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10. There is little possibility that any of the other five radiocarbon samples were so contaminated. First, if they were, it is statistically unlikely that they would form such a uniform group. Second, all charcoal pieces in the samples were very carefully selected for evidence of wood structure. And third, the only sample which did not show such structure was Y-1799, which never should have been submitted. The asphalt occurs in discrete lumps and is usually quite easy to identify; we do not yet know what is was used for, beyond the occasional decoration of figurines.
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14. Research supported by NSF grant GS-715.

8 December 1966

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Shock-Wave Compression and X-Ray Studies of Titanium Dioxide

Abstract. *The Hugoniot of the rutile phase of titanium dioxide has been determined to 1.25 megabars, and data show the existence of a phase change at about 0.33 megabar. The volume decrease associated with this transformation appears to be quite large (approximately 21 percent). Rutile, when recovered from shock-loading in excess of the transformation pressure, is found to be irreversibly transformed to the orthorhombic lead dioxide structure (a distortion of the fluorite structure) with parameters* a, *4.529;* b, *5.464; and* c, *4.905 angstroms and a calculated density of 4.374 grams per cubic centimeter. The new phase reverts to rutile at temperatures above 450°C. It is suggested that the new phase may be another diagnostic indicator of meteorite impact on the earth's surface.*

Rutile, one of the three naturally occurring polymorphs of titanium dioxide, has been studied both with explosive-generated dynamic pressures and by x-ray diffraction at static pressures. The techniques have been described in detail elsewhere (*1*). Dynamic pressure data consist of shock-wave velocities, U_s, measured in the rutile, and the associated shock-particle velocities, U_p, determined from the measured shock strength in a 2024 Al standard and the shock-wave impedance match requirements. The equation of state of the 2024 Al standard needed for this was calculated from the measured 2024 Al Hugoniot

$$U_s = 5.355 \text{ km/sec} + 1.345\ U_p$$

and a Grüneisen ratio, γ, determined from the following relation

$$\rho\gamma = \rho_0\gamma_0 = 6.17 \text{ g/cm}^3$$

where ρ is the density and the subscript 0 refers to standard conditions. Experimental shock-wave velocities are listed in Table 1 together with the particle velocities, pressures, and densities calculated from the Rankine-Hugoniot relationships. These experiments were performed on single crystals cut from boules with unknown orientations, except for two specimens made from naturally occurring polycrystalline samples from Oaxaca, Mexico. No difference in results was observed in the two types of specimens.

The isothermal (25°C) compression of rutile was measured by x-ray diffraction with the use of NaCl for an internal pressure gage (*2*). For this work a new 25°C NaCl isotherm, calculated from Hugoniot data recently measured (*3*) at the Los Alamos Scientific Laboratory, was used for a standard. The compression is not measured with as high precision as we would like because rutile is quite incompressible, with little variation in its lattice parameters. These data, Table 2, are estimated to be valid to less than 1 percent in the ratio between volume and original volume (V/V_0). They are plotted in Fig. 1 with a 25°C isotherm calculated from the Hugoniot:

$$U_s = 6.91 \text{ km/sec} + 1.47\ U_p$$

This Hugoniot was determined from the zero-pressure bulk sound velocity, 6.91 km/sec, computed from measured elastic constants (*4*) and the four low-pressure shock wave data points also plotted in Fig. 1. The x-ray and shock-wave data appear to be in good agreement and are compatible with the initial slope of the calculated isotherm determined from the elastic constants. Data of Clendenen and Drickamer (*5*) have also been plotted in this figure and are, quite obviously, in serious disagreement. They report the onset of a transition at 0.1 megabar (Mb); this is also in contradiction to the pressure-volume (*P-V*) data reported here and to additional static x-ray experiments to pressures of about 0.18 Mb, which also failed to show the existence of a transformation. These particular x-ray experiments were performed without any internal standard for maximum clarity in the films. Pressures were estimated by extrapolating the previously determined compression. We

Table 1. Hugoniot data for TiO_2 (rutile).

ρ_0 (g/cm^3)	U_s std. (km/sec)	U_s (km/sec)	U_p (km/sec)	P (Mb)	V/V_0	ρ (g/cm^3)
4.25		6.91*	0	0	1.000	
4.25	6.29	7.65	0.50	0.162	0.935	4.54
4.25	6.57	7.87	0.66	0.220	0.916	4.64
4.25	6.62	8.18	0.68	0.234	0.917	4.63
4.25	6.65	7.86	0.71	0.237	0.910	4.67
4.25	7.72	8.30	1.38	0.488	0.833	5.10
4.25	9.18	8.26	2.47	0.869	0.701	6.06
4.25	9.26	8.31	2.52	0.891	0.697	6.10
4.25	9.75	8.33	2.91	1.033	0.650	6.54
4.21†	9.86	8.51	2.98	1.068	0.649	6.49
4.25	10.08	8.74	3.11	1.157	0.644	6.60
4.25	10.10	8.77	3.13	1.165	0.644	6.60
4.25	10.11	8.76	3.13	1.165	0.643	6.61
4.25	10.28	9.06	3.22	1.242	0.644	6.60
4.20†	10.25	8.90	3.25	1.212	0.635	6.61
4.25	10.29	8.94	3.25	1.235	0.637	6.67

*Computed from elastic constants (*4*). †Natural rutile from Oaxaca, Mexico.

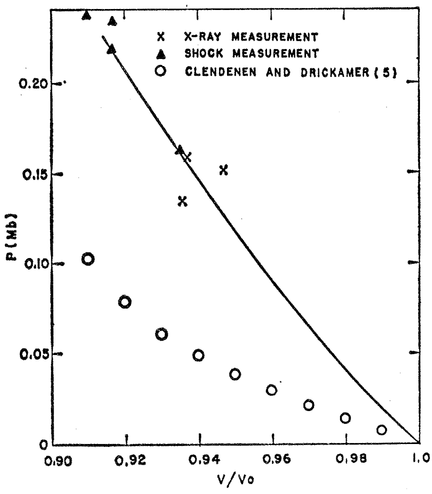

Fig. 1 (left). Isothermal compression of TiO_2 (rutile). The solid curve was calculated from the Hugoniot listed in the text and a Grüneisen ratio of 1.6. For incompressible materials like this the Hugoniot and room temperature isotherm are practically identical in this pressure range.

thus have no evidence that for pressures below 0.33 Mb rutile behaves in any other than a normal fashion.

For shock strengths above 0.33 Mb the Hugoniot data give unmistakable evidence for the existence of a phase change. This is readily seen in Fig. 2 where the shock velocity, U_s, is plotted against the shock-particle velocity, U_p. Three line segments are required to fit the data. The first, originating at the zero-pressure bulk sound velocity, goes through the low-pressure static x-ray points and shock-wave data points. The horizontal segment, drawn with a dashed line, does not represent thermodynamic states but is simply a manifestation of the two-wave structure associated with the transition. In these experiments only the arrival of the first wave is measured. The associated calculated U_p's are meaningful only in the sense that they correspond to variations of the shock strength in the original pressure pulse. The last segment is a fit of the high-pressure data made with the assumption that a transformation has occurred and that the equation of state of the new phase can be represented in the same manner as the first segment. Details of this calculation will be described elsewhere, but the main features have been outlined in interpreting the quartz-stipoverite (stishovite) transformation (*6*).

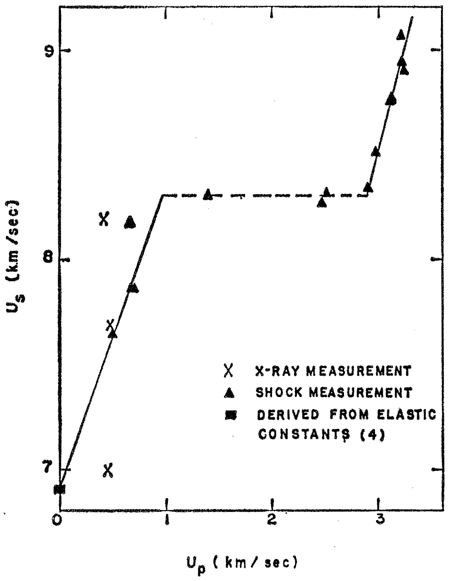

Fig. 2. The U_s-U_p Hugoniot of TiO_2 (rutile). Data points are listed in Table 1 except for those identified as arising from x-ray measurements. The isothermal *P-V* data have been transformed to U_s-U_p data through the Rankine-Hugoniot equations. The rather large scatter (more apparent in this figure than in Fig. 1) is due to the relative stiffness of rutile and the fact that this type of representation of the equation of state corresponds to a differential measurement. The scatter can be accounted for by a volume deviation of only 0.5 percent and a pressure error of 0.3 percent. The shock-wave data determine the compressibility directly and are thus inherently more accurate than measurements of the actual volume.

The *P-V* equation of state for shocked rutile is reproduced in Fig. 3 along with the derived metastable equation of state of the high-density phase. The slope of the phase line at the transition is not known and for these calculations must be guessed. Since there is evidence that the volume change is large with respect to the entropy change, we have arbitrarily used a zero slope. When transitions occur at such high pressures the effect of variation of the slope is not trivial. The effect on the density, compressibility, and volume change due to various assumptions about the slope of the phase line are given in Table 3. It should be noted that the entire region from 0.33 Mb to 1 Mb cannot be examined with the experimental techniques used here and that one has no way of knowing whether there is one large transformation in this region or perhaps several occurring at different pressure levels. The latter case must be considered as a distinct possibility when working with materials that may exist in many phases.

Single crystals of synthetic rutile were shock-loaded above the transition pressure and were recovered. The recovery system was similar to that already described (*1*) except that small [½ inch (1 cm) diameter] samples were placed in the central region. Successful recovery with this system has been made for shock pressures in excess of 0.75 Mb. Although the specimens after shock-loading had nearly the same density (approximately 4.3 g/cm^3) as the original material, it was obvious from their appearance that some irreversible mechanism had taken place. The material as recovered is milky grey and translucent in small flakes. Heating to redness causes the material to become transparent and to transform back to the rutile phase. Heating at 400°C overnight produced no apparent increase in the content of rutile but did serve to improve the quality of the diffraction pattern because of slight annealing of the shock-loading strain. Similar heating times at

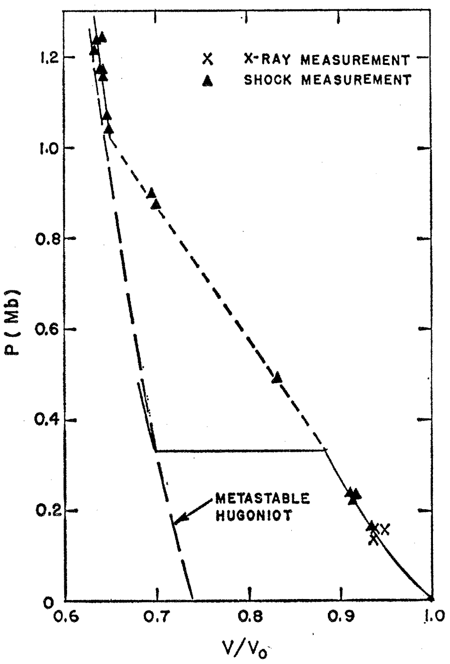

Fig. 3. Pressure-volume Hugoniot for shocked TiO_2 (rutile) and a derived metastable Hugoniot of the possible high-density phase. Beginning of the transition is determined from the intersection of the first two line segments in Fig. 2. This corresponds to a pressure of 0.33 Mb and a calculated temperature of 150°C. The flat horizontal segment represents the isothermal change in volume calculated for this transition. It should be noted that the calculation utilizes only those data points with shock velocities greater than 8.3 km/sec which corresponds to pressures over 1.0 Mb. Thus the derived Hugoniot is subject to considerable uncertainty, which in turn reflects an error in the calculated change in volume. We have assumed that the slope of the U_s-U_p Hugoniot for this Hugoniot and those listed in Table 3 is 1.25, a typical value for minerals.

450°C did increase the rutile content, while 2 hours at 500°C produced almost complete conversion. The recovered fragments showed strong preferred orientation when diffraction pictures were taken of stationary pieces. Even heating and conversion to rutile did not produce a random crystalline array.

Rough measurements of electrical resistance were made on the new material at liquid nitrogen, room, and elevated temperatures. The resistance was fairly high (in the 100,000-ohm range for a grain approximately 5 mm long and 1 mm^2 in cross section) and decreased with a decrease in temperature. The new material is hence probably a semiconductor, but this statement must be qualified. The material is a two-phase mixture, highly strained. A definitive characterization of its electrical properties must await preparation of the pure form.

Recovered material was analyzed by x-ray diffraction in 114.59 powder cameras (Sieman's) with the use of filtered copper radiation. The resultant films were readily indexed as a two-phase mixture of tetragonal rutile (in minor amount) and a new orthorhombic form (see Table 4). Diffraction lines of the sample were broadened and all back-reflection lines were missing; no diffractometer traces of very high quality could be obtained. This highly strained nature is quite characteristic of recovered shocked material in general. To obtain maximum precision in the determination of lattice parameters of the new phase, it was mixed with a small amount of diamond dust, 1 μ in size. The diamond lines served to calibrate the camera as well as to correct for film shrinkage by means of the camera's Straumanis-type film mounting. Spacings for diamond given by Swanson and Fuyant (*8*) were used for this calibration. From the indexing and intensity values in Table 4, it is proposed that the structure of the new phase is isomorphous with those of PbO_2 II and MnF_2 II, isomorphic orthorhombic distortions of the cubic fluorite structure (*9*). Both of these substances exist in the tetragonal rutile phase at room pressure and convert irreversibly to their orthorhombic phases at elevated pressures and temperatures. More recently Kabalkina and Popova (*10*) have confirmed this phase for MnF_2 and also reported its existence in ZnF_2. Still more recently, Bendeliany *et al.* (*11*) have reported quenching this phase in TiO_2 from pressures of 40 to 120 kb and temperatures from 400° to 1500°C, respectively. Hence, the identification of this orthorhombic phase for shock-loaded TiO_2 is quite plausible. Its parameters at room temperature and 1 atm are: *a*, 4.529; *b*, 5.464; and *c*, 4.905 Å. Its space group is *Pbcn*, with four molecules in the unit cell. For comparison, the parameters obtained by Bendeliany *et al.* are: *a*, 4.531 ± .001; *b*, 5.498 ± .001; and *c*, 4.900 ± .001 Å. The discrepancy is probably due to the highly strained nature of our sample and its broadened reflections. No detailed intensity calculations have been made, but the presence of lines such as 121 suggest that the oxygen atoms are in general positions. The new orthorhombic phase has a calculated density of 4.374 g/cm^3, which compares with that of 4.25 g/cm^3 for its parent rutile. A comparison of its diffraction pattern with that of a fifth TiO_2 polymorph, manufacturable from anatase at high pressure (*12*), showed strong resemblances but sufficiently distinct differences to preclude identity.

Table 2. Compression of TiO_2 (rutile) determined by x-ray technique (pressure from NaCl volume variation).

V/V_0 (NaCl)	P (Mb)	c/c_0	a/a_0	V/V_0 (TiO_2)
0.736	0.151	0.990	0.978	0.947
.752	.134	.983	.975	.936
.731	.158	.989	.974	.937

Table 3. Influence of slope of phase line on the calculated transition parameters where (*) identifies parameters of the metastable phase. C_0* is the zero-pressure bulk sound velocity.

dP/dT (kb/°K)	$\Delta V/V_{\text{trans}}$	ρ_0* (g/cm^3)	C_0* (km/sec)
−5	0.15	5.3	9.1
0	.21	5.8	9.9
5	.29	6.5	11.1

The recovery of this new phase of TiO_2 from shock conditions does not necessarily imply that it is the phase indicated in Fig. 2 to which rutile transforms on shock-loading. Vereshchagin *et al.* (*13*) have shown that in rutile-type MnF_2 a new phase appears upon application of pressures above 20 to 30 kb which they have identified as being close to the structure of ZrO_2 in its tetragonal modification. It is only on release of pressure that the orthorhombic α-PbO_2 form appears. The total volume change of MnF_2 (from its value at 1 bar to its tetragonal form) is about 18 percent. This is in agreement with the volume change of 21 percent, as calculated from the shock-wave data. Another possible structure of slightly greater density would be the fluorite structure, since ZrO_2 can exist in a cubic arrangement (*14*) which is 1 percent more dense than the tetragonal distortion. Moreover, in several fluorite-type structures

Table 4. X-ray diffraction pattern of recovered shocked titanium dioxide showing identification as two-phase mixture. Calculated *d* values for the orthorhombic phase are from parameters in the text. The observed rutile values are from Swanson and Tatge (7). Int. is intensity; S, strong; M, moderate; and W, weak.

Orthorhombic				Rutile		
hkl	d_{calc} (Å)	d_{obs} (Å)	Int.	*hkl*	d_{obs} (Å)	Int.
110	3.486	3.494	S			
		3.227	M	110	3.245	100
111	2.842	2.849	S+			
020	2.732	2.739	W−			
002	2.453	2.469	M	101	2.489	41
021	2.387	2.386	W			
200	2.265	2.273	W−	200	2.297	7
102	2.157	2.164	W+	111	2.188	22
121	2.111	2.109	M			
		Not obs.		210	2.054	9
112	2.006	Not obs.				
022	1.825	? Blur				
220	1.743	1.743	W+			
122 130	1.693 1.690	1.693	S−			
202	1.664	1.663	S−	211	1.687	50
221	1.643	1.642	S−			
113	1.480	1.477	W	002	1.480	8
		Not obs.		310	1.453	6
222	1.421	Not obs.				
311	1.395	1.399	M			
132	1.391	Not obs.				
		Not obs.		310	1.360	16

such as CaF_2, CdF_2, and BaF_2, there also exist transitions at high pressures (*15*) to the still denser (about 10 percent) orthorhombic $PbCl_2$-type structure. These might be even more dense than the phase of TiO_2 reached under shock compression, but no positive identification can be made at this time. Similar possibilities exist for the recovery of TiO_2 in the α-PbO_2 structure in the static experiments of Bendeliany *et al.* (*11*), or again this may be a metastable quench product. This seems characteristic of the occurrence of the α-PbO_2 structure in RX_2 compounds.

Another material in the rutile phase, the mineral stipoverite, has become of considerable geologic interest since it has been found at impact sites of meteorite craters, apparently produced by the impact shock. Hence it is possible that this new phase may be of interest because of the common occurrence of rutile as a constituent mineral of sedimentary rocks. Rocks of this type that have been subjected to impact may yield minor quantities of the new orthorhombic phase. The behavior of shocked rutile when considered along with that of quartz (*16*) should give additional evidence of shock conditions. As distances are traversed outward from the point of impact, the new phase should be found coexisting with stipoverite and silica glass (relict of stipoverite) until the shock pressure is decreased below that required for its transformation.

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20 December 1966

Silica in Sea Water: Control by Silica Minerals

Abstract. *Silicate minerals typical of those carried in the suspended load of streams release silica to silica-deficient sea water and abstract silica from silica-enriched sea water. Experimental rates of release and uptake permit the conclusion that the suspended solids carried into the oceans by streams are a major control of the concentration of silica in the ocean.*

This report shows that silicates typical of those carried in the suspended load of streams release dissolved SiO_2 to silica-deficient sea water and take up dissolved SiO_2 from silica-enriched sea water. Experimental concentrations of dissolved SiO_2 in sea water after reaction with silicates are approximately the same as those in the oceans.

We have shown (*1*) that several common silicates rapidly released dissolved SiO_2 to silica-deficient [SiO_2 (aqueous) $\cong$ 0.03 ppm, initially] sea water, and that the final concentrations obtained were near the average concentration of dissolved silica of the ocean [SiO_2 (aqueous) $\cong$ 6 ppm]. We concluded that the ocean must be considered as a chemical system with a rapid response to the detrital silicates carried in by streams.

Our experiments were designed to see whether typical silicates extract dissolved silica from sea water "enriched" with silica. One-gram ($< 62\ \mu$) samples of the minerals kaolinite, montmorillonite, illite, chlorite, muscovite, and glauconite were added separately to 200 ml of silica-enriched [SiO_2 (aqueous) $\cong$ 25 ppm] sea water in polyethylene containers. The sea water was initially

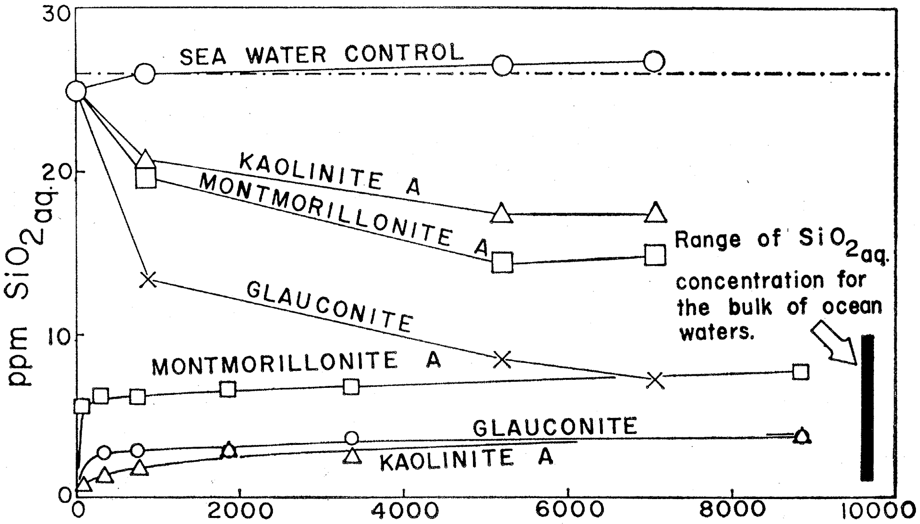

Fig. 1. Concentration of dissolved silica as a function of time for suspensions of silicate minerals in sea water. Curves are for 1-g ($< 62\ \mu$) mineral samples in 200 ml of silica-deficient (SiO_2 in water was initially 0.03 ppm) and silica-enriched (SiO_2 was initially 25 ppm) sea water at room temperature. Size of symbols indicates precision of SiO_2 determinations. Dash-dot line shows minimum SiO_2 concentration of sea water in equilibrium with a hydroxylated magnesium silicate at the *p*H's of our experiments.