noticable changes in lattice parameter are observed. For PuO$_3$–x, for example, a lattice parameter of 5.446 Å is measured: an increase of 0.9% with respect to the lattice constant of stoichiometric PuO$_2$. Here, we have studied the electronic structure of PuO$_{1.75}$. Starting again from the unit cell shown (Fig. 2), the PuO$_7$ supercell has been constructed by removing one of the eight O atoms (marked in dark blue). We subsequently calculated the total energy as a function of lattice parameter, both for the tetravalent Pu$^{4+}$O$_2$ and for the trivalent Pu$_3^{3+}$O$_5$ configurations; the latter has been found to be the ground-state solution. Compared with PuO$_2$, we find that the removal of an O atom results in the localization of one further f electron on each of the Pu sites, i.e., the opposite trend to adding O atom to the PuO$_2$ compound. The increased degree of f-electron localization leads to a distinct increase in the calculated lattice parameter, $a_0 = 5.558$ Å, as the bonding O p electrons are removed and replaced with nonbonding localized Pu f electrons.

The foregoing discussion implies that the increase or decrease in the Pu state of oxidation under O insertion to or extraction from PuO$_2$ can be explained in terms of a localization/delocalization transition by correcting for the self-interaction associated with the strongly correlated f electrons. Whether the oxidation process actually takes place depends on the thermodynamic conditions, in particular the chemical potential of the additional oxygen. We are not able to calculate the entropic contributions to the free energy here; however, the total energy balance of the reaction

$$\text{PuO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{PuO}_{2.25}$$

finds the reduction (left side) to be more favorable by 25 mRy (using an LSD binding energy of the free O$_2$ molecule of 0.7 Ry). Thus, at $T = 0$ the dioxide is stable, in agreement with the observed chemical stability of this compound. Depending on actual conditions (temperature and chemical potential of oxygen), it is conceivable that the oxidation may become favorable, given the small energy barrier. The experimental oxidation process of (2) uses H$_2$O as oxidant, at 32 mbar H$_2$O pressure and at temperatures between 255 and 350°C. In this case oxidation is accompanied by production of H$_2$, which is favored by high entropy.

This study of the electronic structure of PuO$_{1.75}$ did not consider such complex species as O$_3$ and O$_5^2$ as possible candidates for the extra O. Similarly, noncubic distortions of the O sublattice were not considered, although such configurations are often encountered in oxide systems. The relevance of these issues in PuO$_{1.75}$ compounds depends strongly on the energy considerations with respect to the independent interstitial O. The important outcome of this work is that Pu ions play an active role in accommodating extra O in the PuO$_2$ matrix, because their localized f states act as electron reservoirs for the O$^{2-}$ ions: for x greater than 0.5, the added O impurities absorb electrons released by the neighbouring Pu(V) ions in the process of f-electron delocalization leading to the formation of Pu(V) ions. A recent model of corrosion of Pu(III) ions, with the localized f$^5$ configuration, in the vicinity of O vacancies. We find PuO$_2$ energetically stable with respect to interactions with free O$_2$ molecules, consistent with the results from decades of research on this subject. The properties of PuO$_{2.25}$, predicted by our calculations also agree very well with the experimental findings by Haschke et al. Thus, higher oxidation states may be possible under specific experimental or even environmental conditions. Pu oxidation states of 6 and above have not been found in PuO$_{2.25}$, but may be realizable in more exotic circumstances.

References and Notes


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The Archaeology of Ushki Lake, Kamchatka, and the Pleistocene Peopling of the Americas

Ted Goebel, * Michael R. Waters, ** Margarita Dikova ***

The Ushki Paleolithic sites of Kamchatka, Russia, have long been thought to contain information critical to the peopling of the Americas, especially the origins of Clovis. New radiocarbon dates indicate that human occupation of Ushki began only 13,000 calendar years ago—nearly 4000 years later than previously thought. Although biface industries were widespread across Beringia contemporaneous to the time of Clovis in western North America, these data suggest that late-glacial Siberians did not spread into Beringia until the end of the Pleistocene, perhaps too recently to have been ancestral to proposed pre-Clovis populations in the Americas.

Anthropologists have long looked to Siberia for the origins of the first Americans. Much attention has focused on the search for an immediate antecedent of Clovis (1–3), the earliest unequivocal complex of archaeological sites in North America (4). A clear connection between the Siberian Paleolithic and early American sites, however, continues to be elusive.

One Siberian locality pivotal to understanding the peopling of the Americas is the site complex around Ushki Lake, Kamchatka (Fig. 1). Ushki Lake is located in the maritime region of southwestern Beringia, 55°N latitude. Dikova excavated the Ushki sites from 1964 through 1990, revealing two late Paleolithic cultural components in a stratified

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context (5, 6). The earliest, component 7, contained a core and flake industry with small bifacial points and knives that was radiocarbon (14C) dated to about 16,800 calibrated years before present (cal years B.P.) (7), nearly 4000 calendar years earlier than the time of Clovis in North America. Stratigraphically above this, Dikov found a different lithic industry (component 6) characterized by wedge-shaped cores, microblades, and burins that was 14C dated to about 12,600 cal years B.P. Given the age and character of the component 7 lithic industry, Ushki has long been considered not only the earliest archaeological site in Beringia (8) but also a potential Siberian ancestor of Clovis and other early American sites and complexes (7–9). The site has also figured prominently in coastal migration models, because it is the only pre–13,000 cal years B.P. archaeological site along the north Pacific Rim between Hokkaido and central California (10–12).

The Ushki sites, however, are poorly known and controversial. Little information is available in English or Russian, and Dikov never published a final report of his excavations. Concerns about the site were raised because 14C dates conflicted with other contextual information. Mochanov (13) argued that the absence of cryoturbation features in the Ushki sediments meant they could only be Holocene in age. Older carbon in ancient groundwater, he suggested, had contaminated the 14C samples, making them appear much more ancient than they really were.

In 2000, we sampled and mapped Ushki to define the geomorphic and stratigraphic context of the late Upper Paleolithic components, establish the age of each component, and recover diagnostic artifact assemblages from controlled excavations. Our work focused on two sites thought to have contained both late Pleistocene cultural components—Ushki-1 and Ushki-5 (5).

The Ushki sites are buried in alluvial and eolian sediments along the banks of the Kamchatka River (14). At Ushki, there is an active floodplain (T0), low terrace (T1) situated 3 m above the channel edge, and higher terrace (T2) 9 m above the channel edge (Fig. 2). The alluvium under the T1 surface dates to the Holocene and contains several volcanic ashes. The Ushki archaeological components are buried within the alluvium comprising T2 and in overlying eolian sediments that cover the terrace (Fig. 3).

The alluvial sequence of T2, from bottom to top, comprises 2.5 m of coarse to fine sand, followed by 4 m of interbedded very fine sand and silt, which are overlain by 1 m of silt and clay. No evidence of pedogenesis was observed in these sediments. This is a typical alluvial fining-upward textural sequence from lower and middle point bar to upper point bar and overbank sediments. These deposits date to the late Pleistocene, and the upper 1 m of this alluvium contains late Upper Paleolithic components 7 and 6. At the time of occupation, the people at Ushki would have been living on a vertically aggrading floodplain (possibly on the upper portion of a point bar) (15). Ushki Lake, which lies next to the site complex, formed during the late Holocene. Deposition of alluvial sediments appears to have ended around 11,000 cal years B.P. The alluvial sequence is overlain by 2 m of interbedded silt, very fine sand, and volcanic ash separated by numerous thin soils with A horizon development.

These sediments were deposited by eolian processes on the terrace trend during the Holocene and contain cultural components 5 through 1, previously radiocarbon dated by Dikov to 10,000 cal years B.P. and later (5). None of the alluvial or eolian sediments show evidence of cryoturbation.

Our studies at Ushki-1 and -5 confirm the presence of two late Upper Paleolithic cultural components stratigraphically separated by 30 cm of alluvial silt and clay. Components 7 and 6 represent discrete occupations that are separated in time.

To establish the age of components 7 and 6, we dated charcoal samples from four profiles, two at Ushki-1 and two at Ushki-5. To evaluate the possibility that the charcoal samples from Ushki were contaminated by older soluble organics, we dated the base insoluble and soluble fractions from charcoal in both components 7 and 6 (table S1). For component 7, the base insoluble fraction of a sample of hearth charcoal yielded a date of 11,005 ± 115 14C years B.P. (AA-41388), and the base soluble humate fraction of the same sample yielded a date of 11,050 ± 75 14C years B.P. (AA-41389). For component 6, the base insoluble fraction of a sample of hearth charcoal yielded a date of 10,240 ± 75 14C years B.P. (AA-41386), and the base soluble humate fraction of the same sample yielded a date of 9,485 ± 275 14C years B.P. (AA-41387). The base insoluble- and soluble fraction dates from component 7 were essentially identical, and the soluble-fraction date from component 6 was significantly younger than its base insoluble-fraction pair. These results indicate that charcoal from Ushki has not been contaminated by older soluble carbon as Mochanov suggested (13), and that dates obtained from base insoluble charcoal fractions closely approximate the ages of the late Pleistocene cultural components.

To ascertain the ages of components 7 and 6, 15 additional wood charcoal samples (three

![Fig. 1. Map of Beringia, showing extent of Bering Land Bridge during full glacial conditions, and locations of archaeological sites mentioned in the text (1: Ushki; 2: El’gakhchan; 3: Berelekh; 4: Nenana valley sites (Dry Creek, Moose Creek, Owl Ridge, Walker Road); 5: Broken Mammoth; 6: Tangle Lakes sites (Phipps, Whitmore Ridge); 7: Bluefish Caves).](image)

![Fig. 2. Map of Ushki Lake area, showing geomorphic landforms and locations of Ushki Paleolithic sites.](image)
from the stratigraphic unit lying immediately below component 7, five from component 7, and seven from component 6) were \(^{14}\text{C}\) dated by accelerator mass spectrometry (AMS). All resulting \(^{14}\text{C}\) ages are concordant. Ages for the stratigraphic unit immediately underlying component 7 span from 11,870 ± 90 \(^{14}\text{C}\) years B.P. (AA-45711) to 11,200 ± 160 \(^{14}\text{C}\) years B.P. (AA-45712) and average 11,740 ± 60 \(^{14}\text{C}\) years B.P. Ages for component 7 range from 11,330 ± 50 \(^{14}\text{C}\) years B.P. (SR-5810) to 10,675 ± 75 \(^{14}\text{C}\) years B.P. (AA-45710) and average 11,000 ± 30 \(^{14}\text{C}\) years B.P. (16). In calibrated years before present (17), component 7 spans the period from 13,435 to 12,635 cal years B.P., whereas component 6 ranges from 13,175 to 11,255 cal years B.P. The statistical overlap between the ages of the two components is likely due to radiocarbon plateaus coinciding with the times of both occupations (18). Calibration of mean dates of the two components produces ages of 13,130 to 12,900 cal years B.P. for component 7 and 12,355 to 11,955 cal years B.P. for component 6, suggesting that component 7 is 500 to 1000 years older than component 6 (19).

Our archaeological excavations in 2000 focused on Ushki-5, where we opened a 20-m\(^2\) excavation block and exposed both late Upper Paleolithic components. In component 7, which was only 3 cm thick, we unearthed two hearths. Both were unlined smears roughly 1 m in diameter containing charcoal, ash, and burnt bone fragments. Lithic artifacts were dispersed across a distinct living floor around the two hearths.

In component 6, we excavated a well-preserved dwelling. It was roughly 5 m in diameter and was dug into the ground to a depth of about 30 cm below the prehistoric ground surface, at places even cutting into underlying component 7. The floor of the dwelling was marked by a clear band of charcoal and organic residue and contained a single filled post hole. A distinct shoulder was traced around the entire perimeter of the dwelling, and a narrow “arctic entry” passage was noted in its northwest quadrant. An 80-cm-diameter hearth, lined with large stones, was situated near the center of the living space. Thousands of small fragments of burned bone, some of which represent remains of fish and bird, were found in the fill of the hearth. Numerous lithic artifacts including microblades, wedge-shaped cores, and small leaf-shaped bifaces were found clustered near the hearth and around the perimeter of the dwelling.

The component 7 assemblage from the Ushki-5 excavations comprises 332 artifacts. The debitage assemblage (\(n = 318\)) is characterized by numerous biface thinning flakes and pressure flakes, but no microblades and few blades. Flaked-stone tools (\(n = 10\)) include five bifacial points, two bifacial point fragments, two biface fragments, and one leaf-shaped biface (Fig. 4, A, B, and E). The complete points are on flakes and sometimes only partially retouched on their ventral faces. Although Dikov (5–7) described these as “stemmed” points and considered them to be related to Paleoindian stemmed points in western North America, they are much smaller and thinner, and more like notched points than stemmed points. Beads (\(n = 4\)) similar to those found by Dikov at Ushki-1 were also recovered (Fig. 4, C and D). The component 7 lithic assemblage is clearly a nonmicroblade industry, one that is characterized by simple flake and blade tools and small bifacial points and knives. It may have affinities with other early nonmicroblade complexes in Beringia (e.g., the Nenana complex, Alaska, and undated El’gakhchan complex, Chukotka) (2, 8, 20).

The component 6 artifact assemblage recovered from the Ushki-5 excavation consists of 601 articles. Among debitage pieces (\(n = 553\)), microblades as well as biface thinning flakes are common. Cores (\(n = 8\)) include two wedge-shaped microblade cores, one subconical microblade core, and five wedge-
shaped core tablets (Fig. 4, G and J). The tool assemblage ($n = 38$) consists of 12 retouched microblades, six retouched blades and bladelets, six retouched flakes, four burins, three bifaces and biface fragments, two cobbles tools (a hammerstone fragment and ground-stone pestle-like artifact), two side scrapers, one end scraper, one bifacial point fragment, and one smooth-backed knife (Fig. 4, F, H and I, K to M). One small stone bead was also recovered. The character of the component 6 lithic assemblage suggests affinities with other microblade-rich late Paleolithic complexes of Japan, Yakutia (i.e., Diuktai), and Alaska (i.e., Denali) (8, 21).

These findings have significant implications for our understanding of the timing and process of human colonization of Beringia and the Americas. Component 7 at Ushki is nearly 4000 years younger than previously thought and is no longer the oldest site in Beringia (Fig. 5). The earliest unequivocally dated cultural occupation in Beringia is instead the lowest component (unit 4e) of Broken Mammoth (22), central Alaska, 14,000 cal years B.P. Possibly older sites (i.e., Berelekh, Bluefish Caves) have problematic geologic contexts so that $^{14}$C-dated materials cannot be clearly tied to lithic artifacts (2, 11). These data indicate that during the late glacial, humans did not colonize the Bering Land Bridge area until the onset of the Allerod interstadial, only 400 calendar years before the emergence of Clovis in western North America (13,600 cal years B.P.) and 500 to 1000 years after the hypothesized pre-Clovis occupation of Monte Verde, Chile (23).

The confirmed cultural stratigraphy of the Ushki sites—specifically a “nonmicroblade” industry overlain by a microblade industry—replicates the cultural sequence known for central Alaska (24). In age and technological/typological character, component 7 at Ushki relates to the Nenana complex of central Alaska. Cultural occupations ascribed to the Nenana complex range in age from 14,000 to 12,800 cal years B.P. (22, 24), but cluster between 13,400 and 13,000 cal years B.P. Like component 7, Nenana complex industries contain small bifacial points and knives and unifacial tools made on flakes and blades, but lack microblades and burins. Thus, biface-and-blade industries occurred across Beringia during and just before the time of Clovis in western North America.

Microblade and burin industries appear synchronously in the archaeological records at Ushki (component 6) and in Alaska (the Denali complex), shortly after 12,500 cal years B.P. (11, 25). Although this sudden and significant reorganization of technology could be the result of early Beringians adapting to colder conditions of the Younger Dryas (21, 26, 27), it more likely represents a second migration of northeast Asians into the region (28, 29), perhaps antecedents of modern Athabaskan (Na-Dene) peoples of northwest North America (30–32).

The new dates from component 7 at Ushki show that this Siberian bifacial industry cannot by itself be the long-sought Clovis antecedent. Instead component 7 is coeval with the end of Clovis in North America. Thus, we are faced with an apparent dilemma in solving the Clovis-origins question, because there is now no clearly identifiable progenitor in Siberia. Perhaps the biface-and-blade complex of late glacial Beringia (to which we ascribe component 7 of Ushki along with the Nenana complex of central Alaska) did give rise to Clovis (2, 33); however, such a founding migration would have been very rapid, occurring in less than four centuries. Or perhaps Clovis developed in situ within North America and was derived from a much earlier migration from Siberia, a migration that could have occurred before the last glacial maximum ($>24,000$ cal years B.P.) (33–35). Only additional research in northeast Asia and the Americas will resolve this issue.

**Fig. 4.** Lithic artifacts from Year 2000 excavations at Ushki-S [component 7; (A) to (E); component 6: (F) to (M)]. (A and B) "Stemmed" bifacial points; (C and D) stone beads; (E and F) bifaces; (G) wedge-shaped microblade core; (H and K) transverse burins; (I and M) retouched microblades; (J) conical microblade core; (L) end scraper.

**Fig. 5.** Comparison of calibrated AMS $^{14}$C ages from Ushki (components 7 and 6) and archaeological sites in Alaska (Nenana and Denali complexes) (11, 38) and western North America (Clovis complex) (39, 40).
Ecological Consequences of a Century of Warming in Lake Tanganyika

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Deep tropical lakes are excellent climate monitors because annual mixing is shallow and flushing rates are low, allowing heat to accumulate during climatic warming. We describe effects of warming on Lake Tanganyika: A sharpened density gradient has slowed vertical mixing and reduced primary production. Increased warming rates during the coming century may continue to slow mixing and further reduce productivity in Lake Tanganyika and other deep tropical lakes.

Evidence for global climate warming is accumulating, and most of the data that are relevant to inland waters are coming from long-term monitoring records on temperate lakes and glacial and high-latitude systems (1, 2). Tropical ecosystems, including lakes, are less frequently analyzed quantitatively. Consequently, recorded impacts of climatic change on tropical terrestrial and inland water ecosystems are rare. The stratified water column and the large volume and low flushing rates of deep tropical lakes allow them to store heat and furnish a record of long-term trends. Lake Tanganyika records a century-long warming trend, and the impacts on its pelagic ecosystem are evident.

Lake Tanganyika is a large Rift Valley lake (670 km by 50 km) (Fig. 1) in East Africa, just south of the equator (3° to 9°S), with deep basins in the north (maximum depth 1310 m) and the south (maximum depth 1470 m), separated by a sill of 600 m. A few surveys in the past century have published profiles of its nutrients and temperature (3–7). Temperatures in the north basin have increased since 1913 by 0.2°C near the bottom and by 0.9°C at 100 m (8) (Fig. 2A).

Fifty percent of the heat gained by the lake between 1913 and 2000 is in the upper 330 m (8), increasing the vertical temperature gradient (Fig. 2B). Density decreases with increasing temperature and increases with salinity. The temperature gradient largely determines the density gradient at Lake Tanganyika because salinity varies only from 0.57 to 0.63 per mil from the surface to the bottom (9). Although absolute temperature differences are small in this tropical lake [annual mean air temperature was 1.6°C above bottom potential (corrected for pressure) temperature in 2000], density differences per degree Celsius are pronounced at these high water temperatures (10). Between 1913 and 2000, density gradients (8) roughly tripled between 110- and 200-m depth and between 200- and 800-m depth (Fig. 2C). The amount of work required to mix water layers is proportional to the difference in density (10). The density gradient in Lake Tanganyika combined with the extreme depth of the lake impedes vertical mixing.

Global air temperatures correlated well with air temperature at the north end of the lake based on annual means from between 1964 and 1991 (r2 = 0.75, P < 0.0001) (11, 12). Air temperature at the north end of the lake increased by 0.81°C over the 37 years (r2 = 0.56, P < 0.0001), much above the global average (+0.42°C). The lake effect on the surrounding climate should be largest at the north end of Lake Tanganyika.

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