



# Extreme trace elements fractionation in Cenozoic nephelinites and phonolites from the Moroccan Anti-Atlas (Eastern Saghro)



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## ABSTRACT

Nephelinites and phonolites from the Moroccan Anti-Atlas form a cogenetic series of volcanic rocks linked by a fractional crystallization process and showing continuous evolutionary trends for trace-elements. According to partial melting calculations, minor element data in olivine and review of published experimental studies, the most primitive nephelinites are low degree (~2%) partial melts from a carbonated LREE-rich spinel lherzolite. Sr–Nd–Pb isotopic compositions indicate the participation of both DM and HIMU end-members in the mantle source of nephelinites; the HIMU component is here interpreted as a relic of the shallow metasomatized Pan-African mantle. The phonolites show similar isotopic composition except for slightly more radiogenic Sr isotopic values. Fractional crystallization calculations were performed using trace-element mineral/bulk rock coefficients determined with new LA-ICP-MS data on minerals together with published equilibrium partition coefficients. The decrease of LREE, Sr and Ba with increasing differentiation is explained by fractionation of large amounts of apatite. Th, Nb and Zr display a behavior of very incompatible elements, reaching extreme concentration in most differentiated phonolites. Ta, Hf and MREE by contrast are characterized by a moderately incompatible to compatible behavior during differentiation. Fractionation of small amount of titanite, in which Ta, Hf and MREE are highly compatible compared to Nb, Zr and LREE (DNb/DTa: 2, DZr/DHf: 1.5 for titanite/phonolite ratios), explains the observed increase in Nb/Ta and Zr/Hf ratios with increasing silica content, from 18 and 40 in nephelinites to 70 and 80 in phonolites, respectively. Clinopyroxene also contributed to the fractionation of Hf from Zr in the very first steps of crystallization. The low values of Nb/Ta and Zr/Hf ratios observed in the two most differentiated Si-rich phonolites are probably a consequence of late stage segregation of volatile-rich apatitic assemblages in the underlying magma chamber. Two phonolites with extreme Sr contents plot outside fractionation trends, as a result of the remelting of previously crystallized nephelinitic rocks in depth.

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## 1. Introduction

Ultrabasic, strongly alkaline primitive magmas are formed by low partial melting degrees in the mantle (Hirose and Kushiro, 1993), the latter being generally metasomatized (i.e., having experienced infiltration of melts or fluids with “exotic” chemical compositions; Downes et al., 2005; Pilet et al., 2008; Tatsumi et al., 1999). These alkaline melts are typically rich not only in incompatible trace elements but also in mobile components such as CO<sub>2</sub>, H<sub>2</sub>O, F and Cl. Peralkaline rocks are also characterized by a complex mineralogy (Sorensen, 1997) leading to unusual fractional crystallization trends. Fractionation of these mineral assemblages during differentiation of the peralkaline magma leads to the usual enrichment in some very incompatible

elements in the melt but at the same time, depletion in trace elements that are usually considered as incompatible in other less alkaline to non-alkaline magmatic series can occur (Marks et al., 2008). As an example, fractionation of small amounts of apatite and titanite, that are characterized by high LREE and MREE mineral/melt partition coefficients (Olin and Wolff, 2012; Prowatke and Klemme, 2006), can lead to a continuous depletion of melt LREE and MREE contents during fractional crystallization (Marks et al., 2008). Very incompatible elements with similar geochemical characteristic (ionic charge and radius) have a generally similar mineral/melt partition coefficient and as a consequence, their ratios do not change significantly with the degree of partial melting and fractional crystallization (Hofmann and Jochum, 1996). This is particularly the case for the ratio of so-called geochemical twins, namely Nb/Ta and Zr/Hf (Pfander et al., 2007; Weyer et al., 2003). Recent studies however pointed out that in plutonic to subvolcanic alkaline–carbonatitic complexes, Nb/Ta and Zr/Hf ratios increase during differentiation (e.g., Marks et al., 2008), implying that the partition coefficients for both elements are not equal, especially when Ti-rich

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minerals are involved (Green and Pearson, 1987; Olin and Wolff, 2012). Other canonical ratios such as Ce/Pb and Nb/U are also used to estimate the proportion of recycled sedimentary components in the mantle source of primitive basalts (Hofmann, 1997). Differentiation can lead to modification of these ratios and their usefulness as proxies for the amount of recycled crust in the mantle source is biased; this is especially the case of the Si-undersaturated alkaline series such as in the Moroccan Anti-Atlas.

The Mio-Pliocene Saghro Cenozoic volcanic rocks in the Moroccan Anti-Atlas (Berrahma et al., 1993) are amongst the most Si-undersaturated and alkaline-rich volcanic rocks from the Circum Mediterranean volcanic province (Berger et al., 2009; Lustrino and Wilson, 2007). Nephelinites and phonolites are the dominant volcanic products, the former contains scarce wehrlite, pyroxenite and carbonatite xenoliths while the latter frequently shows syenite inclusions (Berger et al., 2009; Ibhi et al., 2002). The nature of these xenoliths indicates that the Saghro lies atop an ultrabasic-alkaline-carbonatitic plutonic complex (Berger et al., 2009; Downes et al., 2005). In this study, new trace element data on bulk rocks and some minerals together with the Sr–Nd–Pb isotopic data are provided and processed to explain the formation of magma with extreme incompatible element concentrations and the fractionation of trace element ratios that are usually unmodified during differentiation.

## 2. Geological context of the Saghro volcanism

The Anti-Atlas uplifted area is located at the boundary between the thick lithosphere of the West African craton toward the South and Peri-Gondwanan-related terranes to the North (Fig. 1). This domain was successively affected by the Eburnean (~2.0 Ga), the Pan-African (760–545 Ma) and the Variscan (420–300 Ma) orogenies (Ennih and Liégeois, 2001, 2008; Gasquet et al., 2008; Hoepffner et al., 2005;

Thomas et al., 2004). The Pan-African event led to the Neoproterozoic magmatic growth by granitoid production and ophiolite/island arc accretion and reworking of the Paleoproterozoic basement by deformation and metamorphism. The Variscan orogeny is only expressed by thick-skin tectonics leading to folding of the Paleozoic sedimentary formations and fracturing of the Precambrian basement (Burkhard et al., 2006). The Triassic to Cretaceous period is characterized by the formation of intra-continental rifts at the location of High Atlas and Middle Atlas, accompanied by Lower Jurassic magmatism (Bensalah et al., 2013, and references therein). The Mesozoic rifts were inverted during the Cenozoic and syn-tectonic sediments were deposited in adjacent sub-Atlasic belts and foreland basins (Frizon de Lamotte et al., 2000; Tesón and Teixell, 2008). According to apatite fission track data and modeling, the High- and Anti-Atlas belts underwent strong uplift during the Neogene (Malusà et al., 2007; Missenard et al., 2008). This uplift event cannot be fully explained by tectonic processes as shortening did not exceed 25% in the High-Atlas belt (Teixell et al., 2003) and because compressional structures (folds, inverse faults) are relatively scarce, as it is in the uplifted Anti-Atlas (Malusà et al., 2007). Modeling of geophysical and topographic data has successfully demonstrated that the elevated areas (Anti-Atlas, central High Atlas and Middle Atlas) lie above a thin lithosphere, characterized by an asthenosphere uplift up to 60 km depth and by the occurrence of alkaline Cenozoic volcanism (Teixell et al., 2005; Missenard et al., 2006; Urchulutegui et al., 2006; Fig. 1). The origin of the thermal uplift is difficult to constrain and it has been the subject to lively debates. It has been related to the horizontal propagation of the Canary plume under the Atlasic corridor (Duggen et al., 2009) but this interpretation has been questioned by Berger et al. (2010) as it does not integrate the Cenozoic geological evolution of the Atlas region and the age distribution of Moroccan volcanism. Recently, Missenard and Cadoux (2012) have proposed that edge-driven convection at the northernmost boundary of the

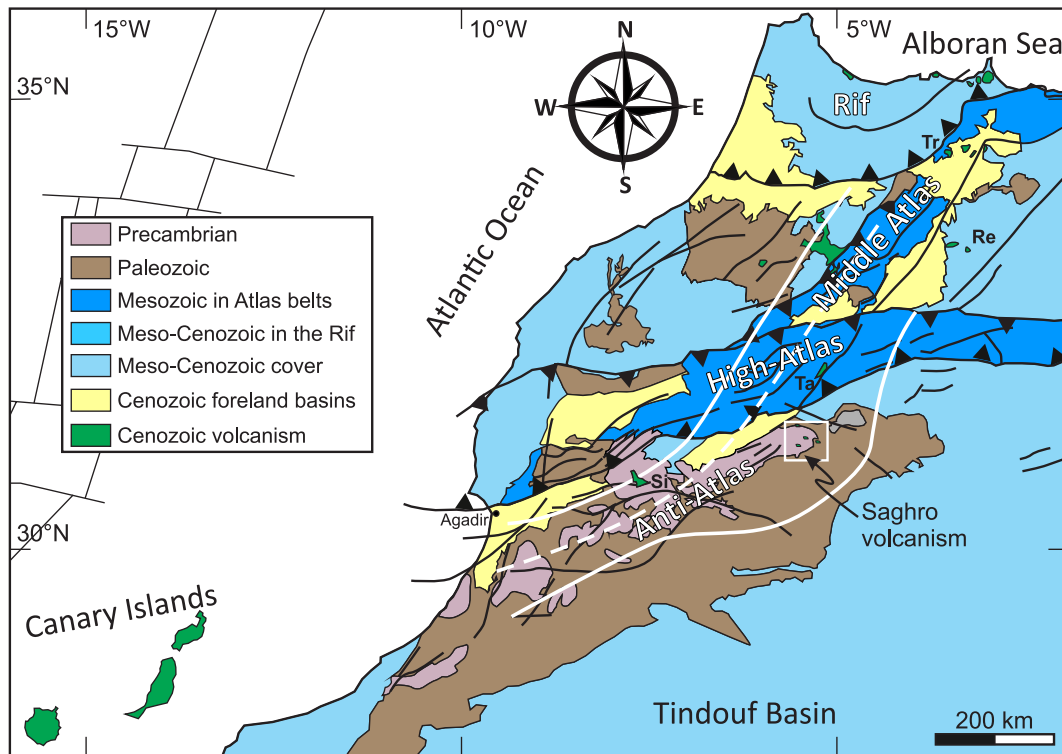


Fig. 1. Simplified geological map of Morocco and bordering regions showing the location of Cenozoic volcanic units. The discontinuous line is the 60 km isodepth contour of the top of the lithospheric anomaly while the continuous lines are representing the 100 km depth for lithosphere–asthenosphere boundary (from Missenard et al., 2006). Re: Rekkame, Si: Siroua, Ta: Tamazight, Tr Taourirt.

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