

raw signal data indicates that generally the values for channels 9 (OG1 filter), 10 (RG8 filter), and 11 (total flux) are within 0.3 percent of the mean for the on-Sun period. After analysis of the data (for example, application of temperature and zero corrections), the mean deviation of corrected signal data for comparable series of measurements is within 0.2 percent. Scrutiny of the X-15 "selected measurement" data give repeatability figures of the order of ± 0.5 percent.

Table 3 summarizes the principal results from all eight flights. The mean deviations of the four sets of average values are rather remarkable: total flux, ± 0.1 percent; ultraviolet plus visible (that is, total minus infrared), ± 0.2 percent; and infrared, $\pm 0.1_5$ percent. The weighted means of all jet-flight series agree with the corresponding X-15 values within 0.2 percent on average. It is difficult to assess absolute accuracy as distinct from the different aspects of precision in measurement, but these figures suggest that the finalized values should be accurate within 1 percent. There is no added complication regarding the broad-band-pass filter channels since the filter factor for this type of filter is essentially the reciprocal of the main-band transmittance.

Comparison with the Johnson curve indicates that Johnson (4) overestimated the total flux by 2.5₅ percent; energy for wavelengths shorter than $\lambda = 607$ nm, by 7.0 percent. On the other hand, the values for $\lambda > 607$ nm are in almost perfect agreement. This significant difference for $\lambda < 607$ nm was confirmed in the analysis of the first series of narrow-band (interference) filter results from the 1966 flights. The weighted mean from five independent filter measurements, covering the spectral range from 295 to 595 nm, is lower by 7.5 percent than the Johnson integral (7). This material (and that from lower tropospheric levels) for the subsequent flights is now being evaluated. The B-57B measurements of total flux have been independently verified (13).

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References and Notes

1. A. J. Drummond, in *Proc. IES-ASTM Int. Symp. Solar Radiation Simulation Los Angeles* (Inst. of Environmental Sciences, Mount Prospect, Ill., 1965).

2. K. Y. Kondratiev, G. A. Nicolsky, I. Y. Badinov, S. D. Andreev, *Appl. Optics* **6**, 197 (1967).
3. K. Y. Kondratiev, personal communication.
4. F. S. Johnson, *J. Meteorol.* **11**, 431 (1954).
5. A. J. Drummond, J. R. Hickey, W. J. Scholes, E. G. Laue, in *Proc. Int. Astronaut. Federation Cong. 17th Madrid 1966* (1967), vol. 2, p. 22 (available from Gordon and Breach, New York).
6. Of the Jet Propulsion Laboratory (California Institute of Technology) and Eppley Laboratory; sponsored by NASA.
7. A. J. Drummond, J. R. Hickey, W. J. Scholes, E. G. Laue, *J. Spacecraft Rockets* **4**, 1200 (1967).
8. R. Penndorf, *J. Opt. Soc. Amer.* **47**, 176 (1957).
9. W. L. Godson, *Quart. J. Roy. Meteorol. Soc.* **86**, 301 (1960).
10. L. Elterman, *U.S. Air Force Cambridge Res. Labs. Environ. Res. Paper No. 46* (1964).
11. P. M. Kuhn and S. K. Cox, *J. Appl. Meteorol.* **6**, 142 (1967).
12. A. J. Drummond, J. R. Hickey, W. J. Scholes, E. G. Laue, in *Proc. Int. Astronaut. Federation Cong. 18th Belgrade 1967*, in press.
13. H. W. Brandhorst, personal communication.
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Glassy Objects (Microtektites?) from Deep-Sea Sediments near the Ivory Coast

Abstract. *Glassy objects of spherical, oval, dumbbell, teardrop, and irregular shapes have been found in a deep-sea sediment core taken off the Ivory Coast. They occur in a layer of sediment that was apparently deposited about 800,000 years ago. Their geographic location, appearance, and physical properties suggest that they are microtektites and that they are related to the tektite-strewn field of the Ivory Coast.*

Several hundred small (<1 mm) glassy objects have been found in deep-sea sediments from north of the Philippines, south of Sumatra and Australia, and southeast of Madagascar. On the basis of their geographic location, age of deposition, and physical properties, it has been suggested that these glassy objects are microtektites and that they represent a portion of the Australasian tektite-strewn field (1). The chemical composition of 60 of the glassy objects was determined by electron-microprobe analysis at the Goddard Space Flight Center (2). In general, they appear to be quite similar in their compositional trends to Southeast Asian and Australian tektites.

Recently, a search was undertaken to see if any glassy objects could be found in the deep-sea sediments near the Ivory Coast of Africa. A few hundred glassy objects were found in one core (V19-297) taken at $2^{\circ}37'N$ and $12^{\circ}00'W$. The appearance and physical properties of these glassy objects are similar to that of the Australasian microtektites.

Out of the 277 glassy objects recovered, approximately 90 percent are spherical in shape, and several hollow hemispheres were found. Most of the remainder are either oval or disc- or dumbbell-shaped (Fig. 1). Only two teardrop-shaped objects were found. In addition, fragments are very abundant.

Like the Australasian microtektites, these glassy objects are mostly less than 1 mm in diameter; however, a few dumbbell-shaped objects are as long as 1.2 mm. They are brittle and break with a conchoidal fracture.

In transmitted light most (~ 70 percent) of the glassy objects are olive brown to olive green in color. A few are colorless, and the remainder are yellowish-green or dark brown to black. Thus, the color of these glassy objects is in contrast to the Australasian microtektites, which are mostly yellowish-brown (from the Wharton Basin) or colorless to yellowish-green; however, they are similar in color to the Ivory Coast tektites which, according to Vand (3), are brownish in thin section.

The surface texture of the glassy objects varies from glassy smooth to very irregular and badly pitted. Unlike the Australasian microtektites, these glassy objects appear to have undergone extensive solution which has resulted in surface markings that are not observed on the Australasian microtektites. Elongated bubble or solution pits, grooves, and flow lines are among the most abundant surface markings (Fig. 1). Like the Australasian microtektites and the Ivory Coast tektites, the glassy objects contain spherical bubble cavities, but no crystalline inclusions. Several of the glassy objects have elevated circular areas. In some instances, these

elevated areas are seen to be hemispherical in shape, with the rounded surface directed in toward the center of the glassy object, and are attached to a short pedestal. These caplike protrusions (Fig. 1) are probably the results of differential solution due to variations in silica content.

The refractive indices of 27 of the Ivory Coast glassy objects were determined. Three of them have rather high refractive indices ranging from 1.581 to 1.592. They are bottle green in color and have a deeply corroded and irregular, but smooth, surface and are thus similar to the bottle-green glassy objects with high refractive indices (1.582 to 1.620) that were found associated with the Australasian microtektites in two of

the cores. The remainder of the glassy objects have a range in refractive index from 1.514 to 1.542 with an average of 1.525. In addition, one spherule has a refractive index of 1.461 ± 0.002 . Electron-microprobe analysis of this spherule indicates that it is nearly pure SiO_2 . Thus the spherule is probably a lechatelierite particle. Other lechatelierite particles were found as inclusions in several of the other glassy objects. The caplike protrusions found have lower refractive indices than the remainder of the glassy object from which they protrude.

From simultaneous paleomagnetic and radiometric studies of Pliocene and recent lavas on land it has been established that the earth's magnetic field

has reversed polarity several times in the last 4 million years (4). Zones of normally and reversely magnetized sediments can be found in many deep-sea sediment cores by determining the polarity of closely spaced samples with a magnetometer (5). The resulting magnetic stratigraphy can then be used indirectly to date certain layers in the cores by correlating the reversal boundaries with those dated on land by the K-Ar method (5, 6).

The magnetic stratigraphy of the core containing the glassy objects found off the Ivory Coast was determined by the use of a spinner magnetometer designed by Foster (7). This core was taken near the magnetic equator, and therefore changes in polarity can be detected only by shifts in declination of 180° , since the inclination is of little use on the equator. Unfortunately, the core was cut into sections, and each section was split in half with a random orientation with respect to the sections above and below it. Therefore, the location of the boundaries between the various sections had to be considered in determining the magnetic stratigraphy of the core. The only 180° shift in declination not associated with one of these boundaries was observed at a depth of 490 cm. That this is indeed a reversal and, in fact, is the last reversal, is indicated by a drop in abundance of the planktonic Foraminifera *Sphaeroidinella dehiscens* just above this depth. Such a decrease in abundance of this species occurs at or just above the last reversal (8). Closely spaced samples taken below the reversal boundary at 490 cm do not reveal the presence of a Jaramillo event, however. This may be due to magnetic instability (although there is no indication of such) or to a hiatus in the sedimentary record.

Although scattered glassy objects were found as high as 40 cm above the reversal, they are most abundant in a layer 15 cm thick that occurs about 40 cm below the reversal. Extrapolation from this reversal indicates that the glassy objects were deposited about 800,000 years ago. This age is somewhat less than the K-Ar age determination of 1.2 ± 0.2 million years (9) given for the Ivory Coast tektites, but it is greater than the age of deposition of the Australasian microtektites (1). The glassy objects were most abundant in a sample taken at 540 to 543 cm. None was found below that depth. Because of the absence of a Jaramillo event, the exact age of deposition is uncertain, but seems to be about 800,000 years.

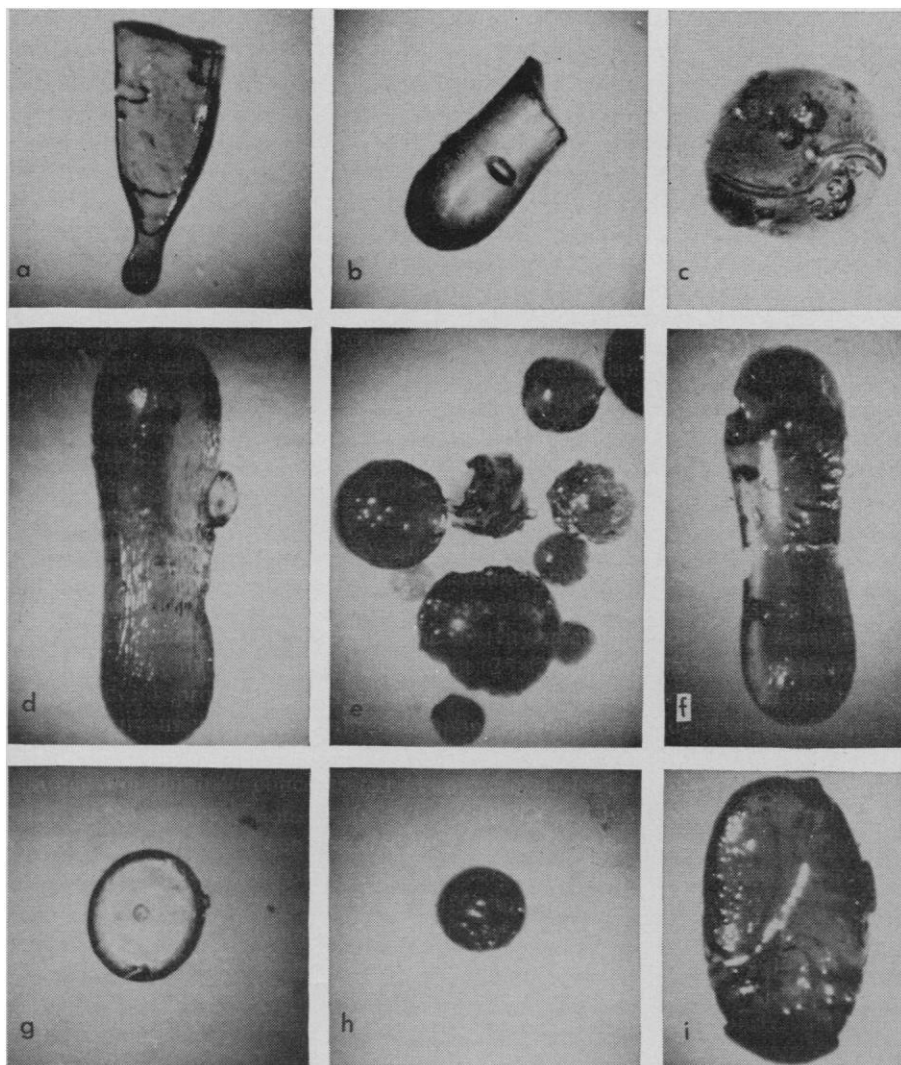


Fig. 1. Glassy objects found in deep-sea sediments from core V19-297 taken near the Ivory Coast. (a) Irregular teardrop-shaped glassy object; length 794μ . (b) Fragment of a dumbbell with large bubble cavity; length 350μ . (c) Sphere with pitted and grooved surface; diameter 280μ . (d) Dumbbell with circular caplike protrusion on right side and flow lines parallel to length of dumbbell; length 1.24 mm . (e) Group of glassy objects; largest diameter, 400μ . (f) Dumbbell with elongated grooves and pits; length 1.14 mm . (g) Disc-shaped glassy object with circular caplike protrusion on right side; maximum diameter, 180μ . (h) Opaque sphere; diameter 160μ . (i) Flattened oval-shaped glassy object with flow structure and large caplike protrusions; length 862μ .

Although the chemical composition has not yet been determined, it is suggested that the glassy objects are microtektites and that they represent a portion of the tektite-strewn field of the Ivory Coast because of (i) their geographic location near the Ivory Coast strewn field; (ii) their apparent age of deposition which is similar to, but somewhat less than, the presently accepted K-Ar age determination of the Ivory Coast tektites; and (iii) their similarity in appearance and physical properties to both the Australasian microtektites and the Ivory Coast tektites. Preliminary chemical analyses, performed with the electron-microprobe at Goddard Space Flight Center, Greenbelt, Maryland, indicate that the glassy objects are also similar to the Ivory Coast tektites in composition.

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References and Notes

1. B. Glass, *Nature* **214**, 372 (1967).
2. W. A. Cassidy, B. Glass, B. C. Heezen, "Physical and chemical properties of Australasian microtektites," in preparation.
3. V. Vand, *Advan. Geophys.* **2**, 1 (1965).
4. A. Cox, R. R. Doell, G. B. Dalrymple, *Nature* **198**, 1049 (1963); *Science* **142**, 382 (1963); R. R. Doell, G. B. Dalrymple, A. Cox, *J. Geophys. Res.* **71**, 531 (1966); I. McDougall and D. H. Tarling, *Nature* **200**, 54 (1963); F. H. Chamalaun and I. McDougall, *Nature* **210**, 1212 (1966). The present normal period of the earth's magnetic history began 700,000 years ago. From 0.7 to about 2.5 million years ago the earth's magnetic field had a polarity opposite to that of the present field, except for two short periods (approximately 50 to 150 thousand years) about 0.95 and 1.9 million years ago, called the Jaramillo and Olduvai events, respectively.
5. N. D. Opdyke, B. Glass, J. D. Hays, J. Foster, *Science* **154**, 349 (1966).
6. D. Ninkovich, N. Opdyke, B. C. Heezen, J. H. Foster, *Earth Planet. Sci. Lett.* **1**, 476 (1966).
7. J. H. Foster, *ibid.*, p. 463.
8. B. Glass, D. B. Ericson, B. C. Heezen, N. D. Opdyke, J. A. Glass, *Nature* **216**, 437 (1967).
9. J. Zähringer, in *Tektites*, J. A. O'Keefe, Ed. (Univ. of Chicago Press, Chicago, Ill., 1963), p. 137; W. Gentner, H. J. Lippolt, O. Müller, *Z. Naturf.* **19a**, 150 (1964); R. L. Fleischer, B. P. Price, R. M. Walker, *Geochim. Cosmochim. Acta* **29**, 161 (1965).
10. I thank Dr. M. Ewing, director of Lamont Geological Observatory, for having taken cores off the Ivory Coast; Dr. N. D. Opdyke, for the use of the facilities of Lamont's paleomagnetic laboratory which were used to determine the magnetic stratigraphy of core V19-297; Drs. Burckle and A. Kaneps, for help with the photographic equipment used to photograph the glassy objects; Drs. B. C. Heezen, J. A. O'Keefe, O. L. Anderson, D. B. Ericson, and J. A. Glass, for discussions and help with the manuscript; F. Wood and Dr. Walter, for help with microprobe analyses. Supported by NSF grant GA 580 and the U.S. Navy, Office of Naval Research. Lamont Geological Observatory Contribution No. 1228.

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High-Pressure Polymorphism of Titanium Dioxide

Abstract. *X-ray diffraction studies made in situ under conditions of high pressure and high temperature revealed the direct transition of rutile to the alpha lead dioxide form in titanium dioxide. Compressibility studies of this alpha lead dioxide form at room temperature showed anomalous behavior in that its molar volume converges close to, but not equal to, that of the rutile form. Under this circumstance an unexpectedly large error appears in the calculations of the equilibrium pressure for the two forms at 298°K.*

Our present knowledge of transformations of the rutile form of TiO_2 (neglecting brookite, anatase, and other "low-pressure" forms) can be summed up very briefly as follows: On shock loading the rutile form undergoes a large volume discontinuity at 0.33 megabar and is recovered in the $\alpha\text{-PbO}_2$ structure (1), some 2.8 percent denser, at 1 atm and room temperature. Thermochemical calculations (2), with the use of calorimetrically obtained data on the enthalpy of the conversion of $\alpha\text{-PbO}_2$ to rutile, placed the equilibrium at 60 ± 20 kb. This is consistent with various reported syntheses (3) of the $\alpha\text{-PbO}_2$ form. High-pressure, x-ray diffraction studies (1) showed no formation (to the limits of detection) of $\alpha\text{-PbO}_2$ from rutile at pressures as high as 0.18 Mb at room temperature. In studies on rutile-type MnF_2 , Vereshchagin *et al.* (4) found that the analogous $\alpha\text{-PbO}_2$ type could be obtained only after the rutile type had been transformed to a third (tetragonal) modification. A similar succession of phases has been reported for ZnF_2 by Kabalkina *et al.* (4). This suggested that the shock-converted TiO_2 , as well as that obtained in the quench studies (3), was derived from a third phase rather than by direct conversion from rutile. We tested this with the use of x-ray diffraction techniques carried out at high pressure and high temperature, as described elsewhere (5).

Runs were made with and without internal (pressure-measuring) standards. In the latter case the pressures were known only grossly, but a gain in pattern clarity was achieved. Patterns taken in several such runs showed the partial formation of the $\alpha\text{-PbO}_2$ form from rutile at temperatures as low as 270°C, as indicated by the presence of its strongest diffraction line, 111. Explorations at 500°C revealed no further transformations. Because of the lack of internal standards, we can only describe our pressures as being within the area of pressure-temperature space delineated by Bendeliani *et al.* (3). To improve this situation, we made one

run with NaF as an internal standard. The observed cubic cell edge of NaF was converted to that of NaCl by use of a room temperature correlation obtained earlier (5). Then, assuming this correlation to be temperature invariant, we entered the tabulation of Decker (6) for the compression of NaCl to obtain an estimate of the pressure. The first picture taken showed the $\alpha\text{-PbO}_2$ form to be present under conditions of

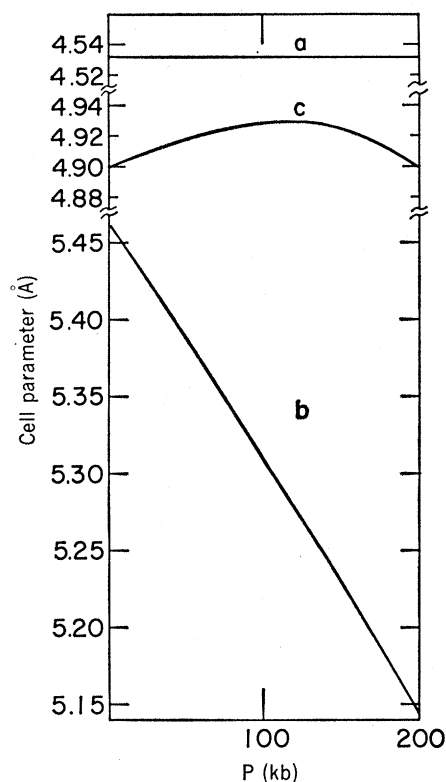


Fig. 1. The variation in the cell parameters of the orthorhombic $\alpha\text{-PbO}_2$ form of TiO_2 as a function of pressure at room temperature. Vertical scales for all three parameters are identical in order to display aberrant behavior of the axes *a* and *c*. This structure may be regarded as a linkage of distorted octahedra, and its pressure behavior is probably a function of the distortion of those chains. However, one parameter is needed to determine titanium positions and three are needed for oxygen positions. Intensity measurements at high pressures are too insensitive to obtain these parameters; therefore, any detailed discussion of atomic movement to explain the lattice parameter behavior would be speculative at this time.