

however, rely on the trophic transfer of peat carbon through the critical link of insect larvae and attain partial independence from the seasonal variation in primary production. This "fossil fuel subsidy" is important in an environment where primary production is essentially nil for about 7 months of the year.

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13. Ratios of ^{13}C to ^{12}C are expressed as $\delta^{13}\text{C}_{\text{PDB}}$, where $\delta^{13}\text{C}_{\text{PDB}} = [(R_{\text{sample}} - R_{\text{std}})/R_{\text{std}}] \times 1000$ and R is the ratio $^{13}\text{C}/^{12}\text{C}$; $\delta^{13}\text{C}$ is reported in parts per thousand (ppt) relative to the Pee Dee belemnite (PDB) standard. The ^{14}C activity of an A.D. 1950 sample is expressed as 100 percent modern, normalized to $\delta^{13}\text{C}$ of -25 ppt to correct for fractionation effects. Modern tundra vegetation is 122 to 140 percent, with lower values in annual grasses, leaves, and aquatic algae. Higher values are found in woody plants, standing dead grasses, and sedges. Marine macroalgae samples (*Laminaria* spp.) are 103 to 107 percent ($N = 4$). "Average peat" was taken to be the mean activity of a uniform layer of peat accumulating at constant rate for 8142 years. Actual basal peats along shorelines and rivers ranged from 3,400 to 12,600 years before present. The mean was 36.3 percent modern ($N = 6$, standard deviation = ± 15.3 percent modern), yielding an average activity of 62.9 ± 10.2 , -11.3 percent modern. This average peat activity is probably lower than the overall activity of peat entering the aquatic systems. An actual particulate sample from the Colville River was 74.4 percent modern. Since no quantitation of modern material in these samples was attempted, the more conservative value of 62.9 percent was used to determine peat carbon content in organisms. Organisms collected for isotopic analyses were frozen until processed in the laboratory. Small organisms such as mysids, amphipods, lemmings, and *Daphnia* were dried whole in vacuo at 70°C . For larger animals muscle tissue was used. Vegetation samples from aquatic and terrestrial sites were dried after any foreign matter was manually removed. Riverborne detritus was collected by suspending a $120\text{-}\mu\text{m}$ mesh plankton net in the Colville River until sufficient material had been collected to provide 5 g of carbon. Isotopic analyses were performed by Beta Analytic, Inc. (BAI), Geochron Division (GD) of Krueger Industries, and Teledyne Isotopes. Precision in ^{14}C analyses was typically ± 1 percent and ^{13}C analyses were ± 0.05 to 0.1 ppt. Costs of analyses limited replication of samples. *Laminaria* from one collection site were sent to each laboratory and yielded the following activities: 105.7 (GD); 105.0, 107.1 (BAI); and 102.8 (Teledyne).

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17. I thank T. Bendock, E. Taylor, S. Johnson, P. Craig, W. Griffiths, and J. Helmericks for providing fish and bird samples for isotopic analyses. M. Miller and S. Johnson kindly reviewed and commented on the manuscript. This study was funded in part by the Bureau of Land Management through interagency agreement with the National Oceanic and Atmospheric Administration, as part of the Outer Continental Shelf Environmental Assessment Program, and in part by the Office of Water Research and Technology, U.S. Department of the Interior.

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Lithium, Compression and High-Pressure Structure

Abstract. *Lithium is found to transform from a body-centered cubic (bcc) to a face-centered cubic (fcc) structure at 6.9 gigapascals (69 kilobars) and 296 kelvin. The relative volume of the bcc structured lithium at 6.9 gigapascals is 0.718, and the fcc structure is 0.25 percent denser. The bulk modulus and its pressure derivative for the bcc structure are 11.57 gigapascals and 3.4, and for the fcc structure are 13.1 gigapascals and 2.8. Extrapolation of the bcc-fcc phase boundary and the melting curve indicate a triple point around 15 gigapascals and 500 kelvin.*

Lithium has three electrons per atom and is thus the most elementary metal available for study. The nature of the forces generated by the electrons in bonding lithium into a solid is partially revealed by studying the structure and density of the metal in response to temperature and pressure changes. In the study described here the structure and density of lithium were measured to 10 GPa (100 kbar, 10×10^{10} dyne/cm²) at an ambient temperature of 296 K.

The technique used in this study has been described (1). Briefly, an annulus of beryllium 2.5 mm in diameter and 0.25 mm thick with a 0.33-mm hole in the center is pressed between two tungsten-carbide Bridgman anvils. The hole is filled with a mixture of Li and LiF powder (pressure indicator). A $\text{CuK}\alpha$ x-ray beam is directed through the annulus, and the diffraction is recorded on a 114.6-mm-diameter cylindrical film sur-

rounding the annulus. Diamond anvils were not used for three experiments because of the very low scattering power of Li.

The diffraction patterns of the Li-LiF mixture exhibited the 110, 200, and 211 diffraction lines of the body-centered cubic (bcc) structure of Li, the 111 and 220 lines of the high-pressure face-centered cubic (fcc) structure of Li, and the 111 and 220 lines of LiF. The pressure is deduced from the LiF volume calculated from the diffraction patterns and correlated with values calculated from a shock compression study of LiF (2).

A preliminary study was made with Li alone to avoid confusing diffraction lines of new structures with those of LiF. Lithium was compressed to a minimum relative volume of $V/V_0 = 0.654$. The ambient bcc structure transformed to a fcc structure at $V/V_0 = 0.712$ (bcc) as the pressure was being increased and trans-

Table 1. Lithium compression data. The ambient (V_0) volume of lithium is 1.876 cm³/g; a is the cubic cell parameter.

Film number	a (LiF) (Å)	a (Li) (Å)	P (GPa)	V/V_0
<i>bcc structure</i>				
2-3	3.968(1)*	3.285(5)*	3.3(1)*	0.820(3)*
4-4	3.965(—)	3.272(0)	3.5(—)	0.811(0)
4-5	3.946(—)	3.216(2)	4.7(—)	0.770(2)
2-4	3.945(2)	3.217(5)	4.7(1)	0.771(3)
2-5	3.919(—)	3.161(—)	6.6(—)	0.731(—)
<i>fcc structure</i>				
4-7	3.900(3)	3.900(3)	8.0(2)	0.687(1)
2-8	3.880(—)	3.855(—)	9.6(—)	0.663(—)
4-9	3.877(3)	3.843(3)	9.8(3)	0.657(1)
4-10	3.876(0)	3.832(2)	9.9(0)	0.651(1)
4-11	3.874(—)	3.828(1)	10.1(—)	0.649(0)

*The standard deviations are listed after each number. They are the uncertainty of the final figure in each number. A dash in parentheses signifies that only one value could be determined because of diffraction line interference.

formed back to the bcc structure at $V/V_0 = 0.723$ (bcc) as the pressure was being released. On exposures that exhibited both structures, the densities of both structures were nearly identical. The fcc structure is only 0.25 ± 0.05 percent denser than the bcc structure.

In the subsequent studies LiF was mixed with Li. The data calculated from the high-pressure x-ray diffraction patterns are listed in Table 1. Using an equation of state as described in (3), the isothermal bulk modulus (B_t) and its pressure derivative (B'_t) for the P - V/V_0 data in Table 1 are $B_t = 10.9 \pm 0.5$ GPa and $B'_t = 3.84 \pm 0.32$. Recently, single-crystal elastic constants for ^7Li have been determined, as well as the temperature and pressure dependences of these constants (to 0.2 GPa) (4). Those measurements yield $B_t = 11.57$ GPa and $B'_t = 3.55$. Because small errors in P and V yield large errors in the values of the moduli near $P = 0$, the value from the elastic constant measurements will be used for B_t . The P - V/V_0 values at high pressure can now be used for determining B'_t . The values thus selected to best represent the compression of bcc Li are $B_t = 11.57$ GPa and $B'_t = 3.39 \pm 0.02$.

The isothermal bulk modulus and its pressure derivative have been measured for Li in the bcc structure by various techniques. The pressure-volume measurements of Bridgman (5) to 4.0 GPa (corrected pressure values) have a bulk modulus and pressure derivative of 11.18 GPa and 3.64. Another set of Bridgman measurements (6) to 10 GPa give 11.58 GPa and 3.74. Bridgman failed to detect the transformation from bcc to fcc, so these values include compression data for the fcc structure. From piston displacement measurements of Swenson (7) to 2.0 GPa, the modulus and its pressure derivative are 11.2 GPa and 3.60. Finally, from a shock compression study by Rice (8), the values are 11.2 GPa and 3.60. Although the shock data go to 27 GPa, temperature calculations for the state of lithium along the Hugoniot show that the data above 5 GPa are for liquid Li. [The melting curve for Li has been measured to 8.0 GPa (9).] The value for B_s was again taken from Felice *et al.* (4) and then the value of B'_s was adjusted to fit the data of Rice (8). The values for the isothermal bulk modulus and its pressure derivative are in excellent agreement among all studies.

With the compression of the bcc structure well defined, the pressure for the transition from the bcc to the fcc structure can be calculated. The data collected on unmixed Li showed that the trans-

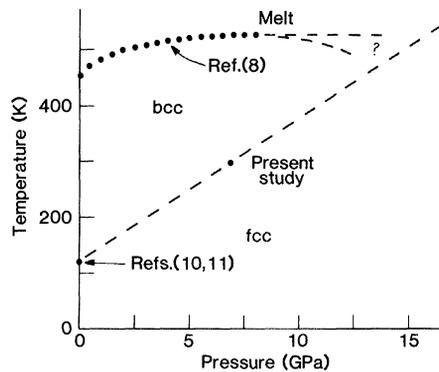


Fig. 1. Suggested phase diagram for lithium.

formation occurs at some pressure corresponding to relative volumes between $V/V_0 = 0.712$ and 0.723 . In the absence of evidence to the contrary, the relative volume at transformation is estimated to be the average, or 0.718 ± 0.008 . From the B_t and B'_t and the equation of state in (3), the pressure for the transition at 296 K is 6.9 ± 0.4 GPa. This value is in excellent agreement with the resistance discontinuity observed at 7.0 GPa and 296 K (10).

From the data on the volume in Table 1 and the correlated pressures established for the bcc structure mixed with the fcc structure we can estimate the bulk modulus and its derivative for the fcc structure. Numerous studies by Barrett (11, 12) on the structures of Li showed that at or below 78 K cold-worked bcc Li partially transforms to an fcc structure whose density is the same, within the error of the measurement, as the density of the bcc structure. This is compatible with our results at high pressure. If we assume that the densities of the bcc and fcc structures are the same at 296 K and $P = 0$, then $B_t = 13.1$ GPa and $B'_t = 2.8$ for the fcc structure. There are larger uncertainties in these values than for the bcc structure because the data span only 3 GPa.

From the data available, an estimate can be made of the pressure-temperature phase boundary between the fcc and bcc structures. Barrett (11, 12) found that on cold-working Li the fcc structure would form, and on heating the fcc structure would transform back to the bcc structure. The narrowest temperature limits between which the fcc structure forms and converts back to the bcc structure are 110 and 135 K, respectively, at zero pressure.

Much of the thermodynamic data collected at low temperatures on the phases of Li is complicated by the appearance of a third phase having a hexagonal close-packed (hcp) structure. The bcc structure transforms spontaneously to the hcp

structure below 71 K. Barrett (11, 12) argues that the hcp structure is metastable and that cold-working at low temperatures, like thermal agitation at high temperatures, promotes the formation of the stable phase, the fcc structure.

The slope of the phase boundary between the bcc and fcc structures is 25.5 K/GPa, if the boundary is assumed to be linear and the temperature of transformation is estimated to be 120 K at zero pressure. From the Clausius-Clapeyron relation, the heat of transformation at 296 K and 6.9 GPa is 40 J/g.

If the phase boundary between the two structures is linear, then it should intersect with the melting curve of Li that was measured by Luedemann and Kennedy (9). Fitting their pressure-temperature data to 8 GPa with a quadratic least-squares fit, the triple point is calculated to be at 13.6 GPa and 466 K. If the melting temperature remains constant to pressures above 8 GPa, as it does between 6.5 and 8.0 GPa, then the triple point is 15.9 GPa and 526 K (see Fig. 1). The existence of a triple point was suggested by Luedemann and Kennedy (9) based on their melting curve and the transformation observed by Stager and Drickamer (10). However the data are extrapolated, we suggest that a triple point should be within reach of static high-pressure equipment.

We have shown that high pressures stabilize an fcc phase of Li, with very little density difference from the bcc phase. The existence of this high-pressure phase suggests that a triple point is responsible for the very flat melting line observed for Li. In this respect the situation is very similar to that for Cs and perhaps Rb, as well.

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