COMPARATIVE STUDY OF DEGRADATION PATTERNS OF PETRIFIED MATERIAL FROM GREEK FOSSILISED FORESTS.

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ABSTRACT
A pilot study of the petrified forests of Lesvos Island and of Kastoria and the application of a non-destructive method for the identification and measurement of soluble salts contained into material fount on both sites are presented here. This method is based on the application of neutral paper pulps impregnated in deionized water on some trunks.
The study includes monitoring of environmental conditions, macroscopic examination and mineralogical study of fossils. Based on climatological data, the period where frost action and temperature variations take place was determined.
The results indicate that in Lesvos Island there is an extensive problem of deterioration due both the crystallisation of soluble salts and the frost action during the winter. In Kastoria there are problems, deterioration caused by the frost action, during the months December to February, the crystallisation of soluble salts and biological depositions.

Keywords: petrified forests, corrosion, deterioration, soluble salts crystallisation, frost action, conservation, preservation.

INTRODUCTION
The fossilised - petrified forest of Lesvos (see fig. 1), which is dated 20 million years, is located in the area of the Northwest part of the island, and according to recent research, it occupies half of the area defined by the imaginary line between Molyvos - Plomari. It is one of the most important natural sites in Europe and a national museum exhibition/display will be created soon, in Sigri (Velitzelos et al., 1997, 1981b, 1981a, 1978) (see fig. 2).

Figure 1. Map of Greece with the areas of Lesvos (1) and Kastoria (2).

Figure 2. Fossilised trunk from Lesvos.

The fossilised - petrified forest of the Kastoria (see fig 1), which is dated 20 - 22 million years, covers an extended area in the regions of Nostimo and Asproklisia. The fossilised trunks are in not so compact sentiments and the degree of fossilisation is either complete or partial (see fig. 3).

Figure 3. Fossilised trunk from Kastoria.

The great importance of the above natural monuments leads to the necessity of a study for the conservation, protection and publicity of those fossilised - petrified forests. The main deterioration factors affecting those materials are soluble salts crystallisation, temperature variations and frost damage in the fossilised forest material.

Soluble salts are one of the main deterioration factors for stone materials and fossils (Torraca 1988, Lampropoulos 1993, Child 1994). Most important are the actions of sodium chloride and sodium sulphate, which under varying temperature and humidity conditions are crystallised into the pores of the material thus developing mechanical stresses.
The action of soluble salts is very decisive for porous materials like fossils (Amoroso and Fasina 1983, Child 1994). Soluble salts that may enter into the pores of the material, are mainly chlorides and sulphates and secondly the carbonates, nitrates and nitrites of alkalis and alkaline earths. Their provenance may be (Lampropoulos 1993, Child 1994) in the case of fossilised - petrified forests:

- The sea, where sodium chloride is contained in a percentage of 3,5% w/v and in non-polluted sea the ratio of sulphate ions to chloride ions is around 0,139. For distances of about 15 km away from the sea, salts can be transported by saltspray phenomenon.
- Underground water, where the soluble salts rise through capillary ascension of water from the underground via the rocks, carrying along -through the soil- the soluble components of aluminium - silica rocks in particular, and other rocks as well, containing diluted salts in various concentrations (see table 1).

- sodium (Na^+)
- potassium (K^+)
- magnesium (Mg^{2+})
- calcium (Ca^{2+})
- sulphates (SO_4^{2-})
- carbonates (CO_3^{2-})
- chlorides (Cl^-)
- silicates (SiO_3^{2-})

Table 1. List of ions of several soluble salts in underground water.

- Possible contact with structure materials or plasters-mortars, i.e. cements, which are important sources of soluble sulphates, carbonates and silicates salts. Additionally, possible contacts of the fossilised material with cement, i.e. from fillings of missing parts, may cause a flow of sulphate salts into the pores of the material.

The most common soluble salts that may form efflorescences (Wheeler, 1993) on the surface and circulate in the pores of the fossilised material are presented. (see table 2).

- sylbite	KCl
- pikromerite	$K_2Mg(SO_4)_2.6H_2O$
- sygenite	$K_2Ca(SO_4)_2$
- glasserite	$(Na,K)_2SO_4$
- polyalite	$K_2Ca_2Mg(SO_4)_4.2H_2O$
- arkanite	K_2SO_4
- halite	$NaCl$
- nitratite	$NaNO_3$
- thermonatrite	$Na_2CO_3.H_2O$
- natrite	$Na_2CO_3.10H_2O$
- tenardite	Na_2SO_4
- mirabilite	$Na_2SO_4.10H_2O$
- nitrocalcite	$Ca(NO_3)_2.4H_2O$
- antarkticite	$CaCl_2.6H_2O$
- gypsum	$CaSO_4.2H_2O$
- bassanite	$CaSO_4.1/2H_2O$
- nitromagnesite	$Mg(NO_3).6H_2O$
- hydromagnesite	$Mg_5(OH(CO_3)_2)_2.4H_2O$
- astrakanite	$MgSO_4.Na_2SO_4.4H_2O$
- magnesite	$MgCO_3$
- kieserite	$MgSO_4.H_2O$
- neskeonite	$MgCO_3.3H_2O$
- epsomite	$MgSO_4.7H_2O$
- bissofite	$MgCl_2.6H_2O$
- kalikinite	$KHCO_3$
- ammonium nitrate	NH_4NO_3
- hexadrite	$MgSO_4.6H_2O$
- nitre	KNO_3

Table 2. The most common soluble salts that may form efflorescences.

When dilution of various salts happens in the pores of a porous material, under saturation or over-saturation point conditions, these salt crystals start to be formed inside the pores. These crystals increase in volume, as they are supplied by the continuous dilution in the capillary network and thus generate/impose pressure-stress on the pore walls. This pressure-stress will increase, the larger the relation will be between the existing salt concentration and its concentration of saturation and it is given by the formula (1):

$$P = (R \cdot T/Us) \cdot \ln(C/Cs) \quad (1)$$

Where:
P = crystallisation pressure in Atms
R = constant of noble gases which equals 0.082 $lt \cdot atm/mole \cdot grad$.
T = absolute temperature in ^oK.
Us = molecular volume of solid salt in lt/mole.
C = present concentration of the salt in moles/lt.
Cs = concentration of the saturated salt moles/lt.

Sodium sulphate which comes in contact with water, inside the pores, at 32,4 ^oC, is transformed from rhombohedric tenardite into monoclinic mirabilite, in according to the following reaction:

$$Na_2SO_4 + 10H_2O \leftrightarrow Na_2SO_4 \cdot 10H_2O$$

At this time there is a corresponding volume increase of 308%, while in the atmosphere this transformation happens in a lower temperature and the maximum of mechanical stresses - pressures occurs at 20 ^oC (Amoroso and Fasina 1983, Lampropoulos 1993).
The volume increase which follows the above mentioned transformations, produces very large mechanical pressures - stresses in the pores, many times greater than the material's resistance, thus resulting in surface fractures and degradation of the material.
Chloride alkalis or alkaline earths salts, due to their greater mobility in relation to sulphate and carbonates, penetrate the pores of the material, where they crystallise and loosen many crystalline structures. They also cause "digestion", that is the dilution of colloidal parts of clays in water and thus facilitate more the dilution of magnesium, which originates from the material.
The deposition of insoluble salts, like siliceous, carbonate, sulphate, on the fossil's surface, apart from causing aesthetic alteration to the material, also creates mechanical stresses on the conduction area by contraction-expansion, and thus leading to degradation of the material.
Exposure in open air may cause degradation of the petrographic material, according to the following procedure:
Under certain conditions of temperature and humidity, soluble salts, which are contained inside the pores, are crystallised, thus resulting in mechanical stresses and fractures, according to the previously mentioned mechanisms (see fig. 4).

Figure 4. Cracking and alveolar corrosion due to crystallisation of the soluble salts in the material of the fossilised forest.

Finally the frost damage, with the increase of the volume of the water about 9,2%, from the fluid to the solid and temperature variations, creates mechanical stresses in the porosity of the material.

OBJECTIVE

The present paper, contributes to developing non-destructive methods for the determining of the presence and crystallisation of soluble salts in the petrographic material of the fossilised forest of Lesvos and Kastoria, so that a conservation strategy can be developed and a formation of a program of action to protect this material. The development of non-destructive methods of determination of the degree and the parameters of degradation-deterioration of monuments of our natural heritage is considered of critical importance for their effective management. An extensive list of accurate identification methods of susceptible minerals has been presented (Howie 1992).

MATERIALS AND METHODS

The presence of soluble salts in the petrographic material of the fossilised forest of Lesvos and Kastoria, was determined by the application of neutral paper pulps wetted in de-ionised water, in various surfaces for one hour and then by analysing the absorbed ions, chloride (Cl^-) and sulphate (SO_4^{2-}), by the use of Analytical Chemistry determination methods, performed in the Laboratory of Inorganic Chemical Analysis of the Food Technology department in T.E.I. of Athens. The measuring of the specific electrical conductivity of the obtained samples/solutions was done in the laboratory of Conservation of Ceramics/Glass-Organic materials in the Department of Conservation of Antiquities and Works of Art, in T.E.I. of Athens.
The above mentioned procedure was applied on four different random samples from the area of Sigri - Lesvos and from the area of Nostimo - Kastoria (see tables 3, 4).

I/n	Cd (μs/cm^2)	Cl^- (ppm)	SO_4^{2-} (ppm)
Sample 1	204	20,5	4,5
Sample 2	258	30,5	5,5
Sample 3	153	31,5	6
Sample 4	219	16	3,5
Sample 5	5	1	0

Table 3. Results of chemical analysis in paper pulps from fossilised trunks of Sigri - Lesvos.

I/n	Cd (μs/cm^2)	Cl^- (ppm)	SO_4^{2-} (ppm)
Sample 1	122	12,5	1,2
Sample 2	135	19,5	1,7
Sample 3	96	21	1,3
Sample 4	127	8,5	0,9
Sample 5	5	1	0

Table 4. Results of chemical analysis in paper pulps from fossilised trunks of Nostimo - Kastoria.

Additionally, climatological data of the area were gathered and tables of temperature and relative humidity were drawn, in order to establish the areas of soluble salt crystallisation and the presence of frost (see fig. 5, 6, 7, 8).

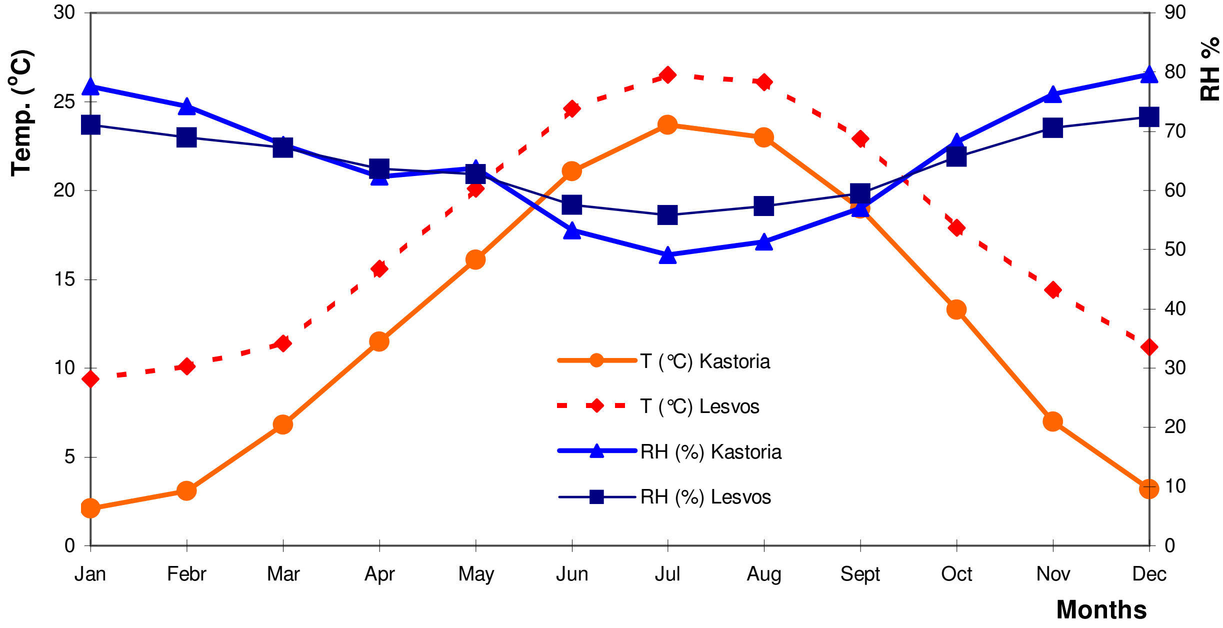

Figure 5. Diagram of mean temperature and relative humidity per month of Lesvos and Kastoria region for the period from 1955 to 1997.

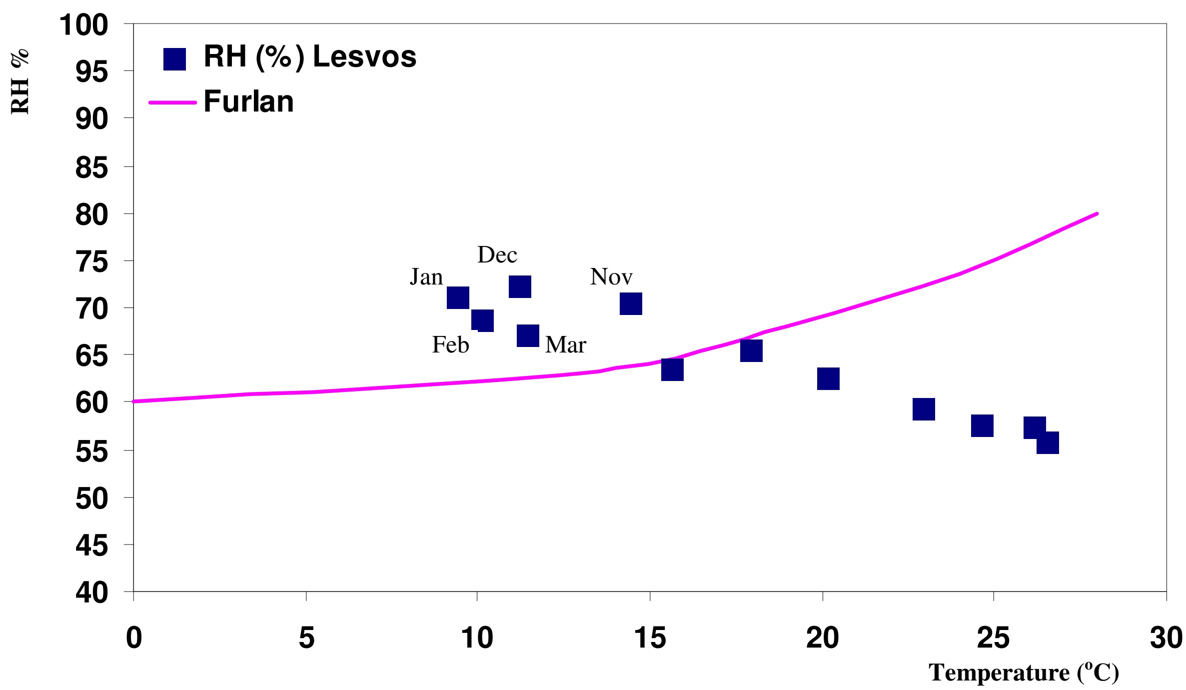

Figure 6. Furlan diagram of fossilised forest of Lesvos, and combination points between temperature and relative humidity per month during the years 1955 - 1997. Every point represents a different month.

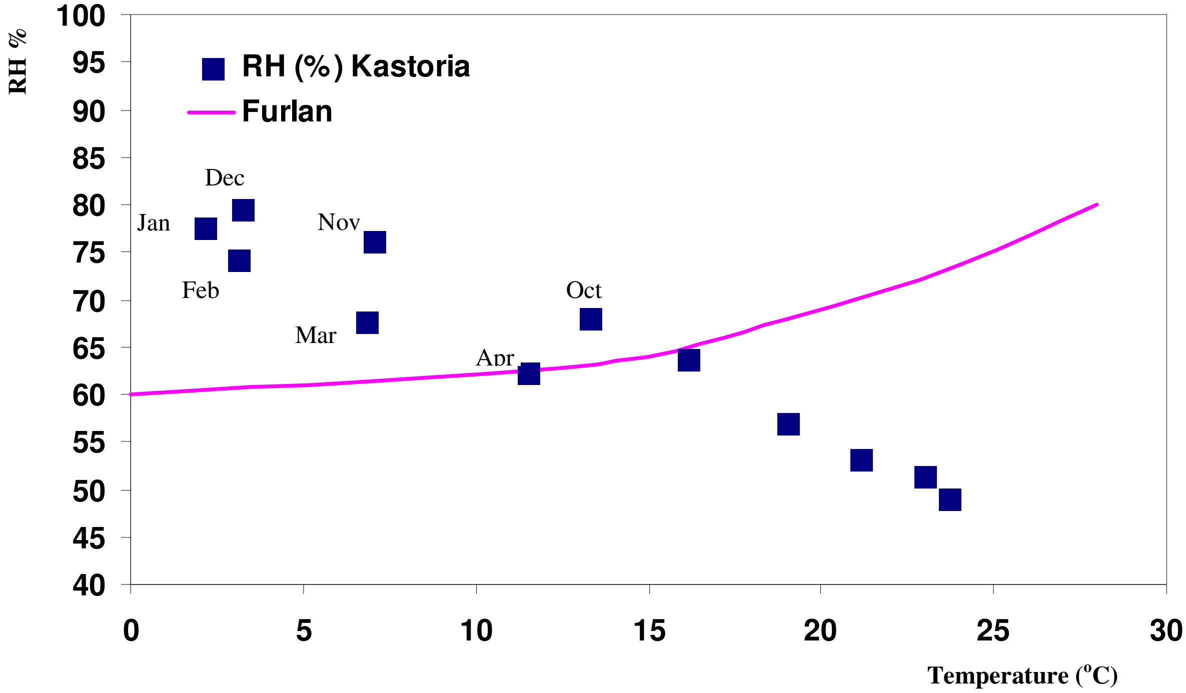

Figure 7. Furlan diagram of fossilised forest of Kastoria and combination points between temperature and relative humidity per month during the years 1955 - 1997. Every point represents a different month.

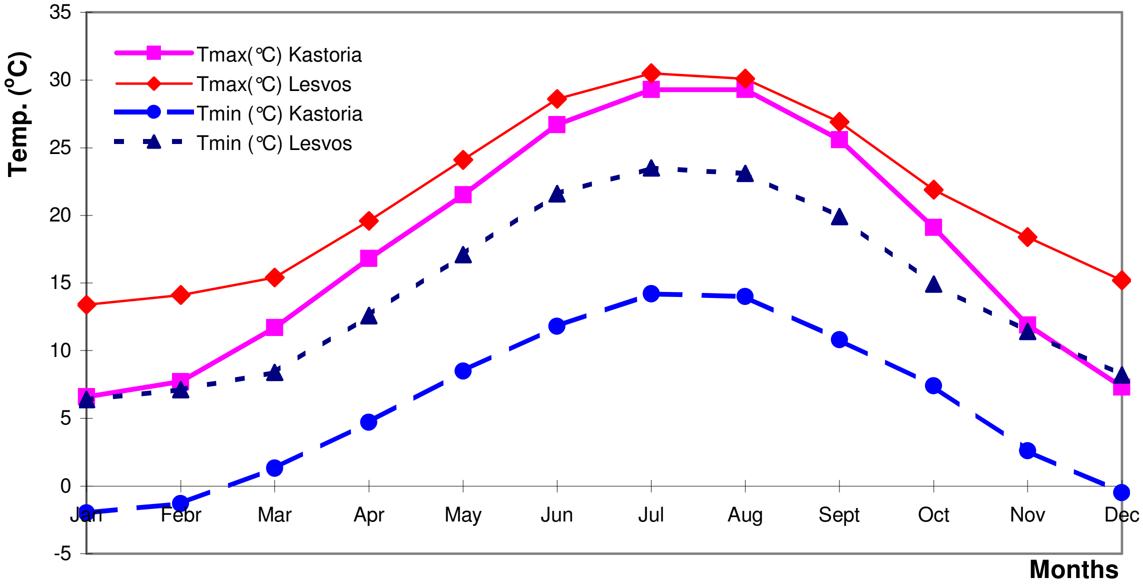

Figure 8. Diagram of average maximum and average minimum temperature per month of Lesvos and Kastoria region for the period 1955 - 1997.

RESULTS

ANALYSIS OF THE FOSSILISED MATERIALS

The relatively high porosity (three samples 19,56 mm^3/gr, 19,24 mm^3/gr, 26,6 mm^3/gr) of the petrographic material of the fossilised forest of Lesvos (Lampropoulos et al., 1997, 1999a) favours the penetration and crystallisation of soluble salts in the structure material of the fossilised forest.
The same material shows in several areas relatively high hardness (7 - 8 Mohs) (Lampropoulos et al., 1997, 1999a) fact which results to a great sensitivity. Additionally, it consists of various different minerals (quartz, tridymite, cristobalite), (Lampropoulos et al., 1997, 1999a), which results to discontinuities in the structure and the formation of cracks produced by mechanical stresses caused by the crystallisation of soluble salts.
In the case of petrified forest of Kastoria, tests were done on 7 samples of estimation of physicochemical properties and analysis structure material (S.E.M., X.R.D., optical microscopy, chemical analysis, water absorption, porosity, and hardness).
The samples consist of 95% SiO_2, which is mostly in the presence of quartz and tridymite. There are also in small quantity oxides of Fe, Al, K, Na, Ti, Ca, Mg, Mn. The porosity of the samples is between 0,85%-15,77% and their hardness is between 6-7 Mohs (Lampropoulos et al., 1999b),.
The macroscopic study of the fossilised forest tree trunks showed the existence of the pattern of alveolar corrosion in many parts of the surface, as well as a large number of fractures.
The analyses of the four samples/solutions of Sigri - Lesvos (obtained by the application of neutral paper pulps wetted in de-ionised water, on the tree trunks of the fossilised forest), by measuring the specific electrical conductivity (cd), of chloride ions (Cl^-) and sulphate ions (SO_4^{2-}), gave the results (see table 3).

Sample 5 is de-ionised water and was used as a comparison towards the other results of the study.
From the previous Table 3 it is clear that important quantities of soluble chloride and sulphate salts exist on the surface and the pores of the material of the fossilised forest of Lesvos.
Then these diagrams were correlated with the V. Furlan diagram, to establish the areas of crystallisation of sodium sulphate, for each month of the year and for the period 1955 - 1997.
Finally the frost damage is not present as is shown from the previous diagrams. Temperature variations, which are present as is shown from the previous diagrams, create mechanical stresses in the porosity of the material.

The analyses of the four samples/solutions of Nostimo of Kastoria (obtained by the application of neutral paper pulps wetted in de-ionised water, on the tree trunks of the fossilised forest near to the soil), by measuring the specific electrical conductivity (cd), of chloride ions (Cl^-) and sulphate ions (SO_4^{2-}), gave the following results on table 4.

Sample 5 is de-ionised water and was used as a comparison towards the other results of the study.
From the previous diagram it is clear that important quantities of soluble chloride and sulphate salts exist on the surface and the pores of the material of the fossilised forest of Kastoria.
Then these diagrams were correlated with the V. Furlan diagram, to establish the areas of crystallisation of sodium sulphate, for each month of the year and for the period 1955 - 1997.
The processing of the climatological data are shown in the previous diagrams for temperature and relative humidity.
Finally the frost damage, during the months January, February and December and temperature variations, which are present as is shown from the previous diagrams, creates mechanical stresses in the porosity of the material.

DISCUSSION - CONCLUSIONS

The action of soluble salts is primarily obvious by macroscopic observation of the alveolar corrosion pattern in many parts of the surface of the tree trunks from the fossilised forest. Then, the presence of soluble salts is also apparent by the presence of chloride and sulphate ions on the surface and in the pores of the material of the fossilised forest. Their crystallisation and their actions are shown in the V. Furlan diagrams, for all months of the year and for the period 1955 - 1997.
From the previous diagrams, in the case of fossilised forest of Lesvos, it is shown that during the months January, February, March, November and December, most plotted dots - combinations of temperature and relative humidity - are falling over the curve and therefore crystallisation of sodium sulphate occurs during these months in the pores of the material of the fossilised forest of Lesvos.
In most tree trunks of the fossilised forest of Lesvos, there are cracks, which are due to the physical disintegration along the wood rays, but also to human intervention, fact, which multiplies the above phenomena.
The transportation of soluble salts to the material of the fossilised forest of Lesvos takes place due to the saltspray phenomenon.
The relatively high porosity of the petrographic material of the fossilised forest of Lesvos (Lampropoulos et al., 1997, 1999a) favours the penetration and crystallisation of soluble salts in the structure material of the fossilised forest.
The same material shows in several parts relatively high hardness (Lampropoulos et al., 1997, 1999a) fact, which results to a great sensitivity. Additionally, it consists of various different minerals (quartz, tridymite, cristobalite), (Lampropoulos et al., 1997, 1999a), which results to discontinuities in the structure and the formation of cracks produced by mechanical stresses caused by the crystallisation of soluble salts.
In the case of fossilised forest of Kastoria the action of soluble salts is primarily obvious by macroscopic observation of the alveolar corrosion pattern in many parts of the surface of the tree trunks from the fossilised forest. Then, the presence of soluble salts is also apparent by the presence of chloride and sulphate ions on the surface and in the pores of the material of the fossilised forest. Their crystallisation and their actions are shown in the V. Furlan diagrams, for all months each year and for the period 1955 - 1997.
From the previous diagrams, in the case of fossilised forest of Kastoria, it is shown that during the months January, February, March, April, November and December, most plotted dots - combinations of temperature and relative humidity - are falling over the curve and therefore crystallisation of sodium sulphate occurs during these months in the pores of the material of the fossilised forest of Kastoria.

Also, the presence of the frost damage and biological organisms was observed, mostly of lichens and moss and as well as the presence of cracking possibly caused by the frost action. It is also possible that soluble salts are transferred by the capillary rising.

The relatively high porosity of the petrographic material of the fossilised forest of Kastoria (Lampropoulos et al. 1999b) favours the penetration and crystallisation of soluble salts in the structure material of the fossilised forest.

The same material shows in several parts relatively high hardness (Lampropoulos et al. 1999b) fact, which results to a great sensitivity. Additionally, it consists of various different minerals (quartz and tridymite), (Lampropoulos et al. 1999b), which results to discontinuities in the structure and the formation of cracks produced by mechanical stresses caused by the crystallisation of soluble salts.

Based on the above mentioned results, the need for a direct study and application of a plan for conservation and protection of the tree-trunks of the fossilised forest of Lesvos and Kastoria, which will be based on thoroughly - detailed study and research of materials and methods for the necessary interventions, becomes obvious and essential. The specific actions should become a priority, in the general presentation policy of the fossilised forests of Lesvos and Kastoria.

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