Fig. 3. Images of gasket **6**. (**A**) AFM images at 1.12 × 1.12 μm and 100 × 100 nm. (**B**) TEM pictures with 50- and 20-nm scale bars for the lower- and higher-resolution images, respectively (all images were obtained unstained). (**C**) UHV-STM images (100 × 100 nm) on a Au(111) surface at 6 K, revealing a line of gaskets settled on a ridge on the gold surface and a color-enhanced and magnified image of a single molecule (scale bar, 3 nm).
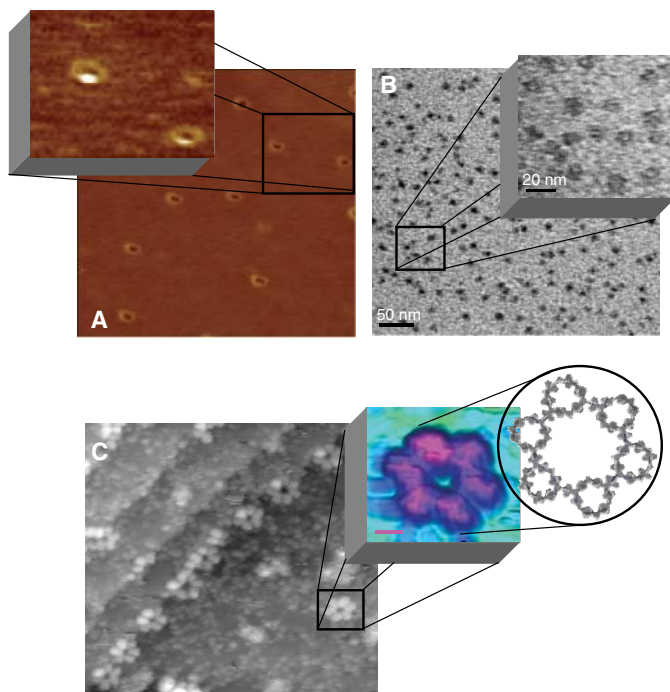
also used to image the structure. This apparatus can generate images with atomic resolution by directly measuring electronic states. UHV allows clean, controlled surface preparation and cryogenic temperatures to help reduce electronic noise and slow molecular motion. Using the same dilution as for the TEM sample preparation, fractal construct **6** in acetonitrile was cast onto a freshly cleaned Au(111) surface. STM images acquired at 6 K (Fig. 3C) verified a hexagonal pattern of the molecule (12 ± 1 nm diameter, and ~0.8 nm in height), which was consistent with the computer-generated model of the structure. Tunneling conductance spectra determined for single mole-cules at 6 K showed a 1-eV energy gap. Traces of linear oligomeric as well as larger macrocyclic assemblies (fractoids) were also observed on the STM images (see supporting online material).

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Middle Paleolithic Shell Beads in Israel and Algeria

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Perforated marine gastropod shells at the western Asian site of Skhul and the North African site of Oued Djebbana indicate the early use of beads by modern humans in these regions. The remoteness of these sites from the seashore and a comparison of the shells to natural shell assemblages indicate deliberate selection and transport by humans for symbolic use. Elemental and chemical analyses of sediment matrix adhered to one *Nassarius gibbosulus* from Skhul indicate that the shell bead comes from a layer containing 10 human fossils and dating to 100,000 to 135,000 years ago, about 25,000 years earlier than previous evidence for personal decoration by modern humans in South Africa.

Early evidence for beads and symbolic behavior by modern humans comes from Blombos Cave, Cape Province, South Africa, where 41 *Nassarius kraussianus* marine shell beads bearing human-made perforations and traces of use are associated with a Still Bay assemblage dated by optically stimulated luminescence (OSL) and thermoluminescence (TL) at ~75 thousand years ago (ka) (*1–3*). No other compelling evidence for bead use exists before about 40 ka, when beads appear at African, Eurasian, and Australian sites (*2, 4*). Other sug-gested early beads lack reliable cultural and chronological context or evidence of human manufacture. Four *Glycymeris* sp. shells with perforations on the umbo come from the Mousterian layers of Qafzeh Cave, Israel (*5*), dated by TL between ~90 and 100 ka (*6*). However, no anthropogenic traces were detected on the perforations, which are known to occur naturally on the umbo of bivalves. Also, the large size of the shells and the presence of pigment on one specimen indicate that they may have been used as ochre containers rather than as ornaments. Here we identify as beads three marine gastropod shells (Fig. 1), two of which come from the Middle Paleolithic site at Es-Skhul, Mount Carmel, and one from the type site of the Aterian industry, Oued Djebbana, Bir-el-Ater, Algeria.

The shelter of Es-Skhul is located at Mount Carmel, Israel, 3 km south of Haifa, in the canyon of Nahal Me'arot (Wadi el-Mughara), and 3.5 km from the Mediterranean shore (*7*). Excavations in 1931 and 1932 identified three main layers (*8, 9*): Layer A (20 to 50 cm of soft

sediment) contained a mixture of Natufian, Aurignacian, and Middle Paleolithic stone tools; layer B (about 200 cm thick and bearing all the human remains) contained Middle Paleolithic stone tools; and layer C (shallow sandy deposits at the base of the sedimentary sequence) yielded only a sparse lithic industry and no faunal remains. Layer B was subdivided into two subunits mainly distinguished by their hardness. The upper hard earth unit B1 resembled plaster of Paris, whereas the lower breccia B2 was similar to concrete. The lithics of Skhul Layer B were attributed to the Levantine Mousterian and have been compared with those of Tabun C and Qafzeh (*7*, *10*), whereas the macrofaunal remains in layer B appeared to correspond with those of Tabun C to D (*11*). Ten individuals (Skhul I to Skhul X), some apparently intentionally buried, were recovered from layer B. They are generally attributed to anatomically modern humans (*12–14*), albeit with some archaic characteristics. A large boar mandible was enclosed in the arms of Skhul V, interpreted as possible grave goods (*8*). Dates obtained for layer B from the use of electron spin resonance (ESR), U-series analysis, and TL on mammalian fossils or burnt flint range from about 43 to 134 ka (*15–17*), but recent ESR and U-series analyses, including direct dating with both tech-

niques of a molar from the Skhul II skeleton, indicate ages between 100 and 135 ka (*18*). Garrod and Bate reported the presence of four marine shell species (*Acanthocardia deshayesii*, *Laevicardium crassum*, *Nassarius gibbosulus*, and *Pecten jacobaeus*), without indicating the number of specimens recovered or their stratigraphic provenance (*7*).

Oued Djebbana is an open-air site, located at Bir-el-Ater, 97 km south of Tebassa, Algeria, close to the Tunisian border and 200 km from the Mediterranean Sea (*19*, *20*). The site contained a 36-m-long by 80- to 100-cm-thick archaeological layer under 3.9 m of sterile alluvial deposits. This layer yielded a lithic assemblage that associates typical Aterian pedunculates with Middle Paleolithic tool types produced in some cases with the Levallois technique. The faunal remains, including *Equus*, *Bubalis boselaphus*, *Bos primigenius*, and *Connochoetes taurinus*, indicate a more humid savannah environment than that at present. The central area of the site, rich in ashes, contained one perforated *N. gibbosulus*. A single infinite conventional radiocarbon date of >35,000 years before the present (MC 657) is available for this site (*21*).

We located the marine shells from Skhul in the Department of Palaeontology, Natural History Museum (NHM), London, and the specimen from Oued Djebbana in the Department of Prehistory, Musée de l'Homme, Paris. The Skhul material includes two perforated *N. gibbosulus*, a valve of *A. deshayesii*, a fragment of *L. crassum*, a fragment of an undetermined shell, and a fragment of a cypraeid. The *P. jacobaeus* mentioned by Garrod and Bate is missing. Only the *N. gibbosulus* bear perforations that could have been used for suspension in a beadwork. However, nonhuman taphonomic processes are known to produce pseudo personal ornaments that can mimic humanly modified and used beads. Ideally, to

determine whether purported ancient beads were used as such requires evidence of human involvement in their selection, transport, manufacture, and use. In the case of the multilayered Skhul site, the stratigraphic origin of the *Nassarius* shells also needs to be established. To address these issues, we analyzed sediment matrix adherent to one *N. gibbosulus* from Skhul (Fig. 1A) and sediment samples from layers A, B1, and B2 kept at the NHM (*22*), and compared the specimens from Skhul and Oued Djebbana to modern reference collections of *N. gibbosulus* shells (*22*).

Sediment samples from layers B1 and B2 cannot be distinguished from one another. The difference in their composition (table S1) appears to be controlled by the varying amounts of silica (predominantly from quartz) and calcium (predominantly from calcite). Rare earth elements (REEs) are essentially parallel. Layer A, in contrast, shows a high concentration of apatite (25% as opposed to 4%) that makes it distinct from layers B1 and B2. Phosphorus in apatite is scattered throughout the sample in the cement rather than being concentrated into discrete grains or bone fragments. This is not the case in samples from B1 and B2. Layer A also has elevated levels of Fe_2O_3, MnO, As, Cu, Mo, Ni, U, and Zn, and to a lesser extent, Al_2O_3, Ba, Li, Rb, and the REEs. The higher Al_2O_3 concentration indicates that layer A is richer in clay. Some of the elevated trace elements correlate independently with Al_2O_3 content (such as Fe_2O_3, Ba, Rb, and the REEs) and are probably contained in the clay minerals.

The hardness and the chemical composition of the sediment adherent to the pierced shell fit in well with samples from B1, B2, and a land snail recorded as coming from the Middle Paleolithic breccia (Fig. 2). This similarity with layer B and difference from layer A are shown in many of the major and trace elements as

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Fig. 1. *N. gibbosulus* shell beads from Es-Skhul (**A** and **B**), Oued Djebbana (**C**), and a present-day shore (**D**). (**E** to **G**) Macrophotos of the perforations on the archaeological specimens. (**H** to **K**) Extent of the ventral shield. Scale bar, 1 cm for (A) to (D), 1 mm for (E) to (G), and 1 cm for (H) to (K).
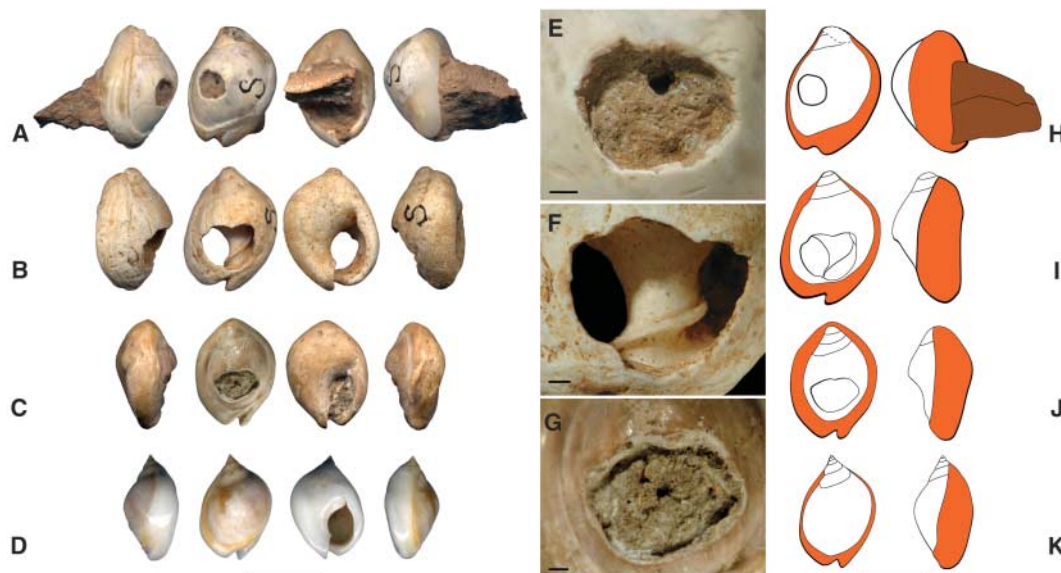
demonstrated in Fig. 2 (*22*). *N. gibbosulus* dated to the last interglacial bear a more developed and thicker parietal shield (*23*), which makes them wider than modern representatives of the species. This feature is observed on the Skhul and Oued Djebbana specimens (Fig. 1) and is particularly evident on the former, showing a width falling outside the modern range (Fig. 3), thus supporting its attribution to marine isotope stage 5.

Nassarius (*Plicarcularia*) *gibbosulus* (Linnaeus, 1758) is a scavenging marine gastropod that lives in shallow waters on pure sand (*24*) and is now confined to the central-eastern Mediterranean. The presence of these shells at Skhul and Oued Djebbana cannot be explained by natural causes. This species, and other closely related species of *Nassarius* (*Plicarcularia*),

originated in the Middle Miocene (*25*), so we can discount derivation of the specimens as fossils from the Cretaceous strata of Mount Carmel or the Eocene rocks of the Nementcha Mountains that are drained by Oued Djebbana. During the accumulation of layers B1 and B2 (100 to 135 ka), the distance of Skhul from the sea varied between 3 and 20 km (*26*, *27*). Oued Djebbana was never, during the whole Upper Pleistocene, closer than 190 km to the sea. The altitude of Skhul (65 m at present and 45 to 150 m between 100 and 135 ka), the good state of preservation of the archaeological shells, their small number, and reduced species spectrum excludes storms as transporting agents (*28*). No known animal predators of *N. gibbosulus* transport these shells into caves or far inland. They can hardly be interpreted as leftovers

from human food, because 100 specimens only provide 4.84 g of dry soft tissue (~20 kcal) and require 30 min to extract (*22*). The *N. gibbosulus* from Skhul do not seem to represent a random sample from a natural living or dead population. Both show a single perforation located in the center of the dorsal side (fig. S1), a feature observed in only 3.5% of modern thanatocoenoses. The Djebbana specimen presents the same rare perforation pattern. Microscopic analysis indicates that the agent responsible for the perforations on the Skhul specimens punched the shell body whorl from the outer dorsal side (Fig. 1). The probability of finding two *N. gibbosulus* with a similar perforation type as those from Skhul in a modern thanatocoenosis is very low (*P* = 0.001). This suggests that the shells were either purposely perforated or deliberately picked out of thanatocoenoses by Skhul inhabitants. We produced perforations similar in size and shape to those on the archaeological specimens by indirect percussion using a flint point as punch and regularizing the resulting hole by rotation. Such perforations are also documented on *N. gibbosulus* used as beads at Upper Paleolithic sites (*29*, *30*). However, considering that natural agents can perforate the shell in the same way, we cannot consider the hole morphology alone as compelling evidence for human agency.

The length of the Skhul specimens (Fig. 3) is significantly larger than that recorded on both reference collections (*P* < 0.01), including the one from the shore close to the site. This does not necessarily imply a preference for large shells, because the variability of size of *N. gibbosulus* shells through time and their size contemporaneous with Skhul layer B is unknown. Our argument for these shells being used as beads relies on the remoteness of the sites from the sea and the rarity of their perforation type in modern thanatocoenoses.

There is substantial uncertainty about the age of the Aterian. Its traditional assignment to a period between 40 and 20 ka (*31*), based on conventional radiocarbon dates from bulk samples of material particularly susceptible to contamination, is now challenged by TL, OSL, and ESR dates, which point to an age of 90 ka to 35 ka (*32*, *33*). This range implies that the age of the Oued Djebbana site, for which only an infinite conventional radiocarbon date is available, could be close to that of Skhul layer B. The shell beads from Skhul and Oued Djebbana belong to the same species as the previous oldest known personal ornaments found in western Eurasia, discovered in the Ahmarian layers of Uçagizli, Turkey, dated to ~40 ka (*34*), and are morphologically similar and belong to the same genus as those from Blombos Cave. The few human remains associated with the Aterian suggest (*35*) that this culture was produced by early anatomically modern human populations, as was the Still Bay culture at Blombos (*36*) and the Ahmarian
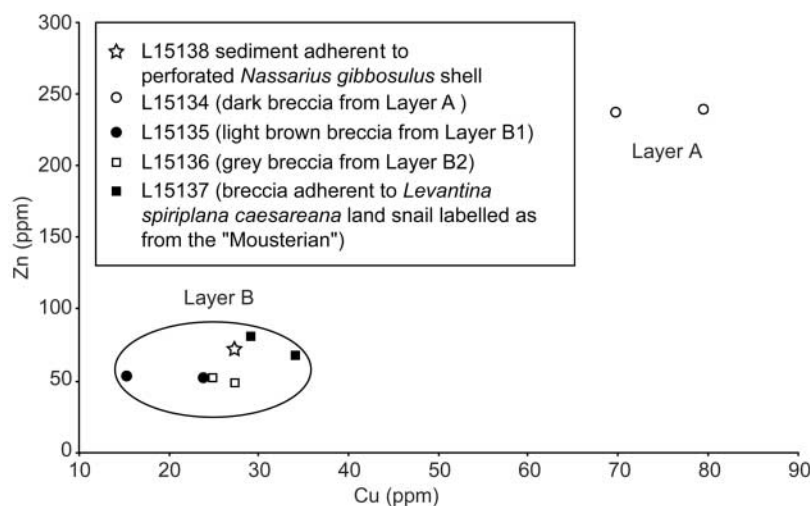
Fig. 2. Variation of Cu and Zn concentrations in Skhul breccias and sediment adherent to the pierced shell. All samples were in duplicate, except for pierced shell sediment, where sample size was insufficient.
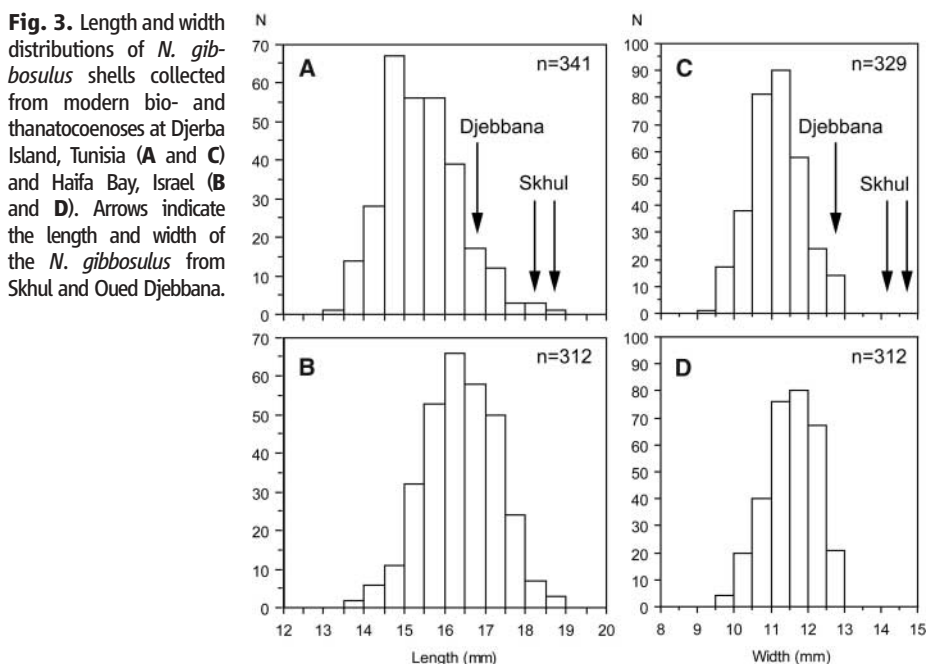
Fig. 3. Length and width distributions of *N. gibbosulus* shells collected from modern bio- and thanatocoenoses at Djerba Island, Tunisia (**A** and **C**) and Haifa Bay, Israel (**B** and **D**). Arrows indicate the length and width of the *N. gibbosulus* from Skhul and Oued Djebbana.

culture at Uçagizli [from correlation with K'sar Akil (*37*)]. Genetic (*38*) and paleoanthropological (*39*) data point to an origin of anatomically modern humans in Africa at ~200 ka. However, evidence for cultural modernity before 40 ka has for long remained limited (*40*). These beads support the hypothesis that a long-lasting and widespread beadworking tradition existed in Africa and the Levant well before the arrival of anatomically modern humans in Europe.

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Phosphorus in Cold-Water Corals as a Proxy for Seawater Nutrient Chemistry

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Phosphorus is a key macronutrient being strongly enriched in the deep ocean as a result of continuous export and remineralization of biomass from primary production. We show that phosphorus incorporated within the skeletons of the cosmopolitan cold-water coral *Desmophyllum dianthus* is directly proportional to the ambient seawater phosphorus concentration and thus may serve as a paleo-oceanographic proxy for variations in ocean productivity as well as changes in the residence times and sources of deep-water masses. The application of this tool to fossil specimens from the Mediterranean reveals phosphorus-enriched bottom waters at the end of the Younger Dryas period.

Phosphorus is a major biolimiting nutrient (*1–3*) that plays a key role in sustaining the biological productivity of the world's oceans. It is rapidly used by marine phytoplankton and exhibits a characteristic depletion in the uppermost surface oceans as a result of export of biomass to the deep oceans. This mechanism may be so efficient that changes in nutrient use in the Southern Ocean are considered to have played an important role in CO_2 sequestration and hence the lower levels of atmospheric CO_2 present during glacial cycles (*4*). Therefore, evaluating and quantifying past changes in the export of biological production to deep waters is a major issue, not only to understand past changes in atmospheric CO_2 but also to help predict how the ocean may buffer future increases in atmospheric CO_2. The P content of the deep-water masses also shows systematic differences across the major ocean basins, with the older deep-water masses in the North Pacific having ~50% higher P concentration than those formed more recently in the North Atlantic, reflecting ongoing remineralization of organic particles in the deep waters. Thus, changes in the P content of deep waters reflect changes in the biological production and cycling in surface waters as well as changes in the residence time of abyssal water masses.

Despite the importance of P, a straightforward approach for quantifying longer term changes in the concentration of this key paleonutrient in seawater is not yet available. The most commonly used proxies, namely carbon isotopes ($\delta^{13}C$) and Cd/Ca ratios in foraminiferal tests, appear to respond to a variety of additional environmental factors, including carbonate ion concentration, $\delta^{13}C$ of foraminiferal diet, and seawater temperature (*5, 6*), although the lack of a significant temperature influence on the incorporation of Cd into benthic foraminiferal tests has been reported recently (*7*). Furthermore, although Ba and organic matter accumulation in marine sediments are recognized as potential tracers of marine biological productivity (*8, 9*), their use as paleoproductivity proxies is dependent on

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