Table 3. Cerium-144, cesium-137, and strontium-90 in samples of patent flour and whole wheat bread, obtained from different locations in 1963.

Sample type	Sampling month	Content of original material (pc/kg)		
		Ce^{144}	Cs^{137}	Sr^{90}
	New York			
Flour	May	15	87	24
Flour	August	10	86	18
Bread	August	17	116	28
	Chicago			
Flour	April	18	35	11
Flour	July	17	45	28
Bread	July	4	122	47
	San Francisco			
Flour	June	9	40	7
Flour	Sept.	8	40	23
Bread	Sept.	19	36	28

values previously found in the patent flour fraction for each of these nuclides for a 1962 Kansas wheat sample (*10*).

Measurements of Ce^{144} and Cs^{137} in patent flour and whole wheat bread samples taken from the open market in three U.S. cities are reported in Table 3. The results for Sr^{90} are listed for comparison. All values are extrapolated to the middle of the month during which the sample was obtained. These samples, though collected in 1963, are not considered representative of the 1963 wheat crop. However, if the milling products on the open market each year are the result of the previous year's harvest, it may be assumed that these products are from the 1962 wheat crop. If this assumption is valid, samples of patent flour and milling products reaching the open market in 1964 will contain more Ce^{144} and Cs^{137} than is reported in Table 3. This prediction seems valid since there is more Ce^{144} and Cs^{137} in the 1963 wheat crop than was reported for wheat samples from the 1962 crop (*10*).

The measurements of Ce^{144} and Cs^{137} reported here were determined by means of radiochemical methods. The procedure, which was reported in detail elsewhere (*11*), was as follows. Cerium and cesium carriers were added to 10 g of dry-ashed sample and equilibrated with Ce^{144} and Cs^{137} by extraction with hydrochloric acid and hydrogen peroxide. Cesium was separated by batch adsorption on ammonium phosphomolybdate and isolated from the alkali metals by selective elution from a phenolsulfonic acid cation exchange resin. After precipitation as cesium tetraphenylborate, Cs^{137} was measured by beta counting under standard conditions with a thin-window Geiger-Muller counter.

After removal of cesium phosphomolybdate, the rare earth and alkaline earth groups were collected as oxalates from the filtrate and ignited to oxides. The two groups were separated by precipitation of the rare earths as fluorides in hydrochloric acid (8*M*). Cerium-144 was isolated from the trivalent rare earths after oxidation with sodium bromate, and was precipitated as iodate. The disintegration rate of Ce^{144} was determined from the counting rate (through 232 mg/cm^2 aluminum absorber) of Pr^{144} under standard conditions with a Geiger-Muller counter. The purity of each nuclide was established by beta absorption measurements. Average chemical recoveries were 82 and 90 percent, respectively, for cerium and cesium. The error due to counting for the tabulated values is within 5 percent.

Material balances of a Kansas wheat sample with its milling fractions show good agreement for both Ce^{144} and Cs^{137} (Table 2). The patent flour fraction contained approximately 10 and 15 percent of the measured Ce^{144} and Cs^{137}. Larger amounts, approximately 45 and 40 percent, respectively, of Ce^{144} and Cs^{137} were found in the bran fraction, which contains the outer layers of the wheat grain. Sampled patent flour and whole wheat bread from three cities contained more Cs^{137} than Sr^{90}, the average Cs^{137}/Sr^{90} ratio for flour and bread being 3.4 and 2.7, respectively. These ratios are not consistent with average ratios reported for rainfall or soil deposition, about 1.7, so that factors other than direct deposition are indicated.

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Magnesium Compounds: New Dense Phases

Abstract. *Magnesium silicide (Mg$_2$Si) undergoes a transformation from a cubic (fluorite) type lattice to a hexagonal lattice at pressures above about 25 kilobars and temperatures above 900°C. There is an increase of density of about 15 percent associated with this structure change. Both the parent and product substances are semiconductors, but of different resistivities. The high pressure phase may be recovered and is indefinitely metastable at normal ambient conditions.*

That substances crystallizing in the fluorite and antifluorite (F_m3_m) lattices might exhibit polymorphic transformations has not previously attracted attention. It is possible that such substances, and particularly intermetallic compounds in this structure class, could undergo any or all of the following types of transformation, but it is not possible to predict which one: (i) a martensitic type transformation to a hexagonal phase, (ii) a polymorphic transformation based on either component, A or B, in such AB$_2$ compounds, and (iii) a second transformation based on the other of the two components. This set of possibilities has been investigated for the interesting semiconducting materials Mg$_2$Si, Mg$_2$Ge, and Mg$_2$Sn, the physical variables employed being the application of high pressures (> 20 kb) and high temperatures (up to $\sim$ 1500°C). New phases of all three substances have been found. All are indefinitely metastable (for more than a year) at ambient conditions after release of the experimental pressures.

The compounds used were vacuum-cast in graphite molds from chemically pure starting materials by J. Kiesler, W. Moore, and W. Baxter of this laboratory. All samples showed a bright, silvery fracture surface when new, but on exposure to summer air, they more or less rapidly became covered with a blue (oxide) film, and foul-smelling hydrides were evolved. The samples were further prepared for examination at high pressure and high temperature by grinding under mineral oil; the suspension thus formed was broken by adding petroleum ether, and the finely crushed solid was then washed repeatedly with this solvent. The powder was dried and transferred to the high-pressure cell only a few minutes before the actual transformations were made. Portions of the original samples were reserved for x-ray, chemical, and metallographic comparisons with the processed material.

Fig. 1. Ordered lamellae of the hexagonal, high-density form of Mg_2Si, formed from a dendrite of normal material in a field of excess silicon. Reaction conditions were 900°C, 30 kb for 5 minutes. The specimen was deliberately held below its melting point during this experiment.

Table 1. X-ray diffraction data for the new dense forms of Mg_2Si, Mg_2Ge, and Mg_2Sn. The *hkl* indices are assigned on the basis of the following diffraction lattices: Mg_2Si, hexagonal, $a = 7.20$Å, $c = 8.12$Å; Mg_2Ge, hexagonal, $a = 7.20$Å, $c = 8.24$Å; Mg_2Sn, hexagonal, $a = 13.09$Å, $c = 13.44$Å. In the case of Mg_2Sn, a less superior fit can be obtained to a lattice isomorphous with that of the new Mg_2Ge, but with $a = 7.6$Å. All the starting materials have an antifluorite lattice (*3*). The increase in density associated with the transformations is from 2.02 to 2.35 g/cm³ (Mg_2Si), and from 3.09 to 3.35 g/cm³ (Mg_2Ge). The increment for Mg_2Sn is not yet known accurately. Commonly, the x-ray patterns also show lines arising from MgO, Si, Ge, Sn, SiO_2 (α-quartz), and GeO_2 (tetragonal), where they may be expected to be formed.

Mg_2Si			Mg_2Ge			Mg_2Sn		
Intensity	*d*, Å	*hkl*	Intensity	*d*, Å	*hkl*	Intensity	*d*, Å	*hkl*
M*	3.55	110	S	3.60	110	W	4.5	003
S	3.40	101	MS	3.50	101	M	3.80	300
MW	2.80		MW	2.90		M	3.70	112
MS	2.70	111	M	2.72	111	W	3.11	213
M	2.46	201	VW	2.60		M	2.65	223
WS	2.34	210	S	2.50	201	M	2.60	320
W	2.20		M	2.06	002, 300	W	2.50	304
M	2.05	300	M	2.05	211	W	2.26	323
MW	2.03	002, 211	M	1.98		M	2.20	
			M	1.90		MW	2.16	404
			M	1.80	220	MW	1.91	007
			W	1.73	310	W	1.84	117
			W	1.68		W	1.80	521
			MW	1.56	212	W	1.66	416
			MW	1.47	401	MW	1.44	703
						W	1.35	731
						M	1.22	823

* VW, W, M, and S stand for very weak, weak, medium, and strong intensity lines, respectively.

The high-pressure equipment was a uniaxial "Belt"-type apparatus. The calibrations used were those of Kennedy and LaMori (*1*) for pressure at room temperature, while H. M. Strong of this laboratory furnished a thermal calibration at pressure based on latent-heat arrests in the melting curves of nickel and iron. The onset of the graphite-diamond reaction in the presence of pure Ni was also used as a calibration at simultaneous high pressures and temperatures.

The samples were contained in capsules of tantalum or titanium placed in alumnia crucibles which in turn were placed in graphite furnace tubes. Thermal insulation of this assembly from the Carboloy apparatus was provided by spools of pyrophyllite. This configuration has been previously referred to as the "indirectly heated cell" (*2*).

Some experiments were done with an alloy of 50 (atomic) percent Mg and 50 (atomic) percent Si at 30 kb, 900°C for 5 minutes. The original material had a markedly dendritic structure, which seemed to persist to some extent in the transformed sample provided that no melting had been allowed to occur. However, the transformed sample also gave a texture remarkably like that of a martensitic steel, showing ordered lamellae of a new phase, with the ordering especially well developed within the faintly visible outlines of the original dendrites (Fig. 1). Examination by x-ray diffraction showed a new and characteristic lattice while float-density measurements showed that a markedly more dense phase had been formed. In subsequent experiments with the compound Mg_2Si, a homogeneous product showing only the new x-ray diffraction behavior was obtained.

With Mg_2Ge or Mg_2Sn rather than Mg_2Si, new phases were found in each after exposure to temperatures of 600° to 1200°C, and pressures of 25 to 55 kb. The x-ray results are summarized in Table 1. All three sets of data may be indexed on the basis of hexagonal lattices.

Transformation occurred readily in all three substances. The rates of transformation were much higher at temperatures above those required for melting, and large grains of the new phases were formed on cooling.

The new forms of each of the substances Mg_2Si, Mg_2Ge, and Mg_2Sn have resistivities in the "semiconducting" range, 10^{-1} to 10^4 ohm cm. All of the new forms exhibit a markedly greater resistance to attack by moist air or dilute mineral acids than the parent materials.

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X-ray Diffraction Data on Two High-Pressure Phases of Calcium Carbonate

Abstract. *X-ray diffraction studies conducted at high pressure with a beryllium pressure vessel show that compression parallel to the* c*-axis of $CaCO_3$-I (calcite), as the phase boundary of $CaCO_3$-II (modified calcite type) is approached, results in a relative reduction of the* c*-axis of phase II of several times that of the* a*-axes. Such data are not consistent with previously proposed anion disorder in $CaCO_3$-II. At 18.7 ± .5 kb and room temperature a new phase of $CaCO_3$ has been observed that is assumed to be phase III found by Bridgman. At this pressure the x-ray diffraction pattern can be indexed as orthorhombic KNO_3-IV type, with $a_0 = 8.90 \pm .01$ Å, $b_0 = 8.42 \pm .01$ Å, and $c_0 = 7.14 \pm .01$ Å (Z = 10).*

The stability regions of $CaCO_3$-II and $CaCO_3$-III with respect to calcite ($CaCO_3$-I) have been worked out by Bridgman (*1*); it was his conclusion that both phases II and III were minor modifications of a calcite structure. Jamieson (*2*) also came to this conclusion from high-pressure x-ray studies of $CaCO_3$ for which he used a single crystal diamond bomb. Jamieson further suggested that the triangular carbonate groups of the phase II structure were in a state of rotational disorder similar to the high-temperature disorder transformations observed in the alkaline earth carbonates by Lander (*3*), and in $NaNO_3$ by Siegel (*4*). Until now, virtually nothing has been learned about the $CaCO_3$-III structure.

The apparatus used in the study reported here consisted of a supported beryllium pressure vessel modified for heating to 600°C. The vessel and press were mounted on the goniometer of a Norelco x-ray diffraction unit; diffraction patterns could thus be obtained from the sample while it was subjected to elevated temperatures and pressures. The vessel design and experimental procedure were described in detail previously (*5*). Pulverized Iceland spar (*6*) or synthetic reagent-grade $CaCO_3$, diluted with cornstarch (*7*), was compressed into thin (less than 1 mm) pellets for sample material.

One of the purposes of this study was to investigate further the possibility of rotational anion disorder in $CaCO_3$-II. In such a process all diffraction peaks with l odd should disappear at the transition inasmuch as the c-axis of the original calcite structure would be halved. Lander (*3*) has shown that such disorder exists in the aragonite-type alkaline-earth carbonates and with increasing temperature results in a marked expansion of the direction (c-axis) normal to the carbonate layers of the structure. Siegel (*4*) also recognized anion disorder in calcite-type $NaNO_3$ with similar expansion of the c-axis (also the direction normal to the anion layers in this structure). This expansion is proportionally much greater than the expansion along other axial directions in these structures, and appears to result from electrostatic repulsion of oxygen ions in "overlap" with cations or other oxygen ions as rotation of the anion groups takes place (*3*, p. 899).

If such disorder exists in $CaCO_3$-II, as Jamieson suggests, then one would expect expansion along the c-axis either at the transition point or as the transition point is approached, depending on whether the transformation is abrupt or gradual.

Table 1. Effect of pressure on the differences in Bragg angle and interplanar spacings for 104 and 006 of calcite.

Internal pressure (kb)	$2\theta_{006} - 2\theta_{104}$ (deg. MoKα)	$d_{006} - d_{104}$ (Å)
0	0.88	−0.092
3.5	0.92	−0.096
7	0.93	−0.097
11	0.95	−0.099
15.5	1.02	−0.106

Table 2. X-ray diffraction data for $CaCO_3$-III at 18.7 ± 0.5 kb and 25°C.

hkl	$d_{\text{obs.}}$ Å	$d_{\text{calc.}}$ Å	I/I_0*
020†	4.22	4.21	10
002†	3.57	3.57	20
220	3.02	3.06	100
030†	2.81	2.81	100
212	2.65	2.64	5
131	2.53	2.51	10
230†	2.37	2.37	15
302	2.28	2.28	10
400†		2.23	
023	2.08	2.07	5
223	1.88	1.88	2
402†		1.89	
313	1.81	1.81	10
042		1.81	
033†		1.81	
412†		1.84	
051	1.64	1.64	5
520		1.64	
024		1.64	

* Relative heights of the peaks. † Indices in common with pattern for KNO_3-IV.

Therefore, several records of the 113 peak of calcite were obtained with increasing pressure up to 15.5 kb at which time this peak could no longer be detected. The transition pressure measured by Bridgman (*1*) is 14.6 kb. The 113 peak was easily recognized at 3.5, 7, and 11 kb. In addition to the loss of 113, a marked difference in the amount of shifting of the 104 and 006 peaks was observed. These data, given in terms of $\Delta 2\theta$ and Δd for one of the experiments, are presented in Table 1, and demonstrate a large contraction of the c-axis relative to the a-axes, rather than expansion. To interpret the data in Table 1 correctly, one should recognize that, for a hexagonal crystal, if $(\Delta c/c_0) \geqq (\Delta d/d_0)_{h0l}$ then $(\Delta a/a_0) \leqq (\Delta d/d_0)_{h0l} \leqq (\Delta c/c_0)$, regardless of the values of the indices h and l (except that they are not both zero). It is also important to note that

$$\lim_{\frac{h}{l} \to 0} \left(\frac{\Delta d}{d_0}\right)_{h0l} = \frac{\Delta c}{c_0}$$

and that

$$\lim_{\frac{l}{h} \to 0} \left(\frac{\Delta d}{d_0}\right)_{h0l} = \frac{\Delta a}{a_0}$$

For the present case not only is d_{006} smaller than d_{104} (as shown by the negative values of the right-hand column of Table 1) but the decrease in d_{006} is