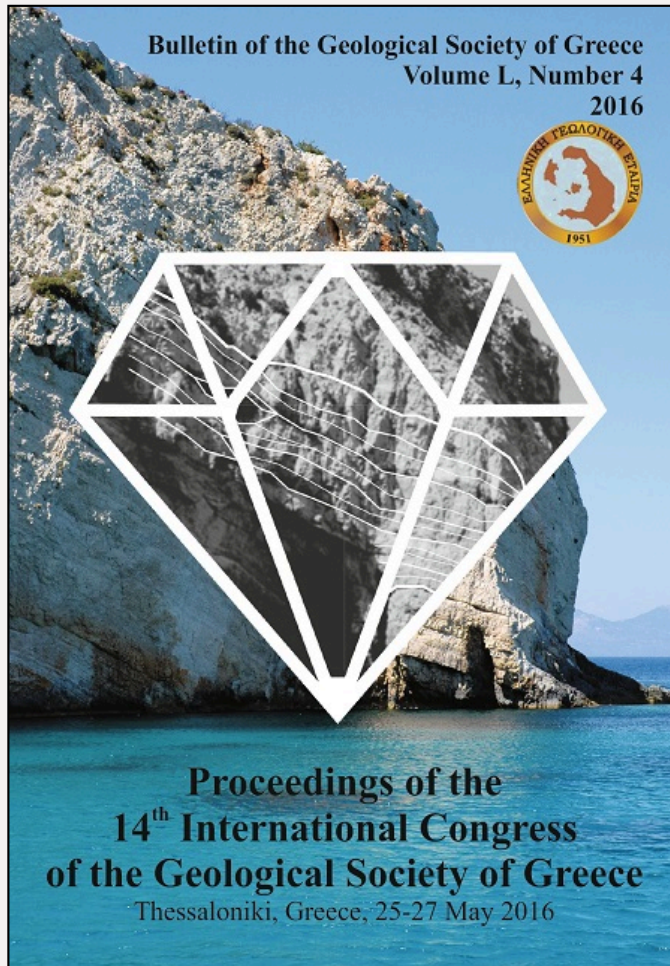


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PRELIMINARY SPECTROSCOPIC STUDY OF FE-BEARING CLAY MINERALS IN ALTERED PILLOW LAVAS FROM LAMIA AREA, GREECE¹

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Abstract

Geological material, of greenish color, filling interspaces in altered Triassic pillow lavas of Lamia area (central Greece) was studied, for the first time in the literature. According to XRD and SEM-EDS data it predominantly consists of calcite, zeolites and clay minerals. The zeolites concern thomsonite and analcime. The clay minerals, on the basis of XRD, FTIR and Mössbauer spectroscopic measurements, constitute a Fe-bearing phase of the illite-glaucanite-celadonite group (most likely Fe-illite).

Keywords: Altered pillow lavas, clay minerals, iron, Mössbauer spectroscopy.

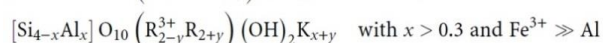
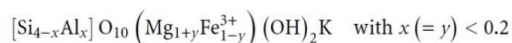
Περίληψη

Γεωλογικό υλικό, πρασινωπού χρώματος, το οποίο απαντά σε εξαλλοιωμένες μαξιλαροειδείς λάβες του Τριασικού στην περιοχή της Λαμίας, μελετάται για πρώτη φορά στη βιβλιογραφία. Σύμφωνα με τα δεδομένα XRD και SEM-EDS αποτελείται κυρίως από ασβεσίτη, ζεολίθους και ορυκτά της αργίλου. Από την ομάδα των ζεολίθων, απαντούν τομσονίτης και ανάλκιμο. Τα ορυκτά της αργίλου, σύμφωνα με XRD και φασματοσκοπικές μετρήσεις FTIR και Mössbauer, συνιστούν Fe-ούχα φάση της ομάδας ιλλίτη-γλαυκονίτη-σελαδονίτη (πιθανότατα Fe-ιλλίτη).

Λέξεις κλειδιά: Μαξιλαροειδείς λάβες, ορυκτά της αργίλου, σίδηρος, φασματοσκοπία Mössbauer.

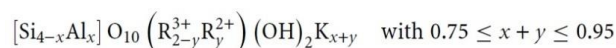
1. Introduction

Iron-bearing clay minerals mainly concern Fe-illite, glaucanite and celadonite (e.g. Buckley *et al.*, 1978; Bailey *et al.*, 1980; Odin *et al.*, 1988; Martin *et al.*, 1991; Meunier, 2005; Zhukhlistov, 2005; Drits *et al.*, 2010). According to the international clay nomenclature (AIPEA committee), celadonite and glaucanite are dioctahedral micas with the following general composition:



¹ Part of the the BSc Thesis of B.K.

Glaucosite is a low-temperature mica that grows at the sediment-seawater interface (the term glaucosity indicate the green pellets either rounded or retaining the form of bioclasts: sponge spicules, foraminifer shells etc). Celadonite-group minerals are extensively occurring in deep-sea floor basalts, such as those sampled in the present study. Fe-bearing (ferric) illites, glaucosite micas, and hyperaluminous glaucosites do not grow in the marine environment like glaucosity but in a continental environment in salt lakes or lagoons, as well as in arid soils. The layer charge of Fe-illites varies from 1 to 0.7 per Si_4O_{10} . The charge originates both in the tetrahedral sheet by substitutions of Al for Si and in the octahedral sheet by substitution of bivalent elements R^{2+} (Mg, Fe^{2+}) for trivalent elements R^{3+} (Al, Fe^{3+}). The iron content ($\text{Fe}^{3+} + \text{Fe}^{2+}$) varies between 0.5 and 1 ion per half unit cell. The presence of a continuous solid solution domain between Fe-illites and glaucosites seems unlikely for crystallographic reasons. In fact, the exact chemical composition of illites is somewhat difficult to define, despite the plenty of data in the literature. Subsequently, under the term "illite" are hidden various phases, according to whether they are defined by X-ray diffraction criteria only (absence of expandable sheets) or by a combination of criteria (XRD, morphology, composition). The general formula unit of an illite is the following:



This formula can be distinguished from that of glaucosites whose charge is predominantly octahedral. There is apparently no continuous solid solution, as mentioned above, between illite and glaucosite. In general, illites form in different natural environments: weathering environments, geothermal fields, and diagenetic environment. The scope of the present paper was a first attempt to characterize, mainly by means of Mössbauer spectroscopy, Fe-clays occurring as interpillow greenish material, together with zeolites, in Triassic pillow lavas in the area north of Lamia city, central Greece (e.g. Pe-Piper and Piper, 2002; Barth, *et al.*, 2003; Barth and Gluhak, 2008; Tsikouras *et al.*, 2008; Koutsovitis *et al.*, 2012). These parent rocks are actually basalts (Figure 1).

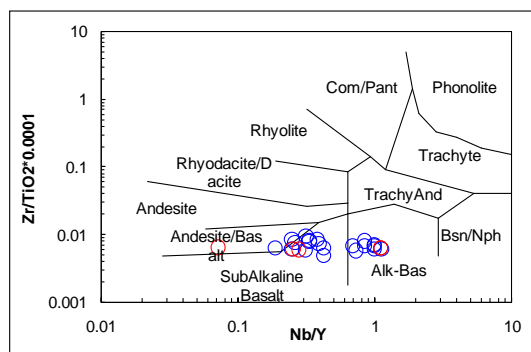


Figure 1 - Discrimination of the parent rocks using analytical data by Tsikouras *et al.* (2008) and Barth and Gluhak (2009).

2. Materials and Methods

The geological material, examined in the present study, was sampled in Triassic pillow lavas occurring in the area north of Lamia (Figure 2). A portion of the material was embedded in epoxy resin and polished, in order to be examined by Scanning Electron Microscope with Energy Dispersive Spectrometer (SEM-EDS). Moreover, the "white" part of the material as well as the greenish part, were carefully separated using an optical stereomicroscope and further pulverized for powder-XRD (PXRD), Fourier-Transform Infrared Spectroscopy (FT-IR) and Mössbauer spectroscopy investigation.

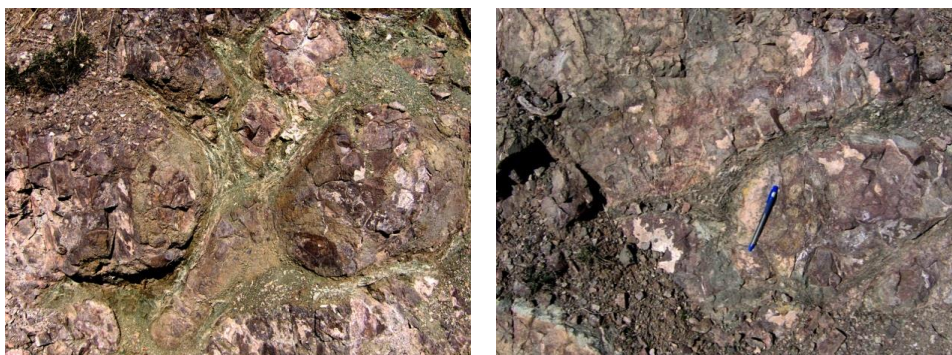


Figure 2 - Altered pillow lavas and the greenish interpillow clayey material.

The PXRD patterns were recorded by means of a Siemens D5005 (Bruker AXS) using $\text{CuK}\alpha$ radiation. The SEM-EDS investigation was carried out using a Jeol JSM-5600 microscope equipped with an Oxford EDS. The FT-IR spectroscopic measurements were performed using a Perkin Elmer Spectrum One spectrometer in the frequency range $4000\text{--}450\text{ cm}^{-1}$, at 2 cm^{-1} resolution, using KBr pellets. The Mössbauer spectra, of the previously characterized Fe-clays, were obtained using a Bruker ER-200D spectrometer at the Institute of Materials Science of NCSR "Demokritos" (Athens, Greece).

3. Results and Discussion

The PXRD of the initial interpillow material, containing both "white" and greenish phases, showed the presence of calcite, zeolites (analcime) and clays of the celadonite group (Figure 3). A further investigation of the "white" part of the material revealed the presence of more zeolite group minerals, namely thomsonite (Figure 4). The presence of zeolites in altered basalts is rather common in the literature (e.g. Keith and Staples, 1985). More detailed study of the separated greenish clayey part of the material proved the existence of illite-glaucanite-celadonite group clay minerals (Figure 5). The chemical composition, and particularly the increased Fe-content of the clays, prior to spectroscopic study, was confirmed by the SEM-EDS investigation (Figure 6). It should be mentioned that it was rather unfeasible to determine the exact phase by conventional SEM-EDS, due to the nature of the clayey material limiting the application of precise microanalyses. That was attempted, after the FT-IR characterization, by cautious Mössbauer spectroscopic measurements.

The FT-IR spectra of the greenish clayey material (Figure 7) showed a peak at 3578 cm^{-1} , featuring the hydrous components (O-H bonds) of Fe-clays and possibly of celadonite. Another characteristic peak at 1000 cm^{-1} is common in many silicate minerals, including Fe-clays, whereas the lack of a peak at 800 cm^{-1} is probably an indication of celadonite (e.g. Slonimskaya *et al.*, 1986 and references therein). Nevertheless, it was not clearly stated, as in the case of SEM-EDS investigation, the exact phase in concern.

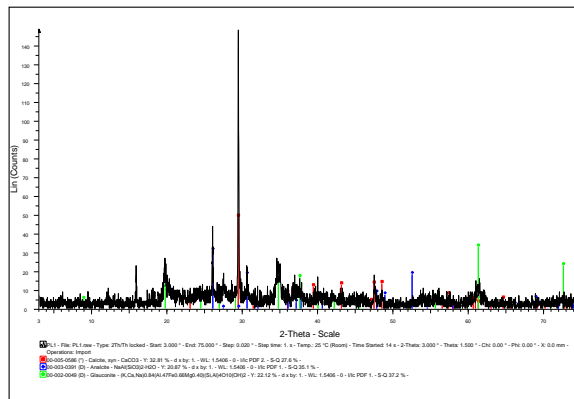


Figure 3 - PXRD pattern of the interpillow material.

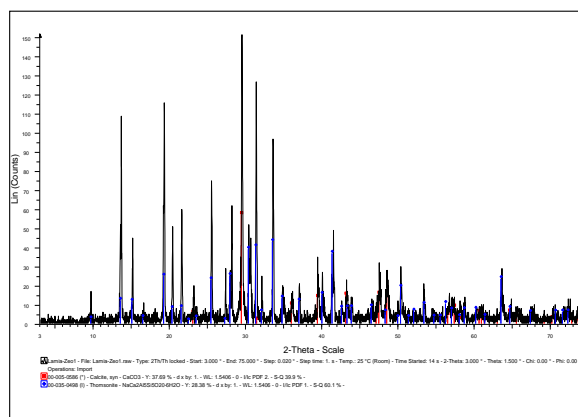


Figure 4 - PXRD of the "white" part of the material.

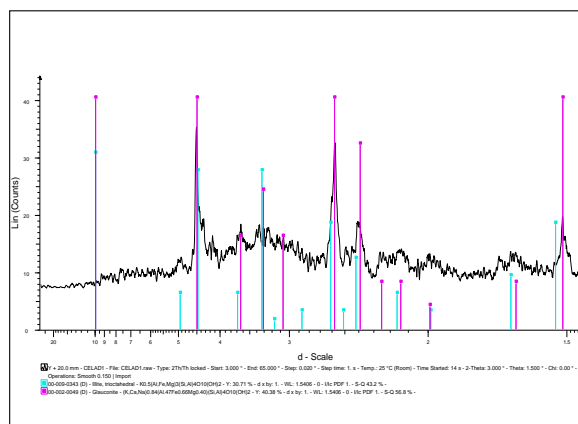


Figure 5 - PXRD of the separated greenish clayey part of the material.

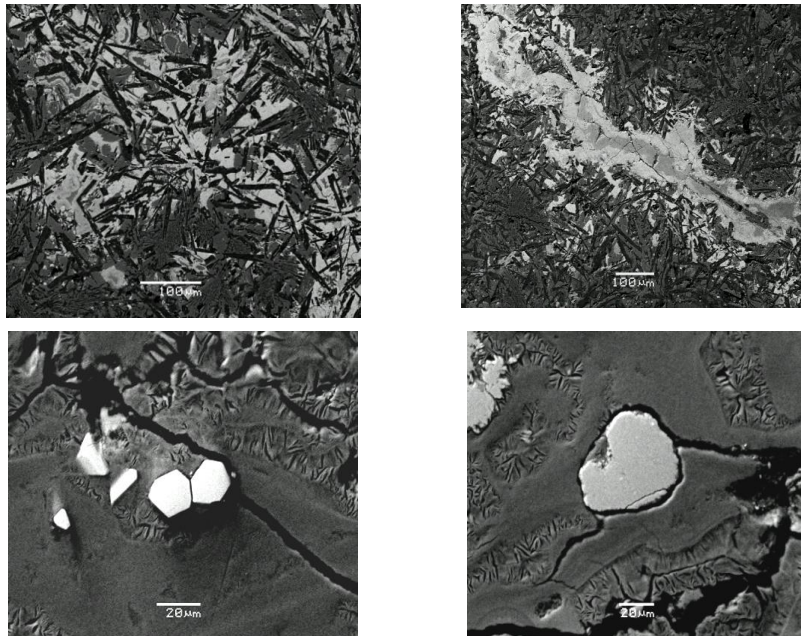


Figure 6 - SEM-EDS data concerning the studied material. Upper left: fresh parent rock; upper right: altered micro-zone containing Fe-oxides/oxyhydroxides; lower left & right: Cr-spinel crystals included into the Fe-clay phase.

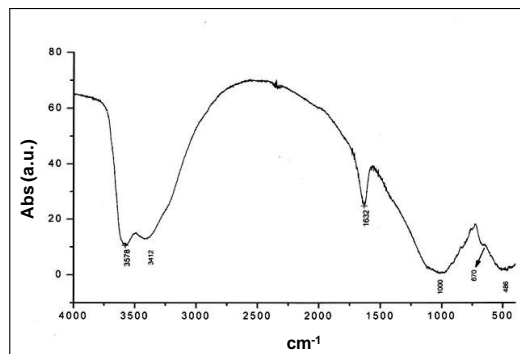


Figure 7 - Representative FT-IR spectrum of the greenish clayey material.

In the subsequent Mössbauer study, it was indicated, for first time in the literature, that the Fe-clays from Lamia altered pillow lavas contain 92% Fe^{3+} and 8% Fe^{2+} and may be Fe-illites than celadonites (Figure 8; Table 1; Figure 9; e.g. Dainyak and Drits, 1987 and references therein; Drits *et al.*, 1997 and references therein; Dyar *et al.*, 2006 and references therein). In particular, the Mössbauer spectra show two quadrupole splitting peaks, where $\delta=0.36$ mm/s and $\Delta E_Q=0.58$ correspond to Fe^{3+} and $\delta=1.15$ and $\Delta E_Q=2.57$ correspond to Fe^{2+} . It should be mentioned, that the above preliminary data, regarding nature of the Lamia Fe-clays, are going to be supported by further research, including X-ray Absorption Spectroscopy measurements in the Fe *K*-edge and Transmission Electron Microscopy (TEM).

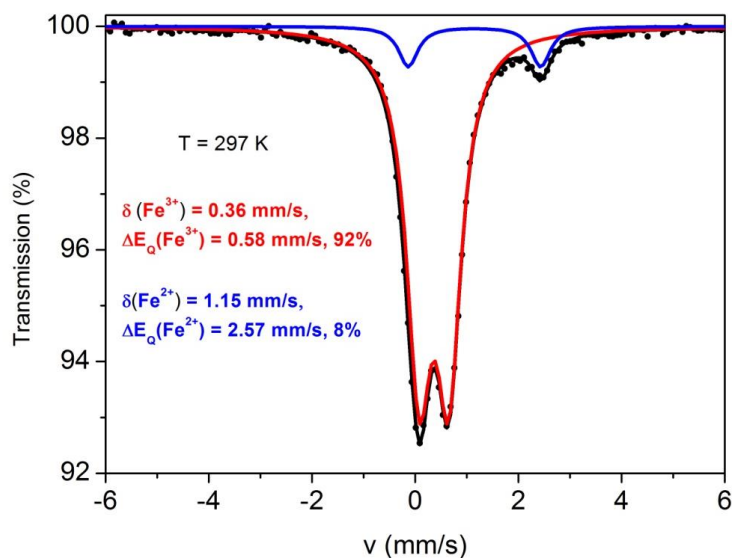


Figure 8 - Mössbauer spectrum of the greenish clayey material.

Table 1 - Fe³⁺ and Fe²⁺ content and Fe³⁺/Fe²⁺ ratios in Fe-illite-glaucanite-celadonite group clay minerals (Bailey *et al.*, 1980; Odin *et al.*, 1988; Martin *et al.*, 1991; Meunier, 2005; Zhukhlistov, 2005; Drits *et al.*, 2010; Dainyak and Drits, 1987 and references therein; Drits *et al.*, 1997 and references therein; Dyar *et al.* 2006 and references therein). 1: Celadonite; 2: Celadonite; 3: Glaucanite; 4: Glaucanite; 5: Celadonite; 6: Fe-illite; 7: Glaucanite; 8: Glaucanite; 9: Fe-illite; 10: Fe-clay from the present study.

Number	Fe ³⁺	Fe ²⁺	Fe ³⁺ %	Fe ²⁺ %	Fe ³⁺ /Fe ²⁺
1	0.96	0.26	78.69	21.31	3.69
2	1.15	0.36	76.16	23.84	3.19
3	0.93	0.21	81.58	18.42	4.43
4	0.89	0.18	83.18	16.82	4.94
5	0.58	0.46	55.77	44.23	1.26
6	0.74	0.07	91.36	8.64	10.57
7	1.10	0.12	90.16	9.84	9.17
8	0.79	0.10	88.76	11.24	7.90
9	0.41	0.13	75.93	24.07	3.15
10	-	-	92.00	8.00	11.50

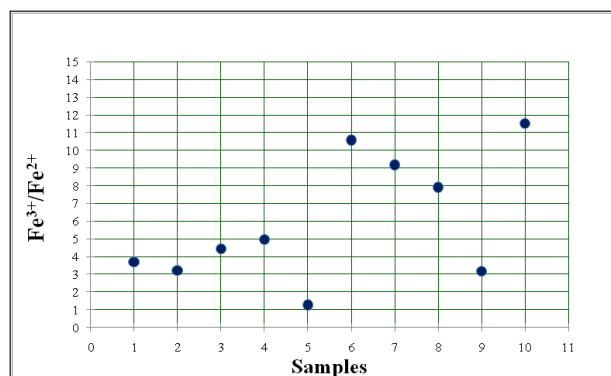


Figure 9 - Fe³⁺/Fe²⁺ ratios in Fe-illite-glaucanite-celadonite group clay minerals on the basis of chemical analyses and Mössbauer spectroscopic data (see Table 1).

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