



Noble gas and carbon isotopic signatures of Cape Verde oceanic carbonatites: Implications for carbon provenance

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ABSTRACT

We discuss noble gas (He, Ne, Ar, Kr, and Xe) and C isotope signatures of carbonatites from the Cape Verde Archipelago. These are the first noble gas compositions ever reported for oceanic carbonatites. The noble gas analyses were performed by crushing the calcite and apatite separates. Some of the analyzed calcites present low $^4\text{He}/^3\text{He}$ ratios (down to 46,700; R/Ra up to 15.5) that cannot be explained by the addition of cosmogenic ^3He , demonstrating that carbonatite magmas came from a reservoir characterised by low time-integrated $(\text{U} + \text{Th})/^3\text{He}$. Such a reservoir is thought to be localised in the deep lower mantle, constraining the depth of origin of the Cape Verde plume. In contrast, apatite samples return highly radiogenic $^4\text{He}/^3\text{He}$ signatures due to their high Th and U contents. An in situ source for ^4He in these apatites is further supported by air-like or lower $^{20}\text{Ne}/^{22}\text{Ne}$ ratios and relatively high $^{21}\text{Ne}/^{22}\text{Ne}$ ratios (up to 0.0485), which result from ^{21}Ne (and ^{22}Ne) formation by nucleogenic reactions. Some apatites plot to the left of the MORB line in the neon three-isotope diagram. This is explained by mass-fractionation processes since these apatites are also characterised by $^{38}\text{Ar}/^{36}\text{Ar}$ ratios lower than the air value or even than the range of values usually used to characterise the MORB–OIB field. Considering that carbonate recycling, which could be characterised by high levels of Te and Ba, would simultaneously increase with time the ^{129}Xe and ^{130}Xe , the observed ^{129}Xe anomalies ($^{129}\text{Xe}/^{130}\text{Xe}$ up to 6.84) cannot be explained by models calling upon crustal carbonate recycling. We attribute these anomalies to an ancient mantle origin by decay of the now extinct ^{129}I . Moreover, experimental work has suggested that crustal carbonates are unlikely to be transported to deep lower mantle depths as a consequence of their removal by melting reactions at subduction. Thus, our noble gas data are indicative of a non-recycled origin for carbon, endorsing the role of primordial carbon in the genesis of Cape Verde carbonatites. This conclusion is supported by typical mantle $\delta^{13}\text{C}$ values (-8.0 to -4.2%) that are lighter than those characterising crustal inorganic carbonates. The fact that He is the noble gas element characterised by the highest solubility in magmas, the faster diffusion and the lower mineral/melt partition coefficients is taken as an explanation for its decoupling from the other noble gases, with He being the one better retaining a deep lower mantle signal.

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1. Introduction

Carbonatites are magmatic rocks containing more than 50% modal carbonate minerals (Le Maitre et al., 2002). The role of the mantle in carbonatite genesis is well established; it serves either as a direct source for carbonate rich magmas generated by a low degree of

melting, or as the source of primary carbonated silicate magmas that, by immiscibility, produce carbonatites in addition to silica-undersaturated magmas (e.g., Mitchell, 2005). However, the ultimate origin of the carbon present in carbonatites has been disputed, and models invoking the role of crustal carbonate recycling are becoming increasingly popular (e.g., Ray et al., 1999; 2009; van Achterbergh et al., 2002; Hoernle et al., 2002; Walter et al., 2008). A crustal origin for carbon in diamonds has also been defended (e.g., Menzies et al., 2003; Tappert et al., 2005; Mohapatra and Honda, 2006).

Noble gases are characterised by chemical inertness, high volatility, and a large range of masses, which induces distinct

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behaviours during physical processes. These characteristics have conferred an important role to the elemental and isotopic composition of noble gases in deciphering the mantle structure. Indeed, their ability to distinguish mantle domains with different degassing histories make noble gases an important tool for unravelling chemical geodynamics (e.g., Zindler and Hart, 1986; Allègre, 1987; Porcelli and Wasserburg, 1995). It has been also demonstrated that carbon and helium correlate in ultramafic xenoliths from some oceanic hotspots, suggesting a coherent behaviour of these elements during fluid migration in the mantle (Trull et al., 1993). Later, Sasada et al. (1997) extended this idea to noble gases as a whole and considered them good tracers of carbon in the mantle.

Considering that noble gases are, like CO₂, volatile elements and that their isotopic compositions in the atmosphere are clearly distinct from mantle ratios (e.g., Moreira et al., 1998), the study of noble gases can be considered of utmost importance for deciphering carbonatite genesis, which in turn plays a major role in understanding the deep Earth carbon cycle. Notwithstanding their potential significance, published studies on the rare gas signatures of carbonatitic rocks are still rare and confined to continental occurrences. These studies revealed that no unique mantle domain can be considered as the ultimate source for carbonatitic magmas. Indeed, although a deep mantle source was invoked to explain noble gas isotopic signatures for occurrences in Kola, Brazil and Canada (Sasada et al., 1997; Marty et al., 1998; Tolstikhin et al., 2002), the role of recycled crustal noble gases introduced into the lithospheric mantle was emphasised for Indian carbonatites (Basu and Murty, 2006; Murty et al., 2007). For the natrocarbonatites expelled by the only active carbonatite volcano (Oldoinyo Lengai, Tanzania), Javoy et al. (1989) identified a ⁴He/³He ratio of 95,000 (or ³He/⁴He = 7.6 Ra, where Ra corresponds to the atmospheric value of 1.384×10^{-6}), similar to the MORB value (e.g. Allègre et al., 1995). For the Oldoinyo Lengai fumaroles, Teague et al. (2008) obtained R/Ra values between 4 and 7. More recently Fischer et al. (2009) presented He isotope ratios ranging from 6.70 to 6.86 Ra, for gases emitted by the Oldoinyo Lengai eruption of July 2005. These results, as well those obtained for CO₂/³He, δ¹⁵N and δ¹³C, were used by the authors to consider such gases indistinguishable from those emitted along mid-ocean ridges.

Reported ages for worldwide carbonatites range from the Archean to the present (e.g., Veizer et al., 1992) and their occurrences are essentially restricted to continental areas (Wooley, 1989). The most notable oceanic exception is the Cape Verde Archipelago, where the presence of “calcareous dykes” and “calcareous mass of volcanic origin” were first described by Bebiano (1932). However, the formal occurrence of carbonatites was only recognised some thirty years later (e.g., Assunção et al., 1965; Allègre et al., 1971). Cape Verde is exceptional in that carbonatites are present in at least 6 of the 10 islands, and because the carbonatite volume is significantly larger than that reported for the Canary Islands (e.g., Hoernle et al., 2002; Muñoz et al., 2005). Despite the extreme rarity of oceanic carbonatites, somewhat contrasting models have been proposed to these occurrences. Hoernle et al. (2002) considered Cape Verde and Canary calcio-carbonatites as resulting from recycling and ageing (≈ 1.6 Ga) of carbonated eclogite, while the model of de Ignacio et al. (2006), for Fuerteventura carbonatites (Canary), implicitly favours a primordial origin for carbon. For the Cape Verde magnesio-carbonatites Hoernle et al. (2002) proposed a source incorporating recycled subcontinental lithospheric mantle.

In this paper, we will focus on the noble gas and carbon isotopic signatures of mineral separates obtained from Cape Verde carbonatites outcropping on 3 of the Southern Islands (Brava, Fogo and Santiago) and one of the Northern Islands (São Vicente), which span an age range of approximately 9 Ma (see below and the Supplementary Material). These are the first noble gas results ever obtained for oceanic carbonatites and aim to contribute to a better understanding of the genesis of the Cape Verde carbonatites and of the deep Earth carbon cycle.

2. Regional geology and geochemistry

The volcanic Cape Verde Archipelago is located in the East Central Atlantic, 600 to 900 km from the western African coast (Fig. 1). It occurs at the southwestern part of the largest oceanic swell (Cape Verde Rise) which is approximately 1200 km wide and characterised by a depth anomaly of 1900 ± 200 m. It is also coincident with important geoid (7.6 ± 0.3 m), heat flow (16 ± 4 mW m⁻²) and gravimetric anomalies (Courtney and White, 1986; Monnereau and Cazenave, 1990; Pim et al. 2008). The lithosphere is 120 to 140 Ma (Williams et al., 1990) and approximately 83 km thick (Cazenave et al., 1988). Crustal thickness is anomalously high (up to 22 km) beneath the islands, which is attributed to magmatic transfer from the plume to crustal levels (Lodge and Helffrich, 2006). However, between the islands the crust has ≈ 7 km thickness, which is normal for oceanic settings (Pim et al., 2008). Crough (1978) first considered the Cape Verde Rise to represent a hotspot swell, associated with an underlying mantle plume, by dynamic uplift (e.g. Courtney and White, 1986; Pim et al., 2008). The plume is, arguably, deep-rooted as imaged by finite-frequency tomography data that show a reasonably resolved P-wave velocity anomaly beneath the archipelago extending down to the core–mantle boundary (cf. Montelli et al., 2006; Zhao, 2007; Helffrich et al., 2010).

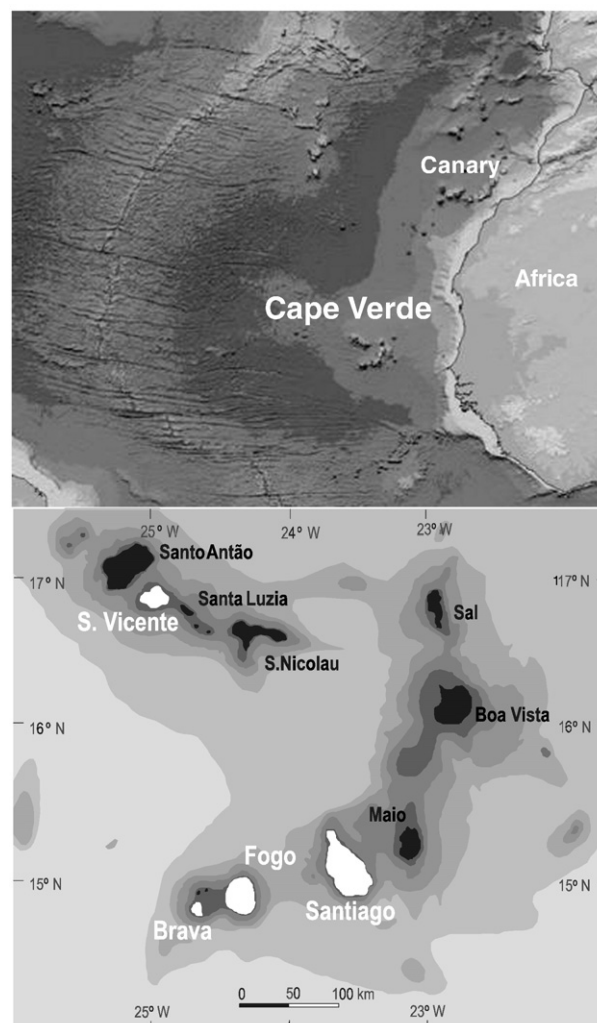


Fig. 1. Map of the Cape Verde Archipelago, where the occurrence of carbonatites was first recognised by Assunção et al. (1965). Carbonatites are now described in the islands of Maio, Santiago, Fogo, Brava, S. Vicente and S. Nicolau and also in the islets neighbouring Brava (see the main text for references). The islands from which the carbonatites studied in this article were collected are shown in white. Location map slightly adapted from Google Earth.

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