Table 3. DDT recovered in August 1960 from soil of experimental stand 4, Maine, sprayed in June 1960 with 3.57 kg of DDT per hectare (4 lb/acre). The stand had never been sprayed before June 1960.

Soil horizon	August 1960
A_{00}	0.034 ± .019
A_0	.013 ± .012
A_2	.080 ± .027
B_2	0
Total	.127 ± .037

than the 10 years previously estimated (*5*).

There is at present no evidence that the persistence of DDT residues in soils is affecting plant populations in any measurable way (*8*). There is abundant evidence, however, that food chains are contaminated in various ways, and the persistence of residues of DDT in soils for as much as a decade is ample reason to examine the cycling of this and other noxious products through ecological systems with great care.

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References and Notes

1. R. F. Morris (Ed.), *Mem. Entomol. Soc. Can.* **31** (1963).
2. H. J. Lutz and R. F. Chandler, Jr., *Forest Soils* (Wiley, New York, 1946); G. Downing and L. B. Norton, *Anal. Chem.* **23**, 1870 (1951); M. S. Schechter, S. B. Soldway, R. A. Hayes, H. L. Haller, *Ind. Eng. Chem. Anal. Ed.* **17**, 704 (1945).
3. Conversion factor: 1 kg/ha = 1.121 lb/acre.
4. T. F. West and G. A. Campbell, *DDT and Newer Persistent Insecticides* (Chemical Publishing Company, New York, 1952).
5. G. M. Woodwell, *Forest Sci.* **7**, 194 (1961). G. L. Mack, New York State Agricultural Experiment Station, Geneva, has pointed out that the residues reported here as *ortho-para* isomer may include DDE [1,1′-dichloro-2,2′-bis(*p*-chlorophenyl)ethylene] which is usually present in soils and cannot be distinguished from *ortho-para* DDT by the Schechter technique.
6. E. P. Lichtenstein and K. R. Schultz, *J. Econ. Entomol.* **52**, 124 (1959); E. P. Lichtenstein and J. B. Polivka, *ibid.*, p. 289; E. P. Lichtenstein, L. J. DePew, E. L. Eshbaugh, J. P. Sleesman, *ibid.* **53**, 136 (1960); E. F. Taschenberg, G. L. Mack, F. L. Gambrell, *Agr. Food Chem.* **9**, 207 (1961); W. E. Fleming and W. W. Maines, *J. Econ. Entomol.* **46**, 445 (1953); and others.
7. J. M. Davis and K. R. Elliott, *ibid.* **46**, 696 (1953).
8. G. M. Woodwell, *Ecology* **43**, 396 (1962).
9. This study was supported by the Conservations Foundation. Various people and organizations have contributed to the study over a period of four years. These include personnel of the New Brunswick International Paper Company, the Forest Pathology and Entomology Laboratory at Fredericton, N.B., Robley Nash of the Maine Forest Service, H. E. Young and Duncan Cameron of the University of Maine, and F. H. Bormann of Dartmouth College.

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13 April 1964

High-Pressure Polymorph of Iron

Abstract. *An x-ray diffraction study of iron under pressure has shown that alpha-iron (body-centered cubic) transforms to hexagonal-close-packing (designated epsilon-iron) at 130 kb, room temperature. The volume change for the transformation is − 0.20 ± 0.03 cm³/mole. The slope for the gamma-epsilon phase boundary has been calculated to be 2 ± 1°C/kb. The molar volume of iron decreases from 7.10 cm³/mole (density = 7.85 g/cm³) at room pressure to 6.10 ± 0.08 cm³/mole (density = 9.1 ± 0.1 g/cm³) at 200 kb and room temperature. The extrapolation of the gamma-epsilon phase boundary, consistent with shock wave data, suggests that it may have an influence on the properties of the earth's core.*

Three polymorphic phases of iron have been recognized: α-iron (body-centered cubic) is stable below 906°C at room pressure, γ-iron (face-centered cubic) is stable between 906°C and 1401°C, and δ-iron (body-centered cubic) is stable between 1401°C and 1530°C, the melting temperature of iron at room pressure. The effect of pressure on the phase boundary between α- and γ-iron has been investigated over a wide range of pressures by means of dilatometry by Birch (*1*), electrical resistivity by Kaufman *et al.* (*2*) and Clougherty and Kaufman (*3*), heat of transformation by Kennedy and Newton (*4*), thermal conductivity by Claussen (*5*), and shock wave propagation by Bancroft *et al.* (*6*) and Johnson *et al.* (*7*). The results of these studies have established that the temperature of the α–γ iron transformation decreases with increasing pressure. The electrical resistivity study of Balchan and Drickamer (*8*) has shown that there is a phase transformation at 130 kb at room temperature. It was considered that, because of the negative slope of the phase boundary, the γ-iron might become the stable phase above 130 kb at room temperature. On the other hand, Johnson *et al.* (*7*) showed that a sharp change occurs in the slope of the α–γ phase boundary at 110 kb and 502°C, and proposed that this inflection point represents a triple point for alpha, gamma and X phases. Jamieson and Lawson (*9*), and Jamieson (*10*) made an attempt to identify this high pressure phase by x-ray diffraction. Working with one diffraction line and the volume change for the phase transformation obtained by Bancroft *et al.* (*6*), they postulated that the high-pressure phase has a hexagonal-close-packed structure. However, the evidence was inconclusive. The purpose of the study reported here was to confirm their hypothesis.

A mixture of powdered iron (purity, 99.8 percent) and sodium chloride was placed between two flat faces (0.5 mm diameter) of diamond anvils in an instrument similar to the one designed by Van Valkenburg (*11*) for his optical work. A finely collimated x-ray beam (0.1 mm diameter, MoKα radiation) was directed to the specimen through the diamond anvil, and the diffracted x-rays were recorded on a flat photographic film. The sodium chloride serves two purposes, being a pressure-transmitting medium and an internal standard for pressure measurements. The pressure to which the specimen was subjected was calculated from the lattice dimensions of the sodium chloride and the available data on density obtained by Bridgman (*12*) for up to 40 kb and by Christian (*13*) for above 40 kb. A 20°C isothermal pressure-volume relation of sodium chloride was derived by Christian from his shock-experiment data by assuming the constancy of the heat capacity and $(\partial P/\partial T)_v$ over the pressure range of present interest. The uncertainty of the pressure-volume relations of Christian is ± 3 percent, and the overall uncertainty of the pressure values reported in this paper is ± 9 percent. Although Evdokimova and Vereshchagin (*14*) reported an extremely sluggish phase transformation of sodium chloride to a cesium chloride type structure below 18 kb, such a transformation was not observed by us.

The photographic records of x-ray diffraction obtained at room pressure,

Table 1. X-ray diffraction data of iron at 192 ± 18 kb and room temperature. MoKα radiation; zirconium filter. Unit cell dimensions were: $a = 2.45 \pm 0.01$ Å, $c = 3.93 \pm 0.01$ Å, $c/a = 1.61$. Molar volume = 6.16 ± 0.08 cm³/mole density = 9.1 ± 0.1 g/cm³. Compressibility $(\beta_{192}) = -(1/V_0)(\partial V/\partial P)_{20°C} = 4.94 \times 10^{-7}$ compressibility at 1 bar and 20°C $(\beta_0) = 5.94 \times 10^{-7}$.

I/I_0	d (Å)	(hkl)	Phase
	2.50	(200)	NaCl std.*
2	2.12	(100)	ε
8	1.97	(002)	ε
10	1.84	(101)	ε
1	1.44	(102)	ε
1	1.234	(110)	ε
1	1.113	(103)	ε

* NaCl internal standard.

130 kb, and 192 kb at room temperature are shown in Fig. 1 (top, middle, and bottom, respectively). At room pressure (Fig. 1, top), three diffraction lines of α-iron, (110), (200), and (211), are clearly discernible. At 130 kb a new line appears just outside the (110) line of α-iron. In Fig. 1 (bottom) taken at 192 kb, the diffraction lines of α-iron have disappeared completely, and the six lines present are all attributed to the high-pressure phase. This pattern has been identified and indexed as hexagonal-close-packing (Table 1). The intensities of the outer lines as reported in Table 1 are reduced by the flat film geometry, otherwise the intensities are consistent with the expected intensities for hexagonal-close-packing. This high-pressure polymorph has been designated ε-iron, analogous with the epsilon phase of cobalt which has a hexagonal-close-packed structure at room pressure and temperature.

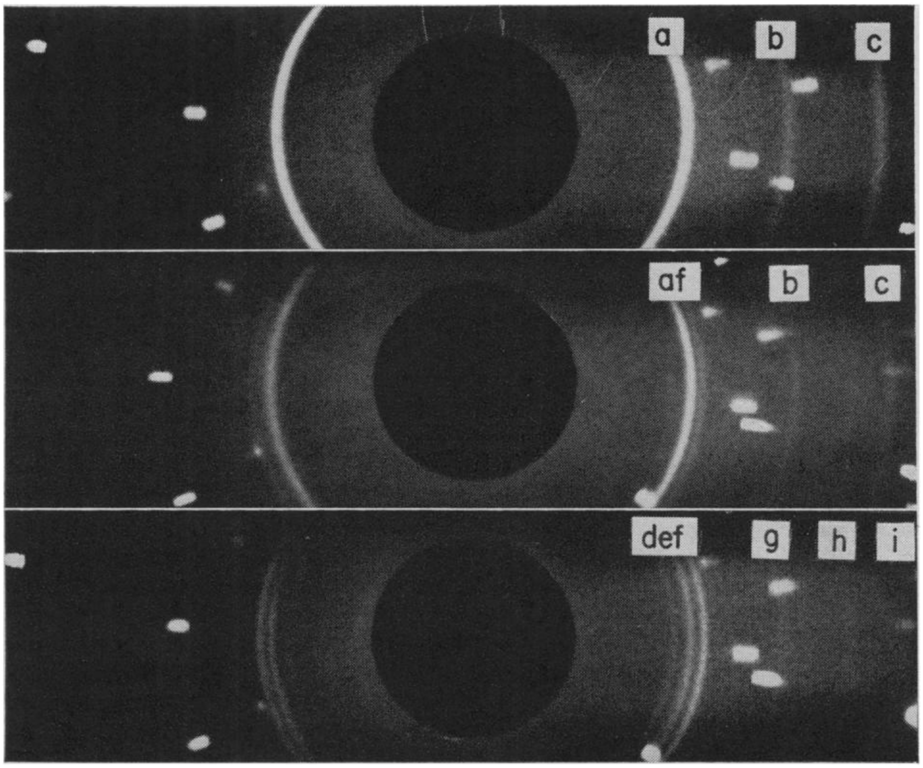

Fig. 1. (Top) Photographic record of x-ray diffraction of iron at room pressure and temperature. The diffraction lines are a = (110) of α-iron, b = (200) of α-iron, and c = (211) of α-iron. (Middle) X-ray diffraction of iron at 130 kb and room temperature. The diffraction lines a, b, and c are the same as in (top), and f, (101) of ε-iron, appears just outside a. (Bottom) X-ray diffraction of iron at 192 kb and room temperature. The diffraction lines are all of ε-iron: d = (100), e = (002), f = (101), g = (102, h = (110), and i = (103).

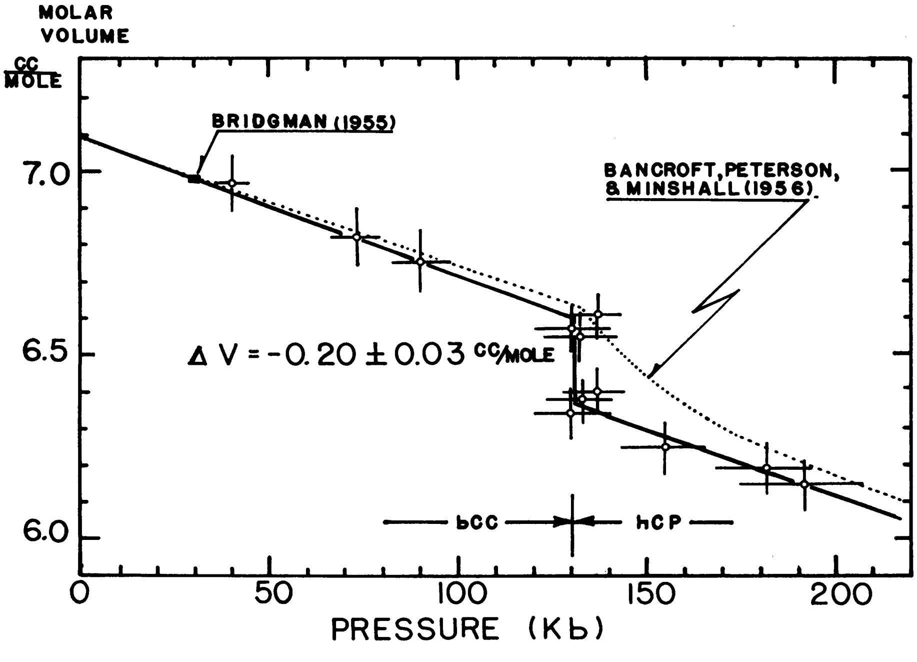

Fig. 2. The molar volume of iron up to 200 kb at room temperature (20° ± 2°C). bCC, body-centered cubic; hCP, hexagonal-close-packed structure.

An x-ray diffraction photograph obtained during an 18-hour exposure period immediately after the pressure was raised above 130 kb showed no lines of α-iron. Upon reduction of pressure, the sample reverted completely from the ε-phase to the α-phase during 18 hours of exposure to x-rays. In a shock wave experiment, the high-pressure phase of iron is detected during an interval of microseconds. Therefore, the α–ε transformation appears to be reversible and rapid.

The effect of pressure on the molar volume of iron is plotted in Fig. 2 along with the data of Bridgman (*15*) and those of Bancroft *et al.* (*6*). Figure 2 shows that below 130 kb our results agree with those of Bridgman and Bancroft *et al.* within 0.5 percent. Above 130 kb, where ε-iron is stable, there are marked differences between our results and those of Bancroft *et al.* The discrepancy at the pressures above 130 kb is probably due to smearing of the phase transformation under the shock conditions used by Bancroft *et al.* Above 170 kb the data of Bancroft *et al.* appear approximately 1 percent higher than our results. Although this difference is not quite outside the experimental uncertainties of our work, it may indicate the thermal expansion of the specimen by adiabatic heating during the shock wave experiments.

The change in volume for the α–ε transformation has been determined from three independent runs to be $-$ 0.20 ± 0.03 cm^3/mole at 130 kb and room temperature. This value is in good agreement with the value, $-$ 0.25 cm^3/mole, obtained by Bancroft *et al.* (*6*) by shock wave techniques.

The shock wave study by Johnson *et al.* (*7*) indicated a triple point of three iron polymorphs at 110 kb and 502°C (775°K). Comparing their data with others obtained under static pressures, they commented that their temperature estimations might be 10° to 50°C too high because of the adiabatic nature of the shock wave experiments. If the α–γ boundary obtained by Johnson *et al.* (*7*) is reduced by 50°C, it can be brought into agreement with the data of Clougherty and Kaufman (*3*), Kennedy and Newton (*4*), and Claussen (*5*). The α–γ phase boundary shown in Fig. 3 was obtained by subtracting 50°C from the data of Johnson *et al.*, and the α–ε phase boundary was also obtained by subtracting 25°C from the α–X phase boundary of Johnson *et al.* (*7*). The triple point can be best estimated to be at 110 kb and 477°C (750°K).

If Clapeyron's equation is applied to the triple point, the slope of the γ–ε phase boundary can be expressed by

$$dT/dP_{\gamma\to\varepsilon} = \{[(V_\varepsilon - V_\alpha) - (V_\gamma - V_\alpha)] \times (dT/dP_{\alpha\to\varepsilon})\,(dT/dP_{\alpha\to\gamma})\} \div [(dT/dP_{\alpha\to\gamma})\,(V_\varepsilon - V_\alpha) - (dT/dP_{\alpha\to\varepsilon})\,(V_\gamma - V_\alpha)],$$

where V is molar volume, T is absolute temperature, and P is pressure. The slope of the phase boundaries for α–γ and α–ε were estimated from the data of Johnson *et al.* (*7*) to be − 2.6°K/kb and − 93.5°K/kb, respectively. According to Kaufman *et al.* (*2*), for temperatures below 1200°K,

$$(V_\gamma - V_\alpha) = -0.312 + 2 \times 10^{-4}\,T \text{ cm}^3\text{/mole}.$$

Substituting the temperature of the triple point, 750°K, into this equation, the volume change associated with the α–γ transformation is calculated to be −0.16 cm³/mole. If this is assumed to be independent of pressure, the slope of the γ–ε phase boundary can be computed to be 2 ± 1°K/kb (Fig. 3).

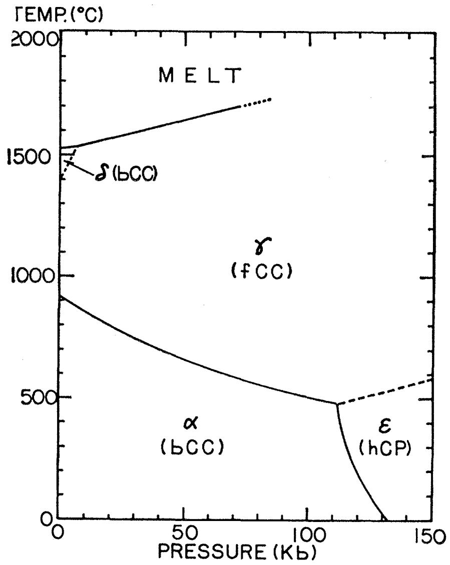

Fig. 3. The phase diagram of iron. The melting curve was determined by Strong (*18*). The α–γ and α–ε boundaries were modified from the data of Johnson *et al.* (*7*). The δ–γ and γ–ε boundaries were calculated. fCC, face-centered cubic; other abbreviations as in Fig. 2.

The slope of the δ–γ phase boundary was calculated to be 19.6°K/kb by using the lattice dimensions of Basinski *et al.* (*16*) and the heat of transformation of Kelly (*17*) (the volume change of 0.08 cm³/mole ,and the heat of transformation of 165 cal/mole at 1673°K). The probable stability field of δ-iron is shown in Fig. 3 along with the melting curve determined by Strong (*18*).

The shock wave studies of iron by Bancroft *et al.* (*6*) and Al'tshuler *et al.* (*19*) have shown that, above 130 kb, the Hugoniot curve has no discontinuity in slope up to 4000 kb, indicating the absence of any rapid phase transformation in iron. This implies that the pressure-temperature conditions of the shock wave experiments are within the stability field of ε-iron. The calculated slope of the γ–ε phase boundary is, in fact, nearly parallel to the slope of the pressure-temperature conditions of the shock experiments (Fig. 4).

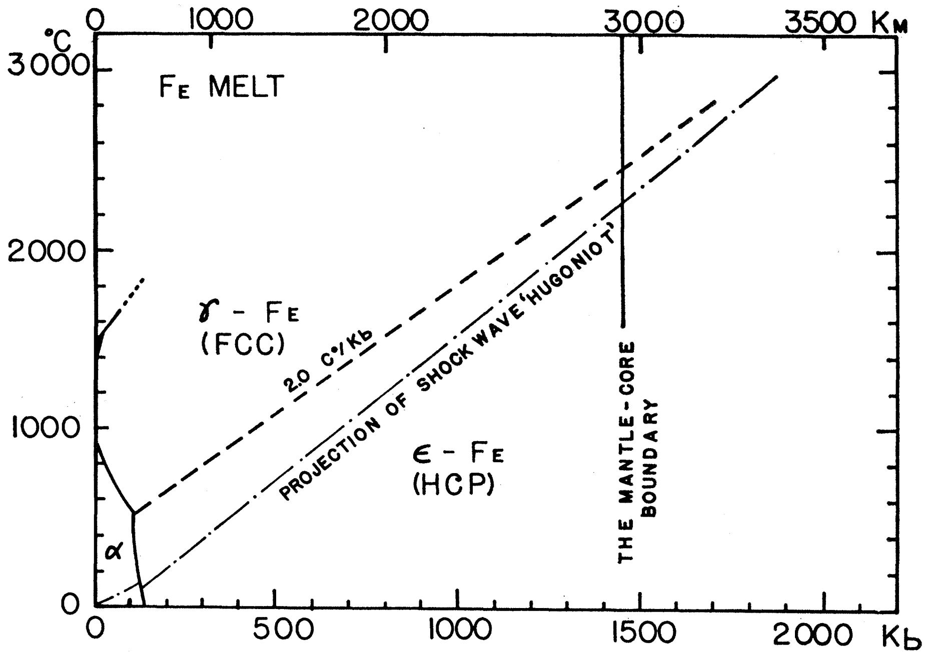

Fig. 4. The extended phase diagram of iron and the projection of shock wave "Hugoniot" (*19*). The calculated boundary between the γ- and ε-phase is nearly parallel to the projection of the shock wave "Hugoniot," and extends to the pressure-temperature conditions within the core of the earth. (Abbreviations as in Figs. 2 and 3.)

The evidence provided by geophysical, geochemical, and celestial mechanical measurements indicates that the core of the earth (2900 km deep to the center of the earth) is composed principally of iron. The pressure and temperature conditions within the core have been estimated by Birch (*20*) and Verhoogen (*21*) to be at the pressures of approximately 1500 kb at the periphery and 3500 kb at the center, and at temperatures of 3000° ± 1000°C. The γ–ε phase boundary, if it extends to the pressure-temperature conditions of the earth's core, may have a significant influence on the core's properties.

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References and Notes

1. F. Birch, *Am. J. Sci.* **238**, 192 (1940).
2. L. Kaufman, A. Leyenaar, J. S. Harvey, in *Progress in Very High Pressure Research,* F. P. Bundy, W. R. Hibbard, Jr., H. M. Strong, Eds. (Wiley, New York, 1962), pp. 90–106.
3. E. V. Clougherty and L. Kaufman, in *High Pressure Measurement,* A. A. Giardini and E. C. Lloyd, Eds. (Butterworth, Washington, D.C., 1963), pp. 152–163.
4. G. C. Kennedy and R. C. Newton, in *Solids Under Pressure,* W. Paul and D. M. Warschauwer, Eds. (McGraw-Hill, New York, 1963), pp. 163–178.
5. W. F. Claussen, in *High Pressure Measurement,* A. A. Giardini and E. C. Lloyd, Eds. (Butterworth, Washington, D.C., 1963), pp. 125–150.
6. D. Bancroft, E. C. Peterson, S. Minshall, *J. Appl. Phys.* **27**, 291 (1956).
7. P. C. Johnson, B. A. Stein, R. S. Davis, *ibid.* **33**, 557 (1962).
8. A. Balchan and H. G. Drickamer, *Rev. Sci. Instr.* **32**, 308 (1961).
9. J. C. Jamieson and A. W. Lawson, *J. Appl. Phys.* **33**, 776 (1962).
10. J. C. Jamieson, in *High Pressure Measurement,* A. A. Giardini and E. C. Lloyd, Eds. (Butterworth, Washington, D.C., 1963), pp. 165–167.
11. A. Van Valkenburg, *ibid.*, pp. 87–94.
12. P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **76**, 1 (1945).
13. R. H. Christian, *Univ. Calif. Rad. Lab. Rept. 4900* (1957).
14. V. V. Evdokimova and L. F. Vereshchagin,

Soviet Phys. JETP (Engl. Transl.) **16**, 855 (1962).
15. P. W. Bridgman, *Am. Acad. Arts Sci.* **84**, 131 (1955).
16. Z. P. Basinski, W. Hume-Rothery, A. L. Sutton, *Proc. Roy. Soc. London Ser. A.* **229**, 459 (1955).
17. K. K. Kelly, *Bull. Bur. Mines* **584**, 94 (1960).
18. H. M. Strong, in *Progress in Very High Pressure Research*, F. P. Bundy, W. R. Hibbard, H. M. Strong, Eds. (Wiley, New York, 1962), pp. 182–193.
19. L. V. Al'tshuler, K. K. Krupnikov, B. N. Ledenev, V. I. Zhuchikhin, M. I. Brazhnik, *Soviet Phys. JETP (Engl. Transl.)* **34**, 874 (1958).
20. F. Birch, in *Solids Under Pressure*, W. Paul and D. M. Warschauwer, Eds. (McGraw-Hill, New York, 1963), pp. 137–162.
21. J. Verhoogen, in *Physics and Chemistry of the Earth*, L. H. Ahrens *et al.*, Eds. (Pergamon Press, London, 1956), vol. 1, pp. 17–43.
22. We thank J. F. Lovering for stimulating discussions and encouragements. This study was supported by NSF grant GP-454.

11 May 1964

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Cerium-144 and Cesium-137 Measurements in the 1963 United States Wheat Crop and Milling Products

Abstract. *The distribution of an abundant short-lived (285 days) nuclide, cerium-144, and a long-lived (30.5 years) nuclide, cesium-137, has been measured in wheat samples and milling products by means of radiochemical methods. The patent flour fraction contained approximately 10 and 15 percent of the measured cerium and cesium.*

Cerium-144 and cesium-137 distributions have not been studied as frequently in environmental samples as strontium-90 since neither of the first two radionuclides are deemed as hazardous to man. They are significant, however, because of their major contribution to world-wide fallout. Cerium-144 and its daughter praseodymium-144 are the most abundant radionuclides in the atmosphere 1 to 3 years after nuclear detonations (*1*). While Cs^{137} is initially a lesser contributor to fallout during this interval, its longer physical half-life, chemical similarity to potassium, and potential as a hazard make necessary more detailed studies. In the study reported here, we measured the amounts of Ce^{144} and Cs^{137} in the 1963 U.S. wheat crop and milling products by means of radiochemical methods.

Table 1. Results of analysis of Ce^{144} and Cs^{137} in samples of wheat grown in the United States during 1963.

Location	Harvest mid-point*	Content of original material (pc/kg)	
		Ce^{144}	Cs^{137}
Indiana	15 July	234	483
Kansas (I)	15 June	474	405
Kansas (II)†	15 June	488	410
Missouri	30 June	210	645
Montana	31 July	411	524
Nebraska	30 June	308	576
North Dakota	14 July	334	466
Ohio	15 July	177	225
Oklahoma	25 May	780	477
South Dakota	31 July	90	309
Texas	15 May	471	322
Washington	31 July	132	342

* The date considered to be about the middle of harvest, for the year 1963. † Duplicate sample of Kansas (II), which is a composite of eight varieties of wheat.

Table 2. Cerium-144 and cesium-137 in Kansas wheat and milling products.

Fraction	Percent of total	Content of original material (pc/kg)		Content of fraction (pc/kg)		Percentage in fraction	
		Ce^{144}	Cs^{137}	Ce^{144}	Cs^{137}	Ce^{144}	Cs^{137}
Wheat (Kansas II)	100	488	410	488	410		
Patent flour	52	84	124	44	64	9	16
1st Clear flour	17	162	166	28	28	6	7
2nd Clear flour	6	184	230	11	14	2	3
Shorts	14	1384	1021	194	143	39	35
Bran	11	1945	1420	214	156	44	39
Total				491	405	100	100

Relatively little has been reported on the distribution of natural cerium and its family, the rare earth elements, in the environment. Late in the 19th century it was reported that "small quantities of the rare earth elements were detected in the ashes of many plants, rice, tobacco and also in human bones" (*2*).

Recently, Nezu *et al.* (*3*) found that the amount of Ce^{144} was one-tenth that of Sr^{90} in mixed animal bone, approximately equivalent to the amount in a root vegetable, and twice as much as the amount of Sr^{90} in a leafy vegetable. It is generally agreed that the rare earth radionuclides are assimilated by the plant root in negligible concentrations and that the association of these radionuclides with plants is due to physical adherence resulting from their particulate origin. However, solubility measurements of fallout debris in New York City indicated that 42 percent of the Ce^{144} was soluble at the time of deposition on the ground (*4*). In studies of the penetration of radionuclides in New Jersey soils it was found that Ce^{144} was measurable down to 30 cm (*5*). Therefore, it seems reasonable to assume that a soluble and exchangeable, as well as a particulate form of cerium, exists in radioactive fallout.

Most of the Cs^{137} is soluble in fallout debris and is strongly adsorbed within the top 5 cm of soil. The removal of Cs^{137} from soils and its availability to plants is retarded by the strong absorptive forces of soil. Two of the factors which tend to reduce these retentive forces, thus making cesium more available to plants, are increases in the concentration of hydrogen ions in the soil (*6*), and increases in the amount of available potassium (*7*).

The degree of radionuclide solubility and the distribution of radioactive elements in soil are only two of the physical parameters of the mechanism of radionuclide transfer from the atmosphere to plants. Another consideration is translocation of radionuclides by plants. Gulyakin and Yudintseva (*8*) observed approximately 2 and 15 percent Ce^{144} and Cs^{137} in wheat grain from plants grown in nutrient solution. The amount was less for soil grown plants. From autoradiographic studies of wheat plants sprayed with Cs^{137}, Middleton (*9*) found dispersion throughout the plant with approximately 10 percent concentrated in the grain.

The amounts of Ce^{144} and Cs^{137} found in samples of the 1963 U.S. wheat crop from eleven states are shown in Table 1. The values are reported as of the date considered to be about the middle of harvest. The states listed produced about 75 percent of all the wheat grown in the United States during 1962. Kansas produced 20 percent of the 1962 wheat crop. Two composite samples were made from eight varieties of Kansas wheat (Table 1). One of the composites (Kansas II) was separated into milling fractions (Table 2). As shown, the patent flour fraction, which is used for human consumption, contained approximately 10 and 15 percent, respectively, of the Ce^{144} and Cs^{137} measured in the grain. This amount is consistent with