The parameters in the least-squares solution were the position and velocity of the spacecraft at the epoch, the gravitational constant $GM_{♂}$ for Mars, the distance off the earth's axis of rotation, and the longitude of each of the five NASA/JPL Deep Space Network tracking stations for which data were available. The statistical properties of the fit, which were good, are summarized in Table 2. The solution for $GM_{♂}$ is $42{,}828.22 \pm 1.83$ km^3/sec^2. A second solution was performed in which the Doppler data were fitted along with nine range measurements taken on 27 July from the NASA/JPL Deep Space Network (Mars tracking facility) at Goldstone, California, with the experimental ranging system used for Mariner 5. The statistical properties of the Doppler fit were not changed appreciably by the addition of the range data. The nine range residuals are shown in Table 3. The value of $GM_{♂}$ for the range and Doppler fit is $42{,}828.48 \pm 1.38$ km^3/sec^2, which is not significantly different, either in size or in estimated standard error, from the value based on Doppler measurements alone. This estimate was computed with a standard error of 62×10^{-9} second on each range point and a standard error of 0.05 hz on Doppler data sampled at 1-minute intervals.

Although the introduction of range data into the fit does not appreciably affect the solution for the mass of Mars, it is of value in the determination of the orbit of the Mariner spacecraft. This has important implications for other Mariner experiments which will require good orbital data for final analysis. Precise knowledge of the orbit is important in relation to information on the ephemeris of Mars and will be significant in later analyses of the tracking data when the nongravitational forces on Mariners 6 and 7 are better understood. At present, we believe that the areocentric orbit for Mariner 6 from the fit to range and Doppler data can be used to predict events along the trajectory to better than 1 second in time or to better than 8 km along the flight path. For example, our best estimate of the time of closest approach to Mars is 31 July 1969, 05:19:06.4 (± 1 second) (UTC).

In addition to Mariners 6 and 7, the only other source for an accurate determination of the mass of Mars is Mariner 4. A recent analysis (*10*) of Doppler data, taken over a 10-day interval during which the spacecraft was centered about a closest approach, has yielded a value for $GM_{♂}$ of $42{,}828.32 \pm 0.13$ km^3/sec^2. Therefore, the masses determined from Mariners 4 and 6 are in agreement, and there is good reason to use the value determined from spacecraft measurements in calculations with other planetary data.

JOHN D. ANDERSON
LEONARD EFRON
S. KUEN WONG
Jet Propulsion Laboratory, California Institute of Technology, Pasadena

References and Notes

1. A. Kliore, G. Fjeldbo, B. L. Seidel, S. I. Rasool, *Science* **166**, 1393 (1969).
2. W. G. Melbourne, paper presented at the 12th plenary meeting of the Committee on Space Research, Symposium C: Space Probes–Part I, Prague, Czechoslovakia, 1969.
3. J. D. Anderson, thesis, University of California at Los Angeles (1967); *Jet Propulsion Lab. Tech. Rep. 32–816* (1 July 1967).
4. G. W. Null, H. J. Gordon, D. A. Tito, *Jet Propulsion Lab. Tech. Rep. 32–1108* (1967).
5. G. E. Pease, *Jet Propulsion Lab. Tech. Rep. 32–1363* (1969).
6. J. D. Anderson and D. E. Hilt, *AIAA* (*Amer. Inst. Aeronaut. Astronautics*) *J.* **7**, No. 6, 1048 (1969).
7. M. E. Ash, I. I. Shapiro, W. B. Smith, personal communication.
8. C. J. Vegos and D. W. Trask, *Ranger Combined Analysis Part II: Determination of the Masses of the Earth and Moon from Radio Tracking Data* [*Jet Propulsion Lab. Space Programs Sum. 37–44* (1967), vol. 3, pp. 11–28].
9. J. Lorell, *Jet Propulsion Lab. Tech. Rep. 32–1387* (1969); W. H. Michael, Jr., W. G. Blackstear, J. P. Capcynski, paper presented at the 12th plenary meeting of the Committee on Space Research, Symposium C: Space Probes–Part I, Prague, Czechoslovakia, 1969.
10. G. W. Null, paper presented at the 130th meeting of the American Astronomical Society, Albany, N.Y., 1969.

11. The authors acknowledge the assistance and support given to the Mariner Mars 1969 Celestial Mechanics Experiment by H. Gordon, D. Curkendall, B. Zielenbach, M. Sykes, S. Reinbold, N. Thomas, and others in both the Mariner Mars 1969 Flight Path Analysis and Command Team and the Precision Navigation Project at JPL. This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under NASA contract No. NAS 7-100.

3 October 1969

■

Silicon: A Possible Factor in Bone Calcification

Abstract. *Silicon, a relatively unknown trace element in nutritional research, has been uniquely localized in active calcification sites in young bone. Silicon increases directly with calcium at relatively low calcium concentrations and falls below the detection limit at compositions approaching hydroxyapatite. It is suggested that silicon is associated with calcium in an early stage of calcification.*

Approximately 5000 quantitative, electron probe microanalyses for calcium, phosphorus, and silicon were made on 50 specimens of normal tibia from young mice and rats (0 to 28 days old) with five different sample preparation techniques. As a result, silicon, a relatively unknown trace element in nutritional research, has been shown to be localized in active calcification sites in young mouse and rat bone. The amount of silicon present in specific regions within the active areas appears to be uniquely related to "maturity" of the bone mineral. In the earliest stages of calcification in these regions, when the calcium content of the preosseous tissue is very low, both silicon and calcium contents rise congruently. In more advanced stages the amount of silicon falls markedly, and, as calcium approaches the proportions present in hydroxyapatite, silicon is present only at the detection limit; the more "mature" the bone mineral the smaller the amount of measurable silicon. Concomitantly maximum amounts of silicon are present at molar ratios of calcium to phosphorus of approximately 0.7, but at ratios of calcium to phosphorus approaching that of hydroxyapatite silicon again falls below the detection limit.

To carry out a study involving quantitative analysis for and precise location of trace elements in biological tissue sections, unusual precautions must be taken to avoid contamination, redistribution, or removal of the elements. This prerequisite cannot be emphasized too strongly in the case of an element such as silicon which is so abundant in the environment (*1*). Modified histological specimen procedures used were (i) freeze-drying and embedding in polymer, (ii) vacuum drying and embedding in polymer, (iii) hand polishing of freeze- and vacuum-dried embedded slices with materials free of silicon, (iv) cryostat cutting with subsequent freeze-drying, and (v) fixation in absolute alcohol and embedding in paraffin. The comparison standard for quantitative electron microprobe analysis was a natural apatite for which a distinctly superior analysis of major and minor elements is available (*2*). There was no measurable wavelength shift between the specimen and the standard. Sequential quantitative analyses

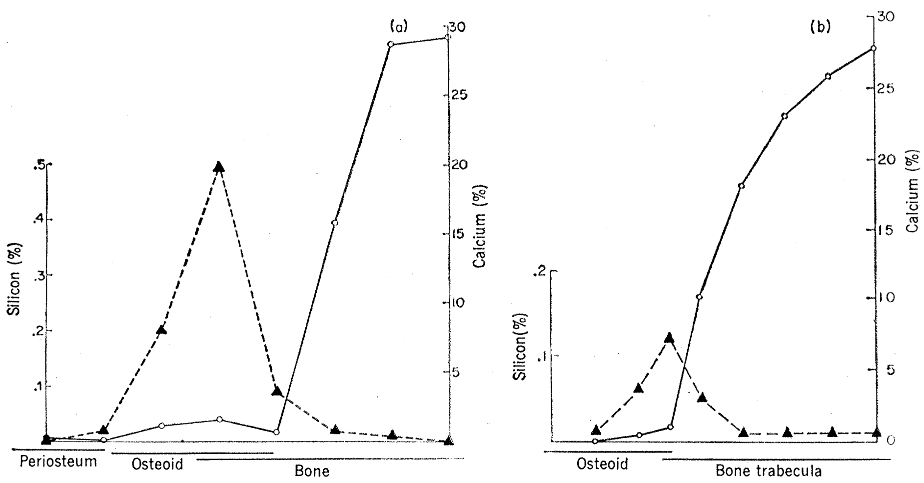

Fig. 1. Spatial relation between silicon (▲) and calcium (○) composition (percent, by weight) in typical traverses across young tibia in (a) a periosteal region (cross section) and in (b) a metaphyseal trabecula (longitudinal section) as obtained by electron-microprobe techniques.

were performed by moving the specimen in 3- to 4-μm steps under a stationary electron beam focused to a diameter less than 2 μm.

The spatial distribution of the changing calcium and silicon compositions in young bone is shown in Fig. 1a, representing one of a great many traverses through sites rich in silicon in the periosteal regions. In the periosteum both the calcium and silicon values are invariably low, whereas in the adjacent osteoid layer of this sample (Fig. 1a), there are silicon-rich sites containing up to 25 times as much silicon and nine times as much calcium as in the periosteum. The silicon content falls again to the original extremely low value as the calcium concentration rises to 15 percent and beyond. Several other traverses across periosteal regions of this sample yield similar results.

A similar relation exists between calcium and silicon in the metaphysis of young bone, the presence of silicon corresponding with the margins of trabeculae and bony spicules in the course of formation. Part of a typical traverse across the metaphyseal region of a longitudinal section of a young tibia (Fig. 1b) shows silicon content rising from 0.01 to 0.06 percent in the preosseous border and to 0.12 percent on the edge of a trabecula but then declining to and remaining at 0.01 percent while calcium content rises progressively from 0.06 to 27.8 percent. This same relation was encountered eleven more times in the continuation of the traverse, not shown in the figure. Calcium contents in the silicon-rich sites, which are abundant in this part of bone, range from 0.15 to 0.70 percent and molar ratios of calcium to silicon range from 1/3 to 3. By comparison, on the edge of the trabeculae where the calcium content is about 1 percent, the molar ratios of calcium to silicon are typically about 5. The decline in silicon, as the traverse progresses into the trabecula, occurs usually at a calcium concentration above 1 percent. Silicon continues to fall and remains at a minimum as the calcium concentration progressively increases with distance from the edge of the trabecula.

The overall relation between silicon and calcium contents, in regions where silicon is found, in both periosteal and endochondral bone can be summarized as follows. At extremely low concentrations of tissue calcium (less than 0.1 percent) little or no measurable silicon is present. Silicon appears where a low to moderate and varying calcium content suggests active calcification. The silicon is not uniformly distributed in these areas but is concentrated in sites containing from 0.08 to 1.0 percent or more silicon and from 0.1 to 2.0 percent calcium on the edge of trabeculae or from 0.5 to about 15 percent calcium in the periosteal areas. Such sites are common. Generally a marked decline in silicon-rich sites occurs at calcium concentrations of 10 to 20 percent, and little or no measurable silicon is present at calcium concentrations above 20 percent, whether in areas of active calcification or not.

To help eliminate the possibility that the silicon increment could be a residual effect as tissue fluid space is replaced by apatite, simultaneous analyses were made in specific areas for silicon and for chloride, an anion not believed to participate in the calcification process (*1*). No correlation with the silicon effect was observed. However, a positive correlation has been established with magnesium, which has been suggested as a factor regulating mineralization in vivo (*3*).

These observations, relating to active bone development, imply that silicon may be allied to the initiation of mineralization of preosseous tissue, whether in periosteal or in endochondral ossification. Further evidence that silicon is involved in calcification at an early stage is provided by molar ratios of calcium to phosphorus. In hydroxyapatite, and in mature bone generally, this ratio is approximately 1.67. In the silicon-rich sites, even though calcium contents range appreciably, these molar ratios are typically in the range 0.6 to 0.8. Silicon-rich sites have yet to be found in bone approaching the composition of hydroxyapatite. Additional information from studies in vivo support the finding that silicon is associated with calcium in the mineralization process (*4*).

EDITH M. CARLISLE
School of Public Health, University of California, Los Angeles 90024

References and Notes

1. E. M. Carlisle, in preparation.
2. E. F. Cruft, C. O. Ingamells, J. Muysson, *Geochim. Cosmochim. Acta* **29**, 581 (1964).
3. R. E. Wuthier, *Calcified Tissue Res.* **4**, 20 (1969).
4. E. M. Carlisle, in preparation.
5. This research was made possible through use of the electron microprobe facilities at the Department of Geology, UCLA, supported in part by NSF grant GA-1503 and in part by the General Research Support grant (FR 05442) of the School of Public Health, UCLA.

30 October 1969

Dimethylpropynylbenzamides: A New Group of Herbicides

Abstract. N-*(1,1-Dimethylpropynyl)-3,5-dichlorobenzamide is representative of a group of benzamides that are herbicidally active on annual and perennial grasses with potential agricultural utility in forage legumes, certain turf grasses, and cultivated crops.*

Several dimethylpropynylbenzamides have shown outstanding activity as selective herbicides. Preeminent among these is *N*-(1,1-dimethylpropynyl)-3,5-dichlorobenzamide (Fig. 1), extensively field tested under the code designation RH-315.

This benzamide was prepared by