



# Petrogenesis of Late Cretaceous A<sub>1</sub>-type alkali monogenetic volcanoes, Wadi Natash, South Eastern Desert, Egypt, and their implications for Nb mineralization and tectonic evolution

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Received: 12 May 2023 / Accepted: 4 August 2023 / Published online: 29 August 2023  
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## Abstract

This article carried out an integrated study of the mineral composition, whole-rock elemental geochemistry, and zircon U-Pb dating for the rift-related alkaline volcanoes at Wadi Natash, South Eastern Desert (SED), Egypt, to investigate their magmatic evolution and origin. The Natash volcanoes (NV) are characterized by explosive and extrusive polyphases trending in NW-SE with a diverse compositional range of basalts, trachyandesites, trachytes, and rhyolites/comendites categorized by distinct high concentration of HFSEs and REEs. Zircon U-Pb dating offers ages of  $96 \pm 2.5$  to  $86 \pm 2$  Ma, constraining Late Cretaceous eruption of the NV. The basalts have high HFSE, REE, and Nb/U ratios similar to Nb-rich basalts derived from OIB source. The trachyandesites/trachytes and rhyolites have high ratios of Ga/Al (8–12), HFSF (Nb = 79–283 ppm, Zr = 433–1807 ppm), and REE (671–728 ppm) and low concentrations of Sr, P, Ti, and Eu which are analogous to typical A<sub>1</sub>-type granites. The Nb enrichment in all rock types (81–283 ppm) is controlled by both magmatic and hydrothermal processes. The NV were originated from an enriched lithospheric mantle source metasomatized by asthenosphere-derived fluids and then experienced fractional crystallization (FC) with no significant input of crustal contamination. Petrographical and geochemical criteria elucidate olivine + clinopyroxene as the main fractionated phases, followed by hornblende + plagioclase + Fe-Ti oxides + apatite during the more evolved stage. In addition to FC, the phenocryst textures conform a variety of magmatic processes, such as multi-crustal storage, crystallization, volatile fluxing, and degassing and magmatic evolution in open systems with a fluctuating temperature, pressure, and water. The geothermobarometric data point to a polybaric-polythermal system with numerous magma residence regions fluctuating from lower-middle (1.4–1.25 GPa and 1154–1136 °C) to shallow crustal levels as demonstrated by plagioclase crystallization (0.75–0.26 GPa and 1048–980 °C) and Fe-Ti oxides (937–904 °C) when magmas ascend to the surface. The evolution of the NV can be linked to mantle plume magmatism and extensive Mesozoic alkaline ring complexes recorded along the Egypt/Sudan border, Northeast Africa, and Northern Arabia in an extensional setting, highlighting that the assembly of the Rodinia supercontinent might have been finalized prior to ca. 86 Ma.

**Keywords** A<sub>1</sub>-type alkaline volcanoes · Nb enrichment · Magma mushes · Intracontinental extension · Alkaline ring complex

Responsible Editor: Domenico M. Doronzo

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## Introduction

Alkaline volcanoes are well-known on Earth's surface and signify low-volume monogenetic magmatism released in a single continuous explosion or in numerous intermittent rhythms in a short time (Németh, 2010). Even though the volume of the alkaline rocks is negligible, they occur broadly in anorogenic, post-collisional, and oceanic island regimes (Zhu et al., 2020; Wang et al. 2021). The rock types of alkaline volcanoes involve multicycles of basaltic, trachytic/phonolitic, and rhyolitic lava flows together with related

pyroclastic deposits, forming diverse landforms like scoria cones, tuff rings, and maar volcanoes (Brenna et al., 2012). The intrusive rocks (e.g. gabbros, syenites, and granites) are sporadically concomitant with the alkaline volcanoes. The alkaline rocks have achieved consciousness scientific and marketable attentiveness worldwide, due to its tendency to enhance total alkali, ratios of both Fe/Mg and Ga/Al, HFSEs (chiefly Nb, Ta, Zr, U), REEs, Sn, and W which characterize A-type granites (Whalen et al., 1987; Eby, 1990; Sheard et al., 2012). Although rare metal mineralizations (e.g. Nb deposits) characterizing alkaline felsic rocks have been broadly examined (Girei et al., 2019), their genesis and advancement remain a theme of controversy. Numerous theories involving a metasomatized lithospheric mantle (Zhu et al. 2016; Girei et al. 2019), lower crustal sources (Harris et al. 2018), and intricate mantle-crust itineraries (Eby 1992) have been proposed for the origin of the parental alkaline magmas.

Radical technology and equipment manufactures broadly use Nb as a vital metal (Weng et al., 2015). On Earth, large quantities of Nb mineralizations are recorded in plutonic rocks like syenites, granites, or carbonatites (Li et al., 2019). On the other hand, a scarce of Nb mineralizations is recognized in extrusive rocks, e.g. the HFSE-REE deposits in the Brockmans, Australia (Chandler and Spandler, 2020), Canada (Miller, 2015), and the Tudiling, China (Yan et al., 2022). However, these deposits are categorized by composite mineralogy with the pouring universal request for rare metals and the development of metallurgical procedures; they have fascinated ample courtesy in recent years due to their abundant assets (Chandler and Spandler 2020; Wang et al. 2021). In the previous studies, mechanisms of Nb deposits that highlight the significance of wide-ranging magmatic differentiation recognized the incompatible behaviour of these elements in rock-forming minerals (Stepanov et al., 2014), while others emphasized the role of hydrothermal alteration in organizing and enhancing rare metals (Ballouard et al., 2016). The Nb mineralization which is either formed by protracted magmatic differentiation or by hydrothermal alteration or by a mixture of both is a key point of argument (e.g. Huang et al., 2014). The role of the magmatic fractionation or hydrothermal alteration or both to increase these incompatible elements to economic ranks, raise rare metal concentrations in natural magmatic systems, and shares in the mineralizations is continually problematic theme (Wu et al., 2023).

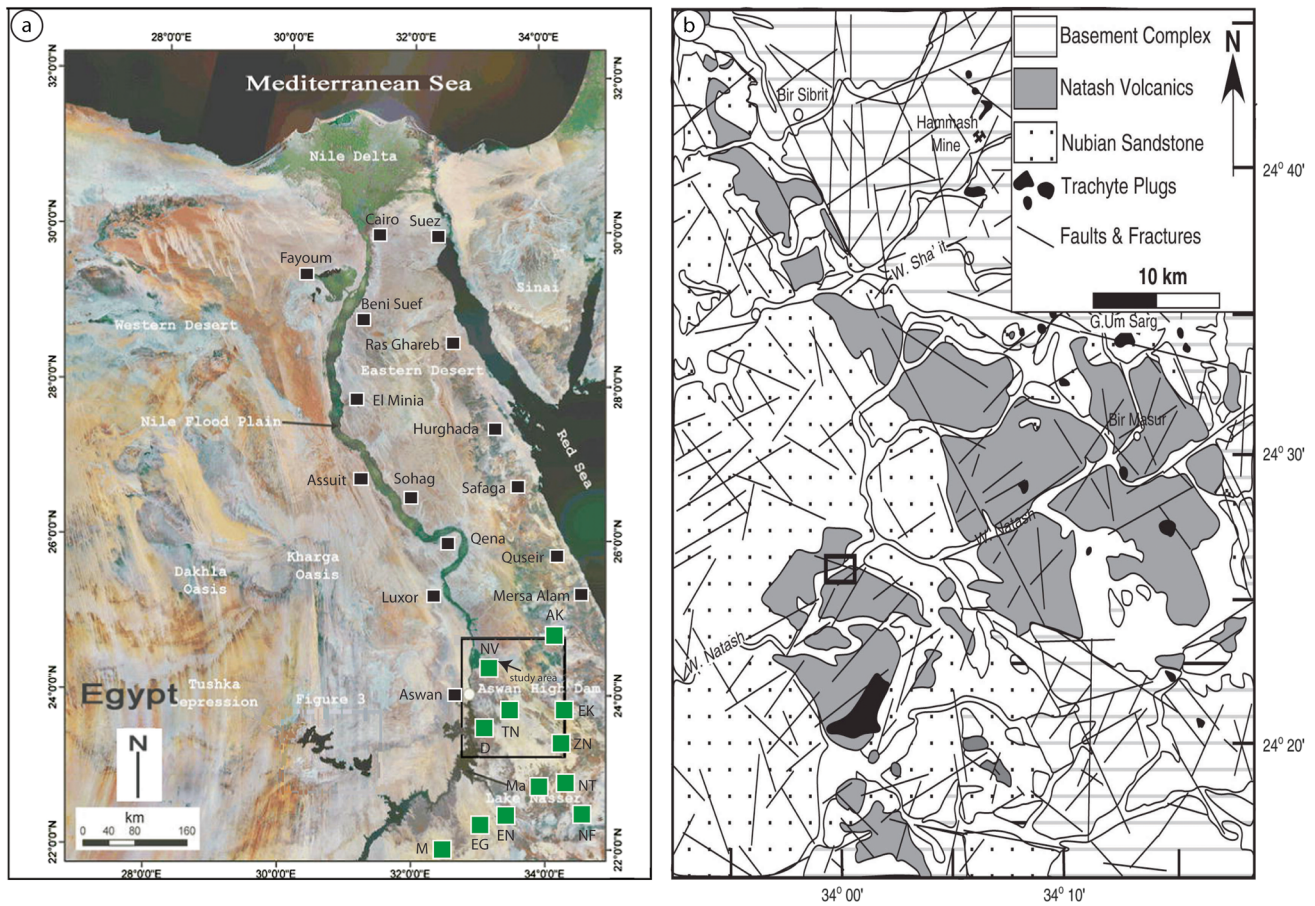
Several alkaline ring complexes (>130 ring) are documented in the northeastern part of Africa that spread from Precambrian (~650 Ma) until Neogene age (~25 Ma, Serencsits et al., 1981; Mohamed, 1998). The alkaline rocks in Egypt form moderately low-volume magmatic assemblages in the form of ring complexes/dykes, plugs, and lava flows associated with alkali granitic/or

syenitic rocks that were erupted after the subducted-related magmatism at the termination of the Neoproterozoic Era (650–500 Ma) until Late Cretaceous. Meneisy (1986) proposed three alkaline volcanic activities involving Early Triassic-Late Permian ( $230 \pm 10$  Ma), Late Jurassic-Early Cretaceous ( $140 \pm 10$  Ma), and Late Cretaceous ( $90 \pm 10$  Ma). Most of these phases are situated in the South Eastern Desert (SED), Egypt (Fig. 1a) that are strictly connected with deep-seated faults/fractures and shear zones (Mohamed 1998). Some of these alkaline ring complexes may comprise both extrusive (like basalts, trachytes, and rhyolites) and intrusive rocks (e.g. gabbros, syenites, and granites, Landoll et al., 1994; Mogahed, 2016). Their rock types with their relatively remarkable minerals have attracted the interest of numerous petrologists, due to their high enrichments in Nb, Ta, Zr, Y, Th, and Cu ore deposits (Hezagy et al., 2016).

The Natash volcanoes (NV) represent one of the largest lava fields (~560 km<sup>2</sup>) in the SED that are located about 125 km ENE of Aswan (Fig. 1a). Several authors discussed the origin of the Natash volcanoes (Crawford et al., 1984; Mohamed, 1998; Abu El-Rus et al., 2016; Khalaf et al., 2018). No researches have been paid a consideration to the genetic affiliation between the Natash volcanoes and its plutonic counterparts (such as the Abu Khruq or El Kahfa ring complex in Egypt, south of Ak, Fig. 1a) in order to understand the whole magmatism during Mesozoic Era. Moreover, the process for Nb enrichment characterizing the alkaline magmas is discreet enigma. In this article, we present an integrated study in terms of zircon U-Pb dating, mineral chemistry, and whole-rock geochemical data for alkaline Natash volcanoes, aiming to (1) constrain the magma source and evolution of the alkaline volcanoes, (2) constrain the mechanisms responsible for Nb enhancement, and (3) propose a detailed framework for the geodynamic evolution and shed new light on the tectono-magmatic development of the Mesozoic magmatism.

## Analytical procedures

The specimen preparation and XRF procedures followed the technique of Sano et al. (2016). In addition to the XRF analyses (Table 1), the rock powders of 19 specimens were used for analysis of trace elements by inductively coupled plasma-source mass spectrometry (ICP-MS). Trace element compositions were determined using a quadrupole Agilent 7700x ICP-MS instrument at the National Museum of Nature and Science, Japan (NMNSJ). Prior to ICP-MS analysis, whole-rock powders were dissolved using a HF-HClO<sub>4</sub>-HNO<sub>3</sub> with ultimate dissolution in 2% HNO<sub>3</sub> plus 0.1% HF spiked with <sup>115</sup>In and <sup>209</sup>Bi.



**Fig. 1** Location of ring complexes and geological map of Wadi Natash. **a** Key map showing the distribution of the main ring complexes in the South Eastern Desert (SED), Egypt: NV, Natash volcanoes (study area); AK, Abu Khrug; ZN, Zargat Naam; TN, Tarbite

North; D, Dahmit; NT, Nigrub El Tahtani; NF, Nigrub El Fokani; EN, El Naga; M, Mansouri; Ma, Malaadob. **b** Geological map of Natash volcanoes (modified after CONOCO 1987)

Analytical precision was appraised using the JB2 and JB2-recom as references. Polished sections for mineral compositions were perceived using a JEOL electron microprobe (JEOL JXA-8230) using 15-kV accelerating voltage, 15-nA beam current, and an analytical spot size of ~1 μm.

Five samples were chosen for zircon U-Pb dating. Full measures for zircon separation and U-Pb analyses are summarized (see Tsutsumi et al., 2012). The FCL zircon ( $^{206}\text{Pb}/^{238}\text{U} = 0.1859$ ; Paces and Miller 1993) and NIST SRM standard glass were used as references. Scanning electron microprobe cathodoluminescence (SEM-CL) apparatus, JSM-6610 (JEOL), and a CL detector (SANYU electron) have been used for backscattered electron and cathodoluminescence (CL) images. U-Th-Pb isotopic analyses were carried out using LAICP-MS (Agilent 7700x with ESI NWR213 laser ablation system). Pb corrections for the concordia diagrams and for each age

were made based on the Pb model planned by Stacey and Kramers (1975). All these analyses were made at NMNSJ.

### Geological background

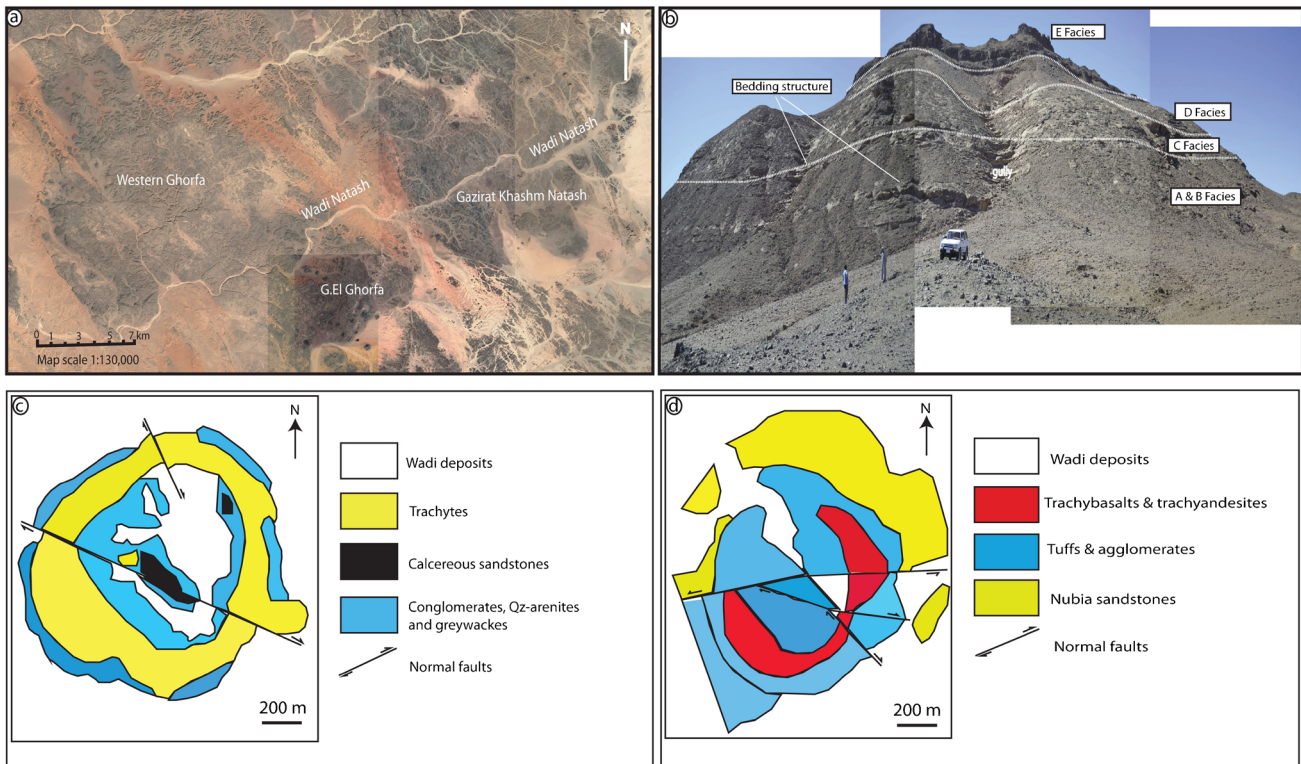
The Natash volcanoes represent one of the most common Mesozoic ring complexes and demonstrate explosive/extrusive low-volume monogenetic eruptions in the SED (Khalaf et al., 2018). These volcanoes are aligned in the NW-SE direction and situated between latitudes 24°15'–24°50' N and longitude 33°40'–34°10' E, unconformably overlying the Precambrian rocks and Nubia sandstone of Upper Cretaceous (Fig. 1b). The lava thickness attains 250 m at the eastern part of Wadi Natash, which declines to about 50 m at its western portion (Crawford et al. 1984). The NV appear in three ring structures that are exposed along Gaziret Khashm



**Table 1** Major trace elements of Upper Cretaceous A-type Natash volcanoes, South Eastern Desert, Egypt

| Element                        | N1    | N2    | N3    | N4    | N5    | N6    | N7    | N8    | N9   | N10  | N11  | N12  | N13  | N14  | N15  | N16  | N17  | N18  | N19  | N20  | N21  | N22  | N23  | N24  | N25  | N26  | N27  | N28  | N29  | N30  |      |
|--------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| SiO <sub>2</sub>               | 41.56 | 45.32 | 46.05 | 49.36 | 49.61 | 49.47 | 50.46 | 52.60 | 55.3 | 55.5 | 52.9 | 56.7 | 57.4 |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| TiO <sub>2</sub>               | 2.03  | 3.11  | 3.35  | 2.72  | 3.54  | 2.72  | 3.35  | 1.79  | 3.63 | 1.72 | 3.54 | 1.58 | 2.27 | 1.25 | 57.8 | 58.0 | 58.1 | 61.8 | 61.8 | 61.8 | 61.9 | 62.7 | 63.6 | 72.1 | 61.0 | 63.1 | 64.0 | 64.3 | 64.6 | 52.9 |      |
| Al <sub>2</sub> O <sub>3</sub> | 15.81 | 15.72 | 15.75 | 15.92 | 15.53 | 15.73 | 16.08 | 16.04 | 17.1 | 15.8 | 16.8 | 16.2 | 12.9 | 16.4 | 17.2 | 17.3 | 16.6 | 15.8 | 15.4 | 15.7 | 16.0 | 15.3 | 16.1 | 12.5 | 16.1 | 16.0 | 15.3 | 15.4 | 15.5 | 16.2 |      |
| FeO                            | 12.88 | 12.84 | 13.63 | 13.41 | 14.47 | 14.55 | 14.07 | 13.45 | 9.23 | 13.1 | 11.4 | 10.3 | 12.5 | 11.2 | 0.47 | 0.47 | 1.26 | 0.20 | 0.40 | 0.19 | 0.19 | 0.18 | 0.21 | 0.41 | 1.15 | 0.2  | 0.23 | 0.23 | 0.23 | 1.58 |      |
| MnO                            | 0.12  | 0.18  | 0.19  | 0.14  | 0.31  | 0.15  | 0.14  | 0.25  | 0.06 | 0.11 | 0.06 | 0.2  | 0.17 | 0.13 | 1.72 | 1.73 | 16.6 | 15.8 | 15.4 | 15.7 | 16.0 | 15.3 | 16.1 | 12.5 | 16.1 | 16.0 | 15.3 | 15.4 | 15.5 | 16.2 |      |
| MgO                            | 11.17 | 5.34  | 5.46  | 1.68  | 3.72  | 1.6   | 1.79  | 1.81  | 0.38 | 0.86 | 0.29 | 1.89 | 0.8  | 0.83 | 1    | 2    | 0    | 5    | 7    | 3    | 9    | 8    | 3    | 6    | 3    | 6    | 3    | 4    | 5    | 2    |      |
| CaO                            | 12.75 | 8.18  | 8.21  | 4.81  | 4.01  | 5.22  | 4.60  | 3.41  | 2.82 | 3.08 | 1.93 | 5.19 | 4.08 | 1.41 | 9.13 | 8.95 | 6.56 | 5.93 | 7.32 | 6.47 | 6.05 | 5.58 | 5.05 | 1.78 | 5.18 | 4.9  | 4.91 | 4.45 | 4.65 | 10.2 |      |
| Na <sub>2</sub> O              | 1.76  | 3.73  | 3.83  | 6.22  | 7.05  | 5.16  | 6.47  | 5.91  | 7.75 | 5.3  | 8.92 | 5.27 | 6.12 | 7.98 | 0.20 | 0.18 | 0.16 | 0.13 | 0.29 | 0.15 | 0.14 | 0.10 | 0.15 | 0.06 | 0.19 | 0.14 | 0.13 | 0.15 | 5    | 5    |      |
| K <sub>2</sub> O               | 0.24  | 1.09  | 1.12  | 1.76  | 0.12  | 1.59  | 0.56  | 1.61  | 0.61 | 2.04 | 0.58 | 2.7  | 0.72 | 1.43 | 0.45 | 0.48 | 0.68 | 0.57 | 1.50 | 0.64 | 0.36 | 0.62 | 0.12 | 0.19 | 0.64 | 0.1  | 0.17 | 0.31 | 0.17 | 0.2  |      |
| P <sub>2</sub> O <sub>5</sub>  | 0.01  | 0.79  | 0.87  | 2.09  | 0.62  | 1.84  | 0.75  | 0.74  | 0.68 | 0.72 | 0.60 | 0.74 | 1.75 | 0.36 | 2.73 | 2.79 | 3.94 | 2.11 | 0.50 | 1.98 | 1.35 | 2.28 | 1.23 | 1.74 | 2.38 | 1.18 | 1.06 | 1.36 | 0.24 | 1.89 |      |
| LOI                            | 1.30  | 3.98  | 2.00  | 2.02  | 1.56  | 2.3   | 2.13  | 2.57  | 2.69 | 2.2  | 1.01 | 3.25 | 1.79 | 1.79 | 7.17 | 7.06 | 6.74 | 5.58 | 4.15 | 5.35 | 6.68 | 5.24 | 6.50 | 4.32 | 6.59 | 6.65 | 6.38 | 5.19 | 1.06 | 5.19 |      |
| Total                          | 99.63 | 100   | 100   | 100   | 100   | 100   | 100   | 100   | 100  | 100  | 100  | 100  | 99.9 | 100  | 3.29 | 3.16 | 0.62 | 4.74 | 5.64 | 4.87 | 5.08 | 3.94 | 5.01 | 4.95 | 3.11 | 5.02 | 5    | 5.76 | 5.18 | 5.27 |      |
| V                              | 614   | 216   | 228   | 99    | 169   | 92    | 227   | 43    | 227  | 44   | 289  | 26   | 86   | 16   | 0.18 | 0.19 | 0.40 | 0.02 | 0.09 | 0.03 | 0.04 | 0.04 | 0.03 | 0.34 | 0.03 | 0.05 | 0.03 | 5.82 | 2.7  | 2.7  |      |
| Cr                             | 179   | 36    | 38    | 8     | 18    | 8     | 23    | 6     | 21   | 6    | 27   | 3    | 7    | 4    | 1.75 | 1.74 | 3.03 | 3.19 | 2.70 | 2.40 | 2.38 | 3.89 | 2.08 | 2.13 | 3.26 | 2.79 | 2.96 | 3.46 | 0.03 | 0.74 |      |
| Co                             | 61    | 54    | 55    | 46    | 46    | 45    | 45    | 38    | 27   | 35   | 30   | 23   | 39   | 38   | 100  | 100  | 100  | 100  | 99.9 | 99.7 | 100  | 100  | 100  | 100  | 100  | 100  | 100  | 100  | 100  | 2.61 | 3.25 |
| Ni                             | 150   | 17    | 17    | 0     | 2     | 0     | 10    | 0     | 4    | 0    | 3    | 0.3  | 0    | 0    | 3    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 100  |
| Rb                             | 4     | 17    | 17    | 22    | 2     | 22    | 8     | 20    | 14   | 40   | 10   | 38   | 10   | 17   | 7    | 7    | 14   | 3    | 10   | 2    | 3    | 2    | 4    | 10   | 16   | 3    | 3    | 3    | 2    | 26   |      |
| Sr                             | 172   | 658   | 634   | 776   | 127   | 886   | 323   | 567   | 401  | 598  | 290  | 658  | 592  | 657  | 2    | 2    | 3    | 1    | 4    | 11   | 1    | 4    | 0    | 2    | 3    | 1    | 2    | 1    | 1    | 3    |      |
| Ba                             | 14    | 229   | 222   | 612   | 4     | 672   | 199   | 591   | 219  | 631  | 141  | 798  | 196  | 1232 | 16   | 16   | 17   | 10   | 7    | 5    | 10   | 12   | 7    | 3    | 13   | 9    | 7    | 17   | 5    | 23   |      |
| Y                              | 11    | 27    | 27    | 36    | 36    | 39    | 39    | 42    | 36   | 54   | 35   | 39   | 35   | 51   | 2    | 1    | 2    | 4    | 4    | 0    | 5    | 7    | 5    | 7    | 3    | 5    | 5    | 5    | 5    | 0.3  |      |
| Zr                             | 15    | 263   | 222   | 291   | 230   | 369   | 264   | 258   | 312  | 485  | 258  | 390  | 249  | 433  | 62   | 60   | 11   | 140  | 120  | 149  | 137  | 119  | 115  | 128  | 56   | 104  | 124  | 140  | 139  | 36   |      |
| Nb                             | 0     | 50    | 38    | 44    | 47    | 67    | 50    | 49    | 42   | 81   | 48   | 84   | 53   | 79   | 418  | 499  | 454  | 52   | 230  | 60   | 62   | 51   | 41   | 22   | 940  | 24   | 19   | 45   | 29   | 595  |      |
| La                             | ---   | 39    | ---   | ---   | ---   | 63.44 | ---   | ---   | ---  | 77   | ---  | 57   | ---  | ---  | 825  | 908  | 202  | 113  | 2136 | 173  | 70   | 75   | 583  | 220  | 1898 | 532  | 48   | 42   | 45   | 798  |      |
| Ce                             | ---   | 88    | 87    | 137   | 99    | 141   | 104   | 142   | 101  | 162  | 100  | 125  | 124  | 160  | 63   | 61   | 66   | 114  | 131  | 124  | 122  | 138  | 104  | 98   | 56   | 115  | 100  | 109  | 107  | 39   |      |
| Pr                             | ---   | 10.45 | ---   | ---   | ---   | 17.07 | ---   | ---   | ---  | 19   | ---  | 15   | ---  | ---  | 653  | 667  | 486  | 1394 | 1297 | 1601 | 1661 | 1807 | 115  | 104  | 522  | 1147 | 1677 | 1567 | 547  | 390  |      |
| Nd                             | ---   | 43.24 | ---   | ---   | ---   | 70.48 | ---   | ---   | ---  | 77   | ---  | 66   | ---  | ---  | 95   | 95   | 99   | 249  | 233  | 256  | 252  | 283  | 225  | 162  | 92   | 201  | 175  | 178  | ---  | 57   |      |
| Sm                             | ---   | 8.97  | ---   | ---   | ---   | 13.7  | ---   | ---   | ---  | 15.5 | ---  | 13   | ---  | ---  | ---  | ---  | ---  | ---  | ---  | ---  | ---  | ---  | ---  | ---  | ---  | ---  | ---  | ---  | ---  | ---  | 126  |
| Eu                             | ---   | 2.89  | ---   | ---   | ---   | 4.74  | ---   | ---   | ---  | 5.63 | ---  | 4.94 | ---  | ---  | 194  | 196  | 170  | 277  | 323  | 299  | 298  | 327  | 285  | 298  | ---  | ---  | ---  | ---  | ---  | 15.8 | 6    |
| Gd                             | ---   | 8.03  | ---   | ---   | ---   | 11.8  | ---   | ---   | ---  | 13.5 | ---  | 11.5 | ---  | ---  | ---  | ---  | ---  | 34.7 | 35.7 | 37.2 | 37   | 42   | 36.4 | ---  | ---  | ---  | ---  | ---  | ---  | ---  | 6    |
| Tb                             | ---   | 1.16  | ---   | ---   | ---   | 1.65  | ---   | ---   | ---  | 2.07 | ---  | 1.65 | ---  | ---  | ---  | ---  | ---  | 126  | 133  | 136  | 135  | 153  | 133  | ---  | ---  | ---  | ---  | ---  | ---  | ---  | 13.4 |
| Dy                             | ---   | 5.97  | ---   | ---   | ---   | 8.11  | ---   | ---   | ---  | 11.2 | ---  | 8.4  | ---  | ---  | ---  | ---  | ---  | 8    | 8    | 8    | 8    | 9    | 4    | ---  | ---  | ---  | ---  | ---  | ---  | ---  | 4.94 |
| Ho                             | ---   | 1.08  | ---   | ---   | ---   | 1.44  | ---   | ---   | ---  | 2.15 | ---  | 1.5  | ---  | ---  | ---  | ---  | ---  | 12.6 | 13.3 | 136  | 135  | 153  | 133  | ---  | ---  | ---  | ---  | ---  | ---  | ---  | 11.5 |
| Er                             | ---   | 2.8   | ---   | ---   | ---   | 3.72  | ---   | ---   | ---  | 5.96 | ---  | 3.96 | ---  | ---  | ---  | ---  | ---  | 25.5 | 27.7 | 27   | 27   | 31   | 25   | ---  | ---  | ---  | ---  | ---  | ---  | ---  | 1.65 |
| Tm                             | ---   | 0.35  | ---   | ---   | ---   | 0.46  | ---   | ---   | ---  | 0.8  | ---  | 0.52 | ---  | ---  | ---  | ---  | ---  | 23.5 | 26.4 | 24.4 | 24.1 | 29   | 21.2 | ---  | ---  | ---  | ---  | ---  | ---  | ---  | 8.4  |
| Yb                             | ---   | 2.1   | ---   | ---   | ---   | 2.7   | ---   | ---   | ---  | 4.9  | ---  | 3.2  | ---  | ---  | ---  | ---  | ---  | 3.87 | 4.49 | 4.07 | 4.08 | 4.85 | 3.49 | ---  | ---  | ---  | ---  | ---  | ---  | ---  | 1.5  |
| Lu                             | ---   | 0.3   | ---   | ---   | ---   | 0.39  | ---   | ---   | ---  | 0.72 | ---  | 0.48 | ---  | ---  | ---  | ---  | ---  | 21.7 | 25.7 | 23   | 23.0 | 27   | 19.2 | ---  | ---  | ---  | ---  | ---  | ---  | ---  | 3.96 |
| Hf                             | ---   | 5.95  | ---   | ---   | ---   | 6.67  | ---   | ---   | ---  | 11.5 | ---  | 8.92 | ---  | ---  | ---  | ---  | ---  | 9    | 1    | 5    | 5    | 5    | 4    | ---  | ---  | ---  | ---  | ---  | ---  | ---  | 0.52 |
| Ta                             | ---   | 2.89  | ---   | ---   | ---   | 3.78  | ---   | ---   | ---  | 4.79 | ---  | 4.66 | ---  | ---  | ---  | ---  | ---  | 4.19 | 4.91 | 4.48 | 4.48 | 5.18 | 3.71 | ---  | ---  | ---  | ---  | ---  | ---  | ---  | 3.2  |
| Ti                             | ---   | 0.06  | ---   | ---   | ---   | 0.03  | ---   | ---   | ---  | 0.03 | ---  | 0.04 | ---  | ---  | ---  | ---  | ---  | 11.8 | 13.7 | 12.6 | 12.6 | 14.2 | 10.5 | ---  | ---  | ---  | ---  | ---  | ---  | ---  | 0.48 |
| Pb                             | 0.8   | 2.1   | 18    | 21    | 22    | 2.82  | 3     | 3.8   | 3.4  | 5.83 | 3.2  | 3.31 | 2.2  | 3.4  | ---  | ---  | ---  | 1.61 | 1.91 | 1.7  | 1.7  | 1.9  | 1.45 | ---  | ---  | ---  | ---  | ---  | ---  | 8.92 |      |
| Th                             | 0.7   | 3.49  | 3.4   | 5     | 3.6   | 5.27  | 4.3   | 5.9   | 4.4  | 7.38 | 3.5  | 6.36 | 4.4  | 7.6  | ---  | ---  | ---  | 1.1  | 11   | 11   | 12   | 9.2  | ---  | ---  | ---  | ---  | ---  | ---  | ---  | 4.66 |      |
| U                              | ---   | 1.05  | ---   | ---   | ---   | 1.59  | ---   | ---   | ---  | 2.37 | ---  | 1.23 | ---  | ---  | ---  | ---  | ---  | 1.39 | 1.96 | 1.43 | 1.47 | 1.59 | 1.33 | ---  | ---  | ---  | ---  | ---  | ---  | ---  | 0.04 |
| Ga                             | ---   | 24.3  | ---   | ---   | ---   | 31.3  | ---   | ---   | ---  | 33.3 | ---  | 28.2 | ---  | ---  | ---  | ---  | ---  | 15.0 | 13.2 | 14.6 | 15.5 | 16.5 | 11.9 | ---  | ---  | ---  | ---  | ---  | ---  | ---  | 11.3 |
| Eu/Eu*                         | ---   | 1.05  | ---   | ---   | ---   | 1.16  | ---   | ---   | ---  | 1.2  | ---  | 1.21 | ---  | ---  | ---  | ---  | ---  | 15.0 | 13.2 | 14.6 | 15.5 | 16.5 | 11.9 | ---  | ---  | ---  | ---  | ---  | ---  | ---  | 0.31 |
| La/Nb                          | ---   | 0.78  | ---   | ---   | ---   | 0.95  | ---   | ---   | ---  | 0.95 | ---  | 0.68 | ---  | ---  | ---  | ---  | ---  | 0.15 | 0.16 | 0.15 | 0.39 | 0.16 | 0.13 | ---  | ---  | ---  | ---  | ---  | ---  | ---  | 6.36 |
| Zr/Nb                          | ---   | 5.26  |       |       |       |       |       |       |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |





**Fig. 2** a Landsat image of Wadi Natash volcanoes. b Photo showing volcanic stratigraphy involving A-B facies (ignimbrite and lapilli-tuff), C facies (hyaloclastites), facies D (conglomerates), and E facies

(lava flows). c, d Geological maps of Gabal El Ghorfa ring dyke and Gaziret Khashm Natash, Wadi Natash, SED, Egypt (Saleh et al. 2021)

lava flows, up to 20 m in thickness, and displays two perpendicular sets of joints along with extremely vesicular exterior, occasionally intercalated with the Nubian sandstones. Subrounded mantle xenoliths are observed in the basaltic lavas, as has been previously detected by many authors (Abu El-Rus et al. 2016, 2018). The third sequence is represented by subvolcanic intrusive plugs which occur as steep-slope massive bodies, attaining up to 100-m height, and its thickness varies from 5 to 10 m. Columnar joints and screes/or talus-rich upper surfaces characterize the intrusive plugs.

Abundant ring complexes are delineated by N60°E- to N30°W-striking lineaments in the SED that were controlled by pre-existing deep crustal faults/fractures within the basement complex (Garson and Krs, 1978; Omar et al., 1987). These complexes were formed during diverse magmatic stages that happened between 230 and 84 Ma in an intraplate environment (Meneisy, 1986). Examples of these complexes are El Kahfa ring complex (ERC), El Gezira (229–230 Ma), El Naga (84–220 Ma), El Mishbeh (141–184 Ma), Shabih (191 ± 7 Ma), Nigrub El Tahiani (139.7 ± 9 Ma), and Nigrub El Fogani (132–142 Ma). ERC is composed of essexitic gabbros and syenitic rocks as well as extrusive rocks of trachyte, rhyolite, and basanite (Hegzay et al. 2016) that are

emplaced at 92 ± 5 Ma, belonging to the Upper Cretaceous ring complexes (Serencsits et al., 1981; Lutz et al., 1988), whereas other ring complexes consist of alkali syenite and granite (Hashad, 1994).

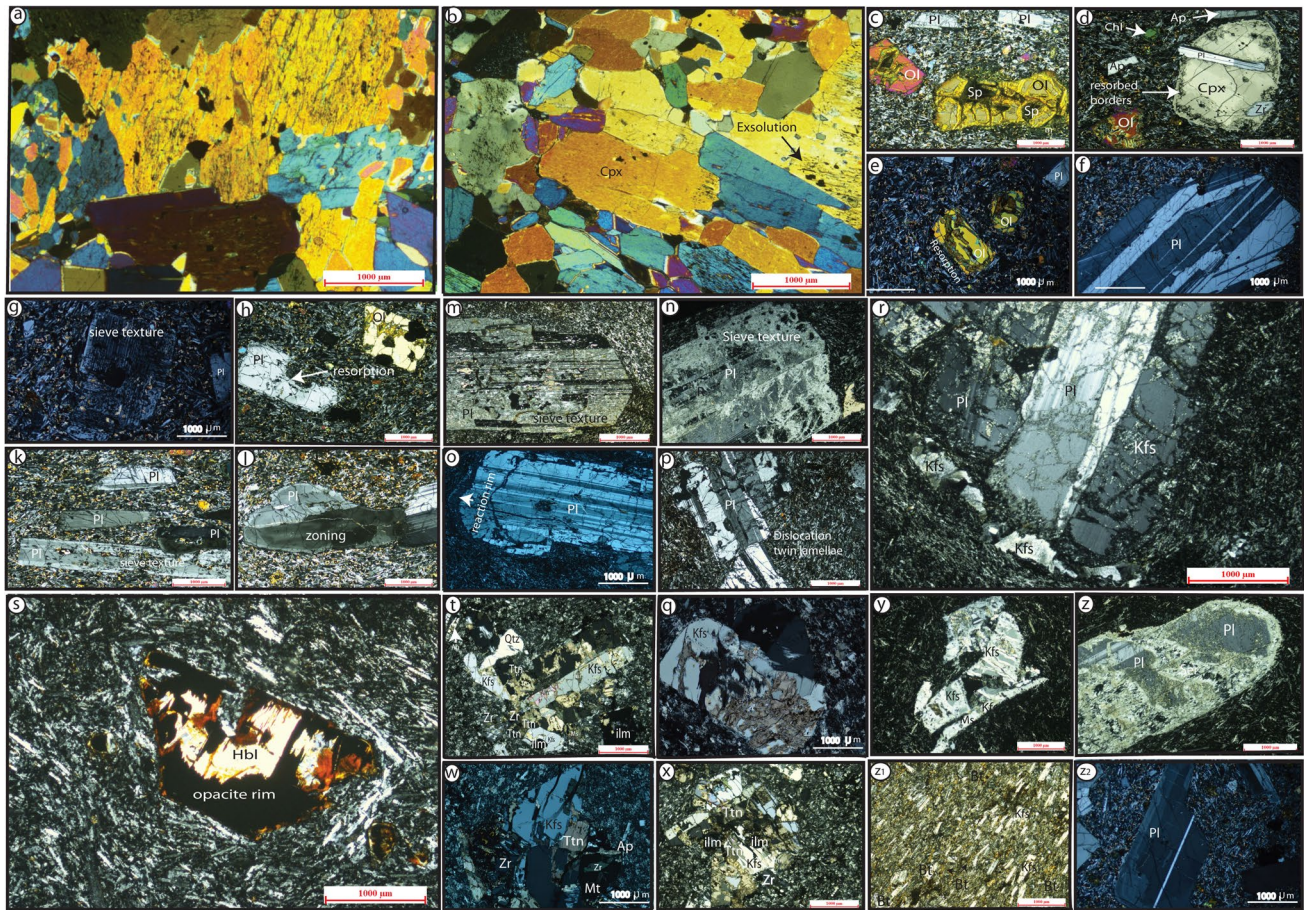
### Petrography

The mantle xenoliths recorded in Natash volcanoes are coarse-grained and composed of clinopyroxene crystals. The latter are holocrystalline, colourless, and subhedral crystals, showing hypidiomorphic equigranular texture and exsolution lamellae (Fig. 3a, b). The main eruptive products of the NV are represented by mafic, intermediate, and felsic types.

### Mafic rocks

These rocks are fine-grained and black in colour with characteristically porphyritic textures. They include ~30% subhedral to anhedral phenocrysts of olivine, clinopyroxene, and plagioclase crystals (Fig. 3c–z). Olivine crystals occur as subhedral to anhedral phenocrysts with distinctive resorption, fractures, embayment, rounded rims, and





**Fig. 3** Photomicrographs showing the main petrographic characters of the Natash volcanoes. **a, b** Photomicrographs showing the subhedral crystals of clinopyroxene forming mantle xenolith. **c** Altered and fractured subhedral-anhedral crystals of olivine (Ol) embedded in a fine matrix. **d** Prismatic euhedral crystals of clinopyroxene with resorption and fine cracks. Notice plagioclase subophitically enclosed with clinopyroxene phenocryst. **e** Resorption along olivine rims. **f** Complex zoning and twinning in plagioclase phenocrysts. **g** Sieve-rich core in plagioclase phenocrysts. **h** Grains of resorbed plagioclase (Pl) and altered olivine (Ol) set in a fine matrix. **k, l** Fine oscillatory zoning observed in plagioclase crystals. **m** Core-rim sieve textures in twinned plagioclase phenocrysts. **n** Sieve-rich rims in plagioclase

iddingisitization especially along their borders and cleavages. Spinel grains occur as inclusions in olivine crystals (Fig. 3c). The crystals of clinopyroxene occur as colourless subhedral crystals and show resorption, embayment, and sieve textures particularly along their rims. They contain zircon, apatite, and Fe-Ti oxides as inclusions and show ophitic texture with lath-shaped plagioclase (Fig. 3d). Plagioclase crystals are fresh, subhedral, and lath-shaped, with 0.5 mm in length. Simple twinning and oscillatory zoning with resorption and sieve texture characterize most plagioclase phenocrysts (Fig. 3g–l). The groundmass is composed of lath-shaped feldspar, olivine, pyroxene, and opaques with typically fluidal texture.

phenocryst. **o** Reaction rims along the borders of twinned plagioclase phenocryst. **p** Deformed twinned plagioclase phenocryst showing dislocated twin lamellae. **r** Antirapakivi texture consisting of K-feldspar (Kfs)-encircled plagioclase (pl). **s** Black opacite rims (encircle) amphibole borders. **t** Altered K-feldspar associated with accessory titanite (Ttn), apatite (Ap), zircon (Zr), and ilmenite (ilm). **q** Simple twinning observed in potash feldspar (Kfs) with accessory minerals involving titanite (Ttn), sphene (Sph), and ilmenite (ilm). **y** Intensive degree of kaolinization affects K-feldspar (Kfs) with corrosive borders. **z<sub>1</sub>** Hydrothermal biotitization observed along feldspar borders. **z<sub>2</sub>** Complex zoning in plagioclase phenocrysts

### Intermediate-felsic rocks

Intermediate rocks of trachyandesitic to trachytic in composition are characterized by enrichment of crystals (>50%), displaying coarse to microporphyratic textures displaying hypocrystalline and trachytic fabric. They contain mineral associations composed of plagioclase and alkali feldspar with subsidiary biotite, aegirine, and amphibole. Their crystals display a wide range in size, varying from megacrysts (>3 mm) through microphenocrysts (0.3–3 mm) to microliths (<0.3 mm). Plagioclase crystals are chiefly subhedral to anhedral megacrysts and phenocrysts as well as lath-shaped outlines in groundmass (Fig. 3m–r). They

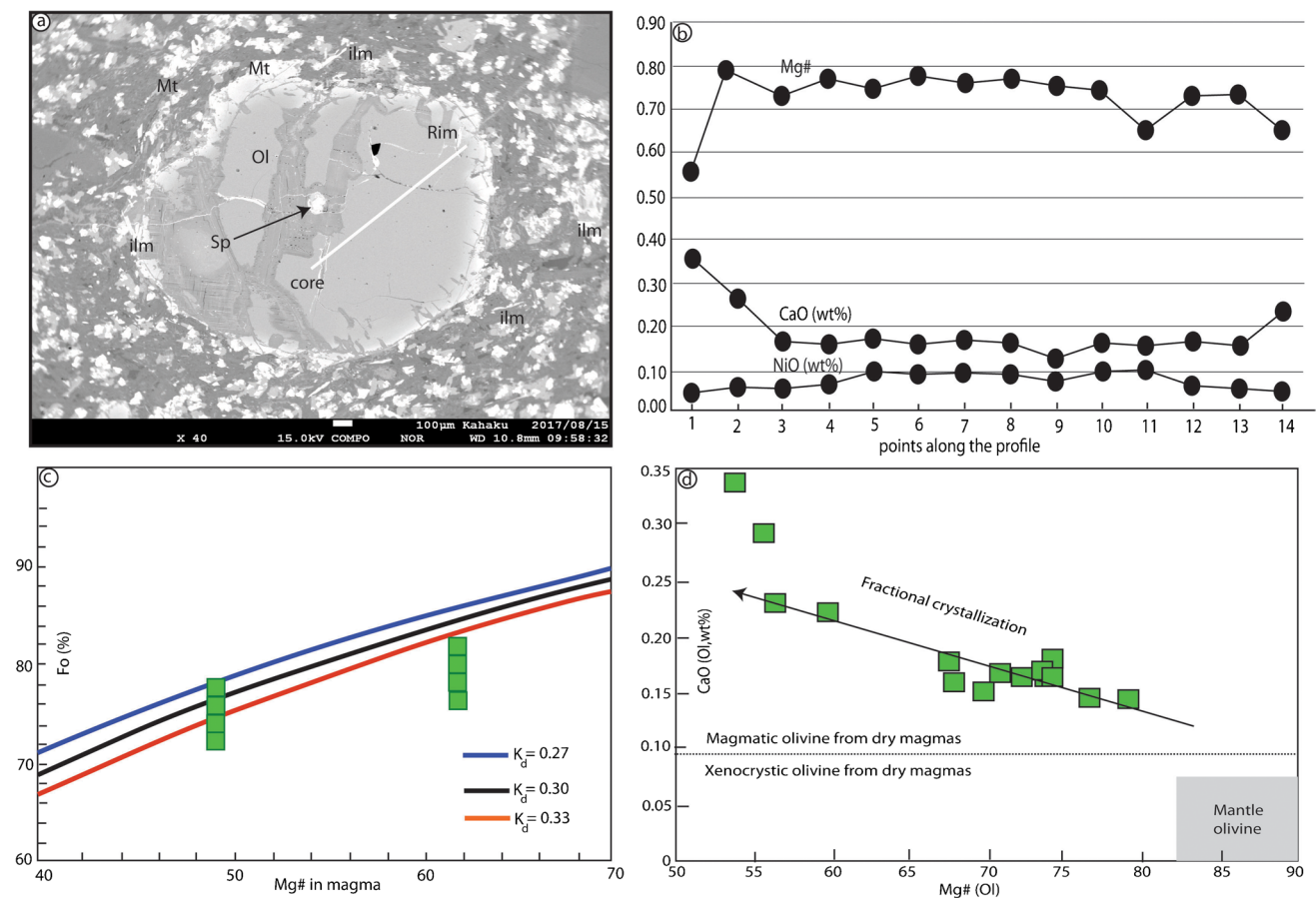


involve melt inclusions and display simple and lamellar twinning as well as composite zoning (Fig. 3n, o). Intensive fractures, bending in twin lamellae, and partial to complete replacement by kaolinite and white mica characterize plagioclase feldspar (Fig. 3p). The latter show marks of disequilibrium features such as fine and coarse-sieve textures, embayment, resorption, dissolution, rounded rims (Fig. 3m, n), and rapakivi/antirapakivi textures (Fig. 3r). Amphibole phenocrysts are dark brown in colour and subhedral crystals and form six-sided or prismatic shape with characteristically simple twinning and colour zoning. They show reaction rims and partial to complete replacement by mica and opaques (Fig. 3s). The phenocrysts of aegirine are subhedral crystals and dark green in colour showing simple twinning and partial replacement by chlorite. Alkali feldspars are subhedral to anhedral twinned crystals and show moderate alteration to sericite and kaolinite (Fig. 3t–y). Accessory zircon, apatite, titanite, rutile, and magnetite along with epidote (allanite) and mica are observed (Fig. 3w, x). The grains of titanite form as subhedral to

euhedral crystals and occur as inclusions in the alkali feldspar (Fig. 3x). Oscillatory zoning and glass inclusions along core and rim of plagioclase crystals forming sieve textures are common (Fig. 3z, z<sub>2</sub>). The groundmass is aphyric and consists of lath-shaped plagioclase, alkali feldspars, mica, biotite flakes encircled the feldspar laths (Fig. 3z<sub>1</sub>), and grains of magnetite and ilmenite demonstrating pilotaxitic and fluidal texture (Fig. 3z<sub>1</sub>, z<sub>2</sub>). The subvolcanic plugs display similar texture and mineral assemblages to those in trachyandesites and trachytes. Alkali feldspar, quartz, and biotite with allanite, zircon, and Fe-Ti oxides characterize the felsic rocks. The quartz phenocrysts are anhedral crystals and show patchy outline.

### Mineral chemistry

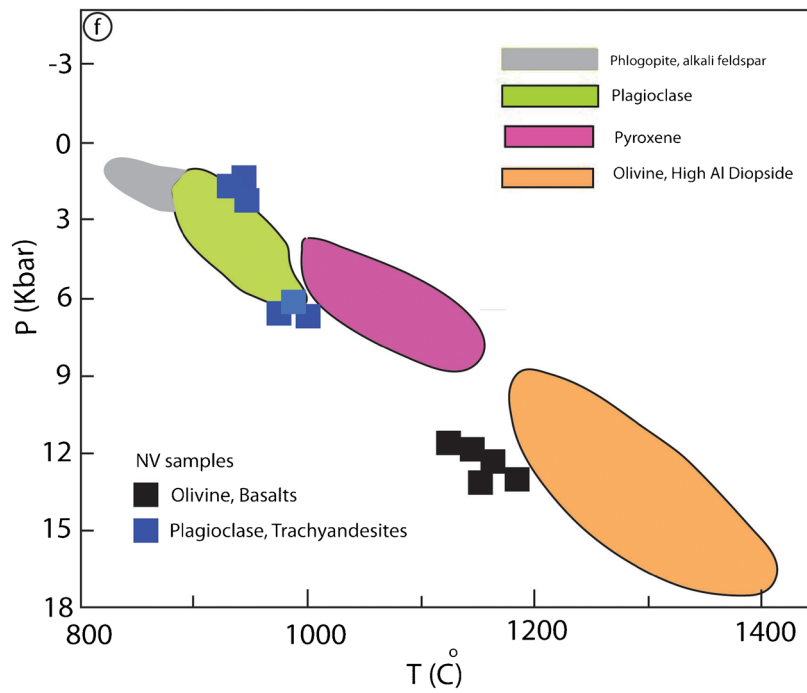
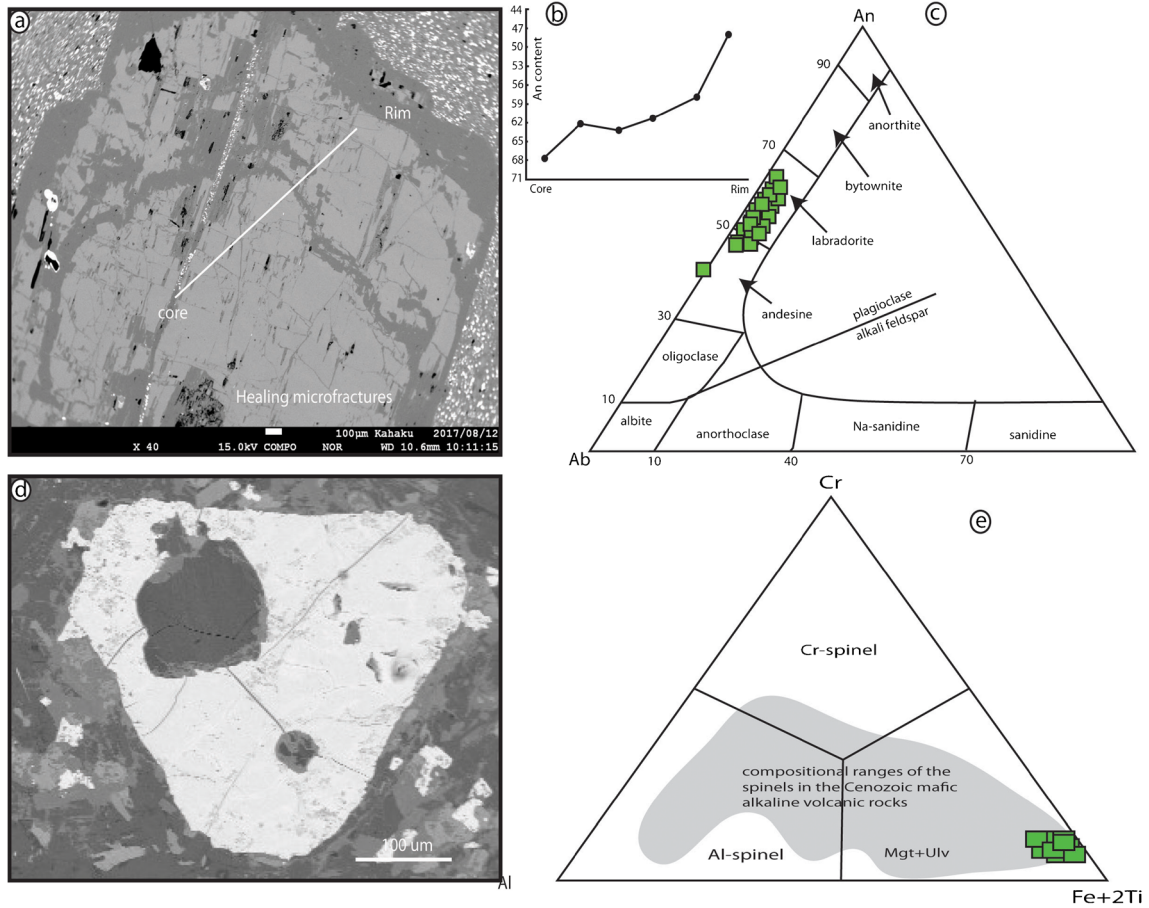
We analysed olivine and opaques from mafic rocks and plagioclase from intermediate rocks. All their compositional data are given in the supplementary Tables 1 and 2.



**Fig. 4** Mineral compositions in the olivine phenocrysts. **a** Normal zoning pattern in rounded olivine with spinel (Sp) as poikilitic inclusion. **b** Mg#, CaO, and NiO variations vs. Fo content for olivine crystals. **c** Fo content of olivine phenocrysts vs. whole-rock compositions

(Mg#). **d** CaO content of olivine versus Fo content of olivine. The solid line separates magmatic and xenocrystic olivine in dry mafic magmas on the basis of CaO content (Foley et al. 2013)





**Fig. 5** Mineral compositions in the plagioclase phenocrysts. **a** Sub-hedral plagioclase showing zoning and resorption with characteristic healing microfractures. **b** The variation of An content along core-rim of plagioclase crystals. **c** Feldspar compositions. **d** Octahedral form of spinel crystals. **e** Iron-titanium-rich spinels. The range of the spinels of other Cenozoic mafic lavas is also shown (Cucciniello et al. 2018). **f** Thermobarometric estimations for the minerals of the Natash volcanoes using equations of Putirka (2008). Field boundaries for the calculated P-T stability of olivine, pyroxene, plagioclase, phlogopite, and alkali feldspar characterized alkaline Damavand volcano (after Eskandari et al. 2018)

## Olivine

Olivine phenocrysts are ubiquitous in mafic rocks (Fig. 4a). The Fo content declines from cores (Fo<sub>77-71</sub>) to rims (Fo<sub>65-60</sub>), demonstrating normal growth zoning (Fig. 4b). The olivine crystals display fluctuation in element concentration. They have increasing CaO (from 0.16–0.27 to 0.23–0.35 wt%) and decreasing Mn (from 0.74–0.58 to 0.25–0.45 wt%), NiO (0.07–0.6 to 0.01–0.04 wt%), and Al<sub>2</sub>O<sub>3</sub> (from 0.04–0.05 to 0.01–0.03 wt%) from their cores to rims (Fig. 4b). The contents of CaO reveal that olivine crystals were formed from magmas (i.e. antecrysts) rather than lithospheric mantle peridotite-derived xenocrysts (Fig. 4d, Foley et al., 2013).

## Plagioclase feldspar

The crystals of plagioclase are recorded in both mafic and intermediate rocks, displaying complex zoning (Fig. 5a). Their An contents (100 × Ca/(Ca+Na) in mole) range from 65 at the core to 45 at the rim, indicating labradorite (An<sub>70</sub>) to andesine (An<sub>45</sub>) in composition with no alkali feldspar (Fig. 5b, c). The K<sub>2</sub>O, MgO, and FeO<sub>T</sub> contents are low and do not display substantial core to rim variations, fluctuating from 0.3 to 0.6, 0 to 0.1, and 0.3 to 0.7 wt%, respectively, in the plagioclase feldspar.

## Spinel

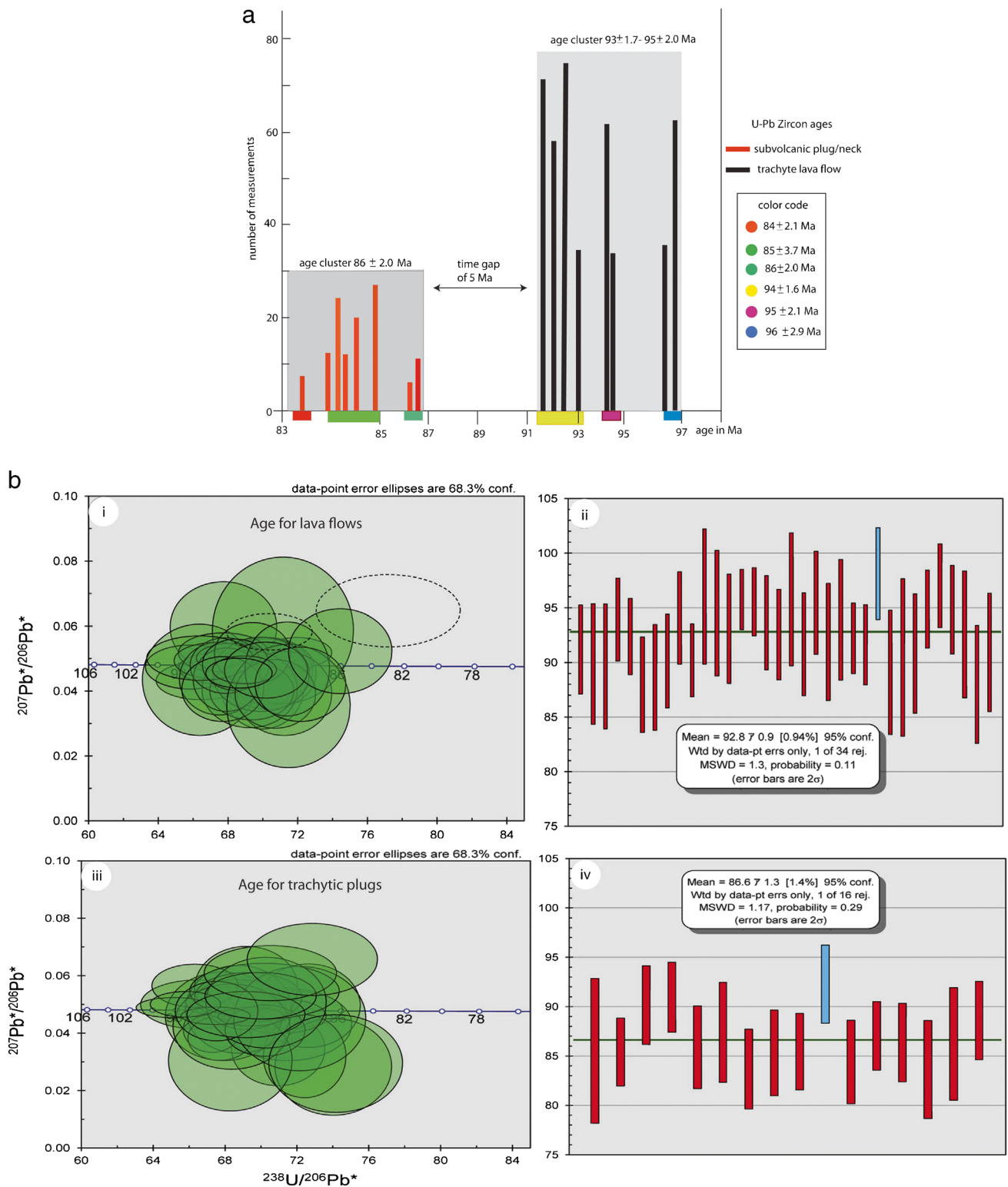
Spinel is found as inclusions in olivine crystals with euhedral octahedral shape (Fig. 5d). They are Ti- and Fe-rich (TiO<sub>2</sub> = 25–27 wt%, FeO = 61–65 wt%) with a homogeneous interior. The Cr<sub>2</sub>O<sub>3</sub> and MnO contents range from 0.6 to 0.83 wt% and from 0.77 to 2.89 wt%, respectively. Their crystals have a limited variation in Al<sub>2</sub>O<sub>3</sub> concentration (from 2.15 to 2.65 wt%), whereas MgO and NiO attain nil values. The enrichment of both Ti and Fe in the studied spinels reflects ulvöspinel composition (Fig. 5e).

## Geothermobarometry

Olivine, plagioclase, and Fe-Ti phases have been used as geothermobarometers in order to evaluate the pressures, temperatures, and crystallization depths at which the magma stagnation regions were situated. The selected minerals advocate that the whole rock characterizes the melt composition wherever the minerals were formed (Coote and Shane, 2018). The method of Roeder and Emslie (1970) has been used (Fig. 4c) in order to test whether the Fo content of the olivine might be in equilibrium with a composition of the whole-rock liquid, relying on the apportioning of Fe-Mg between olivine and liquid which equals to  $^{ol-Liq}D_{Fe-Mg}$  between 0.27 and 0.33 ± 0.03 underneath pressure <2–3 GPa (Roeder and Emslie, 1970). Olivine-melt thermometer (Putirka et al., 2008, Eq. 22) regulated for hydrous systems with its standard error of estimate (SEE) of about ±29 °C (Putirka, 2008) has been used. The Fo contents of the zoned olivine phenocrysts (Fo<sub>77-60</sub>) are not in equilibrium with whole-rock liquid having Mg#62 (Fig. 4c), but equilibrium with the compositional mafic melt having Mg#50 with its K<sub>D</sub> (Fe-Mg) equals to 0.234. Following the equations of Putirka (2008), a pressure of 1.3 GPa and a temperature of 1154 °C have been computed from the composition of olivine cores (Fo<sub>77-71</sub>), declining to a pressure of 1.25 GPa and a temperature of 1136 °C for olivine rims (Fo<sub>65-60</sub>). These calculations overall designate that zoned olivines with Fo<sub>77-60</sub> equilibrated with Mg#50 host melts at 1.3–1.25 GPa (53–43 km) and 1154–1136 °C. Plagioclase-melt equilibrium can be used as thermobarometers and hygrometers which are regulated for hydrous systems with K<sub>D,plag</sub> (K<sub>D</sub> = 0.10 ± 0.05, T < 1050 °C) and SEE at pressure of ±2.47 kbar and a temperature of ±36 °C as well as H<sub>2</sub>O content with a SEE of ±1.1 wt% (Putirka, 2008, Eq. 24a and 25a). A temperature of about 1048 to 980 °C and a pressure of about 0.76 to 0.26 GPa (26–9 km) were supposed for the plagioclase feldspar (An<sub>70-45</sub>), which refer to the middle crustal depth (Murcia et al. 2019) along with crystallization of Fe-Ti oxides at 937–904 °C. By using the plag-melt hygrometer (Putirka 2008), the contents of H<sub>2</sub>O melt are restricted between 1.5 and 2.3 wt%. All these data reflect that there are two storage zones beneath the NV: a deep zone at depths of ~53–43 km and a shallow crustal zone at depth of ~26–9 km.

## SHRIMP U/Pb zircon geochronology

Zircon grains were chosen from the intermediate and felsic rocks for SHRIMP U/Pb dating. Five analyses on 20 zircon grains were done (supplementary Table 1) and shown in histogram (Fig. 6a) and Tera-Wasserburg diagrams (Fig. 6b). The length of these crystals ranges from 100 to 300 µm.



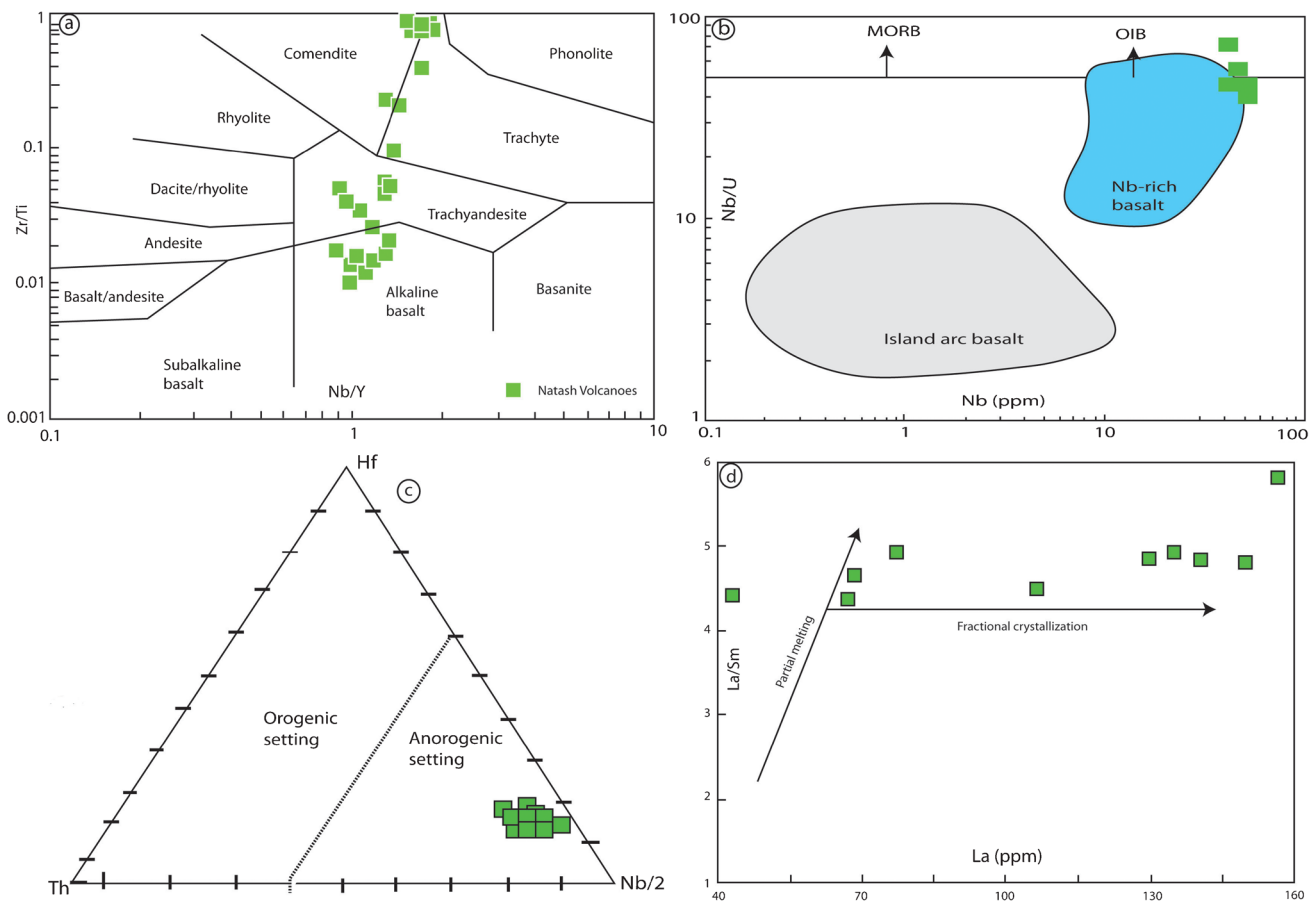
**Fig. 6** U-Pb age dating of the Natash volcanoes. **a** Histogram illustrating U-Pb age for the Natash volcanoes. **b** Tera-Wasserburg U-Pb concordia diagrams (i and ii for trachyandesitic/trachytic flows and iii and iv for trachytic plugs



Euhedral-subhedral short prisms and transparent to translucent with no inclusions characterize the investigated zircon crystals, exhibiting generally magmatic oscillatory and sector zoning. All the results have been revealed that zircons selected from trachyandesitic/trachytic flows have U/Pb ages of  $92\text{--}97 \pm 0.9$  Ma ( $n = 8$ , MSWD = 1.3/1.07) (Fig. 6b (i, ii)), while the youngest U/Pb ages give a period of  $81\text{--}87 \pm 1.3$  Ma ( $n = 8$ , MSWD = 1.17) (Fig. 6b (iii, iv)) for trachytic plugs (Khalaf et al. 2018). This weighted average  $^{206}\text{Pb}/^{238}\text{U}$  age denotes that the age of the NV is reliable with the formerly registered ages of the NV and syenite-granite suites of Abu Khrug and El Kahfa ring complexes ( $93\text{--}85.6 \pm 3$  Ma, El-Shazly and Krs, 1973; Hashad and El Reedy, 1979). Recently, Abu El-Rus et al. (2019) reported the occurrence of Precambrian zircon xenocrysts with U/Pb ages of 681 Ma in some trachyte plugs, typical for Egyptian basement rocks ( $\sim 700$  Ma). The bimodal ages documented by zircons (681 vs. 92 Ma) propose a wide time break ( $>500$  Ma) between the termination of the Neoproterozoic Era and the beginning of unique magmatism in Wadi Natash area during Upper Cretaceous period.

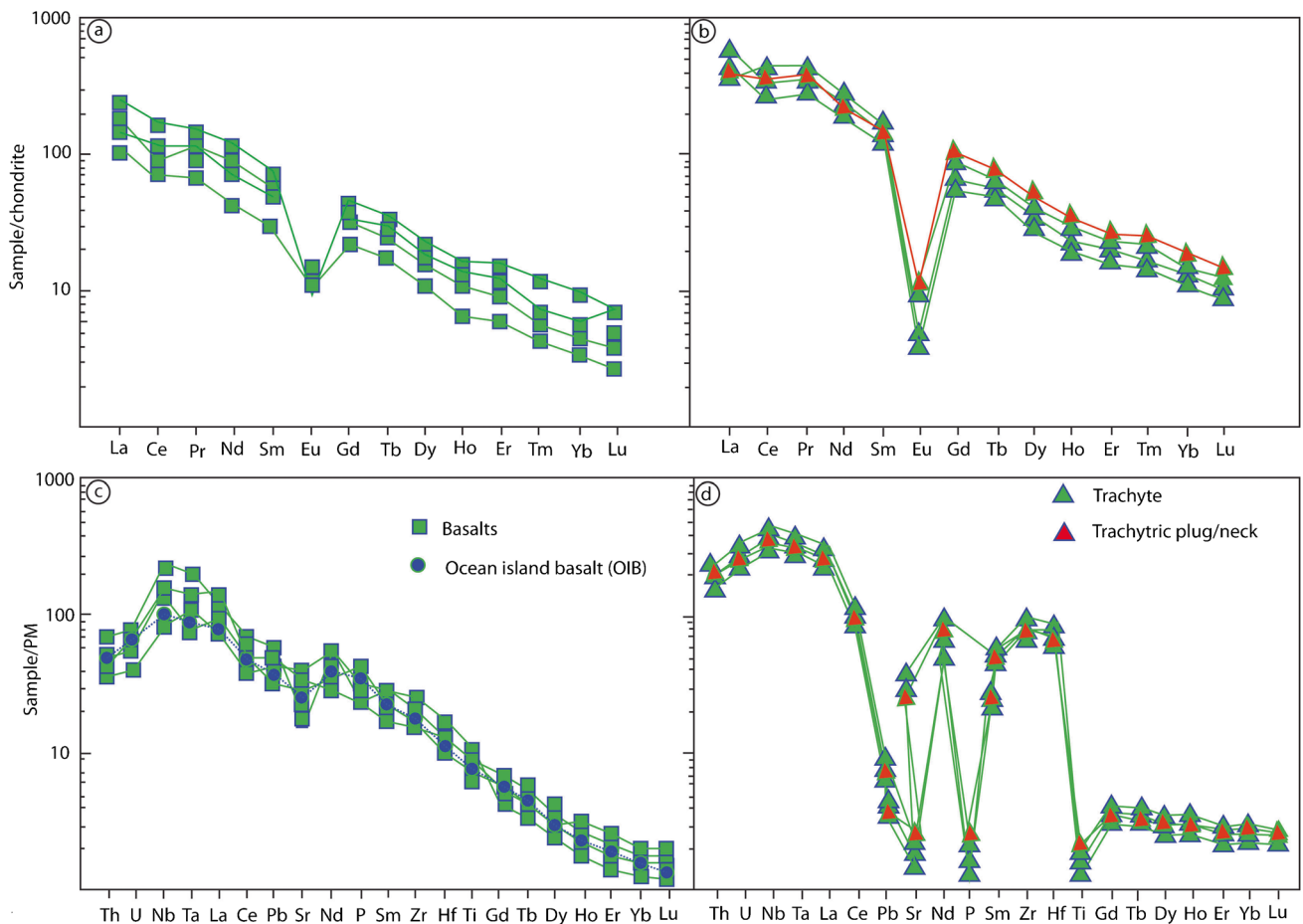
### Whole-rock geochemistry

Most rock specimens have mildly enriched LOI contents ( $>2$  wt%), accredited to secondary minerals like kaolinite, white mica, chlorite, and carbonate. REEs and HFSEs (Zr, Nb, Y) are deliberated as immobile, owing to low correlation coefficients ( $>0.85$ ). The LILEs (such as K, Rb, Ba, and Sr) have been exaggerated to various degrees by metasomatism or metamorphism. The slightly enriched contents of LOI of the Natash specimens probably propose the mobilization of LILEs. So, the immobile elements and its ratios as well as Ti, Ta, and Th elements have been used for geochemical and petrogenetic interpretations. On the Nb/Y vs. Zr/Ti diagram (Fig. 7a), the samples of the NV display a wide compositional array extending from basalts through trachyandesites-trachytes to phonolites-comendites that were formed within plate regime (Fig. 7c). Trachyandesitic/trachytic rocks contain high Zr (522–1807 ppm), Nb (92–283 ppm), Y (58–79 ppm), Rb (60–140 ppm), Ba (70–1889 ppm), Ta (11–16 ppm), Th (16–21 ppm), and U (4–8 ppm) concentrations and



**Fig. 7** Geochemical characteristics of the Natash volcanoes. **a** Zr/Ti vs. Nb/Y diagram (after Winchester and Floyd 1976). **b** Nb/U versus Nb (Xu et al. 2016). **c** Hf-Nb/2-th ternary diagram for distinguish-

ing between orogenic and anorogenic setting. **d** La (ppm) vs. La/Sm binary diagram showing fractional crystallization and partial melting path



**Fig. 8** Trace element normalization diagrams. Chondrite-normalized diagrams for basalts (a) and intermediate/felsic (b). Primitive mantle-normalized multi-element diagrams for basalts (c) and intermediate/felsic (d). The data of OIB along with normalization values of both primitive mantle and chondrite are from Sun and McDonough (1989)

lower Sr contents (52–499 ppm) as compared to the basaltic rocks (Zr = 15–369 ppm, Nb = 44–81 ppm, Y = 11–39 ppm, Rb = 2–39 ppm, Ba = 4–798 ppm, Ta = 3–5 ppm, Th = 4–6 ppm, U = 1–2 ppm, Sr = 127–776 ppm). Compared with trachyandesites/trachytes, the felsic rocks show low contents of LILE and HFSE. The total REE contents increase from the basaltic (180–207 ppm) through the trachyandesitic/trachytic (671–710 ppm) to the felsic rocks (711–728 ppm).

In chondrite-normalized REE plots (Fig. 8a, b), the LREE enrichment and HREE depletion characterize the NV ( $(La/Yb)_N = 10–23$ ;  $(Tb/Lu)_N = 2.29–4.23$ ;  $(Nb/Yb)_N = 16–33$ ;  $(Gd/Yb)_N = 2.3–2.9$ ), similar to the ocean island basalts (OIB, Sun and McDonough, 1989). The ratios of LREE/HREE increase from basalts ( $(La/Yb)_N = 10–15$ ) to trachyandesites/trachytes and rhyolites ( $(La/Yb)_N = 10–21$ ) with moderately low concentration of HREE ( $(Ho/Yb)_N = 1.06–1.14$ ), displaying strong fractionation between LREE and HREE. The basalts fall within the field array of Nb-rich basalts (Fig. 7b). The high concentrations of both Zr/Hf (43) and La/Nb (0.95) ratios in the basalts reflect their

origins from mantle-derived OIB (Taylor and McLennan, 1985). The OIB and the studied basalts show close similarities in Nb/Ta, Nb/U, and Ce/Pb ratios (17.5, 47, and  $25 \pm 5$  vs. 17, 34, and 38, respectively) further reinforcing mantle source for the NV. The most differentiated trachyandesites/trachytes show higher contents of both LREEs and HREEs than the basalts ( $(La/Yb)_N = 19–23$  vs. 15–17, respectively) (Fig. 8a, b). They show weak negative Eu anomalies ( $Eu/Eu^* = 0.36–0.84$ , Fig. 8b) compared to those in basalts (1.16–1.21, Fig. 8a), suggesting that a plagioclase is lacking in the magma source of the basalts, and so, their REE array displays no negative Eu troughs. In mantle-normalized trace element diagrams (Fig. 8c, d, Sun and McDonough (1989), the lava specimens show high enrichment degree for HFSEs (such as Nb, Ta, Zr, and Hf), LILEs, and LREEs with noticeable Pb, Sr, P, and Ti troughs especially in trachyandesites and trachytes (Fig. 8d). Moreover, the trachyandesite/trachyte and rhyolite specimens have higher concentrations of Th, U, Ta, and Hf than the basaltic rocks, demonstrating their high degree of fractionation.

## Composition of primary magmas

The common occurrence of olivine and pyroxene phenocrysts in basalts of the NV and the equilibrium of Fo<sub>77-65</sub> with their host liquids (Mg#55) of olivine crystals are not demonstrative of a primitive magma. In order to remove the fractionation influence and achieve the initial melt composition benchmarks (Mg# = 68–72, 300–500 ppm Ni, 750 ppm Cr; e.g. Green and Falloon 2005), we should add the appropriate fractionated crystal phases into the quantified compositions. Olivine represents the prevailing phenocryst phase in basalts, demonstrating olivine-controlled fractional crystallization. The least-evolved basaltic sample (N<sub>2</sub>) was assumed as the parent magma for the whole NV. The N<sub>2</sub> magma is not compatible with the primary magma that should occur in balance with the mantle because it contains low MgO content (5.34 wt%), as the results of olivine and clinopyroxene fractionation from initial source. In the N<sub>2</sub> melt, the Fo content varies from 77 (core) to 60 (rim). For the melt, a balance (Fe<sup>2+</sup>/Mg) Kd<sub>ol</sub> of 0.3 (Roeder and Emslie 1970) and an Fe<sup>3+</sup>/ΣFe ratio of 0.23 was presumed, according to the Fe<sup>3+</sup>/ΣFe ratios and water content that were calculated by Kelley and Cottrell (2009). The effect of crustal assimilation is neglected in NV based on isotopic data proposed by Abu El-Rus (2016). The positive Eu array characterizing the mafic rocks (Eu\* = 1.05, Fig. 8a) discloses irrelevant separation of plagioclase during fractionation in the formation of their magma. So, the olivine is the only fractionated phase in adjusting the composition of the primary magma. We have used the Petrolog model version 3.1.1.3 (<http://petrolog.web.ru/latest.html>, Danyushevsky and Plechov, 2011) to define an initial magma composition for N<sub>2</sub> melt. This model requires an addition of olivine until a magma composition in balance with the mantle is achieved. The MnO (0.3 wt%) and CaO (0.2 wt%) contents should be constant of the olivines, and the SiO<sub>2</sub>, FeO, and MgO concentrations were calculated as a utility of the content of Fo using 0.3 and 0.23 values for (Fe<sup>2+</sup>/Mg) Kd<sub>ol</sub> and Fe<sup>3+</sup>/ΣFe ratios, respectively, for the melt. This model shows that c. 15–20% olivine requests to be added to attain the balance with mantle olivine composition (Fo<sub>89-90</sub>, Mg# = 73, Mg > 9, K<sub>D</sub> (Fe+Mg) = 0.29). The estimated SiO<sub>2</sub>, FeO, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, and H<sub>2</sub>O contents of the initial magma are 47.2 wt%, 7.73, 11.8 wt%, 10.9, 2.98, 0.13, and 3.1 ± 0.9 wt%, respectively. The calculated temperatures (considering specimens with MgO > 9 wt%, Fe<sup>3+</sup>/Fet = 0.1, and olivine Fo<sub>89-90</sub>) range from 1359 to 1377 °C, by using the equations of Wood (2004) and Putirka's model (2008). Melting pressures vary from 1.6 to 1.77 GPa for the primary magma which corresponds to a mantle source at 16.7–18.7 kb in the temperature ranging from 900 to 1100 °C, near the garnet–spinel peridotite transition boundary

(O'Neill 1981), matching with the pressure estimation (11.7–19.4 kb) determined by the clinopyroxene geobarometer (Nimis 1999). Eskandari (2016) concluded that the depth of magma formation was proposed between 27 and 35 kbar, matching to the deep mantle melting along the lithosphere–asthenosphere boundary melting for the alkaline magmas.

## Discussion

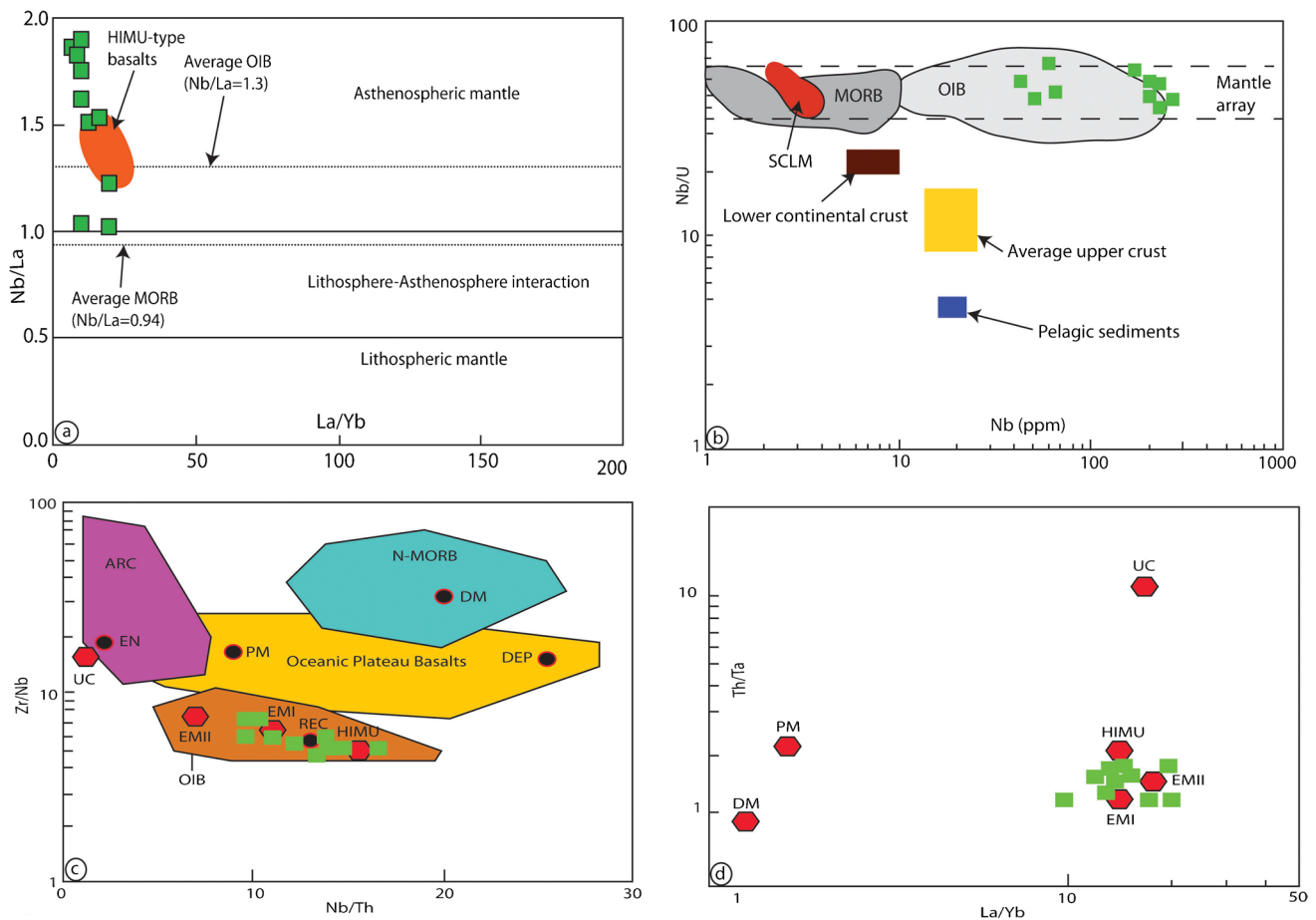
### Petrogenesis

#### Genetic characters of the Natash volcanoes

The ratios of incompatible elements (like La/Yb, Nb/La, Zr/Nb, Nb/Th, Th/Yb, and Nb/Yb) can be used as indicators to trace their mantle source because the processes of partial melting and crystal fractionation have no effect on the behaviour of these ratios (Weaver, 1991). The rock samples of the NV are plotted in OIB field with a HIMU signature based on comparatively high Nb/La (1–2), Th/Y, and Nb/U along with low La/Yb (<50, Fig. 9a, b). The high Nb/Th (10–18) and La/Yb (10–22) ratios along with low Zr/Nb ratios (5–8) of the NV are plotted near OIB source (Fig. 9c, d). The basaltic specimens show much higher Nb (38–84 ppm), Zr (222–369 ppm), and ΣLREE (180–207 ppm) than E-MORB (Nb = 8.3 ppm, Zr = 73 ppm, ΣLREE = 32.35 ppm) and analogous with OIB (Nb = 48 ppm, Zr = 280 ppm, ΣLREE = 165 ppm, Sun and McDonough, 1989). Moreover, NV are categorized by moderately high ratios of Nb/Ta (17–19) which are akin to those of the OIB (15.9; Pfänder et al. 2007) and chondrite (19.9; Münker et al. 2003). In addition, all the NV display moderately high ratios of Zr/Hf (36–67) and Th/Nb (0.06–0.10) which are close to the mantle-derived magma (Zr/Hf = 17.535–45 and Th/Nb = 0.117; Hofmann, 2003) compared with those ratios of continental crust (Nb/U ~ 9, Zr/Hf < 30, Th/Nb = 0.44, Rudnick and Gao, 2003). These geochemical features reflect a fertilized OIB-type mantle source for the NV. Based on Sr–Nd–Pb–Hf isotopic ratios, the NV were chiefly resulted from the HIMU, EMI, and depleted mantle (DM) endmembers, with a large amount of HIMU type (Abu El Rus et al., 2018) as has been previously concluded by Khalaf et al. (2018).

The intermediate and felsic volcanoes in Wadi Natash show high contents of Ga/Al ratio (4–15), HFSEs plus Ce (563–1123 ppm), and REEs (303–564 ppm), representative of A-type granite characters (Fig. 10a–c, Whalen et al. 1987; Eby, 1990). Eby (1990) used the Y/Nb ratio as an imperative key with a value of 1.2 in differentiating between A<sub>1</sub>- and A<sub>2</sub>-type granites. A<sub>1</sub>-type granites





**Fig. 9** Geochemical characters of the Natash volcanoes. **a** La/Yb vs. Nb/La variation in the studied Natash volcanoes showing their affinity to the HIMU-type basalts (Willbold and Stracke 2006). Average Nb/La values for MORB and OIB are from Sun and McDonough (1989), respectively. **b** Nb/U vs. Nb (ppm). **c** Zr/Nb vs. Nb/Th diagram (after Pearce 2008). **d** Th/Ta vs. La/Yb diagram. The shaded field represents the range of MORB, subcontinental lithospheric mantle (SCLM) and oceanic island basalts ( $Ce/Pb = 25 \pm 5$ ; Nb/U

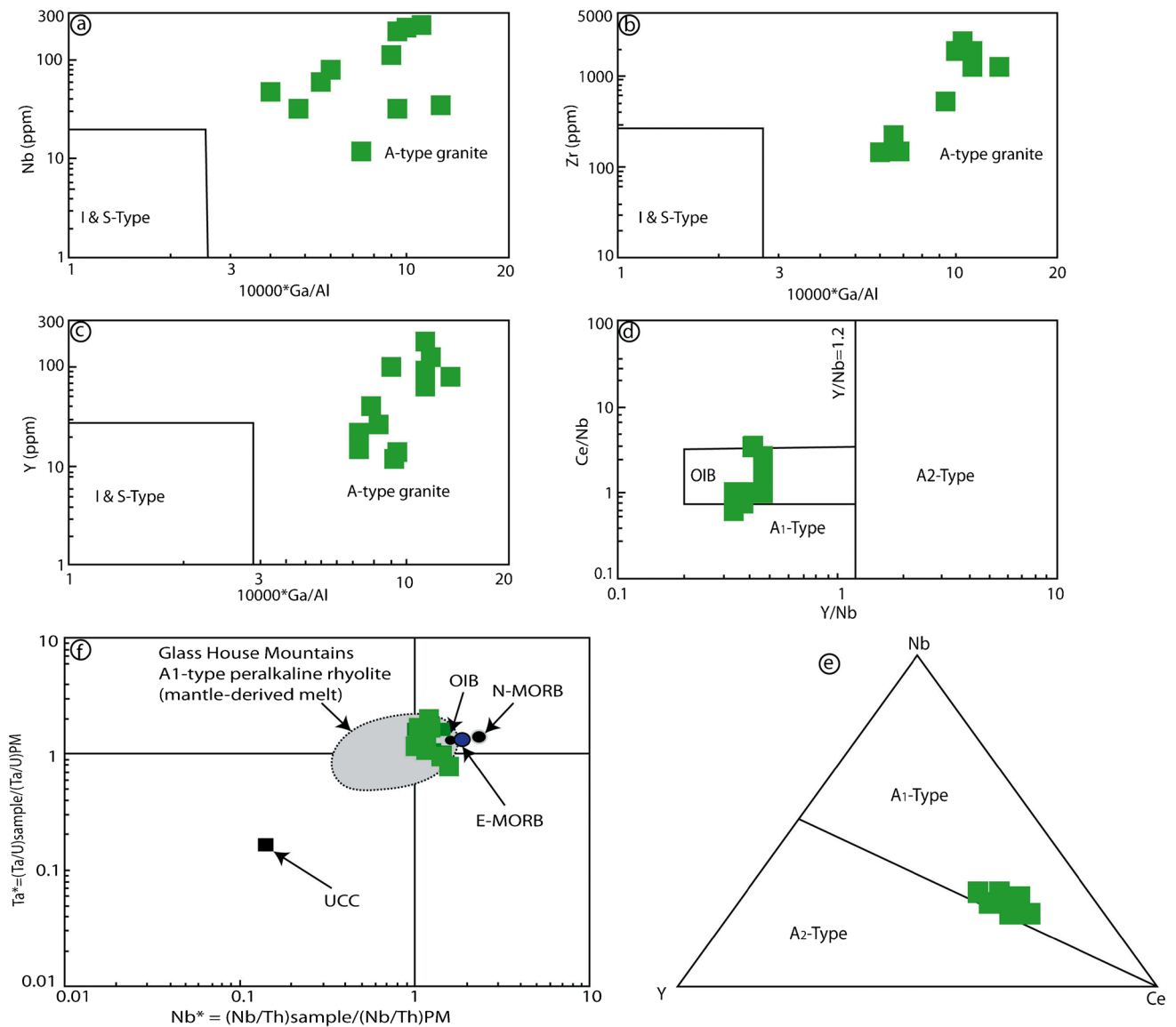
$= 47 \pm 10$ ; Hofmann 2003). The average value of continental crust (Rudnick and Gao 2003) is also included for comparison. MORB, mid-ocean ridge basalt; N-MORB, normal mid-ocean ridge basalt; E-MORB, enriched mid-ocean ridge basalt; OIB, ocean-island basalt; DM, depleted mantle; HIMU, high  $\mu$  mantle; EMI, enriched mantle I; EMII, enriched mantle II; UC, upper continental crust; REC, recycled component; EN, enriched component; DEP, deep depleted mantle

were resulted from OIB sources by fractional crystallization in an intraplate or rift settings, while  $A_2$ -type granites were formed from subcontinental lithosphere or lower crust magmas in post-orogenic settings (Eby 1992). The NV have low Y/Nb ratio ranging from 0.3 to 0.8, similar to the  $A_1$ -type granites ( $Y/Nb < 1$ , Fig. 10d).  $A_1$ -type granite affinity for these volcanoes is confirmed by high Nb concentration relative to Y and Ce contents (Fig. 10e). Furthermore, the NV have high Nb\* and Ta\* values that are similar to the distinctive OIB-derived  $A_1$ -type rhyolites (Fig. 10f, Fan et al. 2021). A-type granites universally need an expressively high temperature, reflecting mantle-derived magmas in their genesis (King et al. 1997). Abu El-Rus et al. (2018) determined the zircon saturation temperatures (ZSTs) for the NV, which range from 830 to 930 °C for trachytes and ~900 °C for

rhyolites that are recorded in A-type granites (>830 °C; Miller et al., 2003).

### Magmatic evolution of the Natash volcanoes

The studied NV show a wide compositional discrepancy (e.g.  $SiO_2 = 45\text{--}72$  wt%; Table 1), proposing that their parent magma-derived melts were affected by different degrees of fractional crystallization (FC, Fig. 11). The proofs of the FC are supported by the following: (1) the felsic rocks are scarce as compared with the basalts that are reliable with a small quantity of magmas formed by FC (Shao et al., 2015) and (2) the NV delineate linear trends on major/trace elements vs. Zr as differentiation index, which are reliable with the trends of FC (Fig. 11). The wide range in La contents (40–150 ppm) and restricted variation of La/

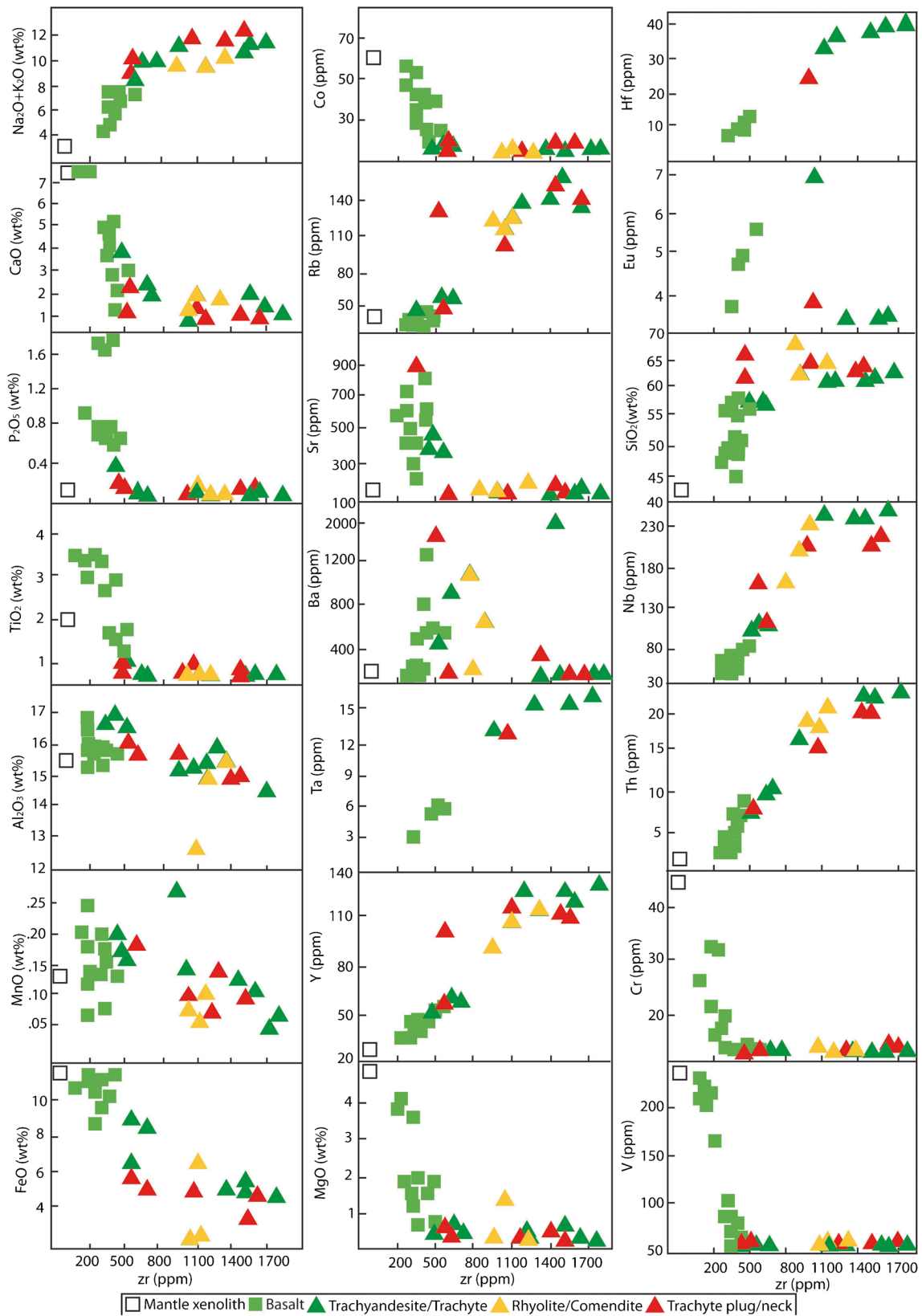


**Fig. 10** A-type characters for the Natash volcanoes. Ga/Al ratio vs. Nb (a), Zr (b), and Y (c). The chemical discrimination diagrams after Whalen et al. (1987) and Eby (1992). d Y/Nb vs. Ce/Nb for discriminating between A<sub>1</sub>- and A<sub>2</sub>-type granite. e Nb-Y-Ce ternary diagram for discriminating between A<sub>1</sub>- and A<sub>2</sub>-type granite. f Ta\* vs. Nb\*

diagram of the Natash volcanoes (after Niu and Batiza 1997; Ta\* = [Ta/U]<sub>sample</sub>/[Ta/U]<sub>PM</sub>; Nb\* = [Nb/Th]<sub>sample</sub>/[Nb/Th]<sub>PM</sub>). The distinctively high Nb\* and Ta\* of A-type alkaline volcanics are inherited from their parental melts with high Nb and Ta. The A<sub>1</sub>-type Glass House Mountains rhyolite are from Shao et al. (2015)

Sm ratio (4–6) together with high Yb contents recorded in high differentiated rocks (9–13 ppm) are further supported for FC (Fig. 7d). The compatible elements like Cr, Co, V, and Sr decrease, while the incompatible elements, such as LILE (like Rb), HFSE (Nb, Ta, Y), and REE, increase from basalts to trachyandesites/trachytes and rhyolites with increasing Zr as abscissa (Fig. 11), signifying a continuous comagmatic evolutionary trend. The decrease of Fe, MgO, and CaO contents joined with Ni and Cr refers to the olivine, clinopyroxene, and spinel fractionation. The decreasing concentration of Eu, Ba, and Sr in the trachyandesites/

trachytes-rhyolites, relative to basalts, designates that their magma underwent fractionation of plagioclase. Furthermore, the low content of Ti presented by these rocks reveals fractionation of amphiboles and/or Fe-Ti oxides. The decrease of TiO<sub>2</sub>, Fe<sub>t</sub>, P<sub>2</sub>O<sub>5</sub>, and SiO<sub>2</sub> contents with increasing fractionation index conforms with the fractionation of titanite, magnetite, and apatite. The trachyandesites/trachytes and rhyolites show high contents of both La/Gd (4.5–6.5) and Lu/Gd (0.03–0.1) ratios along with negative MREE anomaly (Fig. 8), demonstrating a significant participation of amphibole fractionation from the melt because



**Fig. 11** Harker variation diagrams showing Zr used as differentiation index vs. major/trace elements for the Natash volcanoes



the amphibole fractionation causes a decrease in MREE and HREE (chiefly MREE) (Chung et al., 2003).

The high enrichment of Nb, Ta, and Ce contents as well as high Nb/Y ratio (1.3 to 1.88 compared to ~0.4 in continental crust) in the studied NV (Table 1) reflects the absence of any crustal involvements during the arising melt (Rudnick and Gao, 2003). The high Nb/U and Ce/Pb ratios characterizing the NV (34–68 and 28–81, respectively) signify mantle-derived OIB (e.g. Nb/U = 47, Ce/Pb =  $25 \pm 5$  in OIB (Hofmann, 2003), compared to those ratios in the continental crust (9–5, respectively, Rudnick and Gao, 2003)). In the La/Yb vs. Nb/La, Nb/U vs. Nb, and Th/Ta vs. La/Yb plots (Fig. 9), the NV samples supplementarily strengthen its affinities to OIBs with the lacking influences of crustal contamination. The NV are characterized by Nb and Ta enrichment which further support the insignificant contribution of crustal constituents, because the crustal contamination decreases Nb and Ta concentrations and increases the ratios of Th/Ta and Th/Yb during the magma evolution (Niu and O'Hara, 2003). The presented radiogenic data designate that the NV are categorized by their elevated  $^{143}\text{Nd}/^{144}\text{Nd}$  (0.512653–0.512761) and low  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratios (0.7030–0.70286, Abu El Rus et al., 2018), which may confirm that the NV sequences were evolved from OIB-like mafic magmas via fractional crystallization without crustal contamination. The high enrichment in both LILEs and HFSEs as well as isotope ratios characterized the NV, analogous to other alkaline ring complexes from SED ( $^{143}\text{Nd}/^{144}\text{Nd} > 0.51270$  and  $^{87}\text{Sr}/^{86}\text{Sr} = 0.7030$ –0.7050, Landoll et al. 1994), which are reliable with the mantle-derived magmas for the alkaline rocks (Mogahed, 2016). In conclusion, we suggest that the alkali volcanoes in the Wadi Natash were originated from an OIB-derived mantle source and prolonged fractional crystallization with negligible crustal contamination subscribed to the compositional variations from mafic to felsic rocks.

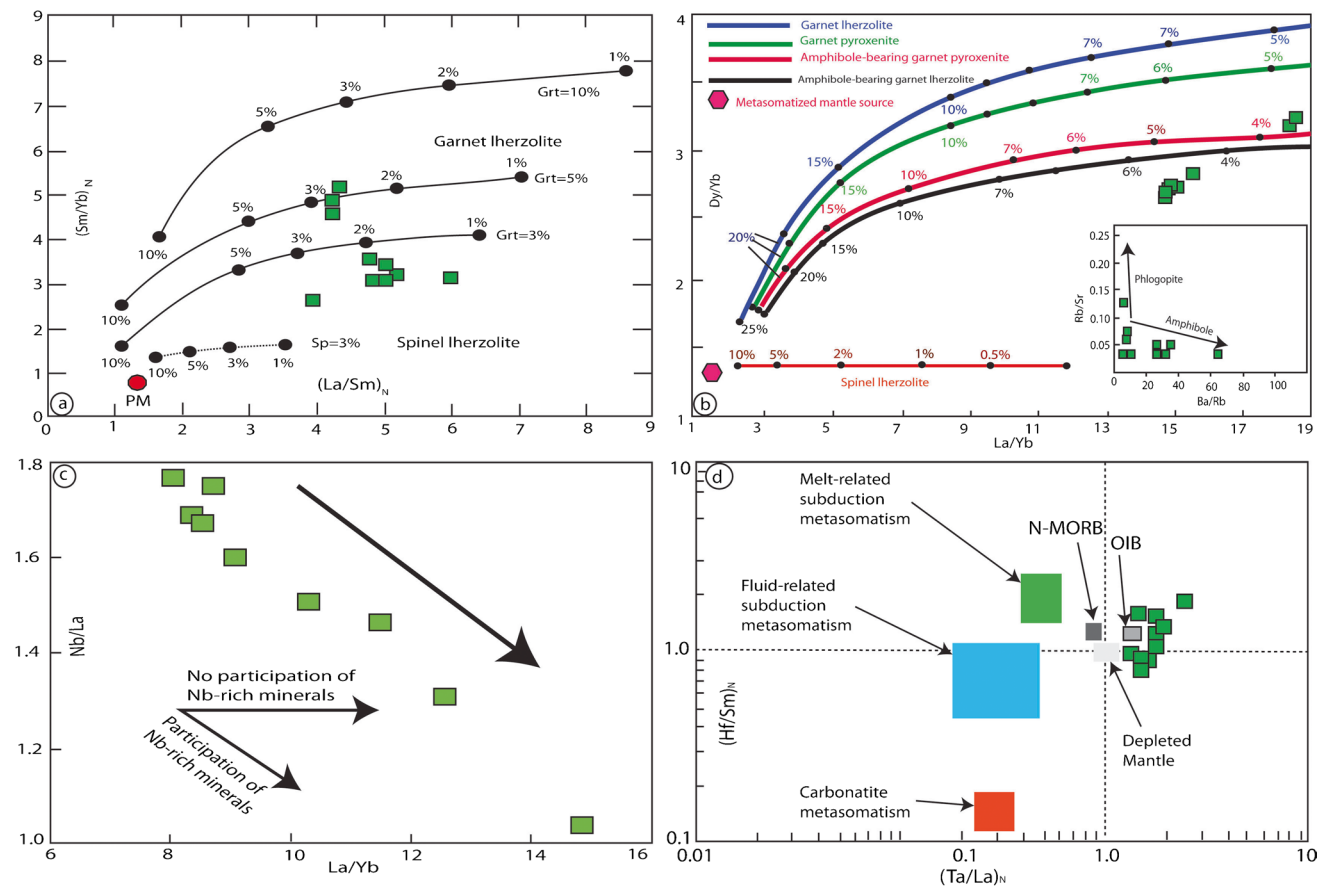
### Mantle metasomatism accompanying Nb mineralization

Natash volcanoes are categorized by LREE enhancement and HREE reduction (Avg.  $(\text{La}/\text{Yb})_{\text{N}} = 9$ ;  $(\text{Dy}/\text{Yb})_{\text{N}} > 2$ ;  $(\text{Sm}/\text{Yb})_{\text{N}} > 1$ ) that are reliable with a garnet-bearing HIMU-OIB-type source (Wang et al., 2009) as the HREE, denoted by Yb, have high partition coefficients to garnet ( $\text{Kd}_{\text{Yb}^{\text{garnet}}} = 5.5$  at 3.0 GPa; Salters and Stracke, 2004). The degree of partial melting of mantle source can be evaluated by the degree of HFSE and LREE enrichment (Fan et al., 2021). The data of the NV display that their source may suffer partial melting via low degree (<5%) in the  $(\text{Sm}/\text{Yb})_{\text{N}}$  vs.  $(\text{La}/\text{Sm})_{\text{N}}$  plot (Fig. 12a). The basalts are linked to Nb-rich basalts (Fig. 7b). Two chief assumptions have been proposed for the origin of Nb-rich basalts: (1) composite mingling of OIB and MORB magmas (model 1, Hastie et al., 2015) or

(2) partial melting of mantle that has been affected by subducted slab melts via metasomatism (model 2, Hastie et al., 2011). Any igneous rocks which were formed by magma mingling have a comprehensive array of Nd isotope (Yang et al., 2006); however, the uniform values of the  $^{143}\text{Nd}/^{144}\text{Nd}$  (0.512653–0.512761, Abu El Rus et al., 2018) do not support the magma mixing in the mantle source for the NV. Model 2 proposes that the Nb-rich basalts are related to Nb-rich minerals of the mantle source, which are created by mantle metasomatism (Hastie et al., 2011). If partial melting of the Nb-poor minerals involved in the mantle source happens, the Nb/La ratios show no variation with discrepancies in the degree of partial melting as shown by La/Yb ratios because of comparable distribution coefficients for Nb and La in the mantle (Sajona et al., 1996). The NV samples show an inverse relationship between the ratios of Nb/La and La/Yb (Fig. 12c), signifying the existence of the Nb-rich minerals in the mantle source that was formed by model 2.

The OIB-like source becomes enriched source when Nb-REE-rich melts intermingle with depleted mantle via mantle metasomatism (Pilet et al., 2011). Many processes have been involved for the extremely enriched geochemical features of OIB like recycled oceanic crust, terrigenous sediments, mantle plume, or asthenosphere-derived melts (Raghuvanshi et al. 2019). The Natash volcanoes show high La/Sm ratio (4–6) which argue against the involvement of old subducted oceanic crusts ( $\text{La}/\text{Sm} < 1$ ) to be source materials for the NV and overall OIB-related constituents ( $\text{La}/\text{Sm} > 1$ , Niu and O'Hara, 2003). Moreover, terrigenous sediments are categorized by Pb enhancement and poor contents of HFSE and REE (Niu et al., 2011), opposing the geochemical features of the NV. The enrichment of LREEs and HFSEs (Fig. 8), joined with high ratios of Nb/La (1.1–1.87) and Nb/U (38–68) as well as low Th/Zr ratios (0.01–0.02) and depletion of Nd isotopic ratios (0.512653–0.512761, Abu El Rus et al. 2018), denotes metasomatized lithospheric mantle triggered by asthenosphere-derived melts as reasonable model (Sahoo et al. 2020). The melt-related metasomatism and fluid-related metasomatism are responsible for the metasomatic lithosphere mantle for NV (Fig. 12d). Such type of metasomatism is common in lithosphere mantle in the ANS that was attributed to fluid released during subduction in Neoproterozoic Era (Shaw et al. 2007) or rising plume through Phanerozoic Era (Rooney et al., 2014).

In a rift regime, outpouring of the asthenosphere can offer a conduit for degassing of Earth (Martin, 2006; Huang et al., 2014), where HFSE-REE-rich melts along with alkali components ascend from the asthenosphere to the lithospheric mantle (Pilet et al., 2008). Such enriched melts interact with the depleted lithospheric mantle as hydrous metasomatic veins composed of amphibole and phlogopite (Pilet et al. 2011; Zhang et al. 2020). The melting of such amphibole-rich metasomatic veins can yield melts with comparable



**Fig. 12** Petrogenetic characters of the Natash volcanoes. **a**  $(\text{Sm}/\text{Yb})_N$  vs.  $(\text{La}/\text{Sm})_N$  trace element binary plot (modified from Li et al. 2019). Batch melting trends depending on the non-modal batch melting equations of Shaw (1970). Melt curves are drawn for spinel-lherzolite (with mode and melt mode of ol53% opx27% cpx17% sp3% and ol6% opx28% cpx67% sp11%; respectively; Kinzler 1997) and for garnet-lherzolite (with mode and melt mode of ol60% opx20% cpx10% gt10% and ol3% opx16% cpx88% gt9%; respectively). The composition of the primitive lherzolitic mantle is plotted (according

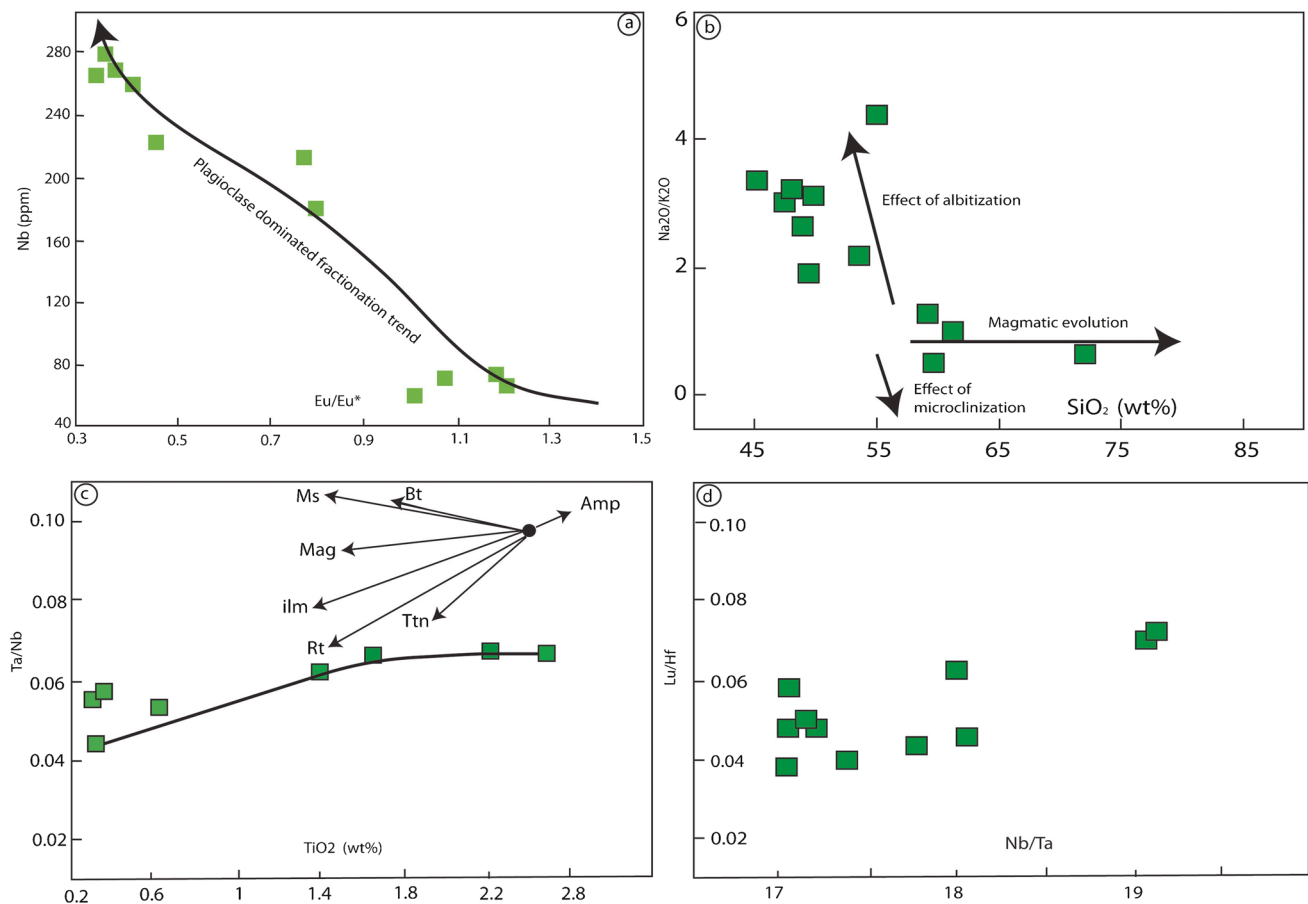
to Sun and McDonough 1989). Partition coefficients for plots **a** and **b** are from McKenzie and O'Nions (1995). **b**  $\text{La}/\text{Yb}$  vs.  $\text{Dy}/\text{Yb}$  ratio showing the fractionation-corrected melts of alkaline Natash volcanoes compared to the non-modal fractional melting trajectories of an amphibole garnet lherzolite (8% modal abundance of amphibole), garnet lherzolite, garnet pyroxenite, and spinel lherzolite (melting trajectories are from McCoy-West et al. 2010). **c**  $\text{Nb}/\text{La}$  versus  $\text{La}/\text{Yb}$  diagram (Sajona et al. 1996). **d**  $(\text{Hf}/\text{Sm})_N$  vs.  $(\text{Ta}/\text{La})_N$  (La Flèche et al. 1998) diagram

geochemical features of alkaline magmas as has evidenced experimentally by Pilet et al. (2008). The low  $\text{K}_2\text{O}$  contents characterized the basaltic rocks (1991–14,604 ppm, Table 1) that strengthen the existence of K-rich hydrous phases (e.g. amphibole or phlogopite) in the mantle source, which are comparable to melts created by partial melting of an amphibole-bearing peridotite ( $K < 20,000$  ppm, Späth et al., 2001). The mafic lavas from NV have low  $\text{Rb}/\text{Sr}$  ( $< 0.1$ ) and high  $\text{Ba}/\text{Rb}$  ( $> 20$ ) ratios (Fig. 12b, inset), proposing the occurrence of amphibole rather than phlogopite in magma source (Furman and Graham, 1999). In the  $\text{Dy}/\text{Yb}$  vs.  $\text{La}/\text{Yb}$  melting model (Fig. 12b), the parent magma of the NV was formed from an amphibole-bearing garnet lherzolite via less than 5% degree of partial melting, compatible with its pervasive existence in the lithospheric mantle of Arabian-Nubian Shield (ANS, Weinstein et al. 2006). Therefore, the

basalts in the Wadi Natash possibly created from an enriched lithospheric mantle via metasomatism subscribed to the HFSE-REE-rich source.

### Mechanisms of Nb enrichment in the Natash volcanoes

Previous studies have proposed that long history of fractional crystallization and hydrothermal metasomatism in combination with partial melting are responsible for the REE and HFSE enhancement in alkaline rocks (Huang et al., 2014; Xiang et al., 2017). The NV are enriched in Nb (80–283 ppm) compared to other ring complexes in SED like El Kahfa ring complex ( $\text{Nb} = 36\text{--}226$  ppm, Hegazy et al., 2016), revealing mineralization potential for Nb deposit. The differentiation paths from basalts to trachytes/rhyolites



**Fig. 13** Diagrams involving various processes responsible for Nb enrichment. **a** Nb vs. Eu/Eu\* presenting an increase of Nb content as the result of Nb-poor plagioclase fractionation. **b** Na<sub>2</sub>O/K<sub>2</sub>O ratio vs. SiO<sub>2</sub> displaying the dominant albitization process during the evolu-

tion of NV. **c** Ta/Nb vs. TiO<sub>2</sub> (after Stepanov et al. 2014) showing increasing of Ta/Nb ratio in residual melt. **d** Nb/Ta vs. Lu/Hf binary diagram

(Fig. 11) are accompanied by an increase of Nb content in the remaining melts as has been documented by Zhu et al. (2020) and Wang et al. (2021). The inverse relation between the whole-rock Eu/Eu\* vs. Nb proposes that the increase of Nb concentrations is well matched with continuous elimination of plagioclase during magma evolution (Fig. 13a). These explanations designate that fractionation processes play an important role in raising the Nb contents during the volcanic evolutions, in which fractionation of Nb-poor feldspars leads to the steady Nb enrichment in the residual melt as crystallization proceeds (Zhu et al., 2020) as has been observed in Late Triassic A<sub>1</sub>-type alkaline volcanoes, East Kunlun Orogen, China (Zhu et al., 2022). Post-magmatic alteration and hydrothermal metasomatism may increase Nb contents, although Nb concentrations are generally enhanced by magmatic processes (Estrade et al., 2014). Some researchers propose that the processes of hydrothermal alteration play a significant role in the enhancement of Nb, REE, and additional rare metal mineralizations (Ballouard et al., 2016), which can produce compounds with ligands (e.g. F<sup>-</sup>, Cl<sup>-</sup>)

and assist their mobilization and concentration (Timofeev et al., 2015; Girei et al., 2019). In the present study, the NV display various features of hydrothermal alteration like the presence of the interstitial biotite flakes along feldspar borders (Fig. 3z<sub>1</sub>), typical characteristics of hydrothermal biotitization. In addition, most of the rock specimens have high Na/K ratios (up to 5), signifying the presence of sodic metasomatism (albitization) that affects the NV (Fig. 13b).

The petrographic observations show the presence of accessory titanite, apatite, zircon, sphene, and ilmenite associated with phenocrysts (Fig. 3). Many authors described and analysed the titanite crystals that are enriched in Nb<sub>2</sub>O<sub>5</sub> (Nb<sub>2</sub>O<sub>5</sub> = 0.5–3.3 and 1.1–3.3 wt% in magmatic and hydrothermal metasomatic crystals, respectively) in Fangcheng alkaline rocks, East Qinling (Zhu et al. 2020, 2022), China. They concluded that the Fangcheng's parent magma was enriched in Nb as the result of the occurrence of an enriched mantle formed by low melting degree. The TiO<sub>2</sub> contents increase (from 0.2 to 2.8 wt%) with an increasing Ta/Nb ratios (from 0.04 to

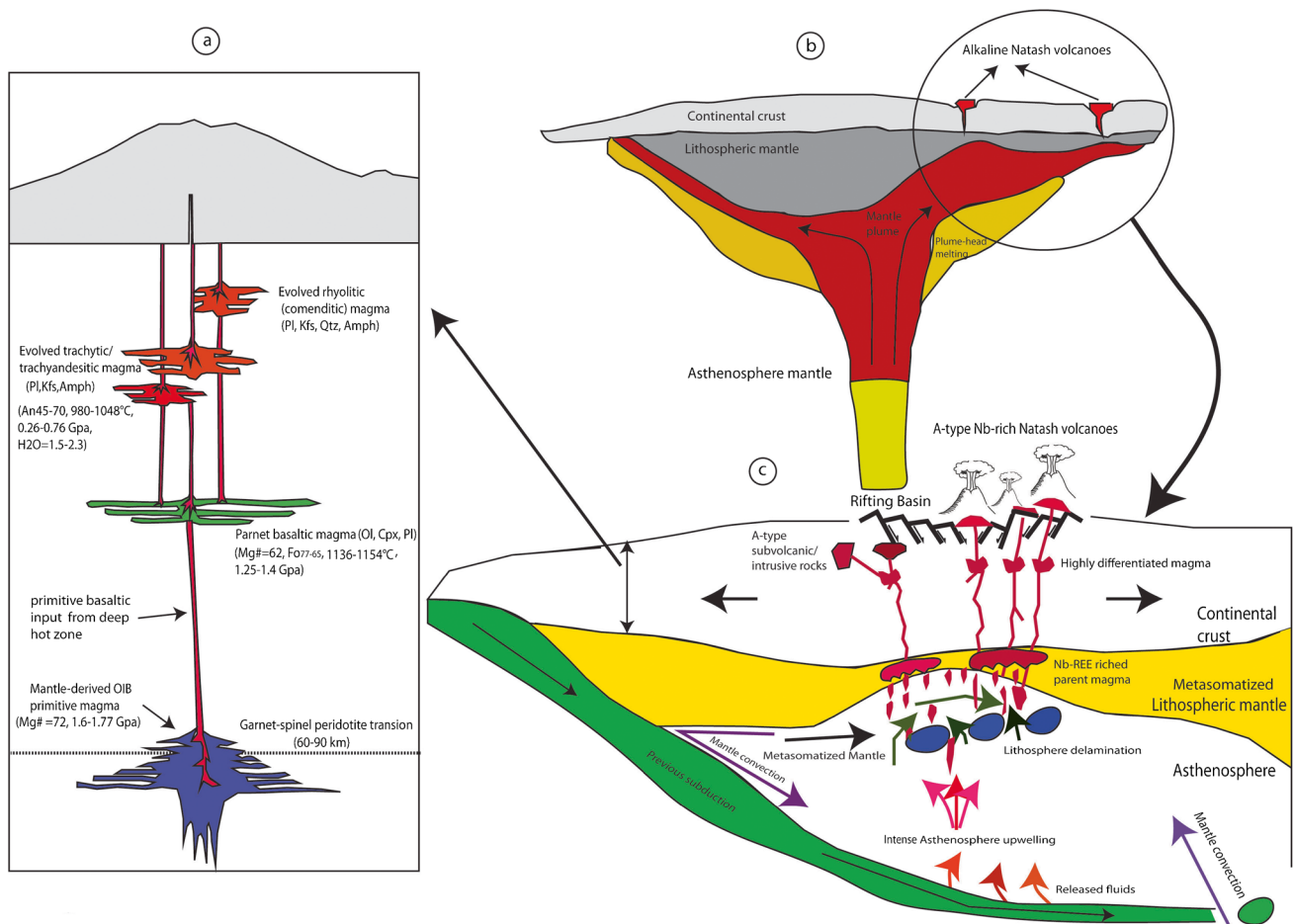


0.06, Fig. 13c), signifying a conceivable role of titanite for presentation the Nb/Ta ratios in partial melts, as has been formerly determined for titanite grains in alkaline rocks (Zhu et al., 2020). Furthermore, ilmenite grains observed in the NV (Fig. 4a) may consider as source of Nb and Ta because ilmenite usually has high contents of Nb and Ta recorded in intermediate-felsic magma. Nb concentrations are commonly enhanced by magmatic processes, although hydrothermal metasomatism may be universally responsible for Nb mineralization (Estrade et al., 2014). The low Zr/Nb (3.5–6.5) along with the positive correlation between Nb/Ta (16–19) and Lu/Hf (0.04–0.06) observed in the Natash lavas (Fig. 13d) deliver supplementary proof that their mantle source was affected by metasomatized fluids that led to the Nb enrichment observed in the subaerial basalts (e.g. Pfänder et al., 2007). The inverse relationship

between Nb/La and La/Yb ratios (Fig. 12c) further supports the occurrence of the Nb-rich minerals in the mantle source that was formed by mantle metasomatism. So, it is concluded that Nb enhancement of the NV is resulted from Nb-rich accessory minerals like titanite/ilmenite crystals inherited from mantle-derived OIB-type parental magma (magmatic processes), fractionation of Nb-poor feldspar, and post-magmatic hydrothermal phenomena that played a role in HFSE remobilization to form Nb-rich minerals as has been proved by Zhu et al. (2020, 2022).

### The nature of Natash plumbing system

Many magma chambers situated at different depths have been recognized underneath intraplate alkaline volcanoes that usually generate from deep mantle and pass over thick



**Fig. 14** Schematic illustration for the Late Cretaceous alkaline magmatism in the Natash area. **a** Cartoon model of the magma plumbing system beneath Natash volcanoes based on geobarometric calculations. **b** A not to scale cartoon (modified after Sen and Chandrasekharan 2011) depicting the plume-induced thinning of the lithosphere that melted at the rift zones to generate alkaline magmatism including Natash volcanoes. **c** Partial melting of a metasomatized mantle triggered via crustal extension and lithospheric thinning,

resulting in the formation of Nb-REE-enriched parent basaltic magma that evolved to mafic-intermediate-felsic magmas (modified after Wu et al. 2023). The asthenospheric upwelling via diapiric mantle and delamination melting prompted by lithospheric thinning into the convecting mantle following ancient subducted-related fluid metasomatism during Pan-African Orogeny has been proposed to create the Natash parent melts along fault-controlled extensional tectonics

crustal successions towards shallower crustal levels (Marzoli et al., 2015). Petrological and geochemical studies reveal that NV display multi-eruptions involving basalts, trachytes, trachyandesites, rhyolites, or comendites (Fig. 7a) that occurred within the Earth's crust (Fig. 14a). The parent magma was created by low degree of metasomatized amphibole-bearing garnet mantle source under high pressure at 1.6–1.77 GPa (>50 km, mantle-crust boundary) similar to the formation of alkaline basaltic melts derived from hydrous phase-rich peridotites at ca. 2.0–2.2 GPa and 1200–1300 °C (Green and Falloon 1998). The Natash parent magma underwent initial fractionation of olivine and clinopyroxene followed by fractional crystallization of plagioclase and amphibole together with apatite and Fe-Ti oxides in more evolved magmas. Thermobarometric outputs give proofs that the NV were evolved through the polybaric fractional crystallization (Fig. 5f). For example, fractionated olivine crystals (Fo<sub>77-65</sub>) suggest stagnation deep zones at 1.4–1.25 GPa (14–12 kbar or 50–43 km), while plagioclase phenocrysts (An<sub>70-45</sub>) reflect shallow crustal levels at 0.76–0.26 GPa (7–2 kbar or 26–9 km) accompanying by H<sub>2</sub>O contents (from 2.5% to 1.5 wt% for high to low An), signifying magmatic injections from deep to shallow H<sub>2</sub>O degassing (Firth et al., 2014; Aiuppa et al., 2019). The shallow depth is reinforced by amphibole occurrence in some evolved trachyandesites and trachytes (Fig. 3s) in which the high melt H<sub>2</sub>O content (≥4 wt%) at mid-shallow depth (~2 kbar) is crucial to stabilize amphibole on intermediate melt compositions (Pontesilli et al. 2022).

The existence of various phenocryst assemblages (particularly feldspar) and their disequilibrium textures in the NV (Fig. 3) propose also that their feeding magma encountered diverse stagnation regions at dissimilar levels of nucleation or dissolution surfaces during rise to the surface. Phenocryst disequilibrium textures like zoning, opacite/reaction rims, and corrosion/resorption designate variations in the magmatic circumstance such as drops of water content, degassing phenomena, and magma dehydration because of pressure and temperature change during magma ascent, or the mixing of compositionally and thermally discrete magmas under open system (Holnes et al., 2019). This is reinforced by the existence of sieve textures in the plagioclase feldspar (Fig. 3g, m–o), which can be interpreted either by compositional variations in magma, magma mixing, or fast decompression of plagioclases to melts where quick ascent of magma may maintain liquid inclusions as glass pockets (e.g. Renjith 2014). The rapakivi and antirapakivi textures observed in feldspar (Fig. 3r) are inferred as the products of magma mixing or convection self-mixing as the result of discrepancies in temperature with no addition of new magma (i.e. recharge). The oscillatory zonation observed in plagioclase (Fig. 3k, l, and z<sub>2</sub>) is the reply of inconsistent external circumstances because of limited convection of the

crystal-derived magmas (Renjith 2014). NV involve highly evolved Hawaiian-Vulcanian crystalline eruptive products (dominant plagioclase) with no mark of primary magma in which crystal-rich lavas require extended residence periods with the prolonged relaxation pause through which volatile flux and melt additions that control eruption frequency and crystal content lead to the complex textures in plagioclase crystals (e.g. McCarthy et al., 2020). So, we infer that the plumbing system of the NV can be interpreted as high crystalline evolved magma mushes (crystal-rich lavas) stagnated and fractionated at dissimilar depths during magmatic evolution preceding to eruption as the result of low volatiles, magma fluxing, and magma frequency with complete absence of primitive mafic rocks (see Ruth and Costa, 2021).

### Regional implications for alkaline magmatism and Nb mineralization

The rock samples of the NV show high concentrations of both HFSE and LREE along with high Ce/Pb ratios (28–42) that infer the existence of garnet and amphibole phase via metasomatism in the HIMU-OIB mantle source, distinctive of within plate regime (Ball et al., 2019). The uniformity of isotope ratios characterizing the NV like  $^{87}\text{Sr}/^{86}\text{Sr} = 0.7030\text{--}0.70286$ ,  $^{143}\text{Nd}/^{144}\text{Nd} = 0.512653\text{--}0.512761$ ,  $^{206}\text{Pb}/^{204}\text{Pb} = 19.28\text{--}19.94$ , and  $^{177}\text{Hf}/^{176}\text{Hf} = 0.28274\text{--}0.28285$  (Abu El Rus et al., 2018) reinforces metasomatized high  $\mu$  HIMU-OIB mantle, similar to Late Proterozoic metasomatized mantle source in many volcanic fields like Mashriq and Bayuda, Sudan (Lotter et al., 2022) and Harrat, Saudi Arabia (Shaw et al. 2007). The metasomatic enhancement is primarily attributed to the emitting of subducted-related fluids/melts that have been proposed for the lithosphere mantle in the ANS during the Neoproterozoic Era (Stein et al. 1997; Abu El-Rus et al., 2018). The isotopic composition and geochemical features of NV along with alkaline ring complexes and Neogene volcanic fields worldwide have been inferred as the sign of the asthenospheric mantle source outpouring from mantle plume region (Fig. 14b, Hofmann, 2003; Niu et al., 2012) emphasizing the existence of high thermal instabilities (i.e. attendance of a deep mantle plume, Abu El Rus et al., 2018; Khalaf et al., 2018), similar to the St. Helena worldwide HIMU in the South Atlantic (Zhu et al., 2022).

The Nb-rich alkaline rocks chiefly extend in various tectonic settings involving craton borders, continental rifts, along with an extensional regime, and rare metal-rich deep source (Ballouard et al., 2020). Adiabatic decompression concomitant with crustal thinning triggers partial melting of the mantle via low degree to produce crucial alkaline melt in the continental rift setting (Khalaf et al., 2018). Temporarily, plate divergence with a low separation rate is encouraging to yield prevalent alkaline magmatism and

prompting provincial rare metal mineralization (Beard et al., 2022). Preceding investigations have revealed that the NE African Terrain (Egypt, Sudan, and Ethiopia) evolved from subduction during Neoproterozoic Era to wide-ranging extensional breakdown and continued until the Mid Neogene (Mohamed, 1998; Vail, 1989). The extensive alkaline magmatism recorded in the SED during the Late Cretaceous, Egyptian/Sudanese borders, Central Africa, Eastern Cameroon, and Kenya, along with Tanzania and Somalia coastal basins indicates that in the Natash area, SED was still in rift-related continental settings (Khalaf et al., 2018). The age resemblance between the NV and the other ring plutons in SED like El Kahfa ring complex (92 Ma, Serencsits et al., 1981; Lutz et al., 1988) infers a widespread alkaline magmatic episode in the Late Mesozoic Era. Regarding the chronological dispersion of alkaline rock assemblages in the SED, the outpouring of the asthenosphere triggered by the lithospheric breakdown protracted a highest during 94–86 Ma. A preferred model for formation of alkaline rocks and Nb-LREE enrichment in the SED is shown in Fig. 14c, as has been proposed for rare metal-rich alkaline rocks (Wu et al. 2023). During the Late Cretaceous, the regional extension of SED triggered the asthenosphere upwelling that is commonly transferred by an outpouring of volatile-rich melts transporting plentiful trace and rare earth elements (like HFSE and REE) from the deep mantle to the shallow lithospheric mantle (e.g. Huang et al., 2014; Yan et al., 2021, 2022). The latter was metasomatized by the continuous rise of such volatile-rich melts and fluids. Delamination and decompression melting into the convecting mantle facilitate the asthenospheric upwelling via diapiric mantle (Nixon et al. 2011). Crustal extension and lithospheric thinning prompted the partial melting of the metasomatic mantle during 96–86 Ma, forming alkaline OIB-like magmas enriched in Nb and REE. When the magmas ascend, fractional crystallization of olivine and pyroxene with exceedingly low  $^{ol/liq}D_{Nb-REE}$  and  $^{px/liq}D_{Nb-REE}$  subscribe the enhancement contents of incompatible rare metal elements (Foley et al., 2013; Beard et al., 2022). The greatly fractionated magmas ascend through the upper crust to create plutons or expelled to yield trachyandesitic/trachytic and rhyolitic extrusions. The HFSE-REE-bearing liquids rise and mingle with feldspar-rich rocks, resulting in the crucial formation of ore-forming elements.

## Conclusion

Pervasive NW-SE trending alkaline rocks are well represented in Wadi Natash area with ages concentrating at 96 to 86 Ma. The Natash volcanoes display a wide compositional range, extending from basalts through trachyandesites and trachytes to rhyolites/comendites. The trachyandesites/

trachytes and rhyolites of the NV show distinctive geochemical features like high HFSE and Ga/Al along with low ratio of Y/Nb and contents of Sr, P, Ti, and Eu, revealing A<sub>1</sub>-type granite. The enrichment of both HFSEs and LREEs, analogous to the OIB-type rocks, shows that NV were produced by partial melting of a metasomatized lithospheric mantle triggered by asthenosphere-derived melts that lead to the Nb and REE-rich primary magma, followed by prolonged fractional crystallization with negligible role of the crustal contamination. Consequences of the geobarometric calculations reveal comprehensive storage zones ranging from the uppermost crust (~26–9 km depth) to deep mid crustal levels (~50–43 km depth), enlightening a crystal-rich magma mushes (dominant feldspar). The NV are enriched in Nb-REEs that were originally dominated by high degree of fractional crystallization and then imposed by the hydrothermal metasomatism. The Natash volcanoes are one of the well-known large-scale alkaline magmatic events generated in an extensional regime in the SED during the Late Mesozoic Era, inferring that the Rodinia assembly had been finalized prior to ca. 86 Ma.

**Supplementary Information** The online version contains supplementary material available at <https://doi.org/10.1007/s12517-023-11637-1>.

**Acknowledgements** We acknowledge Dr. Federico Lucci, Department of Earth and Geoenvironmental Sciences, University of Bari Aldo Moro, Italy, and Dr. Nils Lenhardt, Department of Geology, University of Pretoria, for reading the draft of this manuscript. A lot of thanks to Dr. Yukiyasu Tsutsumi who made geochronological work at the National Museum of Science, Japan. An anonymous reviewer improved the quality of the paper and is gratefully acknowledged.

**Funding** Funding of this research was partly provided by an invitational fellowship for research in Japan from the Japan Society for the Promotion of Science (JSPS S17025).

## Declarations

**Competing interests** The authors declare no competing interests.

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