rials, several samples of green obsidian from the Pachuca source were submitted along with the other samples. The analyst was unaware of the clearly different nature of these samples. These samples have been clearly separated from the other two source materials (Fig. 1).

Most published analyses of Mesoamerican obsidian have until now used only a limited number of chemical elements in the characterization. Most have relied on two, three, or four (*4, 5*). Those elements most frequently tested are Fe, Mn, Na, Rb, Sr, Zr, and Y. On the basis of such analyses, the Otumba obsidian source in the Teotihuacán valley has been identified in recent literature as a major obsidian source during the Early Formative (*5*). We cannot now disagree or agree with the effectiveness of using a limited number of elements, for such an approach may be valid for many sources. However, the Paredón obsidian source cannot be differentiated from Otumba obsidian with the elements most commonly used; at least Ba, As, and Ln are also necessary (Table 1).

Of the 90 obsidian samples analyzed from Chalcatzingo, 10 percent (nine samples) were from Early Formative levels. Without a larger number of elements in this characterization, these would have been identified as Otumba; eight of the nine are actually from Paredón. How closely this high percentage of Paredón obsidian in Chalcatzingo Early Formative levels corresponds to sampling versus reality is a matter for future testing. Twelve nonrandom samples from sites of the same time period in central Morelos (*19*) have recently tested out 33 percent Paredón, 67 percent Otumba (Fig. 1). The larger Middle Formative sample from Chalcatzingo indicates a 32 percent Paredón and 68 percent Otumba exploitation pattern. Nevertheless, it is clear that Paredón is an important obsidian source that has gone unrecognized in previous analyses. Its identification indicates that hypothesized Early Formative obsidian networks will have to be reanalyzed. References in the literature to Otumba obsidian (also termed "Teotihuacán valley" and "Barranca de los Estetes") should be read as Otumba/Paredón until further studies have been carried out.

THOMAS H. CHARLTON
Department of Anthropology, University of Iowa, Iowa City 52242
DAVID C. GROVE
Department of Anthropology, University of Illinois, Urbana 61801
PHILIP K. HOPKE
Institute for Environmental Studies, University of Illinois

References and Notes

1. T. H. Charlton, *Hum. Mosaic* **9**, 59 (1976); "Final report of a surface survey of preconquest trade networks in Mesoamerica" (Department of Anthropology, University of Iowa, Iowa City, 1977).
2. T. H. Charlton, *Science* **200**, 1227 (1978).
3. A. C. Breton [*Proc. 13th Int. Congr. Am.* (1905), p. 265] described the unnamed source as follows (p. 266):
   "To the south of Tulancingo, about four and a half hours' ride on the road to Apam, and beyond the Rancho of Lagunita, there is a ridge of obsidian, which has been worked, partly at so remote a period that a thick lichen has had time to grow on some of the chips in that extremely dry climate.
   "There are some small shady caves in the side of a low hill near, to which the workers brought their roughly shaped pieces to finish, and the fragments are strewn down the slope. There are all sorts of bits, broken and half-finished implements, in fact everything except those many-sided objects which hitherto have been called cores, but which are conspicuous by their absence from all the workings I have seen, except one, . . ."
4. R. H. Cobean, M. D. Coe, E. A. Perry, Jr., K. K. Turekian, D. P. Kharkar, *Science* **174**, 666 (1971); T. R. Hester, R. N. Jack, R. F. Heizer, *Contrib. Univ. Calif. Archaeol. Res. Facil. No. 16* (1972), p. 105; F. H. Stross, J. R. Weaver, G. E. A. Wyld, R. F. Heizer, J. A. Graham, *ibid., No. 5* (1968), p. 59; F. H. Stross, T. R. Hester, R. F. Heizer, R. N. Jack, in *Advances in Obsidian Glass Studies*, R. E. Taylor, Ed. (Noyes, Park Ridge, N.J., 1976), pp. 240–258; F. W. Nelson, K. K. Nielsen, N. F. Mangelson, M. W. Hill, R. T. Matheny, *Am. Antiq.* **42**, 209 (1977).
5. J. W. Pires-Ferreira, *Formative Mesoamerican Exchange Networks with Special Reference to the Valley of Oaxaca* (Memoir No. 7, Museum of Anthropology, University of Michigan, Ann Arbor, 1975); in *The Early Mesoamerican Village*, K. V. Flannery, Ed. (Academic Press, New York, 1976), p. 292.
6. Elevations were obtained from map 14Q-h (3), Depto Cartografico Militar, Mexico (1957), scale 1:100,000.
7. T. H. Charlton, *Am. Antiq.* **34**, 176 (1969).
8. J. Garcia-Barcena G., *Proc. 40th Int. Congr. Am.* **2**, 95 (1973).
9. M. W. Spence and J. R. Parsons, *Anthropol. Pap. Mus. Anthropol. Univ. Mich.* **45**, 20 (1972).
10. J. W. Michels and C. A. Bebrick [in *Dating Techniques for the Archaeologist*, H. N. Michael and E. K. Ralph, Eds. (MIT Press, Cambridge, Mass., 1971), p. 172] illustrate the globulites and trichites which occur in Paredón obsidian.
11. P. D. Sheets, *Curr. Anthropol.* **16**, 375 (1975).
12. D. C. Grove, K. G. Hirth, D. E. Buge, A. M. Cyphers, *Science* **192**, 1203 (1976).
13. P.K.H. conducted this analysis.
14. In addition to source samples provided by T.H.C. a large number of samples were made available by R. Zeitlin.
15. J. M. Ondov *et al., Anal. Chem.* **47**, 1102 (1975).
16. J. P. Maney, J. L. Fasching, P. K. Hopke, *Comput. Chem.* **1**, 257 1977).
17. A. Bieber, personal communication.
18. D. H. Oliver, "Aggregative hierarchical clustering program writeup, preliminary version" (National Bureau of Economic Research, Cambridge, Mass., 1973).
19. D. C. Grove, *San Pablo, Nexpa, and the Early Formative Archaeology of Morelos, Mexico* (Publications in Anthropology No. 12, Vanderbilt University, Nashville, 1974).
20. The trade route surveys and laboratory analyses were made possible by a National Endowment for the Humanities research grant RO-21447-75-138 to the Univeristy of Iowa with T.H.C. as principal investigator. The findings and views presented here do not necessarily represent the views of the Endowment. The University of Iowa provided T.H.C. with a research assignment in 1975. Professor Eduardo Matos Moctezuma of the Instituto Nacional de Antropología e Historia in Mexico City encouraged the fieldwork and was helpful in obtaining the necessary permits (Concesión on Arqueología No. 4/75). C. L. Charlton carried out the detailed studies of the Paredón quarry tools and *débitage*. The Chalcatzingo project, under the direction of D.C.G., was supported by NSF grant GS-31017 with supplementary funds provided by the National Geographic Society. The obsidian characterization was assisted by a grant from Landon T. Clay. P.K.H. thanks L. Tills, S. Gribben, and B. Roscoe for assistance in performing the elemental analyses and the operating staff of the Illinois Advanced TRIGA Reactor for assistance with the sample irradiations.

3 February 1978

Amorphous Ice on Saturnian Rings and on Icy Satellites: Its Formation, Stability, and Observability

Abstract. *Saturnian rings and icy satellites may be covered with amorphous rather than crystalline ice. Its likely source is water molecules sputtered by particles in the radiation belts, it may be stable, and its presence could be deduced from the rate of temperature drop in a shadow. Observation of this effect is, however, difficult, especially for the rings. A possible relation to the brightness anisotropy of ring A is pointed out.*

Recently, detailed studies of the structure and of some of the properties of amorphous ice have been made (*1*). The fact that this ice is formed during slow deposition of H_2O vapor at temperatures below about 150°K makes its properties of great interest for certain astrophysical problems (*1a*). In particular, the rings of Saturn and icy satellites are very likely covered with amorphous ice, and this could be verified by observations from spacecraft.

The existence of amorphous ice on the rings of Saturn and on icy satellites depends on the temperature at which the ice was or is being formed and on its stability. Pollack *et al.* (*2*) have discussed the formation and the probable thermal history of the satellites and the rings of Saturn, which condensed, starting with the outermost ring, at the end of the satellite formation period, close to the time when most of the gas in the nebula was being dissipated. There may have been a period of 2 to 6 × 10^7 years, depending on the opacity, when the temperature of the deposits remained above 150°K, and thus they would be crystalline. In any case, molecules condensing later at lower temperatures would form amorphous grains and would cover the earlier ones with an amorphous coating. Lewis (*3*) analyzed the condensation rate of various molecules of the solar nebula when this process is slow (equilibrium) and when it is fast (disequilibrium). For

0036-8075/78/0901-0809$00.75/0

the equilibrium situation the amorphous ice remains free from admixture of NH_4SH ice, if the temperature does not drop below 150°K at a total pressure of 0.1 bar or below 90°K at 10^{-9} bar. For disequilibrium conditions these limits are 150°K at 3×10^{-4} bar and 120°K at 10^{-9} bar. If this analysis is applicable to the rings and satellites, then there was plenty of time for the formation of amorphous water ice during their accretion. Optical studies of Saturnian rings do not preclude the existence of clathrate water ices with CH_4 or other molecules embedded in them, analogous to cometary ices. The condensation conditions during the formation of the rings were, however, not favorable for the formation of these compounds (*2*). Since clathrate ices, like crystalline and amorphous ices, are tetrahedrally coordinated, it is quite likely that those formed at low temperatures could be amorphous and could contain foreign molecules that would support their basically metastable structure.

Another possible source of amorphous ice is the sputtering of the outside edge of the rings by high-energy protons, as discussed by Cheng and Lanzerotti (*4*). These authors concluded that the flux of water molecules thus formed in the outer portions of the rings is 2×10^9 cm^{-2} sec^{-1} and that most of the molecules are recaptured and redistributed over the inner rings. Because of the low temperature of the rings, the ice thus freshly formed should be amorphous and it should grow at a rate of the order of 1000 Å per year. A similar argument applies to the icy satellites, such as the Galilean satellites, but it has not yet been made quantitative. A slow rate of condensation is favorable for the formation of amorphous ices because of the need to dissipate the heat of crystallization. Visually observable "glassy" ice is actually crystalline on a very fine scale and is not related to the truly amorphous form.

A somewhat similar process was suggested earlier by Banfi (*5*) and then elaborated by Tang (*6*); these authors considered the possibility that H_2O molecules evaporate from the innermost rings, form H^+ and OH^- ions, move along magnetic lines, recombine, and are deposited on the cooler parts of the rings. This process has not as yet been evaluated in detail. The advantage of the last two mechanisms is that fresh amorphous ice is continuously formed and irradiation and meteoritic bombardments (*7*) would not have time to alter its properties.

Several factors affect the stability of amorphous ice. One of them is the radiation belt, which is known for Jupiter but for Saturn is derived from the Jovian belt by using suitable scaling factors. For Saturn this would be applicable at radii comparable to or larger than the outer limits of the rings, and it has been analyzed in considerable detail (*4*). Also, one can conclude (*8*) that solar wind particles can enter the region at smaller radii; either through the high-latitude openings in the magnetic field or by diffusing inward through the tail of the magnetosphere. In either case, one expects a thermal plasma with a kinetic energy of a few electron volts. The likelihood of some of these particles acquiring higher energies by interaction with the magnetic field is negligible, because to do so they would have to cross the equatorial plane several times, which, in view of the high opacity of the rings, is improbable. Electrons and protons with energies of several electron volts cannot penetrate beyond a few times 10^{-8} cm into the ice, so as a result of the extremely low thermal conductivity of amorphous ice, the energy would be confined to a volume of the order of a few atomic sizes. The most likely result of this localized heating would be the escape of one or two molecules of water from the surface. A somewhat similar situation should exist on the trailing side of the satellites.

Another process affecting the stability of the amorphous ice is its spontaneous crystallization. This process is expected to proceed by the usual mechanism of nucleation and growth (*9*), in which the nucleation is most likely heterogeneous rather than homogeneous and plays a small role compared to that of the rate of growth. The order of magnitude of the latter in pure ice can be estimated on the basis of numerous experimental and theoretical studies on similar systems and is given by $G \sim d\,\nu \exp(-E_b/kT)$, where d is the jump distance, ν is the lattice frequency, E_b is the energy necessary to move an H_2O molecule from one site to another as determined from viscosity data, k is the Boltzmann constant, and T is temperature. Putting $E_b = 0.6$ eV (*10*), the growth rate turns out to be less than one intermolecular distance in 10^9 years. On the other hand, if $E_b = 0.3$ eV, which corresponds roughly to breaking a single intermolecular bond, a crystallization rate of several micrometers per year could be expected. Amorphous and hexagonal ice have tetrahedral coordination, however, and thus one does not expect that breaking one bond could lead to significant crystallization. These rates differ very little from what would be expected as a result of zero-point vibration—that is, substituting $\theta_D/2$ (the Debye temperature) for T in the expression for G. Clearly the enormous uncertainty resulting from the unknown effective value of E_b cannot be resolved at present by an unambiguous argument. Even if this were possible, the rates of crystallization of noncrystalline solids are known to be dependent on impurities (*11*), some of which speed the process up, while others slow it down orders of magnitude. There is no information about the sensitivity of amorphous ice in this respect to impurities. This situation is undoubtedly the major source of uncertainty about the persistence of amorphous ice on Saturnian rings and on satellites.

Since there seems to be no simple spectroscopic terrestrial observation for distinguishing between crystalline and amorphous ice, one could rely on the thermal conductivity K, which is known to be very sensitive to the perfection of the crystalline lattice at low temperatures. Recent advances (*12*) in the experimental and theoretical understanding of noncrystalline solids make possible good quantitative estimates of K for amorphous ice. At the temperature of the rings, 90° to 97°K, one obtains $K = 2$ to 5×10^{-4} cal cm^{-1} sec^{-1} deg^{-1}, which is a factor of 50 to 100 lower than the value $K = 2.3 \times 10^{-2}$ cal cm^{-1} sec^{-1} deg^{-1} for crystalline ice.

Aumann and Kieffer (*13*) were the first to analyze the cooling and heating of particles in the Saturnian rings on their entry into and emergence from the planet's shadow, for the purpose of determining the radius R of the particles from the rate of change of the brightness temperature T. They numerically solved the heat conduction equation for the spherical particle and the coupled equation for the balance between the heat input into the particle and the radiative heat loss into space. For sufficiently long times, the change in temperature thus calculated is strongly dependent on R and essentially independent of K. However, if the mean cooling depth is much smaller than R—that is, for times $t < t' = R^2\rho c/4K$ (where ρ is the particle density and c is the specific heat) after the entry into the shadow—the ratio of T to the initial brightness temperature T_0 is given by $T/T_0 = 1-(t/\rho cK)^{1/2}\epsilon\sigma\beta T_0^3$, where ϵ is the emissivity, σ is the Stefan-Boltzmann constant, and β is that fraction of solid angle seen by the particle which is not obstructed by the rest of the ring. As expected, this drop in temperature is dependent on K but not on R. Since the densities and the specific heats of crystalline and amorphous ice differ at most by a few percent, the rate of temperature drop dT/dt, for a given t, should be 7 to 10 times faster for the amorphous ice.

For small R the time t' is too short and for large R the ratio T/T_0 is too close to unity to permit an observation from a fly-by spacecraft. Also, the planet's shadow visible from the earth is too narrow and too close to the bright disk of the planet (*14*) to permit terrestrial measurements. Eclipses of icy satellites (*15*) suggest an overall thermal conductivity lower than that of amorphous ice, indicating that, as for our moon, the intergranular contacts play an important role. Perhaps high-resolution observations of large features from future spacecraft may answer this question.

It is known (*16*) that in contrast to ring B, ring A shows brightness minima at orbital longitudes 70° and 250° and maxima at 160° and 340° (*17, 18*). The diffusion of water molecules from the outer toward the inner rings may contribute to this asymmetry because the differences in their Keplerian velocities would lead to the formation of amorphous ice preferentially on the leading outward and on the trailing inward quarters of particles which are big enough to be facing the planet in a synchronous motion (*19, 20*). Small particles undergo too many collisions to be synchronous (*21*), but they are covered with amorphous ice and would be similarly preferentially deposited, contributing to the brightness anisotropy and increasing the nonsphericity of the large particles (*22*). One expects the fresh ice to be brighter than the old ice, which may be covered with dust and sputtered (*7*). In this model, the absence of brightness asymmetry in ring B could be an indication of collisional destruction of synchronism because of a narrower range of particle sizes (*23*).

R. SMOLUCHOWSKI

Materials Laboratory,
Princeton University,
Princeton, New Jersey 08540

References and Notes

A. H. Narten, C. G. Venkatesh, S. A. Rice, *J. Chem. Phys.* **64**, 1106 (1976).
1a. R. Smoluchowski, in *Comets, Asteroids and Meteorites*, A. H. Delsemme, Ed. (Univ. of Toledo Press, Toledo, 1977), p. 17.
2. J. B. Pollack. A. S. Grossman, R. Moore, *Icarus* **29**, 35 (1976).
J. S. Lewis, *ibid.* **16**, 241 (1972).
4. A. F. Cheng and L. J. Lanzerotti, *J. Geophys. Res.*, in press.
5. V. Banfi, *Mem. Soc. Astron. Ital.* **53**, 247 (1972).
6. C. C. H. Tang, *JPL Rep. 760-134* (1975).
7. A. F. Cook and F. A. Franklin, *Astron. J.* **75**, 195 (1970).
8. J. A. Van Allen, in *Highlights of Astronomy*, E. A. Müller, Ed. (Reidel, Dordrecht, 1978), vol. 4, p. 195; private communication.
9. N. C. Ainslie, C. R. Morelock, D. Turnbull, in *Symposium on Nucleation and Crystallization in Glasses and Melts* (American Ceramic Society, Columbus, Ohio, 1962), p. 97; D. Turnbull, private communication.
10. P. V. Hobbs, *Ice Physics* (Clarendon, Oxford, 1974).
11. D. R. Uhlmann, in *Advances in Nucleation and Crystallization of Glass*, L. L. Hench and S. W. Freiman, Eds. (American Ceramic Society, Columbus, Ohio, 1971), p. 91.
12. R. O. Pohl, in *Phonon Scattering in Solids*, L. J. Challis *et al.*, Eds. (Plenum, New York, 1976), p. 108, figure 1; private communication.
13. H. H. Aumann and H. H. Kieffer, *Astrophs. J.* **186**, 305 (1973).
14. D. Morrison, in *Planetary Satellites*, J. A. Burns, Ed. (Univ. of Arizona Press, Tucson, 1977), p. 269.
15. _____ and D. P. Cruikshank, *Icarus* **18**, 244 (1973).
16. J. B. Pollack, *Space Sci. Res.* **18**, 3 (1975).
17. G. Colombo, P. Goldreich, A. W. Harris, *Nature (London)* **264**, 344 (1976).
18. F. A. Franklin and G. Colombo, *Icarus* **33**, 279 (1978).
19. I. Ferrin, *Nature (London)* **271**, 528 (1978).
20. R. Smoluchowski, *ibid.*, in press.
21. A. Brahic, *Astron. Astrophys.* **54**, 895 (1977); private communication.
22. The presence of many unsaturated and isotropic bonds between amorphous surfaces (*10*) would lead to better adhesion than between randomly oriented crystals.
23. R. Smoluchowski, *Commun. Astrophys. Space Phys.*, in press.
24. Supported by NASA grant NSG-7283, Supplement 1. I wish to thank H. H. Kieffer for his most valuable comments.

3 February 1978; revised 26 June 1978

Age Determination of an Alaskan Mummy: Morphological and Biochemical Correlation

Abstract. *Aspartic acid racemization analysis of a tooth from an Alaskan mummy yielded an age at death of 53 (± 5) years, which correlates well with earlier estimates based on morphological features. This study illustrates the value of integrative approaches to paleopathologic problems and the importance of preserving rare specimens for the application of new techniques.*

A major factor in the success of the recent revival of paleopathology has been cooperation among scientists of many disciplines. The ongoing examination of an Eskimo who died 1600 years ago illustrates the value of this integrative approach in determining the cause and date of death and the age at death.

The body was discovered in a frozen state on St. Lawrence Island, Alaska, in 1972, and remained frozen until it was brought to Fairbanks in 1973. Zimmerman's postmortem examination revealed that the individual was a woman with a skull fracture and aspirated moss fibers in her lungs. These findings indicated that she had been buried alive, probably in a landslide, and suffocated (*1*).

The date of death was determined by two independent techniques. Radiocarbon dating of tissue from the cadaver yielded a date of A.D. 370 to 390 ± 90 (*2*). This date placed the life-span of the individual within the Old Bering Sea cultural phase (*3*) on St. Lawrence Island. The arms of the mummy were covered with tattoos, the details of which were subsequently brought out by infrared photography. The artistic motifs of the tattoos were similar to those seen in a variety of Old Bering Sea artifacts (*4*) and thus correlated well with the radiocarbon date in placing the mummy in this phase of Alaskan prehistory (*5*).

The woman's age at death was initially estimated on the basis of morphological features to be between 50 and 60. The breasts and ovaries were atrophic, there was marked dental attrition, and there was evidence of coronary artery disease, which is rare in premenopausal women. Two years later a second technique was applied to determine the age at death, a microscopic study of cortical bone from a rib specimen. Osteon density was that expected in modern normals in the age range between 50 and 59 (*6*). In 1977, 4 years after the initial examination of the body, a third technique, based on amino acid racemization, was applied to a preserved premolar.

Amino acid racemization dating originated as a method for estimating the age of fossil materials on a scale of 10^3 to 10^6 years (*7, 8*). The dating technique is based on the incorporation of L-amino acids exclusively into proteins by living organisms. Given sufficient periods of time over which proteins are preserved after synthesis, a number of spontaneous chemical reactions take place. Among these is racemization, which converts L-amino acids into their enantiomers, the D-amino acids. The different amino acids racemize at various rates, and these rates, as is the case with all chemical reactions, are proportional to temperature. Aspartic acid has one of the fastest racemization rates (k_{Asp}), and at 20°C the half-life of the reaction is 15,000 years (*9*). Thus, the older a fossilized material is, the higher its D-aspartic acid content or D/L Asp ratio. The age of such a specimen can be calculated from the D/L ratio, once the k_{Asp} for the fossil locality has been determined (*8*).

Recently, this method has been applied to tissues from living humans. At the mammalian body temperature of ~ 37°C, the racemization rate of aspartic

0036-8075/78/0901-0811$00.50/0