Table 1. Heat fluxes (in calories per square centimeter per minute) necessary to maintain an evaporating frost deposit at constant temperature, for various temperatures and pressures.

T_0 (°C)	Heat flux at various pressures P_0 (mb)			
	6	10	15	25
0	1.25	0.76	0.55	0.38
−5	0.62	.41	.30	.21
−10	.33	.22	.17	.12

above the melting level. Let us assume that this water collects by condensation of vapor to ice, and that the vapor must diffuse down from the atmosphere at night. Then, since the partial pressure of water in the atmosphere is some 10^{-4} of the vapor pressure at $-10°C$, the lifetime of the accumulated deposit at $-10°C$ will be only 10^{-4} of the accumulation time. This lifetime is about ½ hour at the pole and 10 seconds elsewhere; thus this mechanism does not increase the likelihood of melting.

This argument applies when the only source of water is the atmosphere. Liquid water from the interior of the planet might occasionally reach the surface to form hot springs (*10*), although there is no indication that such a process occurs on the earth. Most evidence suggests that terrestrial hot springs contain recycled rain water (*11*), although small amounts of juvenile water may also be present.

Water from the interior of the planet might also exist as permafrost at some depth below the surface, and this water might occasionally melt under the action of sunlight. However, temperatures above 0°C occur only at middle and lower latitudes at depths less than about 10 cm. Permafrost this close to the surface must be in equilibrium with atmospheric water, and this is possible only at the poles (*2*). Thus melting of permafrost is extremely unlikely.

Let us now compare the effects of wind with the effects of compositional density differences already mentioned. Measured rates of evaporation under conditions of neutral stability on the earth give (*12*):

$$E = (0.002)\rho_w U \qquad (4)$$

where U is the wind velocity 1 m above the surface. However, even for the case where $U \doteq 100$ m/sec, the additional evaporation due to wind is less than the rates implied in Table 1. The opposite question is whether wind could supply the necessary heat to the surface to melt water ice, but here again the effect appears to be negligible. In fact, the turbulence necessary to mix heat downward to the surface would also cause an increase in evaporation, thus leading to a net cooling. For, if ΔT is the temperature difference between the warm atmosphere and the cool surface, then the flux of heat to the surface will be $\rho U_0 c_p \Delta T$, where c_p is the specific heat of the gas and U_0 is some velocity characteristic of the process. However, at the same time the evaporative cooling will be $\rho U_0 \lambda \Delta \eta$, which is larger than the heating for all reasonable choices of parameters for frost temperatures greater than $-10°C$.

All of the above remarks apply only to pure water ice. Dissolved salts lower both the melting temperature of ice and the pressure of water vapor in equilibrium with ice at a given temperature. As an extreme example, the equilibrium vapor pressure over a saturated solution of $CaCl_2$ is about 1/5 that over pure water at the same temperature, and the melting point of such a solution is some 50°C lower than that of pure water (*13*). Under these conditions the evaporative cooling is negligible, and the lifetime is effectively infinite.

It is probable that pure liquid water does not occur on the martian surface or in the surface soil. The available heat sources cannot balance evaporative cooling, and any frost will evaporate completely before it reaches the melting point. Liquid water might occur in concentrated salt solutions, provided the salts are available in the martian soil.

ANDREW P. INGERSOLL
Division of Geological Sciences, California Institute of Technology, Pasadena 91109

References and Notes

1. L. D. Kaplan, G. Munch, H. Spinrad, *Astrophys. J.* **139**, 1 (1964); T. Owen and H. P. Mason, *Science* **165**, 893 (1969).
2. R. B. Leighton and B. C. Murray, *Science* **153**, 136 (1966).
3. M. Jakob, *Heat Transfer* (Wiley, New York, 1949), vol. 1.
4. The effect of normal velocity in turbulent boundary layers is discussed by E. R. G. Eckert, *Heat and Mass Transfer* (McGraw-Hill, New York, ed. 2, 1959), pp. 462 and 473.
5. S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge Univ. Press, London, 1939), pp. 252–258.
6. W. P. Boynton and W. H. Brattain, in *International Critical Tables*, E. W. Washburn, Ed. (McGraw-Hill, New York, 1929), vol. 5, p. 62; L. L. Bircumshaw and V. H. Stott, *ibid.*, p. 4.
7. A. Kliore, D. L. Cain, G. S. Levy, V. R. Eshleman, G. Fjeldbo, F. D. Drake, *Science* **149**, 1243 (1965); A. Kliore, in preparation.
8. M. J. S. Belton and D. M. Hunten, *Science* **166**, 225 (1969).
9. Leighton and Murray (*2*) estimate that an amount of ice equivalent to a layer 50 μm thick will be deposited annually on the polar caps, if the caps are mainly CO_2.
10. C. Sagan, E. C. Levinthal, J. Lederberg, *Science* **159**, 1191 (1968).
11. B. Mason, *Principles of Geochemistry* (Wiley, New York, ed. 3, 1966), pp. 144 and 205.
12. C. H. B. Priestley, *Turbulent Transfer in the Lower Atmosphere* (Univ. of Chicago Press, Chicago, 1959), p. 93.
13. R. E. Hall and M. S. Sherrill, in *International Critical Tables*, E. W. Washburn, Ed. (McGraw-Hill, New York, 1929), vol. 4, p. 254; H. M. Spencer, *ibid.*, vol. 1, p. 67.
14. Contribution No. 1614 of the Division of Geological Sciences, California Institute of Technology, Pasadena.

2 February 1969; revised 17 November 1969

Metamorphic Waters from the Pacific Tectonic Belt of the West Coast of the United States

Abstract. *Waters unusually rich in ammonia, boron, carbon dioxide, hydrogen sulfide, and hydrocarbons are found in more than 100 localities along the Pacific coast of the United States. The waters are believed to be products of low-grade metamorphism of marine sediments. The marine sedimentary rocks would have to be tectonically emplaced below crystalline rocks in many places. Mercury ore deposits are probably also products of the low-grade metamorphism.*

Natural waters of unusual compositions (examples are given in Table 1) are found in a tectonically active belt about 160 km wide along the Pacific coast of the United States from southern California to Alaska. Although the fluids vary widely in their compositions, they are characteristically rich in CO_2 (up to 15,000 mg/liter HCO_3^-) and may contain as much as several hundred milligrams per liter each of NH_3, H_2S, and B. Commonly I^-/Cl^- ratios are far in excess of that in seawater. In many places hydrocarbons are found associated with the waters, and methane and ethane may be found escaping with the CO_2, as at Wilbur Springs, California. Many of the anomalous fluids are found issuing from known or inferred faults. Volcanic rocks, metavolcanic rocks, mica schist, graywacke, granite, serpentinite, and Mesozoic and Tertiary marine sedimentary rocks are all found to yield these unusual fluids. The anomalous fluids are frequently associated with mercury deposits, as White pointed out (*1*).

At the southern end of this belt in

the United States, in Imperial County, California, a geothermal system has been found in which temperatures as high as 300°C are found at a depth of 900 m (*2*). The surficial expressions of the geothermal system are springs rich in CO_2, NH_4^+, and B, such as the Wister mudpots (see Table 1), at temperatures only a little above the mean annual temperature.

Muffler and White have described metamorphism in the deltaic sediments in the geothermal system (*3*). Simply stated, the reactions are

$$\text{montmorillonite} \rightarrow \text{illite} \quad T < 100^\circ\text{C}$$

$$\text{illite-montmorillonite} \rightarrow \text{K-mica} \quad T < 210^\circ\text{C}$$

$$\text{dolomite} + \text{ankerite} + \text{kaolinite} + Fe^{2+} \rightarrow \text{chlorite} + \text{calcite} + CO_2 \quad 125^\circ\text{C} = T < 180^\circ\text{C}$$

$$\text{calcite} + \text{silicates} \rightarrow \text{epidote} + CO_2 \quad T > 290^\circ\text{C}$$

The compositions of the sediments presently undergoing metamorphism in the Salton Sea area (*3*) show a marked decrease in CO_2 with depth, but no other consistent trend in rock composition is found. Direct proof that carbonate minerals are reacting in the proposed metamorphism is found only in the Salton Sea area. Wilbur Springs (see Table 1) has also been considered to be a connate water modified by metamorphic reactions based upon a high HCO_3^-/Cl^- ratio and high B concentrations (*4*). The similarity of the compositions of fluids yielded on the surface from the Salton Trough metamorphism to the many other CO_2-rich fluids found along the margin of the Pacific Ocean is suggestive of metamorphism occurring throughout the belt. It is probable that part of the very large quantity of CO_2 escaping from the rocks along the Pacific coast is from carbonate minerals reacting to form silicates.

The hydrocarbons frequently found associated with the anomalous waters indicate the presence of organic matter in the metamorphosing materials. High I^-/Cl^- ratios have been ascribed to decomposition of marine biologic remains (*4*). The B concentrations have been explained as due to recrystallization of marine clays with the release of B back into solution. The simplest explanation for the hydrocarbon-ammonia association is the breakdown of proteins to yield CO_2, NH_4^+, and some of the hydrocarbons found. The amino compounds may yield some of the H_2S found in the fluids. Abundant nonprotein original sources for H_2S, CO_2, and hydrocarbons also exist but not for the NH_4^+.

The best present explanation for the anomalous fluids is White's suggestion of metamorphism of sediments deposited under marine conditions. Indeed, there is currently no simple, plausible alternative explanation. One problem with this hypothesis is that the fluids are found issuing not only from marine sedimentary rocks but also from volcanic rocks ranging in age from Holocene to Paleozoic and from fresh to thoroughly altered condition. The anomalous fluids also issue at the surface from granite and serpentinite, which cannot yield the fluid compositions found because the rocks lack sufficient contents of such components as B, NH_4, CO_2, or hydrocarbons. The anomalous fluids also issue from mica schist, biotite gneiss, and Franciscan metasedimentary rocks that have already undergone the metamorphic reactions needed to explain the fluids

Table 1. Compositions and occurrences of anomalous waters, Pacific margin of the United States.

Name (Ref.)	Wister mudpots (*3*)	Wilbur Springs (*4*)	Soda Spring (*6*)	Kennedy Hot Spring (*7*)	Mud Volcano (*6*)	Klawasi Spring (*8*)
Location	Imperial Co., Calif.	Colusa Co., Calif., NW¼ sec. 28, T. 14 N., R. 5 W.	Shasta Co., Calif., NW¼ sec .12, T. 38 N., R. 4 W.	Snohomish Co., Wash., NE¼ sec. 1, T. 5 N., R. 12 E.	Gray's Harbor Co., Wash., sec. 35, T. 22 N., R. 13 W.	Copper River, Alaska, NE¼ sec. 9, T. 3 N., R. 1 E.
Rock	Alluvium	Knoxville Formation (marine sandstone and shale)	Altered volcanic	Biotite gneiss	Marine shale and sandstone	Mesozoic marine sedimentary rocks overlain by Pleistocene glacial deposits
Age	Holocene	Jurassic	Devonian(?)		Miocene	Mesozoic and Pleistocene
Temp. (°C)	21.	57.	11.	30.	Cool	21.
*p*H	7.1	7.24	6.5	7.7	8.4	7.7
			Concentrations in milligrams per liter			
SiO_2	59.	190.	81.	136.	5.	123.
Fe	0.8				0.06	0.0
Mn	0.9		184.			0.0
Ca	79.	1.4	184.	37.	21.	31.
Mg	325.	58.	235.	48.	17.	136.
Sr	4.	10.	2.4	2.1		8.
Na	6,470.	9,140.	1,200.	655.	3,150.	10,000.
K	466.	460.	40.	64.	26.	271.
Li	9.6	14.		3.3		6.9
NH_4	34.	303.	6.3	0.02	6.	0.0*
B	54.	293.	55.	8.9	113.	169.
HCO_3	4,340.	7,390.	3,060.	1,190.	2,380.	7,230.
SO_4	900.	23.	3.8	3.	14.	664.
Cl	8,480.	11,000.	1,140.	643.	3,500.	12,100.
F	14.	1.1				0.3
Br		15.	4.3		18.	29.
I		16.	0.5	0.1	5.3	6.8
H_2S		178.	<0.1			

* Although NH_4 is reported 0.0, the 17 mg/liter of NO_3^- reported were probably NH_4^+ in the natural water.

they yield. It is therefore postulated that marine sedimentary rocks have been underthrust below the igneous and metamorphic rocks that crop out and that the sedimentary rocks are currently undergoing metamorphism and are yielding the anomalous fluids. The metamorphic fluids may serve to aid tectonism as their pressures are limited only by the strength of overlying rocks.

Rising magmas may in some places supply the elevated temperatures necessary for metamorphism. In the Clear Lake area of California, CO_2-, B-, and NH_3-rich fluids are associated with recent volcanic rocks (*5*). However, similar fluids are found in many other areas where no young volcanic rocks are found, so that magma in the Clear Lake area and elsewhere may be regarded as a heat source rather than the source of the fluids that came from reacting sedimentary rocks. The mercury deposits of the coast ranges of the western United States may be products of low-grade metamorphism. Mercury may be an early metal removed from the source rocks during a thermal (metamorphic) event. Thus, mercury deposits may be found unassociated with other economic metal deposits.

In summary, it is proposed that the anomalous fluids so common in the Pacific coastal belt of the United States result from metamorphism of marine sedimentary rocks. Both inorganic materials and biologic remains are affected by the metamorphism, which yields various amounts of NH_4^+, H_2S, CO_2, B, and hydrocarbons to the fluids that escape in some places along faults. The metamorphic fluids in some places yield mercury deposits. The metamorphically derived fluids may also serve as a hydraulic medium for tectonic activity in the belt where the fluids are found.

IVAN BARNES

U.S. Geological Survey, Menlo Park, California 94025

References

1. D. E. White, in *Geochemistry of Hydrothermal Ore Deposits*, H. L. Barnes, Ed. (Holt, Rinehart & Winston, New York, 1967).
2. H. C. Helgeson, *Amer. J. Sci.* **266**, 129 (1968).
3. L. J. P. Muffler and D. E. White, *Geol. Soc. Amer. Bull.* **80**, 157 (1969).
4. D. E. White, *ibid.* **68**, 1659 (1957).
5. ——— and C. E. Roberson, in *Petrologic Studies: A Volume in Honor of A. F. Buddington* (Geological Society of America, New York, 1962).
6. J. B. Rapp, unpublished data.
7. R. W. Tabor and D. F. Crowder, *U.S. Geol. Surv. Prof. Pap. 604* (1969).
8. A. Grantz, D. E. White, H. C. Whitehead, A. R. Tagg, *Amer. Ass. Petrol. Geol. Bull.* **46**, 1990 (1962).

15 December 1969

Megafauna and Man from Ayacucho, Highland Peru

Abstract. Crude unifacial tools, choppers, and a burin have been uncovered in association with megafauna in a buried stratum that was radiocarbon dated at 12,200 B.C. in a cave in highland Peru. The tool types, megafauna, and date are significant with regard to the problem of the antiquity of man and his culture in the New World.

During 1969 preliminary archeological investigations in the Ayacucho Valley of highland Peru, crude tools were found in direct association with the bones of extinct animals not previously found with human remains. A portion of humerus of a Megatheriidae from a stratum with tools has been dated by a relatively new radiocarbon determination technique as 12,200± 180 B. C. (UCLA 1464) (*1*). This is the earliest date on human remains in South America, and the find has implications for both New World prehistory and paleontology.

The purpose of this Peruvian research is to obtain information about the development of agriculture and the concomitant rise of prehistoric civilization in the second major nuclear area of the New World that can be compared with the long sequence previously found in Tehuacan, Mexico (*2*). So far about 450 sites have been found and there has been some testing of stratified sites (mainly dry caves or rock shelters) (*3*). The testings have revealed some early domesticated plants and a long pre-ceramic cultural sequence (Puente complex, 8000 to 6400 B.C.; Jaywa complex, 6400 to 5000 B.C.; Piki complex, 5000 to 3800 B.C.; Chihua complex, 3800 to 2700 B.C.; and Cachi complex, 2700 to 1700 B.C.).

One test in the south end of one of the caves, Pikimachay Cave (Ac 100), however, revealed a very much earlier artifact complex in its earliest stratum. In this test the stratigraphy was as shown in Table 1.

In the three lowest strata, Zones H, H1, and H2, 51 crude artifacts occurred in direct association with bones of extinct animals, two of which have not been previously found in association with man. In Zone H, 34 artifacts occurred with extinct animal bones; and Figs. 1 and 2 show a pebble chopper and a side scraper with a sloth rib. In Zone H1 there were 17 artifacts, and in Zone H2, one piece of polished bone was uncovered. The artifacts from the upper two zones are relatively similar and have been classified as the Ayacucho complex. They belong to six general categories.

The first and largest category (25 specimens) is unifaces which have been struck from ellipsoidal pebble cores by a blow against some part of the narrower axis and have large curved striking platforms. They consist of one thin flake retouched on one edge, 11 thick flakes retouched along one or more portions of the flake, five large flakes retouched on two opposite edges of the flake, four very large slabs (almost half a pebble) retouched along one concave edge with two additional ones retouched in such a manner as to have a concave cutting edge, one flake with a blunted or battered back edge with a concave retouched edge opposite it, and one smaller flake with a convex retouched cutting edge.

The second group (19 specimens) is made from the pebbles themselves and have large portions of the pebble's cortex still adhering. Most numerous were seven thick bifacial core choppers with battering along most of their edges, but there were five pebbles with bifacial retouching or battering along a single narrow portion or end of the ovoid pebble. Also, four pebbles had been retouched in such a way as to have two or three spurs along their cutting edges (denticulates?), two had concave retouched edges (gouges), and one had a narrow and deep concave retouched edge (spokeshave).

Another category is represented by four drill-like unifacial tools which had been manufactured from flakes struck from the longitudinal axis of pebbles, with the pebble's cortex still adhering

Table 1. Stratigraphy in south end of Pikimachay Cave.

Zone	Composition	Thickness (cm)	Content
A	Modern dung	5–10	
B	Light gray ash	5–20	Initial Period artifacts
C	Dark gray ash	20	
D	Light gray ash	5–10	
E	White ash	5–10	
F	Rock and gray ash	5–10	
G	Large rock fall	100–200	
H	Dark clayish stratum	5–10	Ayacucho artifact complex
H1	Yellowish loess stratum	5–20	
H2	Dark yellow soil	< 5	