BGSG

Volume 56

Research Paper

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DOI number:
http://dx.doi.org/10.12681/bgsg.20706

Keywords:
Clinoptilolite, fibrous zeolites, mordenite, analcime. phillipsite, chabazite, quartz, clay minerals

Citation:
Filippidis A., Kantiranis N., Mytiglaki C. and Tsirambides A. (2019), The Mineralogical Composition of Samos Zeolitic Rocks and Their Potential Use as Feed Additives and Nutrition Supplements. Bulletin Geological Society of Greece, 56, 84-99.

Publication History:
Received: 30/06/2019
Accepted: 03/04/2020
Accepted article online: 06/04/2020

The Editor wishes to thank two anonymous reviewers for their work with the scientific reviewing of the manuscript and Ms Emmanouela Konstantakopoulou for editorial assistance.

THE MINERALOGICAL COMPOSITION OF SAMOS ZEOLITIC ROCKS AND THEIR POTENTIAL USE AS FEED ADDITIVES AND NUTRITION SUPPLEMENTS

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Abstract

Fifteen (15) zeolitic rocks from Karlovassi-Marathokampos basin of Samos Island (Greece) were investigated for their mineralogical composition by X-Ray Diffraction (XRD) method. According to EU Regulation No 651/2013, clinoptilolite of sedimentary origin with ≥80 wt% clinoptilolite, ≤20 wt% clay minerals, free of fibres and quartz, can be used as feed additive for all animal species. Depending on the zeolites, the zeolitic rocks are grouped to those containing: Clinoptilolite (33-86 wt%), clinoptilolite (59 wt%) + mordenite (20-21 wt%), clinoptilolite (22 wt%) + analcime (29 wt%), clinoptilolite (17 wt%) + phillipsite (27 wt%), analcime (29-70 wt%), mordenite (62%) and chabazite (63 wt%). None of the clinoptilolite-containing rocks (10 samples) meet the requirements of the EU Regulation No 651/2013, and thus cannot be used as feed additives for all animal species and consequently as nutrition supplements, since all of them contain 2-5 wt% quartz, two of them 20-21 wt% mordenite (fibrous zeolite), nine of them <80 wt% clinoptilolite (17-73 wt%) and two of them >20 wt% clay minerals (27-42 wt%). Although the EU Regulation No 651/2013 refers to clinoptilolite of sedimentary origin, using the presence or absence of quartz and fibrous minerals, none of the five mordenite, analcime and chabazite containing zeolitic rocks, can be used as feed additives and nutrition supplements, since all of them contain 2-6 wt% quartz and one of them contains 62 wt% mordenite (fibrous zeolite).

Key words: *Clinoptilolite, fibrous zeolites, mordenite, analcime. phillipsite, chabazite, quartz, clay minerals*

Περίληψη

Μελετήθηκαν 15 δείγματα ζεολιθικού τόφφου από τη λεκάνη Καρλοβασίου-Μαραθόκαμπου της νήσου Σάμου, ως προς την ορυκτολογική τους σύσταση με τη μέθοδο της περιθλασιμετρίας ακτίνων-Χ (XRD). Σύμφωνα με την ευρωπαϊκή οδηγία No 651/2013, η χρήση ζεολιθικών πετρωμάτων ως συμπληρώματα ζωοτροφών επιτρέπεται μόνο αν το πέτρωμα περιέχει τουλάχιστον 80 wt% κλινοπτιλόλιθο, λιγότερο ή μέχρι 20% κ.β. αργιλικά ορυκτά και είναι απαλλαγμένο από ινώδη ορυκτά και χαλαζία. Ανάλογα με τους τύπους ζεόλιθου που εντοπίστηκαν τα εξεταζόμενα ζεολιθοφόρα πετρώματα ταξινομήθηκαν ως εξής: με κλινοπτιλόλιθο (33-86% κ.β.), με κλινοπτιλόλιθο (59% κ.β.) και μορντενίτη (20-21% κ.β.), με κλινοπτιλόλιθο (22% κ.β.) και ανάλκιμο (29% κ.β.), με κλινοπτιλόλιθο (17% κ.β.) και φιλλιψίτη (27% κ.β.), με ανάλκιμο (29-70% κ.β.), με μορντενίτη (62% κ.β.) και με χαμπαζίτη (63% κ.β.). Τα κλινοπτιλολιθικά πετρώματα (10 δείγματα) περιέχουν 2-5% κ.β. χαλαζία, δύο από αυτά περιέχουν ινώδη ζεόλιθο (μορντενίτη), σε εννέα από αυτά το ποσοστό του περιεχόμενου κλινοπτιλόλιθου είναι λιγότερο από 80% κ.β. και σε δυο δείγματα το ποσοστό των αργιλικών ορυκτών ξεπερνάει το 20% κ.β.. Ως αποτέλεσμα δεν μπορούν να χρησιμοποιηθούν ως πρόσθετα ζωοτροφών και κατά επέκταση ούτε ως συμπληρώματα διατροφής, αφού δεν πληρούν την ευρωπαϊκή οδηγία. Παρόλο που η ευρωπαϊκή οδηγία No 651/2013 αναφέρεται σε ζεολιθικά πετρώματα με κλινοπτιλόλιθο, εάν λάβουμε υπόψη μόνο το ποσοστό του χαλαζία και την παρουσία ινώδων ορυκτών κανένα από τα υπόλοιπα πέντε ζεολιθικά πετρώματα δεν μπορεί να χρησιμοποιηθεί ως πρόσθετο ζωοτροφών ή ως συμπλήρωμα διατροφής αφού όλα περιέχουν 2-6% κ.β. χαλαζία και ένα από αυτά περιέχει ινώδη ζεόλιθο (μορντενίτη 62% κ.β.).

Λέξεις κλειδιά: *Κλινοπτιλόλιθος, ινώδης ζεόλιθοι, μορντενίτης, ανάλκιμο, χαμπαζίτης, φιλλιψίτης, χαλαζίας, αργιλικά ορυκτά*

1. INTRODUCTION

The zeolitic volcaniclastic rock deposit corresponds to a rock which contains high amounts of one or more from the different (>65) phases of zeolites. The zeolite with the numerous applications is the HEU-type zeolite (clinoptilolite-heulandite) that shows tabular crystals and contains micro/nano-pores in a framework of channels with 10 - and 8-member rings, in dimensions of 7.5x3.1 Å, 4.6x3.6 Å and 4.7x2.8 Å (e.g., Misaelides et al. 1995; Baerlocher et al. 2007; Filippidis & Kantiranis, 2007; Filippidis et al., 2008, 2010, 2013, 2015a,b, 2016b; Filippidis 2010, 2013; Mitchell et al., 2012; Vogiatzis et al., 2012; Hatzigiannakis et al., 2016; Papastergios et al., 2017; Floros et al., 2018).

Clinoptilolite of sedimentary origin with ≥80 wt% clinoptilolite, ≤20 wt% clay minerals, free of fibres and quartz, can be used as feed additive for all animal species (EU Regulation No 651/2013, Filippidis et al. 2016a) and consequently as nutrition supplement. In humans and animals, inhaled or injected or swallowed, fibrous zeolites (mainly erionite and mordenite, and to a lesser extent roggianite and mazzite), as well as the SiO_2 minerals (quartz, cristobalite, tridymite), were found to be toxic, carcinogenic and highly pathogenic (Davis, 1993; Driscoll, 1993; Ross et al., 1993).

On Samos Island two main Neogene basins were developed, the Mytilinii basin in the east and the Karlovassi basin in the west (Figure 1a). During the Miocene the Karlovassi basin was filled successively with carbonates, ash-fall tuffs and tuffites, marlstones, claystones, siliceous limestones, porselanites (with abundant opal) and cherts (with abundant chalcedony) (IGME 1979; Stamatakis 1989a). The tuffaceous horizons of the Karlovassi-Marathokampos basin underwent extensive diagenetic alteration in a saline-alkaline lake environment, resulting in the formation of rocks containing zeolites and evaporate minerals (colemanite, ulexite, celestite). The zeolitic rocks of the basin have been investigated for their mineralogy, petrology, geochemistry and possible industrial or environmental applications by many authors (e.g., Stamatakis 1989a,b; Pe-Piper & Tsolis-Katagas, 1991; Hall & Stamatakis, 1992; Stamatakis et al., 1996; Filippidis & Kassoli-Fournaraki, 2002;

Kantiranis et al., 2002, 2004b, 2006, 2010, 2011; Filippidis et al., 2005, 2007; Tsirambides & Filippidis, 2012; Mitiglaki et al., 2015).

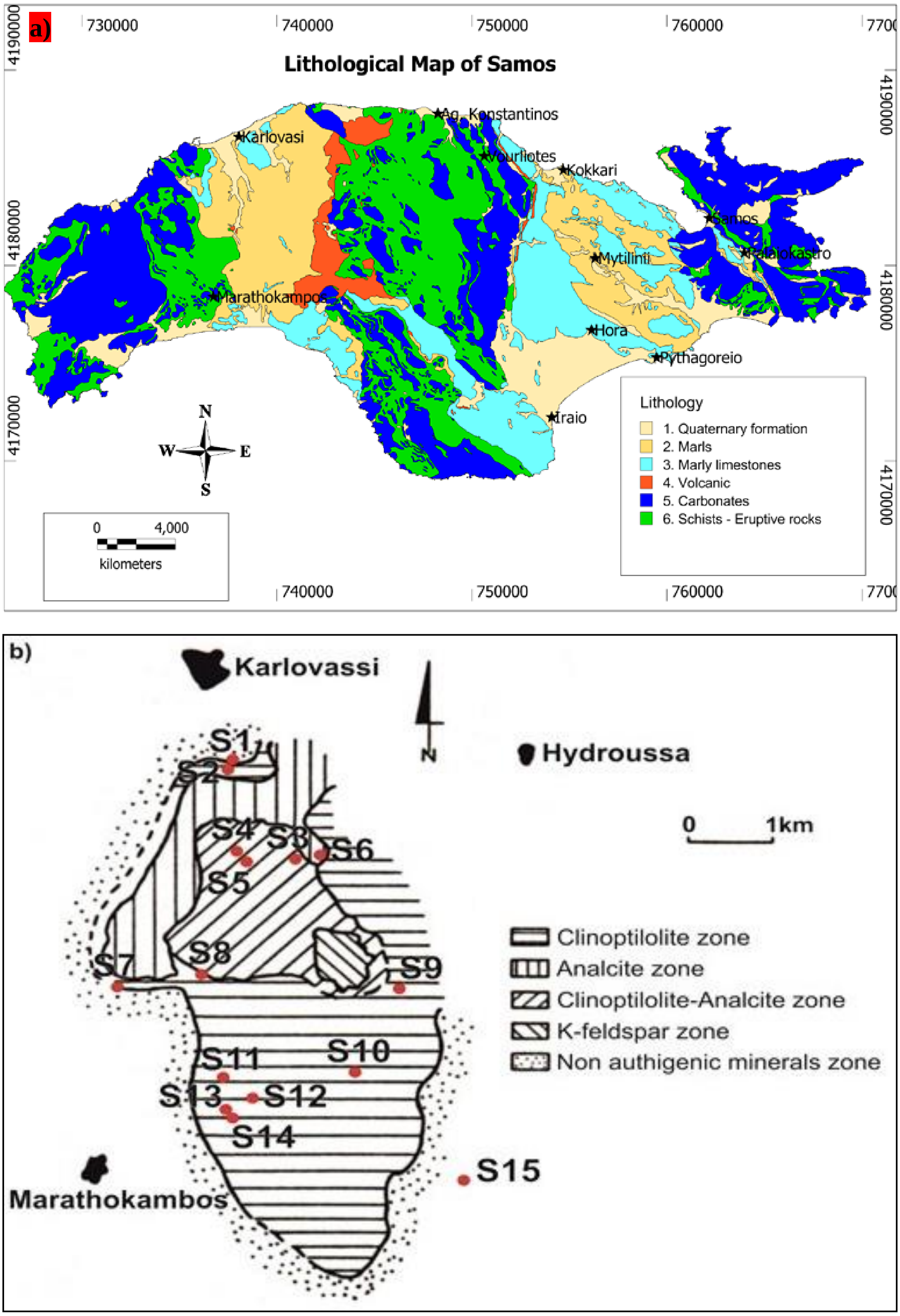

Fig. 1: (a) Lithological map of Samos island (Gournelos et al., 2014). **(b)** Location of the 15 samples in a direction from Karlovassi in the North (S1) to Marathokampos in the South (S15) (Kantiranis et al., 2007).

Studies on the use of zeolitic rocks as feed additives in different animals show negative, neutral and positive effects on the production and quality of livestock products (e,g., Mumpton, 1977; Pond & Mumpton, 1984; Tsitsishvili et al., 1992; Tserveni-Gousi et al., 1997; Yannakopoulos et al., 2000; Bish & Ming, 2001; Deligiannis et al., 2005; Filippidis, 2010). In most studies the quality characteristics (EU Regulation No 651/2013, Filippidis et al., 2016a) of zeolitic rocks are not mentioned. The aim of the present study is to investigate the mineralogical composition of the zeolitic rocks from the Karlovassi-Marathokampos basin of Samos Island and evaluate their potential use as feed additives (in accordance with the EU Regulation No 651/2013) and as nutrition supplements (Filippidis et al., 2016a).

2. MATERIALS AND METHODS

Fifteen (15) representative samples (S1-S15) were collected from the zeolitic rocks of Karlovassi-Marathokampos basin of Samos Island, in a direction from Karlovassi in the north (S1) to Marathokampos in the south (S15) (Figure 1b). The mineralogical composition was determined by the X-Ray Diffraction (XRD) method. The XRD analysis was performed using a Philips PW1710 diffractometer with Ni-filtered CuK_{α} radiation on randomly oriented powder samples. The samples were scanned 3-63^o 2θ at a scanning speed of 1.2 ^{o}/min and 3-33^o 2θ at a scanning speed of 0.24 ^{o}/min.

Semi-quantitative estimates of the abundance of the mineral phases were derived from the XRD data, using the intensity (counts) of certain reflections, the density and the mass absorption coefficient of the identified minerals for CuK_{α} radiation (corrected using external standards), the software MAUD-Material Analysis Using Diffraction with the RIETVELD method. The semi-quantitative estimation of the percentage of total amorphous materials was achieved by comparing the area of each broad background hump, which represents the amorphous materials in each sample, with the analogous area of standard mixtures of minerals with different contents of natural amorphous material, scanned under the same conditions (Kantiranis et al., 2004a, 2005).

3. RESULTS

The semi-quantitative mineralogical composition of the zeolitic rock samples are presented in Table 1, while in Figures 2-4 representative XRD patterns are given. Concerning the zeolite contents, in the Karlovassi-Marathokampos basin of Samos Island, six samples (S3, S4, S7, S9, S10, S12) of the zeolitic rocks contain clinoptilolite (33-86 wt%), three samples (S2, S5, S14) contain analcime (29-70 wt%), one sample (S15) contains mordenite (62%), one sample (S8) contains chabazite (Figure 2) (63 wt%), two samples (S1, S11) contain clinoptilolite (59 wt%) + mordenite (20-21 wt%), one sample (S13) contains clinoptilolite (22 wt%) + analcime (29 wt%) (Figure 3), one sample (S6) contains clinoptilolite (17 wt%) + phillipsite (27 wt%) (Figure 4).

Table 1. Mineralogical composition (wt%) of the zeolitic rocks from Karlovassi-Marathokampos basin of Samos Island

Sample	Cpt	Mor	An	Ph	Cha	M	CM	Qz	F	Am	Total
S1	59	21	-	-	-	4	8	5	3	-	100
S2	-	-	70	-	-	5	3	6	12	4	100
S3	86	-	-	-	-	2	2	2	8	-	100
S4	33	-	-	-	-	9	27	5	18	8	100
S5	-	-	29	-	-	6	29	3	30	3	100
S6	17	-	-	27	-	2	42	2	10	-	100
S7	54	-	-	-	-	10	4	2	30	-	100
S8	-	-	-	-	63	2	23	4	8	-	100
S9	43	-	-	-	-	14	11	2	26	4	100
S10	67	-	-	-	-	7	4	2	20	-	100
S11	59	20	-	-	-	4	8	4	5	-	100
S12	73	-	-	-	-	11	4	5	7	-	100
S13	22	-	29	-	-	8	15	2	24	-	100
S14	-	-	68	-	-	4	2	6	11	9	100
S15	-	62	-	-	-	1	1	2	12	22	100

Cpt: Clinoptilolite, Mor: Mordenite, An: Analcime, Ph: Phillipsite, Cha: Chabazite, M: Micas, CM: Clay Minerals, Qz: Quartz, F: Feldspars, Am: Amorphous material.

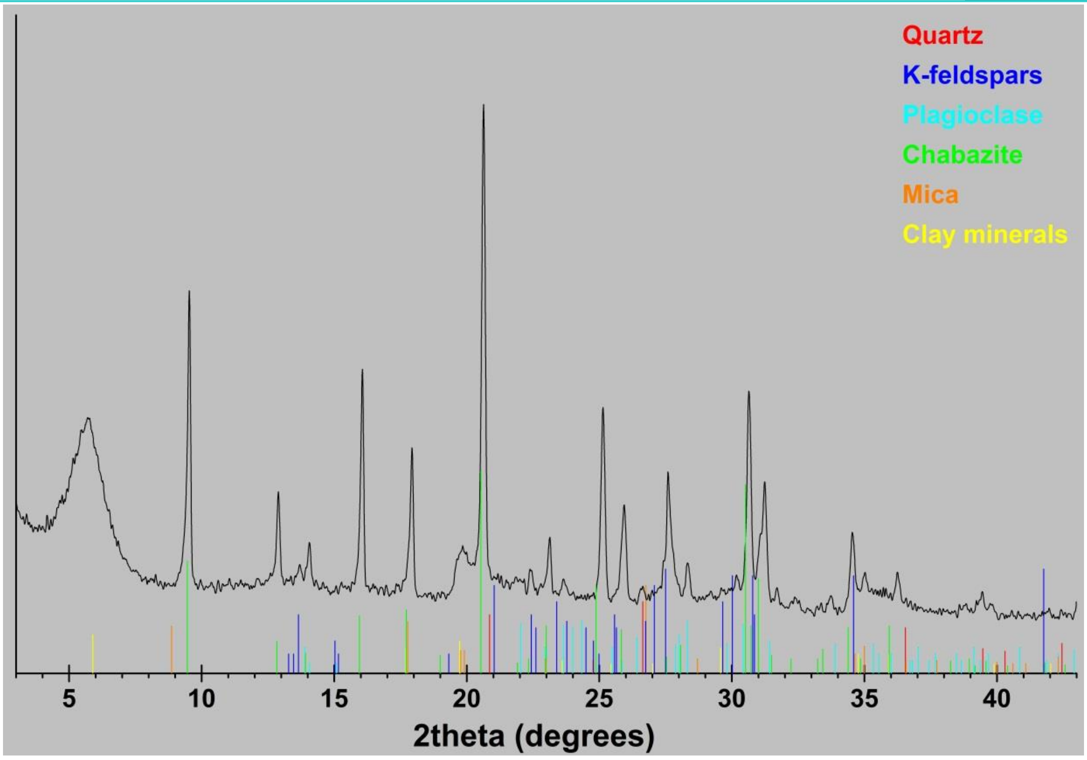

Fig. 2: X-Ray diffraction pattern of sample 8 with containing zeolite and chabazite.

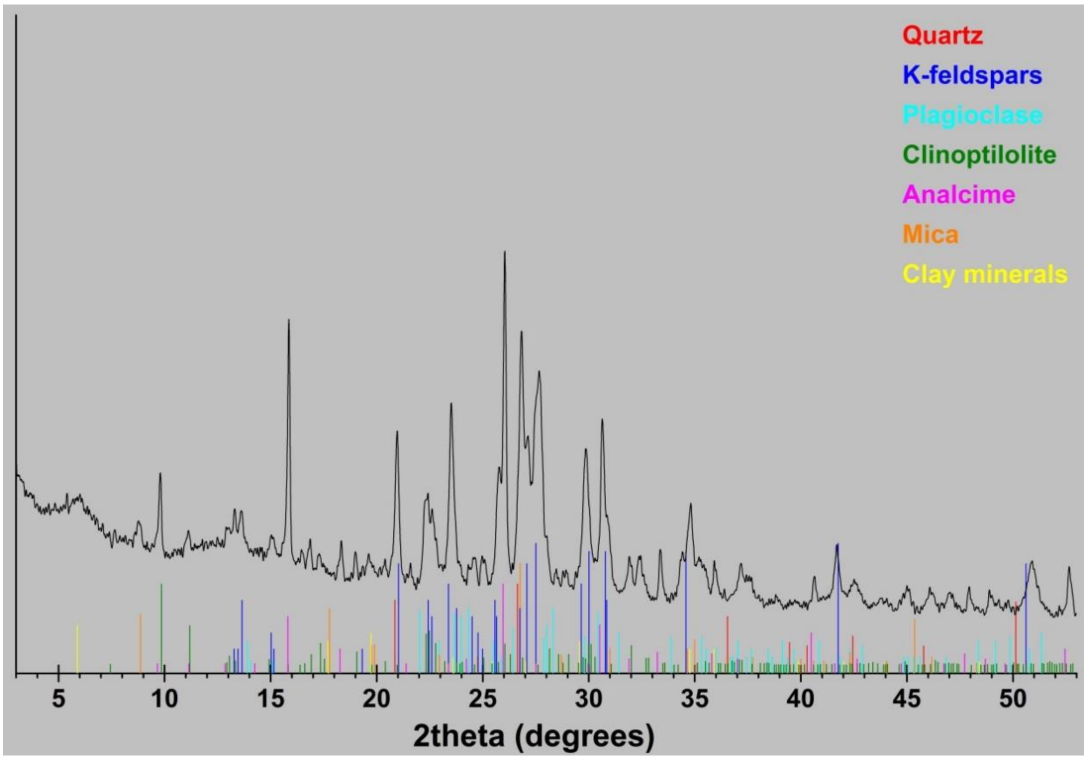

Fig. 3: X-Ray diffraction pattern of sample 13 with containing zeolite clinoptilolite and analcime.

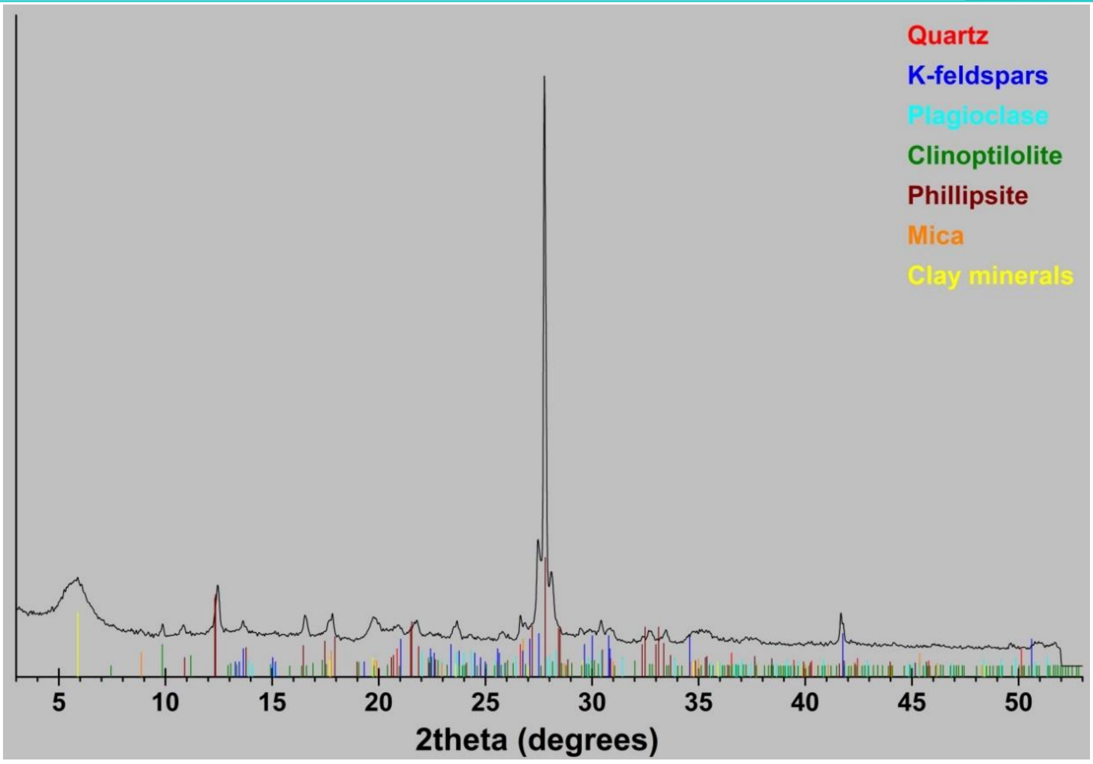

Fig. 4: X-Ray diffraction pattern of sample 6 with containing zeolite clinoptilolite and phillipsite.

Only sample S3 of the zeolitic rocks contains ≥80 wt% clinoptilolite (86 wt%), ≤20 wt% clay minerals (2 wt%), is free of fibres (fibrous zeolites such as mordenite), but unfortunately is not free of quartz (SiO_2), containing 2 wt% quartz. Three samples (S1, S11, S15) contain the fibrous zeolite mordenite (20-62 wt%), four samples (S4, S5, S6, S8) contain 23-42 wt% clay minerals and all samples contain quartz (2-6 wt%).

4. DISCUSSION AND CONCLUSIONS

Clinoptilolite of sedimentary origin with ≥80 wt% clinoptilolite, ≤20 wt% clay minerals and free of fibres and quartz, can be used (in powder form) as feed additive for all animal species (EU Regulation No 651/2013) and consequently as nutrition supplements. Clinoptilolite of sedimentary origin, belonging to the additive category “technological additives” and to the functional groups “binders” and “anticaking agents”, is authorised as an additive in animal nutrition with the conditions laid in the EU Regulation No 651/2013, which is binding in its entirely and directly applicable in all Member States. The EU

Regulation No 651/2013 also defines the X-Ray Diffraction (XRD) as analytical method for the determination of clinoptilolite.

Fibrous zeolites (mainly erionite, mordenite, roggianite and mazzite) and the SiO_2 minerals (quartz, cristobalite, tridymite), were found to be toxic, carcinogenic and highly pathogenic for humans and animals (Davis, 1993; Driscoll, 1993; Ross et al., 1993). Since the EU Regulation No 651/2013, concerns the clinoptilolite of sedimentary origin, the 15 samples of the Karlovassi-Marathokampos zeolitic rocks can be grouped in those containing clinoptilolite and those without clinoptilolite. Concerning the clinoptilolite-bearing rocks, two samples, (S1, S11) contain the fibrous zeolite mordenite (20-21 wt%), five samples (S7, S9, S10, S12, S13) contain <80 wt% clinoptilolite (22-73 wt%), two samples (S4, S6) contain <wt% clinoptilolite (17-33 wt%) and >20 wt% clay minerals (27-42 wt%), one sample (S3) contain >80 wt% clinoptilolite (86 wt%) and all samples contain quartz (2-5 wt%).

Considering the mineralogical composition (Table 1) none of the clinoptilolite-containing rocks meet the requirements of the EU Regulation No 651/2013, and thus they cannot be used as feed additives and nutrition supplements, since all of them contain 2-5 wt% quartz, two of them 20-21 wt% mordenite (fibrous zeolite), nine of them <80 wt% clinoptilolite (17-73 wt%) and two of them >20 wt% clay minerals (27-42 wt%).

Concerning the non clinoptilolite-bearing rocks one sample (S15) contains 62 wt% the fibrous zeolite mordenite, three samples (S2, S5, S14) contain 29-70 wt% analcime and one sample (S8) contains 63 wt% chabazite, two samples (S5, S8) contain >20 wt% clay minerals (23-29 wt%) and all samples contain quartz (2-6 wt%).

Although the EU Regulation No 651/2013 refers to clinoptilolite of sedimentary origin, using the presence or absence of quartz and fibrous minerals, we could evaluate the potential use of the non clinoptilolite-containing rocks, as feed additives and as nutrition supplements.

Considering the mineralogical composition (Table 1), none of the mordenite, analcime and chabazite containing zeolitic rocks, can be used as additives in animal nutrition and as nutrition supplements, since all of them contain 2-6 wt% quartz and one of the contains 62 wt% mordenite (fibrous zeolite).

5. ACKNOWLEDGMENTS

The authors express many thanks to the two anonymous reviewers for their useful and constructive comments which improved our manuscript.

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