ARCHAEOLOGY

Pigments of the imagination

Paul Bahn

THE first direct dating of Ice Age cave-art in Europe has been carried out as part of a French programme of pigment analysis in the Quercy region of France[1] and the French Pyrenees[2,3]. These results follow the recent discovery of human blood in red pigments in some Australian caves and rock-shelters, which was dated by radiocarbon to 10,730 and 20,320 years before present (BP)[4], and show that the study of cave art has entered a new and highly promising phase of research.

As in Australia, it was the discovery of organic material in pigment used in French caves which produced the radiocarbon date. Analyses of pigments have consistently revealed the use of iron oxide (red) and manganese dioxide (black). But the improved analytical methods of recent years have produced far more detailed results, most notably from Lascaux cave[5], and some years ago it was discovered that some of the black figures in the Pyrenean cave of Niaux contained charcoal[6].

The research programme of pigment analysis in the decorated caves of Quercy[7] revealed that charcoal was used here too, in the cave of Cougnac. It is a sample of 100 mg from a black dot on the cave wall, between a megaloceros (giant deer) figure done in charcoal and a 'speared human' figure, that has produced a radiocarbon date of 14,300 ± 180 years BP[1].

Samples of pigment from red figures on Cougnac's walls were compared with a deposit of red ochre on the cave floor, and with ochre sources outside the cave and 15 km away; the floor deposit was probably related to production of the red figures, and the ochre used was most likely obtained from local clays. Two points to emerge are that the large red animal figures in the centre of the cave's main panel were drawn with the same pigment and were therefore probably a composition, done in a single production event. And whereas stylistic studies had assigned Cougnac to the Early Magdalenian period, the date (together with one of 15,000 years BP from a reindeer bone in the cave) points to the Middle Magdalenian. Further dates, however, will be needed for confirmation.

Similar results have emerged from pigment analyses in the Pyrenees[2,3], especially in the caves of Niaux and Réseau Clastres. Dates have not yet been obtained from the charcoal figures at Niaux, but analyses of samples, carried out by scanning electron microscopy, X-ray diffraction and proton-induced X-ray emission, have revealed four specific 'recipes' of pigments mixed with mineral 'extenders' and binders: talc; baryte with potassium feldspar; potassium feldspar; and potassium feldspar with biotite (a kind of black mica). Beyond making paint go further, extenders have other advantages; for example, adding biotite makes red paint spread easily when wet, produces a darker colour than pure red ochre, improves adhesion to the wall and stops the paint cracking as it dries.

In Niaux's famous 'Salon Noir', most of the animal figures were first sketched out in charcoal, and then manganese paint using recipe 4 was added on top. It therefore seems that the Salon Noir was indeed a 'sanctuary', a special place where the figures were carefully planned ahead of execution. The figures in all other parts of this huge cave were done more spontaneously, without preliminary sketches.

So these analyses are helping to establish how the caves were decorated: the Salon Noir contains all four recipes, though most of it was done with number 4, as was a sign at the far end of the cave; the Réseau Clastres, on the other hand, had only recipe 4, without preliminary sketches, confirming that it was visited very briefly. Another important application is helping in the detection of fakes: only one painting in Niaux, a red-painted fissure interpreted as a vulva, proved to have no extender. As the figure was not mentioned by the first scholars to study the cave, and there are initials nearby, it is clearly modern.

It is possible to 'date' recipe 4, because the occupation site of La Vache, directly across the valley from Niaux, has that same extender used with red and black paint on bones from layers dating to 12,850–11,650 years BP[8], the Upper Magdalenian; Niaux had traditionally been assigned to the Middle Magdalenian on the basis of style. Recipe 2 does seem to belong to the Middle Magdalenian, as it has been found on a bead from the cave of Enlène in levels of 13,940–12,900 years BP, and also in the Middle Magdalenian of the cave of Le Mas d'Azil.

One difference between the two projects is that the Quercy team believe the composition of its pigments to be entirely natural, because the mineral components discovered exist in the same proportions in local sediments. The Pyrenean team, on the other hand, insist that their compositions and recipes contain associations of components which it is quite impossible to find in nature. These claims are not necessarily contradictory — artists in Quercy may have been content to use natural pigments, whereas those in the Pyrenees may have concocted new ones.

Pigment analysis is providing a tool, applicable at least regionally, for dating Magdalenian paintings, and is revealing that behind apparent stylistic homogeneity there is technological heterogeneity. Styles lasted longer than was thought, and are of limited use in dating. □

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BLACK HOLES

Making a compelling case

Charles D. Bailyn

BLACK holes, although perhaps the most spectacular theoretical constructs in astrophysics, are by their nature elusive to observers. They can be detected only indirectly, by their gravitational influence on their surroundings. Currently the most convincing black hole candidate is one member of a binary star system known to X-ray astronomers as A0620–00. New work by Haswell and Shafter[1] adds yet another brick to what has become an impressive edifice of data demonstrating that this system must contain a black hole.

Strong compact X-ray emitting objects are good places to start looking for black holes. The energy requirements for producing large numbers of X-rays in a small volume are severe. The only viable energy source for such emission is the gravitational energy released by material accreting onto a compact object. Models along these lines have been used to account for quasars (sufficiently far away from us to require galaxy-sized black holes to account for their apparent luminosity) and for compact X-ray sources in our Galaxy. In a few cases, detailed studies of the latter systems have produced virtually airtight evidence for the existence in nature of black holes.

The strongest galactic X-ray sources are binary stars bound sufficiently closely for one member of the system to accrete material from the other. The accreting gas typically forms a disk around the accreting star, and becomes hotter as it spirals inwards. The immense X-ray emission observed from these systems implies that the accreting star must have an enormous gravitational field, and hence must be extraordinarily dense. Only black holes, or neutron stars, in which the protons and electrons in ordinary matter are crushed together to produce an object with densities as high as several hundred million tons per cubic centimetre, will suffice.

Although various indications suggest that most of the compact objects in X-ray binaries are neutron stars, there is a strong limit on the mass a neutron star can attain. Models of the equations of state likely to pertain inside neutron stars[2] as well as more general relativistic constraints[3] show that neutron stars with masses greater than three times that of the Sun cannot exist; such objects would inexorably collapse to become black holes. The object of the game in galactic black-hole hunting is therefore to find a compact object in an X-ray binary whose mass exceeds three times the Sun's.

A0620−00 commanded the immediate attention of X-ray astronomers when it erupted in 1975, becoming for a short while the brightest object in the X-ray sky. The optical counterpart was readily identified as a nova star called V616 Mon, which had been seen to erupt once before in 1917. Observations following the object's return to its quiescent level led to the determination of the binary's orbital period as about 8 hours[4]. At the same time, the companion star was shown to have velocity variations of almost 1,000 kilometres per second during each orbit[4]. With this information, a simple application of Kepler's laws demonstrated that the mass of the compact object could be no lower than 3.18 ± 0.16 times the Sun's. Very reasonable assumptions regarding the nature of the secondary star and the origin of the orbital luminosity variations then sufficed to put the minimum mass of the compact object unambiguously over the three-solar-mass limit.

Now, Haswell and Shafter[1] have measured the velocity variations of the emission lines associated with the accretion disk around the compact object. Because they originate in a disk which has gas flowing at high speeds both towards and away from the observer, these spectral lines are extremely broad (owing to Doppler shifting). Indeed the breadth of the lines, which indicates the velocity of the innermost edge of the accretion disk, has itself been used as an indication that the compact object must be significantly more massive than three solar masses[5]. By using simple models of the complex structure of the disk emission lines, Haswell and Shafter have shown that the accretion disk, and presumably the compact object which it surrounds, have orbital variations of about one-tenth the amplitude of those of the comparison star. This factor of ten represents the mass ratio between the compact object and its companion.

This information increases the minimum mass of the compact object to 3.82 ± 0.24 times the Sun's. Thus unlike Cygnus X-1 and LMC X-3, the more familiar black-hole candidates usually invoked in textbooks and popular articles, the compact object in A0620−00 can be demonstrated to be above the three-solar-mass limit from the dynamics of the binary system alone.

In fact, it seems likely that the black hole is substantially more massive than that. If the companion has the mass usually associated with stars of its spectral type, then the compact object must be at least four times the solar mass[1]; the very plausible models of the accretion disk structure used by Johnston, Kulkarni and Oke[5] lead to a similar limit. The final piece of information required for an accurate measurement of the mass of the compact object would be the inclination of the orbital plane to the line of sight. In principle this can be determined from the ellipsoidal variations, small changes in brightness caused by our changing angle of view during an orbital period.

Preliminary measurements[4] of these variations suggest a mass for the object of about seven times the solar mass. Several groups are currently observing these variations, but as yet the results do not appear to be totally self-consistent and repeatable (J.E. McClintock, personal communication). But even without this last piece of the puzzle, the case for a black hole in A0620−00 seems compelling: any alternative would be even more bizarre, and would probably result in severe damage to much of current astrophysical theory. □

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PALAEOCLIMATOLOGY

Estimating atmospheric CO_2

N. J. Shackleton

ONE of the great surprises from studies of the ice-age climates was the discovery, made from bubbles of fossil air trapped in the great ice sheets[1], that there was less CO_2 in the atmosphere during glacial periods than in interglacials. As well as contributing to our understanding of climate change (especially important given current fears about the effect of anthropogenically generated greenhouse gases), the discovery offers a means for integrating studies of the different contributions of the ocean, atmosphere and biosphere. Now, on page 462 of this issue[2], Jasper and Hayes report a new approach to estimating the history of CO_2 partial pressure in the ocean surface waters. The method should extend the CO_2 record well beyond the start of the ice-core record. Also, it should enable us to elucidate the changes in the dynamic equilibrium of CO_2 between the atmosphere and the sea surface.

Previous attempts to explain natural variations in atmospheric CO_2 have been based on Broecker's discussion[3] of the oceanic 'biological pump' whereby marine photosynthesis removes carbon from the surface waters of the ocean and hence holds atmospheric CO_2 below the level it would attain if the ocean were abiotic. Previous attempts to apply his arguments have involved measuring variations in the ^{13}C content ($\delta^{13}C$) of planktonic and benthonic foraminifera from a low-latitude deep-sea sediment core. The history of changes in the $\delta^{13}C$ difference between warm surface waters (monitored by the planktonics) and ocean deep water (monitored by the benthonics) can be interpreted as a history of changes in the efficacy of the biological pump and hence provides a record of variations in the equilibrium CO_2 partial pressure in ocean surface water[4]. But the complexities of carbon isotope gradients within the ocean and of isotopic exchange with the atmosphere severely limit this approach.

Jasper and Hayes[2] instead estimate the amount of isotopic fractionation that occurs in the photosynthetic step in which marine algae use sunlight to incorporate dissolved CO_2. This fractionation depends on the concentration of dissolved CO_2. Jasper and Hayes' analysis requires separate estimates of $\delta^{13}C$ of dissolved CO_2 in the surface water, and $\delta^{13}C$ in the organic material formed by photosynthesis, as a function of geological age. The first estimate is the easy one to make: it is obtained by measuring $\delta^{13}C$ in the carbonate shells of planktonic foraminifera. The more difficult measurement is of $\delta^{13}C$ for the photosynthesized organic carbon. Jasper and Hayes measure this for selected organic molecules by combining mass spectrometry with gas chromatography. The molecules that they chose are C_{37} alkadienones, which are specifically associated with the prymnesrophyte algae (coccoliths).

Earlier work[5] gave an approximate form for the relationship between the degree of photosynthetic fractionation and the concentration of CO_2 in sea water. Jasper and Hayes estimate the two