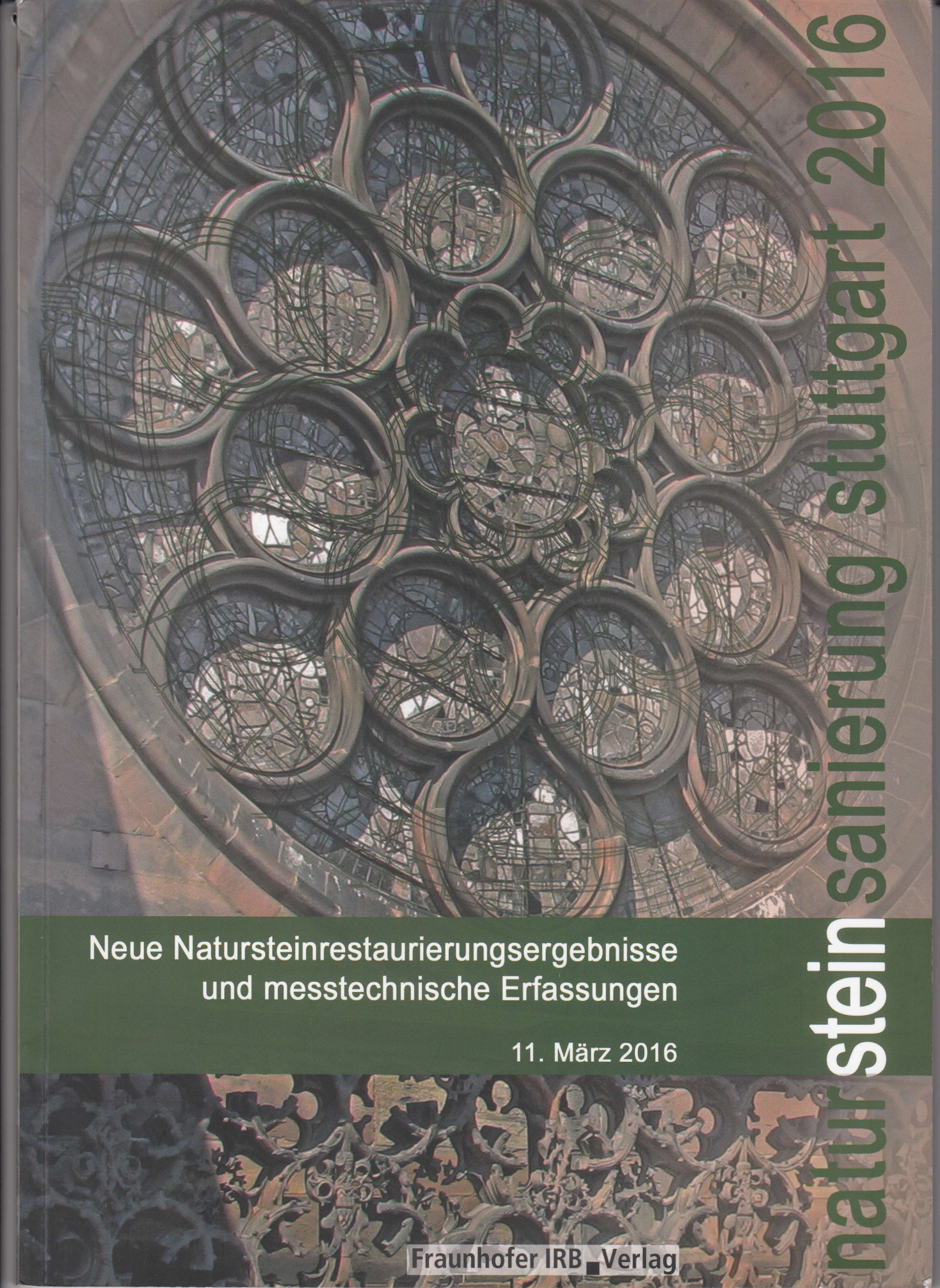


naturstein sanierung stuttgart 2016

Neue Natursteinrestaurierungsergebnisse
und messtechnische Erfassungen

11. März 2016

Fraunhofer IRB Verlag



Gabriele Patitz, Gabriele Grassegger, Otto Wölbert (Hrsg.)

Natursteinsanierung Stuttgart 2016

Neue Natursteinrestaurierungsergebnisse und messtechnische Erfassungen
sowie Sanierungsbeispiele

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Liebe Teilnehmerinnen und Teilnehmer, liebe Leserinnen und Leser,

herzlich Willkommen zur 22. Fachtagung Natursteinsanierung an der HFT in Stuttgart. Wir wünschen Ihnen einen interessanten und abwechslungsreichen Tagungstag. Mit den zusammengestellten Beiträgen aus der Forschung und Praxis möchten wir Ihnen viele neue Anregungen und Ideen für Ihre tägliche Arbeit mitgeben.

Die Fachbeiträge und weiterführenden Informationen finden Sie in dem vorliegenden Tagungsband. In Ergänzung dazu können Sie sich in der Fachausstellung über neue und altbewährte Produkte und Arbeitsmaterialien informieren. Fachliteratur bieten Ihnen die Informationsstände des Fraunhofer IRB Verlages und der Stand des Landesdenkmalamtes Esslingen an.

Die diesjährige Exkursion führt uns zum Straßburger Münster und wurde von den Mitarbeitern der Fondation de l'Œuvre Notre-Dame organisiert und vorbereitet. Wir erhalten Einblicke in die Werkstätten der Straßburger Münsterbauhütte und werden die Baustellen an der Südquerhausfassade und an der Galerie Goetz besichtigen. Eine geführte Turmbegehung sowie eine Führung zum europäischen Steinhandwerk mit Schwerpunkt Tradition & Brauchtum – Rituale & Zeremonien – Symbole & Allegorien runden das Tagungsprogramm ab.

Die Vorträge in Stuttgart spannen einen Bogen von der Verfugung des Natursteinmauerwerks auf der Wartburg über die Sanierung von hydrophobierten Sandsteinfliguren am Schloss Weißenstein, das Schadensbild und die Schadensentwicklung eines Marmorgrabmales in der Schweiz, die Steinrestaurierung am Hauptportal der Stiftsbasilika St. Martin in Landshut und Forschungsarbeiten zu Untersuchungen der Natursteinverwitterung mit Ultraschall-Oberflächen-Messungen.

Mit den ausgewählten Themen und Informationsständen wollen wir Ihnen zwei spannende und inspirierende Tage bieten.

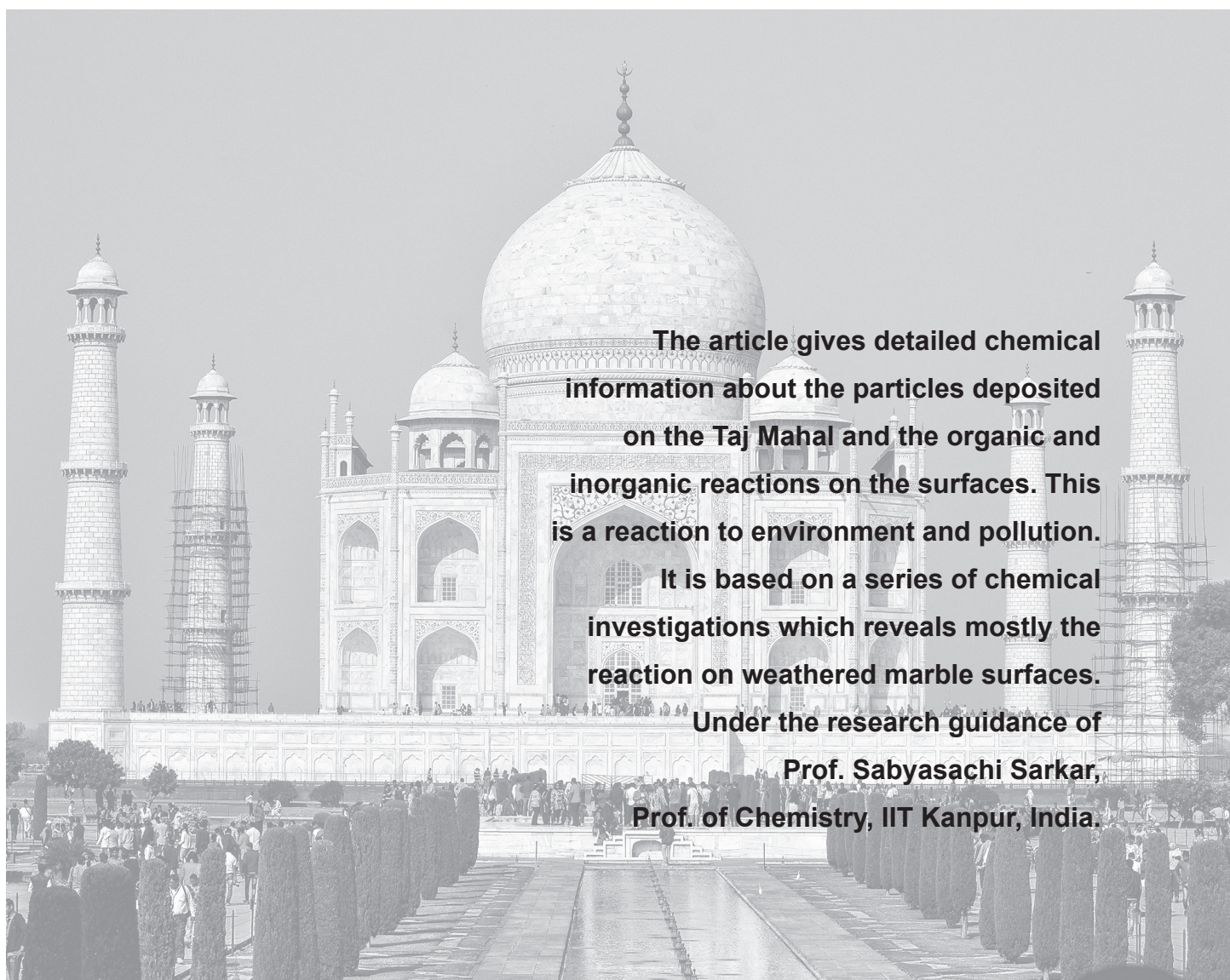
Wir wünschen Ihnen einen interessanten fachlichen Austausch und viele neue Anregungen und Ideen für Ihren Alltag!

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Chemistry and Deposition of Airborne Particulates on the Taj Mahal at Agra/India

Investigations on Soiling at Monuments in a Semi-Arid Zone of India.

von Deepankar Banerjee



The article gives detailed chemical information about the particles deposited on the Taj Mahal and the organic and inorganic reactions on the surfaces. This is a reaction to environment and pollution.

It is based on a series of chemical investigations which reveals mostly the reaction on weathered marble surfaces.

Under the research guidance of Prof. Sabyasachi Sarkar, Prof. of Chemistry, IIT Kanpur, India.

1 Introduction

The environmental species impacting upon the Taj Mahal at Agra have been studied. In this research endeavour based on research projects in different aspects of aerosol-substrate reaction studies, the impacts and implications of various phenomena have been considered. Thus impact of precipitation, determination of origin of aerosols, impact of pollutants, impact of dust, marble weathering phenomena, filter analysis and impact of bacteria and related micro flora have been studied in the light of existing research methodologies and sampling profiles. The pollution grade and situation can be obtained from the Central Pollution Control Board (C.P.C.B.) under Ministry of

Environment and Forests, Government of India (Table 1).

2 Methodology and samples

The elemental profile and morphology of aerosols and marble were studied by the SEM-EDS (Scanning Electron Microscopy and Energy dispersive spectroscopy), the mineralogical profile was studied by XRD (X-ray diffraction), the organic matter of aerosols, algae were studied by FTIR (Fourier Transform Infrared Spectroscopy). The water soluble fractions of the organic aerosols were analysed by NMR Spectroscopy.

Tab. 1 Pollution grade and situation, Central Pollution Control Board (C.P.C.B.) under Ministry of Environment and Forests, Government of India. Explanation: SPM = Suspended Particulate Matter

Parameters → Years ↓	SO2 µg/m ³	NO2 µg/m ³	SPM µg/m ³
2002	5	22	376
2003	4	22	352
2004	5	18	309
2005	9	22	306
2006	6	22	316
2007	6	23	296
2008	7	22	304
2009	6	20	334
2010	5	20	333
2011	4	20	290
2012	5	18	322
2013	4	17	275
2014	4	15	277



Fig. 1 Location of the samples investigated: water spout with and without black crusts (left side), pieces of crusts (right side)

Samples and Sampling

Micro samples of crust particles have been collected as a result of natural weathering phenomena. Micro samples peel off or give away from places such as water spouts or water passage areas (Fig 1). Dust fall is a monthly measurement of dust deposited on a monthly basis. The algal input into the dust fall, soluble organic and inorganic content of aerosols from dust fall have been studied. Dust from high volume filter samples (Dust collected by High Volume Sampler, Particle diameter is on the coarse mode. The height of the sampling station is 20 meters from the ground level.), coarse dust from High Volume Samplers have been collected and studied. Marble with algal growth have been collected from the monument stores and studied. The equipment used for dust sampling was located at the north-west corner of the monument and height of 20 meters from the ground level, the equipment was an "Envirotech" make High Volume Sampler.

Chemical Composition of the Dust by different methods

The samples studied were :

1. **Dust** was characterised for seasonal, morphological, mineralogical, elemental profiles. (Particle size has not been measured but it is in the coarse mode). Grain size has not been measured.

- A **Composite dust**: Composite dust represents the dust profile of an entire year. The XRD (X-ray diffraction) results of this dust gave the presence of Kaolinite, Microcline, Quartz, Calcite, Hematite, Magnetite and Iron Oxide Hydroxide (Table 2).
- B Composite dust represents the dust of all seasons (summer, winter and rainy). **Seasonal profiles of the dust**:
- I. Summer dust: the summer dust analysed by XRD gave the presence of Kaolinite, Microcline, Quartz, Calcite, Hematite (Table 3).
 - II. Winter dust: the winter dust analysed by XRD gave the presence of Kaolinite, Microcline, Quartz, Calcite, Hematite, Magnetite (Table 4).
- C **Elemental profile**: of the dust analysed by SEM-EDS system gave the percentage composition of Na, Mg, Al, Si, S, Cl, K, Ca, Fe and Mn (Table 5). The SEM images of the dust showed a Silicate matrix in which soil oriented minerals with Si/Al elements have appearances of Iron oxide particles. The Iron oxide particles show a typical particle morphology along with soil oriented particles. Soil oriented geometrical patterns like rectangular, rhomboidal and other irregular shaped particulate patterns could be seen^{2,3} (Fig 2).

Tab. 2 X-ray Data of the composite dust (I. Expt. = Intensity of Experimented Sample, I. Std. = Standard Value of Intensity as per JCPDS Software, dA° Expt. = d Values of Experimented Sample, dA° Std. = Standard d Values)

Name of Mineral	P.D.F. Card	I. Expt.	I. Std.	dA° Expt.	dA° Std.
Kaolinite $Al_4(OH)_8Si_4O_{10}$	78-2110	52.43	100	7.23	7.12
Potassium Aluminium Silicate (Microcline) $KAlSi_3O_8$	19-926	49.02	100	4.22	4.20
Quartz SiO_2	46-1045	100	100	3.31	3.34
Calcite $CaCO_3$	05-0586	39.15	100	3.00	3.03
Hematite Fe_2O_3	33-0664	29.62	100	2.68	2.70
Magnetite Fe_3O_4	77-1545	25.46	100	2.53	2.53
Iron Oxide Hydroxide $FeOOH$	18-639	28.06	100	2.50	2.50

Tab. 3 X-ray data of summer dust

Name of Mineral	P.D.F. Card	I. Expt.	I. Std.	dA Expt.	dA Std.
Kaolinite $Al_4(OH)_8Si_4O_{10}$	78-2110	62	100	7.7	7.12
Potassium Aluminum Silicate (Microcline) $KAlSi_3O_8$	19-926	66	100	4.2	4.22
Quartz SiO_2	46-1045	100	100	3.32	3.34
Calcite $CaCO_3$	05-0586	69	100	3.01	3.03
Hematite Fe_2O_3	33-0664	65	100	2.72	2.70

Tab. 4 X-ray data of winter dust

Name of Mineral	P.D.F. Card	I. Expt.	I. Std.	dA° Expt.	dA° Std.
Kaolinite $Al_4(OH)_8Si_4O_{10}$	78-2110	60	100	7.5	7.12
Potassium Aluminium Silicate (Microcline) $KAlSi_3O_8$	19-926	62	100	4.22	4.22
Quartz SiO_2	46-1045	77	100	3.32	3.34
Hematite Fe_2O_3	33-0664	62	100	2.85	2.70
Magnetite Fe_3O_4	19-629	61	100	2.40	2.53

Tab. 5 EDS data of dust (calibrated)(Wt % = weight percent)

Element	Wt %
Na	01.50
Mg	02.76
Al	19.30
Si	39.51
S	00.58
Cl	01.03
K	13.93
Ca	01.76
Mn	01.38
Fe	11.74
Ni	01.58
Cu	02.95

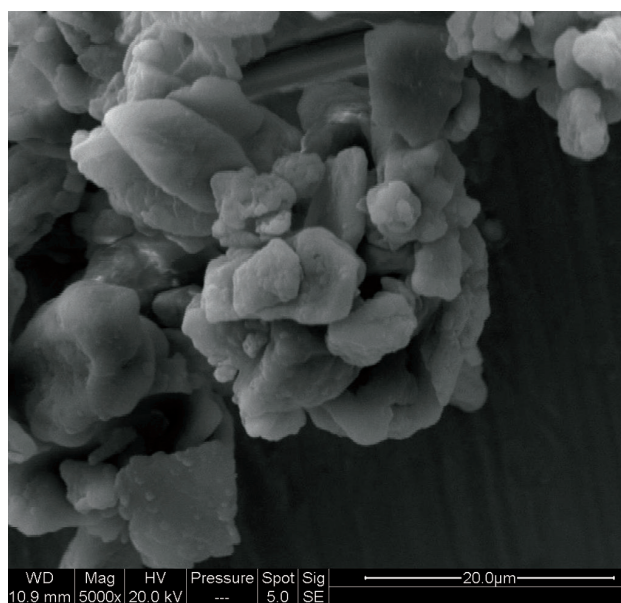


Fig. 2 SEM- Image of dust

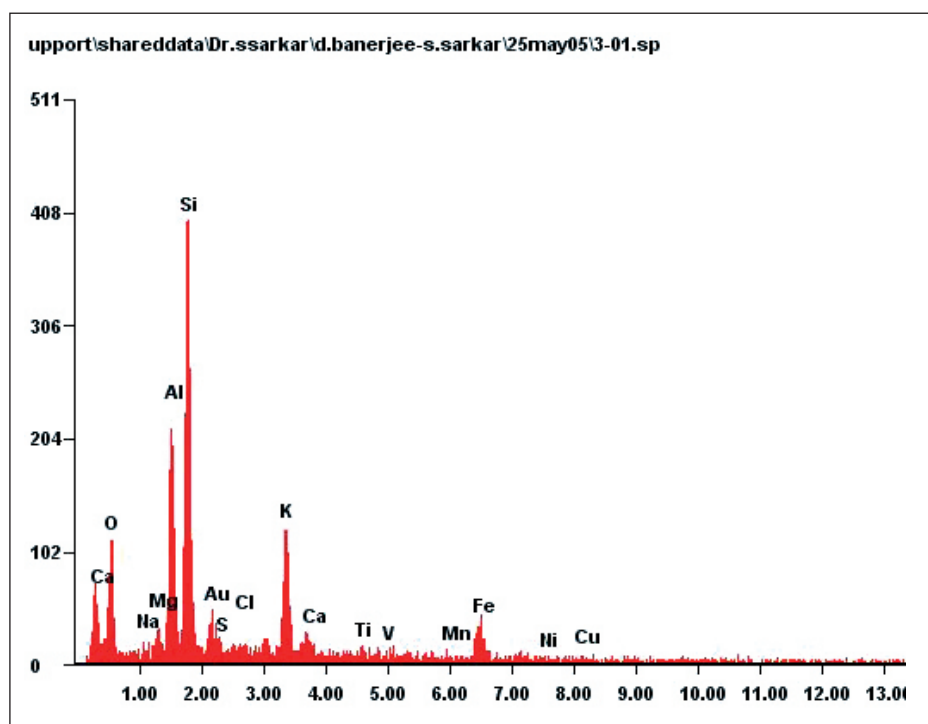


Fig. 3 EDS spectra of dust

Tab. 6 X-Ray data of High volume filter sample dust

Name of Mineral	P.D.F. Card	I. Expt.	I. Std.	dA° Expt.	dA° Std.
Kaolinite $Al_4(OH)_8Si_4O_{10}$	78-2110	62.23	100	7.16	7.12
Potassium Aluminium Silicate (Microcline) $KAlSi_3O_8$	19-926	56.43	100	4.26	4.22
Quartz SiO_2	46-1045	64.37	100	3.30	3.34
Calcite $CaCO_3$	05-0586	46.64	100	3.03	3.03
Hematite Fe_2O_3	33-0664	42.86	100	2.77	2.70
Hematite αFe_2O_3	13-534	33.52	100	2.69	2.69
Iron Oxide Hydroxide $\delta FeOOH$	13-87	36.98	100	2.55	2.55

Tab. 7 X-Ray data of fresh marble (marble used in conservation)

Name of Mineral	P.D.F. Card	I. Expt.	I. Std.	dA° Expt.	dA° Std.
Calcite	05-0586	100	100	3.00	3.03
$CaCO_3$		16.46	14	2.45	2.49
		20.77	18	2.27	2.28
		19.44	18	2.10	2.09
		23.59	17	1.90	1.91
		21.53	17	1.87	1.87

Tab. 8 X-Ray data of weathered marble

Name of Mineral	P.D.F. Card	I. Expt.	I. Std.	dA° Expt.	dA° Std.
Calcium Oxalate Hydrate Whewellite $CaC_2O_4 \cdot H_2O$	20-231	35.95	100	5.93	5.93
Calcium Carbonate Hydrate $CaCO_3 \cdot H_2O$	15-20	16.31	100	4.39	4.33
Calcite $CaCO_3$	05-0586	100	100	3.01	3.03
Calcium Iron Magnesium Carbonate Ankerite [Ca(Fe, Mg) (CO ₃)]	33-282	49.8	100	2.86	2.9
Calcium Carbonate Hydrate $CaCO_3 \cdot H_2O$	24-513	11.00	100	2.66	2.63
Magnetite Fe_3O_4	19-629	8.27	100	2.56	2.53

2. Analysis of High volume filter sample:

The High volume filter sample was analysed by XRD and the minerals identified were Kaolinite, Microcline, Quartz, Calcite, Hematite, Magnetite and Iron Oxide Hydroxide. Thus the mineralogical profile of the composite dust and the High volume filter sample were similar (Table 6).

3. Mineralogical analysis of marble:

- A Mineralogical analysis of fresh marble (marble used in conservation and restoration): The XRD results of such marble gave the presence of Calcite phases in relative intensities (Table 7).
- B Mineralogical analysis of weathered marble with black crust: The XRD results of such marble specimen gave the presence of Whewellite, Calcium carbonate hydrate, Ankerite and Magnetite (Table 8).

Tab. 9 FTIR band assignments for organic content of marble crust

Bands cm^{-1}	Functional groups
2924	CH_2 symmetric
2852	CH_2 asymmetric
1748	C=O stretching of esters
1561	Substituted aromatics
1460 } 1377 }	C-H deformation of CH_3 and CH_2
1146	C-O-C asymmetric or symmetric stretching of esters and carbohydrates
739	Aryl mono-substituted or C-H

Tab. 10 EDS of fresh marble

Element	Wt %
Si	02.95
Ca	97.05

Tab. 11 Analysis of weathered marble with black crust by EDS

Element	Percentage
AL	1.30
Si	0.0
Ca	84.77
Mn	6.74
Fe	7.20

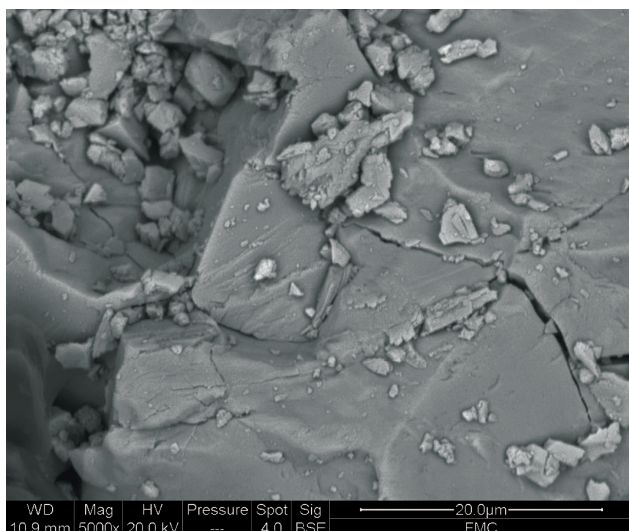


Fig. 5 SEM-image of fresh marble

4. Weathering of the Marbles and analytic results

The marbles exposed were investigated for organic composition of the crusts, the overall composition of the marbles and chemical reactions due to soiling and biological attack.

5. Analysis of organic content of the weathered marble crust by FTIR spectroscopy:

Crust is considered a general term of a fallen micro marble sample. In some cases the crusts also contain biological matter like algae. The FTIR analysis gave the presence of CH_2 symmetric and asymmetric stretch, C=O stretching of esters, substituted aromatics, C-H deformation of CH_3 and CH_2 , C-O-C asymmetric or symmetric stretching of esters and carbohydrates, Aryl mono-substituted or C-H stretch⁴ (Table 9).

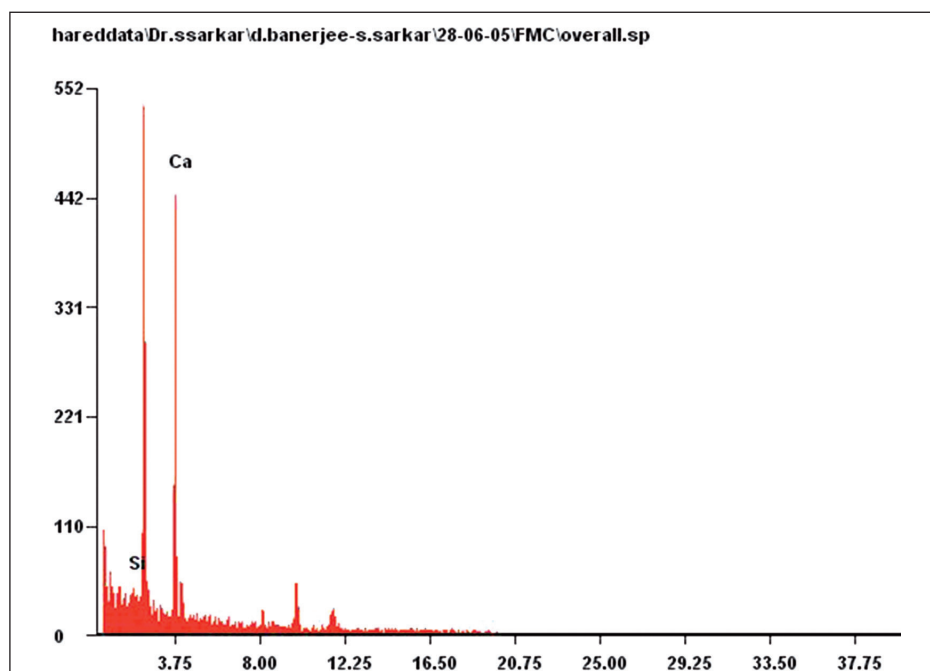


Fig. 4 EDS spectra of fresh marble (marble used in conservation and restoration)

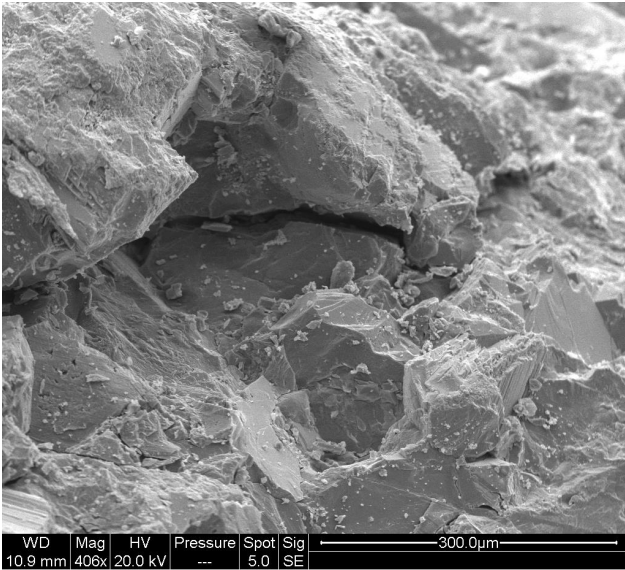


Fig. 6 SEM image of weathered marble with black crust

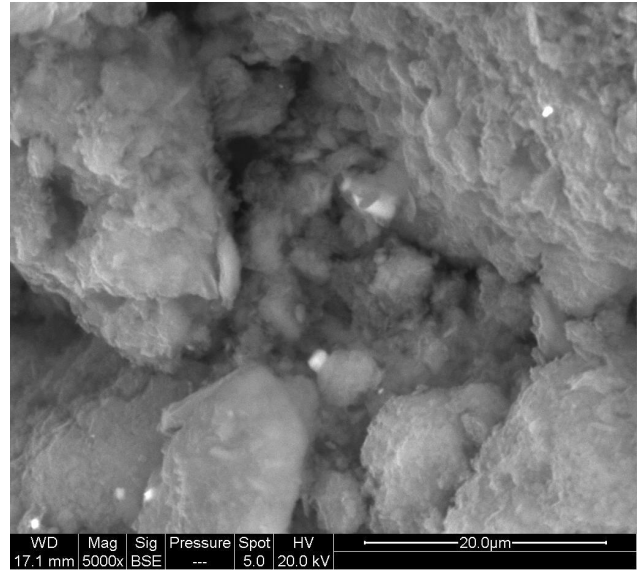


Fig. 7 SEM image of Algal growth on marble crust

Tab. 12 X-ray data of marble with algal crust

Name of Mineral	P.D.F. Card	I. Expt.	I. Std.	dA° Expt.	dA° Std.
Calcium Oxalate Hydrate Whewellite $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	75-1313	10.66	100	5.94	5.92
Calcium Silicate CaSiO_3 (Wollastonite)	27-88	5.86	100	2.92	2.97
Calcium Carbonate Hydrate $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$	34-513	11.15	100	2.65	2.63

6. Elemental analysis of marble:

A Analysis of fresh marble (marble used in conservation and restoration)

The analysis of fresh marble by a SEM-EDS system gave the presence of Calcium 97.05% and Si-2.95%, the SEM images revealed a Calcite matrix in which the grains are in different forms without any cracks, gaps or pores (Table 10, Fig 5). Analysis of a fresh marble already done by Energy Dispersive Spectroscopy. (Relative percent because of the EDS-method, which can not detect $-\text{CO}_3$, water and oxide.)(Fig 4)

Analysis of weathered marble crust by a SEM-EDS system gave the presence of Calcium 84.7%, Al- 1.3% , Fe -7.2% and Mn- 6.7%, the SEM images showed weathering profiles. Pits, pores were visible. Micro and macro pores were visible with different shapes. Such pores might have occurred due to fracturing mechanisms. The marble showed preliminary weathering profiles (Table 11, Fig 6).

7. Mineralogical profile of marble with black crust:

Marble with algal crust was analysed by XRD and the phases found were Whewellite, Wollastonite (standard high pressure and temperature formation within the metamorphic process) and Calcium carbonate hydrate (Table 12).

Wollastonite may have been formed by changes in temperature witnessed by the geographical area where temperature variations are between 1 °C in winters to 45 °C in summer. Calcium carbonate hydrate may have been formed by the action of water on the marble. The impact of algal growth on the weathered marble can be seen by the presence of its metabolic product Whewellite.

8. Analysis of weathered marble encrusted with algae (algal growth on marble):

SEM images of algal growth on weathered marble were examined. The Calcite grains were intermixed with the bioorganic cellular material of the blue-green algae. The algal mass had penetrated into the weak zones of the calcitic mass. The

Tab. 13 EDS analysis of seasonal soluble dust from dust fall

Element	Summer	Winter	Rainy
	Wt %	Wt %	Wt %
Mg	11.0	13.5	9.66
Al	3.75	1.01	6.3
Si	32.5	5.3	31.0
K	12.0	0.0	13.48
Ca	13.4	76.48	18.2
Fe	27.0	3.7	21.3

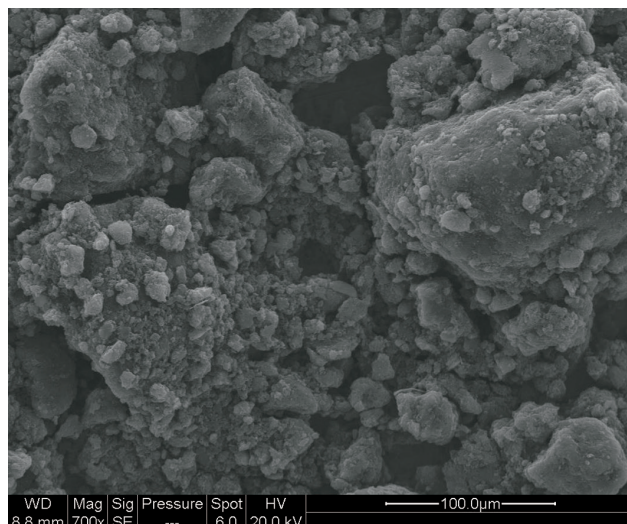


Fig. 8 SEM image of soluble summer dust from dust fall

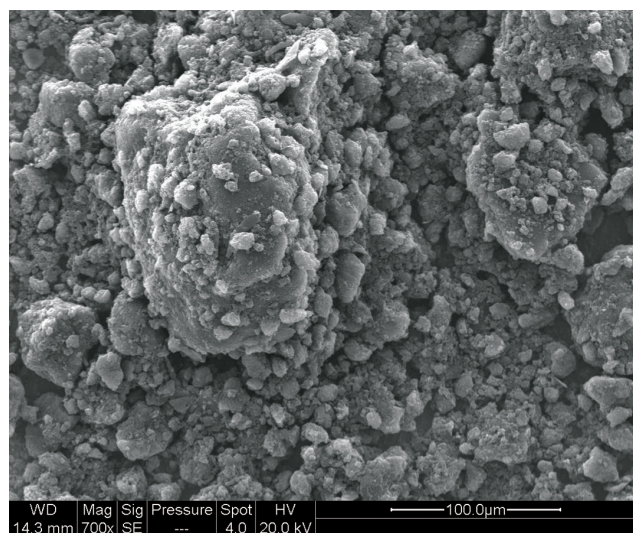


Fig. 9 SEM image of soluble winter dust from dust fall

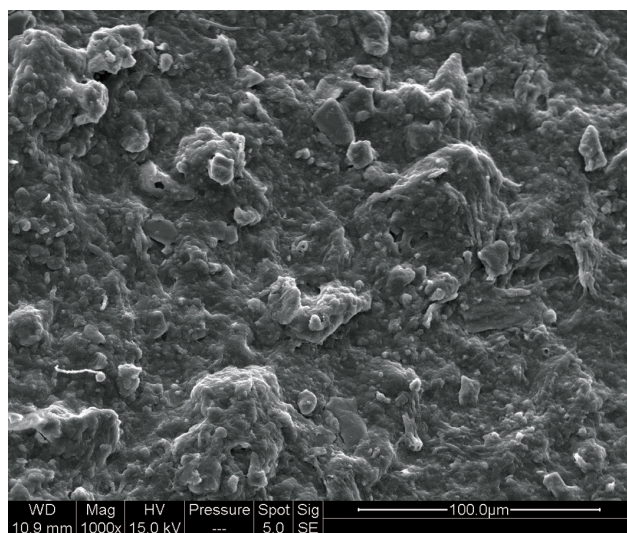


Fig. 10 SEM image of algae

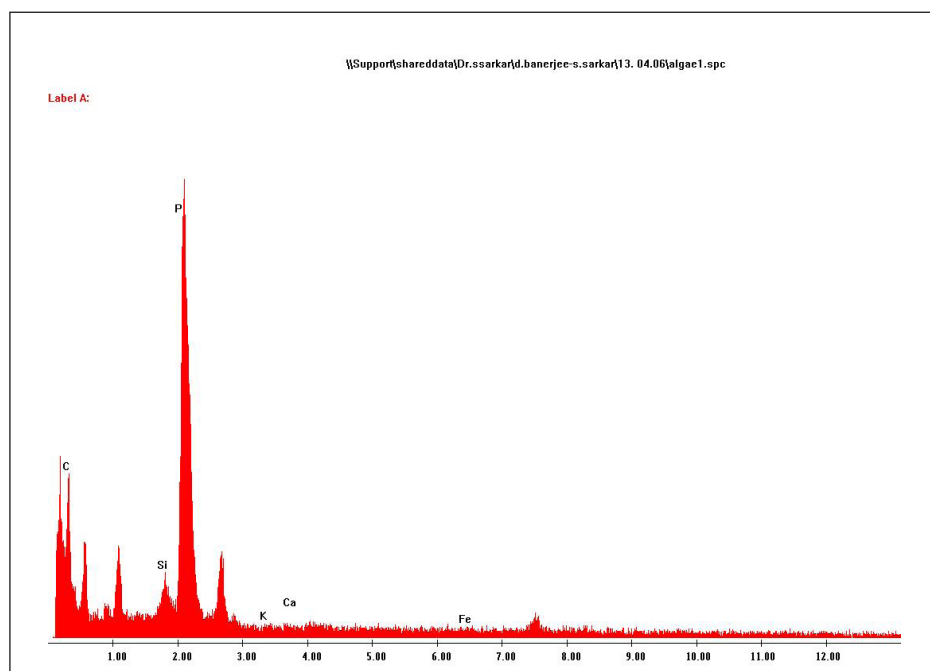


Fig. 11 EDS spectra of algae

resulting topography was a organo-mineral complex. The fibrillar material of the algal cell wall had become interspersed with the micron sized calcite grains. Calcite grains had been impregnated with algal filamental invasions, which had encrusted the small pits and pores of the calcitic mass (Fig 7).

9. The chemical composition of the soluble dust:

The dust was investigated by XRD, the soluble part of the dust was estimated as soluble dust fall by filtering the soluble part of the dust fall sample through a Whatman 42 filter paper. The soluble content of the dust from the dustfall was analysed by SEM-EDS method. The soluble dust from the dust-fall thus represents the water soluble fraction.

10. Analysis of soluble dust

A The soluble dust from the dust fall samples was analysed by a SEM-EDS system. **Seasonal profiles of the soluble dust:-**

- I. **Summer season soluble dust:** Summer soluble dust gave the percentage composition of Mg-11 %, Al-3.75 %, Si-32.5 %, K-12 %, Ca-13.4 % and Fe-27.4 %
- II. **Rainy season soluble dust:** Rainy season soluble dust gave the percentage composition of Mg-9.66 %, Al-6.3 %, Si-31 %, K-13.4 %, Ca-18.2% and Fe-21.3 %.
- III. **Winter season soluble dust:** Winter season soluble dust gave the percentage composition of Mg-13.5 %, Al-1 %, Si-5 %, K-0 %, Ca-76.5 % and Fe-3.7 % (Table 13).

The SEM images of all the seasonal profiles of soluble dust show agglomerated clay structure in which the soil particles were closely attached to each other, micro and macro grains were visible. Fragmental evidences of Iron oxide particles along with the basic soil oriented Si/Al elemental profiles of particles were visible. Clay particles in different irregular sizes-

Tab. 14 FTIR analysis of algae

Bands cm^{-1}	Functional groups
3418 cm^{-1}	O - H and N - H of water Amide A
2923 cm^{-1}	CH_2 stretch of Fatty acids
2853 cm^{-1}	CH_2 stretch of Fatty acids
1637 cm^{-1}	Amide I of Protein of β pleated sheet structure.
1463 cm^{-1}	CH_2/CH_3 of Lipids Amide II
1026 cm^{-1}	Carbohydrates
583 cm^{-1}	} Mixed Si - O deformations and Octahedral sheet vibrations
519 cm^{-1}	
467 cm^{-1}	

micro, medium and large particles can be seen. These particles were identical with the morphological structure of the airborne dust particles (Fig 8, 9).

The clay profiles are identical of a typical soil oriented particle matrix.

11. Analysis of algae from dust fall deposits:

The algae from the dust fall samples was analysed by SEM-EDS, thus the algae analysed was from the dust fall deposit and not from the marble crust.

I. Algae chemical analysis by SEM-EDS:

The blue green algae which grow on the Calcitic mass of the monument showed a Chlorophyllous cell structure matrix based on natural organic polymers like Proteins, Sugars and Phosphates. Some evidences of other microbial mass like fungal strains can also be ascertained. Evidences of metal particulates embedded on the algal mass can be seen in the SEM images (Fig 10).

Tab. 15 NMR of water soluble summer aerosol

ppm values	Functional Groups	Identifications
0.9–1.9ppm	C-H	Purely aliphatic moieties
1.9–3.2ppm	H-C-C=	Protons bound to aliphatic carbon atoms adjacent to unsaturated groups like Alkenes (allylic protons) Carbonyl or Imino groups (heteroallylic protons) or aromatic rings (benzylic protons)
3.3–4.1ppm	H-C-O	Protons bound to oxygenated aliphatic Carbon atoms (hydroxy or alkoxy groups)
6.5–8.3ppm	Ar-H	Aromatic protons
4.1–4.5ppm		Organo Nitrates

Tab. 16 NMR of water soluble rainy season aerosol

ppm values	Functional Groups	Identifications
0.9–1.9PPM	C-H	Purely aliphatic protons
1.9–3.2ppm	H-C-C=	Protons bound to aliphatic carbon atoms adjacent to unsaturated groups like Alkenes (allylic protons) Carbonyl or Imino groups (heteroallylic protons) or aromatic rings (benzylic protons)
3.3–4.1ppm	H-C-O	Protons bound to oxygenated aliphatic Carbon atoms (hydroxy or alkoxy groups)
6.5–8.3ppm	Ar-H	Aromatic protons

Tab. 17 NMR of water soluble winter season aerosol

ppm values	Functional Groups	Identifications
0.9–1.9PPM	C-H	Purely aliphatic protons
1.9–3.2ppm	H-C-C=	Protons bound to aliphatic carbon atoms adjacent to unsaturated groups like Alkenes (allylic protons) Carbonyl or Imino groups (heteroallylic protons) or aromatic rings (benzylic protons)
3.3–4.1ppm	H-C-O	Protons bound to oxygenated aliphatic Carbon atoms (hydroxy or alkoxy groups)
6.5–8.3ppm	Ar-H	Aromatic protons

The elemental analysis by EDS gave imprints of Phosphates, Carbon and silica absorbed on the surface of the algae (Fig 11).

II. Algae analysis by FTIR spectroscopy:

The algae gave signatures of water absorption on proteins, CH₂ stretch of fatty acids, Amide I of Proteins of β pleated sheet structure, CH₂/CH₃ of Lipids Amide II, Carbohydrates, Mixed Si-O deformations and Octahedral sheet vibrations (Table 14).

12. Organic aerosols – chemical composition of the water soluble and insoluble fractions

The organic aerosol was collected from the Glass Fiber filter paper from the High Volume Samplers and the organic matter taken was the water soluble fraction.

13. Analysis of water soluble fractions of Organic aerosols:

The water soluble fraction of the organic aerosols extracted from filters (qualitative) were analysed based upon seasonal profiles by NMR spectroscopy:

I. Water soluble summer aerosol:

Functional groups identified were purely aliphatic moieties, Protons bound to aliphatic carbon atoms adjacent to unsaturated groups like Alkenes (allylic protons) Carbonyl or Imino groups (heteroallylic protons) or aromatic rings (benzylic protons), Protons bound to oxygenated

aliphatic carbon atoms (hydroxyl or alkoxy groups), Aromatic protons and Organo Nitrates (Table 15).

II. Water soluble rainy season aerosol:

Functional groups identified were purely aliphatic Protons, Protons bound to aliphatic carbon atoms adjacent to unsaturated groups like Alkenes (allylic protons) Carbonyl or Imino groups (heteroallylic protons) or aromatic rings (benzylic protons), Protons bound to oxygenated aliphatic carbon atoms (hydroxyl or alkoxy groups), Aromatic protons (Table 16).

III. Water soluble winter season aerosol:

Functional groups identified were purely aliphatic Protons, Protons bound to aliphatic carbon atoms adjacent to unsaturated groups like Alkenes (allylic protons) Carbonyl or Imino groups (heteroallylic protons) or aromatic rings (benzylic protons), Protons bound to oxygenated aliphatic carbon atoms (hydroxyl or alkoxy groups), Aromatic protons. (Table 17)

14. Analysis of total insoluble matter in the dust fall:

The analysis of the total insolubles have been studied in the seasonal patterns by FTIR spectroscopy.

I. Summer season total insoluble matter:

The band assignments gave imprints of absorbed water on polymeric compounds, CH₂ symmetric and CH₂ asymmetric, Amide I and

Tab. 18 FTIR analysis of total insoluble matter in summer dust fall

Bands cm^{-1}	Functional groups
3690 cm^{-1}	Outer Hydroxyl groups
3401 cm^{-1}	3402-3344 cm^{-1} OH stretching of Polymeric compounds.
2924 cm^{-1}	CH_2 Group Symmetric
2855 cm^{-1}	CH_2 group A symmetric
1651 cm^{-1}	Amide I band
1546 cm^{-1}	C-N stretching vibration of Peptidic band of Proteins Amide II band.
1424 cm^{-1}	1424-1417 cm^{-1} Phenolic OH C=O stretching of Carboxylates.
1384 cm^{-1}	Nitrates
1254 cm^{-1}	Sulphonic group of Polysachcharides
1019 cm^{-1}	Silicates Kaolinite structure
465 cm^{-1}	Quartz

Amide II, nitrates, Phenolic OH C=O stretching of Carboxylates, Sulphonic group of Polysachcharides, Silicates with Kaolinite and Quartz. (Table 18)

II. Winter Season total insoluble matter:

The band assignments gave imprints of absorbed water on polymeric compounds, CH_2 symmetric and CH_2 asymmetric, Amide I and Amide II, nitrates, Sulphonic group of Polysachcharides, Carbonyl COO-vibration, Kaolinites well ordered, Quartz. (Table 19)

3 Conclusions for the weathering of the surfaces at the Taj Mahal

The pollution load on the site can be assessed as natural and indicative also of possible anthropogenic inputs. Iron from the dust gets settled on the weak zones of the monument and can aid in crust formation. The organic fraction of the soluble dust resembles Humic like substances. Such organic compounds can also settle on the weak and weathered zones of the monuments. Emissions from industry, vehicular exhausts, burning of biomass by municipal or domestic purposes can also contribute to the chemical nature of the pollution. Such airborne anthropogenic particulate inputs have not been quantified yet in terms of magnitude, actual dispersion rates, deposition and residence time. In the overall scenario it seems that the

Tab. 19 FTIR analysis of total insoluble matter in winter dust fall

Bands cm^{-1}	Functional groups
3690 cm^{-1}	Outer Hydroxyl groups
3401 cm^{-1}	3402-3344 cm^{-1} OH stretching of Polymeric compounds.
2924 cm^{-1}	CH_2 Group Symmetric
2852 cm^{-1}	CH_2 group A symmetric
1649 cm^{-1}	Amide I band
1541 cm^{-1}	Amide II band
1385 cm^{-1}	Nitrates
1255 cm^{-1}	Sulphonic group of Polysachcharides
1240 cm^{-1}	1240-1237 cm^{-1} COO-Vibration.
1031 cm^{-1}	Kaolinites well ordered
469 cm^{-1}	470 cm^{-1} Quartz.

natural effects of aerosols seem to have a long term impact on the monument. This study has attempted to determine all possible particulate impact by analysis.

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