

Fig. 1. Spectra of the quasars 1146+111B and C, and their ratio (B/C). The positions of the redshifted ( $z=1.0115 \pm 0.0003$ ) emission lines of H $\gamma$ , H $\delta$  and O III in 1146+111B, the atmospheric A and B bands, and two cosmic-ray events (C.R.) are indicated.

The observations were made in the period 14–16 April 1986, using the European Southern Observatory faint object spectrograph and camera (EFOSC) on the 3.6-m telescope at La Silla. A red grism providing a dispersion of  $270 \text{ \AA mm}^{-1}$  was used with a slit width of 1.5 arc s, resulting in a spectral resolution of  $18 \text{ \AA}$  (full width at half-maximum) throughout the wavelength range 5,600–9,300  $\text{\AA}$ . Both objects were observed simultaneously. Standard flat-fielding, sky subtraction, and wavelength and intensity calibration techniques were applied, and the resulting spectra are shown in Fig. 1.

Many features are common to both spectra, particularly the ubiquitous Fe II multiplets<sup>10</sup>. There is, however, a significant difference: the H $\gamma$  4,340  $\text{\AA}$  and H $\delta$  4,102  $\text{\AA}$  emission lines are prominent in the spectrum of B and not seen in that of C (H $\gamma$  equivalent widths of  $\sim 26 \text{ \AA}$  in B and  $< 4 \text{ \AA}$  in C). The ratio of the two spectra reveals a third possible difference, an emission feature in the spectrum of B at 6,301  $\text{\AA}$ , probably the O III, 3,133  $\text{\AA}$  Bowen fluorescence line which is sometimes seen in quasar spectra.

In view of these spectral differences, it seems unlikely that the two objects are different images of one quasar. Even allowing for possible intrinsic variations and path-length differences, it is improbable that the hydrogen lines could have varied by a factor of 6–7 relative to both the continuum and the Mg II emission line over the suggested<sup>1</sup> delay time of  $\sim 10^3$  yr. The spectra are different, and the most straightforward interpretation is that the objects are two different quasars. The similarity in redshift is not at all surprising for a physical pair: there are enough close pairs (in redshift and projected separation) in the Véron catalogue<sup>11</sup> that the probability of at least one of them having a redshift difference  $\leq 100 \text{ km s}^{-1}$  is essentially unity. There is another quasar pair, of separation 1 arc min, which was also suggested to be due to a gravitational lens<sup>12</sup>, but closer

scrutiny revealed significant spectral differences in that case also<sup>13</sup>. In the absence of any compelling evidence to the contrary, therefore, we conclude that 1146+111B,C are simply two separate quasars located close to each other.

We thank John Danziger, Bob Sanders and Joe Wampler for useful comments and discussions.

Received 15 May; accepted 16 May 1986.

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## Natural ventilation of the Paintings Room in the Altamira cave

P. L. Fernández\*, I. Gutierrez†, L. S. Quindós†, J. Soto† & E. Villar\*

\* Fundamental Physics Department, Science Faculty, and † Medical Physics Department, Medicine Faculty, University of Santander, 39005 Santander, Spain

The Altamira cave (Santillana del Mar, Santander, Spain) is famous for the ceiling of one of its chambers, the Paintings Room, which is decorated with palaeolithic paintings. However, the massive influx of visitors resulted in deterioration of these rupestrian paintings and the cave was closed in 1977 to determine both the causes and the maximum number of visitors that could visit the cave without putting the paintings at risk<sup>1–3</sup>. The natural ventilation of the Paintings Room is one of the most important factors in formulating the maximum occupational index for visitors to the cave. The emission of carbon dioxide and water vapour by visitors inside the chamber is directly proportional to the number of visitors and the time spent in the room. By ventilating the room, these components should be removed from the air within a short period of time, thus returning the chamber to the prevailing conditions before visitors were allowed in. We report here variations in the <sup>222</sup>Rn concentration in the air of the Paintings Room which we use as a quantitative index of the natural ventilation existing in this chamber. We carried out parallel studies of the temperature at different points in the cave and the evolution of the carbon dioxide concentration in the air of the Paintings Room, and hence established the maximum number of people per hour that should be allowed to visit this chamber.

Radon-222 is a noble gas of the radioactive series of <sup>238</sup>U, an element that occurs in rocks in the Earth's crust with a concentration between 2 and 5 p.p.m. (parts per 10<sup>6</sup>). Because of its gaseous nature and its greater concentration within the Earth, radon escapes through the interstices of the soil to the atmosphere, with an exhalation rate of  $\sim 1 \text{ atom cm}^{-2} \text{ s}^{-1}$ . When this exhalation occurs in places with little ventilation, the radon concentration of the air may be high.

The <sup>222</sup>Rn concentration of the air of the Altamira cave was measured by scintillation cells with a capacity of 500 cm<sup>3</sup>, in which a vacuum had been created down to a pressure of 50 torr. These scintillation cells were made of transparent plastic and

**Table 1** Mean monthly  $^{222}\text{Rn}$  concentration in the air of the Hall and Paintings Room; and the natural ventilation rate in the Paintings Room

Month	Location	$^{222}\text{Rn}$ concentration (pCi/l $^{-1}$ )	Ventilation rate (m $^3$ h $^{-1}$ )
February 1983	Hall	47 $\pm$ 3	10.3 $\pm$ 1.6
	Paintings Room	76 $\pm$ 4	
March 1983	Hall	149 $\pm$ 8	9.2 $\pm$ 1.3
	Paintings Room	159 $\pm$ 8	
April 1983	Hall	162 $\pm$ 8	6.9 $\pm$ 1.0
	Paintings Room	171 $\pm$ 9	
May 1983	Hall	159 $\pm$ 9	1.0 $\pm$ 0.2
	Paintings Room	185 $\pm$ 12	
June 1983	Hall	43 $\pm$ 4	13.4 $\pm$ 2.1
	Paintings Room	67 $\pm$ 5	
July 1983	Hall	6 $\pm$ 1	20.3 $\pm$ 3
	Paintings Room	27 $\pm$ 3	
August 1983	Hall	13 $\pm$ 2	16.9 $\pm$ 2.4
	Paintings Room	37 $\pm$ 5	
September 1983	Hall	16 $\pm$ 2	17.9 $\pm$ 2.6
	Paintings Room	38 $\pm$ 5	
October 1983	Hall	37 $\pm$ 5	16.4 $\pm$ 2.3
	Paintings Room	58 $\pm$ 6	
November 1983	Hall	117 $\pm$ 7	5.1 $\pm$ 0.8
	Paintings Room	143 $\pm$ 8	
December 1983	Hall	173 $\pm$ 9	5.7 $\pm$ 0.8
	Paintings Room	180 $\pm$ 9	
January 1984	Hall	177 $\pm$ 9	9.3 $\pm$ 1.2
	Paintings Room	181 $\pm$ 9	

their internal walls were covered with a film of  $\text{SZn(Ag)}$ . The emission of  $\alpha$  radiation by the radon ( $t_{1/2} = 3.8$  days) contained in the air filling the cell leads to this radiation falling onto the film of  $\text{SZn(Ag)}$ , where it produces fluorescence. The light thus emitted can be detected using a photomultiplier tube and the pulses produced can be recorded.

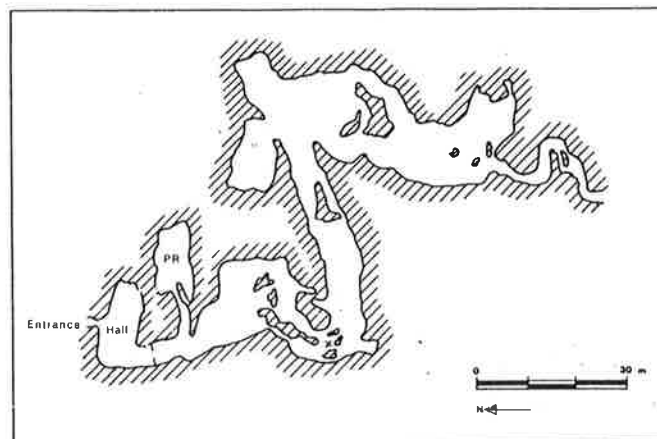
Because two of the short-lived radon daughters,  $^{218}\text{Po}$  and  $^{214}\text{Po}$ , are also  $\alpha$  emitters, their contribution to the total counting supplied by an air sample increases with time until a radioactive equilibrium is reached between the radon and the two daughters. This equilibrium is reached 3 h after the sample is taken only if, initially, radon gas was present in the air sample. Therefore, to calculate the radon concentration, we carried out a 10-min counting 3 h after the collection of the air sample assuming that there was a radioactive equilibrium between the radon and its daughters. The number of counts obtained from the scintillation cell when empty was subtracted from each measurement resulting from fluorescence of the  $\text{SZn(Ag)}$ .

The  $^{222}\text{Rn}$  concentration was measured in two chambers within the cave: the Hall chamber, located at the entrance to the cave; and the Paintings Room (see Fig. 1). Measurements were made three times per week over a period of 1 yr between February 1983 and January 1984. From these results, we calculated the monthly average radon concentrations (Table 1).

To calculate the natural ventilation in the Paintings Room from the radon concentrations, we used the simplified model proposed by Wilkening<sup>4</sup>, which is based on the fact that the temporal variation in the radon concentration ( $C$ ) in the air of this chamber can be expressed as the sum of the production caused by radon exhalation from the rock surfaces, the radioactive decay and the radon losses resulting from the natural ventilation:

$$\frac{dC}{dt} = E \frac{S}{V} - \lambda C - \frac{Q}{V}(C - C_h) \quad (1)$$

where  $E$  is the radon exhalation rate,  $S$  and  $V$  the surface and volume of the Paintings Room, respectively,  $Q$  the ventilation rate in this chamber,  $\lambda$  the radon decay constant and  $C_h$  the radon concentration in the Hall chamber.

**Fig. 1** Map of Altamira cave. PR, Paintings Room.

In stationary conditions, and assuming that  $Q \cong 0$  when the radon concentration reaches its maximum value  $C_{\text{max}}$  (in our case 196 pCi l $^{-1}$ ), then

$$E \frac{S}{V} = \lambda C_{\text{max}} \quad (2)$$

We can calculate the ventilation rate as

$$Q = \lambda V \frac{(C_{\text{max}} - C)}{(C - C_h)} \quad (3)$$

To apply this model to the experimental values obtained in the Altamira cave, we calculated the natural ventilation in the Paintings Room. Table 1 shows that values obtained for the ventilation rate are low throughout the whole year. Taking into account the volume of the Paintings Room,  $\sim 330$  m $^3$ , it would take  $\sim 16$  h to totally renew the air in the chamber by natural ventilation in July, the period of maximum ventilation rate, and  $\sim 330$  h in May, the period of minimum rate.

At the same time as measuring the radon concentration, we studied two variables that may be related to the ventilation rate: air-temperature differences between the Paintings Room and the Hall chamber and the carbon dioxide concentration in the air of the Paintings Room.

The Altamira cave has a single entrance. In such a static cave, ventilation currents are principally caused by convective air movements that basically depend on the temperature gradients between the different points into the cave. In the Altamira cave, the air temperature differences between the Paintings Room and the other chambers, with the exception of the Hall chamber, are always very small<sup>5</sup>. Temperature differences between the air in the Paintings Room and that in the Hall chamber are appreciably caused by the influence of the outside temperature on the latter so convective interchanges can be expected.

Figure 2 shows the monthly mean values obtained for the ventilation rate in the Paintings Room and the temperature differences between the air of the Paintings Room and the air of the Hall chamber throughout the measurement period. The correspondence can be observed between the annual variations in both ventilation in the Paintings Room is basically determined by convective processes between these two areas.

The carbon dioxide concentration in the air of the Paintings Room has its origin from the gas dissolved in the infiltration waters that flows into this enclosure. In the same way as the radon gas, the carbon dioxide concentration in the Paintings Room is eliminated by natural ventilation as the air interchanges with the outside atmosphere. The experimental measurement of the carbon dioxide concentration was carried out using an infrared analyser connected to a continuous trace graph plotter.

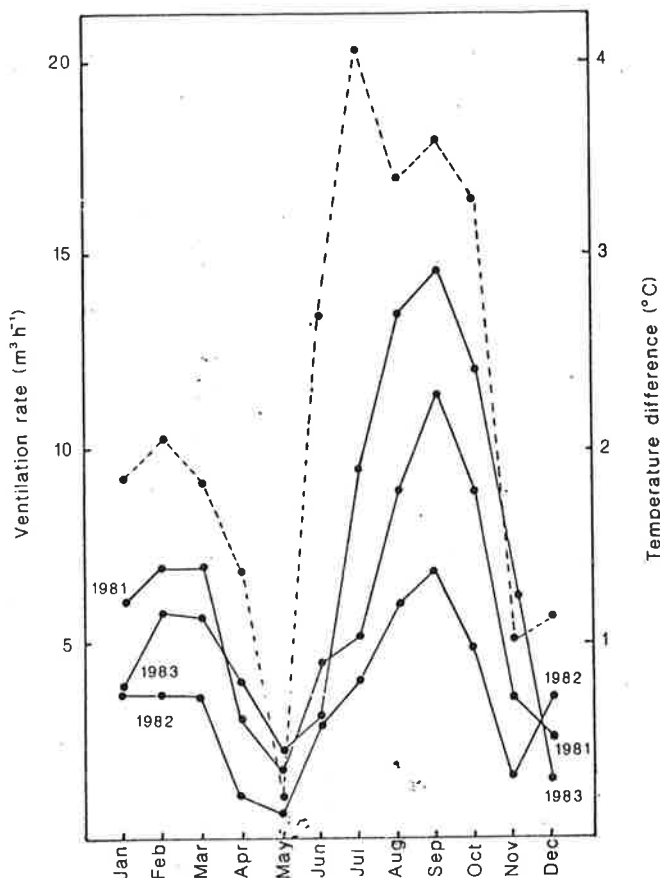


Fig. 2 Variations in the ventilation rate (dashed line) and the temperature differences (solid lines) between the Paintings Room and the Hall chamber.

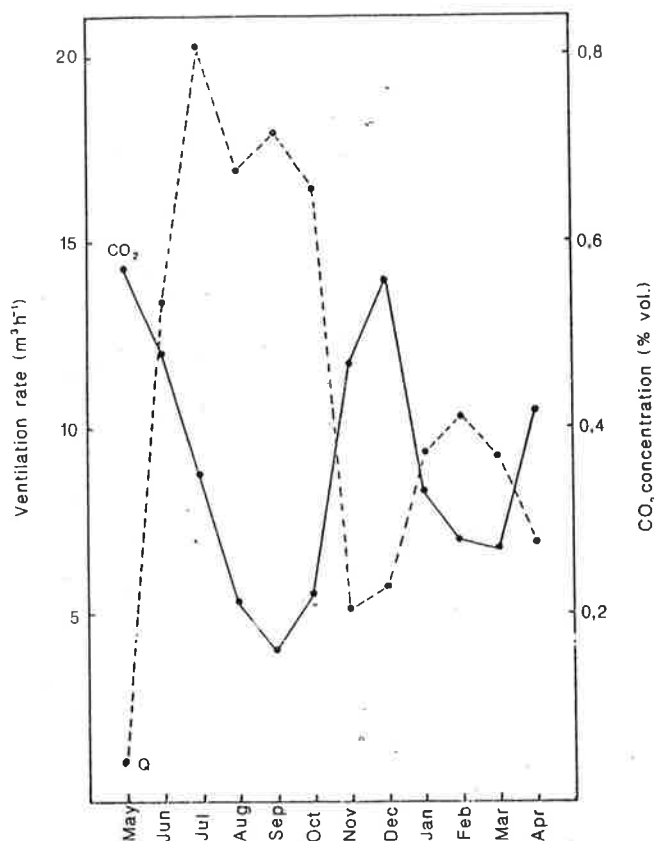


Fig. 3 Variations in the ventilation rate (dashed line) and carbon dioxide concentration (solid line) in the Paintings Room.

Figure 3 shows the ventilation rate calculated previously together with the monthly mean carbon dioxide concentrations measured in the Paintings Room. The inverse relationship between both variables consistent both with the variations in the temperature differences between the Hall chamber and the Paintings Room and with the fact that natural ventilation is the major factor affecting changes in the carbon dioxide concentration.

Taking into account that a person exhales an average carbon dioxide volume of  $\sim 17 \text{ l h}^{-1}$  (ref. 6) our results show that the maximum number of people that could visit the Paintings Room for a period of one hour each day in the summer months without raising the carbon dioxide concentration higher than that seen in May are 43, 74 and 80 visitors in July, August and September, respectively.

Our results indicate a weak natural ventilation in the Paintings Room throughout the whole year. The ventilation rate shows minimum values in May and November and maximum values in the summer months. These results agree with the estimations obtained from the temperature differences between the air of the Paintings Room and that of the Hall chamber and of the carbon dioxide concentration in the air of the Paintings Room. The minimum radon concentration and maximum ventilation rate, found in July, match the maximum absolute value of the temperature difference between the Hall chamber and the Paintings Room and the minimum carbon dioxide content in the air of the latter, found in the same month. In the same way, the maximum radon concentration and minimum ventilation rate recorded in May match the minimum absolute value of the temperature difference between the Hall and the Paintings Room and the maximum carbon dioxide concentration measured in this month.

Received 19 December 1985; accepted 17 March 1986.

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## Global distribution of peroxyacetyl nitrate

Hanwant B. Singh\*, Louis J. Salas† & William Viezee†

\* NASA-Ames Research Center, Moffett Field, California 94306, USA

† SRI International, Menlo Park, California 94025, USA

Nitrogen oxides ( $\text{NO}_x$ ) have a central role in the chemistry of the atmosphere, especially in key processes relating to ozone, hydroxyl-radical (OH) and acid formation<sup>1-7</sup>. High reactivity of  $\text{NO}_x$  (lifetime of 0.5-2 days) precludes hemispheric-scale transport and it has been proposed that non-methane hydrocarbons present in the troposphere can transform  $\text{NO}_x$  into its organic forms principally as peroxyacetyl nitrate (PAN)<sup>8,9</sup>. PAN is highly stable in the colder regions of the middle and upper troposphere and can provide a mechanism for  $\text{NO}_x$  storage and transport. Once transported, PAN and its homologues can easily release free  $\text{NO}_x$  in warmer atmospheric conditions. PAN is probably ubiquitous and its concentrations could exceed those of  $\text{NO}_x$  in clean tropospheric conditions<sup>10-12</sup>. Here we present the first view of the global distribution of PAN based on extensive shipboard and aircraft measurements. PAN is more abundant in the Northern than in the Southern