MINERALOGICAL, PETROLOGICAL AND GEOCHEMICAL FEATURES OF THE UNIQUE LAPIS LACEDAEMONIUS (KROKEATIS LITHOS) FROM LACONIA, GREECE: APPROACH ON PETROGENETIC PROCESSES WITHIN THE TRIASSIC VOLCANIC CONTEXT

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Abstract

The Lapis Lacedaemonius (krokeatis lithos) is a well-known meta-volcanic rock of great historical importance. Petrographic observations, mineral chemistry data, as well as geochemical analysis of selected samples, reveal that these rocks are porphyritic metabasaltic rocks which have been significantly affected by saussuritization and also by restricted silicification processes. They represent subduction related calc-alkaline volcanic rocks which also appear in the adjacent Hellenic Triassic volcanic outcrops, and appear to be associated with the rift/drift phase within the Pindos oceanic realm. The unique features of the Lapis Lacedaemonius, when compared to geochimically similar volcanic rock outcrops, are mainly attributed to their distinct porphyritic textures, predominantly with microlithically textured groundmass along with the coarse grained plagioclase, and to saussuritization processes. The Lapis Lacedaemonius seems to have been formed in a sub-volcanic system closely associated with epidotes, suggesting that metasomatism occurred within hydrothermal upflow zones.

Keywords: Lapis Lacedaemonius, Krokeatis lithos, Saussuritization, Subduction, Triassic volcanism.

Περίληψη

Ο Κροκεάτης Λίθος είναι ένα έντονα γνωστό μετα-ηφαιστειακό πέτρωμα με μεγάλη ιστορική σημασία. Οι πετρογραφικές παρατηρήσεις, οι ορυκτοχημικές δεδομένες καθώς και οι γεωχημικές αναλύσεις επιλεγμένων δειγμάτων, δείχνουν ότι το πέτρωμα αυτό είναι πορφυρικός ηφαιστειακός ο πορφυρικός του εκφραστής, οι ηφαιστειακές διαδικασίες καθώς και οι αναλυτικές σημασίες τους. Η καταλληλότητα του Κροκεάτης Λίθου σε υδροθερμικές περιοχές συνδέεται με την διάκριση του ειδικού πορφυρικού της στέγης, καθώς και με τη διακρίσιμη αναλυτική της. Αποτελεί ένα ενισχυμένο ηφαιστειακό πλημμυρισμό, συνδεόμενο με την αναλυτική του διακρίσιμης καταλληλότητα, τον πορφυρικό και τον ειδικό πορφυρικού, την αναλυτική της διακρίσιμης καταλληλότητα. Οι αναλυτικές δεδομένες συνδέονται με την διακρίσιμη της διακρίσιμης καταλληλότητα.
1. Introduction

Lapis Lacedaemonius (Krokeatis lithos) is a well-known volcanic rock since the ancient times. Although it was very difficult material to process, in antiquity it was used for the manufacture of vases, seals, and for the decoration of buildings. It is referred by Pausanias who noted the outcrops locality, as well as its importance in ancient times, since it had been used as raw material since the Minoan period. Later on, the Romans largely extracted this stone for decorative elements. Few of the noteworthy monuments where the Lapis Lacedaemonius has been found are: the ancient acropolis of Mycenae, the palace of King Minos (Knossos, Crete), the baths next to the temple of Poseidon (Corinth), Basilica of Saint Peter, (Rome), Agia Sofia church (Constantinople), Westminster Abbey (London), the ruins of ancient Pompeii and Saint Marc church (Venice). Consequently, it is known with several names; Krokeatis lithos, Porfido verde antico, Marmor Lacedaemonium, Spartan basalt, green stone from Taygetus, Green Porphyry, Viride or Porfido serpentino verde, Krokeischer Stein (e.g. Zezza and Lazzarini, 2002; Wilson, 2013; Kokkorou-Alevra, 2014). The only known occurrence of Lapis Lacedaemonius is near the village of Krokees (old name Levetsova) in Laconia, Northern Southern Peloponnese.
From a geologic aspect, this metavolcanic rock occurrence is part of the Triassic volcanism, which is widespread throughout the mainland of Greece, as part of the Sub-Pelagonian Zone. These volcanic occurrences, which mostly include pillow lavas and massive flows, are associated with the rift/drift phase within the Pindos oceanic realm. In the past, several studies were conducted focusing mostly to the entire Triassic volcanism of the area (Panagos, 1979; Thiebault, 1982; Pe-Piper et al., 1982; Gerolymatos, 1994; Pe-Piper and Piper, 2002). The current study aims to characterize mineralogically and geochemically the Lapis Lacedaemonius (Krokeatis lithos), in an attempt to interpret from a geological scope the reasons for its uniqueness and its absence in other Triassic volcanic localities. In order to accomplish the aforementioned, scientists with different scientific specialization have collaborated to achieve a multidiscipline approach.

2. Geological Setting

Lapis Lacedaemonius is an altered porphyritic basaltic rock which occurs near the village of Krokees (Fig. 1) and is considered as being part of the rift/drift related Triassic volcanism of the Hellinides, which in geotectonic terms may be considered as part of the Sub-Pelagonian Zone (Sharp and Robertson, 2006). The Triassic nappes in the region are termed as the Phyllite-Quarzite Series (Thiebault, 1982; Pe-Piper and Piper, 1991, 2002). These include Paleozoic to Early Triassic pelagic brecciated limestones/marbles and metasedimentary rocks (phyllites, metaconglomerates, metasandstones). The overlaying Tyros beds, mostly exposed in Lakonia, comprise a volcanic and sedimentary sequence, which includes altered basaltic/andesitic pillows, thick pyroclastic series, as well as minor basaltic, dacitic or rhyolitic massive flows and hypabyssal intrusions, while the sedimentary rocks include minor dolomite, sandstone and shale fragments (Gerolymatos, 1994; Pe-Piper and Piper, 2002 and references therein). This nappe is locally conformably overlain by Triassic limestone, passing up into the Tripolitsa limestone (Thiebault, 1982). The volcanic rocks in Lakonia and subsequently in Krokees are basaltic rocks that have undergone low-grade metamorphism (Fig. 2) and are often accompanied by epidotes, which formed by pervasive alteration of the basalts. These volcanic rocks lack significant penetrative deformation features (Thiebault, 1982; Gerolymatos, 1994).

3. Materials and Methods

Thin polished sections were made from three selected samples and examined by transmitted light microscopy and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), using a JEOL JSM 5600 scanning electron microscope, equipped with an automated energy dispersive analysis system ISIS 300 OXFORD, with the following operating conditions: 20 kV accelerating voltage, 0.5 nA beam current, 20 s time of measurement and 5 μm beam diameter. The spectra were processed using the ZAF program (3 iterations). The mineralogical composition of the samples was also investigated by powder X-ray diffraction (XRD). The XRD study was carried out using a Philips X'Pert Panalytical X-ray diffractometer, operating with Cu radiation at 40 kV, 30 mA, 0.020 step size and 1.0 sec step time. The XRD patterns were evaluated using the DIFFRACplus EVA software v.11 (Bruker-AXS, USA) based on the ICDD Powder Diffraction File (2006). Part of these three samples were pulverized to <200 mesh in an agate mill and were digested with a mixture of HCl-HNO₃-HF acids and was analyzed for a series of trace elements by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-MS) and a series of major elements by X-ray fluorescence (XRF). All samples were analyzed at the Laboratories of the Institute of Geology and Mineral Exploration (I.G.M.E.).

4. Results and Discussion

4.1. Petrography and mineral chemistry

The Lapis Lacedaemonius samples consist of altered prismatically lath-shaped subhedral plagioclase phenocrysts, with their size reaching up to 2 cm, as well as of a groundmass exhibiting microphitic or symplectitic textures (Fig. 3). Based upon petrographic observations (Fig. 3), XRD peak patterns (Fig. 4) and mineral chemistry (Table 2), it is determined that the groundmass consists
mainly of albite, clinopyroxene, epidote, magnetite, quartz, titanite and rare devitrified glass composed of chlorite. In particular, clinopyroxene grains are found only within the groundmass and are classified as augite, exhibiting moderate TiO$_2$ (0.35-0.72 wt. %), Al$_2$O$_3$ (1.75-2.28 wt. %) and low Na$_2$O and Cr$_2$O$_3$ contents (representative analyses in Table 2). The groundmass along with the coarse grained plagioclase crystals forms characteristic porphyritic and also glomeroporphyritic textures. The medium to coarse grained plagioclase crystals have undergone extensive saussuritization processes, including albite/oligoclase relics, epidote, pumpellyite, sericite, quartz and magnetite. Epidote and prehnite, pumpellyite are more frequent within the cores of the former basic plagioclase feldspars but they also appear within the groundmass. The occurrence of epidote, pumpellyite, prehnite, pumpellyite and sericite strongly suggests that these rocks underwent low-grade metamorphic/metamorphic processes. Despite the prevailing metasomatism, metamorphic degrees are restricted, which is confirmed by the absence of secondary amphibole. Secondary amygdales (1-2 mm) are filled with mixtures of epidote, chlorite, pumpellyite and rarely calcite (Figure 3B, C).  

Table 1 - Representative microanalyses of Lapis Lacedaemonius samples.

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Note: PL: plagioclase; Ab: albite; An25: oligoclase; Cpx: clinopyroxene; Ep: epidote; Ser: sericite; Chl: chlorite; Mag: magnetite; Pmp: pumpellyite; Prh: prehnite; Qtz: quartz; Aug: augite.
Figure 3 - Photomicrographs and back-scattered electron (BSE) images of Lapis Lacedaemonius samples; (A) Altered plagioclase phenocrysts within the micritic groundmass; (B) Altered plagioclase phenocrysts and amygdale within the groundmass; (C) Amygdale within the groundmass. (D) Micritic groundmass area; (E) Altered plagioclase phenocrysts with relict albite; (F) BSE image within the center of the plagioclase phenocryst.
4.2. Whole-rock geochemistry

Rock classification of the studied metavolcanic Lapis Lacedaemonius (Krokeatis lithos) samples was based upon the binary diagram of Winchester and Floyd (1977), modified by Pearce (1996), which incorporates relatively immobile elements, since Lapis Lacedaemonius have been affected by low-grade metamorphic and metasomatic processes. Based upon this diagram (Fig 5A) and on their petrographic features, samples are classified as porphyritic basalts. These rocks are regarded by many authors (e.g. Pe-Piper et al., 1982; Zezza and Lazzarini, 2002) as porphyritic andesites. However, this classification has been based upon their silica and alkali contents that were affected by metamorphic and metasomatic processes. On a volatile free basis, the rocks of this study have relatively high Al₂O₃ contents (19.39-19.93 wt. %), as well as rather high TiO₂ (0.84-0.89 wt. %) and low MgO (3.45-3.68 wt. %) contents. Their TiO₂ contents, as well as their relatively high FeO/MgO ratio values (2.35-2.37), can classify them as being Fe-Ti-rich, based upon the criteria of Melson et al. (1976) and Sinton et al. (1983) (FeO/MgO>1.75). Their relatively high SiO₂ contents (53.33-54.24 wt. %) and the occurrence of CIPW normative quartz, would classify these rocks as andesites, however, this is most likely the result of restricted silification, as confirmed from the petrographic observations. Their geochemical character can be regarded as transitional calc-alkaline, as shown on the Y vs. Zr binary plot (Fig. 5B).

Their MORB-normalized MREE and HREE patterns are subparallel (0.66-1.90 and 0.50-0.77×MORB respectively; Fig. 5C), while their LREE are moderately enriched ([La/Yb]MORB=0.66-1.90) (Fig. 5C). Eu anomalies vary from moderate to significant negative ([Eu/Eu⁰]=0.66-0.84) which may be due to plagioclase fractionation, changes in fO₂ conditions or crustal contamination of the source. The Middle to Upper Triassic calc-alkaline rocks from Lakmon (Pindos region), Gionna (Central Greece), Glykomilia (Kozakas region) (Magganas et al., 1997; Pomonis et al., 2004), South Othris (Koutsovitis et al., 2009), as well as from the eastern and south-western Peloponnese region (villages of Platano and Kokkino respectively) (Pe-Piper and Piper 1991, 2002) show similar and subparallel REE patterns, although the latter seem to be more comparable. On the other hand, the MORB-normalized incompatible trace element patterns (Fig. 5D) reveal that Th and K have higher normalized values than Nb and Ta. Zr exhibits significant negative anomalies, while Ti shows moderate negative anomalies. Furthermore, the incompatible Cs and Rb are relative to other elements enriched. The calc-alkaline rocks from the referred adjacent localities present comparable enrichments and depletions, especially regarding the immobile elements.
4.3. Geotectonic and Mantle source interpretations

In the MORB-normalized incompatible trace element patterns of the studied samples (Fig. 5D), the higher normalized values of Th and K relative to Nb and Ta most likely account for influence of subduction or crustal contamination processes (Pearce and Peate, 1995). Negative HFSE anomalies, such as those of Ti and Zr, most often point to supra-subduction zone magmas (e.g. Saunders et al., 1991; McCulloch and Gamble, 1991). Similar assumptions can be inferred from the LILE Cs and Ba enrichments; however, secondary processes most likely affected their original magmatic values. The Ti–V–Sm ternary discrimination diagram (after Vermeesch, 2006; Fig. 5E), which incorporates immobile elements, clearly suggests that subduction related processes had a significant effect during rock formation. Similar assumptions can be made from the binary diagram of Th/Yb vs. Nb/Yb (Fig. 5F), in which the studied samples plot above the MORB-OIB mantle array, but also from the strikingly low Nb/Th ratio values, which are below the value of 4, characterizing arc-related rocks (Sun and McDonough, 1989). From the same binary diagram, apart from the effect subduction, it seems that the samples were derived from an enriched mantle source.

The occurrence of alkaline and E-MORB lavas along with the calc-alkaline basalts and trachyandesites in Triassic localities in Greece, such as in Pindos (Pe-Piper and Piper, 2002; Pe-Piper et al., 2004), Koziakas (Magganas et al., 1997; Pomonis et al., 2004) and South Othris (Koutsovitis et al., 2012), further supports this assumption. In addition, the Zr/Nb ratios of the studied samples, which are almost independent from fractional crystallization and slab dehydration processes (e.g. Thirlwall et al., 1994; Pearce and Peate, 1995; Kamber and Collerson, 2000), may provide information concerning the nature of the mantle source. In particular, their Zr/Nb ratios range between 10.9 and 15.2, which may be considered as very low, pointing to derivation from an enriched mantle source. This enriched source is most likely linked to the Early Triassic upwelling of plume-related asthenospheric OIB melts, shown by the high estimated mantle potential temperature (~1,370°C; Magganas and Koutsovitis, 2015). Addition of slab related sedimentary components seems to have also taken place as implied by the relatively high Th/La ratios (0.25-0.41) (Plank, 2005). A plausible scenario to interpret the geotectonic setting for the formation of the Triassic studied rocks, as well as other comparable Triassic calc-alkaline lavas, is the occurrence of intra-oceanic local compressional tectonics, possibly related with a breakup of the early formed oceanic crust forming an infant subduction zone. This scenario has successfully interpreted the unusual Triassic ultramafic-mafic-felsic suite in Othris (Koutsovitis et al., 2012).

4.4. Unique features of the Lapis Lacedaemonius

The question which obviously arises is what are the reasons for the unique appearance of the Lapis Lacedaemonius (Krokeatis lithos) and why is it absent in other Triassic volcanic localities. The fact that this rock occurrence presents obvious geochemical similarities with other Triassic calc-alkaline volcanics reported throughout the Hellenic mainland, makes it even more difficult to interpret. Small differences in their chemistry and possibly variability in the influence of subduction or sediment components cannot explain this alone. What makes the Lapis Lacedaemonius unique compared to the other Triassic calc-alkaline volcanic rocks is the absence of K-feldspar, the presence of fewer clinopyroxene crystals and the higher modal composition of the groundmass, the larger in size plagioclase phenocrysts, the silicification processes and also the infrequency of calcite in comparison to sericite. The most reasonable explanation that can be given is related to the fact that the other Triassic calc-alkaline volcanic rocks appear mostly in the form of pillow lavas, whereas the Lapis Lacedaemonius seems to be part of a subvolcanic suite. Thus, large sized plagioclase crystals were most likely formed in relatively deeper levels before being brought to shallower levels by a differentiated melt. Their association with epidotes in veins and crosscutting intrusions indicates that metasomatism occurred within hydrothermal upflow zones, comparable to those occurring in sheeted dykes of SSZ ophiolites (Banerjee et al., 2000; Gillis, 2002).
Figure 5. Lapis Lacedaemonius samples plotted on the: (A) Zr/Ti vs. Nb/Y diagram (Winchester and Floyd, 1977, modified by Pearce, 1996). (B) Y (ppm) against Zr (ppm) diagram (Barrett and Maclean, 1999). (C) MORB-normalized REE patterns. (D) MORB-normalized incompatible trace element patterns [normalization factors after Pearce and Parkinson (1993)]. (E) Ti–V–Sm diagram (after Vermeesch, 2006); (F) Th/Yb vs. Nb/Yb diagram (after Pearce, 2008). Triassic cale-alkaline volcanic rocks from Kozakas (Magganas et al., 1997; Pomonis et al., 2004), South Othris (Koutsovitis et al., 2009), Pindos (Lakmon) and Giona Mountain (Pe-Piper and Piper, 1991, 2002), Peloponessos (Messinia–Kokkino, Arcadia–Platanos villages) (Pe-Piper and Piper, 1991, 2002) are shown.

5. Conclusions

The Lapis Lacedaemonius (Krokeatis lithos) is a meta-volcanic rock of great historical importance. Its impressive and unique appearance was known even since the Minoan period and was used throughout ancient and medieval times as a raw material source. The studied samples reveal that...
Lapis Lacedaemonius is a subduction affected, transitional calc-alkaline basalt, formed during the Triassic volcanic period.

They exhibit many similarities compared with other Triassic calc-alkaline volcanic rocks from adjacent localities, showing that they were formed after interaction between E-MORB type volcanism and subduction related processes. Their differences which make the Lapis Lacedaemonius unique are mostly petrographic, accommodating higher modal plagioclase phenocrysts and micritic groundmass, both affected by saussuritization and restricted silicification processes, as well as the absence of clinopyroxene phenocrysts. It seems to have formed in a subvolcanic system closely associated with epidotes in the area, indicating that metasomatism occurred within hydrothermal upflow zones. In order to confirm these assumptions a more detailed study is anticipated in the short future so as to further investigate and unravel these processes.

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7. References


