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Methods used for the determination of soluble salts into the material of fossilised trees. Case study of the fossilised forest in Lesbos Island.

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Summary

The soluble salts crystalization under various conditions of temperature and humidity, consists one of the major deterioration factors of the porous materials as in the case of the structure material of the fossilized forests.

The determination of the presence of soluble salts into the porous material can be used as an indicator for the estimation of the state of preservation of the fossilized trees and therefore it is necessary for the planning of conservation and preservation treatments.

In this study it is presented a pilot application of a non-destructive method for the identification and measurement of soluble salts contained into the structure material of the fossilized forest of Lesbos Island. The method is based on the application of neutral paper pads impregnated in deionized water on the tree trunks. Afterwards the pads were put and stirred into deionized water and solubilisation of the absorbed ions took place. The specific electric conductivity as well as the sulphur (SO_4^{2-}) and chlorine (Cl^-) ions were determined from the resulted solutions.

Introduction

The fossilised - petrified forest of Lesvos, 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).

Soluble salt crystallisation in the fossilised forest material.

Soluble salts are one important deterioration factor for stone materials and fossils (Torraca 1988, Lambropoulos 1993, Child 1994). Most important are the actions of sodium chloride and sodium sulphate, which under particular 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 (Lambropoulos 1993, Child 1994):

1. **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.

2. **Underground waters**, 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 analogies the following ions:

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

3. **Acidic air pollutants**:

- sulphur dioxide (SO_2)
- sulphur trioxide (SO_3)
- nitrogen oxides (NO_X)
- hydrochloric acid (HCl)

Which attack the carbonate admixtures and the alkali compounds of the material and form the corresponding sulphate, nitrate or chloride salts, and contribute to the disintegration of the fossilised material. This case is very general and it is therefore obvious that it does not apply on the case of the petrographic material of the fossilised forest in Lesvos.

4. **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:

- 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

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:

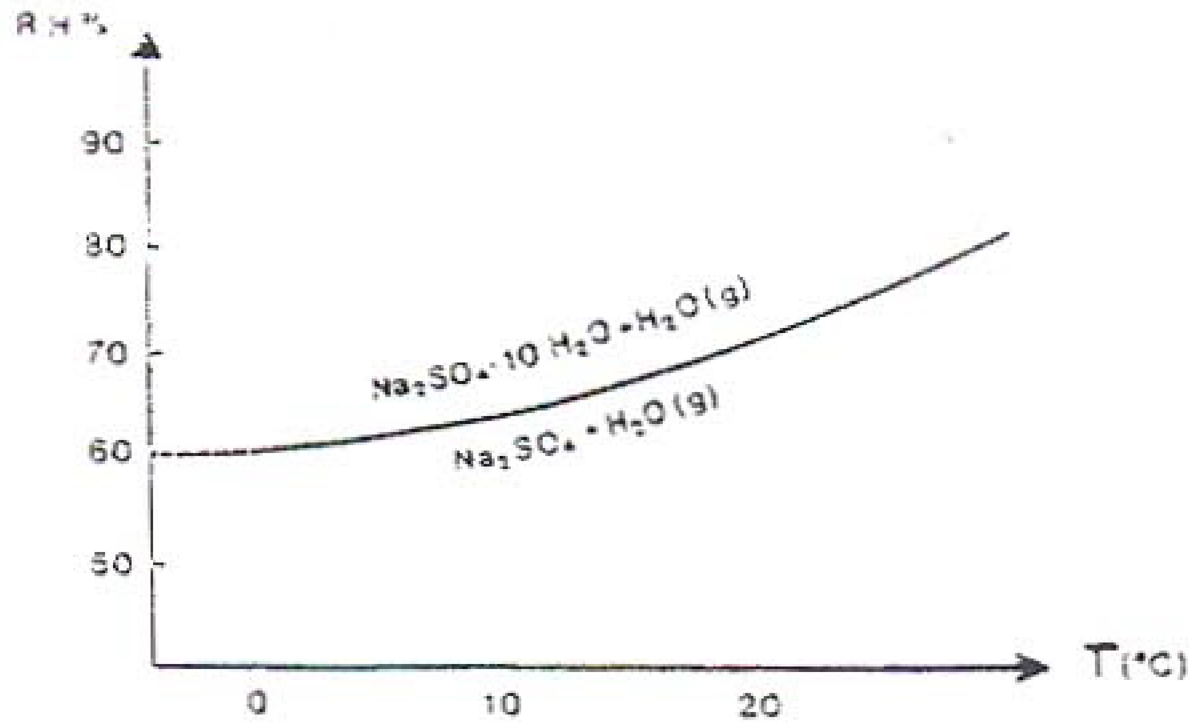
$$P = (R \cdot T/Us) \cdot \ln(C/Cs)$$

Where:
P = crystallisation pressure in Atms
R = constant of noble gases which equals 0.082 lt·Atm/mole·grad.
T = absolute temperature in °K.
Us = molecular volume of solid salt in lt/mole.
C = present concentration of the salt.
Cs = concentration of the saturated salt.

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

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

and 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 °C (Amoroso and Fasina 1983, Lambropoulos 1993).



Stability regions of anhydrous Na_2SO_4 and of $Na_2SO_4 \cdot 10H_2O$ in correlation with the temperature and the relative humidity of the atmosphere (V. Furlan).

Sodium carbonate in contact with water, over 32 °C appears as thermonatrite and below 32 °C as natrite. In the atmosphere, for relative humidity 50-80%, in the period 0-30 °C we have the transition from monoclinic decahydrite, into trigonal heptahydrite and into rhombohedric monohydrite.

Magnesium sulphate hydrate (microcrystallic kieserite) in contact with water, at 1,8 °C, is transformed into rhombohedric epsomite which is stable up to 45 °C, with a corresponding volume increase of 170%.

The transformation of gypsum into anhydrite in contact with distilled water, happens at 45 °C, while in saturated solution of sodium chloride, the corresponding temperature is 18 °C. 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 to surface disintegration 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 contuction area by contraction-expansion, and thus is causing disintegration and degradation of the material.

Exposition in open air may cause degradation of the petrographic material, according to the following procedure:

In appropriate-particular conditions of temperature and humidity, soluble salts which are contained inside the pores are crystallised, thus resulting to mechanical stresses and fractures, in according to the previously mentioned mechanisms.

Aim

An extensive list of accurate identification methods of susceptible minerals has been presented (Howie 1992). The present paper, aims at the development of non-destructive methods for the determination of the presence and crystallisation of soluble salts in the petrographic material of the fossilised forest of Lesvos, in a way that the formation of a program of action for its protection will be possible. 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.

Materials and Methods

The presence of soluble salts in the petrographic material of the fossilised forest of Lesvos, was determined by the application of neutral paper compresses 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.

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.

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 (obtained by the application of neutral paper compresses 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 following results:

I/n	Cd (μs/cm²)	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

Sample 5 is de-ionised water and was used as a comparison towards the other results of the study.

From the previous table 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.

The processing of the climatological data are shown in the following tables for temperature and relative humidity.

Then these tables 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 1955-1993.

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 each year.

From the previous diagrams 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 (Lambropoulos et al., 1997) 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 (Lambropoulos et al., 1997) fact which results to a great sensitivity. Additionally, it consists of various different minerals (quartz, tridymite, cristobalite, (Lambropoulos et al., 1997), 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 - conclusions, 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, 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 forest of Lesvos.

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