

VOLCANIC GLASS (PERLITE) OF KIMOLOS ISLAND, GREECE: MINERAL CHEMISTRY AND STRUCTURE

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ABSTRACT

The structure and mineral composition of Kimolos perlite is examined in this paper. Kimolos perlite is produced during the last volcanic episode in the island, dating between 2.0 and 0.9 m.y. ago. Kimolos perlite mainly consists of glass (>85%) which demonstrates the typical onion-skin perlitic structure. The volcanic glass includes two water modes: the weakly bound water, which corresponds to the lattice water, and the strongly bound water, which corresponds to the monomeric OH. Kimolos perlite mineral phase consists of plagioclase (with oligoclase-andesine composition), quartz, biotite, titaniferous magnetite, and pyroxene.

KEY WORDS: volcanic glass; Kimolos island; Aegean Sea; perlite mineralogy; perlite geochemistry.

1. INTRODUCTION - GEOLOGICAL SETTING

Perlite is a volcanic glass of rhyolitic composition, containing 2 to 5 percent of combined water. In a commercial sense the term perlite is used to describe any glassy volcanic rock which has the ability to expand to about 20 times its volume when quickly heated to a temperature above its softening point, and to form a light-coloured lightweight, frothy material (Plate 2). Greece is the largest European producer and exporter of perlite. The most commercially important deposits occur on the island of Milos (Provatas and Trachilas areas) and to a lesser extent on Kimolos, Kos, Lesvos islands. Kimolos island is part of the Aegean volcanic arc which formed during the Pliocene as a consequence of the northward subduction of the African plate beneath the Aegean one (Fytikas et al., 1976).

The pre-volcanism background of Kimolos island consists of schists and Neogene sediments and granitic intrusions. Volcanics mainly consists of dacitic and andesitic lavas. Submarine pyroclastic series can be found underlain by basic hyaloclastite products. Above the pyroclastic series (lower lavas), dacitic and andesitic domes and lava flows occur and form the central frame of Kimolos island (Fytikas et al., 1986). The volcanic activity took place during the Upper Pliocene and Lower Pleistocene (between 3.5 and 0.9 m.y.). Two cycles of volcanic activity are distinguished (Fytikas and Vougioukalakis, 1992). The first cycle, between 3.5 and 2.0 m.y., comprises the lower lavas and the andesitic-dacitic lavas of Kimolos. The second cycle, between 2.0 and 0.9 m.y., comprises many areas of Kimolos, including the Xaplovouni area where the perlite occurs (Fig. 1). A NE-SW trending tectonic lineament, along which the volcanic centres of Milos island group were arranged, appears to be still active (Fytikas and Vougioukalakis, 1992). Hydrothermal alteration occurs in many parts of the island, where bentonite and kaolinite deposits are found. The minerals montmorillonite, kaolinite, zeolites, K-feldspar and alunite have been recorded (Minopoulos, 1981).

Perlite formed during the second cycle of the volcanic activity, and outcrops NNE from Kimolos village, on the Xaplovouni hill (Fig.1). The Kimolos perlite dips in beds, in the field. It has rhyolitic composition (Koukouzas, 1994)(Table 1).

2. ANALYTICAL TECHNIQUES

The analyses of perlite were carried out in the Departments of Geology and Chemistry at Leicester University. Optical microscope was used to identify the mineral composition of perlite. A Hitachi Scanning Electron Microscope, model S-520, with an attached 'Link' Energy Dispersive X-ray Detector was used to determine the perlite structure. A Philips X-ray Diffractometer (PW 1716), with a generator Philips PW 1729, and a goniometer Philips PW 1050/25, was also used for the study of Kimolos perlite mineralogy. A Stanton Thermal Analyser, model 1500, was used for the Differential Thermal and Thermogravimetric Analyses (D.T.A./T.G.A.). Two infra-red spectrophotometers, a research infra-red Perkin-Elmer 580B and an automatic infra-red Perkin-Elmer 1600 series FTIR, were used for the Infra-red (I.R.) analysis of Kimolos perlite. Polished thin sections were analysed using the JEOL JXA-8600 Electron Microprobe. All analyses were made using 15 kV accelerating potential. The problems that appeared in the preparation and the running of the polished thin sections were overcome by using blue dyed araldite to fill the holes and bubbles in the sections, which were very unconsolidated.

3. STRUCTURE OF THE VOLCANIC GLASS

Perlite mainly consists of glass, which comprises the groundmass. Perlite is characterised by a system of concentric, spheroid cracks called perlitic structure. This onion-skin perlitic structure is better developed on Kimolos than on the other Greek island perlites (Koukouzas, 1994, Koukouzas and Dunham, 1994) (Plate 1). Where the perlitic cracks are rarer a glassy texture is produced, whilst vesiculation is increased, leads to the vesiculated texture. Alteration may appear in the internal part of the perlitic cracks or in the glassy groundmass. These textures are derived by microscopic observations.

Quartz, feldspars, biotite, and opaque minerals are present in the Kimolos perlite. Quartz occurs either in the form of inclusions in feldspars or individual small crystals which are rounded in shape. Feldspars are plagioclases (oligoclases) with extinction angle of 5-7 degrees. They are euhedral and small in size (0.2-1mm). Biotite is very small in size (0.1-0.2mm) distinguished with difficulty. The opaque minerals, present in perlite, are magnetites and ilmenites, which are small in size (0.1-0.3mm).

The glass and the mineral composition of Kimolos perlite was identified by X-ray diffraction analysis, as well. The glass is indicated by a broad halo between 18 and 35 two theta angles. Quartz intensities were measured at the highest peak (3.34 Å d-spacing), which is the strongest reflection and can be observed when less than 1% is present. Biotite intensities were measured at the highest peak (10.07 Å d-spacing). Feldspars gave three or four sharp strong reflections in the d-spacing range 3.33-3.18 Å. Cristobalite (opal-C) presents the highest reflection at 4.05 Å d-spacing. XRD analysis of Kimolos perlite demonstrates variation of the mineral phase intensities. Feldspars give the strongest peaks, quartz and cristobalite moderately strong peaks, and biotite weak peaks.

4. WATER CONTENT

Differential thermal and thermogravimetric analyses (D.T.A./T.G.A.) were carried out in order to identify the thermal behaviour and the water content of Kimolos perlite. D.T.A. and T.G.A. also yield information on the temperature where phase changes or decompositional reactions took place, producing either endothermic or exothermic peaks. The main peaks which were found in the D.T.A. profiles and the loss of weight which was found in the T.G.A. profile are described as follows.

An endothermic peak appears at about 100 degrees Centigrade which represents the release of superficial water. This is the weakly bound water. At that temperature, the loss of weight ranges between 0.10 and 0.20%. An endothermic peak at about 400 degrees, which should present more clearly in the D.T.A. profiles, indicated the release of most of the water included in the perlite. However, that peak corresponds to the strongly bonded water in the form of hydroxyl (OH). Nevertheless the loss of weight appeared very clear, ranging between 1.80 and 3.20%. Kimolos perlites showed the highest loss of weight, among the Greek perlitic rocks. The mineral and glass proportion

(Koukouzas, 1994). At 580 degrees, the flat endothermic peak indicated the a-b quartz inversion. Even though that peak did not appear very clearly, it exists in Kimolos perlite. At 880-920 degrees, the endothermic peak corresponded to the conversion of alkalis and silica phases to an amorphous glassy phase (Mackenzie, 1957). This peak indicates the complete conversion to the glassy phase. This is crucial, because after that point, expansion takes place. At 1000 degrees, the endothermic peak represents the conversion of the amorphous silica to cristobalite (Mackenzie, 1957). That peak also appeared more clearly in Kimolos than the other Greek perlites (Koukouzas, 1994). Despite the appearance of the peaks mentioned above, a broad exothermic effect in the temperature range from 200 to 600 degrees was also present. This is a result of the diminution of the internal surface of the glass on annealing. Similar observations have been referred by Nasedkin and Piloyan (1983) from Chuguev and Arteni perlite deposits in Russia.

5. MODE OF WATER

Infra-red analysis was used to identify the mode of water contained in perlite. The infra-red method identified the species of water in perlite and revealed an important parameter in determining their relative concentrations.

Two main water peaks were identified in Kimolos perlite (Fig.2). First, an approximately symmetrical band at 1630 cm^{-1} . This is weakly bound H_2O and corresponds to the lattice or co-ordinated water (less energy). This water band results from the fundamental bending mode of water molecules (Nakamoto, 1978). The bending mode is less energetic, involving oblique movement directions of the atoms with respect to the positions of the others in the vibrating unit (Velde, 1992). Second, a broad asymmetric band at about 3570 cm^{-1} . This is strongly bonded H_2O and corresponds to the monomeric OH. In general, asymmetric vibrations give the strongest I.R. absorption peaks (Putnis, 1992). This water band is attributed to the fundamental OH-stretching vibration (Nakamoto, 1978). The stretch mode is the most direct and the highest energy vibrational mode. It involves the motion of one atom against another or of several atoms against a single atom (Velde, 1992). In addition to these two main water peaks, another occurred at about 3000 cm^{-1} . This band is probably produced by the combination stretching plus bending mode of water molecules. The noise at about 2350 cm^{-1} , appearing in all the perlite traces, is due to incomplete purging of CO_2 from the spectrometer (Newman et al, 1986).

6. MINERAL CHEMISTRY

Glass, plagioclases, magnetite and pyroxene from Kimolos perlite were analysed by Electron Microprobe in order to identify volcanic glass and mineral phase chemistry (Tables 2, 3, 4, 5). The total of the glass analyses is 96-97%, as a result of the lost water (3-4%). Statistics were made in the glass analyses in order to determine the variation of glass composition in Kimolos perlite (Table 2). Previous work on the accuracy and precision of electron microscope analyses of silicates and glasses has been carried out by Dunham and Wilkinson (1978).

Kimolos plagioclases range for 16-47% An in composition, although most of them give 20 to 30% An. Therefore, Kimolos plagioclases are mainly in the oligoclase-andesine range. Kimolos magnetite is titaniferous, while the pyroxene is of orthopyroxene composition (enstatite).

7. DISCUSSION

Although perlitic cracks and perlitic textures are well known, as characteristic feature of some volcanic rocks (Mackenzie et al., 1991, Shelley, 1993), few publications refer to the variation of perlite textures (Kadey, 1963, Whitson, 1982). Kimolos perlite develops very well the perlitic cracks, identified by the optical and the Scanning Electron Microscope. In addition it shows clearly the vesiculation process affecting the volcanic glass.

The abundance of volcanic glass in Kimolos perlite is indicated by the X.R.D analysis. The determination of the volcanic glass by X.R.D. techniques is also reported in other perlite studies (Naert, 1974, Lorenz and Muller, 1982, Buriesci et al., 1985). The comparison of glasses among the Greek perlites and the relation with their mineral phases (Koukouzas, 1994) demonstrates the high glass content in Kimolos perlite.

D.T.A. and T.G.A. help us to confirm the existence of two modes of water (molecular and hydroxyl) and to estimate the proportion of each one in perlite. The molecular water is 0.10% in Kimolos perlite. The hydroxyl water, of the Greek perlites, ranges between 1.40 and 3.20% approximately (Koukouzas, 1994). Higher values correspond to Kimolos perlites (3.20%) which contains more glass. The only previous data on D.T.A./T.G.A. analyses on Kimolos perlite is provided by Shackley (1988) who analysed some random Greek perlite samples. However, he identified an endothermic peak at 120-133 degrees for all the perlites, the main endothermic peak at 254 degrees, and an other endothermic peak at 844-908 degrees for the Kimolos perlite.

The Infra-red analysis indicated and confirmed the abundance of water in Kimolos perlite, compared with the other Greek perlites (Koukouzas, 1994), which recorded as strongly bound water. Although there is no previous data for the infrared analysis of the Greek perlites, the I.R. results are confirmed by other world-wide perlite deposit reports (Keller and Pickett, 1954, Lehmann and Knauf, 1973, Lehmann and Rossler, 1974, Naert, 1974, Wu, 1980, Acocella et al., 1984).

The previous microprobe analyses of Kimolos perlite (Koukouzas, 1994) indicated the low Al_2O_3 , CaO, K_2O , and the high TiO_2 and FeO proportions of Kimolos perlitic glass compared with the other Greek perlites. The glass analyses are closely related to the Na_2O and K_2O changes found in obsidian and perlite studies (Jezek and Noble, 1978). However, more titaniferous magnetite is found in Kimolos perlites than the other Greek deposits (Koukouzas, 1997).

8. CONCLUSIONS

The Kimolos perlite is produced during the second cycle of the volcanic activity in Kimolos (2.0-0.9 m.y. ago) and covers a small part of the island. The volcanic formation is a typical exogenous lava dome with peripheric flows some time finished to water domain. Pyroclastic formations from previous explosion of the dome are also present (Fytikas and Vougioukalakis, 1992). Columnar forms of the lava flows are well preserved.

The onion-skin perlitic structure is very well developed on Kimolos volcanic glass. Furthermore, the vesiculation process that affected the volcanic glass is clearly present under the optical and the scanning electron microscope. The abundance of volcanic glass is also identified with X.R.D. analyses. Kimolos glass has high proportion of FeO and TiO_2 .

Two main water peaks were identified in Kimolos volcanic glass. An approximately symmetrical band at 1630 cm^{-1} , which is the weakly bound water and corresponds to the lattice or co-ordinated water (less energy), and a broad asymmetric band at about 3570 cm^{-1} , which is strongly bounded water and corresponds to the monomeric OH. The first water bands results from the fundamental bending mode of water molecules, and the second water band is attributed to the fundamental OH-stretching vibration.

The main water peaks present at 100 deg. C. and correspond to the release of superficial water, and at 400 deg. C. indicating the release of the strongly bonded water in the form of hydroxyl (OH).

The mineral phases that are included in the Kimolos perlite comprises small proportion (less than 15%) compared with the volcanic glass. The main mineral phase, plagioclase, is of oligoclase-andesine composition. Few biotite crystals and many titaniferous magnetites are also appear. The pyroxene is enstatite.

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Table 1: Representative chemical analyses of Kimolos perlite

	KIM1	KIM2
SiO ₂	75.40	73.93
TiO ₂	0.15	0.15
Al ₂ O ₃	12.67	12.67
Fe ₂ O ₃	1.19	1.19
MnO	0.06	0.06
MgO	0.09	0.09
CaO	0.96	0.96
Na ₂ O	3.69	3.69
K ₂ O	3.71	3.71
P ₂ O ₅	0.03	0.03
LOI	2.54	2.54
Total	100.49	100.49

Table 2: Representative analyses of Kimolos perlite volcanic glass

	K1	K2	K3	K4	K5	K6
SiO ₂	76.42	75.65	76.34	76.21	75.92	76.27
TiO ₂	0.10	0.11	0.12	0.12	0.09	0.08
Al ₂ O ₃	12.01	11.96	12.02	12.12	11.96	12.06
FeO	0.56	0.87	0.43	0.69	0.71	0.47
MnO	0.05	0.09	0.02	0.04	0.02	0.08
MgO	0.07	0.12	0.03	0.06	0.09	0.04
CaO	0.67	0.68	0.63	0.68	0.65	0.61
Na ₂ O	3.63	3.33	3.72	3.37	3.36	3.70
K ₂ O	3.89	3.82	3.99	3.85	3.85	3.92
SrO	0.03	0.06	0.06	0.06	0.06	0.06
BaO	0.14	0.05	0.11	0.01	0.08	0.15
Total	97.64	96.74	97.47	97.21	96.79	97.44

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Table 3: Statistical analysis of volcanic glass composition

	mean	s.d.	min.	max.
SiO ₂	75.95	0.79	74.27	79.35
TiO ₂	0.11	0.03	0.03	0.18
Al ₂ O ₃	12.04	0.13	11.03	12.51
FeO	0.69	0.17	0.28	1.36
MnO	0.06	0.02	0.00	0.16
MgO	0.08	0.04	0.00	0.87
CaO	0.65	0.11	0.46	1.08
Na ₂ O	3.59	0.77	2.40	6.38
K ₂ O	3.66	1.01	0.37	4.73
SrO	0.03	0.03	0.00	0.06
BaO	0.09	0.08	0.00	0.23
Cr ₂ O ₃	0.01	0.01	0.00	0.04
NiO	0.01	0.01	0.00	0.04

Note : s.d. = standard deviation, min. = minimum, max. =maximum, Sixty one (61) perlite samples were examined

Table 4: Representative analyses of Kimolos perlite feldspars

	FLD1	FLD2	FLD3	FLD4	FLD5	FLD6	FLD7	FLD8
SiO ₂	63.65	57.64	61.39	61.90	62.04	62.61	62.45	61.66
TiO ₂	0.00	0.03	0.00	0.03	0.00	0.02	0.01	0.01
Al ₂ O ₃	21.96	25.53	23.44	23.11	23.14	23.19	23.40	23.62
FeO	0.16	0.30	0.25	0.15	0.18	0.16	0.17	0.20
MnO	0.02	0.04	0.00	0.03	0.03	0.03	0.02	0.01
MgO	0.00	0.01	0.02	0.00	0.00	0.00	0.01	0.00
CaO	3.65	8.97	5.60	5.41	5.19	5.29	5.46	5.83
Na ₂ O	8.90	6.48	7.87	8.38	8.36	8.43	8.42	8.08
K ₂ O	1.10	0.29	0.56	0.60	0.59	0.59	0.60	0.57
SrO	0.06	0.12	0.05	0.07	0.07	0.04	0.02	0.10
BaO	0.42	0.16	0.08	0.02	0.07	0.06	0.23	0.01
Total	99.92	99.57	99.26	99.70	99.67	100.42	100.79	100.09
Oxygens	32.000							
Si	11.38	10.32	11.00	11.05	11.07	11.09	11.04	10.97
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	4.56	5.60	4.95	4.86	4.87	4.84	4.87	4.95
Fe ²⁺	0.02	0.05	0.04	0.22	0.03	0.02	0.02	0.03
Mn	0.00	0.01	0.00	0.00	0.00	0.00	0.03	0.00
Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00
Ca	0.69	1.72	1.07	1.03	0.99	1.00	1.03	1.11
Na	3.04	2.25	2.74	2.90	2.89	2.89	2.88	2.78
K	0.25	0.06	0.12	0.14	0.13	0.13	0.13	0.13
Sr	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.01
Ba	0.03	0.01	0.00	0.00	0.00	0.00	0.01	0.00
Total	19.98	20.03	19.95	20.03	20.06	20.00	20.03	20.00

	MAG1	MAG2	MAG3		PYR1	PYR2
SiO ₂	0.21	0.54	0.30	SiO ₂	51.08	49.78
TiO ₂	7.44	7.36	6.93	TiO ₂	0.13	0.11
Al ₂ O ₃	1.61	1.73	1.64	Al ₂ O ₃	0.67	0.64
Cr ₂ O ₃	0.00	0.00	0.03	FeO	21.21	20.32
Fe ₂ O ₃	47.08	45.64	45.21	MnO	2.64	2.64
FeO	33.33	33.35	31.75	MgO	18.75	18.34
MnO	1.18	1.27	1.14	CaO	0.73	0.75
MgO	0.92	0.86	0.98	Na ₂ O	0.03	0.15
CaO	0.03	0.09	0.03	K ₂ O	0.04	0.09
Na ₂ O	0.01	0.02	0.06	Total	95.31	92.88
K ₂ O	0.01	0.02	0.01			
Total	87.35	86.52	83.55			
Oxygens	4.000			Oxygens	6.000	
Si	0.01	0.02	0.01	Si	2.01	2.01
Ti	0.23	0.23	0.22	Ti	0.00	0.00
Al	0.08	0.08	0.08	Al	0.03	0.03
Cr	0.00	0.00	0.00	Fe ²⁺	0.70	0.69
Fe ³⁺	1.45	1.41	1.45	Mn	0.09	0.09
Fe ²⁺	1.14	1.15	1.13	Mg	1.10	1.10
Mn	0.04	0.04	0.04	Ca	0.03	0.03
Mg	0.06	0.02	0.06	Na	0.00	0.01
Ca	0.00	0.00	0.00	K	0.00	0.00

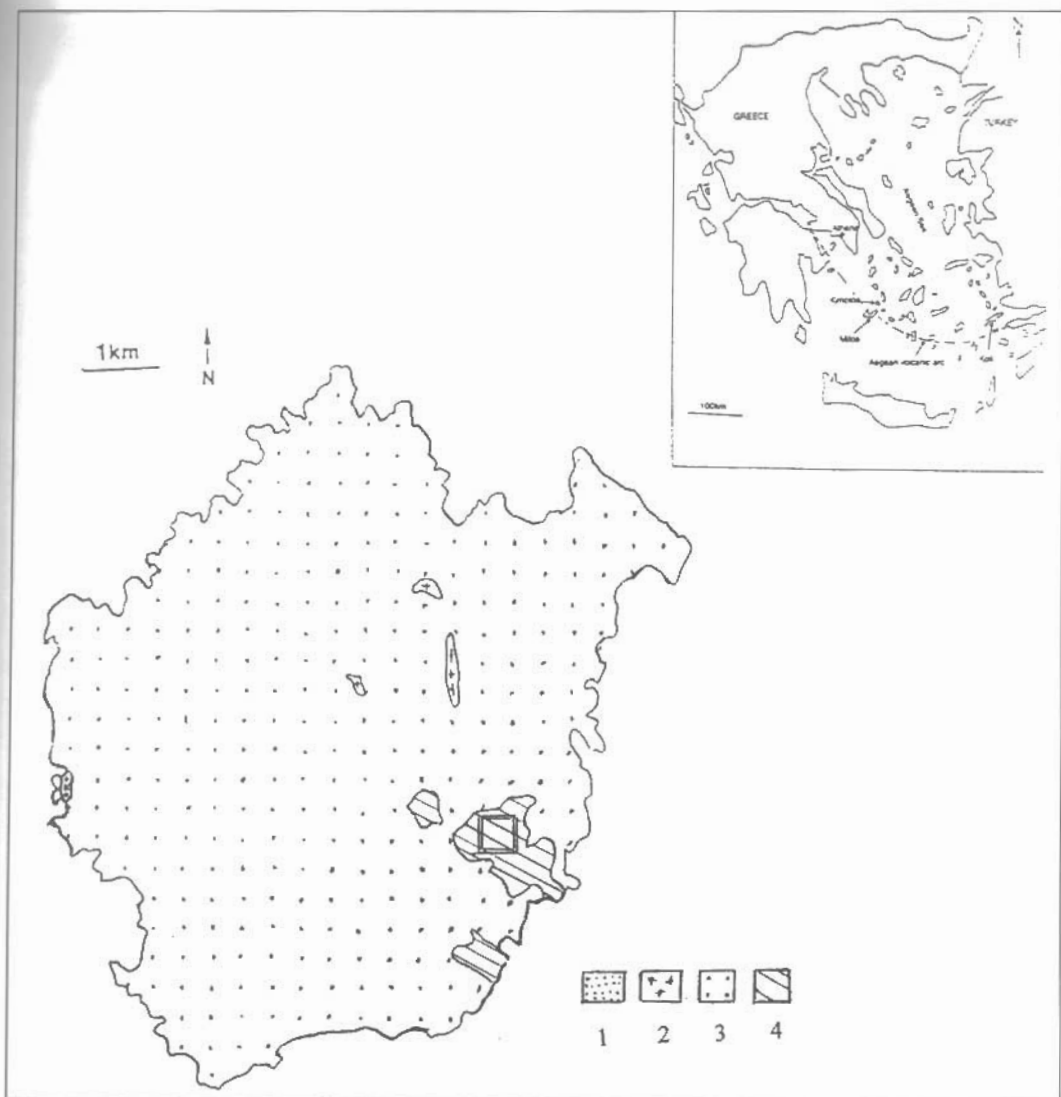


Fig. 1: Location of Kimolos island in the Aegean volcanic arc and simplified geological map of Kimolos island (after Fytikas and Vougioukalakis, 1992), modified with the sample locations of the perlite deposit (frame) (1=Schists and Neogene sediments, 2=Granitic body, 3=Lower lavas, Kastro ignimbrite, hydrothermally altered volcanics, andesitic and dacitic dykes, lava flows and domes, Kimolos village breccia, Prassa ignimbrite flow and surge units, pumice flows, Filakopi submarine pyroclastics, Geronikola tuff ring and lava flows, Korakies nuee ardente and reworked pyroclastic breccia, Psathi pyroclastics, alluvial deposits and marine sediments, scree, eluvial and beach deposits, 4=Xaplovouni-Psathi rhyolitic lava domes and flows (where perlite occurs).

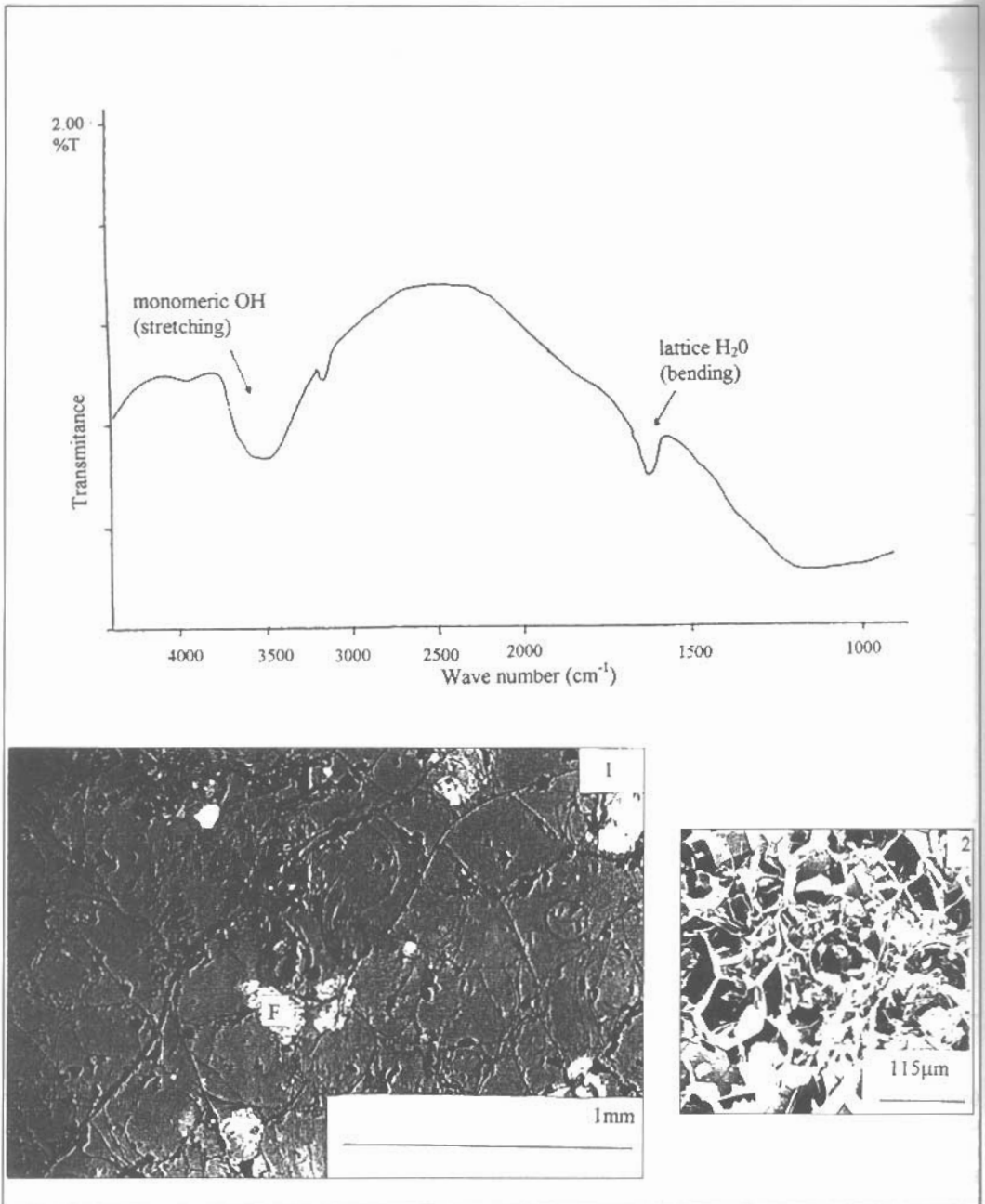


Fig. 2: Infra-red analysis of Kimolos perlite.

Plate 1. Perlitic cracks are dominant in the glassy groundmass of Kimolos perlite. The small-sized phenocrysts are feldspars (F)

Plate 2. Kimolos expanded perlite structure under the Scanning Electron Microscope (S.E.M.).