

Editorial

Editorial for the Special Issue “Minerals of Alkaline Igneous Rocks: Chemical and Isotopic Features as Tracers of Magmatic Processes”

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This Special Issue aims to highlight the pivotal role of the minerals found in alkaline igneous rocks in tracing magmatic processes. In different geodynamic contexts, minerals such as alkali-feldspar and clinopyroxene exhibit a largely variable chemical and isotopic composition. Such a variability can be profitably employed to investigate the evolution processes undergone by magmas during their movement from the mantle source up to the surface, especially when magma evolution occurs in open-system conditions.

One of the most relevant aspects of the minerals of alkaline igneous rocks is that most of them are solid solutions involving several pure components of different composition. This holds for olivine, clinopyroxene, feldspars (including alkali-feldspar and plagioclase solid solutions), black mica, amphibole, as well as several accessory mineral phases of variable composition, such as opaque oxides (including magnetite- and ilmenite-series). In every igneous rock, either plutonic or volcanic, several of these minerals may occur together, in many cases testifying to the achievement of an equilibrium state during the evolution history of the magma. Hence, the chemical composition of minerals coexisting in an igneous rock can yield estimates of the pressure-temperature-oxygen fugacity (P–T–fO₂) conditions established during specific stages of magma crystallization (e.g., [1,2]). Moreover, minerals in alkaline igneous rocks usually host melt and fluid inclusions entrapped during magma differentiation. These inclusions help to acquire useful information on magma pre-eruptive conditions (composition, dissolved volatile content, crystallization depth and equilibration temperature) from which the nature of primary magmas and their source regions, the physical-chemical conditions of magma chambers, the pre-eruptive volatile contents, and degassing processes can be assessed (e.g., [3–9]).

Secondly, the isotopic composition of relevant radiogenic elements, e.g., Sr and Nd, measured in such minerals are additional parameters that may indicate hidden aspects of the magmatic processes under study (e.g., [10–12]). Furthermore, combining the radiogenic and stable isotopic, and chemical composition of minerals may further elucidate the plumbing system of a volcano (e.g., [13–15]) as well as provide information on the Earth’s interior. In this perspective, the minerals of alkaline igneous rocks are precious archives of the history of their host rocks, recording a variety of magmatic processes including closed-system fractional crystallization, and open-system processes such as mingling/mixing among magmas of different composition, and the assimilation of continental crust.

There is an additional aspect of some minerals of alkaline igneous rocks that makes them powerful tracers of magmatic processes that precede the onset of volcanic eruptions, events that may threaten people living in the vicinity of active volcanoes. Diffusion of major and trace elements through the lattice of minerals such as alkali-feldspar, olivine and clinopyroxene yields timescale estimates of several magmatic processes occurring from



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nucleation until the growth of the very last rim of a crystal, providing important insights for volcanic hazard assessments (e.g., [16–22]).

In the Special Issue titled “Minerals of Alkaline Igneous Rocks: Chemical and Isotopic Features as Tracers of Magmatic Processes”, some interesting case studies that apply of the above-mentioned geochemical tools to alkaline igneous rocks are illustrated.

Di Renzo et al. [23] present a detailed study on the clinopyroxenes of lavas of variable ages from Somma-Vesuvius, one of the most well-known volcanoes of Southern Italy. In particular, several single clinopyroxene crystals collected from three lava flows cored in a deep borehole on a flank of the volcano were analyzed using an electron microprobe for major elements and by thermal ionization mass spectrometry for the Sr-isotopic composition. The minerals are rather variable in chemical (Mg# = 92–69) and isotopic ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70681\text{--}0.70781$) composition, suggesting that the magma evolution processes occurred in open-system conditions, due to either magma mixing or crustal contamination. The chemical and Sr-isotopic features of the studied clinopyroxene crystals, integrated with volcanological, geochemical and geochronological data from the literature, imply that a significant change in the eruptive dynamics of Somma-Vesuvius occurred during a period of multiple caldera formation since the Pomici di Base Plinian eruption (ca. 22 ka). The study of Di Renzo et al. [23] illustrated how minerals of igneous rocks may help to improve the knowledge of the past behavior of a dangerous volcano, with the aim of mitigating the volcanic risk in case of the renewal of volcanic activity.

Pelullo et al. [24] combined various equilibrium tests and geothermobarometric methods, which they applied to a suite of Campi Flegrei volcanic rocks and related minerals spanning the activity period from ~59 ka to 1538 A.D. (for a review see [25] and references therein), constituting a large set of mineral and bulk-rock chemistry data from the literature. The aim was to evaluate the reliability of the various methodologies in inferring pre-eruptive magma storage conditions. A first interesting result was the evidence for two “magmatic environments”, each characterized by a prevalent set of P–T conditions of magma storing. One magmatic environment is represented by mafic magmas ponding in a widely distributed, deep crustal reservoir; the other should be envisaged as a series of small-volume, shallow reservoirs, where evolved magmas stagnate. Batches of magmas of variable composition from both environments had the chance to interact several times during the Campi Flegrei history, especially during the past 12 ka, when several tens of eruptions occurred, with variable energies and volumes of emitted magma, including Plinian eruptions. The interaction (i.e., mingling/mixing) among different magma batches at Campi Flegrei was accompanied by other open-system processes such as crustal contamination and CO₂ flushing, as well as the removal of earlier grown crystals from their equilibrium melts. Another important finding of Pelullo et al. [24] was the acknowledgment that using one single geothermobarometer does not constrain with certainty the magma storage conditions. Rather, a combination of various methods provides more reliable P–T estimates that, in the case of the Campi Flegrei complex volcanic system, are in agreement with independent estimates based on petrological and geophysical methods.

An interesting study was carried out by Donato et al. [26] on the heavy mineral fraction of sands from the Ofanto river basin, located in Southern Italy. These sands are made up of mostly clinopyroxene, melanite garnet and amphibole, and subordinate volcanic lithic fragments. In the study, the chemical and Sr-Nd isotopic composition of the variable minerals was used as a “geofingerprint” to identify the volcanic rock source. Most likely, the provenance of such mineral fragments should be found in one of the Quaternary volcanic centers located in Southern Italy, i.e., Mt. Vesuvius, Campi Flegrei, Ischia Island and Procida Island in the Campania region, and Mt. Vulture in the Basilicata region. All these volcanoes were fed by alkaline magmas, either potassic (e.g., [13,27–30]) or sodic (e.g., [31,32]). The Ofanto river basin includes Mt. Vulture and a provenance of the sands from this volcano was likely. In comparison to the products of all the mentioned volcanoes, the combined chemical and isotopic characterization of the Ofanto river heavy minerals highlighted the occurrence of two distinct populations. One population of heavy minerals, separated from

sands of the central and final sectors of the river, shows chemical and isotopic features similar to those of Mt. Vulture volcanic rocks, as expected; the other population, found in sands from the upstream sector of the Ofanto river, exhibits a geofingerprint pointing to a volcanic source located in Campania. An in-depth investigation allowed Donato et al. [26] to suggest Mt. Vesuvius as the most likely source. Another interesting inference of this study concerns the absence of minerals from the Campania volcanoes in the sands of the central and final sectors of the Ofanto river basin. This might be the result of either dilution by the dominant mineral component from Mt. Vulture or the trapping of a large sedimentary load from the river by many dams located along its course.

Another geofingerprint was described by D'Antonio et al. [33] in a detailed characterization of the petrography and mineral chemistry of products of the Monte Epomeo Green Tuff (MEGT) eruption, an explosive volcanic event generated at the Ischia island (Southern Italy) 56 ka ago. The MEGT eruption has, for several decades, been known to have left an ash fall deposit across Southern Mediterranean area, which is one of its main stratigraphic markers and used in many tephrochronological studies (e.g., [34–39]). In most of these studies, the MEGT was usually described as being recognizable by the occurrence of aegirine pyroxene, as initially defined by Keller et al. [34]. The detailed mineral chemistry characterization carried out by D'Antonio et al. [33] instead highlighted that the clinopyroxene present in the MEGT products collected near the vent area on Ischia, which is still variable, never reached the aegirine composition. This feature will help in future studies to discriminate the MEGT deposit in distal outcrops from other aegirine-bearing, distal tephra layers that were erroneously attributed to the MEGT eruption in the literature. Moreover, a more precise attribution of distal tephra layers to either the MEGT eruption or other eruptions generated at Ischia will provide a better definition of the areal distribution of the explosive deposits of the island.

Vlach [40] presents a case-study of crypto- and microcrystalline hydrothermal zircons from peralkaline granites of the Graciosa Province (Southern Brazil). These fine zircon aggregates occur in association with typical hydrothermal minerals, including alkali-feldspars, quartz, fluorite, epidote-group minerals, phyllosilicates, and Fe oxides, filling micro-fractures and tiny miarolitic cavities in the host rock. The author combines morphological and textural features of hydrothermal zircons with the results of their thorough geochemical (major, minor and trace elements) and Lu-Hf isotopic characterization. Peculiar geochemical characteristics of the hydrothermal zircons, namely high amounts of Fe, Al, and Ca, not usually hosted in the zircon lattice, as well as of High Field Strength Elements (HFSE), and Light and Medium Rare Earth Elements, provide evidence for an origin by precipitation from a hydrothermal fluid, which is a result of the interaction between a F- and HFSE-bearing orthomagmatic fluid and a meteoric fluid circulating in the country rocks. The Ti-in-zircon crystallization temperatures of the analyzed magmatic crystals are estimated to be between 772 and 708 °C. The author interprets the obtained temperature range as an upper limit to the granite solidus. Conversely, geothermometry of chlorite from the main syenites provides hydrothermal temperature values in the range of 250–300 °C. These temperatures agree with the available experimental data, which suggest that hydrothermal zircon may precipitate in a large range of temperatures from the solidus down to 150 °C [41,42], and at the temperature at which zircon re-equilibrates as a result of diffusion–reaction processes that may take place even under weathering conditions [43].

An interesting study concerning a thorough chemical characterization of pyrochlore supergroup minerals hosted in alkali granites and syenites of the Boziguoer deposit in Southwest Tianshan, China, is presented by Sun et al. [44]. The Boziguoer Nb (Ta-Zr-Rb-REE) deposit was discovered in 1998 and is currently China's largest Nb deposit. It is also a 'type' example of Nb deposits associated with alkaline magma. The main Boziguoer lithofacies are alkaline granite and syenite, characterized by albite, K-feldspar, quartz, arfvedsonite and aegirine as the main minerals. The Nb of the deposit is mainly hosted in pyrochlore supergroup minerals, which are ubiquitous in both alkaline granite and syenite, and is thought to be the result of magmatic evolution. Sun et al. [44] performed a highly accurate

mineral chemistry investigation and found an unusual mechanism of substitution in these pyrochlore supergroup minerals involving Nb and REE. The authors conclude that the crystallization of pyrochlore supergroup minerals in the differentiating Boziguoer alkaline magma was significantly different from that occurring in other pyrochlore-bearing rocks such as carbonatite and nepheline syenite, playing a role in the Nb enrichment of the Boziguoer deposit.

Kamali et al. [45] carried out mineralogical and mineral chemical characterization of diorite dikes hosting enclaves and loose pyroxene crystals from the Sungun Cu-Mo Porphyry deposit, located in East Azerbaijan (Iran). Like other porphyry copper deposits, formed mostly in subduction-related settings [46], the Sungun porphyry deposit is thought to have developed in a post-collisional environment, and to be related to alkaline magmas [47].

Several distinct minerals (dominant plagioclase, hornblende and biotite; accessory sphene, quartz and apatite) are associated in the diorite enclaves, and their chemistry, along with that of pyroxene crystals, constrained both the nature of magmas and their main thermodynamic parameters. The pyroxene was found to be an igneous augite equilibrated at a large and variable depth (33–45 km), over a wide range of high temperatures (1100–1400 °C), and in highly oxidizing conditions, as suggested by its high ferric iron content. High oxygen fugacity conditions were also detected in the analysis of amphibole, which equilibrated at a much lower temperature (714–731 °C). The results of the investigations led Kamali et al. [45] to infer that the Sangun porphyry magmas and their Cu-Mo ores equilibrated in a sector of the lower continental crust. Studies such as that of the Sangun plutonic rocks and porphyry deposit provide the opportunity to assess petrological and geochemical factors controlling mineralization in post-collisional environments.

In summary, the Special Issue “Minerals of Alkaline Igneous Rocks: Chemical and Isotopic Features as Tracers of Magmatic Processes” describes how the chemical and isotopic features of many of these minerals can be employed for a variety of purposes, including (i) determining P–T–fO₂ conditions of magma cooling, unveiling pre-eruptive magmatic processes and their timescales with critical implications for volcanic hazard assessment; (ii) identifying the provenance and fate of river sands; (iii) constraining the conditions of hydrothermal alteration and the composition of the fluids involved; (iv) reconstructing the behavior through time of the magma plumbing system of complex explosive volcanoes; (v) building useful geofingerprints to identify the volcanic source of tephra layers found in distal outcrops; (vi) understanding the mechanisms of the formation of economic ore deposits.

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