MICRO-SCALE CHEMICAL AND ISOTOPIC VARIATIONS IN THE PRODUCTS OF THE 1650 C.E. EXPLOSIVE ERUPTION REVEALING THE BEHAVIOR OF KOLUMBO SUBMARINE VOLCANO, GREECE

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INTRODUCTION AND GEOLOGICAL BACKGROUND

Kolumbo is a submarine volcano located about 7 km NE of Santorini, it is the largest of more than twenty submarine volcanic cones, aligned in the transtensional Anydros basin, one of the most seismically active zones in the South Aegean Volcanic Arc. Kolumbo explosively erupted in 1650 CE, causing the death of about 70 people on Santorini.

Explorative cruises employing ROVs discovered a high temperature (up to 220°C) hydrothermal field (Sigurdsson *et al*., 2006; Carey *et al*., 2011) with CO_2-rich discharges and accumulation of acidic water at the bottom of the crater (505 m bsl), increasing the related hazard. A possible magma chamber was recognized below the crater by seismic data (Schmid *et al*., 2022). Other studies unveiled that the cone is possibly polygenetic (Hübscher *et al*., 2015; Preine *et al.*, 2022). The eruption sequence was reconstructed by Cantner *et al*. (2014), considering historical accounts and footage from the ROVs. After a period of intense seismic activity, the eruption started with a submarine phase in September 1650 and became subaerial after the formation of a small islet from the eruption products. The activity ended in December 1650.

Kolumbo is possibly the most dangerous volcano in the Aegean Sea, so it is fundamental to understand its behaviour and to know its history. The aim of this work is to provide a model that could explain the Kolumbo plumbing system prior to the 1650 CE eruption through petrographic, geochemical, and state-of-the-art isotopic analyses, to better understand the behaviour of this active volcano. Another objective of this work has been to set up a method for the micro-analysis of Sr and Nd isotope ratios on small samples, such as single crystals, containing small amount of these elements (down to 2 ng of Sr and 100 pg of Nd), and, to apply this procedure to submarine products for the first time.

METHODS AND MATERIALS

The Kolumbo volcano samples were collected during explorative cruises with ROVs and by divers in the shallower portion of the cone. Kolumbo products are highly heterogeneous juvenile pumices and dense clasts. The latter are both juvenile products from the 1650 CE eruption and fresh lithic lavas. Forty-five samples were cut to obtain thin sections for petrographic and mineral chemistry analyses; 23 samples without clear signs of alteration or features from mingling processes, were prepared for bulk geochemical and isotopic analyses.

In addition to whole-rock geochemical and Sr-Nd-Pb isotope analyses, detailed petrographic, mineral chemistry and micro-analytical isotopic investigations on selected samples have been performed. Based on the methods reported in Koornneef *et al*. (2014, 2015), Plomp *et al*. (2017), Jansen *et al*. (2018) and Di Salvo *et al*. (2018), it was possible to set up the micro-analytical Sr-Nd isotopic procedure on single crystals at the "Filippo Olmi" Laboratory of the Department of Earth Sciences of the University of Florence, due to the availability of the New Wave-Merchantek MicroMill™ micro-sampling device and the New Thermo Triton Plus equipped with four amplifiers with 10^{13} Ω resistors. Particular attention has been paid to the blank contribution because of the small amounts of sample investigated but also because of the possible contamination by seawater. Procedures to reduce the blank contributions included: an improved cleaning of the equipment used for the micro-sampling procedure, at least three or four ultrasonic baths with MilliQ of the sample thin sections (150 μm thick) and a particular leaching procedure of the sampled powder with MilliQ.

RESULTS AND DISCUSSION SUMMARY

The analysed whole-rock samples of Kolumbo are classified by their chemical composition as shown in Fig. 1.

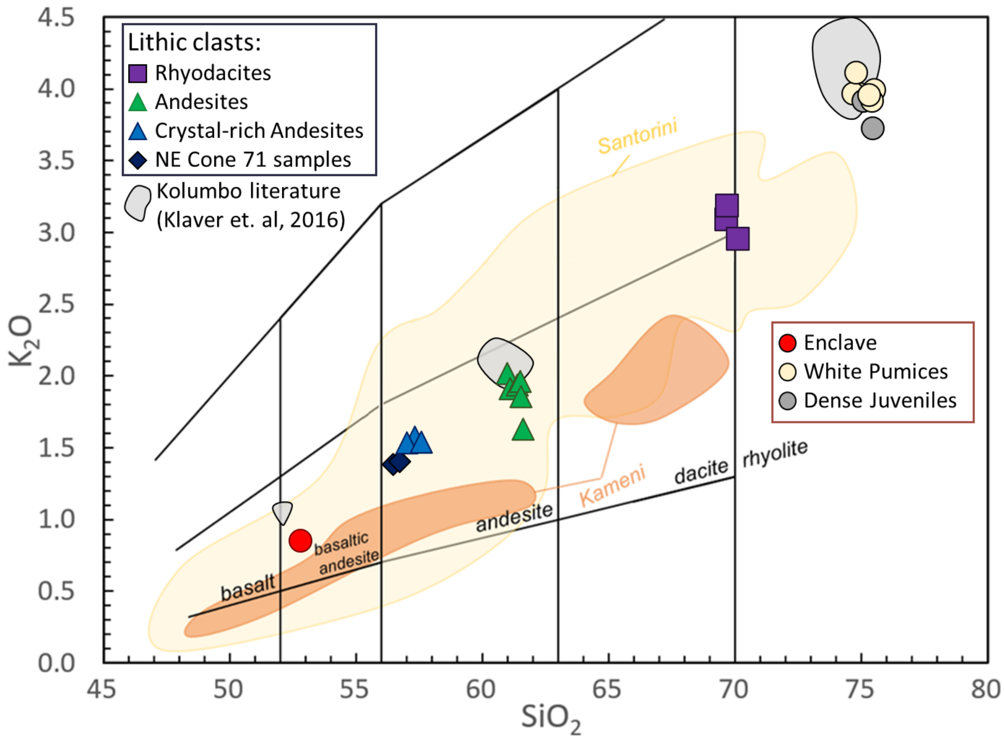

Fig. 1 - SiO_2 *vs*. K_2O classification diagram (Peccerillo & Taylor, 1976) for Kolumbo volcanic products. Data are reported on water-free basis. Kolumbo literature data from Klaver *et al*. (2016; grey fields). Other fields represent Santorini volcanic products (Kameni products in orange).

The rhyolitic samples with mafic enclaves represent the juvenile products of the 1650 CE activity, attesting the interaction (mingling) of different magmas before the eruption. Rhyolites are compositionally homogeneous but show different structures, they have been subdivided in: White, Light Grey, Banded and Convoluted pumices and Dense juvenile samples. $^{87}Sr/^{86}Sr$ ratio in rhyolites varies from 0.70409 to 0.70419, with Dense Juveniles slightly less Sr radiogenic than White Pumices, while $^{143}Nd/^{144}Nd$ is almost identical (0.51272-0.51273). The analysed enclave sample has quite different isotope signature with lower $^{87}Sr/^{86}Sr$ (0.70357) and higher $^{143}Nd/^{144}Nd$ (0.51283) than the rhyolitic host rocks. The main mineral phases of rhyolitic samples are plagioclase, biotite, orthopyroxene. Plagioclase, amphibole, clinopyroxene and olivine are found in the mafic enclaves, often characterized by diktytaxitic texture. Transport of minerals from the enclaves to the rhyolitic host is often observed. Minerals show a large compositional variability. In the juvenile samples, plagioclase displays distinct populations based on chemical composition: a Low-An group (An_{15-25}) for rhyolitic samples and a High-An group for the enclaves (An_{80-95}). Some rhyolitic samples show also an intermediate An_{25-40} population, together with more abundant orthopyroxene and higher-Mg# biotite (Group-B samples, Fig. 2) than samples with only An_{15-25} plagioclases. The latter are instead richer in enclaves (Group-A samples, Fig. 2). The An_{25-40} plagioclase have usually a lower-An rim and the zonation is well distinct, furthermore the cores are less Sr radiogenic than the rims (and the whole-rock values) possibly testifying a mixing process with a less Sr radiogenic melt. We distinguished also different types of enclaves, based on their petrography and degree of evolution. Their crystals show complex zoning and considerable isotopic variations, suggesting the presence of a complex and dynamic mafic system characterized by the occurrence of multiple mafic magmas with different isotope composition.

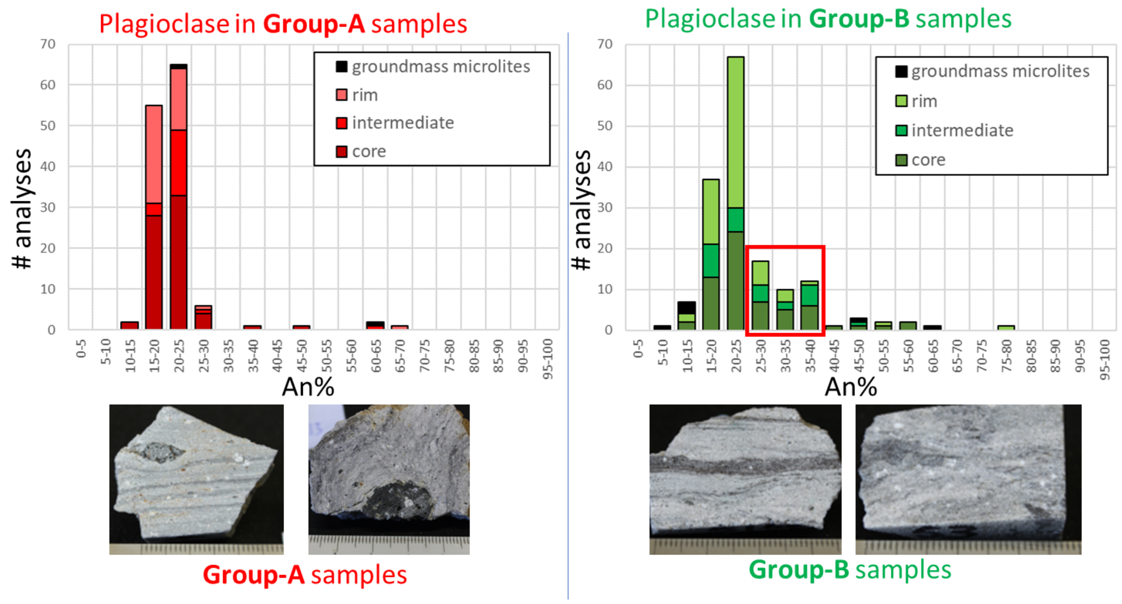

Fig. 2 - Histograms for plagioclase compositions (An%) in Group-A and Group-B rhyolites. Photos are examples of clasts belonging to the two Groups.

The sampled fresh lithic lavas can be subdivided in three groups with characteristic petrographic textures that are well reflected in their different chemical compositions. We distinguished: Crystal-rich Andesites, Andesites and Rhyodacites. They can give information on the early history of the volcano and on how the rhyolitic magma could have been generated. Calculated pressures from amphibole compositions show that they could possibly derive from different reservoirs at different depth, shallower for Andesites and Rhyodacites and deeper for Crystal-rich Andesites. On the basis of major and trace elements and isotope ratios, we propose a two steps differentiation process to produce the rhyolitic samples (Fig. 3): first Andesites may reach compositions similar to those of the Rhyodacites by AFC (fractionating plagioclase, amphibole, clinopyroxene, oxides and apatite) and, successively in a shallower reservoir the magma evolve to a rhyolitic composition with a AFC processes characterized by different fractionating phases (plagioclase, biotite, orthopyroxene oxides, apatite and zircon).

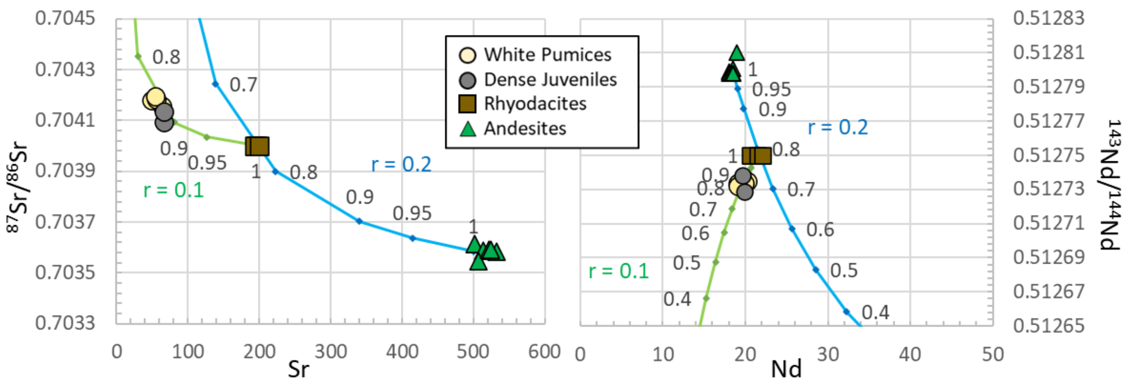

Fig. 3 - Two steps AFC evolution from Andesites to rhyolitic samples. Equations from De Paolo (1981). Blue line is the first AFC step from Andesites to Rhyodacitic compositions, after about 23% of FC and 5% assimilation. Green line is the second AFC step from rhyodacite to rhyolite, after about 10-15% FC and 1-1.5% assimilation; r is the ratio of the mass assimilation rate to the fractional crystallization rate.

CONCLUSIONS

Our data suggest the presence of a complex storage system. We propose that the 1650 CE eruption was fed by two close, shallow rhyolitic reservoirs (possibly set in a crystal mush), receiving different input of mafic melts. These different mafic inputs interacted to various degree with the host rhyolites of the two reservoirs. The early batches of the new melts mixed with the resident ones, whereas the later ones mingled with the rhyolitic magma. A final input of basaltic andesite melts reached both reservoirs and helped the system to reach eruptive conditions. The heterogeneous structures observed in the rhyolitic samples may derive from syn-eruptive conduit processes. White pumices are more vesiculated and show less interactions with mafic inputs, they may represent the shallower portions of the rhyolitic reservoirs. The grey and denser rhyolites may be originated deeper in the reservoirs. Their peculiar vesiculation and microlite-rich groundmass might derive from the slower ascent rate near the wall of the conduit.

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