

Certain additives (NaCl , NH_3 , FeCl_2) in the water covering the hydrocalcite favor the transformation process, and other additives (Na_2SO_4 , SrCl_2 , FeSO_4 , NH_4NO_3 , MgCl_2 , BaCl_2 , sugar, polyphosphates) impede it. An increase in the concentration of these additives causes a corresponding acceleration or deceleration of the transformation in all samples investigated. Observations over a period of 3 months revealed that the presence of either <0.1 mole percent MgCl_2 , <0.01 mole percent BaCl_2 , or <100 parts per million of Calgon in the covering water entirely prevents the transformation of $\text{CaCO}_3 \cdot \text{H}_2\text{O}$. Air-dried hydrocalcite kept in a dry place over a period of 3 months also remained unchanged. No vaterite or any other hydrate of CaCO_3 formed in any of the transformation experiments.

These results suggest that nesquehonite forms in scales under conditions similar to those in nature. Analogously, it may be assumed that hydrocalcite also forms in nature by precipitation from cold water in its contact zone with air, as in the spray zone of waterfalls, in nearshore parts of a lake, and in stalactites and stalagmites. Hydrocalcite is less likely to form from water rich in NaCl (seawater).

Transformation of $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ into calcite takes place only as a result of dry heating; transformation into aragonite takes place only in the presence of H_2O (the exception being water rich in NH_3). Thus complete transformation into aragonite takes place even at temperatures below 0°C and in the presence of additives such as NaCl , despite the fact that in the direct crystallization of anhydrous CaCO_3 from solution low temperatures and the presence of NaCl favor the formation of calcite and suppress the formation of aragonite. It may thus be assumed that aragonite, whose origin in nature and in technical plants cannot be explained by the temperature and the ion content of the precipitating medium, does not form directly; rather it forms by way of a carbonate hydrate phase.

HANNELORE MARSCHNER*
Laboratorium für Sedimentforschung,
University of Heidelberg,
Heidelberg, Germany

References and Notes

1. R. Brooks, L. M. Clark, E. F. Thurston, *Phil. Trans. Roy. Soc. London Ser. A* **243**, 145 (1951).
2. G. Baron and M. Pesneau, *Compt. Rend.* **243**, 1217 (1956); R. van Tassel, *Z. Anorg. Chem.* **319**, 107 (1962).

3. H. Menzel, A. Brückner, H. Schulz, *Z. Elektrochem.* **36**, 188 (1930); M. R. Kinsolving, C. MacGillavry, R. Pepinsky, *Amer. Mineral.* **35**, 127 (1950).
4. American Society for Testing and Materials Powder Diffraction File Card No. 1-0130 (1960).
5. F. Krauss and W. Schriever, *Z. Anorg. Chem.* **188**, 259 (1930).
6. I thank A. Fritz for supplying samples, M.

Gastner for chemical analyses, B. Nuber for calculating the crystallographic data, and Dr. G. Müller for many stimulating discussions. Supported by the Deutsche Forschungsgemeinschaft.

* Present address: National Building Research Institute, P.O. Box 395, Pretoria, South Africa.

20 March 1969; revised 17 June 1969

Strength-Density Relations in Particulate Silicates of Complex Shape and Their Possible Lunar Significance

Abstract. *Some terrestrial particulate silicate rocks with complex particle shapes have internal friction angles over 45° and cohesion of about 0.1 newton per square centimeter at bulk densities of 0.6 to 0.8 gram per cubic centimeter. Mechanical and other properties of the lunar surface layer, observed with spacecraft, may be consistent with a low bulk density and complex reentrant shapes for the fine particles.*

Earth-based measurements of the photometry and infrared emission of the lunar surface long ago suggested that the surface is covered with fine particles with very low packing density and complex, highly irregular particle shapes. Subsequent radio emission and radar measurements seemed consistent with this hypothesis.

The Surveyor landings confirmed the presence of the fine particle cover. However, the larger surface blocks, over 1 mm in diameter, were shown in Luna and Surveyor pictures to have generally convex surfaces and to look rather solid. Furthermore, the density of one block was measured as 2.8 ± 0.4 g/cm³, an indication that it is solid or nearly solid (1). As a consequence, in recent discussions of the structure and properties of the fine matrix material it has generally been assumed that the fine particles, too, have convex, rounded, surfaces and are essentially solid. On this assumption, bulk densities have been calculated for the surface layer from the mechanical properties determined with the Surveyor spacecraft (1, 2). The results are not in good agreement with some earth-based data and with the Luna 13 measurement of bulk density (3).

This discrepancy raises the possibility that the shapes and perhaps the internal porosity of the fine particles, predominantly 2 to 60 μm in diameter (4), which constitute the bulk of the surface layer, are different from those of the larger blocks. Consideration of the size-frequency distribution of the larger pieces and its extrapolation downward has already led to some doubt as to whether the fine and coarse fractions

can be considered to come from the same population (5). It thus seemed worthwhile to examine further the mechanical property-density relations for silicates composed of particles with highly irregular reentrant shapes. Measurements of shear strength for such material have been reported (6), but data on cohesion and internal friction are desirable for comparison with lunar observations.

Volcanic ash and lapilli deposited by the 1959 activity of Kilauea Iki in Hawaii were used as an experimental material; the site of the sample was approximately 1 km southwest of the crater (7). The particles are essentially tholeiitic basaltic glass, with a solid density of about 2.8 g/cm³. Figure 1 shows typical particle shapes, and Table 1 gives the particle size distribution. The material is much coarser than the fine lunar matrix but is of interest because

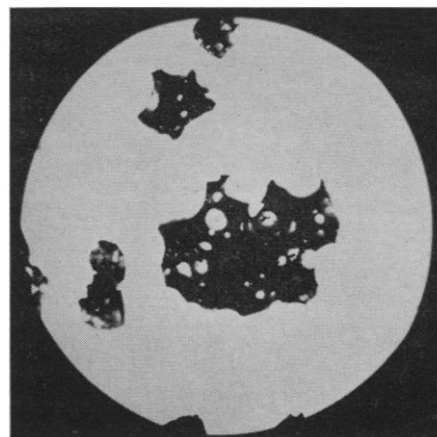


Fig. 1. Micrograph of ash particles. Diameter of the field is 2.2 mm. [Courtesy of J. Green]

of the irregular particle shapes. The tests described below were made both with the as-received particle size distribution and after sieving to remove particles coarser than 3.3 mm and finer than 0.83 mm. Two packing

Table 1. Size distribution of ash particles.

Size (mm)	Percentage of mass smaller than indicated size
0.42	0.1
0.83	0.5
1.0	1.1
1.4	2.3
2.0	4.7
2.8	10.
3.3	15.
4.0	24.
5.6	52.
6.7	65.
7.9	78.
9.4	88.
13.	95.
19.	97.
27.	98.6

states were used: (i) uncompacted, produced by gently pouring the particles into a container from a height of a few centimeters, and (ii) compacted, produced by vibrating the material in the container. Vibration times were limited to minimize separation by particle size. The bulk densities ranged from 0.6 to 0.8 g/cm³ corresponding to 23 to 30 percent solid; the vibration produced only a small change.

Using a shear box of the conventional soil-mechanics design, I determined the load necessary to shear samples as a function of the normal (compressive) load. Normal loads were generally limited to 3 newton/cm² (4 lb/in.²), since noticeable crushing of the particles occurred at higher loads. Two to five tests were made at each of the normal loads, particle size distributions, and compaction states: considerable scatter occurred. The median

values are plotted in Fig. 2. Cohesion was read as the zero intercept and internal friction angle was read as the initial slope of each curve. Cohesion was also determined separately with a vane penetrometer; the two sets of measurements were in good agreement. Though experimental scatter introduces some uncertainty in internal friction angle, the value is at least 45° for all conditions tested. Table 2 summarizes the results.

The internal friction angles are strikingly high for rock particles of such low bulk density. It seems highly possible that the Surveyor observations of the lunar surface material are consistent with a material having mechanical properties resembling those of these laboratory samples.

Porosity of the individual particles is partly responsible for the low bulk density of the material tested; poor packing due to the complex irregular shapes is also important (6). If the lunar surface layer was formed by ash deposits, particles with internal porosities and shapes resembling those in the terrestrial ash could occur. If, as seems more likely, the surface layer was produced or reworked by meteoroid impact, the impact process itself could produce complex, highly reentrant particle shapes (8). It must be admitted that one would expect both the internal porosity of the particles and the complexity of their shapes to decrease as the particle size decreases. Nevertheless, the possibility that the properties of the fine lunar matrix are associated with complex particle shapes should not be ruled out.

LEONARD D. JAFFE

Jet Propulsion Laboratory,
California Institute of Technology,
Pasadena 91103

Table 2. Summary of results of measurements of cohesion and internal friction.

Size distribution (mm)	Compaction	Bulk density* (g/cm ³)	Percent-age of solid†	Cohesion		Internal friction angle (deg)
				In newton/cm ²	In lb/in. ²	
Unsieved	Uncompacted	0.63	23	0.1	0.2	47
Unsieved	Compacted	.67	24	.2	.3	54
0.83 to 3.3	Uncompacted	.70	25	.06	.09	49
0.83 to 3.3	Compacted	.83	30	.2	.3	54

* Uncertainty, ± 0.03 . † Uncertainty, ± 2 .

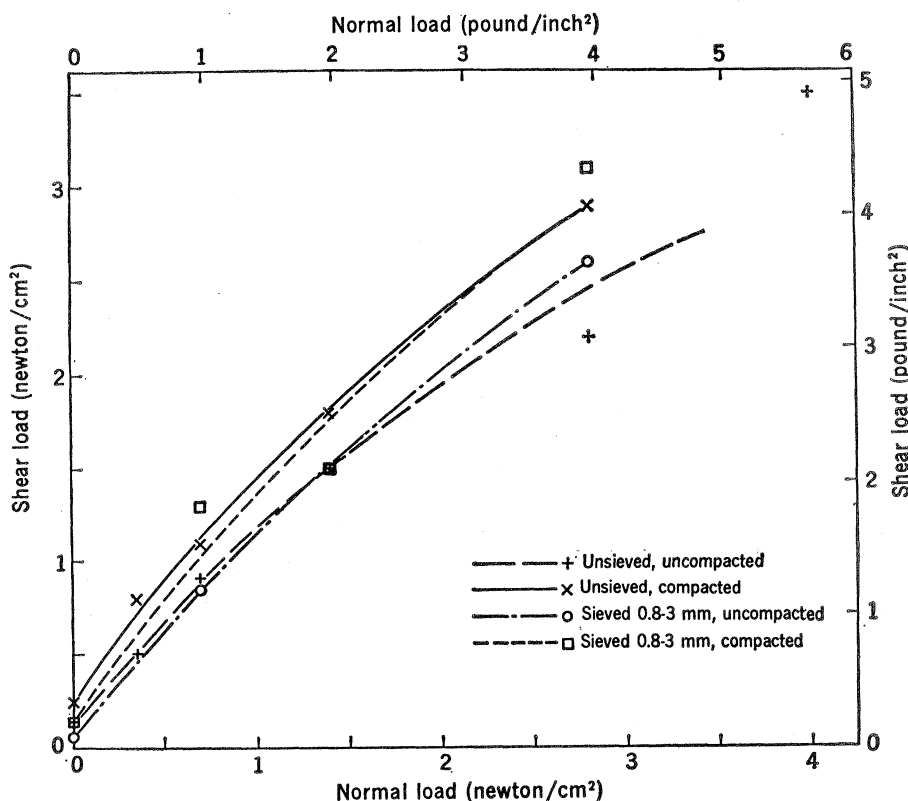


Fig. 2. Shear load as a function of normal load.

References and Notes

1. R. F. Scott and F. I. Roberson, *NASA (Nat. Aeronaut. Space Admin.) SP-173* (1968), pp. 121-161.
2. E. M. Christensen, S. A. Batterson, H. E. Benson, C. E. Chandler, R. H. Jones, R. F. Scott, E. N. Shipley, F. B. Sperling, G. H. Sutton, *J. Geophys. Res.* **72**, 801 (1967); R. F. Scott and F. I. Roberson, *ibid.* **73**, 4045 (1968); E. M. Christensen, S. A. Batterson, H. E. Benson, R. Choate, R. E. Hutton, L. D. Jaffe, R. H. Jones, H. Y. Ko, F. N. Schmidt, R. F. Scott, R. L. Spencer, F. B. Sperling, G. H. Sutton, *NASA (Nat. Aeronaut. Space Admin.) SP-166* (1968), pp. 41-95; L. D. Jaffe, *Science* **164**, 1514 (1969).
3. V. S. Troitsky, *J. Res. Nat. Bur. Stand. D. Radio Sci.* **69-D**, 1585 (1965); Yu. G. Matveev, G. L. Suchkin, V. S. Troitsky, *Astron. Zh.* **42**, 810 (1965) [*Soviet Astron. AJ Engl. Transl.* **9**, 626 (1966)]; T. Hagfors, R. A. Brockelman, H. H. Danforth, L. B. Hanson, G. M. Hyde, *Science* **150**, 1153 (1965); L. D. Jaffe, *Icarus* **6**, 75 (1967); I. I. Cherkasov, A. L. Kemurjian, L. N. Mikailov, V. V. Mikheyev, A. A. Morozov, A. A. Musatov, I. A. Savenko, M.

- I. Smorodinov, V. V. Shvarev, *Kosm. Issled. Akad. Nauk SSSR* 5, 746 (1967) [transl. in *Cosmic Res.* 5, 636 (1967)]; A. A. Morozov, M. I. Smorodinov, V. V. Shvarev, I. I. Cherkasov, *Dokl. Akad. Nauk SSSR* 179, 1087 (1968) [*Soviet Phys. Dokl. Engl. Transl.* 13, 348 (1968)]; R. F. Scott, *J. Geophys. Res.* 73, 5469 (1968).
4. E. M. Christensen, S. A. Batterson, H. E. Benson, R. Choate, R. E. Hutton, L. D. Jaffe, R. H. Jones, H. Y. Ko, F. N. Schmidt, R. F. Scott, R. L. Spencer, G. H. Sutton, *J. Geophys. Res.* 73, 7169 (1968); E. M. Christensen, S. A. Batterson, H. E. Benson, R. Choate, L. D. Jaffe, R. H. Jones, H. Y. Ko, R. L. Spencer, F. B. Sperling, G. H. Sutton, *ibid.*, p. 4081; L. D. Jaffe, *ibid.* 72, 1727 (1967); D. E. Gault, R. J. Collins, T. Gold, J. Green, G. P. Kuiper, H. Masursky, J. A. O'Keefe, R. A. Phinney, E. M. Shoemaker, *ibid.* 73, 4115 (1968).
5. E. M. Shoemaker, R. M. Batson, H. E. Holt, E. C. Morris, J. J. Rennilson, E. A. Whitaker, *NASA (Nat. Aeronaut. Space Admin.) SP-173* (1968), pp. 13-81; L. D. Jaffe, *Science* 164, 774 (1969).
6. J. H. Osgood and J. Green, *Geophysics* 31, 536 (1966).
7. I thank J. Green, who collected, characterized, and provided the material.
8. D. E. Gault, E. D. Heitowit, H. J. Moore, *Trans. Amer. Geophys. Union* 45, 74 (1964); L. D. Jaffe, *Appl. Phys. Lett.* 11, 328 (1967).
9. Sponsored by NASA under contract NAS7-100.

19 May 1969

Carbon-14 in Patagonian Tree Rings

Abstract. The radiocarbon activity found in tree rings from southern Argentina shows secular fluctuations which are synchronous with and of the same amplitude as those known for the Northern Hemisphere. Comparable measurements indicate that the activity in Patagonian trees is about five per mil lower than in European trees.

Natural radiocarbon allows dating of carbonaceous materials up to about 50,000 years old (1). One of the assumptions on which the method is based is the constancy of the specific activity of the isotope present in atmospheric carbon dioxide, independent of time and locality. A permanent record of the annual activity of the atmosphere has been kept by the carbon assimilated in the growth rings of trees. Analyses of Northern Hemisphere trees showed that the initial C^{14} content varies slightly with time (2-5), causing errors in radiocarbon dating of as much as 150 years

for the last millennium. It was expected that secular variations would show synchronism over the globe, but their existence still had to be demonstrated for the Southern Hemisphere. Furthermore, de Vries (2) reported a "local effect"—the C^{14} activity in a tree from Colorado apparently being about 1 percent higher than that in contemporary samples from central Europe. It was thus deemed desirable to undertake a worldwide survey of samples from different localities and dates. We now summarize our results from some Argentine trees and compare them with

those of other authors (see 2, 4, 6-8).

A survey in the rain forests of the north Patagonian Andes in 1961 was guided by the report of Schulman (9). Only unexplored regions offered possibilities of finding millenary trees (10). The main difficulty was that either the old trees have decayed wood in the center of the trunk or that they are completely hollow. Several specimens were obtained, however (11). They belong to indigenous species, *Fitzroya cupressoides* (lahuán, alerce), *Araucaria araucana* (pehuén, araucaria, pino de los Andes), and *Nothofagus dombeyi* (coigüe or coihue). The samples provided tree rings apparently spanning more than 1700 years (ascertained by ring counting alone). The real ages after A.D. 1400 should, however, be accurate to at most a few tens of years because of the agreement of the different C^{14} analyses at the three selected dates mentioned below. The specimens discussed here are named after the National Parks in which they grew. Los Alerces F 63: *Fitzroya* from the left bank of Arroyo Le Goufre (42°36'S, 72°3'W), west of Lake Cisne, at 550 m altitude. It had a diameter of 2 m and a rotten or missing pith of 40 cm. Its span of preserved year-rings (more than 1700) is the longest known from a Southern Hemisphere tree. It was felled in 1962 (12). Los Alerces F II: *Fitzroya* with a diameter of 65 cm and 300 rings, from the shore at the end of the southwest

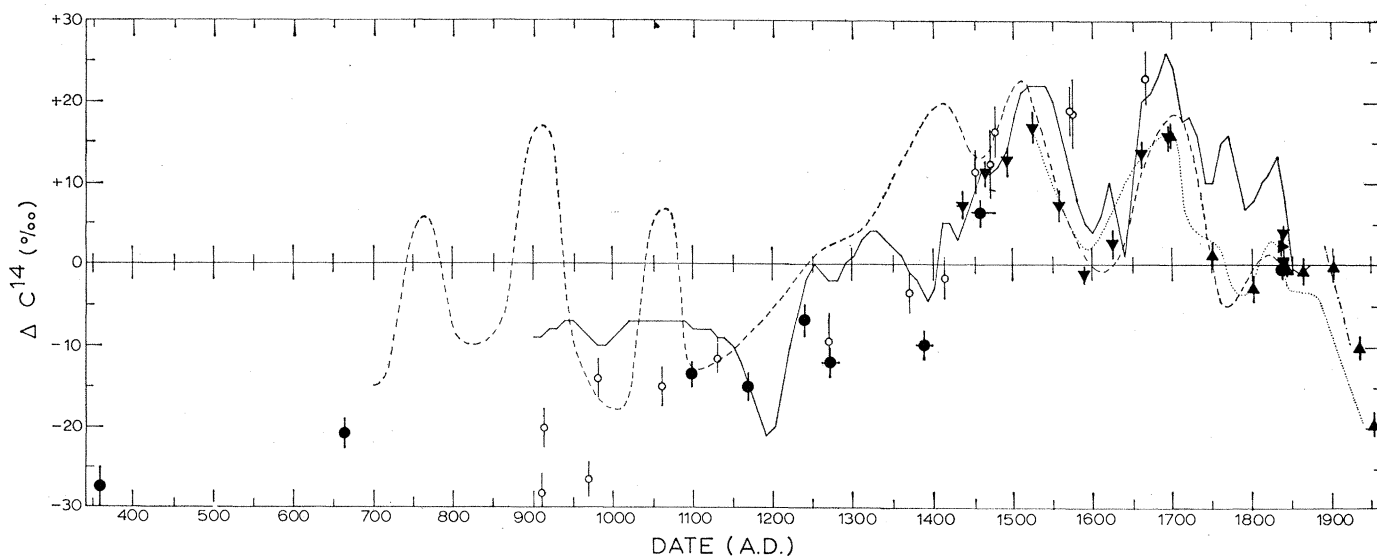


Fig. 1. Secular fluctuations of carbon-14 in tree rings from Patagonia compared with measurements of others. The absolute value of the reference axis for each series of data is explained in the text. The vertical error bars indicate the standard deviations (σ) calculated as the internal error of the mean value. The horizontal bars indicate, when the scale allows for it, the number of rings in the samples. Data from previous publications of Northern Hemisphere (Europe and North America) samples are represented by: dotted line, de Vries (2) corrected; dashed line, Willis *et al.* (4); dash and dot line, Lerman *et al.* (17). The Southern Hemisphere is represented by measurements of a New Zealand tree $\circ$ by Jansen (7, 8), and of the Patagonian trees mentioned in the text: $\blacktriangle$, Los Alerces F II; $\bullet$, Los Alerces F 63; $\blacktriangledown$, Nahuel Huapi B; $\blacktriangleright$, Nahuel Huapi J; $\bullet$, Lanín.