

**Monitoring Air Pollution Impacts on Anasazi Ruins  
at Mesa Verde National Park, Colorado, USA.**

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**INTRODUCTION**

The four corners region of the United States contains some of North America's most treasured cultural resources in the form of dwelling ruins of prehistoric Anasazi civilization. These ruins have been exposed for a thousand years to an atmospheric environment which was largely unaffected by human activity. However, in very recent years rapidly increasing visitation of cultural sites in the area, construction and operation of large industrial installations such as power plants and smelters, as well as rapid regional population growth have changed this situation. Local air chemistry may have been sufficiently altered as to affect the mode of deterioration of the masonry of the ruins. At the request of the National Park Service, a system was developed for monitoring the effects of the deposition of airborne pollutants on these resources. A mechanism of deterioration by acid-deposition caused acceleration of natural erosion processes is hypothesized.

Gaseous and particulate pollutant concentrations and micro-climatological variables are measured at Spruce Tree House ruin, Mesa Verde National Park, Colorado. Two test walls, closely resembling Anasazi structures, have been constructed of sandstone specimens typical of masonry units found at Mesa Verde. This allows intensive study of the material of interest without the danger of disturbing the archaeological integrity of the ruins proper. Deterioration of the stone occurs by a combination of chemical and mechanical processes which weaken the material which bonds the quartz grains. The surface recession rate is periodically recorded using microphotography, and chemical and microstructural alterations in the bonding phase are observed using optical and electron probing techniques.

The ultimate objective is an assessment of the influence of local air and precipitation chemistry on the rate of deterioration. Two hypotheses are posed: (1) Correlations between the rate of deterioration of the sandstone masonry and fluctuations in the concentrations of acidic components delivered by the local atmosphere can be detected, and (2) Inputs of acidic components accelerate deterioration by natural processes by increasing the rate of dissolution of the bonding phases in the sandstone microstructure.

## METHODS

The monitoring consists of a coordinated program of non-destructive materials deterioration monitoring and highly detailed environmental characterization measurements at one location. The rates of surface erosion and chemical and microstructural alterations have been investigated with respect to: 1) pollutant chemical constituents of the atmosphere (primarily sulfate and nitrate), 2) microclimate variables such as temperature and relative humidity, and 3) parameters of eolian and hydraulic erosion.

### Sandstone Masonry Deterioration Monitoring

To periodically assess any changes in the chemistry of the sandstone masonry in the Anasazi cliff dwelling ruins, and measure the rate of physical deterioration, a monitoring system based on microphotography of stone surfaces and the chemical analyses of specimens collected at regular intervals was devised. The deterioration data is examined as a potential function of variations in the air chemistry and meteorological conditions. A series of five stones were selected for each test wall, from a source of actual Anasazi-dressed masonry which had lost archaeological context. One wall was built on a rock ledge fully exposed to the elements. Thirty-five meters away, the second wall site was located at the extreme down-canyon side of Spruce Tree House Ruin, protected from rain and snow.

At each site, an array of sandstone specimens cored out of a single sandstone block are mounted in fused quartz holders which are held in an acrylic rack. Four cores are removed each month and subjected to a variety of chemical analyses. An assumption was made that any effect that atmospheric pollutants may have on the stones' integrity will appear at or near the surface. In the relatively arid climate of Mesa Verde, it is not a common occurrence that the masonry would be saturated throughout by water. Consequently, the predominant expression of deterioration is the rate of recession of the surface. Here, the bonding material is dissolved or disrupted by repeated exposures to moisture which may contain chemicals which accelerate the process. The rate of recession is expressed macroscopically as the rate at which the loosened quartz grains are subsequently removed. The erosion of sandstone presents a peculiar problem in measuring recession rates. Erosion involves the removal of individual quartz grains. On a macroscopic scale, the rate of degradation, or the rate of surface recession, is perceived to be a continuous process where the removal of many individual grains will yield a macroscopically measurable result. At the microscopic level, examination of a single event reveals that no erosion occurs until an entire grain is removed. Erosion, therefore, is measured in discrete steps.

The rate of recession is measured by periodically examining selected sandstone surfaces. Photographs are made at magnifications of 8X and 32X. Sapphire and polycrystalline alumina rods, about 1-mm diameter, are embedded in the sandstone surfaces to provide positional references. By comparing photographs taken at monthly intervals, it is possible to determine when each surface grain disappears from the surface. This allows an average recession rate to be calculated. Under some circumstances, agglomerates of several grains will dislodge from the surface at once. It appears that monthly intervals provide sufficient temporal resolution for observation of the erosion events.

Chemical changes in the sandstone are monitored by a combination of procedures. One of the most important tools is the use of backscattered electron imaging microscopy (BSEI) of prepared cross sections of sandstone specimens. It is also important to assess what atmospheric contaminants are deposited on the surface. The contaminants of greatest concern are those which are water soluble. Therefore, sandstone cores are pulverized and dispersed in distilled water. After centrifugation and filtering, the decanted liquid is analyzed for sulfate, nitrate and chloride using ion chromatography. Finally, the surfaces of the cores are examined both optically and by secondary electron microscopy to determine the extent of microstructural changes that are occurring due to atmospheric exposure. Energy dispersive analysis of x-rays (EDAX) also serves to detect atmospheric particles which have deposited onto the core surface. All this information can then be used to at least qualitatively identify deterioration processes that may be occurring.

### Microclimate and Air Chemistry Monitoring

The environmental characterization measurements system was designed to provide adequate temporal resolution for the observation of features in the atmospheric signals that may drive the hypothesized mechanism of accelerated sandstone deterioration. It is important to note that while the sandstone deterioration measurements are taken monthly, the environmental data are of much finer temporal resolution. This is done to allow the investigation of variations in deterioration rates with respect to not only long-term means in the atmospheric parameters, but also extreme variations and the range of diurnal cycles.

Microclimatological parameters monitored at Spruce Tree House include temperature, relative humidity, the three-dimensional wind field, solar radiation, and rainfall rate. These data are digitally sampled and processed by an on site datalogger, and recorded as hourly averages. The meteorological sensors are mounted at the top of a 7 m tower, located in a clearing 40 m south of Spruce Tree House. The sensors are thus about 5 m above the elevation of the test walls, and just above the forest canopy within the canyon. This exposure of the instruments was chosen to be representative of the local environment experienced by the test walls and Spruce Tree House. In addition, temperature transducers and surface wetness sensors have been mounted within and on the test walls. Signals from these sensors are also computerized and recorded on digital tape. An active air sampling system is also located at the base of the meteorological tower.

Atmospheric chemistry is monitored in several ways. Precipitation and actively sampled air chemistry are collected weekly. The chemical composition of precipitation is obtained from a National Atmospheric Deposition Program regional rain sampling station, located 1.6 km north of the ruins site. At the test walls, a four stage series-filtration system collects particulate and gaseous pollutant samples. Aqueous extracts of the filters are analyzed by automated ion chromatography. The method provides airborne concentration data for total (gaseous plus particulate) nitrate large- and small-particle associated sulfate, and sulfur dioxide gas.

## PRELIMINARY RESULTS

Prototype instrumentation for both materials and aerometric aspects of the project was installed in late 1983. A preliminary testing period of the procedures and equipment was conducted for an the first year of on-site operation. The sandstone deterioration monitoring began a continuous record of surface recession rates in 1985. This paper discusses the data gathered through fall, 1986. Monitoring is continuing at the site.

Although there is some variability, the sandstones found in Mesa Verde are relatively uniform in terms of general composition and microstructure when compared to the broad spectrum of sandstone types. Principally, they consist of a narrow size distribution of quartz grains (100-150 microns) that account for about 80 to 90% of the mineral content. The grains are rounded to subangular, due to authigenic quartz overgrowths. The remainder of the mineral content consists of 5 to 10% clay minerals, 3 to 8% potassium feldspar, a combined 5% of hematite ( $Fe_3O_4$ ) and calcite ( $CaCO_3$ ), and a combined 1% of such accessory phases as zircon ( $ZrSiO_4$ ), tourmaline, apatite and barite ( $BaCO_3$ ). A major component of the sandstone is porosity, which ranges between 21 to 36 volume percent. Because of this, structural integrity owes much to the interlocking packing of the grains. The dominant cementing material is the authigenic quartz. Although normally a very strong and chemically stable bonding material, it does not provide an extensive matrix of bonding material and thereby leaves the stones in a friable state. Other cementing materials, of secondary importance on a volume percentage basis, may be important with respect to the resistance of the stone to weathering process. Clay mineral bonding occurs to a much lesser extent and generally appears in interstitial patches. Normally, calcite and hematite phases appear as discrete grains, however, some stones have been found to contain appreciable amounts as a cement.

The variability of the sandstones found in the Park is a function of the relative proportions of the secondary bonding material. This influences the apparent integrity of ruins stones exposed to natural weathering processes. Frequent observations have been made where an individual masonry unit in a ruins wall deteriorates rapidly, even though neighboring blocks are relatively unaffected. The erosion mechanism of greatest concern to this project is the chemical alteration of the bonding matrix of the sandstone. If cementing material is dissolved, the individual quartz grains on the surface are laid bare to mechanical elements of the erosion process. The time dependence of various elements in this process is currently unclear, although the dissolution of the bonding material is presumably sufficiently slow to be controlling. This is the most likely and feasible mechanism of natural erosion. The important question is whether it is accelerated by chemical pollutants.

The annual median pH of precipitation at Mesa Verde is pH 4.4. Also, dry-deposited accumulations of acidifying pollutants such as nitric acid and sulfur dioxide, which subsequently are dampened by dew and rain can yield solutions of high acidity on a localized scale. This would act particularly strongly on such compounds as the carbonates and have decreasingly less effect on feldspars, clays, ferrous compounds and the accessory phases. Least affected would be quartz. At first glance, it would seem that acidic

environments should not be particularly important considering the preponderance of loose quartz cementation. However, there is some evidence that these sandstones are susceptible at least to some degree. Previous preliminary investigations have indicated that the cohesive strength of sandstone cores soaked in mild acid solutions is 10 to 90% lower than those soaked in neutral solutions. This would indicate that bonding material is weakened particularly in those cases where significant quantities of carbonates are present. However, it is indeed difficult to apply such observations to the current situation since the manner of delivery of acidic components and degree of uniform exposure is quite uncertain.

Figures 1 and 2 display some of the typical erosion data collected at the Spruce Tree House site. The linear recession rate data can be seen to be quite variable from month to month, although comparing block F5 to block RH3, no obvious seasonal trend exists in the first completely monitored annual cycle. Other blocks also show the same degree of variation; the protected test wall produced somewhat lower rates of recession.

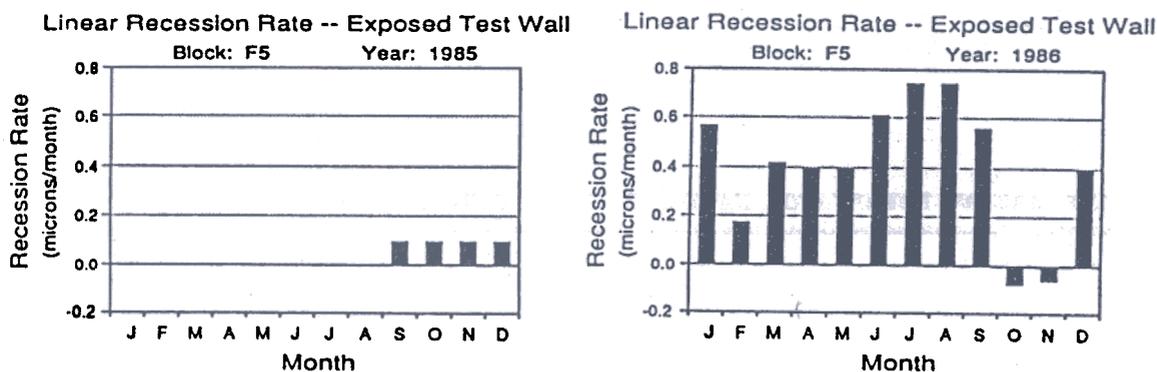


Figure 1. Measured linear recession rate (microns/ month) during 1985 and 1986 for a single sandstone block, designated F5, in a test wall at Mesa Verde National Park, Colorado, which is exposed to rainfall.

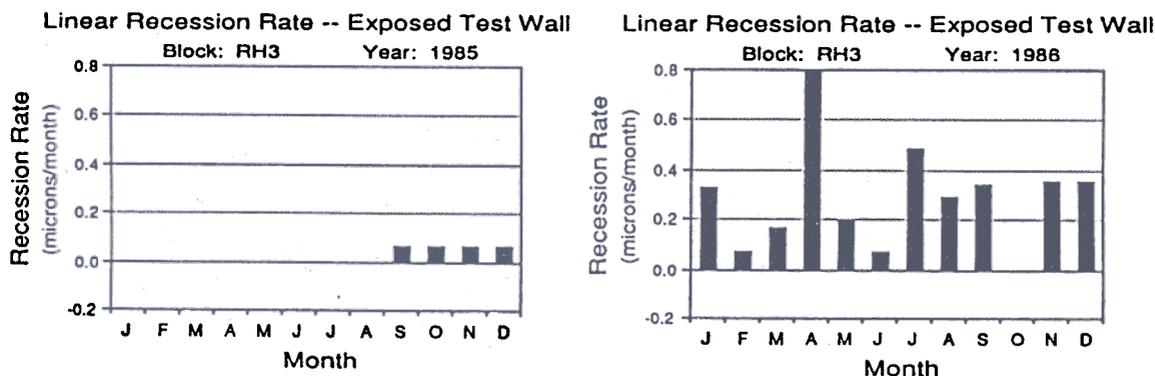


Figure 2. Measured linear recession rate (microns/ month) during 1985 and 1986 for a single sandstone block, designated RH3, in a test wall at Mesa Verde National Park, Colorado, which is exposed to rainfall.

The concentrations of the acid-deposition associated pollutants measured at the Spruce Tree House site are also highly variable throughout the course of the year. Figure 3 presents airborne concentration data for total nitrate and for sulfur dioxide versus time during the year. Included in this figure are data from mid-1984 through late 1986, so that nearly two years of weekly-averaged values are plotted. Note that this does not correspond one-to-one with the time period presented in Figures 1 and 2.

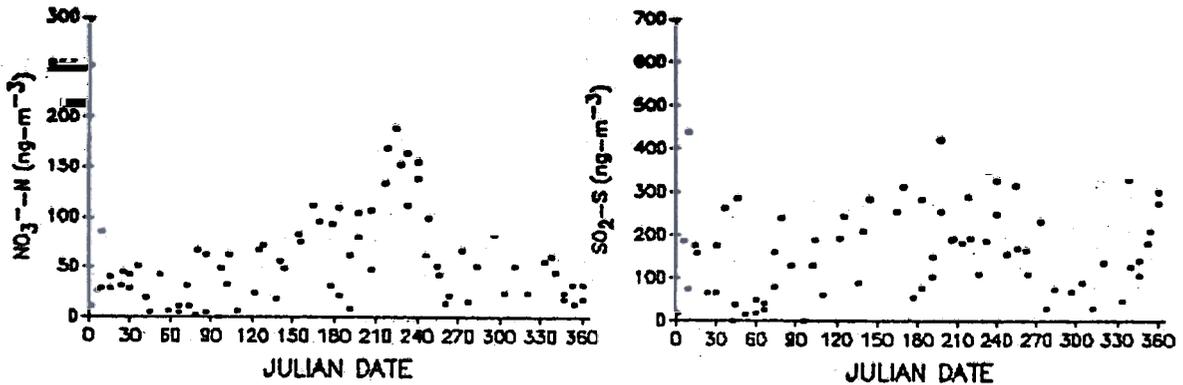


Figure 3. Measured airborne concentrations (nanogram / cubic meter) for the period 1984 through 1986, of total (gaseous plus particulate) nitrate, and sulfur dioxide gas at Mesa Verde National Park, Colorado.

#### DISCUSSION AND CONCLUSIONS

The first full year of coordinated materials deterioration and environmental characterization data collection at the Mesa Verde field site was completed in fall, 1986. The data collection rate of the project is necessarily a very slow one; this corresponds to the long-term nature of the effects the project is attempting to elucidate. For the purposes of addressing the ultimate objective of the project, that is, with respect to direct air pollution damage, but one data point per month results from the considerable efforts of many persons. Therefore, constraints of multivariate statistical analysis require that at least several years of sampling be completed before any mathematically significant interpretation can be made regarding possible direct effects of acid deposition on the sandstone masonry. However, it appears that a qualitative analysis of the results assembled to date would suggest that the monitoring system design has proven to be an appropriate one for the investigation of the problem originally delineated in the objectives of the project. The ongoing tasks of this research effort are: 1) assembling and organizing the extensive database into a form that will facilitate the planned statistical interpretation, 2) adding at least one more year's sequence of data points, and 3) developing a broader descriptive interpretation of the data as a baseline statement of the physical and chemical microenvironment of Spruce Tree House ruin during the mid-1980's.

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SUMMARY

Some of the most ancient cultural resources in the United States are located in the Four Corners region of the southwest. Ruins of sandstone masonry buildings constructed by the Anasazi civilization have been exposed for a thousand years to a relatively pristine environment. In very recent times, however, population growth and rapid industrial development have led to increased pollutant emissions in the area. Because pollutants may accelerate the natural sandstone weathering processes, a monitoring system has been installed at Mesa Verde National Park, Colorado, a World Heritage site since 1978. Two test walls were constructed of sandstone masonry blocks which were once part of Anasazi buildings that had collapsed. Thus, cores can be removed and electronic temperature and moisture sensors have been embedded in the blocks without disturbing any actual intact cliff dwelling ruins. One test wall is located within the Spruce Tree House ruin, in an area that is protected from direct impact of rain and snow. A second wall is located about 40 meters south of the ruin, exposed to rain and snow in a clearing along the canyon wall, along with microclimate and air-quality monitoring instruments. At regular intervals, photomicrographs are made of reference areas on each block in the test walls. Successive photomicrographs are compared and the removal of individual grains of the sandstone is thus observed. From the grain-loss counts, it is possible to determine even very small average erosion rates for the surface, because the Mesa Verde sandstones have very uniform grain sizes. The linear recession rates are highly variable on a month-to-month or seasonal time scale. The departures of recession rate from longer-term averages will be examined in relation to microclimate and air quality data collected on site. Electron microscopy and other microanalysis methods are used to observe minute changes in the chemical, mineralogical, and physical makeup of the sandstone as it exposed to the environment. The quartz grains in the sandstones at Mesa Verde are held together by physical interlocking, overgrowth of silicate and other minerals, and some cementing by clay minerals. Laboratory experiments demonstrated that these sandstones are greatly weakened by acidic solutions. The ultimate objective of this research is to determine whether airborne acidic pollutants can accelerate the alteration of the cementing phases by natural weathering processes, thereby hastening the deterioration of the masonry walls.

L'Enregistrement des Effects de la Pollution de l'Air sur les d'Anasazi au Parc National de Mesa Verde, Colorado, Etats-Unis

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### Résumé

Certaines des références culturelles les plus anciennes des Etats-Unis se trouvent dans la région des Four Corners (Quatre Coins) du sud-ouest. Les ruines en maçonnerie de grès qui datent de la civilisation Anasazi ont été exposées à un environnement isolé depuis un millénaire. Très récemment cependant l'augmentation de la population et le développement industriel rapide ont donné comme résultat l'augmentation des agents de pollution dans l'air. Comme les agents de pollution risquent d'accélérer la détérioration du grès, un système de monitoring a été installé dans le Parc National de Mesa-Verde, dans l'état de Colorado, un des sites du Patrimoine Mondial depuis 1978.

Deux murs d'essai ont été construits en blocs de grès récupérés des ruines qui se sont écroulées à travers les siècles. Ainsi des perforations ont été effectuées pour installer des enregistreurs électroniques de température et d'humidité sans nuire aux ruines intactes sur les rochers. Un mur d'essai est situé dans les ruines même de Spruce Tree House (La Maison de l'Épicéa) dans un emplacement protégé des effets directs de la pluie et de la neige. Un deuxième mur est placé à peu près à 40 mètres au sud des ruines, exposé aux effets de la pluie et de la neige, dans une clairière, le long du mur du cañon avec des instruments d'enregistrement de micro-climat et de la qualité de l'air. A intervalles réguliers des photomicrographies sont faites des zones de repère sur chaque bloc des murs d'essai. C'est en comparant ces photomicrographies qu'on arrive à établir les pertes moyennes de grains de grès, cela d'une façon assez minutieuse du fait que les pierres de Mesa-Verde sont composées des grains très uniformes. Les taux de récession linéaire sont très variables dans un contexte mensuel aussi bien que saisonnier. Ainsi les variations importantes avec les moyennes à long terme seront examinées à la lumière des données du micro-climat et de la qualité de l'air enregistrée sur place. Des méthodes d'électron microscopie aussi bien que d'autres systèmes de micro-analyses sont mis à l'œuvre pour observer les changements les plus infimes dans la composition du grès du point de vue chimique, minéralogique et physique dans le contexte de son contact avec l'environnement. Les grains de quartz contenus dans le grès de Mesa-Verde se tiennent par un engrenage physique, par l'expansion du silicate et des autres minéraux et un certain processus d'adhésion des minéraux contenus dans l'argile. Des tests de laboratoire ont montré que ces blocs de grès sont très affaiblis par des solutions acides. Le but ultime de cette recherche est d'établir si les polluants acides peuvent accélérer l'altération des phases d'agglomération par effritement, dépechant, ainsi, la détérioration des murs de maçonnerie.