



90134

1352-2310(95)00495-5

## EXPERIMENTAL STUDY OF LIMESTONE AND SANDSTONE SULPHATION IN POLLUTED REALISTIC CONDITIONS: THE LAUSANNE ATMOSPHERIC SIMULATION CHAMBER (LASC)

P. AUSSET,\* J. L. CROVISIER,† M. DEL MONTE,‡ V. FURLAN,§  
 F. GIRARDET,§ C. HAMMECKER,† D. JEANNETTE† and R. A. LEFEVRE\*

\*Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA, URA CNRS 1404), Université de Paris XII, 94010-Créteil, France; †Centre de Géochimie de la Surface (CGS, CNRS), 1 rue Blessig, 67000-Strasbourg, France; ‡Dipartimento di Scienze Geologiche (DSG), Università di Bologna, via Zamboni, 67, 40127-Bologna, Italy; and §Laboratoire de Conservation de la Pierre (LCP), Département des Matériaux, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015-Lausanne, Switzerland

(First received 12 March 1995 and in final form 30 November 1995)

**Abstract**—The Lausanne Atmospheric Simulation Chamber (LASC) has been constructed with the aim of studying the SO<sub>2</sub> effects on different materials. It allows the carrying out of numerous measurements on large stone samples simultaneously and on line. The behaviour of two carbonatic stone types (limestone and sandstone), either naked or covered with fly ash or soot particles, exposed at the following conditions, SO<sub>2</sub> = 125 ppb (340 µg m<sup>-3</sup>), NO<sub>2</sub> = 50 ppb (98 µg m<sup>-3</sup>), relative humidity = 79%, temperature = 13°C, has been studied. This experiment has been carried out over a 1 yr period. It has been observed that SO<sub>2</sub> deposition velocity decreases with time and in different ways for each of the two stone types, naked or covered with fly ash or soot particles. During the first four months, the deposition velocity is higher on naked stones; later on, it is higher on the stone samples covered with fly ash. Throughout the experiment the SO<sub>2</sub> deposition velocity on stone samples covered with soot particles is lower than on naked samples and those covered by fly ash. Finally, the values of SO<sub>2</sub> deposition velocity are confirmed by the chemical analysis of sulphur in the samples. Sulphur is present from the stone surface down to about 0.8 mm depth. Copyright © 1996 Elsevier Science Ltd

**Key word index:** Atmospheric simulation chamber, sulphur dioxide, limestone, sandstone, fly ash, soot particles, SO<sub>2</sub> deposition velocity, sulphur fixation.

### INTRODUCTION

Gaseous pollutants (SO<sub>2</sub>, NO<sub>x</sub>, O<sub>3</sub>, etc.), microparticulate carbonaceous matter (particularly fly ash), and water are, according to the literature, today's most active factors in the deterioration of building stone surfaces in areas where air quality is bad. In these areas and for materials containing calcium carbonate, the most important degradation is identified with sulphation.

The sulphation has been described by some authors as a development of black crusts (Kieslinger, 1932; Jeannette, 1981; Camuffo *et al.*, 1982; Del Monte and Sabbioni, 1984; Ausset *et al.*, 1991). These crusts are found mainly in areas protected from rain wash-out and their thickness grows as the air pollution increases.

Other authors observed stone sulphation with no formation of black crusts, as if stones could have the capacity of drawing and storing sulphur without any visible transformation of the surfaces concerned (Winckler, 1966; Braun and Wilson, 1970; Furlan and Girardet, 1988).

These two phenomena can be easily observed in the natural environment but are very difficult to be interpreted and above all to be quantified. Sulphation depends on numerous factors including the stone type, the concentration of polluting elements (gas, particles), temperature and humidity. It is difficult to identify the role played by these different factors and it is therefore necessary to carry out simulations in laboratories, under very precise conditions, in order to understand their activity.

In the literature there are some studies simulating the stone alteration caused by sulphur dioxide. Speeding (1969) and Breccia *et al.* (1975) have reproduced in a simulation chamber the degradation of limestones and marbles under the effect of <sup>35</sup>SO<sub>2</sub> with high humidity. After some hours of exposition the formation of Ca<sup>35</sup>SO<sub>4</sub> has been observed. Judeikis and Stewart (1976) and Cobourn *et al.* (1993) showed that the deposition velocity of SO<sub>2</sub> varies, depending on the nature of exposed materials (marbles and dolomites). Similar studies (Serra and Strarace, 1978) on calcium carbonate and SO<sub>2</sub> demonstrated



3197

Fonds Documentaire ORSTOM  
 Cote: Bx16468 Ex: 1

that not only is an important quantity of carbonate transformed into calcium sulphate, but that this reaction does not occur completely in the absence of humidity. The works by Spiker *et al.* (1992a, b) show that the deposits of SO<sub>2</sub> on limestones and marbles increase exponentially when the relative humidity increases. Johansson *et al.* (1988) show that limestones exposed to a gaseous mixture of SO<sub>2</sub>-NO<sub>2</sub> and at a relative humidity of 90% form gypsum on their surface: according to these authors, NO<sub>2</sub> acts as a catalyst of oxidation of sulphur dioxide on the stone surfaces.

In addition to these experiments in simulation chambers, numerous studies on black crusts have been performed. These crusts, besides their gypsous nature, contain fly ash emitted during fuel oil and coal combustion. Camuffo *et al.* (1983) and Del Monte and Sabbioni (1984) also assert that a small amount of gypsum forming sulphur and calcium could be carried by microparticulate aerosol carbonaceous matter and

simulation chamber reproducing urban pollution in order to study the different factors leading to stone sulphation. Contrary to the previous authors, with the exception of Spiker *et al.* (1992a, b), we chose much lower SO<sub>2</sub> concentrations which are similar to the ones in urban polluted atmospheres.

The stones chosen for the experiment are a limestone and a sandstone, the behaviour of which has been previously studied in the field (Furlan and Girardet, 1992). These rocks were utilized both naked and covered with fly ash (produced by heavy fuel oil combustion) or soot particles (from light fuel oil combustion in diesel motors). Both types of particles are present in relevant quantities in polluted urban atmospheres.

The aim of this experience was to study:

(1) the behaviour of the two types of stones and of an inert substrate (quartz fibres) in the presence of gas:

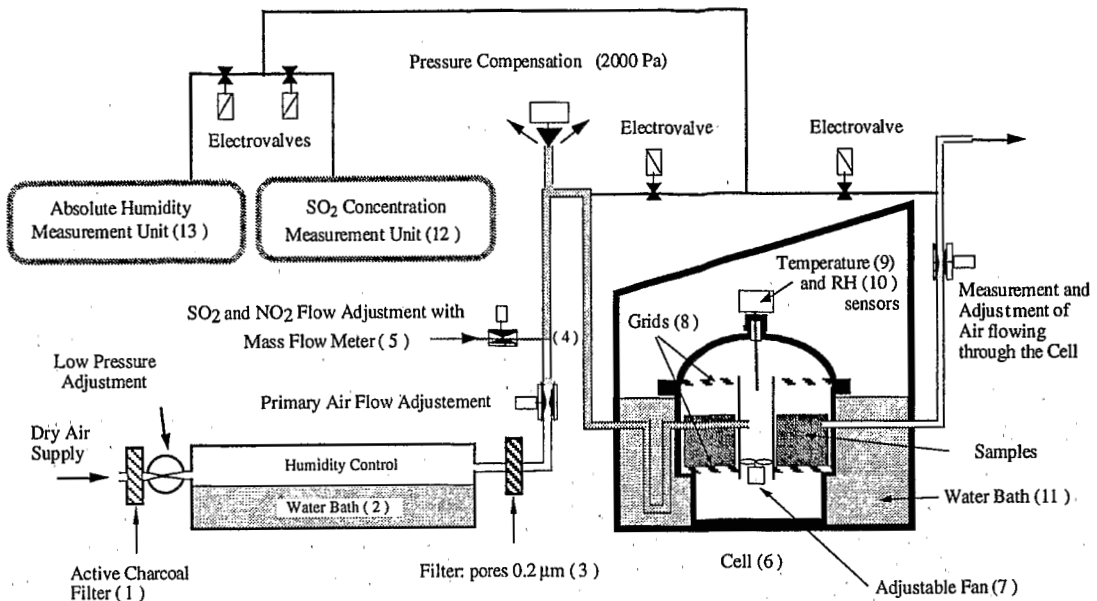


Fig. 1. Scheme of one of the 10 cells and of its running: gas injection system (1 to 5), main part (6 to 11) and measurement system (12 and 13).

7.2 W. Grids (8) assure atmospheric homogenizing. The speed of the fans is adjustable for each cell. This enables the resistance of the boundary layer to be regulated between 1 and 4 s cm<sup>-1</sup> after setting. These values have been determined experimentally by means of test samples of fibreglass impregnated with a solu-

tion is performed at the inlet of each cell only. A set of programmed measures as well as periodical setting of the measure instruments are enabled by a control unit. A microcomputer works out all operating data.

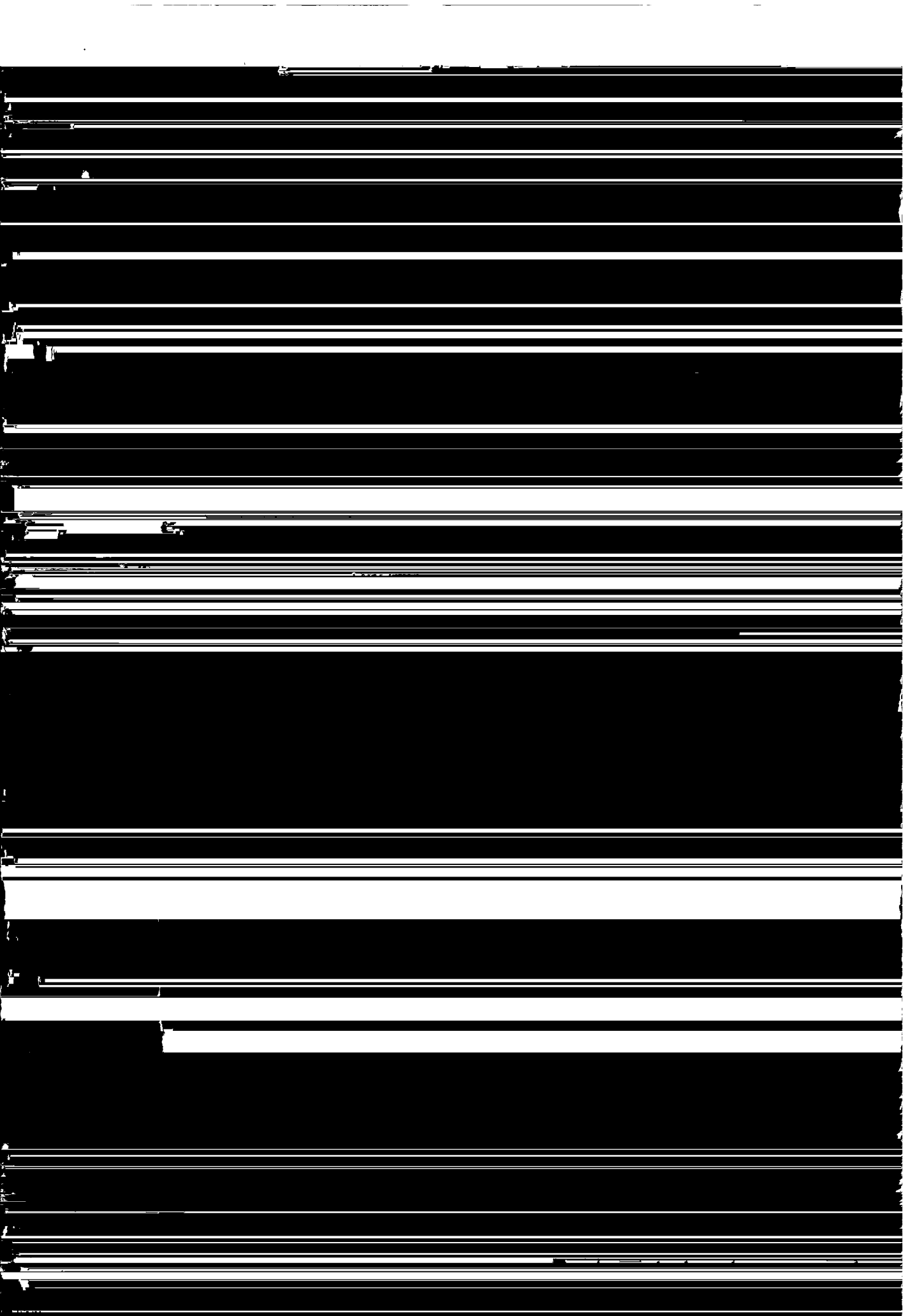
Table 1. Physical and chemical parameters inside each cell

Temperature	$13 \pm 0.2^\circ\text{C}$
Relative humidity	$79 \pm 1\%$
SO <sub>2</sub> concentration	$125 \pm 5 \text{ ppb} = 340 \pm 13 \mu\text{g m}^{-3}$
NO <sub>2</sub> concentration	$50 \pm 2 \text{ ppb} = 98 \pm 4 \mu\text{g m}^{-3}$
Boundary layer resistance	$1.3 \text{ s cm}^{-1}$
Exposure	3, 6, 9 and 12 months

are recorded. It shows the good stability of the system, with the exception of some accidents which we will comment upon later.

cement. The porosity of this limestone derives from the addition of a macroporosity and a microporosity with low connectivity. Macroporosity consists of large pores of about 200  $\mu\text{m}$  deriving from the dissolution of bioclasts edges. Petrophysical studies show that all macroporosity is trapped. Microporosity in porous areas either in the centre of bioclasts or in microspartitic cement is a free porosity.

The Berne sandstone is a calcareous sandstone (calcite = 23%; quartz = 40%). Two types of porosities affect it. Microporosity derives from uneven contact among the grains from microporosity of feldspars



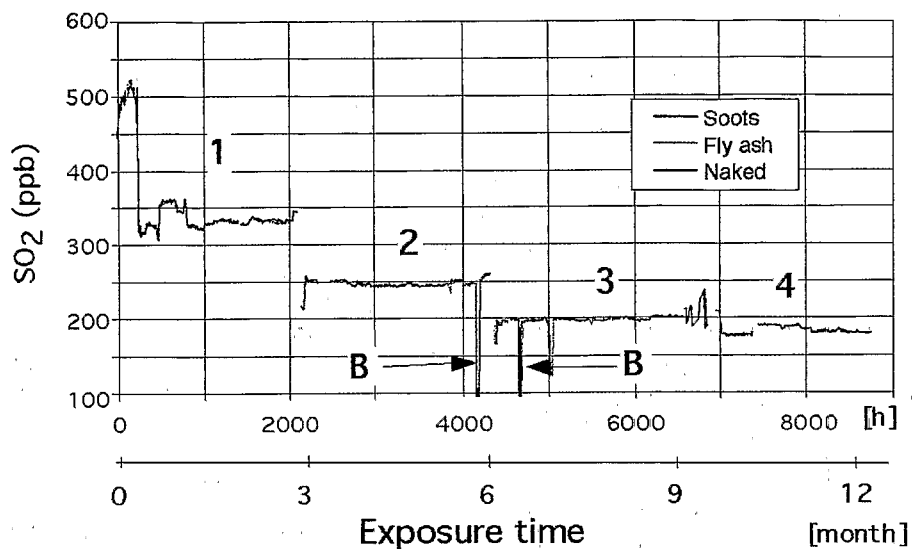
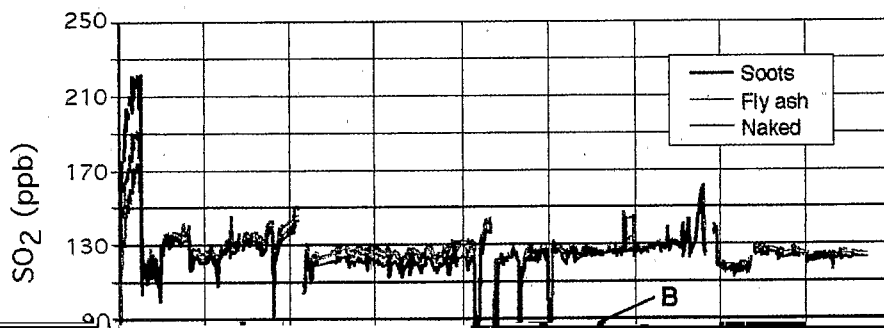
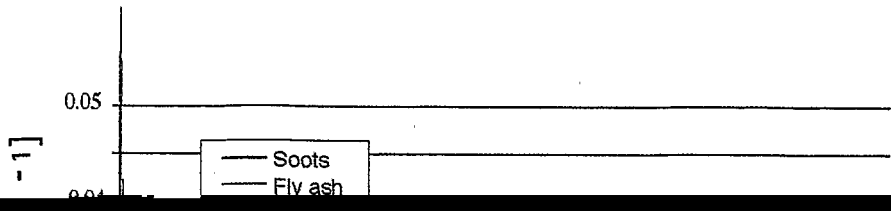


Fig. 3. Variation of the SO<sub>2</sub> inlet concentration in three cells containing Berne samples naked, covered with fly ash or with soot particles. The very weak differences among the three curves indicate the good working of the SO<sub>2</sub> dilution and measurement system. The four flats correspond to the periodical adjustments of the inlet concentration because of the decrease of the number of stone samples in the cells after the quarterly drawings (B: drop of the concentration as a consequence of an accidental stop of SO<sub>2</sub> injection).





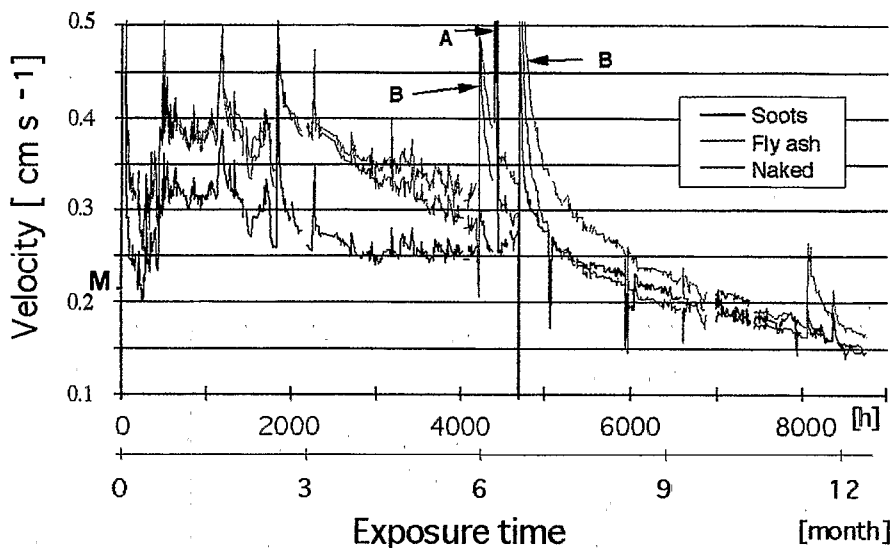


Fig. 7. Deposition velocity of  $\text{SO}_2$  on the Jaumont limestone, naked, covered with fly ash or with soot particles during the 12 experimental months (A: accidental increase in relative humidity. B: accidental interruption of  $\text{SO}_2$  injection in the cells; M: average annual deposition velocity of  $\text{SO}_2$  measured in Milan) (Furlan and Girardet, 1992).

in Figs 5, 6 and 7). The peaks correspond to abnormal and short variations in humidity or  $\text{SO}_2$  concentration. These accidents do not seem to have a long incidence on the deposition velocity on the Berne sandstone. They have, on the contrary, a very remarkable effect on the Jaumont limestone; a drop of  $\text{SO}_2$  concentration of some hours caused an activation of the deposition velocity for several hundreds of hours. This fact indicates that the two materials have a remarkable difference in their behaviour when they are moved from a stationary condition: the explanation lies in their different physical and chemical properties.

In the case of humidity variations, the deposition velocity attains its previous speed quickly again.

#### Determination of sulphur deposition

A set of two sample stones were drawn out from each cell every three months. The preparation of stone samples for analysis was performed by milling  $10 \text{ cm}^2$  of the surface of the stones in subsequent steps of  $0.1 \text{ mm}$  on  $2.5 \text{ mm}$  depth. The sulphur concentrations were determined by pyrolysis and Infra Red (elementary analyser of C and S: CSA 2003 Leybold-Heraeus) directly on small amounts of powder.

The results for the 3, 6, 9 and 12 months of exposition for each stone, naked or covered with fly ash or with soot are reported in Fig. 8. The values plotted in these diagrams correspond to the S quantity actually fixed, i.e. after deducting the sulphur contained in the stones, fly ash or soot particles. A regular decrease of

Table 2. Flux of fixed sulphur on the two stones ( $\text{g m}^{-2} \text{ yr}^{-1}$ ), after 3, 6, 9 and 12 months of experiment for the three different situations

Stones	Time (month)	Naked	Fly-ash	Soot particles
--------	--------------	-------	---------	----------------



sulphur fixation from the surface towards the depth can be observed in the case of the Berne sandstone. On the contrary, for the Jaumont limestone a weaker sulphur fixation in the first layer (100  $\mu\text{m}$ ) than in the second one is systematically observed. This last result can be explained by the structure of the stone material which shows on its surface large open pores with an average diameter of 200  $\mu\text{m}$ . Inside the pores,  $\text{SO}_2$ ,  $\text{NO}_2$  and  $\text{H}_2\text{O}$  concentrations are slightly higher and, because of a higher number of active sites, there is a higher probability that the reaction of  $\text{SO}_2$  fixation occurs.

Table 2 indicates the total sulphur fluxes calculated starting from the preceding data, by integrating the different distribution curves of Fig. 8.

It can be observed that:

- (1) The flow increases with time but not in a linear way: the speed increase lessens, depending on time, whatever the nature of stone is or if it is coated or not.
- (2) The Jaumont limestone is, in any case, more reactive than the Berne sandstone. This is quite obvious if we consider that the active mineralogical surface of the Jaumont limestone is much higher than that of Berne sandstone (94% and 23% calcite, respectively): the probability that one  $\text{SO}_2$  molecule interacts with one of  $\text{CaCO}_3$  and fixes as  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is much higher on the first. Besides, the large pores acting as traps further increase the probability of reaction in the Jaumont limestone.
- (3) After six months, the fly ash has an activating role.
- (4) The soot particles, on the contrary, protect the stones surface all over the experiment.
- (5) The sulphur deposition in relation to depth in the stone samples (Fig. 8) and the flow calculations of deposited sulphur (Table 2) agrees with the measure of

measurement method allows us to quantify the atmosphere-material exchanges on each cell instantaneously and on line.

The analysis of the first results concerning the behaviour of the exposed materials, i.e. Jaumont limestone and Berne sandstone, over a 1 yr period and under conditions similar to reality, points out remarkable modifications. Such modifications can be compared with the ones produced on the same materials in a polluted urban area.

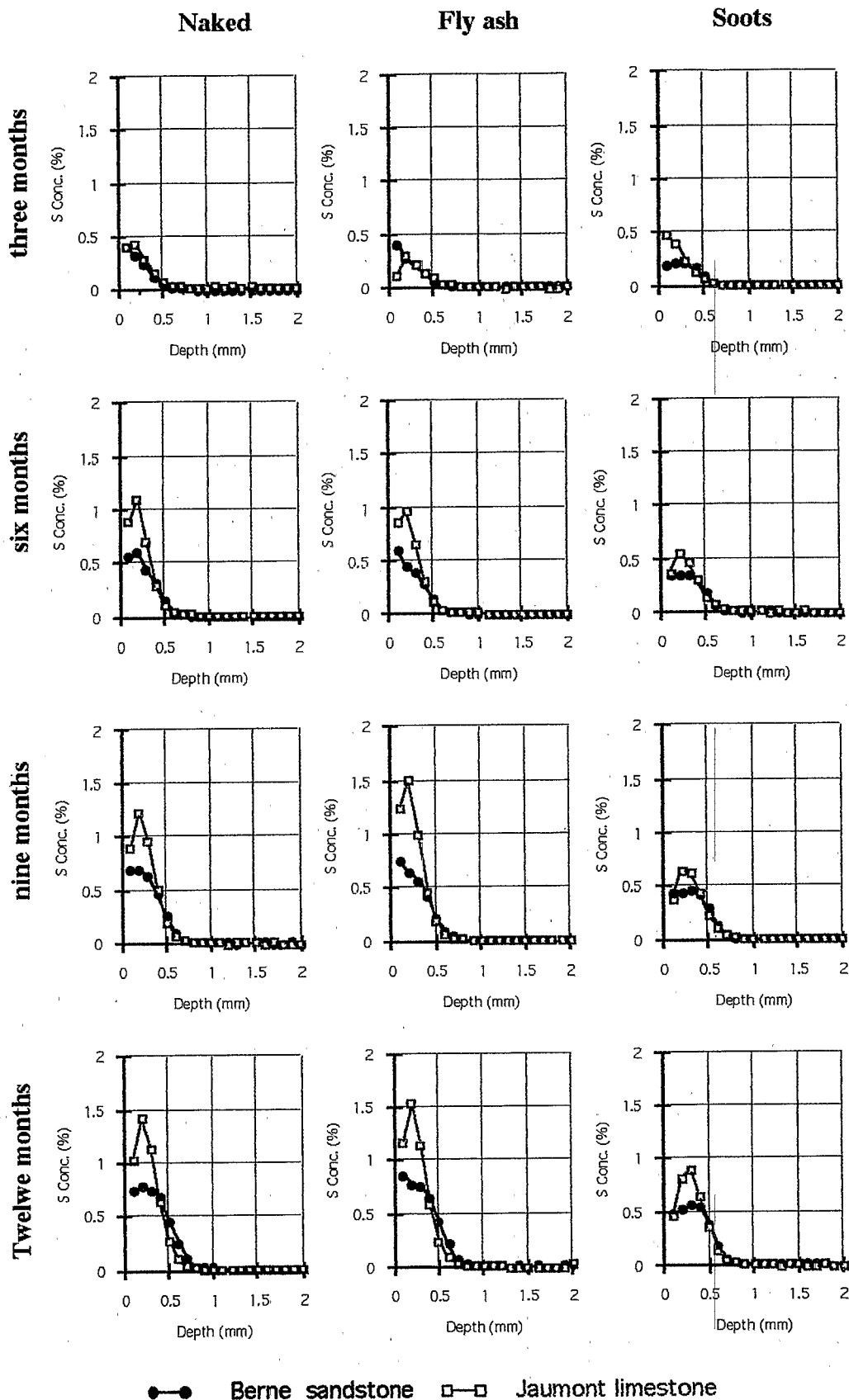
Jaumont limestone and Berne sandstone have different  $\text{SO}_2$  deposition velocities when exposed naked. This can be explained by their different chemico-mineralogical and petrophysical characteristics.

As far as  $\text{SO}_2$  deposition velocity is concerned, fly ash particles do not change the behaviour of Jaumont limestone, during the first three or four months. From this time, the  $\text{SO}_2$  deposition velocity increases. The same behaviour can be observed on the Berne sandstone, but the increase of  $\text{SO}_2$  deposition velocity caused by fly ash is less revealing.

Throughout the experiment, the  $\text{SO}_2$  deposition velocity on stones covered with soot particles is lower, especially during the first six months. Soot particles seem to play an important screening role during this time interval.

In general, a decrease of  $\text{SO}_2$  deposition velocity can be observed in all cases, i.e. in samples exposed naked or covered with fly ash or soot. It shows a passivation phenomenon that decreases sulphation velocity with time.

Sulphur deposition into the stones occurs from the surface down to about 0.8 mm depth. In samples exposed naked or covered with fly ash or soot, this sulphur fixation tends to decrease with time. These measurements seem to indicate a decrease of stone sulphation with time too.



●—● Berne sandstone □—□ Jaumont limestone  
 Fig. 8. Depth sulphur distribution in the Berne and Jaumont samples after 3, 6, 9 and 12 months of experiment.

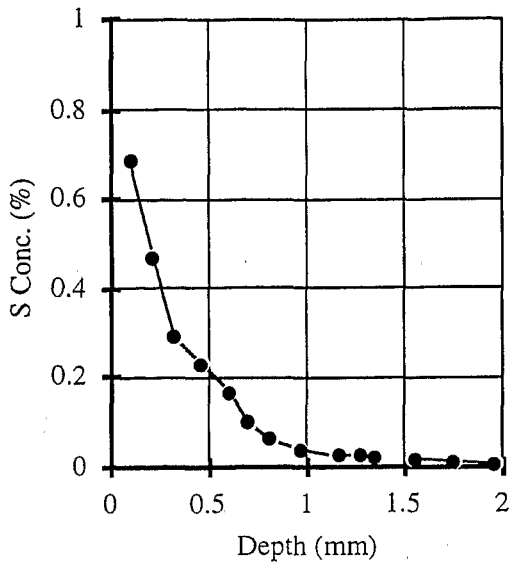


Fig. 9. Curve of sulphur distribution in relation to depth in a naked Berne sample exposed in Milan over 1 yr (1986-1987).

- Cofer W. R. III, Schryer D. R. and Rogowski R. S. (1980) The enhanced oxidation of  $\text{SO}_2$  by  $\text{NO}_2$  on carbon particulates. *Atmospheric Environment* 14, 571-575.
- Cofer W. R. III, Schryer D. R. and Rogowski R. S. (1981) The oxidation of  $\text{SO}_2$  on carbon particles in the presence of  $\text{O}_3$ ,  $\text{NO}_2$ , and  $\text{N}_2\text{O}$ . *Atmospheric Environment* 15, 1281-1286.
- Craig N. I., Harker A. B. and Novakov T. (1974) Determination of the chemical states of sulfur in ambient pollution aerosols by X-Ray Photoelectron Spectroscopy. *Atmospheric Environment* 8, 15-21.
- Del Monte M. and Sabbioni C. (1984) Gypsum crust and fly ash particles on carbonatic outcrops. *Arch. Met. Geoph. Biocl. Ser.* B35, 105-111.
- Del Monte M. and Sabbioni C. (1987) Nucleazione di cristalli da particelle carboniose. *Atti del XVI Cong. di M.E.*, Bologna, pp. 23-24.
- Del Monte M., Sabbioni C., Ventura A. and Zappia G. (1984) Crystal growth from carbon carbonaceous particles. *Sci. Total Envir.* 36, 247-254.
- Fisher G. L., Prentice B. A., Silberman O., Ondov J. M., Biermann A. H., Ragaini R. C and Mc. Farland A. R. (1978) Physical and morphological studies of size-classified coal fly-ash. *Envir. Sci. Technol.* 12, 447-451.
- Furlan V. and Girardet F. (1988) Vitesse d'accumulation des composés atmosphériques du soufre sur diverses natures de pierre. *6th Int. Cong. Deterior. Conserv. Stone*, Torun, pp. 187-196.
- Furlan V. and Girardet F. (1992) Pollution atmosphérique et réactivité des pierres. *7th Int. Cong. Deterior. Conserv.*

18798

28

10  
u. entomol  
10. 102

102  
102