Barbero et al., 2020b); b) structural sketch

1207   map showing the different tectono-stratigraphic domains of the Makran Accretionary

1208   Wedge (modified from Burg et al., 2013); c) simplified geological-structural map of the

1209   North Makran Domain showing the different tectonic units (modified from Eftekhar-

1210   Nezhad et al. 1979; Burg, 2018; Samimi Namin, 1982, 1983; Barbero et al., 2020b).

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1212   **Figure 2**. Simplified geological map of the western part of the Durkan Complex

1213   (based on Samimi Namin, 1982 and modified according to our original fieldwork and

1214   photointerpretation with satellite images). The locations of the sampled areas are also

1215   shown.

1216

1217   **Figure 3**. a) Schematic stratigraphic column and ages for the three different types of

1218   successions in the western part of the Durkan Complex; b) vesicle volume % vs. depth of

1219   eruption for basalts from the different successions. The different curves indicate the depth-

1220 vesicles percent for tholeiitic (solid line, from Moore and Schilling, 1973) and alkaline

1221 (dashed line, from Moore, 1970) volcanic rocks. Modified from Barbero et al., (2021).

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1224 **Figure 4**. Nb/Y vs. Zr/Ti discrimination diagram of Winchester and Floyd (1977)

1225 modified by Pearce (1996) for volcanic and metavolcanic rocks from the western part of

1226 the Durkan Complex.

1227

1228 **Figure 5**. N-MORB normalized incompatible element patterns (left column) and

1229 Chondrite-normalized rare earth element patterns (right column) for volcanic and

1230 metavolcanic rocks from the part of the Durkan Complex. Normalizing values are from

1231 Sun and McDonough (1989). Compositions of average plume-influenced mid-ocean ridge

1232 basalt (P-MORB) from the Southwest Indian Ridge and typical alkaline oceanic within-

1233 plate basalt (OIB) are from Janney et al. (2005) and Sun and McDonough (1989),

1234 respectively.

1235

1236 **Figure 6**. Chondrite-normalized $(Sm/Yb)_N$ vs. $(La/Yb)_N$ (a), $(Sm/Yb)_N$ vs. $(Sm/Dy)_N$

1237 (b), and $(La/Yb)_N$ vs. Yb_N (c) diagrams for the volcanic and metavolcanic rocks of the

1238 western part of the Durkan Complex. Normalizing values are from Sun and McDonough

1239 (1989).

1240

1241 **Figure 7**. N-MORB normalized Th vs. Nb discrimination diagram of Saccani (2015)

1242 for volcanic and metavolcanic rocks from the western part of the Durkan Complex.

1243 Vectors indicate the trends of compositional variations due to the main petrogenetic

1244 processes. Abbreviations, AFC: assimilation-fractional crystallization; OIB-CE: ocean

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island-type (plume-type) component enrichment; FC: fractional crystallization; MORB: mid-ocean ridge basalt; N-: normal type; E-: enriched type; P-: plume type; D-: depleted type; IAT: island arc tholeiite; CAB: calc-alkaline basalt; AB: alkaline oceanic within-plate basalt; MTB: medium titanium basalt. Normalizing values, as well as the composition of typical N-MORB (white star), E-MORB (grey star), and OIB (black star) are from Sun and McDonough (1989).

Figure 8. Diagram showing the variation of TiO_2, CaO, and Na_2O contents vs. Mg# for clinopyroxenes from the basaltic and metabasaltic rocks of the western part of the Durkan Complex. Arrows represent the average trends of variation for clinopyroxene from the different geochemical groups of rocks.

Figure 9. a) Ti vs. (Ca + Na) and b) (Ti + Cr) vs. Ca discrimination diagrams of Leterrier et al. (1982) showing the compositions of clinopyroxenes from the volcanic and metavolcanic rocks from the western the part of the Durkan Complex.

Figure 10. Compositions of clinopyroxenes from the basaltic and metabasaltic rocks from the western the part of the Durkan Complex plotted in the TiO_2–Na_2O–$SiO_2/100$ diagram for discriminating clinopyroxenes in basalts from different oceanic settings (Beccaluva et al., 1989). Abbreviations, E-MORB: enriched mid-ocean ridge basalt; N-MORB: normal mid-ocean ridge basalt; WOPB: within oceanic plate basalts; ICB: Iceland basalts; and SSZ: supra-subduction zone basalts.

Figure 11. Variation of TiO_2 (a), CaO (b), and Al_2O_3 (c) contents in clinopyroxenes from basaltic and metabasaltic rocks from the western the part of the Durkan Complex vs.

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1270   the Nb/Y ratios of their hosting rocks. Only clinopyroxene with Mg# in the range 0.74 –

1271   0.80 are plotted to allow comparison between the different chemical groups.

1272

1273   **Figure 12**. a) Nb vs. Zr and b) Zr/Y vs. Zr/Nb diagrams for volcanic and metavolcanic

1274   rocks from the western part of the Durkan Complex. N-MORB, E-MORB and OIB end-

1275   members are from Sun and McDonough (1989). Fields showing the compositional

1276   variation of different types of basalts from subduction-unrelated ophiolites and modern

1277   oceanic setting are shown for comparison in Panel b) (data from Saccani et al., 2013, Le

1278   Roex et al., 1983; Hanan et al., 2000; Chauvet et al., 2011). The dashed line in b)

1279   represents the mixing curve calculated using OIB and N-MORB end-members (from Le

1280   Roex et al. 1983).

1281

1282   **Figure 13**. a) Nb/Yb vs. TiO$_2$/Yb diagram showing the isobaric melting curves for

1283   theoretical mantle sources S1 and S2 calculated for different pressures according to Pearce

1284   (2008); b) Nb/Yb vs. Th batch melting curve for the theoretical mantle source S1 and S2

1285   calculated for both spinel- and garnet-facies conditions. The dashed line represents the

1286   mixing line of various melt fractions from garnet- and spinel-facies mantle. S1 and S2

1287   represent theoretical mantle sources calculated by assuming different degrees of

1288   enrichment by an OIB-type chemical component (Lustrino et al., 2002) of a sub-oceanic

1289   slightly depleted lherzolite residual after small volume of MORB melt extraction

1290   (lherzolite ZB2, Barbero et al., 2020c). Depleted MORB mantle (DMM) and primitive

1291   mantle (PM) compositions are also shown in Figure 13a (data from Workman and Hart,

1292   2005 and Sun and McDonough, 1989, respectively). Input parameters (source modes,

1293   melting proportions, and partition coefficients, source compositions) for the model in

1294   Figure 13b are given in Supplementary Table S2. Volcanic and metavolcanic rocks from

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the western part of the Durkan Complex are plotted in both diagrams. The relatively less

fractionated basalts of each rock type are shown with large symbols, whereas other

samples are shown with small, grey symbols.

Figure 14. Calculated chondrite-normalized (Sun and McDonough, 1989) rare earth

element (REE) liquid composition for parental melts derived from mantle sources S1 and

S2, assuming various degrees of non-modal batch partial melting in the spinel- and garnet-

facies mantle, as well as different proportions of melt fractions from garnet- and spinel-

facies mantle. S1 and S2 represent theoretical mantle sources calculated by assuming

different degrees of enrichment by an OIB-type chemical component (Lustrino et al., 2002)

of a sub-oceanic slightly depleted lherzolite residual after small volume of MORB melt

extraction (lherzolite ZB2, Barbero et al., 2020c). Abbreviations: EM: enriched mantle

source (from Lustrino et al., 2002); DMM: depleted MORB mantle (Workman and Hart,

2005). Input parameters for the REE models (source modes, melting proportions, and

partition coefficients), as well as compositions of the different mantle sources are shown in

Supplementary Table S2. The comparison between the composition of the relatively less

fractionated basalts of Group 1, Group 2a, and Group 2b and the calculated melts are

shown in panels a), b), c), respectively. Representative examples of the mixing of various

melt fractions from garnet- and spinel-facies mantle are shown in a1).

Figure 15. Conceptual cartoon showing the petrogenetic processes operating during

the shallow-water (a) and deep-water (b) stages of growth of the Durkan seamounts. The

depositional positions of the different types of successions within the seamount chain is

modified from Barbero et al. (2021). Abbreviations, MORB: mid-oceanic ridge basalt;

OIB: ocean island basalt; S1 and S2: enriched mantle sources derived from different

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1320   degrees of enrichment by an OIB-type chemical component of a sub-oceanic slightly

1321   depleted lherzolite residual after small volume of MORB melt extraction; spl: spinel; gt:

1322   garnet.

Figure 1

Figure 2

Figure 4 for Online publication only

Figure 4

Figure 5 for Online publication only

Figure 8 for Online publication only

Figure 9

Figure 10 for Online publication only

Figure 11 for Online publication only

Figure 12 for Online publication only

Figure 13 for Online publication only

a *Shallow-water shield stage (Cenomanian)*

Type-II succession Type-III succession Type-II succession
(seamount slope) (seamount summit) (seamount slope)

Depth (km)

sea level

OIB crust

MORB crust

higher lithospheric load

Sub-oceanic lithospheric mantle

S2

spl facies
gt facies

shorter melting column

Sub-oceanic asthenospheric mantle

OIB-type components (mantle plume?)

b *Deep-water stage (Coniacian - early Campanian)*

Depth (km)

non-active seamount

oceanic plate movement

Type-I succession

sea level

MORB crust

lower lithospheric load

Sub-oceanic lithospheric mantle

spl facies
gt facies

longer melting column

S1
S2

Sub-oceanic asthenospheric mantle

OIB-type components (mantle plume?)

S1
S2 Thermically and chemically plume-influenced mantle
S1: Enriched mantle source S2: Strongly enriched mantle source

Transitional melts (P-MORB)

Alkaline melts (OIB)

Figure 2

Figure 3

Figure 4 grey tone for printed version

Figure 6 grey tone for printed version

Figure 7 grey tone for printed version

Figure 9

Figure 10 grey tone for printed version

Figure 11 grey tone for printed version

a *Shallow-water shield stage (Cenomanian)*

Type-II succession (seamount slope) Type-III succession (seamount summit) Type-II succession (seamount slope)

sea level

OIB crust

MORB crust

higher lithospheric load

Sub-oceanic lithospheric mantle S2

spl facies
gt facies

shorter melting column

Sub-oceanic asthenospheric mantle

OIB-type components (mantle plume?)

Depth (km)

b *Deep-water stage (Coniacian - early Campanian)*

non-active seamount

oceanic plate movement

Type-I succession

sea level

MORB crust

lower lithospheric load

Sub-oceanic lithospheric mantle

spl facies
gt facies

longer melting column

S1
S2

Sub-oceanic asthenospheric mantle

OIB-type components (mantle plume?)

Depth (km)

S1
S2 Thermically and chemically plume-influenced mantle
S1: Enriched mantle source S2: Strongly enriched mantle source

Transitional melts (P-MORB)

Alkaline melts (OIB)

Table 1 (1/4)   **Table 1 (2/4)**

Rock Group	Group 1 (P-MORB)											Group 1 (
Sample	MK364	MK365*	MK369	MK370*	MK483	MK484	MK485	MK493*	MK867	MK282	MK338	MK795
Rock	bas and	bas	bas	bas	bas	Fe-bas	bas	bas	bas	meta-bas	eta Fe-bas	tra
Texture	aphiric	aphiric	aphiric	aphiric	doleritic	doleritic	doleritic	doleritic	aphiric	foliated	foliated	aphiric
Succession type	Type-I	Type-I	Type-I	Type-I	Type-II	Type-II	Type-II	Type-II	Type-II	Type-I	Type-II	Type-I
XRF analyses:												
SiO_2	53.3	51.4	43.3	51.8	47.2	44.6	47.2	47.6	49.5	52.3	50.9	66.9
TiO_2	2.29	2.27	2.19	2.27	1.64	1.68	1.90	2.01	1.69	1.20	2.24	0.32
Al_2O_3	16.5	14.8	15.9	16.4	15.6	16.3	17.2	16.7	14.9	12.2	13.3	14.7
Fe_2O_3	1.17	1.24	1.36	1.27	1.57	1.68	1.55	1.46	1.57	1.04	1.70	0.75
FeO	7.82	8.28	9.06	8.44	10.46	11.19	10.33	9.75	10.47	6.93	11.30	5.02
MnO	0.05	0.09	0.21	0.17	0.16	0.17	0.15	0.16	0.16	0.15	0.17	0.05
MgO	4.93	5.11	10.53	5.03	7.00	8.34	5.30	5.50	9.89	11.90	6.87	0.02
CaO	4.19	6.70	6.77	5.21	8.67	7.77	8.27	9.04	4.38	9.53	7.17	1.39
Na_2O	5.32	5.78	2.20	4.05	3.04	2.71	3.21	2.70	3.88	2.28	3.65	9.74
K_2O	0.97	0.81	1.28	1.40	1.59	1.11	1.54	1.28	0.18	0.09	0.97	0.06
P_2O_5	0.51	0.47	0.43	0.43	0.28	0.31	0.32	0.34	0.23		0.25	0.09
LOI	2.54	2.69	6.57	3.43	2.99	3.6	2.99	3.03	2.92	2.31	1.67	0.57
Total	99.53	99.66	99.86	99.94	100.18	99.48	100.04	99.56	99.75	99.92	100.17	99.62
Mg#	52.9	52.4	67.4	51.5	54.4	57.0	47.8	50.1	62.7	75.4	52.0	0.7
Zn	202	170	120	118	102	114	107	106	104	60	112	133
Cu	72	59	60	75	123	125	125	125	113	75	105	3
Sc	29	26	35	30	26	25	21	24	34	34	45	n.d.
Ga	17	17	22	19	20	19	23	21	16	12	19	37
Ni	56	47	214	101	66	55	30	32	84	108	28	n.d.
Co	57	60.5	71	53	45	42	38	42	57	31	45	n.d.
Cr	160	143	353	259	153	112	58	51	378	456	79	3
V	239	230	244	273	244	245	236	227	227	247	292	21
Ba	155	219	290	186	231	184	323	227	120	44	261	26
Pb	12	8	6	7	8	9	8	9	18	10	10	26
ICP-MS analyses:				*(XRF)*								
Rb	18.5	18.6	14.0	27	31.7	24.4	32.0	27.1	5.21	1.39	19.9	3.72
Sr	817	669	417	419	258	492	500	499	105	329	278	80.5
Y	30.9	26.9	33.5	25	20.8	23.8	21.9	22.2	21.9	17.0	25.4	58.0
Zr	216	164	220	182	134	149	148	164	130	88.0	157	701
La	19.1	18.2	21.4	20	14.2	16.2	19.5	16.6	15.1	8.95	20.5	68.9
Ce	38.7	34.5	44.4	48	31.6	35.8	18.1	32.4	32.4	19.8	41.3	146
Pr	4.84	4.48	5.63		4.03	4.65	35.5	4.52	3.98	2.60	4.90	13.9
Nd	18.6	18.2	21.9	21	16.7	19.5	4.41	18.5	15.9	10.8	18.8	44.0
Sm	4.84	4.74	5.48		4.33	5.48	18.3	5.03	3.97	2.85	4.76	8.91
Eu	1.43	1.46	1.61		1.49	1.67	4.86	1.68	1.12	0.834	1.46	0.97
Gd	4.41	4.52	4.86		4.37	4.81	1.59	4.81	4.05	2.83	4.31	7.96
Tb	0.695	0.738	0.778		0.703	0.792	4.63	0.766	0.671	0.458	0.681	1.49
Dy	4.13	4.25	4.57		3.97	4.50	0.701	4.32	4.06	2.71	4.06	9.45
Ho	0.854	0.870	0.941		0.771	0.866	4.10	0.827	0.812	0.556	0.785	2.13
Er	2.32	2.36	2.55		1.98	2.19	0.760	2.06	2.11	1.54	2.05	6.71
Tm	0.333	0.342	0.366		0.281	0.303	2.02	0.305	0.288	0.224	0.289	1.16
Yb	2.16	2.22	2.35		1.75	1.93	0.278	1.90	1.79	1.44	1.87	8.39
Lu	0.319	0.317	0.345		0.257	0.279	1.76	0.273	0.258	0.204	0.274	1.33
Nb	25.1	26.2	32.6	25	20.1	23.8	0.246	20.6	17.5	13.5	25.4	103
Hf	5.93	3.93	6.68	4	4.29	3.68	4.27	4.72	3.97	2.74	6.12	17.9
Ta	1.67	1.98	1.92		1.42	1.53	1.34	1.29	1.37	0.916	1.62	4.41
Th	3.58	3.60	3.66	3	1.97	2.21	1.96	2.12	2.28	1.49	3.48	12.8
U	0.748	1.08	0.783		0.641	0.489	0.479	0.593	0.613	0.356	0.764	0.809
Nb/Y	0.81	0.98	0.97	1.00	0.97	1.00	0.89	0.93	0.80	0.80	1.00	1.77
Zr/Y	6.98	6.11	6.57	7.34	6.46	6.26	6.75	7.39	5.93	5.19	6.20	12.10
Ti/V	59	61	58	52	42	43	50	55	46	30	47	95
$(La/Sm)_N$	2.55	2.48	2.52		2.12	1.91	2.40	2.12	2.45	2.03	2.78	4.99
$(Sm/Yb)_N$	2.49	2.37	2.59		2.75	3.16	3.06	2.94	2.46	2.19	2.83	1.18
$(La/Yb)_N$	6.35	5.90	6.53		5.83	6.03	7.36	6.25	6.04	4.44	7.86	5.89
$(Sm/Dy)_N$	1.95	1.85	1.99		1.81	2.02	1.97	1.93	1.62	1.75	1.95	1.57

Table 1 — Click here to access/download;Table;Table_01_R.xls

P-MORB)	Group 2a (Alkaline)							
MK797	MK372	MK373*	MK375	MK376	MK490	MK870	MK876	MK879
bas	bas	bas	Fe-bas	Fe-bas	Fe-bas	Fe-bas	Fe-bas	Fe-bas
aphiric	aphiric	aphiric	aphiric	aphiric	doleritic	porphyritic	porphyritic	doleritic
Type-I	Type-I	Type-I	Type-I	Type-I	Type-II	Type-II	Type-II	Type-II
51.1	47.6	48.2	46.3	46.2	45.1	46.5	45.6	47.9
1.23	2.96	2.72	3.09	3.00	5.13	2.60	3.21	2.65
13.9	14.2	14.3	14.5	15.0	13.9	12.6	15.9	13.2
1.12	1.51	1.39	1.71	1.58	2.02	1.72	1.70	1.68
7.48	10.04	9.30	11.43	10.54	13.44	11.47	11.33	11.22
0.20	0.19	0.13	0.13	0.15	0.14	0.14	0.15	0.13
9.07	5.89	6.35	5.31	6.84	6.12	8.54	10.59	8.57
9.20	10.45	8.47	9.82	8.20	8.27	8.60	3.24	7.92
3.05	3.09	3.55	2.42	2.56	1.83	2.10	2.04	2.30
1.08	0.65	0.38	0.56	1.34	0.89	0.24	1.54	0.94
0.24	0.33	0.35	0.35	0.33	0.51	0.48	0.48	0.42
1.98	2.80	4.27	4.10	3.88	2.04	4.91	4.13	3.05
99.66	99.65	99.45	99.69	99.60	99.39	99.87	99.96	99.98
68.4	51.1	54.9	45.3	53.6	44.8	57.0	62.5	57.7
52	97	105	113	119	148	79	113	54
74	38	93	59	112	158	65	24	9
31	24	23	31	32	34	29	23	27
14	20	16	27	23	25	23	24	24
95	82	51	76	91	99	45	21	39
23	48	42	40	52	55	49	54	44
301	110	92	93	101	46	25	29	26
257	302	268	357	348	518	284	291	297
203	122	161	156	255	315	134	212	232
8	7	8	7	8	6	10	7	9
19.0	8.76	7.16	6.94	12.4	23.3	13.8	20.6	19.7
275	422	318	270	170	716	705	114	1016
20.8	23.1	21.2	27.9	24.0	30.5	28.4	23.9	23.9
89.8	238	242	223	219	301	259	220	204
18.3	24.7	26.6	31.6	24.2	47.3	27.3	28.9	29.3
13.3	51.0	58.0	64.1	50.9	43.6	57	61.3	61.6
27.4	6.35	6.92	7.83	6.56	89.4	7.17	7.31	7.95
3.51	23.9	26.2	29.0	24.8	10.6	27.4	28.1	29.7
13.8	6.00	6.58	6.78	6.12	41.7	6.82	6.76	7.60
3.50	1.69	1.75	1.95	1.77	9.73	2.14	2.14	2.22
1.07	4.68	5.37	5.69	5.16	2.96	5.95	6.24	6.60
3.59	0.658	0.785	0.820	0.738	7.96	0.841	0.903	0.981
0.583	3.70	4.11	4.35	3.89	1.17	4.63	4.80	5.20
3.50	0.679	0.720	0.814	0.720	6.35	0.852	0.905	0.964
0.706	1.69	1.73	2.00	1.73	1.16	2.01	2.17	2.30
1.94	0.226	0.232	0.266	0.234	2.87	0.280	0.287	0.311
0.281	1.33	1.33	1.62	1.39	0.379	1.60	1.61	1.80
1.77	0.188	0.183	0.230	0.193	2.25	0.224	0.193	0.250
0.255	29.9	33.6	35.8	32.4	0.310	32.7	36.5	30.3
3.22	6.38	6.71	7.14	6.56	10.2	6.83	6.28	7.20
1.38	2.16	2.21	2.52	2.33	3.56	2.12	2.53	2.22
2.16	4.11	3.11	4.89	4.15	6.26	3.20	3.49	2.69
0.668	0.980	0.981	1.28	1.19	1.55	0.685	1.07	0.752
0.88	1.30	1.59	1.28	1.35	1.55	1.15	1.52	1.27
4.32	10.3	11.4	7.98	9.12	9.87	9.09	9.18	8.53
29	61	64	54	54	61	58	69	55
2.46	2.66	2.61	3.01	2.55	2.89	2.58	2.76	2.49
2.20	4.68	5.48	4.36	4.59	4.81	4.72	4.66	4.69
5.42	12.42	14.28	13.13	11.72	13.92	12.20	12.86	11.69
1.66	2.69	2.66	2.58	2.61	2.54	2.44	2.34	2.42

Table 1 (3/4)

Rock Group	Group 2a (Alkaline)										
Sample	MK491*	MK480	MK494	MK479	MK291	MK339	MK340	MK342	MK500	MK506	MK507
Rock	Fe-bas	bas	Fe-bas	bas	:ta-Fe-bas	neta-a-rhy	meta-bas	:ta Fe-bas	Fe-bas	Fe-bas	bas
Texture	doleritic	doleritic	doleritic	aphiric	foliated	foliated	foliated	foliated	aphiric	aphiric	aphiric
Succession type	Type-II	Type-II	Type-II	Type-III	Type-II	Type-II	Type-II	Type-II	Type-II	Type-II	Type-II
XRF analyses:											
SiO_2	44.3	52.8	46.9	51.7	46.4	66.8	41.9	45.4	42.0	46.4	45.7
TiO_2	2.25	2.04	3.34	3.06	2.91	0.05	2.03	3.65	2.60	3.15	2.75
Al_2O_3	14.3	14.5	13.7	13.9	14.5	15.2	13.4	13.3	14.1	13.6	14.8
Fe_2O_3	1.74	1.15	1.80	1.42	1.73	0.57	1.38	2.23	1.66	1.80	1.56
FeO	11.60	7.65	12.03	9.49	11.54	3.77	9.17	14.86	11.06	12.02	10.38
MnO	0.14	0.12	0.13	0.14	0.19	0.04	0.13	0.21	0.18	0.16	0.18
MgO	14.08	7.05	7.99	7.30	7.84	3.37	12.49	6.63	6.04	10.52	7.43
CaO	5.75	8.08	7.38	5.61	8.31	0.24	6.68	7.78	9.75	5.69	8.47
Na_2O	1.67	5.31	2.28	2.93	3.24	8.76	1.67	2.14	2.57	2.55	2.90
K_2O	0.44	0.38	1.03	0.29	0.02	0.10	0.66	0.22	n.d.	0.03	0.03
P_2O_5	0.30	0.28	0.66	0.35	0.32	0.02	0.23	0.38	0.40	0.30	0.30
LOI	3.13	1.30	2.37	3.51	2.96	1.18	9.97	2.76	9.13	3.47	5.21
Total	99.76	100.61	99.56	99.71	99.92	100.07	99.70	99.51	99.55	99.70	99.68
Mg#	68.4	62.2	54.2	57.8	54.8	61.4	70.8	44.3	49.3	60.9	56.1
Zn	122	39	137	126	141	208	86	167	110	110	119
Cu	116	56	91	44	110	5	147	121	71	93	101
Sc	27	22	23	27	33	n.d.	47	42	24	33	23
Ga	18	12	22	15	24	33	17	24	20	19	19
Ni	356	26	46	70	48	n.d.	97	36	59	38	45
Co	67	30	55	32	35	n.d.	51	50	53	36	39
Cr	412	237	19	193	94	40	152	54	65	38	94
V	294	265	310	267	315	42	312	376	318	325	277
Ba	204	351	293	135	91	26	202	198	74	95	90
Pb	9	10	7	7	8	5	9	8	9	9	10
ICP-MS analyses:											(XRF)
Rb	7.00	5.46	13.8	4.69	2.92	0.955	14.3	9.19	1.13	1.51	2
Sr	826	405	866	106	612	17.3	171	610	1010	595	588
Y	21.5	23.4	28.4	18.5	25.5	69.9	19.1	33.0	27.0	26.9	21
Zr	192	162	303	194	212	609	139	259	180	218	206
La	22.1	29.3	33.7	24.7	21.7	93.2	20.2	44.9	24.9	24.0	18
Ce	49.5	62.2	74.7	51.3	47.9	155	37.4	35.4	49.9	53.0	51
Pr	6.16	7.32	9.60	6.40	6.13	15.3	4.50	75.3	6.08	6.41	
Nd	24.7	29.3	37.7	24.4	24.0	50.3	16.1	9.67	24.4	26.2	20
Sm	6.17	7.13	9.13	6.10	6.10	11.2	4.06	39.7	5.91	6.85	
Eu	1.75	2.06	2.68	1.48	1.78	1.40	1.16	9.44	1.86	2.00	
Gd	5.18	5.78	8.02	5.08	5.39	11.0	3.33	2.83	5.30	5.71	
Tb	0.775	0.841	1.15	0.746	0.803	1.74	0.512	8.62	0.814	0.863	
Dy	4.18	4.68	5.84	4.10	4.38	10.3	2.80	1.20	4.51	4.88	
Ho	0.815	0.874	1.06	0.728	0.782	1.93	0.546	6.63	0.853	0.908	
Er	2.00	2.22	2.46	1.81	1.90	4.88	1.41	1.20	2.13	2.28	
Tm	0.278	0.299	0.309	0.241	0.258	0.654	0.188	2.85	0.277	0.283	
Yb	1.63	1.85	1.75	1.37	1.58	3.70	1.16	0.347	1.63	1.55	
Lu	0.225	0.257	0.249	0.188	0.210	0.477	0.158	1.98	0.230	0.229	
Nb	30.2	40.6	42.4	26.0	30.0	165	23.6	0.268	41.9	31.5	30
Hf	5.09	4.45	7.29	6.12	5.45	16.2	3.00	6.28	4.18	4.72	7
Ta	2.24	2.71	2.94	2.02	1.98	10.5	1.42	3.08	2.69	2.24	
Th	2.95	3.87	3.54	3.06	3.05	21.4	2.84	5.00	4.20	2.62	3
U	0.697	0.990	1.07	0.993	0.932	5.01	0.663	1.24	1.33	0.869	
Nb/Y	1.41	1.74	1.49	1.40	1.18	2.37	1.24	1.36	1.55	1.17	1.44
Zr/Y	8.94	6.95	10.7	10.5	8.33	8.71	7.31	7.83	6.69	7.53	9.83
Ti/V	48	46	67	71	57	7	43	60	54	61	63
$(La/Sm)_N$	2.31	2.66	2.38	2.62	2.30	5.39	3.21	2.42	2.64	2.26	
$(Sm/Yb)_N$	4.21	4.28	5.79	4.95	4.28	3.35	3.89	5.30	4.14	4.92	
$(La/Yb)_N$	9.74	11.4	13.8	12.9	9.84	18.08	12.5	12.84	10.92	11.11	
$(Sm/Dy)_N$	2.45	2.53	2.60	2.47	2.31	1.80	2.40	2.37	2.24	2.33	

Table 1 (4/4)

Rock Group	
Sample	MK482
Rock	bas
Texture	doleritic
Succession type	Type-II
XRF analyses:	
SiO_2	48.6
TiO_2	3.06
Al_2O_3	15.8
Fe_2O_3	1.43
FeO	9.52
MnO	0.13
MgO	6.74
CaO	5.15
Na_2O	2.05
K_2O	3.08
P_2O_5	0.78
LOI	3.05
Total	99.44
Mg#	55.8
Zn	113
Cu	61
Sc	19
Ga	27
Ni	71
Co	33
Cr	68
V	290
Ba	395
Pb	8
ICP-MS analyses:	
Rb	55.8
Sr	581
Y	33.8
Zr	403
La	59.2
Ce	119
Pr	14.5
Nd	53.0
Sm	12.0
Eu	3.02
Gd	9.60
Tb	1.35
Dy	6.85
Ho	1.28
Er	3.07
Tm	0.402
Yb	2.34
Lu	0.336
Nb	71.8
Hf	11.4
Ta	5.13
Th	8.74
U	2.00
Nb/Y	2.13
Zr/Y	11.9
Ti/V	66
$(La/Sm)_N$	3.17
$(Sm/Yb)_N$	5.72
$(La/Yb)_N$	18.16
$(Sm/Dy)_N$	3.07

	Group 2b (Alkaline)								
MK496*	MK497*	MK499	MK855*	MK859*	MK860	MK894*	MK907*	MK910	MK818
bas	bas	bas	bas	Fe-bas	Fe-bas	bas	bas	meta-bas	bas
porphyritic	porphyritic	porphyritic	porphyritic	porphyritic	porphyritic	aphiric	aphiric	foliated	aphiric
Type-II	Type-II	Type-II	Type-II	Type-II	Type-II	Type-III	Type-III	Type-III	Type-III
46.7	50.8	48.4	45.1	42.1	45.4	51.8	51.8	53.5	53.1
3.41	2.25	1.55	3.28	3.41	3.77	3.41	4.61	3.98	3.54
15.2	14.2	14.9	12.8	13.1	13.8	14.8	14.2	13.0	12.8
1.36	1.15	1.22	1.49	1.69	1.72	1.33	1.39	1.32	1.29
9.09	7.65	8.11	9.92	11.26	11.48	8.86	9.28	8.83	8.60
0.17	0.14	0.15	0.14	0.16	0.18	0.19	0.32	0.13	0.14
9.88	7.35	13.61	8.39	11.82	9.19	4.06	3.39	5.03	6.22
8.63	9.51	7.09	11.97	10.17	8.22	8.72	6.08	8.05	8.33
2.79	4.74	2.81	1.75	0.91	1.59	4.75	5.50	3.78	3.51
0.25	0.12	0.11	1.79	1.80	2.10	0.54	1.08	0.76	0.66
0.55	0.27	0.20	0.54	0.40	0.60	0.79	1.10	0.49	0.46
1.62	1.93	2.06	2.66	3.14	1.76	0.43	1.11	1.10	1.04
99.65	100.11	100.25	99.87	99.97	99.85	99.62	99.89	99.96	99.63
66.0	63.2	74.9	60.1	65.2	58.8	45.0	39.4	50.4	56.3
72	39	64	60	90	66	104	97	63	42
102	74	89	125	108	44	10	33	55	32
20	22	25	24	34	30	12	12	27	27
11	10	10	16	19	16	16	13	14	15
66	40	285	53	134	113	n.d.	33	28	15
40	37	49	48	63	45	27	37	37	14
85	246	959	42	280	270	5	4	97	56
336	303	228	406	373	408	190	424	311	267
610	153	170	267	370	172	421	142	244	173
7	10	8	7	9	9	12	10	11	12
(XRF)			*(XRF)*						
6	2.80	1.70	36	20.7	59.4	23.8	45.9	17.4	11.0
570	204	138	584	591	208	198	128	1458	1123
21	15.9	15.9	19	18.3	26.0	17.3	19.3	24.7	18.1
313	201	148	320	246	317	306	398	288	274
59	31.9	27.1	45.0	45.5	54.5	35.8	50.7	53.3	44.6
129	64.4	53.6	119	94.4	62.8	68.9	84.8	55.1	90.6
	7.58	6.18		11.0	121	8.41	8.72	110	10.3
31	27.5	22.0	39	41.8	14.7	34.3	28.8	12.6	39.2
	6.69	4.93		8.75	51.6	8.24	7.05	44.9	8.37
	1.92	1.29		2.26	10.9	2.33	1.81	9.83	2.19
	5.21	3.62		5.61	3.62	5.65	4.68	2.74	5.62
	0.722	0.516		0.765	7.46	0.774	0.651	6.63	0.796
	3.73	2.78		3.90	0.992	3.70	3.37	0.903	4.08
	0.681	0.546		0.711	5.07	0.624	0.620	4.81	0.733
	1.73	1.38		1.57	0.886	1.44	1.55	0.839	1.73
	0.230	0.184		0.212	2.05	0.200	0.218	2.00	0.235
	1.38	1.13		1.16	0.262	1.20	1.39	0.254	1.40
	0.193	0.168		0.159	1.55	0.161	0.200	1.58	0.208
67	36.5	39.2	58	57.9	0.215	40.3	57.1	0.225	44.0
8	6.00	4.48	8	8.66	10.1	7.33	8.71	11.5	6.50
	2.76	2.66		4.39	4.97	2.93	5.03	3.88	3.01
6	4.05	4.46	5	7.33	8.37	3.77	6.75	5.56	5.50
	1.31	1.23		2.17	2.42	1.20	1.76	1.69	0.969
3.13	2.29	2.47	3.02	3.16	2.10	2.33	2.96	2.16	2.43
14.6	12.6	9.30	16.7	13.4	12.20	17.7	20.6	11.67	15.1
62	45	41	50	57	57	51	66	78	81
	3.08	3.81		3.35	3.74	2.81	4.64	3.62	3.44
	5.39	4.15		8.37	7.77	7.66	5.65	6.91	6.66
	16.61	15.81		28.07	29.04	21.50	26.24	25.03	22.92
	3.06	2.94		3.73	3.56	3.70	3.48	3.39	3.40

Table 2 (1/2)

Rock Group	Group 1 (P-MORB)												Group 2a (alkaline)							
Sample-rock	MK483-basalt						MK485-basalt						MK491-ferrobasalt						MK479-basalt	
Mineral-site	2-1 r	2-10 c	3-2	4-4	5-3 r	5-8 c	2-2 c	2-6 r	1-2	4-2	5-7	6-2	1-3	3-1 c	3-7 r	5-3 c	6-1 c	6-4 r	3-3	4-3
Note																				
SiO_2	50.50	49.84	50.94	48.59	49.94	48.85	50.00	50.08	49.64	49.02	49.77	50.00	50.27	49.33	48.76	49.80	49.86	47.62	49.26	49.99
TiO_2	1.22	0.96	1.12	1.45	1.31	1.01	0.91	1.03	1.33	1.36	1.13	0.91	1.17	1.68	1.82	1.29	1.60	1.86	1.54	1.32
Al_2O_3	2.53	2.40	2.70	2.51	2.53	2.73	1.44	1.74	2.63	2.83	3.06	1.90	2.98	3.30	3.19	2.93	3.46	3.63	3.82	3.47
Cr_2O_3	0.07	0.05	0.13	0.04	0.00	0.25	0.00	0.05	0.02	0.04	0.16	0.15	0.38	0.27	0.19	0.40	0.41	0.28	0.26	0.36
FeO	9.02	11.67	9.01	12.28	11.35	8.42	13.82	11.58	11.57	10.78	9.49	8.72	6.46	8.56	8.51	6.77	7.79	8.60	6.98	6.49
MnO	0.12	0.31	0.14	0.21	0.28	0.23	0.30	0.21	0.25	0.19	0.19	0.15	0.06	0.16	0.13	0.19	0.12	0.15	0.07	0.16
MgO	15.34	14.08	15.58	14.44	14.95	15.89	14.26	15.29	14.41	14.83	15.51	16.32	16.46	14.51	14.94	16.09	15.27	14.04	15.88	16.22
CaO	20.89	19.96	20.86	19.42	20.32	21.11	19.26	19.48	20.22	20.36	20.29	20.69	21.58	21.40	21.79	21.32	21.39	21.02	21.34	22.05
Na_2O	0.28	0.46	0.33	0.40	0.36	0.38	0.35	0.34	0.39	0.37	0.32	0.30	0.37	0.44	0.43	0.41	0.50	0.50	0.33	0.35
K_2O	0.00	0.00	0.01	0.00	0.02	0.01	0.01	0.00	0.01	0.02	0.03	0.04	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.01
Total	99.95	99.73	100.81	99.33	101.07	98.88	100.36	99.80	100.46	99.80	99.94	99.17	99.71	99.65	99.76	99.18	100.42	97.70	99.50	100.43
A.p.f.u.																				
Si	1.873	1.868	1.871	1.830	1.842	1.821	1.873	1.870	1.846	1.828	1.844	1.859	1.849	1.837	1.811	1.845	1.834	1.809	1.821	1.828
Ti	0.034	0.027	0.031	0.041	0.036	0.028	0.026	0.029	0.037	0.038	0.031	0.025	0.032	0.047	0.051	0.036	0.044	0.053	0.043	0.036
Al	0.110	0.106	0.117	0.111	0.110	0.120	0.064	0.076	0.115	0.125	0.134	0.083	0.129	0.145	0.140	0.128	0.150	0.163	0.166	0.150
Cr	0.002	0.001	0.004	0.001	0.000	0.007	0.000	0.001	0.001	0.001	0.005	0.004	0.011	0.008	0.005	0.012	0.012	0.008	0.008	0.010
Fe^{3+}	0.095	0.136	0.100	0.175	0.159	0.202	0.165	0.150	0.145	0.170	0.135	0.166	0.124	0.112	0.163	0.128	0.117	0.141	0.124	0.138
Fe^{2+}	0.185	0.230	0.176	0.212	0.191	0.060	0.268	0.212	0.215	0.166	0.159	0.105	0.074	0.155	0.101	0.081	0.123	0.132	0.092	0.061
Mn	0.004	0.010	0.004	0.007	0.009	0.007	0.009	0.007	0.008	0.006	0.006	0.005	0.002	0.005	0.004	0.006	0.004	0.005	0.002	0.005
Mg	0.848	0.787	0.853	0.810	0.822	0.883	0.796	0.851	0.799	0.824	0.857	0.905	0.902	0.806	0.827	0.889	0.837	0.796	0.875	0.884
Ca	0.830	0.801	0.820	0.783	0.803	0.843	0.773	0.779	0.806	0.814	0.805	0.824	0.850	0.854	0.867	0.846	0.843	0.856	0.845	0.864
Na	0.020	0.034	0.023	0.029	0.026	0.027	0.025	0.025	0.028	0.027	0.023	0.021	0.026	0.032	0.031	0.029	0.036	0.037	0.024	0.025
K	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.000	0.000	0.001	0.001	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000
Total	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000
Al (IV)	0.110	0.106	0.117	0.111	0.110	0.120	0.064	0.076	0.115	0.125	0.134	0.083	0.129	0.145	0.140	0.128	0.150	0.163	0.166	0.150
Al (VI)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Wo (%)	42.0	40.3	41.6	39.0	40.1	41.8	38.1	38.6	40.4	40.7	40.7	40.8	43.0	43.6	43.6	42.9	43.1	43.6	43.1	43.8
En (%)	42.9	39.6	43.2	40.3	41.1	43.8	39.3	42.2	40.1	41.2	43.3	44.8	45.6	41.1	41.6	45.0	42.8	40.6	44.7	44.8
Fs (%)	9.6	13.7	10.1	17.6	16.0	20.2	16.6	15.1	14.6	17.1	13.6	16.7	12.5	11.3	16.4	12.9	11.7	14.2	12.4	13.8
Acm (%)	1.0	1.7	1.2	1.5	1.3	1.4	1.2	1.2	1.4	1.3	1.1	1.1	1.3	1.6	1.6	1.5	1.8	1.9	1.2	1.3
Mg#	0.75	0.68	0.76	0.68	0.70	0.77	0.65	0.70	0.69	0.71	0.74	0.77	0.82	0.75	0.76	0.81	0.78	0.74	0.80	0.82

Table 2 (2/2)

	Group 2a (alkaline		Group 2b (alkaline)																
Rock Group	MK479-basalt		MK859-ferrobasalt						MK855-basalt						MK910-meta basalt				
Mineral-site	5-3	12-3	1-10 c	1-14 r1	1-7 r2	1-13 r3	4-2	5-1	1-5 c	1-12 r	2-6 c	2-10 r	4-4 r	4-9 c	1-3 c	1-4 ec	1-6 r	3-2	7-3
Note			profile core-rim												profile core-rim				
SiO_2	50.01	48.03	50.11	44.68	49.14	46.32	46.20	45.83	48.33	45.80	45.55	45.78	49.73	48.15	47.66	46.06	45.40	48.72	49.02
TiO_2	1.01	2.11	1.26	3.69	2.03	2.44	2.87	3.47	1.99	3.30	2.97	3.49	1.29	2.21	1.95	2.48	3.05	1.49	1.43
Al_2O_3	2.66	4.39	2.88	7.08	3.75	5.59	5.89	6.17	4.13	5.72	5.92	5.65	2.92	5.13	4.38	5.70	6.39	3.54	3.30
Cr_2O_3	0.67	0.12	0.98	0.00	0.37	0.42	0.31	0.01	0.20	0.07	0.03	0.09	0.56	0.28	0.30	0.29	0.16	1.00	0.56
FeO	5.75	7.78	4.25	7.12	5.83	6.49	6.72	7.57	5.87	8.08	6.81	8.18	4.79	6.19	6.02	7.30	7.46	5.18	5.74
MnO	0.13	0.10	0.10	0.07	0.08	0.07	0.12	0.09	0.08	0.09	0.06	0.11	0.01	0.07	0.00	0.12	0.08	0.09	0.15
MgO	16.68	14.91	16.02	12.52	15.09	13.67	13.52	12.75	14.60	13.16	13.55	13.60	16.02	13.61	14.89	14.05	13.71	15.17	15.03
CaO	22.32	22.09	23.91	23.48	23.91	24.20	24.34	23.58	24.06	22.55	23.38	21.76	23.12	23.76	23.67	22.59	22.81	23.61	23.30
Na_2O	0.37	0.34	0.32	0.56	0.38	0.39	0.44	0.46	0.36	0.66	0.60	0.39	0.36	0.41	0.28	0.46	0.47	0.38	0.55
K_2O	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.01	0.00	0.01	0.02	0.02
Total	99.62	99.87	99.82	99.20	100.57	99.57	100.40	99.95	99.61	99.43	98.85	99.07	98.79	99.81	99.15	99.04	99.53	99.20	99.10
A.p.f.u.																			
Si	1.837	1.779	1.839	1.675	1.801	1.722	1.706	1.708	1.789	1.713	1.704	1.720	1.843	1.786	1.771	1.720	1.690	1.806	1.819
Ti	0.028	0.059	0.035	0.104	0.056	0.068	0.080	0.097	0.055	0.093	0.084	0.099	0.036	0.062	0.055	0.070	0.085	0.042	0.040
Al	0.115	0.191	0.125	0.313	0.162	0.245	0.256	0.271	0.180	0.252	0.261	0.250	0.127	0.224	0.192	0.251	0.280	0.155	0.144
Cr	0.020	0.003	0.028	0.000	0.011	0.012	0.009	0.000	0.006	0.002	0.001	0.003	0.016	0.008	0.009	0.009	0.005	0.029	0.016
Fe^{3+}	0.161	0.155	0.121	0.171	0.141	0.192	0.196	0.150	0.151	0.183	0.206	0.138	0.125	0.102	0.170	0.195	0.198	0.148	0.163
Fe^{2+}	0.016	0.086	0.009	0.052	0.037	0.010	0.011	0.085	0.031	0.070	0.007	0.119	0.024	0.090	0.017	0.033	0.034	0.013	0.015
Mn	0.004	0.003	0.003	0.002	0.002	0.002	0.004	0.003	0.002	0.003	0.002	0.004	0.000	0.002	0.000	0.004	0.003	0.003	0.005
Mg	0.914	0.823	0.877	0.700	0.824	0.757	0.744	0.709	0.806	0.733	0.756	0.762	0.885	0.753	0.825	0.782	0.761	0.839	0.831
Ca	0.879	0.876	0.940	0.943	0.939	0.964	0.963	0.942	0.954	0.903	0.937	0.876	0.918	0.944	0.942	0.904	0.910	0.938	0.926
Na	0.026	0.024	0.022	0.041	0.027	0.028	0.032	0.033	0.026	0.048	0.043	0.028	0.026	0.029	0.020	0.034	0.034	0.027	0.039
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.001
Total	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000
Al (IV)	0.115	0.191	0.125	0.313	0.162	0.245	0.256	0.271	0.180	0.252	0.261	0.250	0.127	0.214	0.192	0.251	0.280	0.155	0.144
Al (VI)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.010	0.000	0.000	0.000	0.000	0.000
Wo (%)	44.0	44.6	47.7	49.5	47.7	49.4	49.5	49.1	48.5	46.6	48.1	45.6	46.4	49.2	47.7	46.4	47.0	47.7	46.9
En (%)	45.8	41.9	44.5	36.7	41.9	38.8	38.2	36.9	41.0	37.9	38.8	39.6	44.8	39.2	41.8	40.2	39.3	42.7	42.1
Fs (%)	16.1	15.5	12.1	17.1	14.1	19.2	19.6	15.1	15.1	18.4	20.6	13.9	12.5	10.2	17.0	19.5	19.8	14.8	16.3
Acm (%)	1.3	1.2	1.1	2.1	1.4	1.5	1.6	1.7	1.3	2.5	2.2	1.5	1.3	1.5	1.0	1.7	1.7	1.4	2.0
Mg#	0.84	0.77	0.87	0.76	0.82	0.79	0.78	0.75	0.82	0.74	0.78	0.75	0.86	0.80	0.82	0.77	0.77	0.84	0.82

Supplementary Figure S1

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

On behalf of the co-authors
Emilio Saccani