Geology, Zircon Geochronology, and Petrogenesis of Sabalan Volcano (Northwestern Iran)

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Abstract

Sabalan Volcano (NW Iran) is an isolated voluminous (4821 m elevation; $>800 \text{ km}^2$) composite volcano that is located within the Arabia-Eurasia collision zone. Its edifice was assembled by recurrent eruptions of trachyandesite and dacite magma falling into a relatively restricted compositional range (56-67% SiO_2) with high-K calc-alkaline and adakitic trace element (Sr/Y) signatures. Previous K-Ar dating suggested protracted eruptive activity between 5.6 and 1.4 Ma, and a two stage evolution which resulted in the construction of the Paleo- and Neo-Sabalan edifices, respectively. The presence of a topographic moat surrounding Neo-Sabalan and volcanic breccias with locally intense hydrothermal alteration are indicative of intermittent caldera collapse of the central part of Paleo-Sabalan. Volcanic debris-flow and debris-avalanche deposits indicate earlier episodes of volcanic edifice collapse during the Paleo-Sabalan stage. In the Neo-Sabalan stage, three dacitic domes extruded to form the summits of Sabalan (Soltan, Heram, and Kasra). Ignimbrites and minor pumice fall-out deposits are exposed in strongly dissected drainages that in part have breached the caldera depression. Lavas and pyroclastic rocks are varyingly porphyritic with Paleo-Sabalan rocks being trachyandesites carrying abundant phenocrysts (plagioclase + amphibole + pyroxene + biotite). The Neo-Sabalan rocks are slightly more evolved and include dacitic compositions with phenocrysts of plagioclase + amphibole $\pm$ alkali-feldspar $\pm$ quartz. All Sabalan rock types share a common accessory assemblage (oxides + apatite + zircon). High spatial resolution and sensitivity U-Pb geochronology using Secondary Ionization Mass Spectrometry yielded two clusters of zircon ages which range from 4.5 to 1.3 Ma and 545 to 149 ka, respectively (all ages are averages of multiple determinations per sample). U-Th zircon geochronology for selected Neo-Sabalan rocks agrees with the U-Pb ages, with the youngest zircon rims dating to ca. 110 ka. Because zircon

crystallization predates eruption, this age represents the upper limit for the youngest eruptions of Sabalan. Valley-filling ignimbrites yielded variable U-Pb zircon ages which argue against these pyroclastic rocks being generated in a single caldera forming event. These results indicate that eruptions occurred more recently than previously indicated by K-Ar dating. Paleo-Sabalan and Neo-Sabalan volcanic rocks have similar geochemical characteristics, including enrichment of LILE and LREE relative to HFSE and HREE, respectively, and prominent negative Ti, Nb, and Ta anomalies. The trachyandesitic to dacitic rocks of Sabalan also share negative Eu anomalies. This, together with horizontal or slightly increasing Y vs. Rb trends, indicates fractionation of plagioclase-amphibole or plagioclase-clinopyroxene assemblages with negligible crustal assimilation (based on low and invariant Rb/Th). High degrees of mantle partial melting are inferred from high $(La/Yb)_N$ (from 28 to 48). Overall, the subduction-affinity of Sabalan volcanic rocks agrees with models of melt generation following a Quaternary slab break-off event coeval with continental collision.

Key words: Quaternary volcano, U/Pb dating, Zircon, Subduction, Collision, Iran

1. Introduction

Northwestern Iran is located in a broad zone of continental collision and deformation between the African-Arabian and Eurasian plates. This area experienced a compressional tectonic regime from early Mesozoic to present where compression has resulted from subduction of Neo-Tethyan oceanic crust under the Iranian microplate and the subsequent collision between the Arabian and Eurasian plates along the Zagros suture zone (Sengor and Kidd, 1979; Dewey et al., 1986; Dilek et al., 2009). Volcanism is present in this area, with Sabalan volcano (Fig. 1) representing the

easternmost volcano in an approximately E-W trending belt of Quaternary volcanoes built on the Turkish-Iranian plateau (Dilek et al., 2009). Its nearest volcanic neighbors are Sahand (also in NW Iran), as well as Ararat, Tendürek, Süphan, and Nemrut in eastern Anatolia (Turkey) which all lie within the Arabia-Eurasia collision zone (Fig. 1) (Kheirkhah et al., 2009).

Despite the importance of Sabalan for the geology of Iran and the adjacent regions, limited data is available regarding the ages and compositions of volcanism which are critical to infer magma origins and tectonic setting of the volcano. Existing geochronology is limited to four K/Ar whole-rock age determinations on volcanic rocks by Alberti et al. (1980) suggesting that the initial activity of Sabalan volcano occurred between 5.6 to 2.9 Ma. The Neo-volcanic rocks are inferred to have erupted at 1.6 to 1.4 Ma, following subsidence of a magma chamber roof and caldera formation. Several geochemical models for the origin of Sabalan magmas were put forward in the 1970's to 1980's. In these early studies, Didon and Gemain (1976) postulated that the Pliocene to Quaternary activity of Sabalan volcano was due to tectonic breakup of the Azerbaijan platform which followed Late Cretaceous to Eocene rifting and was fueled by alkaline magma generation in a continental rift zone. According to this model, rifting was related to mantle heating underneath Azerbaijan which started in the Eocene, but terminated before leading to full-scale oceanic spreading. Didon and Gemain (1976) also asserted that Sabalan rocks are sodic-alkaline (latite to andesite) and that compositional variation was controlled by magmatic fractionation and crustal contamination. By contrast, Alberti et al. (1975) described Sabalan volcanic rocks as calc-alkaline with orogenic affinities. Dostal and Zerbi (1978) further established that Sabalan magmatic compositions are dominated by high-K calc-alkaline andesites and dacites, with rare rhyolites present. According to this research, the major and trace element compositions of the rocks are consistent with the derivation of a parental magma by partial

melting of garnet peridotite enriched in large-ion-lithophile elements (LILE) in the upper-mantle, presumably in a region overlying a former subduction zone (Dostal and Zerbi, 1978). In this model, differentiation of primary magmas of Sabalan volcano was related to low-pressure amphibole-dominated fractional crystallization (Dostal and Zerbi, 1978). Lescuyer et al. (1978) supported this view by suggesting that Sabalan magmatic compositions resemble those of orogenic volcanic systems. Alberti et al. (1980) further postulated that eruptions at Sabalan resulted from the opening of fissures as a relaxation of compressional stresses in central and western Iran above a former Benioff zone that would facilitate the rise of mantle-derived magma. Subsequent research on Sabalan has mostly focused on its geothermal potential (e.g., Noorollahi et al., 2009).

To amend this critical lack of geochronological and geochemical data on Sabalan volcano, we present initial results from field, petrographic and whole rock geochemical (including a wide range of trace elements) data for several key stratigraphic units of Sabalan volcano. These data are also chronologically constrained by new U-Pb and U-Th zircon ages. The application of zircon geochronology for Quaternary volcanic rocks has many advantages compared to more traditionally used K-Ar (Ar-Ar) techniques, especially as zircon is impervious to alteration and also because individual crystal domains can be targeted by high spatial resolution analytical techniques (here: Secondary Ionization Mass Spectrometry; SIMS), thus permitting to easily identify potential contaminants (xenocrysts) which - if unrecognized - could bias age interpretations.

2. Regional geology

Sabalan (Savalan in Turkish pronunciation) volcano is located in Ardebil province, northwestern Iran. With 4821 m in elevation it is the second largest (after Damavand) volcano in Iran. The

central and highest parts of the volcano consist mainly of glacially eroded remnants of lava domes that form three prominent peaks named Soltan, Heram, and Kasra (Fig. 2).

Sabalan volcanic rocks overly Eocene to Miocene magmatic rocks covering an area of approximately 800 km². The volcanic activity of Sabalan initiated with andesitic eruptions during the early Pliocene. During this phase, andesitic to dacitic ash flow and ignimbrite deposits, as well as lava-flows, accumulated to great thickness (locally up to 3000 m). These rocks probably erupted from several centers forming an extensive composite volcanic complex (Alberti et al., 1980) which experienced collapse probably during early Pleistocene time leading to the formation of a roughly circular “caldera” depression ~12 km in diameter (Alberti and Stolfa, 1973; Didon and Gemain, 1976). Despite younger activity concealing parts of the depression walls and erosion having destroyed them, the topographic expression of the collapse structure is still easily recognizable in many places although the exact timing of the collapse remains unknown. The subsequent eruption of rhyodacitic to andesitic volcanic domes and flows in central part of the crater (the "Upper Series" of Alberti and Stolfa, 1973) formed a second, major cone. The youngest eruptions of trachyandesitic lava flows occurred mainly within the caldera boundaries, but in places have breached the caldera margins. Small summit craters as well as lateral flows of post-glacial age were also recognized by Alberti et al. (1980), although these morphologic interpretations lack confirmation through radiometric dating.

3. Field evidence and Petrography

3.1. Paleo-Sabalan volcanic rocks

Based on our field investigation and mapping, we follow the classification of Alberti et al. (1973; 1975; 1980) of subdividing the eruptive stratigraphy into two main groups: the Pre-

Caldera/Lower series and the Post-Caldera/upper series. We, however, prefer a non-genetic terminology and thus have dubbed these groups Paleo- and Neo-Sabalan volcanic rocks, respectively. We did not follow the subdivision by Didon and Gemain (1976) who assigned ignimbrites and other pyroclastic deposits to an intermediate “syn-caldera” stage because we do not find evidence for a single large explosive eruption accompanying crater collapse. We instead assign most pyroclastic rocks to the Neo-Sabalan stage (equivalent to the post-caldera stage in Didon and Gemain, 1976) based on our new geochronology which suggests a prolonged hiatus in activity between Paleo-Sabalan lavas and the eruption of the widespread ignimbrites and pyroclastic deposits (Fig. 2).

Paleo-Sabalan rocks are trachyandesites with abundant phenocrysts (plagioclase + amphibole + pyroxene + biotite). They include lava with porphyritic textures composed of phenocrysts of plagioclase, hornblende, pyroxene and biotite in a hyalo-microlitic groundmass. Common petrographic features of the lavas are euhedral to anhedral (with rounded rims) plagioclase (oligoclase-andesine in composition) with common albite and Carlsbad twinning and oscillatory zonation. Oxides, apatite, and zircon are characteristic accessory minerals (Fig. 3a). These lavas are associated with pyroclastic rocks (ash tuffs and ash to lapilli fall-out deposits) with outcrops around Sabalan caldera in the Aighar area, Qarahghol and Ghezelbara mountains and Shahneshin and Balujeh villages (Fig. 2). Lava flows are regionally widespread and cover older (Cretaceous to Miocene) magmatic rocks. In the northwest and to the west of the caldera, Paleo-Sabalan volcanic successions are intruded by andesitic-dacitic domes which pre-date Neo-Sabalan (Fig. 2).

To the east of Sabalan caldera, in the Ghezelbara mountains, the Paleo-Sabalan volcanic succession consists of intercalated lavas and ash tuffs reaching >500 m in thickness. The basal

layers are locally altered and impregnated by sulfide mineralizations which are likely associated with the younger stages of Sabalan activity. Around Shahneshin village southeast of the caldera, the Paleo-Sabalan volcanic succession includes three trachyandesitic lava flows that are interbedded with ash fall-out and ash-tuff beds. The middle lava flow contains fine grained and rounded magmatic enclaves. Paleo-Sabalan volcanic beds are covered by Neo-Sabalan ignimbrite and/or trachyandesite lava flows that erupted from lateral craters.

3.2. Neo-Sabalan volcanic rocks

Neo-Sabalan comprises the main edifice and adjacent cover, and is composed of subvolcanic domes and related lavas, and locally ignimbrites and block-and-ash flow deposits, as well as pyroclastic fall-out deposits. Neo-Sabalan includes pyroclastic rocks (ignimbrites) that are present in three major lobes in northern part of caldera, and in outcrops with a small map footprint between the southeastern caldera margin and Shahneshin village. These pyroclastic rocks cover the Paleo-Sabalan volcanic successions with contacts exposed in the Ghotuorsouei to Balujeh areas (Fig. 2). In addition, there are several major lava flows which erupted along the caldera margins, in part flowing outside and breaching the caldera walls (Fig. 2). The most recent components of Neo-Sabalan are lavas which form a central cluster of flows and domes. These are often highly dissected and eroded by past and ongoing glacial activity, including the domes that form the center of the volcano and which make up the prominent Soltan, Kasra, and Heram summit crests. Many of these flows show contacts where they extruded over older volcanic rocks, often with auto-brecciated basal zones. They also frequently preserve well-developed ogive structures on their surfaces attesting to their comparatively recent emplacement.

The central domes of Sabalan are dacitic to trachyandesitic in composition. Their porphyritic texture is composed of euhedral-anhedral plagioclase, biotite and hornblende phenocrysts in a

hyalo-microlitic groundmass with alkali feldspar, plagioclase, and quartz microlites (Fig. 3b and 3c). Pyroxene phenocrysts are less abundant in Neo-Sabalan lavas compared to Paleo-Sabalan. Plagioclase is andesine-oligoclase in composition with sieve-textured cores and common sodic plagioclase overgrowths. Euhedral to anhedral poikilitic hornblende phenocrysts up to 2 mm in size with chadacrysts of plagioclase and apatite are characteristic for Neo-Sabalan lavas. These phenocrysts are enclosed by a glassy groundmass with microlites of alkali feldspar, plagioclase, and quartz. Apatite, opaques, and zircon are present as accessory minerals (Fig. 3d).

White-colored ignimbrites (mostly cropping out in the Shirvandarasi valley in the vicinity of the villages of Ghotuorsouei and Valhezir, north and west of caldera, respectively) are pumice-rich pyroclastic flow deposits ranging in thickness from few centimeters to 15 meters. The ignimbrite deposits are unwelded, poorly consolidated, and matrix-supported lapilli tuffs containing pumice and lithic clasts of non vesicular cognate lavas (containing non-vesiculated glass and phenocrysts of plagioclase, quartz, and biotite) in a fine-grained (ash-sized) matrix. The phenocrystic crystal content is mainly plagioclase and amphibole. Single subhedral to anhedral crystal fragments of plagioclase are typical, but glomerocrystic aggregates of plagioclase also exist, whereas amphiboles are typically euhedral to subhedral. Accessory minerals comprise opaques, apatite (often as inclusions in phenocrysts), and zircon. The matrix contains glass shards with a pristine morphology (including cusped X- and Y- shaped vesicle wall fragments), but the glass is usually replaced by fine silica and alkali feldspar (adularia) aggregates, clay minerals, or carbonates (Fig. 3e).

4. Geochronology

4.1. Published K-Ar Geochronology

K-Ar whole rock geochronological data for Paleo-Sabalan (Pre-caldera/ lower series in the nomenclature of Alberti et al., 1975) volcanic rocks suggested that the first eruption of Sabalan volcano occurred at ca. 5.6 Ma, with ages extending down to ca. 2.9 Ma. Whole rock K-Ar age determinations of Neo-Sabalan (Post-caldera/ Upper series in the nomenclature of Alberti et al., 1973 and 1980) lavas are between 1.6 to 1.4 Ma (Alberti et al., 1980). Prior to this study, no other published radiometric ages were available for Sabalan.

4.2. Methods for ion-microprobe U-Pb and U-Th zircon geochronology

Zircon U-Pb and U-Th ages for selected samples (Table 1) are based on U, Pb, and Th isotopic measurements by SIMS (or ion microprobe). We employed spot analyses using the CAMECA IMS 1270 ion microprobe at the University of California, Los Angeles (UCLA) following procedures described in Quidelleur et al. (1997), Schmitt et al. (2003), and Schmitt (2011). Following mineral separation using conventional liquid and magnetic techniques, zircon grains were hand selected, mounted in epoxy, and sectioned by grinding with abrasives and polishing with diamond suspension. The mounts were sputter-coated with a conductive layer of high-purity gold in an argon atmosphere. A mass-filtered $^{16}\text{O}^-$ primary ion beam was focused to an ~20-30 μm diameter spot and the resulting secondary ion beam (at 10 keV with an energy window of 50 eV) was mass-separated at a mass resolving power of 5000. For U-Pb analysis (Table 2), a pre-sputtering period of ~180 sec was applied in order to remove surficial Pb, and data were collected during 8–10 magnet cycles using a single electron multiplier detector. The sample chamber was flooded with oxygen at $\sim 3 \times 10^{-5}$ Torr to enhance secondary Pb^+ ionization. The

reported weighted-mean ages are based on $^{206}\text{Pb}/^{238}\text{U}$ ages calculated using zircon standard AS3 (1099 ± 0.5 Ma; Paces and Miller, 1993). Common lead corrections were made using the measured values of ^{207}Pb and a composition of anthropogenic Pb in Southern California (Sanudo-Wilhelmy and Flegal, 1994). A ^{230}Th disequilibrium-correction (leading to a deficit in ^{206}Pb compared to equilibrium) was based upon an estimated initial $(^{230}\text{Th})/(^{238}\text{U})$ of 0.2 (Schmitt, 2011). Selected zircons with young and comparatively imprecise $^{206}\text{Pb}/^{238}\text{U}$ ages which straddled the limit of U-Th disequilibrium dating (200-300 ka; Schmitt, 2011) were also analyzed by U-Th methods (Table 3). This method is based on the determination of $(^{230}\text{Th})/(^{238}\text{U})$ in zircon (parenthesis indicating activities). U-Th model ages are then calculated as two-point isochrons involving the measured $(^{230}\text{Th})/(^{238}\text{U})$ in zircon and a calculated (based on whole rock U and Th abundances) melt composition.

The U-Pb and U-Th ages reported here need to be considered as maximum values for the eruption because zircon is well-known to crystallize significantly before the eruption with their ages recording pre-eruptive crystallization (e.g., Fukuoka and Kigoshi, 1974; Reid et al., 1997). Moreover, the U-Pb data reported here are for sectioned zircon crystals, and although the analysis spots targeted the tips of the crystals, there is still considerable beam overlap covering interior domains which may record older phases of zircon crystallization. To obtain some constraint on the youngest, and possibly near-eruption zircon crystallization (e.g., Wright et al., 2015), we also explored depth profiling analysis of zircon rims for the youngest samples where crystals were pressed in indium metal, gold coated, and analyzed without sectioning or polishing. All zircon ages are reported as estimates for the time of magmatic zircon crystallization. Future work on young zircons from Sabalan using U-Th and (U-Th)/He dating (e.g., Schmitt, 2011) is anticipated to better constrain the eruption ages for the youngest lavas from Sabalan which are

possibly late Pleistocene in age, or younger. All age uncertainties for weighted averages are reported at the 95% level together with their mean square of weighted deviates (MSWD), and the number of analysis used to average vs. those that were rejected as antecrystic (i.e., predating the latest phase of zircon crystallization in a sample; Table 1).

4.3. U-Pb and U-Th zircon geochronology results

Five zircons separates from Paleo-Sabalan volcanic rocks (S15, S22, S10B, S39, and S42 from Ghezelbara mountain and Shahneshin village, NE and SW of caldera, respectively) yielded ages between 4.51 ± 0.13 Ma ($n = 12$; MSWD = 0.68) and 1.26 ± 0.07 Ma ($n = 7$; MSWD = 1.4).

Although crudely consistent with the vintage K-Ar whole rock ages, the U-Pb zircon ages are a significant improvement because of their considerably smaller uncertainties. The next younger age group is defined by three samples from ignimbrite deposits outside the northern (S33 and S34) and southeastern (S23) caldera margin. S23 and S34 are composite pumice samples, whereas S33 is a bulk ignimbrite sample. S33 yielded a homogeneous zircon age population with an average age of 545 ± 40 ka (MSWD = 1.1; $n = 8$). The sample from the overlying ignimbrite deposit (S34) yielded a stratigraphically consistent younger age of 402 ± 42 ka (MSWD = 0.59; $n = 5$), excluding some zircons with ages that are close to the average of S33 and which are consequently interpreted as recycled antecrysts. The southeastern ignimbrite sample (S23) has several antecrystic grains with ages between ca. 320 ka and 1.2 Ma; a single young zircon age of 183 ± 121 ka was obtained for S23 which we interpret as the maximum age for the eruption.

Zircon separates from trachyandesitic flows (S10, S24, S25, and S11) yielded U-Pb ages between 481 ± 69 ka (sample S10; MSWD = 0.02; $n = 5$) and 149 ± 31 ka (sample S25; $n = 1$). The dominant zircon populations in S11, S24, and S25 ka are essentially indistinguishable in age although they are from widely separated locations around the central edifice and represent flows

directly on or outside the inferred caldera margins. The oldest sample S10, by contrast, is from a flow well inside the caldera margin. This flow is also remarkable because it shows mingling between crystal-rich and crystal-poor magmas, and the presence of a bimodal zircon age population: besides the five grains averaged at 481 ± 69 ka, there is a second well-defined cluster of zircon crystallization ages averaging 3.03 ± 0.10 Ma (MSWD = 0.75; $n = 9$). We did not attempt to physically separate the two intermingled lava types before crushing and separating zircon, but we suspect that each zircon age population represents the zircon cargo of the crystal-rich and crystal-poor magmas, respectively. Four samples of dacitic dome lavas (S26, S35, S37, and S38) within the caldera boundaries yield ages between 257 ± 21 ka (sample S38; MSWD = 0.65; $n = 11$) and 188 ± 20 ka (sample S35; MSWD = 1.0; $n = 11$). This group also includes sample S26 which was collected from high elevation at the Soltan crest, and whose age falls into the same age range (234 ± 16 ka; MSWD = 0.53; $n = 12$). This indicates that trachyandesitic and dacitic eruptions overlapped.

Our reconnaissance U-Th zircon rim model ages are consistent with the U-Pb zircon results. Samples S10 and S34 (U-Pb ages of ca. 481 and 402 ka, respectively) yielded $(^{230}\text{Th})/(^{238}\text{U})$ close to secular equilibrium. Samples S25 and S35 with slightly younger U-Pb ages (ca. 149 and 188 ka, respectively) have U-Th zircon interior ages that are on average older than those of the rims. This attests to protracted zircon crystallization, and possibly recycling of antecrysts which are overgrown by new zircon at a later stage. The youngest U-Th rim ages for trachyandesitic flows and dacitic dome lavas (represented by samples S25 and S35) are ca. 110 ka. The most recent activity at Sabalan thus involves the eruption of lava flows within the central complex at or after ca. 110 ka. If this includes post-glacial activity (Alberti et al., 1980) remains to be confirmed through further study.

These first geochronological results since the late 1970's confirm that the Sabalan edifice was built in two main stages. The Paleo-Sabalan stage has maximum ages of 4.5-1.3 Ma, with the actual eruption probably close to these limits at the stated uncertainties. Neo-Sabalan zircon ages are between 481 and 149 ka (U-Pb) or 111 ka (U-Th rims). Because of the strong evidence of zircon recording multiple pre-eruptive crystallization events, these ages are almost certainly overestimating the actual eruption age. Both stages are separated by several explosive eruptions at 545 ka, 402 ka, and 183 ka deduced from U-Pb zircon ages of valley-filling ignimbrites and fall-out deposits which are persevered in the N and SE parts of the caldera, respectively. These units could represent deposits associated with one or more caldera-forming explosive eruptions.

5. Whole rock geochemistry

5.1. Sampling and analytical methods

Samples were collected with the goal to evaluate the variability of rock compositions over a large geographical extent and the entire radiometrically dated strata of the volcano. Analyses of a selection of 34 representative samples from the different layers are presented in Table 2. Major and trace elements were analyzed by SGS (Canada) using inductively coupled plasma (ICP) atomic emission spectroscopy (AES) and ICP mass spectrometry (MS) analytical protocols, respectively, after lithium metaborate fusion.

5.2. Major elements chemistry

Rocks from the Sabalan volcano have SiO₂ contents ranging from 56 to 67 wt% (Table 2). Paleo-Sabalan rocks have generally lower SiO₂ (55–60 wt%) compared to Neo-Sabalan (60–67%). On the total alkali vs. silica plot, the compositions of Paleo-Sabalan rocks classify as trachyandesitic,

whereas the Neo-volcanic rocks are trachyandesitic to dacitic (Fig. 7a). On the basis of the Le Maitre et al. (1989) classification, the rocks of Sabalan volcano are assigned to the high-potassium calc-alkaline suite (Fig. 7b). On selected Harker diagrams (Fig. 8), the Paleo- and Neo-Sabalan rocks define fields that show gradual systematic compositional variations between both sample suites. This suggests derivation from a single parental magma-type, with Neo-Sabalan rocks tending to be slightly more differentiated than Paleo-Sabalan rocks.

5.3. REE and trace element chemistry

Primitive mantle-normalized trace element variation diagrams (Sun and McDonough, 1989) highlight the geochemical resemblances between the Paleo- and Neo-Sabalan rock suites (Fig. 9a). As for the major elements, similar features of the trace element abundance patterns for Paleo- and Neo-Sabalan rocks imply that they are derived from a single parental magma undergoing differentiation by fractional crystallization. Both volcanic suites show spider diagrams with prominent enrichments in large ion lithophile elements (LILE) which are characteristic for enriched mantle sources or continental crustal contamination, unlike mid ocean ridge basalt (MORB)-type or mature rift-related magmas that originate from the depleted upper mantle. Enriched mantle sources or continental crustal influences are also supported by chondrite-normalized rare earth element (REE) patterns which are characteristically enriched in light REE (LREE) relative to heavy REE (HREE) (Fig. 9b). In addition, the Paleo- and Neo-Sabalan spider diagrams display negative Ti, Nb, and Ta anomalies (Fig. 9a) which suggest either a subduction-modified mantle source that became enriched in fluid/melt mobile incompatible elements, or some degree of continental crustal contamination.

In addition, Sabalan samples show a marked positive Sr anomaly resulting in elevated Sr/Y vs. Y or Sr/(Na₂O+K₂O) (Fig. 10a and 10b). When plotted on the adakite discrimination diagrams of Denfant and Drummond (1990) all of the samples plot within the adakitic field (Fig. 10a). The Sr versus Na₂O+K₂O and MgO versus SiO₂ diagrams for Sabalan volcanic rocks indicate that these rocks have compositions equivalent to the high-silica group of Martin et al. (2005; Fig. 10b and 10c).

6. Discussion

Paleo-Sabalan and Neo-Sabalan volcanic rocks have similar geochemical characteristics, so that they are presumably derived from a long-lived and homogeneous source producing similar parental magmas. All Sabalan rocks have low MgO (<3.12 wt.%), and direct derivation via partial melting of peridotite-mantle parental magma can thus be ruled out. Based on systematic variations of major elements with increasing SiO₂ (increasing Na₂O, Al₂O₃ and K₂O with and decreasing TiO₂, MgO, P₂O₅, Fe₂O₃ and CaO; Fig. 8), fractional crystallization is identified as a major factor controlling the compositional diversity. Based on higher SiO₂ in Neo-Sabalan rocks compared to Paleo-Sabalan, the Neo-Sabalan phase generally produced more evolved magma compositions, but systematic trends in age vs. composition are lacking for the Neo-Sabalan phase itself.

The abundance patterns of trace elements can be summarized as follows for all Sabalan rocks: 1) strong enrichment of LILE relative to high field strength elements (HFSE); 2) prominent negative Ti, Nb, and Ta anomalies; and 3) chondrite-normalized REE patterns with LREE strongly enriched relative to HREE. Based on the tectonic setting of Sabalan volcano in a continental collision zone we consider four major sources as potential contributors to magmatism at Sabalan: 1) crustal sources (lower continental crust, and subducted oceanic crust), 2) primitive

mantle, 3) enriched mantle (similar to an ocean island basalt OIB source), and 4) subduction-metasomatized mantle.

6.1.1. Crustal sources

Figure 6 represents the comparison between compositions of Sabalan volcanic rocks and inferred lower crustal composition (after Rudnick and Gao, 2003). In a primitive mantle normalized multi-element diagram (Fig. 9a) Sabalan magmas deviate from lower crust by having higher LILE and lower Eu, Ti, Dy, Y, Yb and Lu abundances. Chondrite-normalized REE patterns of Sabalan volcanic rocks indicate that they are more enriched in LREE (and complementarily more depleted in HREE) than lower crust (Fig. 9b). According to these geochemical characteristics, whole-scale melting of the lower crust cannot be the sole magmatic process generating Sabalan volcanic rocks.

Because of high ratios of Sr/Y and Na₂O/K₂O (Fig. 10a and 10b) Sabalan volcanic rocks could be related to adakitic magmatism which has been proposed to result from partial melting of subducted oceanic crust in the eclogite or garnet-amphibolite stability fields (Defant and Drummond, 1990; Martin, 1993, 1999). Alternatively, differentiation of subduction-derived basaltic magma beneath a thick continental crust could produce such adakitic melts (Atherton and Petford, 1996) (Fig. 10c). The strong enrichment of LREE and depletion of HREE and Y in adakites has been linked to residual garnet in the magma sources. The complementary high abundances of Sr (and low abundances of Ti, Nb, or Ta) are thought to result from the absence of plagioclase and presence of Fe-Ti oxides in the source (Martin, 1999). Adakitic rocks are present in different tectonic environments (Maury, 1996) where deeply subducted oceanic crust undergoes partial melting. These melts can be generated during the initial stages of subduction (e.g., Sajona et al., 2000), in subduction zones with fast and oblique convergence (e.g., Peacock

et al., 1994), or after subduction has ceased (e.g., Prouteau et al., 1999; Sajona et al., 2000). According to the MgO vs. SiO₂ compositional variation diagram (after Martin et al., 2005), Sabalan volcanic rocks are similar to adakites derived from garnet-amphibolite and/or eclogitic sources (Fig. 10c). Although they are indistinguishable in the MgO vs. SiO₂ diagram from compositions generated by partial melting of thickened lower crust, the obvious trace element differences between Sabalan volcanic rocks and global lower crust (Fig. 9), lead us to explore an origin of the Sabalan parental magmas from partially melted metabasaltic sources in a subduction environment.

A problem with this interpretation of generating Sabalan parental magmas via partial melting of metabasaltic (garnet-present) sources in a subduction environment, although supported by the chemical characteristics of Sabalan rocks, is that subduction of the Neo-Tethyan oceanic crust has long finished after continental collision occurred at ca. 13 Ma (Dilek et al., 2009). Melting of the detached Tethyan slab cannot be ruled out, but before discussing the merits and shortcomings of such a scenario, we discuss alternative petrogenetic models that could satisfy the geochemical characteristics of Sabalan rocks, in particular melting of a subduction modified mantle as the parental magma source for Sabalan volcanic rocks.

6.1.2. Mantle sources and partial melting

Of the three potential mantle sources (primitive, enriched OIB-like, and subduction-metasomatised), primitive mantle and OIB sources can be readily dismissed based on the high abundances of LILE and LREE in Sabalan rocks relative to primitive mantle and their prominent negative Ti, Nb, and Ta anomalies that are untypical for OIB sources (Fig. 9a). This is supported by chondrite-normalized REE patterns where Sabalan volcanic rocks have low contents of

MREE and HREE relative to OIB compositions (Fig. 9b). Metasomatised mantle has a composition similar to primitive mantle, but mobile incompatible elements are enriched.

On the basis of the Th/Yb versus Ta/Yb diagram (after Pearce, 1983), the parental magma sources of Sabalan volcanic rocks are similar to those producing magmas in an active continental margin setting with enrichments of Th/Yb and Ta/Yb typical for within-plate (W vector) or crustal contamination (C vector) (Fig. 11). Sabalan samples plot above the compositional array defined by basalts from non-subduction settings (MORB - within-plate basalts). This supports that sub-continental mantle sources were involved in generating Sabalan magmas genesis leading to enrichments of Th and Ta relative to less incompatible trace elements.

The range of $(La/Yb)_N$ (from 28 to 48) for Sabalan rocks, and the relatively high La_N (from 58 to 98) and low Yb_N (from 1 to 3) are indicative for the degree of partial melting, or the composition of the mantle source. $(La/Yb)_N$ decreases with increasing degrees of partial melting (Pankhurst, 1977; Saadat and Stern, 2011). To produce $(La/Yb)_N$ between 28 and 48, unusually low degrees of depleted mantle partial melting would be required, and it therefore seems more likely that the mantle has become enriched in LREE relative to HREE. In this scenario, the sub-continental mantle below Sabalan must have been somewhat, but not excessively, enriched with La ($La_N \sim 3$ in primitive mantle) relative to Yb ($Yb_N \sim 3$) resulting in $(La/Yb)_N \sim 1$. If the subcontinental mantle sources were even more enriched in La (La_N : from 58 to 98) and other LIL elements, e.g., due to addition of these elements via transport in aqueous fluids derived from dehydration of subducted oceanic lithosphere, higher degrees of partial melting in the mantle sources would be permitted.

6.1.3. Assimilation and fractionating differentiation

Phenocryst assemblages in Paleo- (plagioclase + amphibole + pyroxene + biotite) and Neo-Sabalan (plagioclase + amphibole $\pm$ alkali-feldspar $\pm$ quartz) samples suggest that amphibole, plagioclase, and to a lesser extent clinopyroxene may have been important fractionating phases. Th and Rb behave largely equally incompatibly during fractional crystallization of these assemblages and their ratio should remain constant (Fig. 12). By contrast, increasing Rb/Th could result from crustal assimilation, because Rb/Th is higher in continental crust than in the least evolved Sabalan volcanic rocks (Keskin et al., 1998). To investigate the role of fractional crystallization (FC) and assimilation (A) in Sabalan magmatism, we monitored Rb/Th in Paleo- in comparison with Neo-volcanic rocks. AFC modeling (Fig. 12a) suggests that over the compositional range from trachyandesite to dacite crustal assimilation is negligible because of the very low r values ($r < 0.1$; r = rate of assimilation to rate of fractional crystallization) that are required to match the observed Rb/Th.

Although the highly incompatible element Rb is a useful fractionation index for mafic differentiation, it is less indicative for acid magmas which have experienced biotite fractionation. For modeling the hydrous vs. anhydrous crystallization assemblage (e.g., Keskin et al, 1998) of the more evolved Sabalan rocks, we instead use Y as a fractionation index and plot it against Rb on a log–log diagram which also indicates modeled Rayleigh fractionation vectors (Fig. 12b). The positive correlation of Paleo-Sabalan volcanic samples in the Rb vs. Y diagram is consistent with fractionation of plagioclase + clinopyroxene (Pl + Cpx) or plagioclase + amphibole (Pl + Amp), whereas the horizontal or slightly negative trend shown by the Neo-Sabalan volcanic samples can be best explained by a larger proportion of amphibole in the fractionating assemblage.

6.2. Geodynamic context

In our model, we envision that the Neo-Tethyan oceanic slab experienced roll-back and ultimately break-off after the end of subduction in the Upper Miocene (Dewey et al., 1986; McQuarrie et al., 2003) and/or Middle-Upper Eocene (Hempton, 1987; Vincent et al., 2005; Hessami et al., 2011). The detached remnants of steeply dipping subducted oceanic crust became stranded beneath the Eurasian plate in the region of Azerbaijan. Because of subduction and associated metamorphism, the basaltic rocks of the Neo-Tethyan oceanic crust transformed into amphibolite and ultimately eclogite. In this process, fluids and/or partial melts that were enriched in LILE and LREE were generated and metasomatized the lithospheric mantle. High degrees of partial melting of the metasomatized mantle generated the parental magma of Sabalan volcano which inherited a subduction component (Fig. 13). This model is in accordance with similar scenarios previously proposed for calc-alkaline post-collisional magmatism in Iran (e.g., Berberian and Berberian, 1981; Agard et al., 2011). Pearce et al. (1990) in their study of young volcanoes in SE of Turkey proposed lower crust delamination for Upper Cenozoic magmatism in Eastern Turkey and NW Iran. Keskin et al. (2006), however, suggested that Neo-Tethyan oceanic slab break-off beneath Eurasia plate was the trigger for Quaternary magmatism in this region. Although there is no clear-cut distinction between both scenarios that can be petrologically resolved, we tentatively side with the model of oceanic crust breakoff because the slab remnant has been tomographically detected in seismic studies (Lee and Zaho, 2007).

7. Conclusions

According to our field investigations and newly established zircon geochronology, Sabalan volcano has erupted in two major episodes spanning the Pliocene-Pleistocene. Pliocene-Pleistocene activity at Sabalan volcano initiated with the eruption of trachyandesites to andesites,

mostly preserved as lava flows. Ages for these flows are between ca. 4.5 and 1.3 Ma. After a gap of ca. 0.7 Ma, eruptive activity re-initiated violently at ca. 550 ka with a series of explosive eruptions which produced widespread ignimbrites and fall-out deposits surrounding Sabalan. One or more of these eruptions might be associated with caldera collapse. Neo-Sabalan activity continued with emplacement of trachyandesitic to dacitic domes which form the eroded crest of the volcano. The youngest activity of Sabalan volcano is represented by trachyandesite lavas which erupted from several lateral craters and flowed down the flanks of the volcano as thin flows. The youngest eruption of lava occurred as recent as ca. 110 ka, or could be even younger.

Paleo-Sabalan and Neo-Sabalan volcanic rocks have similar geochemical characteristics, and they are presumably derived from a long-lived and homogeneous source producing similar parental magmas. Strong enrichment of LILE relative to HFSE; prominent negative Ti, Nb, and Ta anomalies, and chondrite-normalized REE patterns with LREE strongly enriched relative to HREE support a subduction-metasomatized mantle origin. Higher LILE (including LREE) and lower Eu, Ti, Dy, Y, Yb and Lu in Sabalan magmas compared to lower crustal compositions argue against whole-scale melting of lower crust. Although Sabalan volcanic rocks have adakitic affinity, they are not the result of partial melting of subducted oceanic crust in the eclogite or garnet-amphibolite stability fields.

High $(La/Yb)_N$ (from 28 to 48) and the relatively high La_N (from 58 to 98) and low Yb_N (from 1 to 3) abundances suggest that Sabalan magmas originated from high degrees of partial melting of enriched mantle. This enrichment is due to addition of aqueous fluids and/or melts derived from dehydration of the subducted ocean lithosphere to lithosphere mantle beneath Sabalan. Neo-Tethyan slab roll-back and break-off, after the termination of subduction and continental collision, resulted in a steeply dipping slab remnant beneath Eurasia. The localized release of

fluids and/or melts from this slab imprinted a subduction signature (high LILE and LREE and negative Ti, Nb, and Ta anomalies) onto the parental magmas of Sabalan volcano. Petrographic evidence, low Rb/Th and mildly positively to negatively correlated Y and Rb indicate that the subsequent evolution of parental magmas into the trachyandesitic to dacitic compositions erupted at Sabalan were controlled by the crystallization of plagioclase-clinopyroxene and to lesser extent plagioclase-amphibole assemblages with negligible crustal assimilation, and in the absence of garnet.

8. Acknowledgments

We thank Ms. Razieh Chaharlang for assistance in drawing part of the artwork for this paper.

The ion microprobe facility at UCLA is partly supported by a grant from the Instrumentation and Facilities Program, Division of Earth Sciences, National Science Foundation.

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Figures captions:

Fig. 1. Google Earth Satellite imagery showing Quaternary volcanic complexes (outlined in white) in northwestern Iran, Armenia, and southeastern Turkey. Neo-Tethyan suture and major faults are indicated in red.

Fig. 2. Simplified geological map of Sabalan volcano, and location of samples dated by U-Pb and U-Th zircon methods.

Fig. 3. Photomicrographs of selected Sabalan volcano samples in crossed polarized light: a) Paleo-Sabalan trachyandesite with abundant plagioclase (Pl), amphibole (Amp) and biotite (Bio) phenocrysts in a hyalo-microlitic groundmass (Ghezelbara lava sample No. S1); b) plagioclase, biotite and hornblende phenocrysts in hyalo-microlitic groundmass of Soltan dacitic rocks (sample No. S35); c) porphyritic texture in trachyandesitic to dacitic rocks of a central dome. Alkali feldspar, plagioclase, quartz are present as microlites in a partially glassy groundmass (sample No. S38); d) Neo-Sabalan lavas of trachyandesitic to dacitic composition with a porphyritic texture composed of euhedral-anhedral plagioclase and biotite phenocrysts in a hyalo-microlitic groundmass. Plagioclase is mostly oligoclase-andesine in composition with sieve textures being common (sample No. S24) and e) unwelded ignimbrite containing a fine-grained (ash-sized) matrix with glass shards and phenocrysts of plagioclase, quartz, and biotite (sample No. S25).

Fig. 4: U-Pb zircon results for Sabalan early (Paleo-Sabalan) to mid Pleistocene volcanic rocks. Dashed line indicates fixed-intercept (common $^{207}\text{Pb}/^{206}\text{Pb} = 0.8283$) regression through the youngest zircons in each population.

Fig. 5: U-Pb zircon results for Sabalan mid to late (Neo-Sabalan) Pleistocene volcanic rocks. See Fig. 4 for explanation.

Fig. 6: U-Th zircon rim (on unsectioned crystals) and interior (sectioned crystals) data for Sabalan mid to late (Neo-Sabalan) Pleistocene volcanic rocks. Dashed line indicates model isochron that is defined by the average of the youngest zircons (those farthest from the equiline). Isochron is anchored at a model melt composition defined by (^{238}U)/(^{232}Th) of the whole rock calculated from ICP-MS U/Th analyses for each sample.

Fig. 7. a) Rock classification $\text{Na}_2\text{O}+\text{K}_2\text{O}$ versus SiO_2 diagram with compositional domains after Cox et al. (1989); b) Rock classification K_2O versus SiO_2 diagram after Rickwood (1989). Filled diamond and open circle symbols are Paleo- and Neo-Sabalan volcanic samples respectively.

Fig. 8. Major element variation diagrams. Symbols as in Fig. 7.

Fig. 9. a) Trace element variation diagrams (Primitive mantle normalization after Sun and McDonough, 1989). Right upper diagram is a composition comparison between primitive mantle-normalized Paleo- (dark grey) and Neo-Sabalan (light grey) with lower crust data after Rudnick and Gao (2003); b) Chondrite- normalized (Nakamura, 1974) REE comparison of Sabalan volcanic rocks with lower crust. Right upper diagram is a composition comparison between Chondrite- normalized Paleo- (dark grey) and Neo-Sabalan (light grey) with Lower crust data after Rudnick and Gao (2003).

Fig. 10. a) Plot of Sr/Y versus Y for the Sabalan volcanic rocks discriminating between normal calc-alkaline rocks and adakites (adakitic field after Denfant and Drummond, 1990); b) Chemical variations among the Sabalan volcanic rocks adakitic samples. All the samples plot within the fields of typical high SiO_2 adakites (HSA; fields drawn after Martin et al., 2005); c) Chemical variations among the Sabalan volcanic rocks adakitic samples. All the samples plot within the fields of typical high SiO_2 adakites (HSA; fields drawn after Martin et al., 2005).

Fig. 11. Th/Yb versus Ta/Yb diagram used to distinguish between subduction-enrichment and compositional heterogeneity in the mantle (after Preace, 1983). Sabalan samples plot in the field for active continental margins suggesting a subduction-derived component in the parental magmas.

Fig.12. Compositional vectors derived from assimilation-fractional crystallization of a model parental magma and an upper crustal contaminant (Keskin et al., 1998) in comparison to Sabalan compositions. a) Rb/Th vs. Rb model curves suggest that crustal assimilation in dacite to trachyandesite magmas is negligible because of the very low r (ratio assimilation over fractional crystallization) values ($r < 0.1$); b) Rb vs. Y model curves for hydrous (amphibole) vs. anhydrous (clinopyroxene) fractional crystallization (starting composition randomly chosen). The positive trend for Paleo-Sabalan samples and the horizontal to slightly negative trends for Neo-Sabalan samples suggest a progressive change to the fractionating mineral assemblage becoming more hydrous with time. Thick marks on each vector correspond to 5% crystallization intervals (Amp: amphibole; Pl: plagioclase; Ol: olivine; Cpx: clinopyroxene; Opx: orthopyroxene; Gt: garnet; B: basic; I: intermediate; A: acidic; numbers refer to phase proportions).

Fig. 13. Schematic geodynamic setting for Sabalan volcanism in the context of the Arabia–Eurasia collision zone in NW Iran.

Table 1. Summary of U-Pb and U-Th zircon ages for Sabalan volcano.

Table 2. Whole rock geochemical analyses of representative samples from the Sabalan volcano.

Sabalan volcano

Neo-S.

- Dacitic to trachyandesite lava flow
- Dacitic volcanic dome and related flows
- Ignimbrite, tuff and lahar
- Trachyandesitic lava and pyroclastics
- Pyroclastic and ignimbrite
- Pliocene dacitic dome
- Eocene-Miocene volcanic rocks

- Caldera
- City, village and local name
- Sabalan crests
- Sample No-age in Ma

Table 1. Summary of U-Pb and U-Th zircon ages for Sabalan volcano.

Sample	w.m.	1 s.e.	2 s.e.	MSWD	n grains	U-Th
S35	0.188	0.009	0.020	1.0	11	111 ka
S37	0.228	0.023	0.053	0.19	10	
S26	0.234	0.007	0.016	0.53	12	
S11	0.237	0.008	0.018	0.66	9	
S25	0.149	0.016	0.031	-	1	110 ka
S38	0.257	0.009	0.021	0.65	10	
S24	0.230	0.023	0.063	0.00	5	
S23	0.183	0.061	0.121	-	1	
S34	0.402	0.015	0.042	0.59	5	s.e.
S10A	0.481	0.025	0.069	0.02	5	s.e.
S33	0.545	0.016	0.040	1.10	8	
S39	1.262	0.024	0.070	1.43	7	
S42	2.909	0.046	0.084	0.63	9	
S10B	3.030	0.044	0.102	0.75	9	
S22	3.452	0.046	0.113	1.27	12	
S15	4.513	0.060	0.132	0.68	12	

Table 2. Whole rock geochemical analyses of representative samples from the Sabalan volcano.

Sample suite	S01 Paleo.	S02 Paleo.	S03 Paleo.	S04 Paleo.	S12 Paleo.	S14 Paleo.	S15 Paleo.	S16 Paleo.	S17 Paleo.	S18 Paleo.	S19 Paleo.	S21 Paleo.	S22 Paleo.	S30 Paleo.	S39 Paleo.	S40 Paleo.	S41 Paleo.	S42 Paleo.
SiO ₂	64.6	58.7	57.7	56.5	57.9	60.4	59.7	57.2	59.2	58.6	57.3	56.5	60.6	58.5	62.1	60.6	59.5	58.8
TiO ₂	0.46	1.04	1	1.24	0.9	0.91	0.79	0.88	0.81	0.9	0.89	0.84	0.74	1.21	0.68	0.84	0.93	0.93
Al ₂ O ₃	15.1	16.1	16.2	15.7	16.2	16.8	15.8	16.6	16	16	15.4	15.5	16.1	16.1	15.6	16.8	16.6	16.2
CaO	3.12	5.55	6.03	6.2	5.55	5.71	4.6	5.17	4.85	4.65	6.63	6.6	4.3	5.5	4.23	5.64	5.73	6.08
Fe ₂ O ₃	2.76	5.37	5.58	6.05	5.96	5.42	4.98	5.15	4.78	5.54	5.07	4.83	4.46	5.49	4.04	5.25	5.26	5.61
K ₂ O	3.26	3.24	2.98	2.89	2.55	2.43	3.41	2.46	2.79	3.45	2.95	2.88	2.96	2.9	3.12	2.49	2.58	2.42
MO	1.13	2.85	2.74	3.12	2.57	2.1	2.27	2.35	1.98	1.94	2.57	2.49	1.21	2.7	1.95	2.68	2.47	2.42
MnO	0.05	0.08	0.08	0.09	0.1	0.08	0.09	0.08	0.06	0.08	0.08	0.08	0.07	0.08	0.07	0.08	0.08	0.08
Na ₂ O	4.6	4.7	5	4.9	4.7	5.1	4.4	4.7	4.5	4.6	4.5	4.4	4.6	5	5.2	5.1	5.1	5
P ₂ O ₅	0.28	0.56	0.72	0.76	0.55	0.51	0.47	0.54	0.44	0.64	0.55	0.51	0.38	0.78	0.53	0.56	0.57	0.59
LOI	1.7	0.48	0.3	0.48	0.7	0.69	0.78	1.03	0.87	1.11	1.99	2.17	0.71	0.93	0.34	0.07	0.3	0.41
Total	97.06	98.67	98.33	97.93	97.68	100.15	97.29	96.16	96.28	97.51	97.93	96.8	96.13	99.19	97.86	100.11	99.12	98.54
Ba	630	720	750	760	670	760	770	690	680	830	720	700	650	760	890	710	720	710
Rb	77.1	77.3	57.6	55.2	57.5	47.6	86.7	40.8	72.3	92.9	61.5	57	69.9	48.5	67.5	48.1	50.6	45.6
Sr	860	1260	1610	1700	1170	1190	860	1140	1000	1040	1230	1270	1000	1640	1230	1180	1310	1310
Y	7	12.9	13.1	13.4	12.9	12.4	15.2	11.7	12	16	12.3	11.6	11.4	11.4	10.1	11.5	11.6	11.2
Zr	117	187	154	164	146	169	210	171	158	266	155	131	131	154	159	145	142	135
Nb	18	27	25	26	20	22	32	25	24	35	24	22	21	27	21	20	19	19
Ta	1.3	1.9	1.7	1.7	1.4	1.3	2.2	1.6	1.6	2.2	1.6	1.5	1.6	1.4	1.3	1.3	1.2	1.1
Th	14.5	19.9	13.6	13	11.9	10.1	20.2	14.2	15.8	19.4	14.9	14.2	16.2	8.2	13.7	11.3	11.5	10.9
a	18	19	19	19	19	20	20	21	19	19	19	19	19	20	19	19	19	19
Zn	48	72	81	82	72	88	72	82	78	90	73	67	64	85	62	74	76	77
Cu	13	56	56	62	51	42	42	59	45	60	57	45	53	21	33	29	42	51
Ni	12	35	39	45	50	30	30	46	34	33	41	40	47	23	21	38	27	27
V	49	109	120	127	114	106	91	81	73	101	92	101	70	114	55	104	92	105
Co	7.1	17.7	17.1	20.2	19	15.1	14.6	16.6	13.4	17.4	16.3	15.9	14.3	15.6	11.4	15.7	15.1	15
Hf	3	5	4	4	4	4	5	4	4	6	4	4	3	4	4	4	4	3
Cs	2.6	2.3	1.4	1.4	1.2	1	3.3	0.4	1.5	2.2	2.1	2.1	2.1	1.3	2	1	1	0.7
U	4.69	5.83	3.78	2.83	3.17	2.38	5.38	3.69	4.04	5.94	3.43	3.68	4.14	2.55	3.64	3.12	3.09	2.91
W	2	2	2	1	2	1	2	3	2	2	1	1	3	1	<1	1	1	<1
La	40.9	53.5	59.9	64.6	45.6	51.7	59	51.2	48.1	66.2	51.5	50.8	44.7	59	53.8	45.6	47.8	47.6
Ce	67.1	98.1	112	120	83.1	90.5	103	94.3	83.7	119	94.2	91.7	78.3	114	91.9	81.5	87.7	87.1
Pr	6.57	10.7	12.4	13.9	8.99	9.65	10.8	9.95	8.96	12.5	10.4	9.9	8.19	12.9	9.46	8.75	9.73	9.62
Nd	21.9	38.2	44.6	50.2	32.4	34.4	35.9	34.6	31.7	42.9	37.1	35.3	28.7	46.2	32.5	31	35.2	34.8
Sm	3.1	5.8	6.6	7.7	5.1	5.2	5.6	5.4	5	6.5	5.6	5.3	4.3	6.8	4.5	4.7	5.6	5.3
Eu	0.88	1.59	1.87	1.98	1.5	1.49	1.47	1.45	1.34	1.61	1.49	1.46	1.26	1.91	1.27	1.29	1.52	1.49
d	2.28	4.04	4.48	5.07	3.85	3.87	4.23	3.76	3.3	4.58	4.03	3.77	3.22	4.34	3.13	3.41	3.75	3.69
Tb	0.29	0.54	0.57	0.64	0.51	0.5	0.58	0.5	0.49	0.65	0.51	0.48	0.46	0.52	0.4	0.42	0.49	0.47
Dy	1.39	2.84	2.83	3.03	2.67	2.54	3.11	2.56	2.46	3.39	2.73	2.39	2.38	2.56	2.03	2.53	2.51	2.5
Ho	0.24	0.53	0.51	0.53	0.51	0.47	0.58	0.48	0.44	0.67	0.48	0.45	0.43	0.47	0.38	0.45	0.45	0.43
Er	0.78	1.34	1.35	1.36	1.31	1.23	1.62	1.21	1.22	1.67	1.3	1.08	1.16	1.15	1	1.19	1.12	1.15
Tm	0.09	0.2	0.19	0.19	0.19	0.17	0.23	0.16	0.17	0.24	0.17	0.17	0.2	0.15	0.14	0.16	0.14	0.15
Yb	0.7	1.2	1.2	1.2	1.3	1.1	1.6	1.1	1.1	1.7	1.1	1.1	1.1	0.9	0.9	1	0.9	1
Lu	0.09	0.2	0.17	0.18	0.2	0.16	0.23	0.2	0.17	0.22	0.16	0.16	0.17	0.12	0.18	0.16	0.16	0.12

Table 2 (Continued)

Sample suite	S23 Neo.	S24 Neo.	S25 Neo.	S26 Neo.	S27 Neo.	S28 Neo.	S29 Neo.	S31 Neo.	S32 Neo.	S33 Neo.	S35 Neo.	S36 Neo.	S37 Neo.	S38 Neo.	S10 Neo.	S11 Neo.
SiO2	61.2	59.8	64	62.3	63.1	62.4	64.1	64.8	65.5	64.4	63.3	64.4	62.1	62.9	65	62.8
TiO2	0.53	0.65	0.46	0.61	0.65	0.63	0.56	0.49	0.53	0.55	0.61	0.68	0.6	0.6	0.5	0.61
Al2O3	14.6	15	15.3	15.7	15.2	16.1	15.4	15.3	15.1	15.5	16	16.1	15.8	15.8	14.8	16.2
CaO	3.42	4.75	3.08	4.6	4.01	4.55	4.02	3.16	2.88	3.32	4.2	3.99	4.09	4.02	2.91	4.17
Fe2O3	3.19	3.71	2.74	3.78	3.75	3.66	3.26	2.99	3.08	3.29	3.5	4.08	3.44	3.78	3.15	3.77
K2O	3.14	3.05	3.19	2.54	3.07	2.4	3.42	3.24	3.52	3.3	2.63	3.23	2.54	3.11	3.4	2.7
MO	1.42	1.78	1.16	1.77	1.68	1.71	1.33	1.18	1.21	1.29	1.58	1.9	1.62	1.76	1.25	1.81
MnO	0.06	0.07	0.05	0.06	0.06	0.06	0.06	0.05	0.06	0.05	0.06	0.06	0.06	0.07	0.06	0.06
Na2O	4.3	4.4	4.6	4.9	5	4.9	4.7	4.7	4.7	4.6	5	5.3	4.8	5	4.6	4.8
P2O5	0.34	0.44	0.32	0.4	0.5	0.34	0.34	0.3	0.3	0.33	0.35	0.55	0.38	0.46	0.33	0.39
LOI	4.15	2.4	1.83	0.23	0.57	0.73	1.9	1.3	0.96	1.89	0.49	1.08	0.78	0.19	0.97	0.42
Total	96.35	96.05	96.73	96.89	97.59	97.48	99.09	97.51	97.84	98.52	97.72	101.37	96.21	97.69	96.97	97.73
Ba	660	710	770	640	760	640	670	730	680	620	650	810	660	870	690	670
Rb	75.5	63.3	77.8	53	70	50.6	76.2	76.1	84.7	80	56.1	65.1	51.7	66.3	86.6	57.1
Sr	920	1080	990	1150	1130	1000	970	840	960	1130	1230	1080	1160	850	1060	1060
Y	7.9	8.7	7	8.3	9.1	7.7	8.1	7.4	7.8	7.8	8.1	8.3	7.7	9.1	7.7	8.5
Zr	136	127	121	190	166	125	134	158	154	153	164	187	116	159	139	132
Nb	19	20	17	16	21	15	19	17	21	19	17	19	15	22	20	18
Ta	1.3	1.2	1.1	1	1.2	0.9	1.2	1.1	1.4	1.3	1	1.1	1	1.3	1.3	1.1
Th	14.2	12.5	13.3	10.8	12.5	9.1	14.7	13.4	17.1	15.1	10.8	13.1	9.6	12.2	16.9	11.2
a	18	18	18	19	20	19	18	18	18	19	19	20	17	18	18	19
Zn	56	58	44	58	61	60	56	50	50	48	57	62	56	63	52	62
Cu	36	32	12	36	30	32	16	57	21	24	31	17	28	30	20	30
Ni	17	24	12	25	17	20	15	84	14	45	16	24	15	21	21	31
V	57	70	48	64	68	71	58	51	51	58	61	69	58	47	55	85
Co	8.9	10.5	7.2	10.8	10.2	10.2	8.6	7.7	7.5	8.7	9.8	10.6	8.9	9.8	7.9	10.6
Hf	3	3	3	5	4	3	3	4	4	4	4	4	3	4	4	3
Cs	2.5	2	2.5	1.4	2.2	1.4	2.6	2.4	2.9	4.2	1.7	1.9	1.5	1.7	3	1.2
U	4.45	3.78	4.32	2.85	3.93	2.69	4.44	4.22	5.35	4.73	3.19	3.71	2.9	3.4	5.33	3.37
W	2	2	2	1	2	1	2	2	2	2	1	1	1	1	2	2
La	44.9	46.9	44.9	43.2	52.6	39.2	45.2	41.4	44.8	42.3	42.1	48.1	40.6	54.4	44.9	45.4
Ce	75.4	82	72	73	90.9	67.6	76.1	70.3	75.2	70	73.4	82.8	70.8	93	75.2	77.8
Pr	7.59	8.48	7.28	7.6	9.38	7.04	7.73	7.14	7.55	7.01	7.62	8.47	7.32	9.38	7.41	8.07
Nd	25.9	29.4	23.9	26	31.7	24.5	26.2	24.3	24.8	24.1	26.2	28.6	25.3	31.1	24.7	27.2
Sm	3.9	4.4	3.4	4	4.4	3.8	3.8	3.5	3.5	3.6	3.8	4.3	3.8	4.5	3.5	4.1
Eu	1.01	1.19	0.94	1.1	1.22	1.01	0.98	0.95	0.96	0.99	1.1	1.17	1.07	1.17	0.88	1.09
d	2.49	2.87	2.22	2.73	3.01	2.5	2.51	2.36	2.57	2.34	2.54	2.85	2.46	2.95	2.43	2.75
Tb	0.33	0.37	0.28	0.34	0.4	0.32	0.33	0.33	0.33	0.34	0.34	0.38	0.32	0.37	0.3	0.37
Dy	1.62	1.95	1.55	1.81	1.95	1.66	1.76	1.47	1.63	1.66	1.71	1.8	1.71	1.87	1.58	1.85
Ho	0.29	0.36	0.27	0.31	0.33	0.29	0.3	0.27	0.31	0.29	0.3	0.34	0.31	0.37	0.28	0.33
Er	0.75	0.81	0.72	0.83	0.89	0.79	0.8	0.73	0.82	0.81	0.82	0.86	0.75	0.98	0.77	0.87
Tm	0.1	0.12	0.1	0.12	0.13	0.11	0.11	0.11	0.11	0.12	0.11	0.11	0.1	0.14	0.11	0.12
Yb	0.8	0.8	0.7	0.8	0.9	0.7	0.8	0.8	0.8	0.8	0.8	0.8	0.7	0.9	0.8	0.8
Lu	0.12	0.19	0.11	0.11	0.12	0.11	0.12	0.14	0.12	0.11	0.11	0.09	0.12	0.16	0.14	0.13