no trace of these features was discernible. It should be remembered in this respect that the visibility of many Martian surface features, including the "canals," is variable with time. No Earth-like features, such as mountain chains, great valleys, ocean basins, or continental plates were recognized. Clouds were not identified, and the flight path did not cross either polar cap.

Although it may be difficult to ever arrive at an unambiguous identification and interpretation of all the features recorded on the Mariner photographs, we feel that the existence of a lunartype cratered surface, even in only a 1-percent sample, has profound implications about the origin and evolution of Mars and further enhances the uniqueness of Earth within the solar system. By analogy with the Moon, much of the heavily cratered surface of Mars must be very ancient-perhaps 2 to 5  $\times$  10<sup>9</sup> years old (1). The remarkable state of preservation of such an ancient surface leads us to the inference that no atmosphere significantly denser than the present very thin one has characterized the planet since that surface was formed. Similarly, it is difficult to believe that free water in guantities sufficient to form streams or to fill oceans could have existed anywhere on Mars since that time. The presence of such amounts of water (and consequent atmosphere) would have caused severe erosion over the entire surface. The principal topographic features

of Mars in the areas photographed by

## Rock Degradation by Alkali Metals: A **Possible Lunar Erosion Mechanism**

Abstract. When rocks melt under ultrahigh-vacuum conditions, their alkali components volatilize as metals. These metal vapors act to comminute polycrystalline rocks to their component minerals. The resultant powder is porous and loosely packed and its characteristics may be compatible with the lunar surface as revealed by the Ranger photographs. If meteorite impact or lunar volcanism has produced vaporization or areas of molten lava, alkali erosion may have given dust of this character in adjacent solid areas.

The unusual phenomena which might attend the melting of lunar rocks under high-vacuum conditions due to volcanism or meteoric impact have received some attention (1). In addition to observing the usual rock gases, we have noted the evolution of vapors of alkali metals from rocks melted in the laboratory under ultrahigh vacuum Mariner have not been produced by stress and deformation originating within the planet, in distinction to the case of Earth. Earth, of course, is internally dynamic, giving rise to mountains, continents, and other such features, whereas Mars has evidently long been inactive. The lack of internal activity is also consistent with the absence of a significant magnetic field on Mars, as determined by the Mariner magnetometer experiment.

As we had anticipated, Mariner photos neither demonstrate nor preclude the possible existence of life on Mars. Terrestrial geological experience would suggest that the search for a fossil record appears less promising if Martian oceans never existed. On the other hand, if the Martian surface is truly "near pristine," that surface may prove to be the best-perhaps the only -place in the solar system still preserving clues to primitive organic development, traces of which have long since disappeared from Earth.

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conditions. Polycrystalline rock ma-

terials were rapidly eroded by these

metal vapors at moderate temperatures.

It is possible that this erosion phenome-

non may have contributed to the pro-

duction of a lunar dust layer. That

such a dust layer exists on the lunar

surface is supported by the recent

Ranger photographs (2), although the

depth and bearing quality of the layer are still matters of some controversy. Previously, this dust has been attributed variously to cosmic material swept up by the moon, to volcanic ash eruptions, or to the erosion of the lunar surface by various agents such as solar radiation, meteoritic impacts, and the rock-fracturing effects of rapid changes in temperature (3).

Dissociation of the common alkali oxides on vaporization under laboratory conditions is known to occur (4) and similar dissociation of silicates might be anticipated. When we made a rough calculation of equilibrium vapor pressures, using available thermodynamic data for silicates and making estimates for unavailable figures, we found that a partial pressure of approximately  $10^{-5}$  mm would be expected for potassium at 1500°K above the surface of a potassium-aluminum silicate (kaliophilite) of about the acidity of basalt. This vapor pressure can be used to estimate the maximum evaporation rate of the potassium from such a silicate (5), which, for a reasonable eruptive period of about a month, would amount to 0.25 g/cm<sup>2</sup>. In actual rock melts maintained at a temperature of 1500° to 1900°K for periods as long as 1 hour, visible alkali vaporization occurs which is independent of the material of which the crucible containing the melt is constructed (molybdenum, platinum, and alumina). A basalt with a Na/K ratio of about 7 gives a vaporized film with a Na/K ratio of approximately 3, this ratio reflecting the higher dissociation vapor pressure of the potassium compound (4).

Of particular interest is the eroding behavior of metallic sodium and potassium in contact with rock materials. The disintegration of ceramic bodies by grain-boundary attack by liquid sodium was noted previously (6), but the effect on rock materials as described below seems not to have been observed.

When the alkali metals were deposited under vacuum conditions on pieces of broken rock, or on polished sections of rock, and the glass or quartz containers sealed off under vacuum and exposed at 100°C, disintegration of the rock to a powder became evident after about 2 weeks. Exposure to the vapor of the metal at 350°C or higher produced evident erosive effects within an hour, and complete disintegration of the rock was accomplished by exposure for 12 hours. For convenience, most of our experiments were conducted under the hightemperature conditions producing more rapid attack. Work thus far has been mostly qualitative, but the observations on the characteristics of the erosion effect may be of general interest.

Sequential studies of the comminution showed that the rock was progressively sundered or peeled off into large pieces, with a popping-out of crystals occurring and the material finally being broken up to a powder. When remaining lumps of rock were exposed to alcohol or moisture, microbubbles of hydrogen were rapidly released at grain boundaries and along certain cracks, seemingly from the interior of the rock pieces. This indicated that the alkali metal itself is effective as a penetrating agent. No similar attack was induced by aqueous or molten alkali ionic media, such as potassium acetate or lithium-potassium nitrate eutectic. which are known to produce reaction and swelling in certain silicates (7), even when heated for many days at temperatures up to 500°C. Rocks were not affected by reagents such as anhydrous FeCl<sub>3</sub> and bromine which, along with the alkali metals, form nonstoichiometric intercalation compounds with graphite. We also tested the effects of alkali metals on various natural and synthetic glasses and found no evidence of disintegration, but a slow, uniform chemical attack occurred at temperatures above 350°C. The glassy reaction-product layer on the surface showed contraction spalling and cracking on cooling, particularly at corners or edges. Basic rocks disintegrated more readily than silicious or acidic types, but certain polycrystalline aggregates of a single mineral, either natural (quartz) or artificially prepared as a sintered pellet (forsterite), did not disrupt. The size distribution in the erosion product was the same as that of the component crystals of the parent rock, as judged microscopically, so that attack along the grain boundaries between dissimilar minerals seemed to predominate. For a carefully measured sample of basalt, the weight after reaction and washing of water-soluble product increased by 0.02 percent. Also, x-ray diffraction examination by the powder technique revealed no significant difference between a powdered sample of the parent rocks, the reaction product, and the reaction product after it was washed. Thus, by a conservative estimate, the reaction of alkali-metal vapor on this rock must result in the alteration of less



Fig. 1. Rock powder produced by the erosive effect of potassium on olivine basalt. Photographed within high-vacuum system.

than 5 percent of the parent material.

Natural rocks exhibit a certain degree of fracture and porosity and seldom achieve the theoretical composite density of their component minerals. They contain gas vesicles, fractures, parting cracks, inclusions, grain boundaries of varying degrees of disorder, and other kinds of internal surfaces, all of which may be available as avenues of rapid surface or dislocation diffusion. As has been noted, there is evidence in alkali metal-rock interactions that at least a portion of the alkali is diffused in the form of the metal or its vapor. One can hypothesize that the observed degrading of rocks by sodium and potassium takes place as a result of vapor or capillary penetration by the metal along cracks, grain boundaries, and intercrystalline defects; by the subsequent reaction of the metal with the silicate, a non-adherent product is formed which disrupts the layers binding the rock minerals. This effect may be of interest to mineralogists as a nonmechanical method of rock comminution which may have special applications. For example, we have used the technique for the separation of chondrules from chondritic meteorites.

Figure 1 shows the typical appearance of the rock powder which results from potassium attack on tholeitic basalt; the sample is within the experimental evacuated system and is untamped. The open structure of the powder brings to mind the type of lunar surface, predicted by Hapke ( $\delta$ ) and others, which would be necessary to achieve the observed optical properties. In the ultrahigh-vacuum (about  $10^{-11}$  torr) conditions of the lunar surface, magnification of the alkali vaporization effect would be expected from molten rock sources. Such melting would be encountered at volcanic centers, or during lava-flooding which has been invoked to explain the maria (1). Also, the impact of meteorites would volatilize rock materials, and would lead to instability and melting of the lunar crust (9).

In addition, sputtering of metal oxides by simulated solar wind bombardment produces surfaces enriched in metals (10), and presumably this mechanism might also be operative on the lunar surface in producing the alkalis.

In the lunar vacuum, then, the alkali metals should be added to the volcanic volatiles familiar to us under terrestrial conditions. A fraction of these volatiles would in time escape to space, but reactive substances such as the alkalies, with large accommodation coefficients, would remain. These would be spread as a surface deposit over many kilometers around the source because of the very large mean free path. Temperatures reached during the lunar diurnal cycle (maximum about 127°C) would be sufficient to assure the comminuting attack on crystalline rock materials by the condensed alkalies in a relatively short period. If terrestrial lava flows can be used as models for similar lunar surfaces, the bulk of the matrix crystals of lunar lava beds would average about 10  $\mu$ in diameter and on alkali attack would yield a powder of this average size. This has been estimated as a reasonable size for the particles of the lunar dust layer (11).

One might conclude that alkali-metal erosion may be added to the list of possible agents contributing to the production of a lunar dust layer. Also this would add a metallic component to the material of the surface which has been postulated as necessary to explain the high electrical conductivity deduced from radio measurements (12), and it seems to impart certain physical peculiarities giving a cohesive powder of open structure, whose properties may be compatible with the moon's optical characteristics.

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## Stability of Lakes near the **Temperature of Maximum Density**

Abstract. In deep lakes that are near the temperature of maximum density, stability is greatest when the decrease of temperature with depth is about onehalf of the decrease in temperature of maximum density with depth. Observed temperature decreases in lakes under such conditions tend to follow the curve that produces greatest stability.

It was shown (1) that a simple equation of state for water, valid at moderate pressures and near the temperature of maximum density, could be derived from compressibility data; the latter were computed from sonic velocities. The equation of state yielded a rate of decrease of temperature of maximum density with increase of pressure of 0.021°C/bar.

If the equation of state is valid, then other inferences drawn from the equation should be consistent with observation. My purpose is to propose three corollaries and to show that they explain observed temperature profiles in deep lakes near maximum density. These corollaries are:

I) If a column of water is mechanically stable, the temperature-depth curve must change its sign of slope where it crosses the line of maximum density.

II) A lake that is at the temperature of maximum density throughout is not mechanically stable.

III) If the surface of a lake is at maxi-

mum density, stability is greatest when the change of temperature with depth is one half of the change in temperature of maximum density.

The equation of state previously derived is

$$v = v_0 [1 - p(a + b\theta) + c\theta^2]$$
(1)

where v is specific volume,  $v_0$  is specific volume at 4°C and atmospheric pressure, p is "gauge" or "lake" pressure,  $\theta$  is (4.00-T) °C, *a* is 49.458  $\times$  10<sup>-6</sup>/bar, *b* is  $0.327 \times 10^{-6}$ /bar°C, and c is 7.8  $\times$  $10^{-6}/(^{\circ}C)^2$ . It was shown by partial differentiation of Eq. 1 that the line of maximum density has a slope of b/2c or 0.021°C/bar. Thus, if  $\theta'$  is defined as the temperature of maximum density,

$$\theta' = (b/2c)p \tag{2}$$

In general, an equation of state is  $v = f(p,\theta)$ . From differential calculus

$$\mathrm{d}\boldsymbol{v} = \left(\frac{\partial\boldsymbol{v}}{\partial\boldsymbol{p}}\right)_{\boldsymbol{\theta}} \mathrm{d}\boldsymbol{p} + \left(\frac{\partial\boldsymbol{v}}{\partial\boldsymbol{\theta}}\right)_{\boldsymbol{p}} \mathrm{d}\boldsymbol{\theta}$$

or

$$\frac{\mathrm{d}\nu}{\mathrm{d}p} - \left(\frac{\partial\nu}{\partial p}\right)_{\theta} = \left(\frac{\partial\nu}{\partial\theta}\right)_{p}\frac{\mathrm{d}\theta}{\mathrm{d}p} \tag{3}$$

 $\partial$  and d being partial and total derivatives, respectively. The left side of Eq. 3 provides a standard of stability, for dv/dp is an observed change of specific volume with pressure, or depth, in a lake, and  $(\partial v/\partial p)_0$  is the corresponding isothermal change. The latter is related to the isentropic derivative by the equation

$$\left(\frac{\partial v}{\partial p}\right)_{\theta} = \left(\frac{\partial v}{\partial p}\right)_{S} - \frac{T}{c_{p}} \left(\frac{\partial v}{\partial T}\right)_{p}^{2}$$

whose last term becomes vanishingly small near the temperature of maximum density (S denotes entropy). This equation shows that there is no internal heating or cooling when water at the temperature of maximum density is compressed or expanded adiabatically; therefore the adiabatic and isothermal processes are identical.

An observed temperature profile, dv/dp, is stable if, and only if,

$$\frac{\mathrm{d}\nu}{\mathrm{d}p} - \left(\frac{\partial\nu}{\partial p}\right)_{\theta} < 0$$

That is, for stability a small displacement must induce a restoring force. Therefore, from Eq. 3, stability also implies that

$$\left(\frac{\partial v}{\partial \theta}\right)_p \frac{\mathrm{d}\theta}{\mathrm{d}p} < 0 \tag{4}$$

Corollary I is proved in the following manner. Partial differentiation of Eq. 1 gives

$$\left(\frac{\partial v}{\partial \theta}\right)_p = v_0(-bp + 2c\theta)$$

But from Eq. 2,  $bp = 2c\theta'$ , so that

$$\left(\frac{\partial v}{\partial \theta}\right)_p = 2cv_0(\theta - \theta')$$

Equation 3 then becomes

$$\frac{\mathrm{d}v}{\mathrm{d}p} - \left(\frac{\partial v}{\partial p}\right)_{\theta} = 2cv_0(\theta - \theta')(\mathrm{d}\theta/\mathrm{d}p)$$

or, in temperatures Celsius for easier visualizing,

$$\frac{\mathrm{d}v}{\mathrm{d}p} - \left(\frac{\partial v}{\partial p}\right)_T = 2cv_0(T - T')\frac{\mathrm{d}T}{\mathrm{d}p} \qquad (5)$$

Then from Eqs. 4 and 5 the column of water is stable if, and only if,

$$2cv_0(T-T')\frac{\mathrm{d}T}{\mathrm{d}p}<0$$
 (6)

If the temperature profile crosses the line of maximum density so that (T-T')reverses sign, then, by Eq. 6, dT/dp must also reverse sign to maintain stability. Thus corollary I is proved.

If a lake is isothermal, so that in Eq. 5

 $\frac{\mathrm{d}T}{\mathrm{d}p}=0,$ 

the condition of Eq. 6 is not satisfied and the lake is not stable. Physically, a vertical displacement of a volume of water in an isothermal (adiabatic) lake profile would not result in a return force. Likewise, if a lake is at maximum density,

$$(T-T')=0;$$

nor is the condition of Eq. 6 satisfied, and a lake at maximum density does not possess stability. In this case, the lack of a return force is strictly true only for a small vertical displacement. However, the absence of such a return force is equivalent to an absence of stability, and corollary II is therefore proved.

Corollary III is proved by defining a family of linear temperature profiles passing through 4°C at atmospheric pressure, and with the equation

$$\theta = (rb/2c)p \tag{7}$$

Note that when the parameter r = 0 the profile is isothermal, whereas when r = 1the profile is at maximum density. Let  $\phi$  represent the right side of Eq. 3, so that

$$\phi = \left(\frac{\partial v}{\partial \theta}\right)_p \frac{\mathrm{d}\theta}{\mathrm{d}p}$$

Maximum stability occurs when the value of  $\phi$  is minimum. Again by partial differentiation of Eq. 1

$$\left(\frac{\partial v}{\partial \theta}\right)_p = v_0(-bp + 2c\theta)$$

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