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Carbonate assimilation during magma evolution at Nisyros (Greece), South Aegean Arc: Evidence from clinopyroxenite xenoliths

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ABSTRACT

To contribute to the understanding of magma evolution in arc settings we investigate the oldest volcanic unit (Kanafià Synthem) of Nisyros volcano, located in the eastern Aegean Sea (Greece). The unit consists of porphyritic pillow lavas of basaltic andesite composition with trace element signatures that are characteristic of island-arc magmas. Two lava types are distinguished on the basis of geochemistry and the presence or absence of xenoliths, with the xenolith-bearing lavas having distinctly elevated Sr, MREE/HREE and MgO/Fe_2O_3 compared to the xenolith-free lavas. Xenoliths include relatively rare quartzo-feldspathic fragments that represent continental-type material, and coarse clinopyroxenite xenoliths that consist largely of aluminous and calcic clinopyroxene, and accessory aluminous spinel. Anorthite–diopside reaction selvages preserved around the clinopyroxenite xenoliths demonstrate disequilibrium between the xenoliths and the host magma. The xenolith clinopyroxene is distinctly enriched in most lithophile trace elements compared to clinopyroxene phenocrysts in the host magmas. A notable exception is the Sr concentration, which is similar in both clinopyroxene types. The high Al and low Na contents of the clinopyroxenites preclude a cumulate, deep metamorphic, or mantle origin for these xenoliths. Instead, their composition and mineralogy are diagnostic of skarn rocks formed by magma–carbonate interaction in the mid/upper crust.

The Kanafià lavas are interpreted to have undergone crystal fractionation, magma mixing/mingling and crustal assimilation while resident in the upper crust. We show that magma–carbonate reaction and associated skarn formation does not necessarily result in easily recognised modification of the melt composition, with the exception of increasing Sr contents. Carbonate assimilation also releases significant CO_2, which will likely form a free vapour phase due to the low CO_2 solubility of arc magmas. In the broader context, we stress that the effects of carbonate assimilation by arc magma may be more significant than currently recognised. Carbonate assimilation may modify key trace element ratios, such as Sr/Y, in arc magmas, and will liberate significant CO_2 as vapour, which may influence eruption dynamics, estimates of subduction zone volatile budgets, and deep mantle CO_2 recycling.

1. Introduction

The diversity of magmatic rocks preserved in active and ancient arcs makes our comprehension of arc crust construction and evolution particularly challenging. Deciphering the origin and evolution of arc volcanic rocks requires consideration of the compositions and melting conditions of mantle and/or crustal sources, contributions from the subducting slab, and fractional crystallisation, mixing, assimilation and degassing of the magma prior to eruption (e.g., see Stern, 2002). Trace-element and isotope geochemistry coupled with petrological knowledge can be effective tools in this endeavour, although distinguishing the contributions from the subducting crust or from the overlying arc crust can be especially problematic, particularly in continental arc settings (e.g., Davidson, 1987; Leeman, 1983).

Arc magmatism is also responsible for most of the volatile release from deep Earth to the atmosphere and oceans (Fischer, 2008; Sano and Williams, 1996), but like the trace element signatures, the source of volatiles such as CO_2 from arc magmas remains a contentious issue (e.g., Fischer, 2008). Understanding volatile fluxes and sources in these environments not only is important for global volatile budgets, but also is crucial for understanding and predicting explosive volcanic eruptions. Large volumes of carbon and H_2O are drawn into subduction zones in hydrous and carbonate minerals (Plank and Langmuir, 1998; Seto et al., 2008) and there is consensus that much of the water is recycled back to arc magmas (van Keken et al., 2011). The case for carbon is less certain. Isotopic studies indicate that most of the CO_2 degassing from arcs is derived from carbonate-rich sedimentary sources (Fischer, 2008; Hilton et al., 2002; Sano and Williams, 1996), which are widely assumed to reside in subducting slabs. However, experimental

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studies (Molina and Poli, 2000) and thermodynamic calculations (Kerrick and Connolly, 2001) concur that carbonate in deep slabs are more resistant to decomposition and volatile release than their hydrous counterparts, which raises the question of whether the substantial CO_2 flux from arc magmas is due to CO_2 recycling from the slab and mantle wedge, or whether other sources are required. Sourcing CO_2 from the upper plate is often considered unimportant (e.g., Sano and Williams, 1996; Snyder et al., 2001), despite the fact that many modern arcs are built on carbonate platform sequences (e.g., Iacono-Marziano et al., 2009; Mitropoulos et al., 1987; Snyder et al., 2001; van Soest et al., 1998). Carbonate–silicate magma interactions have been documented in intrusive complexes (Barnes et al., 2005; Wenzel et al., 2002) and carbonate assimilation has been proposed to influence the composition of some potassic volcanic rock suites, such as at Merapi Volcano in Java (Chadwick et al., 2007), Vesuvius (Iacono-Marziano et al., 2009; Savelli, 1967) and the Colli Albani Volcanic District, central Italy (Gaeta et al., 2009). However, the importance of carbonate assimilation to the composition and eruption dynamics of arc magmas in general has remained ill constrained.

In this paper, we describe the petrology and geochemistry of the oldest volcanic unit exposed on the active volcano of Nisyros of the South Aegean Arc. In particular, we focus on unusual ultramafic xenoliths that are hosted by these lavas that we interpret as products of carbonate–magma interaction in the plumbing system of the volcano. We discuss the implications of these results for magma evolution, magma geochemistry and CO_2 fluxing from Nisyros and other arc volcanos.

2. Geological setting

The South Aegean Arc extends over 500 km through the Aegean Sea and includes active volcanic centres on the islands of Milos, Santorini and Nisyros (Keller, 1982; Fig. 1a). The arc has developed over the last 3 m.y. in response to north-easterly subduction of the Mediterranean seafloor beneath the South Aegean microplate (Mitropoulos et al., 1987). Extensional regional tectonics since the mid Tertiary has produced a substantially thinned crustal basement to the arc (Pe-Piper et al., 2005). Quaternary volcanism at the easternmost extent of the arc culminated at 161 ka, with explosive eruption and caldera collapse at Kos that produced the extensive Kos Plateau Tuff (Allen, 2001; Bachmann et al., 2011; Smith et al., 1996; Fig. 1b). Post Kos Plateau Tuff volcanism in this region has been focused at the southern rim of the now-submerged caldera and has led to development of Nisyros Island; an 8 km wide symmetrical strato-volcano that is still active (Marini et al., 1993). The steep flanks of the volcano comprise thick sequences of lava flows and pyroclastic deposits that vary in composition from basaltic andesite to rhyolite, while at the centre of the island is a circular caldera of about 4 km diameter that has been partly filled by late-stage dacitic domes that reach a maximum elevation of ~700 m above sea level (Fig. 1c). Hydrothermal venting from the crater floor continues to this day (Brombach et al., 2003), with the last significant hydrothermal eruption occurring in 1887. The basement beneath Nisyros is known from two deep geothermal drillholes, each reaching over 1500 m below sea level (Marini et al., 1993). The boreholes intersected units of diorite, limestone, and marble and skarn formed by contact metamorphism and hydrothermal alteration of the limestones. Similar carbonate-rich rock-types are found as xenoliths in some pyroclastic deposits on the island (Di Paola, 1974; Francalanci et al., 1995; Limburg and Varekamp, 1991; St. Seymour and Vlassopoulos, 1992).

The volcanic stratigraphy of Nisyros has been described by many authors (e.g., Di Paola, 1974; Limburg and Varekamp, 1991; Volentik et al., 2002), but most recently by Volentik et al. (2005a). Here we only present a simplified outline of the geology of the island. The earliest magmatism at Nisyros occurred as submarine flows that deposited porphyritic pillow lavas of basaltic-andesite composition that crop out on the north-western shore, as a result of active uplift of this section of the island (Nomikou and Papanikolaou, 2011; Tibalbi et al., 2008). There is evidence of erosion and reworking of these volcanic rocks, indicating exposure above sea level for part of the depositional history (Volentik et al., 2005a). This unit, referred to by

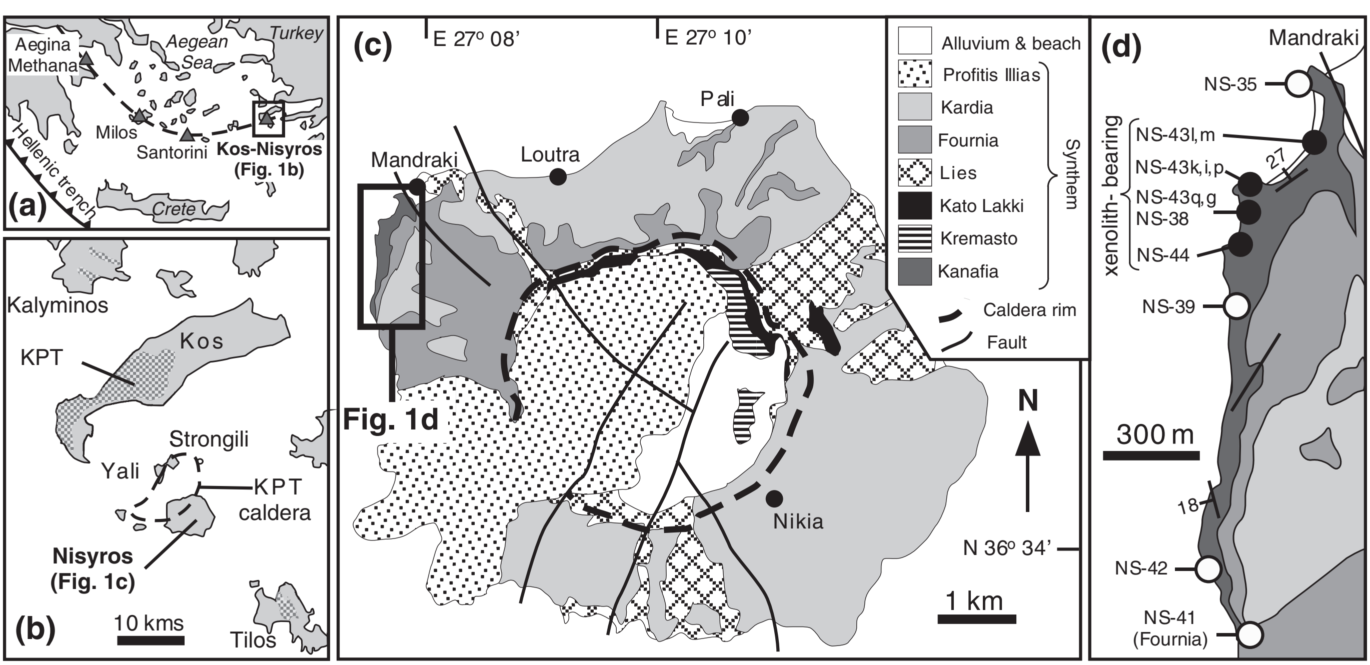

Fig. 1. Location and simplified geological map of Nisyros. The Kos–Nisyros volcanic system (b) represents the eastern-most volcanic centre of the South Aegean Volcanic Arc (a). KPT = Kos Plateau Tuff. Distribution and caldera location for the KPT are taken from Pe-Piper et al. (2005). (c) Geological map of Nisyros, adapted from Volentik et al. (2005b). The volcanic geology is crosscut by major faults defined by Nomikou and Papanikolaou (2011). Details of the geology of the Synthems can be found in Volentik et al. (2005a). (d) Geology of the coastline to the southwest of Mandraki village where the Kanafià volcanic rocks are exposed. The locations of samples analysed in this study are indicated. The open dots mark sampling sites of xenolith-free lavas, while the black dots mark sites of xenolith-bearing samples.