[CONTRIBUTION FROM THE K-25 TECHNICAL DIVISION, CARBIDE AND CARBON CHEMICALS COMPANY]

Variation in the Natural Abundance of the Lithium Isotopes[1]

BY A. E. CAMERON

RECEIVED OCTOBER 15, 1954

Lithium samples from commercial and from known minerological sources have been investigated and the variation in the $\mathrm{Li^7/Li^6}$ ratio with origin is established. Measurements have been made on the $\mathrm{Li^6Li^7I^+}$ and $\mathrm{Li^7Li^7I^+}$ ions at masses 141 and 140. Sublimation of the iodide is free from discriminatory effects and no corrections need be applied. This ratio has been shown to be unaffected by variations in instrumental conditions and is believed to be reliable. The variation of $\mathrm{Li^7/Li^6}$ ratio in commercial chemicals has been observed to be between 12.44 and 12.93. Minerals examined show variations in the 7/6 ratio between 12.47 and 12.72. Partial precipitation of lithium as phosphate or carbonate is shown to effect an isotope separation.

No systematic examination of the lithium isotopic ratio has been reported in the literature. Many mass spectroscopists have made and reported measurements but these have been, with one exception, upon commercial chemicals of unknown origin. The failure of the determinations to agree among themselves or with the ratio calculated from the accepted atomic weight determination of Richards and Willard[2] indicates difficulty in the mass spectrometry or a variation with origin or chemical history of the sample. The writer has made an investigation, both of the mass spectrometry and of the isotopic ratio as a function of origin of the sample and of its chemical history.

Mass Spectrometry.—Measurements have been made with two 60° sector instruments of 15 cm. radius. These were equipped with a solid sample handling source which is described elsewhere.[3] Lithium iodide has been chosen as the sample form. It gives adequate vapor pressure at 320 to 380°, depending upon the sample surface area. The spectrum of this compound when sublimed and ionized by slow electrons, shows $\mathrm{Li^+}$, $\mathrm{LiI^+}$, $\mathrm{Li_2I^+}$ and $\mathrm{Li_2I_2^+}$ with the latter ion in very low abundance. No detectable $\mathrm{LiI_2^+}$ is observed. $\mathrm{I^+}$ is observed in large abundance and $\mathrm{HI^+}$ when water vapor is present in the spectrometer. The mixed ions such as $\mathrm{LiNaI^+}$ are observed if other alkali metals are present. The molecular ions have been observed in the vapor of the alkali metal halides by Ionov[4] and by Dukyelskii, Zandberg and Ionov.[5] L. Friedman of the Brookhaven National Laboratory presented a paper on the mass spectrum of lithium iodide at the Pittsburgh Meeting of ASTM committee, E-14 on Mass Spectrometry in March, 1953. He determined the partial heats of sublimation to monomer and to dimer and the heat of dissociation of the gaseous $\mathrm{(LiI)_2}$ into monomer.

The indications are strong that the reliable ion in this system is the dimer ion $\mathrm{Li_2I^+}$. The "dimer-monomer" ratio, mass 141/mass 134, varies between samples in a manner which has not been found controllable. In samples which are fused in quartz tubes in high vacuum, the concentration of the dimer ion usually is low, *ca.* 0.2 of the intensity of the monomer ion. If dehydration is carried out without fusion, the dimer ion will be ten times greater. Experimental observations have established that the $\mathrm{Li^6I^+/Li^7I^+}$ ratio is a function of the dimer–monomer ion ratio, while the $\mathrm{Li^6Li^7I^+/Li^7Li^7I^+}$ ratio is not affected. Furthermore, no change in instrumental conditions has proven to have any significant effect upon this ratio. The instruments have been operated with and without source magnets, with deliberately altered focussing conditions, with different receiver slit widths, with different electron energies from 20 volts to above 75 volts, with different accelerating voltages and with different ion lens arrangements. No significant alteration in the ratio was produced by any of these changes, or by variation in the intensity of the ionizing current. Both tubes were removed from the instruments, and changes made in the geometry of the receivers without effect upon the results. This is good evidence that no spurious or reflected ion beams were impinging on the collector plate and altering the ratio. Several different 4×10^{10} ohm resistors were employed without any evidence of non-ohmic behavior found.

Cross-contamination or "memory" between samples was avoided by thorough cleaning of the stainless steel ion chambers. After usage they were washed with water and dilute hydrochloric acid. They were then electrostripped in glycerol and phosphoric acid bath with an electrode arrangement inside and outside to secure uniform deplating. They were water washed thoroughly and oven dried. No evidence of memory has been observed with this type of ion source over a twofold change in isotopic concentration of any element examined.

The two ion beams to be compared were brought alternately upon the receiver slit by variation in the strength of the magnetic field, all other conditions being left unaltered. The voltage developed in the 4×10^{10} ohm input resistor of the FP-54 electrometer tube was bucked with voltage from a pair of parallel connected, battery operated precision decade potentiometers. One of these potentiometers was connected automatically in the circuit when a "mass select" switch was thrown to read peak A or peak B. Residual galvanometer deflections were converted into potentiometer readings by interpolation factors experimentally determined after each set of readings. It was customary to make alternately a minimum of eleven readings of the small peak and ten of the large peak. The calculation scheme was essentially to average two consecutive readings of the "A" peak and divide by the intervening "B" peak. This tended to correct for slow intensity drifts with time because of changes in surface area of the sample being sublimed, or shifts in the heater voltage on the sample furnace. The ten ratios were then treated as independent readings for statistical purposes. The standard deviation was calculated and multiplied by the appropriate factor, 2.26 in the case of ten readings, to give the 95% confidence interval of the set of readings. The 140/141 ratio is divided by two to give the 6/7 ratio.

Chemistry of Sample Preparation.—Initially it was customary to fuse the iodide in 5 mm. o.d. Pyrex tubes attached to a high vacuum system. The tubes were then sealed off until ready for use, at which time the lower 8–10 mm. of the tube was cut off and placed in the sample retort. The high sodium content of the samples finally pointed to attack of the lithium upon the glass with consequent formation of a silicate phase and alteration of the isotopic abundance. This procedure was abandoned in favor of fusion in quartz or Vycor, although this technique was not entirely free from troubles, or support of the sample on a porous substrate.

Iodide was prepared from lithium sulfate by addition of purified hydriodic acid and evaporation just to dryness on a hot plate. The sulfate is reduced and iodine liberated. This procedure should be carried out three times to ensure complete conversion and elimination of free sulfur. Preparation from carbonate or hydroxide is, of course, very simple. Commercial hydriodic acid is stabilized by the addition of about 1.5% hypophosphorous acid ($\mathrm{H_3PO_2}$). The distillation to free the acid from this stabilizer was not entirely

---

(1) This work was done at the Oak Ridge Gaseous Diffusion Plant operated for the Government by Union Carbide and Carbon Corporation.

(2) T. W. Richards and H. H. Willard, THIS JOURNAL, **32**, 4 (1910).

(3) A. E. Cameron, "Electron-Bombardment Ion Source for Mass Spectrometry of Solids," Carbide and Carbon Chemicals Company, K-25 Plant, June 19, 1953, (K-1021), *Rev. Sci. Inst.* **25**, 1154 (1954).

(4) N. I. Ionov, *Proc. Acad. Sci., USSR*, **59**, 467 (1948).

(5) V. M. Dukyelskii, E. A. Zandberg and N. I. Ionov, *Proc. Acad. Sci., USSR*, **62**, 323 (1948); *ibid.*, **68** (1949).

satisfactory and, in any case, should be done in an inert atmosphere. A preferable procedure was to add elemental iodine to the refluxing acid in an all-glass apparatus until the color of free iodine persisted. This should convert the hypophosphorous acid to phosphoric and eliminate decomposition troubles during the distillation. The acid was then distilled through a short bead packed column and the first and last 15% were discarded. Tests for phosphoric acid indicated the presence of at most a few parts per million. It was stored in dark bottles out of light.

Standard practice was to add an amount of ammonium iodide approximately equal to the iodide being prepared to prevent hydrolysis. The samples were carefully evaporated to dryness on a hot plate and gave a product probably between a mono- and trihydrate. These were then dissolved in absolute ethyl or methyl alcohol and sample "sponges" of rolled fine nickel screen or pieces of porous alundum were dipped into the alcohol solution. These sample "sponges" had been hydrochloric acid washed, extracted with distilled water and oven dried. The impregnated porous substrates were dried over a hot plate until no longer wet and dropped into 8 mm. test-tubes attached to a high vacuum system. They were flamed carefully until well evacuated and the ammonium iodide sublimed out to the upper part of the tube. They were then sealed off under vacuum until ready for use. No evidence of difficulty from reaction with the substrate was detected. Check samples were prepared which contained large amounts of free iodine and of hydriodic acid. Formation of nickel iodide was evidenced by a dark sublimate which appeared during the sample flaming, but no effect on the lithium ratio was detectable. Addition of one drop of hydriodic acid to the alcohol solution was considered to be good practice.

Treatment of Ore Samples. Spodumenes: ($LiAlSi_2O_6$).—Portions of single crystals were ground in a boron carbide mortar and ignited in platinum to convert to β-spodumene which is more reactive chemically. The silicate was decomposed by addition of sulfuric and 40% hydrofluoric acid followed by evaporation to fumes of sulfur trioxide. The cake was slurried in water and filtered. Most of the residue was aluminum oxide and carried no lithium. Ammonium hydroxide was added to the diluted filtrate and the excess boiled off. The solution was filtered and the lithium sulfate recovered by evaporation to dryness and fuming off the ammonium salts. The entire sulfate residue was then converted to iodide.

Lepidolites: $K_2Li_3Al_4Si_7O_{21}(OHF)_3$.—These ores in genreal carried sodium, potassium, rubidium and cesium in addition to lithium. The chemical treatment was the same as for the spodumenes, care being taken to avoid fusion of the mica in the initial heating. The alkali metal sulfates were treated by ion-exchange chromatography with Dowex-50 resin to separate lithium. The entire lithium peak was collected when eluted with 0.5 *N* HCl to avoid any possibility of isotope separation. Sodium was discarded, but the other alkali metals were recovered. The elution of the column was monitored by flame tests.

Phosphates: Amblygonite ($LiAlFPO_4$), **Triphylite** ($LiFePO_4$) **and** Li_2NaPO_4.—These compounds were treated both by conventional phosphate chemistry, adding an excess of ferric ion and then precipitating phosphates in an ammonium acetate–acetic acid buffer, and by ion exchange–fixing the lithium on Dowex-50 resin and washing out the phosphate ion. The lithium was then eluted with dilute hydrochloric acid.

Experimental Results

The ores and some of the commercial chemicals which have been measured are reported in the following table. It is apparent that there is a large variation in materials of commercial origin, from a 7/6 ratio of 12.44 for lithium carbonate from Searles Lake origin to 12.93 for the carbonate which was initially chosen as the laboratory standard. By contrast the variation in the ores is from 12.47 for a single crystal of Kings Mountain spodumene to 12.72 for a lepidolite from Nepora, P. E. A. The averages of the spodumenes and of the lepidolites are rather close, 12.61 compared to 12.63 and the difference is probably not significant. However, the phosphate ores appear to run somewhat lower in 7/6 ratio with the exception of the High Climb Mine amblygonite.

TABLE I

ABUNDANCE OF LITHIUM ISOTOPES IN CERTAIN LITHIUM MINERALS

Sample and origin	Li^7/Li^6
Spodumene, Kings Mountain, N. C.[a] (Mine operated by Foote Mineral Co.)	
Single crystal, surface ore	12.54 ± 0.03[e]
	12.54 ± .06
Single crystal, unweathered	12.47 ± .04
	12.48 ± .05
Single crystal, unweathered	12.52 ± .02
	12.51 ± .03
Spodumene, Harding Mine,[b] Dixon County, New Mexico	
Single crystal	12.60 ± .05
	12.65 ± .04
	12.57 ± .07
Spodumene, Helen Beryl Mine,[c] Custer County, South Dakota	12.71 ± .11
	12.71 ± .06
Spodumene, Pseudomorph,[c] Helen Beryl Mine	12.66 ± .02
Lepidolite, Colorado[d]	12.61 ± .04
	12.58 ± .05
Lepidolite, Niaja Loaf,[d] P. E. A.	12.71 ± .06
	12.63 ± .08
	12.66 ± .04
	12.68 ± .04
	12.68 ± .02
	12.68 ± .04
Lepidolite, Bolidens, Sweden[d]	12.57 ± .04
	12.53 ± .06
Lepidolite, Nepora, P. E. A.[d]	12.70 ± .02
	12.75 ± .30
Lepidolite, Ingersoll Mine, Custer County, South Dakota[c]	
Preparation A	12.69 ± .02
Preparation B	12.71 ± .02
Lepidolite, Spain[d]	12.57 ± .03
Lepidolite, Auburn, Maine[b]	12.60 ± .03
	12.60 ± .04
Amblygonite, Colorado[d]	
By phosphate precipitation	12.57 ± .05
	12.52 ± .02
	12.45 ± .02
By ion exchange only	12.46 ± .03
	12.48 ± .04
Amblygonite, Hugo Mine, S. Dakota[c]	
By ion exchange only	12.51 ± .02
	12.54 ± .09
	12.49 ± .04
Amblygonite, High Climb Mine, Custer County, S. Dakota[c]	
By ion exchange	12.63 ± .06
	12.66 ± .03
Triphylite, Bodenmais, Bavaria[b]	
By ion exchange—Preparation A	12.58 ± .04
	12.47 ± .02
	12.43 ± .05
Preparation B	12.48 ± .02
	12.48 ± .02

TABLE I (*Continued*)

Sample and origin	Li^7/Li^6
Li_2NaPO_4, Searles Lake, from American Potash Company, Los Angeles	
By ion exchange	12.91 ± .02
	13.05 ± .03
By phosphate precipitation	12.82 ± .05
	12.94 ± .10
Li_2CO_3, Searles Lake, from Pacific Coast Borax Co.	12.42 ± .03
	12.47 ± .02
	12.43 ± .03
Li_2CO_3, Bureau of Standards	12.48 ± .03
	12.49 ± .03
	12.51 ± .03
	12.51 ± .03
Laboratory Standard, Li_2CO_3—Av. of 10 measurements	12.93 ± .03

[a] Collected June, 1953. [b] From T. F. Bates, Pennsylvania State College. [c] From T. I. Taylor, Columbia University. [d] From A. B. Chandler, Foote Mineral Company. [e] Error stated represents limits of the 95% confidence interval for the stated ratio; for calculation method see section this article titled mass spectrometry.

A few experiments were made to show the effect of chemical treatments upon the isotopic ratio. Precipitation of 10% of the lithium present in a 5 *N* nitrate solution by addition of sodium carbonate and heating for an hour, followed by rapid filtration gave lithium carbonate in which the 7/6 ratio was 13.07 compared to a starting material of 12.87. Wagner, Pelz and Higatsberger[6] have recently reported this same observation, although they carried the process through repetitive stages and secured a change from 12.48 to 14.03 in the 7/6 ratio. Heating a solution of lithium carbonate which was saturated at room temperature gave a product not significantly different from the starting material, although the indicated direction of separation was that observed in the above experiment.

Precipitation of 66% of the lithium present in 0.7 *N* lithium nitrate solution by addition of orthophosphoric acid effected a separation with the same direction as that obtained with carbonate. The 7/6 ratio in the liquor was 12.82 and that in the precipitate 12.90. The effects observed upon fusion of iodide in glass where there is the possibility of formation of an insoluble silicate phase indicate an effect in the opposite direction, with the iodide being impoverished in Li^6. The differences observed in the ores may well be ascribed to chemical effects, although much more work will be required to establish this completely. There is indication from the measurements upon the three Kings Mountain spodumene crystals that variations occur in a single mineral deposit. The two minerals from the Helen Beryl Mine in Custer County, South Dakota also appear to be significantly different. Only one determination was made on the spodumene pseudomorph because of the small lithium content. The two preparations made on the lepidolite from the Ingersoll Mine were carried through chemistry and ion exchange separately. The agreement is very satisfactory. The variability observed in the measurements upon the phosphate ores may be ascribed to incomplete phosphate removal.

The results obtained for the natural abundance are at variance with many of the published determinations. The measurements of Hintenberger[7] on lithium metal and on lithium chloride give an abundance of 12.4 to 12.52 after correction of the metal measurements for free evaporation. White and Cameron[8] sublimed the heavy molecule $LiAlCl_4$, but made measurements at masses 6 and 7 where instrumental discriminations might be appreciable. Their result of 12.70 ± 0.07 lies in the range of the variations observed as does Inghram's value of 12.53 on lithium chloride of unknown origin[9] and Hibbs'[10] measurement of 12.46 ± 0.03 on lithium iodide measuring masses 133 and 134. The accepted value in the summary compiled by Bainbridge and Nier[11] is the measurement by Hoff Lu on amblygonite of unspecified origin.[12] Lu reported 12.29 ± 0.20, correcting for drift in the ratio during the long period of thermal ion production.

The atomic weight determination of Richards and Willard leads to a value of the ratio of 12.11 ± 0.20. Their lithium salt was purified by several partial precipitations of lithium fluoride to free it from other alkali metals, followed by recrystallizations as perchlorate or nitrate. These steps, involving incomplete recovery of the lithium, could well introduce a very appreciable shift in the isotopic abundance. A recent publication by Hutchison[13] argues for a value of 11.50 for the 7/6 ratio on the basis of an atomic weight calculated from X-ray measurements and the determination of crystal densities. One would wish to know the history of the lithium fluoride used, since the ratio in that particular crystal could well have been altered by its chemical history.

One concludes on the basis of the data presented for the ores in the table that the natural abundance lies between 12.47 and 12.72 for the 7/6 ratio, with an average number for silicate ore being perhaps 12.60.

OAK RIDGE, TENNESSEE

---

(6) G. Wagner, A. Pelz and M. J. Higatsberger, *Monatsh.*, **85**, 464 (1954).

(7) H. Hintenberger, *Naturwiss.*, **34**, 52 (1947).

(8) J. R. White and A. E. Cameron, *Phys. Rev.*, **74**, 991 (1948).

(9) M. G. Inghram, ANL-4012 (1947).

(10) R. F. Hibbs, Y-602 (1950).

(11) K. T. Bainbridge and A. O. Nier, "Relative Isotopic Abundances of the Elements," Preliminary Report No. 9, Nuclear Science Series, National Research Council, December, 1950, (NP-1971).

(12) Hoff Lu, *Phys. Rev.*, **53**, 845 (1938).

(13) D. Hutchison, THIS JOURNAL, **76**, 967 (1954).