spectrum of different complex urates or other nitrogen compounds is present (*2*), all combining to give one very strong peak, perhaps corresponding to some spacing between rings of atoms. If uric acid is present at all, it is merely one among many compounds.

There also can be no doubt that the white, crystal-aggregate (not "amorphous") spheres that comprise bird urine go into true solution, although there is much variation in the amount of solubility from one bird to another. If you place a tiny speck of white material on a glass slide and add weak acid, you can watch under the microscope as a sphere shrinks and totally disappears, and elsewhere on the slide a new, much larger, bladed, perfect crystal will start to grow where no solid was visible before. I believe this is commonly accepted as evidence of true solution and reprecipitation. This process goes on in a matter of a few seconds to a few minutes, before any water or acid has evaporated. Of course, after the acid has stood for an hour or so and totally evaporated, many more crystals form. Biologists have not realized this, because they have never watched the material under the microscope.

I do not simply "feel" that the addition of water or acid alters the nature of bird droppings; anyone can "see" for himself if he will take parrot's excrement and mix it with vinegar, and then watch the spectacular microscopic display.

The "acceptable" biochemical methods cited by Poulson and McNabb involve mixing the bird urine with various chemicals, adjusting the *p*H (*3*), attacking it with enzymes, and measuring the surviving chemical wreckage colorimetrically, manometrically, spectrophotometrically, and so forth. In my opinion, the drastic wet chemical method of analysis converts the material from whatever it is originally *into* uric acid before the identification part of the analysis. Although, indeed, most of my studies have been on air-dried excrement of uncertain history (from bottoms of bird cages, chicken coops, and others), I have also looked at freshly excreted material and found no essential difference (except in the case of Australian eagle droppings). But the biochemists have been equally vague about the time elapsing between urination and eventual analysis, a rare exception being Nechay and Nechay (*4*) who analyzed the material the day of excretion. In view of the bacteriological changes that may go on in the material (*5*), possible changes in *p*H, oxidation-reduction potential, and rapid loss of water as the material is excreted, falls through the air, and dries, it behooves the biochemist to analyze it as rapidly as possible by x-ray diffraction, as that is the only way to conclusively discover what the material really is without altering it by the very method of analysis.

The two papers that Poulson and McNabb cite identifying the presence of uric-acid secreting enzymes in birds are dated 1904 and 1936, and hopefully the identification of urine components was much cruder then than it is even today. Needham (*6*) stresses again and again that it is the *insoluble* nature of uric acid that allowed the development of the terrestrial egg—a "closed box" in which embryonic waste products had to be retained, but kept in inert form; for example, he says (p. 1144), "the only solution to the problem of getting rid of nitrogen by the embryo is through uric acid." The whole evolutionary theory of development of terrestrial oviparous vertebrates is based on this purported insolubility; I claim it is not uric acid, but is mainly acid-soluble compounds, probably largely urates.

Poulson and McNabb's final structural argument is not pertinent, because obviously the material is a solid precipitate, whatever its composition, or I could not have seen crystalline spheres with the microscope.

Anyone must conclude that this is a subject that needs to be studied by non-alterative methods (x-ray) on many kinds of birds; the whole subject of urine diagenesis with time, from embryo, liver, kidney, and cloaca to wet splashes and "lithified" hard white crusts, is a wide-open field. To the multitude who have a vested interest in the presumptive predominance of uric acid in bird urine: I challenge you to prove it by x-ray diffraction if you are that confident of being right!

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References and Notes

1. For example, a recent confident statement by I. H. Krakhoff and R. L. Meyer [*J. Pharmacol. Exp. Ther.* **149**, 417 (1965)]: "Birds are known to excrete uric acid as the principal end-product of nitrogen metabolism."
2. R. L. Folk, *Texas J. Sci.* **21**, 125 (1969).
3. For example, G. L. O'Dell, W. D. Woods, D. A. Laerdal, A. M. Jeffay, J. E. Savage [*Poultry Sci.* **39**, 426 (1960)] added HCl to bring the *p*H to between 1 and 2 before analyzing for uric acid.
4. B. R. Nechay and L. Nechay, *J. Pharmacol. Exp. Ther.* **126**, 291 (1959).
5. F. Liebert, *Koninkl. Akad. Wetenschap. Amsterdam Proc. Sect. Sci.* **12**, 54 (1909).
6. J. Needham, *Chemical Embryology* (Macmillan, New York, 1931), vol. 2.
7. I acknowledge Professors L. S. Land and E. C. Jonas (geology department, Univ. of Texas) and W. F. Bradley (chemical engineering) for discussion of chemical questions.

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Obsidian Hydration Rates

Johnson (*1*) reports a series of obsidian hydration readings from a site in northern California which are explained in terms of the Friedman hydration formula:

$$x^2 = kt$$

where x is the thickness of hydration band in microns, k is a constant for a given temperature, and t is the time in years. These readings convinced Johnson that the Friedman rate formula is universally valid: "It is important to underline, for archeologists, the universality of Friedman's equation." I must dissent, because, regardless of the universality of the equation, archeologists who rely on it for determining the age of obsidian specimens will get wrong answers some of the time. Empirical evidence that not all obsidian forms hydration bands as explained by Friedman has been presented by Clark for California (*2*) and Meighan *et al.* for western Mexico (*3*). Johnson does not discuss Clark's evidence, even though it applies to obsidian from other California sites (*4*), and he doubts the evidence from west Mexico. The same kind of criticism was presented by Friedman and Evans (*5*) against the data from west Mexico, namely, that the archeology had been incorrectly interpreted and that a proper interpretation would bring the dating into line with the Friedman formula.

Figure 1 shows the differences in interpretation between the linear rate for west Mexico and two rates proposed for temperate areas by Friedman. Table 1 presents two new groups of hydration readings for which the linear rate

Table 1. Obsidian hydration dates from Casas Grandes, Chihuahua, Mexico, and Snaketown, Arizona.

Site	No. of readings*	Range (μ)	Average (μ)	Known age† (A.D.)	Age, linear rate‡ (A.D.)	Age, Friedman rate§
Casas Grandes	70	1.4–4.0	2.05	1340–1660	1365–1409	A.D. 1304
Snaketown (total)	18	3.4–5.0		500–1100	468–1066	1896 B.C. to A.D. 172
Breakdown						
Mound 39, col. 2	2			700–1100	740– 897	
Mound 39, col. 3	1			900–1100	767– 897	
Mound 40, test 1	1			500– 700	382– 554	
Mound 40, pit 42	1			700– 900	630– 774	
House 7 : 5 F, floor	1			900–1100	822– 946	

* The hydration readings (but no age interpretations) for Casas Grandes are those of Dixon (*7*). The readings for Snaketown were done at UCLA by L. Foote and include all the obsidian found in Haury's recent excavations. † Ages are calculated on the basis of the average reading for Casas Grandes and the total range of hydration for Snaketown because of the small sample from the latter. The "known ages" were provided by the excavators: E. W. Haury for Snaketown (based on ceramic crossties and other evidence) and C. C. DiPeso for Casas Grandes (based on tree-ring chronology and other evidence). Only 6 of the 18 readings from Snaketown are treated in the breakdown because the other specimens are from the surface or other contexts in which a "known age" of reasonable precision could not be supplied. ‡ There is a ± factor which indicates the time period in which the true age is believed to fall (*3*). § The Snaketown age is derived from Friedman and Smith's age estimates for three specimens from a colonial Hohokam site (*8*) with the use of the Temperate No. 1 rate (see Fig. 1). The same rate has been used for the nearby Hohokam site of Snaketown. Friedman and Smith recognized that their Hohokam samples yielded ages that were too old and commented: "Older than the estimated dates, possible exposure to hot sun might have increased the rate of hydration, possibly re-use of older artifact." Ages determined by use of the Friedman rate formula are not given for the individual Snaketown readings, but, like the overall readings, they would all be too old by as much as 2000 years.

formula yields hydration ages that are correct according to other dating evidence. Use of the Friedman rate equation for these examples, as well as for those mentioned above, will yield erroneous dates. When the hydration bands are small, as they are at Casas Grandes, *any* of the proposed rate formulas will give ages fairly close to the expected age. The results with small hydration readings do not validate any rate formula, and it is only with the larger bands (over about 5 μ) that major differences in the obsidian ages appear with the differences dependent upon the rate formula used to calculate age.

Although a linear rate formula definitely yields more correct ages with some obsidian, some of the time, this does not mean that one rate formula is right and the other wrong. It does provide strong evidence that there is another variable, not accounted for in the Friedman formula, which can affect the results either to a negligible extent (in which case the Friedman formula can yield correct estimates of age), or to a major extent (in which case the Friedman formula can yield highly erroneous age determinations).

The mechanism of hydration formation is not yet explainable, but several investigators are developing evidence that the chemical composition of the obsidian has an effect on the hydration process, and it is likely that this evidence will reveal an important variable missing from the Friedman formula (*6*). Until the variable is understood and taken into account, application of obsidian dating to chronological problems in archeology can only be done if the archeologist has sufficient empirical evidence to determine the nature of the obsidian hydration rate for his area. The rate formula may turn out to be the unmodified Friedman formula, a linear rate formula, or anything in between. Empirical determination of the hydration rate on a small sample of obsidian from a particular site does *not* indicate discovery or validation of a universal law applicable to all other obsidian.

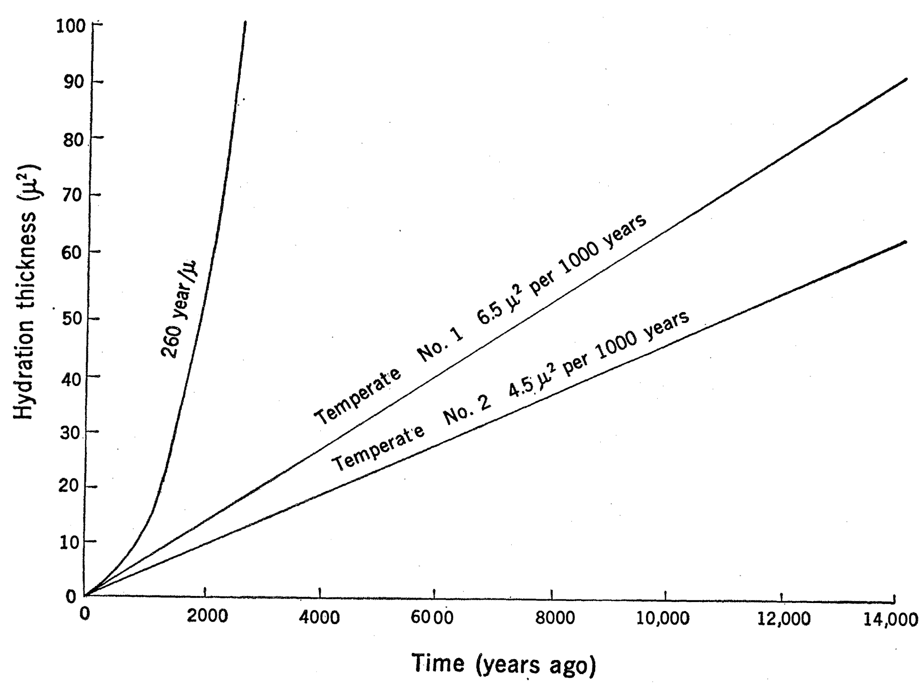

Fig. 1. Obsidian hydration rates. At the left is shown the linear rate for west Mexico. The other two rates are for the temperate zone and are based on the Friedman formula (*8*).

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3. C. W. Meighan, L. J. Foote, P. V. Aiello, *Science* **160**, 1069 (1968).
4. I. Friedman, R. L. Smith, D. Clark, in *Science in Archaeology*, D. Brothwell and E. Higgs, Eds. (Basic Books, New York, 1963). In this article the authors used the Clark hydration rate for California obsidian and the Friedman rate for all other areas.
5. I. Friedman and C. Evans, *Science* **162**, 813 (1968).
6. Among the students working on the problem of chemical variability are three UCLA graduate students whose reports show how chemical variability in the obsidian greatly alters the hydration rate. The manuscripts include: P. V. Aiello, "The chemical composition of rhyolitic obsidian and its effect on hydration rate" (1969); J. E. Ericson, "Obsidian dating: A geological, chemical, and physical approach" (1969); and J. Kimberlin, "Chemical characterization of obsidian artifacts" (1969).
7. L. E. Dixon, *Catalog of Obsidian Hydration Measurement Data for Mexico* (Smithsonian Institution, Washington, D.C., 1969).
8. I. Friedman and R. L. Smith, *Amer. Antiquity* **25**, 476 (1966).

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