opinions are (i) scars of very similar size and (ii) precise alternation. It is in these opinions that scholars disagree, especially if the qualitative statements regarding size and precise alternation are not backed up by quantitative data.

Regarding the more than 600 "tools" selected by the late L. S. B. Leakey, it should be pointed out that Leakey's selection is made from a larger selection made by the excavators and that he did not personally inspect each of the thousands of pieces that the excavators rejected as not being demonstrably artifacts. It would be instructive to know (i) the total number of pieces of chert excavated and (ii) the number selected from this total population by the excavators for presentation to Leakey for his selection. It is apparent that both the number of "tools" and the individual specimens selected will vary significantly with the authority making the selection.

I disagree with Wade's opinion that natural processes producing flaked cherts "would form them indiscriminately from any quality of chert." The physical properties that make a piece of chert knapable are the same regardless of whether man or nature is doing the knapping; therefore, those pieces that are more homogeneous, with fewer flaws, and more glasslike in regard to pressure and percussion fracturing are going to be the ones showing the most flake scars in a natural mixture.

Regarding the concentrations of artifacts in the lower Yermo formation, there should be published quantitative data on patterns of distribution and relative frequencies of artifacts, chert clasts, and nonchert clasts in various size ranges per unit volume of the deposit. Unfortunately, the only published data in this regard are mostly generalized statements such as "a tremendous concentration of material occurs at 6 and 9 feet below the fan surface" (*1*, p. 39). In the only published stratigraphic section I know of, I see no obvious concentration at 2 and at 3 m below the ancient fan surface (*2*, p. 72). The distribution appears to be random over a vertical interval of at least 8 m.

Wade is absolutely correct that my statement regarding some of the more diagnostic Paleolithic artifacts is an opinion. It was not meant to be anything else and is based upon examination of *typical* specimens in various parts of Europe and Africa. But opinions, no matter how experienced the authority may be, do not constitute proof, as the Calico site controversy so ably demonstrates. As for the opinion poll of "professionals" offered by Wade, it is indeed fortunate that we do not settle scientific questions by the votes of experts. No doubt others could come up with a three-quarters majority who would *not* accept the flints as man-made, and the names of the authorities would be just as impressive as those mentioned by Wade.

The point of my article is that the evidence for human manufacture of flints at Calico Hills is not compelling and is not likely to be at a site where more than 10 percent of the matrix of the controversial specimens is composed of the same chert, and where all were deposited in a sedimentary environment in which few, if any, angular pieces of chert are apt to have survived unchipped (*3*).

In conclusion, I would add that, while the possibility of very early man in the New World is real, it can only be established as fact where incontrovertible evidence is found. Were this not true, then the case for very early man in America would have been won in the last century (*4*), and maybe in the opinion of some it was.

VANCE HAYNES
Department of Geological Sciences,
Southern Methodist University,
Dallas, Texas 75222

References

1. L. S. B. Leakey, R. D. Simpson, T. Clements, R. Berger, J. Witthoft, and participants, *Pleistocene Man at Calico* (San Bernardino County Museum Association, San Bernardino, Calif., 1972).
2. L. S. B. Leakey, R. D. Simpson, T. Clements, in *The 1970 Britannica Yearbook of Science and the Future* (Praeger, New York, 1969).
3. V. Haynes, *Science* **181**, 305 (1973).
4. G. F. Wright, *Man and the Glacial Period* (Appleton, New York, 1896).

29 October 1973

Low-Temperature Thermal Decomposition of Water

It is eminently worthwhile to consider chemical processes whereby hydrogen could be generated directly from a primary heat source, so that hydrogen could be efficiently used as an energy carrier and as a versatile, clean fuel (*1*). However, the three-reaction process that Abraham and Schreiner (*2*) have proposed is not achievable.

The authors point out that the critical reaction is

$$LiNO_2 + I_2 + H_2O \xrightarrow{300°K} LiNO_3 + 2HI \quad (1)$$

and appear to be discussing this reaction in aqueous solution. The solution will be acidic and nitrite will almost completely be in the form of the weak acid HNO_2 (dissociation constant = 4×10^{-4}). The appropriate electrode potential for the oxidation

$$HNO_2(aq) + H_2O(l) \rightarrow NO_3^-(aq) + 3H^+(aq) + e^- \quad (2)$$

is − 0.94 volt (aq, aqueous; l, liquid). For the overall reaction

$$HNO_2(aq) + I_2(c) + H_2O(l) \xrightarrow{298°K} NO_3^-(aq) + 2HI(aq) + H^+(aq) \quad (3)$$

the standard Gibbs free energy ΔG^0 (298°K) = + 18.8 kcal/mole (c, crystalline). Reaction 1 will not go in acid solution.

The "oxidation-reduction potential of the nitrite-nitrate couple" to which Abraham and Schreiner refer is that observed in basic solution, where hydriodic acid would be neutralized to iodide (which in essence provides the driving force for the reaction). Thus the reaction proposed will not proceed in acidic solution and will not produce the desired HI in basic solution. In actuality, nitrous acid oxidizes iodide to iodine in acid solution.

There are review references to oxidation of nitrous acid by iodine (*3*). But the literature (*2, 4*) describes measurements made in neutral or basic solution.

If reaction 1 were to be attempted heterogeneously, with $LiNO_2(c)$ and $LiNO_3(c)$, then enthalpy and Gibbs free energy changes, ΔH and ΔG, for reaction 1 would be 62.3 and 45.0 kcal/mole, respectively. (Entropies for lithium compounds must be estimated, but it is clear that this reaction is impossible.)

A possible modification to the proposed reaction might be to make the solution basic by adding ammonia. If $NH_4I(c)$ could be isolated from the solution, it might be decomposable under appropriate high-temperature conditions as follows

$$NH_4I(c) \rightarrow NH_3(g) + H_2(g) + I_2(g) \quad (4)$$

(g, gas) although ammonia also begins to decompose appreciably above 675°K.

Any reaction sequence which sums only to the decomposition of water must involve highly endothermic reactions driven at high temperatures by large increases in entropy. Reaction 4 is such a reaction, although I am not able to comment on the practicality of the overall reaction sequence.

LESTER R. MORSS
School of Chemistry,
Rutgers University,
New Brunswick, New Jersey 08903

References

1. W. E. Winsche, K. C. Hoffman, F. J. Salzano, *Science* **180**, 1325 (1973).
→ B. M. Abraham and F. Schreiner, *ibid.*, p. 959.
3. J. W. Mellor, *Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry* (Wiley, New York, 1967), vol. 8, suppl. 2, p. 362.
4. G. G. Durrant, R. O. Griffith, A. McKeown, *Trans. Faraday Soc.* **32**, 999 (1936); E. Abel, *Monatsh. Chem.* **81**, 7 (1950).

9 July 1973

We welcome this opportunity to clarify the question raised by Morss, which has also been raised by others. The key to the cycle we proposed is the reaction

$$LiNO_2 + I_2 + H_2O \rightarrow LiNO_3 + HI \quad (1)$$

which is also the one being questioned. This reaction can just as well be written

$$NO_2^- + I_2 + H_2O \rightarrow 2I^- + NO_3^- + 2H^+ \quad (2)$$

Since it is well known that NO_2^- oxidizes I^- to iodine in acid solution, and further since the solution becomes acid as reaction 1 progresses and there is a surfeit of NO_2^- present, the obvious conclusion seems to be that only the parasitic reaction 3 will occur

$$H^+ + HNO_2 + I^- \rightarrow \tfrac{1}{2}I_2 + NO + H_2O \quad (3)$$

for which the standard Gibbs free energy $\Delta G^0 = -42.46$ kjoule. That conclusion is, however, a little hasty. The first question to ask is, What is the pH value for which ΔG of reaction 1 will be zero?

The solution of $LiNO_2$ will initially be alkaline because the dissociation constant of HNO_2 is small, 4×10^{-4}. Reaction 2 can be rewritten

$$NO_2^- + I_2 + 2OH^- \rightarrow NO_3^- + 2I^- + H_2O \quad (2a)$$

for which $\Delta G^0 = -104.22$ kjoule. Assuming that the activities (a) of I^- and NO_3^- are equal and that the activity of NO_2^- remains close to unity, we obtain after appropriate substitutions

$$pH = 4.8656 + 3/2 \log a_{I^-} \quad (4)$$

For unit activity of I^-, reaction 2a will have $\Delta G = 0$ at a pH of 4.9. We have thus established thermodynamically that reactions 1, 2, and 2a will go as written, which is one of the points at issue. Further, Berthoud and Berger (*1*) reported that in a solution of NO_2^- buffered to the acid side (pH 6.5) iodine was completely transformed to iodide.

The second question is whether there are reasonable conditions which will make $\Delta G = 0$ for the parasitic reaction 3. If it is assumed that the activities of I_2, H_2O, and I^- are unity and that a small amount of NO will be generated to develop a pressure of 1 atm then ΔG for reaction 3 will be zero at pH 5.4. Then reaction 1 is thermodynamically possible and conditions can be found which suppress reaction 3. Furthermore, the matter of relative rates also enters the picture, about which we can say nothing.

We have not succeeded in maintaining conditions that will make reaction 1 practical, although we have extracted HI by distillation. We have found that the reactions we suggested in our report (*2*) will not go under conditions that will make a practical cycle. Our work has, however, produced the following modified sequence, which is much more promising

$$2KNO_3(m) + I_2(c) = 2KI(c) + 2NO_2(g) + O_2(g) \quad (5)$$

$$2NO_2(g) + \tfrac{1}{2}O_2(g) + H_2O(l) = 2HNO_3(aq) \quad (6a)$$

$$2HNO_3(aq) + 2NH_3(g) = 2NH_4NO_3(aq) \quad (6b)$$

$$2KI(aq) + 2NH_4NO_3(aq) = 2KNO_3(ppt) + 2NH_4I(aq) \quad (7)$$

$$2NH_4(c) = 2NH_3(g) + I_2(g) + H_2(g) \quad (8)$$

where m means molten; c, crystalline; g, gas; l, liquid; aq, aqueous; and ppt, precipitate. The potassium salts were used in this sequence because the solubility characteristic of KNO_3 permits the efficient conversion of NH_4NO_3 into iodide (reaction 7).

BERNARD M. ABRAHAM
FELIX SCHREINER
Chemistry Division,
Argonne National Laboratory,
Argonne, Illinois 60439

References

1. A. Berthoud and W. Berger, *Helv. Chim. Acta* **11**, 364 (1928).
2. B. M. Abraham and F. Schreiner, *Science* **180**, 959 (1973).

9 July 1973 ■

Keweenawan Volcanic Sequence

Baksi and Watkins (*1*) state that there are only four plateau basalt accumulations that exceed 2×10^5 km^3 in volume, and do not list one that might even be the largest one of all—the Keweenawan volcanic sequence of the Lake Superior region. Although their source, Holmes (*2*), gives only 1.2×10^5 km^3 for the Keweenawan, one of the more active workers in the field, White (*3*), estimates a volume in excess of 4×10^5 km^3 for the Keweenawan in the Lake Superior area alone, a volume second only to that cited by Holmes for the Deccan of India (7×10^5 km^3). This was probably a conservative estimate; inasmuch as the Keweenawan volcanic sequence probably extends from Lake Superior as far as Kansas along the midcontinental gravity high and perhaps into the lower peninsula of Michigan in the other direction, its volume may even exceed that of the Deccan.

This does not affect the data or conclusions of Baksi and Watkins, but we who toil with the Keweenawan hate to see our favorite sequence of rocks downgraded.

N. KING HUBER
HENRY R. CORNWALL
Geologic Division,
U.S. Geological Survey,
Menlo Park, California 94025

References

1. A. K. Baksi and N. D. Watkins, *Science* **180**, 493 (1973).
2. A. Holmes, *Principles of Physical Geology* (Ronald, New York, 1965), p. 301.
3. W. S. White, *Am. J. Sci.* **258**, 367 (1960).

18 May 1973