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Petrology and geochemistry of the Crommyonia volcanic rocks north of the Saronic Gulf, Greece

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Introduction

The Saronic Gulf is traditionally regarded as the westernmost part of the present-day South Aegean arc. This continental arc developed from the Pliocene onwards as a result of (1) the northward subduction process of the African plate beneath the Eurasian plate, and (2) slab-rollback of the African plate with respect to the Eurasian plate, which led to regional extension of the continental crust (van Hinsbergen et al., 2005; Jolivet & Brun, 2010). The Pliocene volcanism of the Saronic Gulf ceased in the Pleistocene on the islands of Aegina and Poros, but continued on Methana peninsula into historic times. North-west of the Saronic Gulf is a small volume of volcanic rocks (<1 km³) which are largely deposited along major extensional faults. These Crommyonia lavas have a Pliocene-Pleistocene eruption age which is contemporaneous with volcanism in the Saronic Gulf and coincides precisely with episodes of increased local basin subsidence (Fytikas et al., 1976; Schroder, 1976; Bellon et al., 1979; Collier & Dart, 1991; Pe-Piper & Piper, 2002). Previous studies proposed that the geochemistry of these volcanic rocks could be explained as subduction magmas which experienced a strong degree of assimilation and fractionated crystallization and could therefore be considered as part of the Saronic Gulf volcanics (Fytikas et al., 1986; Pe-Piper & Hatzipanagiotou, 1997). More recently, however, Pe-Piper & Piper (2005) proposed an alternative petrogenesis involving crustal melting based on the similarities in trace element contents and Sr-Nd isotopes between the mid-continental crust and the Crommyonia volcanic rocks. As literature data on the Crommyonia volcanic unit are limited, the here presented study complements the existing petrographic-geochemical database significantly. This new information is used to further elucidate the petrogenetic evolution of the Crommyonia volcanic rocks as well as their relationship to the Saronic Gulf volcanics.

Methodology

A total amount of 43 rock samples, deemed to represent the variations within the Crommyonia volcanic deposits, was collected during fieldwork in July 2014. Sample locations

were selected based on the geological map and the available literature data (Pe-Piper & Hatzipanagiotou, 1997). Thirty-six thin sections were thoroughly examined for their mineralogical and textural content with an Olympus™ BH-2 BHTP polarization microscope. Thirty rock samples were consecutively devolatilized, digested in mineralogical acids and prepared for flux-melting to determine major element compositions with a Varian™ 720 ES Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES) at the Department of Geology, Ghent University. The same rock samples were digested in mineralogical acids for trace element analysis using a Thermo Scientific™ XSeries II Inductively Coupled Plasma – Quadrupole – Mass Spectrometer (ICP-Q-MS) at the Department of Analytical Chemistry, Ghent University. Based on the major and trace element composition of the aforementioned samples, a selection of 16 rock samples was chosen for Sr-Nd-Pb-Hf isotope analysis. Sample powders were digested in mineralogical acids and the considered elements were isolated from their matrix through cation- or anion exchange chromatography. Measurements were performed on a Thermo Scientific™ Neptune Multi Collector – Inductively Coupled Plasma – Mass Spectrometer (MC-ICP-MS) at the Department of Analytical Chemistry, Ghent University for Sr-Nd-Pb isotopes and the Department of Geology and Geochemistry, VU Amsterdam for Hf isotopes.

Results and discussion

The whole rock major and trace element concentrations of the Crommyonia lavas (66-72 wt% SiO₂) plot at the more evolved end of the differentiation trend defined by the Saronic Gulf volcanic deposits (50-69 wt% SiO₂) whose geochemical-petrographic data are collected in Smet (2014). The Crommyonia high-K rhyodacites-rhyolites show similar to higher ⁸⁷Sr/⁸⁶Sr ratios (0.7071 - 0.7139) and Pb isotopic compositions (²⁰⁶Pb/²⁰⁴Pb: 18.76 - 18.88; ²⁰⁷Pb/²⁰⁴Pb: 15.71 - 15.72; ²⁰⁸Pb/²⁰⁴Pb: 39.14 - 39.21), and similar to lower Nd-Hf isotope ratios (¹⁴³Nd/¹⁴⁴Nd: 0.5121 - 0.5122; ¹⁷⁶Hf/¹⁷⁷Hf: 0.2824 - 0.2827) than the Saronic Gulf volcanic deposits. Whole rock compositions and radiogenic isotope geochemistry thus seem to support a petrogenesis as arc magmas with a higher degree of crustal differentiation-contamination. The Saronic Gulf volcanic suite is further characterised by the abundance of mafic enclaves, which are interpreted as relics from a mafic magma that replenished and remobilised a more felsic crystal mush (Smet, 2014). Mafic enclaves are however scarce and very small within the Crommyonia rhyodacites-rhyolites, which implies a distinct difference in the petrogenesis of the two volcanic centres. From a mineralogical point of view, the Crommyonia rhyodacites-rhyolites contain a large variety of continental crust-related minerals (e.g., garnet, sillimanite, muscovite, monazite/xenotime), which are absent in the Saronic Gulf volcanic rocks. Petrographic textures commonly observed within the Crommyonia lavas include resorption features in quartz and K-feldspar (macro)phenocrysts and a combination of sieve textures and reverse zonation patterns in plagioclase (macro)phenocrysts. These textural features suggest the occurrence of a high-temperature process that destabilized the aforementioned mineral phases. We thus favour the hypothesis of Pe-Piper & Piper (2005) that crustal melting was the principal driving mechanism behind the petrogenesis of the Crommyonia rhyodacites-rhyolites. Their magma genesis is however linked to the region's subduction magmatism (cf. synchronicity with volcanism in the Saronic

Gulf), whereas their eruption at the Earth's surface was facilitated by regional extension tectonics (cf. correlation with local faults and basin subsidence). The strong similarity between Hercynian basement paragneiss (Pe-Piper, 2000; Stouraiti et al., 2010) and the Crommyonia rhyodacites-rhyolites in terms of their garnet chemistry, bulk geochemistry and Sr-Nd-Hf isotopic compositions suggests that the former potentially served as the protolith that underwent crustal melting. The significant enrichment in hydrosoluble elements (e.g., Large Ion Lithophile Elements – LILEs, Dotsika et al., 2009) could be representative of interaction between the Crommyonia magmas and hydrothermal fluids, and/or incorporation of hydrothermally altered country rocks, in the upper portions of the crust. Given the above considerations, we propose that the Crommyonia volcanic field needs to be regarded as a volcanic unit which is separate from the Saronic Gulf arc volcanics.

Conclusions

Pliocene to present-day magmatism in the South Aegean Sea is driven by the ongoing subduction of the African plate beneath the Eurasian plate, which resulted in the development of a continental volcanic arc. Petrographic and geochemical characteristics of the Crommyonia rhyodacites-rhyolites suggest that crustal melting processes were the principal driving mechanism behind their petrogenesis. Subduction magmatism did however play a vital role by providing the required amount of heat to produce the crustal melts which were presumably sourced from a Hercynian basement paragneiss. Extensional faulting provided the necessary pathways for the Crommyonia magmas to reach the surface and allowed the percolation of hydrothermal fluids which altered the geochemical and isotopic composition of the upper crust and Crommyonia magmas. We thus conclude that the Crommyonia volcanic deposits are not a part of the active South Aegean arc and are only indirectly linked to the area's ongoing subduction tectonics.

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Characterization and genesis of Cu-Pb-Zn-V-Fe-Mn supergene ore deposits in the area of Bou Arfa (Oriental High Atlas, Morocco)

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Keywords: weathering, calamine, non-sulfide deposits, mottramite, supergene enrichment, Atlas uplift.

Introduction

Renewed interest is shown to supergene ore deposits over the last years. This is mainly due to 1) the high cost effectiveness of these deposits (metal contents are generally 2 to 5 times higher than in hypogene mineralization), 2) the easier and faster extraction process, 3) the softened host rocks, and 4) the location close to the surface (Arndt & Ganino, 2010).

The ore deposits of Jbel Klakh, Jbel Haouanit and Jbel Rhals are located at the northern edge of the Oriental High Atlas (Morocco), close to the city of Bou Arfa. Few studies have been carried out since their closure over the years 1950-1970. Jbel Klakh and Jbel Rhals deposits were mainly mined for their copper mineralization; Jbel Rhals is currently the subject of new prospections. Jbel Haouanit was mined for lead and zinc, and is still exploited by artisanal miners.

Methods and aims

A total of 130 samples have been collected from the three sites. Numerous investigations were carried out: observations with transmission and reflection optical microscopes and with a scanning electron microscope, and X-Ray diffraction analyses. The various mineral phases and their relationships with the host rock and between themselves were characterized, in order to decipher the mineral sequences (parageneses) and their relative chronology. The geochemical analyses highlighted some processes of the ore formation.

Results and discussion

Jbel Klakh

The mineralized veins are located in Jurassic dolomitized host rocks. From the bottom to the top, four zones have been identified, based on the various mineral phases: the hypogene sulfides zone, the secondary sulfides enrichment zone (or cementation zone), the oxidized zone, and the leached zone (or gossan). Chalcopyrite is

the main primary sulfide. Bornite, digenite, chalcocite and djurleite successively precipitated in the secondary sulfides zone, where percolating Cu-rich acidic fluids reached the slightly reduced conditions near and under the water table level (Chávez, 2000; Van Langendonck et al., 2013). Another secondary sulfide, covellite, formed afterwards in some locally Cu-depleted environments. The presence of these sulfides indicates that the buffering capacity of the acidic fluids, by the dissolution of carbonated host rocks, was not sufficient to hinder the fluids from reaching the water table level (De Putter et al., 2010; Decrée et al., 2010). Then, malachite, azurite, brochantite and copper silicates were found in the oxidized zone: they precipitated under near neutral pH conditions. Finally, the leached zone contains the iron oxides and hydroxides.

Jbel Haouanit

The ores are located in Jurassic dolomitized host rocks; primary sulfides are galena and sphalerite. Sphalerite is completely weathered in smithsonite, and later in hydrozincite. Galena is usually weathered in cerussite, but an intermediary, anglesite, may form in local acidic environments, such as in cleavages and fractures (Sangameshwar & Barnes, 1983). The higher resistance of galena to weathering is due to the relatively low mobility of lead in supergene fluids, and to the *in situ* precipitation of the secondary minerals (Reichert & Borg, 2008). The large amount of iron oxides and hydroxides capping the sequence may indicate that pyrite was also a primary sulfide.

Few occurrences of copper mineralizations show veins of chalcocite weathered in covellite, malachite and iron oxides and hydroxides. A Pb-Cu vanadate, mottramite, is also found, associated with dolomite. The occurrence of mottramite highlights that slightly reduced V-rich fluids have circulated in the ores during the weathering (Boni et al., 2007).

Integration of the weathering in the geodynamic context

The High Atlas intracontinental mountain belt is the result of two major events: the Triassic to Liassic rifting which led to the opening of the Atlantic and Tethys Oceans, and the Cenozoic tectonic inversion, caused by the convergence of the African and Iberian plates, and resulting in the uplift (e.g. Mattauer et al., 1977; Frizon de Lamotte et al., 2000; Leprêtre et al., 2015). Those events are of great importance for the genesis of ore deposits. The precipitation of primary sulfides in both Jbel Klakh and Jbel Haouanit deposits is probably related to the Triassic rifting (Choulet et al., 2014). The Cenozoic uplift of the Atlas belt led to the exhumation and fracturing of the series which were then exposed to weathering. Hence, host rocks were dissolved and sulfides were oxidized. The relatively hot arid climate, punctuated with short wet periods, and the fracturing of the rocks may have provided the optimal conditions for the concentration of metals in solution and the precipitation of massive supergene ores.

Jbel Rhals

The Jbel Rhals ores are located in Paleozoic schists capped by Permo-Triassic basalt flows. The mineralization is totally different from the ores described above, and it is difficult to identify the original primary ore. As two types of veins have been observed, a two-step formation sequence has been identified. Most veins are large and contain massive goethite, and dendritic pyrolusite, often developed at the surface of goethite and in cavities. Thin calcite veins have been cutting the large ones; malachite laths grew from the outer edges of the veins to the center. Therefore, the first step is associated with the massive crystallization of goethite, rapidly followed by pyrolusite, while the second is characterized by the precipitation of calcite and malachite.

Conclusion and perspectives

The Jbel Haouanit and Jbel Klakh deposits experienced the same geological ore processes: the hypogene sulfides underwent several periods of weathering related to the High Atlas uplift, resulting in the successive formation of various secondary minerals, i.e. secondary sulfides, oxidized phases (carbonates, silicates, vanadates,...), and finally iron oxides and hydroxides. The

precipitation in the oxidized zones could only occur when the acidity of the fluids was buffered, by the host rock dissolution.

The Jbel Rhals ore deposit is different. Two generations of supergene minerals were identified; their formation may also be related to the High Atlas uplift, but the refined processes were not identified.

New dating of the supergene processes ($^{40}\text{Ar}/^{39}\text{Ar}$ or K/Ar on K-rich Mn-oxides and (U-Th)/He on iron oxides and hydroxides) would provide useful information, to integrate the weathering events in their geodynamical and paleogeographic contexts.

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