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CN[−] as a suitable leaving group. This enables arylation of amines with chloro-substituted caffeine, benzoxazole, benzothiazole, and *N*-Boc benzimidazole (entries 12 to 15). Lastly, the direct derivatization of pharmaceutical agents has been demonstrated by using linezolid, an antibiotic that undergoes direct heteroarylation in 58% yield (entry 16). This result further demonstrates the capacity of druglike molecules to readily participate in this C–H functionalization reaction.

Our proposed mechanistic explanation for the C–H arylation process is described in Fig. 5. Triscyclometalated Ir(III) complexes, such as Ir(ppy)₃ (**3**), are reversibly promoted to their excited state form [^{*}Ir(ppy)₃] (**4**) upon absorption of a photon from the 26-W light source (**30**). ^{*}Ir(III)(ppy)₃ (**4**) is a powerful reductant [oxidation potential (*E*_{1/2ox}) = −1.73 V versus saturated calomel electrode (SCE) in CH₃CN] (**30**, **31**) and, upon encountering 1,4-DCB (*E*_{1/2red} = −1.61 V versus SCE in CH₃CN) (**32**), could donate an electron to form the corresponding arene radical anion **5** (**33–35**). The resultant Ir^{IV}(ppy)₃ (**6**) is a strong oxidant (*E*_{1/2red} = +0.77 V versus SCE in CH₃CN) (**30**, **31**) and would be capable of undergoing a single-electron transfer event with amine **7**, generating amine radical cation **8**, as well as re-forming Ir^{III}(ppy)₃ (**3**) and thereby completing the photoredox cycle. The C–H bonds adjacent to the nitrogen atom in **8** are weakened by about 40 kcal/mol and so could undergo deprotonation by NaOAc (where OAc is an acetoxyl group) to give α-amino radical **9** (**19**, **36**). A radical-radical coupling reaction could then unite intermediates **5** and **9**, representing the key bond-forming step (**15–19**, **37–43**). Elimination of CN[−] from **10** would then form the aromatized benzylic amine product **11**.

In summary, the concept of accelerated serendipity has been successfully executed, resulting in the discovery of a photoredox amine C–H arylation reaction. Requiring only commercially

available materials, mild conditions, and operationally trivial reaction protocols, we anticipate this carbon-carbon bond-forming protocol will be widely used in the synthesis of benzylic and heterobenzylic amines.

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Pelagic Fishing at 42,000 Years Before the Present and the Maritime Skills of Modern Humans

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By 50,000 years ago, it is clear that modern humans were capable of long-distance sea travel as they colonized Australia. However, evidence for advanced maritime skills, and for fishing in particular, is rare before the terminal Pleistocene/early Holocene. Here we report remains of a variety of pelagic and other fish species dating to 42,000 years before the present from Jerimalai shelter in East Timor, as well as the earliest definite evidence for fishhook manufacture in the world. Capturing pelagic fish such as tuna requires high levels of planning and complex maritime technology. The evidence implies that the inhabitants were fishing in the deep sea.

Although humans were able to travel hundreds of kilometers over the ocean by 50,000 years ago (ka), as required for the colonization of Australia, global evidence

for fishing is rare before about 12 ka (*1*, *2*). Middle Stone Age sites in southern Africa, such as Klais River Mouth Main Cave, Pinnacle Point, and Ysterfontein 1, contain evidence of shellfish

predation and the remains of marine mammals such as seals, but evidence of fishing before the Holocene is absent or exceptionally rare (*1*, *3*, *4*). Whether this reflects real behavioral changes or the loss of coastal archaeological sites as sea level rose is unknown. A record of early marine fishing is found at Blombos Cave dating between ~140 and 50 ka, but the fish represented are shallow-water species and would not have required boats or complex technology for their capture (*5*).

At Jerimalai shelter in East Timor, evidence exists for systematic pelagic fishing from 42 ka, showing the high level of maritime capacity

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possessed by early colonists moving into, and through, the islands of Wallacea (Fig. 1 and Table 1).

During Pleistocene low sea stands, the southernmost extension of the Eurasian continent comprised Sumatra, Java, Bali, Borneo, and the now-drowned shelf in between (Sunda). New Guinea, Australia, and the Aru islands were joined as a separate continent, Sahul. Between these two landmasses stretches the 1500-km-wide Wallacean Archipelago (Fig. 1), with more than 17,000 islands. It includes the Lesser Sunda islands as well as Sulawesi, Maluku (excluding the Aru Islands), and the Philippines east of Palawan. During the human time span, Sunda, Sahul, and the islands of Wallacea were not connected by a land bridge. The human colonization of Wallacea and Sahul must have been undertaken by boat, but there is little in the way of archaeological evidence to attest to the marine skills of the early colonists.

Along the northern coasts of some Wallacean islands and of mainland and island Papua New Guinea (Fig. 1), cave sites with evidence of Pleistocene coastal exploitation proximal to current shorelines are locally preserved. However, even in these regions, evidence for Pleistocene fishing is absent or sparse. The caves preserve a variety of marine shell species (6, 7), and a few have low quantities of fish and shark remains dating back to 40 ka (8), but the remains are not suggestive of developed maritime skills (9, 10). A more convincing case for systematic fishing comes from Kilu Cave in the northern Solomon Islands, dated to 32 ka. Kilu contains a larger quantity of fish bone, including some pelagic species, but overall fishing at Kilu seems to have been inshore (11).

At the eastern end of East Timor, Pleistocene raised coralline terraces run parallel to the present coastline and contain many caves and shelters (12–15). At one such cave, Jerimalai (15) (Fig. 1 and figs. S1 and S2), excavation of two 1 × 1 m test pits (squares A and B) in 2005 produced a rich assemblage of cultural material, including well-preserved faunal remains, a large number of stone artefacts ($n = 9752$), bone points, fishhooks, and shell beads dating to the terminal Pleistocene (figs. S3 and S4) (15). Much like other assemblages associated with early modern humans in South and Southeast Asia, the lithic assemblage is characterized by faceted radial and rotated core technology and an informal scraper assemblage (figs. S6 to S8 and table S1) (16–18). The assemblage is made from high-quality chert and is one of the only large and well-dated palaeolithic assemblages in Southeast Asia dating to the period of modern human colonization. Among the faunal remains, the number and weight of fish bones far exceeds those of other fauna, averaging 56% (range, 16.7 to 80.0%) by weight of the total vertebrate remains between spit 3 and spit 55. Bones from pelagic fish, such as tuna, compose almost 50% of the total fish assemblage in the earliest occupation levels (Fig. 2).

Where fish are less dominant, the remains of marine turtles predominate. Unlike the marine fauna, the terrestrial faunal remains indicate op-

portunistic exploitation of the limited range of vertebrates found on Timor at the time. They comprise small quantities of murid rodents, bats, birds, and various terrestrial reptiles (mainly py-

thons, with small quantities of other snakes and monitors and smaller lizards) (15, 19). We recovered a total of 38,687 fish bones from square B. 19,252 of these were identified at

Fig. 1. Map showing Sunda, Wallacea, Sahul, and the location of sites.

Table 1. Accelerator mass spectrometry radiocarbon dates from Jerimalai shelter, East Timor. Dates were calibrated to 2σ with the program OxCal 4.1, using the Marine09 calibration curve, ΔR = 0. cal yr B.P., calendar years before the present.

Spit no.	Material	Age (yr B.P.)	C ¹⁴ 2σ cal yr B.P.	Specimen lab code
Jerimalai shelter square A				
3	Charcoal	2570 ± 34	2759–2695 (63.0%)	Wk-19224
			2638–2613 (13.4%)	
			2595–2501 (19.0%)	
5	Charcoal	3245 ± 39	3562–3385	Wk-19225
6	Turbo	5341 ± 41	5835–5598	Wk-18154
12	Turbo	5567 ± 44	6101–5866	Wk-18155
13	Turbo	5549 ± 62	6115–5762	Wk-17829
21	Turbo	5909 ± 40	6422–6245	Wk-19226
26	<i>Haliotis cf. varia</i>	10,110 ± 79	11,245–10,870 (92.4%)	Wk-18156
			10,862–10,802 (03.0%)	
27	Turbo	19,952 ± 235	23,935–22,564	Wk-17830
38	Turbo	13,658 ± 91	16,761–15,455	Wk-19227
46	<i>Trochus</i>	38,255 ± 596	43,381–41,616	Wk-17831
Jerimalai shelter square B				
3	Charcoal	124 ± 32	273–184 (34.0%)	Wk-19228
			179–173 (01.1%)	
			151–54 (45.0%)	
			48–10 (15.2%)	
4	Turbo	4962 ± 50	5455–5167 (93.5%)	Wk-19229
			5160–5131 (01.9%)	
9	<i>Trochus</i>	4580 ± 42	4900–4640	Wk-19230
16	<i>Trochus</i>	4867 ± 42	5293–5032	Wk-18157
21	<i>Trochus</i>	5595 ± 43	6123–5887	Wk-18158
23	<i>Trochus</i>	5694 ± 45	6232–5972	Wk-18159
33	<i>Trochus</i>	5939 ± 45	6455–6265	Wk-17832
34	Shell bead/ <i>Nautilus</i>	6118 ± 41	6654–6434	Wk-19316
40	<i>Trochus</i>	8879 ± 78	9776–9393	Wk-19231
49	<i>Haliotis cf. varia</i>	14,007 ± 146	17,083–16,151	Wk-18160
56	Turbo	35,387 ± 534	41,217–38,853	Wk-19232
66	<i>Trochus</i>	37,267 ± 453	42,475–41,125	Wk-17833

least to anatomical element. (Table 2). The total minimum number of individuals (MNI) of fish remains identified to family was 796, and the number of individual specimens (NISP) was 2822. Twenty-three taxa were identified, including 22 families and 1 species (*Monotaxis granoculis*). The MNI of Scombridae (tunas) is greatest in most of the spits, almost to the base of the site, accounting for approximately 16% of total MNI. Scaridae (parrotfish), Carangidae (trevallies), Balistidae (triggerfish), and Serranidae (groupers) follow in MNI and NISP. These species make up about 12 to 15% of the total MNI. Other major fish families identified are Lethrinidae (emperors), Lutjanidae (snappers), Acanthuridae (unicornfish), Labridae (wrasses), and Tetradontidae (puffers). For Elasmobranchii (rays and sharks), both are recognized, and some shark vertebra were identified as Carcharhinidae.

At least 15 fish taxa were exploited during the earliest period of occupation, from 42 to 38 ka

(phase I), although the quantity of fish bones from this phase is limited (Table 3). Although this may in part be a consequence of less intensive occupation of the site at this time, it is more likely due to the cemented nature of the deposit, which made recovering and extracting small bones problematic (see methods in the supporting online material). The prominent feature during this earliest occupation phase is the intensive focus on pelagic fish species, particularly Scombrids. The ratio of pelagic species (49%) and inshore species (51%) based on MNI is almost equal (Fig. 2). Sharks and rays were also exploited (Table 3). At present the site appears to have little evidence of occupation between ~38 and 24 ka. This may be due to sea level retreat rendering the shelter farther from the coast during this time; however, research at other nearby coastal sites such as Lene Hara Cave suggests that it more likely reflects limited sampling due to the small size of the excavation (20).

Between 17 and 9 ka (phase II), sea level rose, and by 9 ka Jerimalai would have almost been as close to the coast as it is today. In terms of offshore fish exploitation, in phase II the ratio of pelagic species in the total MNI remained high (46%), but the number of Carangids (trevallies) dramatically increased, whereas the exploitation of Scombrids (tunas) remained similar. There is also a marked change in the evidence of inshore fishing. Parrotfish were still intensively exploited, but the number of groupers and triggerfish increased.

The mid-Holocene assemblage (phases III and IV) is different. The most prominent change is the dramatic increase (66 to 76%) in the total MNI and lower ratio of pelagic fish species (34 to 24%) (Fig. 2). Pelagic species were still targeted, but inshore fish dominate the assemblage. The increase of inshore species may reflect the stabilization of sea level, warmer temperatures, and the establishment of reef habitats.

Because no direct evidence of fishing technology has been found in the earliest occupation period, it is uncertain how and by which method the occupants at Jerimalai captured pelagic and other species. Tuna can be caught in purse seines or leader nets (21). Simple fish-aggregating devices such as tethered log floats can be used to attract tuna (21, 22). The small size of the pelagic bones (individuals of ~50 to 60 cm in length) indicates that mostly immature individuals were taken, which may favor an interpretation of netting over line fishing as the capture method.

Zooarchaeological and ethnoarchaeological studies in Southeast Asia and Oceania suggest that the parrotfish and unicornfish would likely have been caught by netting or spearing, whereas

Fig. 2. Graph showing changing ratios of pelagic and inshore fish species through time (in percent based on MNI). cal BP, calendar years before the present.

Table 2. Fish bone assemblage from square B Jerimalai shelter by anatomical element.

Anatomy	Left	Right	n	Anatomy	n	Anatomy	n
Premaxilla	109	118	227	Scale	131	Vertebra (Scombrids)	1181
Dentary	102	97	199	Scute (Acanthurids)	16	Vertebra (Carangids)	240
Quadrate	79	102	181	Scute (Carangids)	100	Vertebra (Scarids)	145
Maxilla	52	48	100	Scute (unknown)	3	Vertebra (Balistids)	12
Articular	54	43	97	Tooth (Balistidae)	65	Vertebra (Lethinids)	8
Pharyngeal (lower)			56	Tooth (bony fish)	73	Vertebra (Lobotidae)	7
Pharyngeal (other part of pharyngeal cluster)			6	Tooth (shark and ray)	1	Vertebrae (Elasmobranchii)	7
Pharyngeal (upper)			113	Dentary/premaxilla	98	Vertebra (Muraenidae)	6
Scapula			56	1st fin spine (Balistidae)	89	Vertebra (flathead)	6
Hyomandibular			48	1st fin spine (Acanthurids)	73	Vertebra (Diodon?)	2
Cleithrum			42	Spine (Diodontidae)	5	Vertebra (Sphyracidae)	2
Opercle			30	Spines	2096	Vertebra (5–10 mm)	4546
Palatine			24	Unknown (skull)	584	Vertebra (5 mm)	2892
Preopercle			17	Vomer	38	Vertebra (10 mm)	516
Epihyal			18	Specific fragments	106	Vertebra (broken)	4585
Ceratohyal			17			1st vertebra	131
Posttemporal			6			Caudal vertebrae	236
Supracleithrum			15				
Subtotal (identified)					19,252		
Subtotal (unidentified fragments)					19,435		
Total					38,687		

Table 3. MNI and NISP of identified fish taxa from the 1 × 1 m excavation, square B, Jerimalai shelter, East Timor.

Cultural phase	I				II		III		IV		Total
Age (cal yr B.P.)	42,000–38,000				17,000–9000		6500–5500		5500–modern		
	Genus/ species	MNI (NISP)	%	MNI (NISP)	%	MNI (NISP)	%	MNI (NISP)	%	MNI (NISP)	%
					</						

Fig. 3. A broken shell fish-hook dated between ~23 and 16 ka from square A, spit 29, Jerimalai shelter, East Timor (scale is in millimeters).

trevallies, triggerfish, snappers, emperors, and groupers are most commonly captured by angling using a baited hook, but netting and trapping can be successful depending on species and body size (23–28). A broken hook in square A, spit 29, is dated between ~23 and 16 ka (specimen lab codes Wk-17830 and Wk-19227) (Fig. 3.). This is the earliest definite evidence for fishhook manufacture in the world. Another hook fragment in square A, spit 26, is dated ~11 ka (Wk-18156) (fig. S5 and Table 1), as is one from nearby Lene Hara Cave (13). The dra-

matic increase of trevallies and groupers in phase II is consistent with the appearance of angling technology. All are *Trochus* shell single-piece baited hooks and do not seem suitable for pelagic fishing; however, it is possible that other types of hooks were developed at the same time. Bone points made on the spines of large fish first appear at Jerimalai in phase II. Their function is uncertain, but they clearly represent a component of a composite tool, such as fine barbs for fish spears, or part of complex hooks for trolling. The number

of bone points increases dramatically in the mid-to late-Holocene levels (phases III and IV). No artefacts related to netting have yet been recovered, but the manufacture of strong fiber line is implied by the hooks, so knowledge of netting seems probable. The finds from East Timor demonstrate the high level of maritime skills and technology possessed by the modern humans who colonized Wallacea. These skills would have made possible the occupation of the faunally depauperate islands of Wallacea and facilitated the early maritime colonization of Australia and Near Oceania.

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Supporting Online Material

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Phanerozoic Earth System Evolution and Marine Biodiversity

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The Phanerozoic fossil record of marine animal diversity covaries with the amount of marine sedimentary rock. The extent to which this covariation reflects a geologically controlled sampling bias remains unknown. We show that Phanerozoic records of seawater chemistry and continental flooding contain information on the diversity of marine animals that is independent of sedimentary rock quantity and sampling. Interrelationships among variables suggest long-term interactions among continental flooding, sulfur and carbon cycling, and macroevolution. Thus, mutual responses to interacting Earth systems, not sampling biases, explain much of the observed covariation between Phanerozoic patterns of sedimentation and fossil biodiversity. Linkages between biodiversity and environmental records likely reflect complex biotic responses to changing ocean redox conditions and long-term sea-level fluctuations driven by plate tectonics.

Identifying the causes of changes in biodiversity and mass extinctions in Earth history is a central goal of paleobiology (1, 2). However, patterns of taxonomic richness and turnover derived from paleontological data covary with changes in the sedimentary rock record, thereby raising the possibility that the fossil record is strongly overprinted by geologically controlled sampling biases (3–6). An alternative hypothesis is that large-scale geological processes cause physical environmental changes that influence both patterns of sedimentation and macroevolution (3, 7). The sampling bias and common-cause hypotheses are not mutually exclusive, and a critical unanswered question is their overall relative importance during Earth's history.

To address this question, we used a recent compilation of geographically and temporally explicit co-occurrences of Phanerozoic rocks and fossils in North America (7). We compared fossil diversity and sedimentary rock quantity according to the common analytical currency provided by macrostratigraphy: The total number of fossil taxa in

a time interval is commensurable with the total number of hiatus-bound rock packages, which relate to the underlying geological processes that control the spatial and temporal distribution of sedimentation (8). To evaluate the possible role of common-cause interactions in driving both the macroevolutionary history of marine animals and continent-scale patterns of sedimentation, we compared the rock and fossil records to a global database of isotope ratios in marine carbonates (9) and to estimates of relative global sea level (10, 11), all of which have been linked to biological turnover. We restricted our analysis to the marine component of the stratigraphic and fossil data (Fig. 1A), which dominates the North American record (7, 12).

In the Phanerozoic, fluctuations (but not the trend) in low-latitude carbonate $\delta^{18}\text{O}$ (Fig. 1B) reflect global climate change, which has been linked to biodiversity patterns (13) and some mass extinctions (14). Changes in $\delta^{13}\text{C}$ (Fig. 1C) are controlled by the exchange of carbon between isotopically depleted organic and isotopically enriched inorganic reservoirs (15, 16), and $\delta^{13}\text{C}$ excursions commonly coincide with turnover events in the fossil record (17). The burial efficiency of pyrite formed through microbial sulfate reduction plays a key role in the Phanerozoic $\delta^{34}\text{S}$ pattern (Fig. 1D) (18, 19). Seawater $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. 1E) is

governed by the flux and composition of Sr from midocean ridge volcanism and from continental weathering (20). Both $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{34}\text{S}$ covary with generic origination rate over the Phanerozoic (21). Finally, global long-term sea level, expressed geologically as the extent of continental flooding (Fig. 1F), has been recognized as a potential control on marine diversity via a species-area effect (3, 22).

Interval-to-interval changes (i.e., first differences) in the number of marine animal genera (G; representing face-value range-through diversity) were positively correlated with first differences in the total number of marine sedimentary rock packages (P). We found the highest Spearman rank-order correlations between the G and P records, between P and sea level, and between $\delta^{34}\text{S}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ (table S1). Multiple linear regression of the six detrended environmental variables on G (adjusted $R^2 = 0.28$; $P = 0.00004$) similarly showed P as the dominant explanatory variable ($P = 0.00004$), with the next strongest contribution from $\delta^{34}\text{S}$ ($P = 0.09$). Simple correlation and regression analyses of detrended data seemed to support aspects of the rock-record bias hypothesis. However, first differences emphasize only the shortest-term variability in the data, which is expected to be strongly overprinted by variability in sampling. Moreover, simple correlation and regression analyses are only sensitive to linear or monotonic relationships among variables.

To overcome these limitations, we used a non-parametric measure of information transfer (IT) to assess the relative strength and directionality of interactions among G, P, and several global environmental records (23). Unlike correlation, the IT between two variables, A and B, is nonsymmetric ($A \rightarrow B \neq B \rightarrow A$) and can be used to distinguish a driving variable from a response variable, even in short and unevenly sampled time series (fig. S1) (24). We first quantified the relative strength of IT from each potential driving factor on a response variable, while excluding any IT that may arise from common interaction with other factors (e.g., does sea level contain significant information on generic richness beyond any mutual correlations with the sedimentary rock

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