K-1168
Physics

# THE NATURAL ABUNDANCE OF THE LITHIUM ISOTOPES

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Date of Issue: September 15, 1954

Report Number: K-1168

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## ABSTRACT

Lithium samples from commercial and from known minerological sources have been investigated and the variation in the $Li^7/Li^6$ ratio with origin is established. Measurements have been made on the $Li^6Li^7I^+$ and $Li^7Li^7I^+$ 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 $Li^7/Li^6$ 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.

# THE NATURAL ABUNDANCE OF THE LITHIUM ISOTOPES

Many mass spectrometric measurements of the ratio of the two lithium isotopes have been reported in the literature. An examination immediately indicates that there is no good agreement between the results quoted. It is not clear whether this may be caused by differences in mass spectrometers, or whether there is a variation in the abundance with origin of the samples. The following table includes the more recent determinations.

TABLE I

MEASUREMENT OF THE NATURAL ABUNDANCE OF THE LITHIUM ISOTOPES

| Worker | Sample | Ionization Method | Mass Measured | 7/6 |
|---|---|---|---|---|
| Richards and Willard (13) (1910) | LiCl | (atomic weight determination) | | 12.11 ± 0.2 |
| Bondy and Vanicek (2) (1936) | glasses | Thermal | 6-7 | 12.0 |
| Brewer (3) (1936) | salts | Thermal | 6-7 | 11.6 - 12.52 |
| Hoff Lu (12) (1939) | amblygonite | Thermal | 6-7 | *12.29 ± 0.20 |
| Hintenberger (8) (1947) | Li, LiCl | Electron | 6-7 | 12.4 ± 0.20<br>(12.4 to 12.52) corr. |
| Inghram (10) (1947) | LiCl | Electron | 6-7 | 12.53 |
| White and Cameron (16) (1948) | $LiAlCl_4$ | Electron | 6-7 | 12.70 ± 0.07 |
| Hibbs (7) (1950) | LiI | Electron | 133-134 | 12.46 ± .03 |

*Accepted value, Bainbridge and Nier (1)

With the exception of the one measurement reported by Hibbs, the measurements have been made on the metal ion at low mass where discriminations in ion lenses and geometry will be most apparent. Corrections should be applied to the results obtained with thermal ionization to account for preferential evaporation of the low mass isotope. The measurement of White and Cameron involved sublimation of a salt of high molecular weight, but the masses measured were 6 and 7. Hibbs' measurement was made at high mass, and the sublimation of the lithium iodide should be free from any separative effects. Of all the determinations reported, only that of Hoff Lu was on a material other than a commercial chemical of unknown origin. He does not, however, report the geological origin of the mineral which he used.

It appeared that it should be a simple matter to clarify these discrepancies, since an ion source structure had been developed specifically for sublimation of solid samples and slow electron ionization of the vapors. This source has been described elsewhere (4). The results of the measurements, and the experimental difficulties--both instrumental and chemical--will be discussed in some detail in the following sections.

## MASS SPECTROMETRY

Lithium iodide was chosen as the sample form. It sublimes readily to give adequate vapor pressure at moderate temperatures, 320-400°C, depending upon the surface area. It is readily prepared from lithium sulfate by reaction with hydriodic acid. Details of the chemistry will be discussed in the following section. The spectrum shows the following ions: $Li^+$, $LiI^+$, $Li_2I^+$ with only a very small $Li_2I_2^+$ and no detectible $LiI_2^+$. The ions $I^+$ and $HI^+$ are always observed as are the mixed ions, e.g., $NaLiI^+$, when another alkali metal is present. No anticipated interferences exist at masses 133 and 134 ($LiI^+$) except for $Cs^+$ which is a monobar of mass 133. At masses 140 and 141 ($Li_2I^+$) there are no interferences from other alkali metal-halogen combinations. Since iodine is monobaric no corrections need be made for halogen isotopes.

It was initially believed that measurements of the 133/134 ratio were reliable in the absence of cesium. Lithium iodide, essentially as trihydrate, was fused in glass tubes of 5 mm o.d. attached to a high vacuum system. When a quiet melt was obtained, the tube was sealed off. Sodium was always observed to be present but no significance was ascribed to the observation until it was realized that this indicated that the lithium iodide had attacked the glass. There was thus the possibility of formation of a solid lithium silicate phase and segregation of the isotopes between the melt and this more complex compound. Fusion of the same iodide in quartz or in Vycor gave consistently different answers, confirming the hypothesis.

In samples prepared by fusion in glass or in quartz, the "dimer-monomer" ratio, the ratio of the mass 141 to mass 134, was observed to be generally between 0.2 and 0.5. If the iodide had not been fused the ratio tended to be 2.0 to 2.5. Variations had been observed in measurements of the 133/134 ratio which seemed to correlate with variation in the "dimer-monomer" ratio. A series of samples were prepared from the same iodide which were spiked with increasing amounts of sodium to determine whether the presence of this element had any effect upon the isotopic ratio. The results of this experiment are given in table II.

## TABLE II

## LITHIUM IODIDE WITH ADDED SODIUM, FUSED IN QUARTZ SAMPLE TUBES

| Mole Fraction Lithium | 133/134 | $\frac{140/141}{2}$ | Dimer-Monomer Ratio |
|---|---|---|---|
| 1.00 | 0.07822 | 0.07876 | 0.80 |
| .83 | .07843 | .07891 | .79 |
| .71 | .07764 | .07882 | 1.65 |
| .50 | .07779 | .07887 | 1.32 |
| .33 | .07864 | .07878 | .39 |

An examination of the data shows immediately that the 133/134 ratio varies, but that this variation does not correlate with the sodium content. If, however, a plot is made of both the 133/134 and $\frac{140/141}{2}$ ratio as a function of the "dimer-monomer" ratio, it will be observed that the latter ratio is independent of the concentration of the bi-molecular species, while the 133/134 ratio is practically a linear function of the dimer-monomer ratio. Various methods of sample preparation have been investigated, but no sure means of controlling the concentration of the mono- and the bi-molecular species has been found. Fusion tends to eliminate the dimer ion. Vacuum drying of the salt, without fusion, in general gives an observed "dimer-monomer" ratio of 2.0 or above.

The formation of the molecular ions in vapors of the alkali metal halides, both positive ions and negative ions, had been observed and reported by Ionov (11) and Dukyelskii, Zandberg, and Ionov (5). In March, 1953, Dr. Lewis 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. This will shortly appear as a report from the Chemistry Department of the Brookhaven National Laboratory. The observations in this laboratory agree in general with those which he made. Variation in the dimer-monomer ratio was observed in different experiments, but never with a specific sample of salt in a fixed geometry of oven and ion source. No change was observed in the ratio during a run. Elementary kinetic theory considerations rule out secondary reactions of ions, atoms or molecules in the small volume of the chamber at the low pressures encountered--estimated to be on the order of $1 \times 10^{-5}$ mm. or less. Additional evidence that recombinations did not account for the "dimer" ion is that no shift in the "dimer-monomer" ratio is observed with change in the current of ionizing electrons from 10 microamperes to 500 microamperes.

Thus, it appears well established that two molecular species are present in the vapor. Friedman determined the partial heats of sublimation to monomer and dimer at 0° K to be 44.5 ± 7 and 45.0 ± 2 kcal, respectively. The heat of dissociation of $(LiI)_2$ into gaseous monomers was found to be

44.0 ± 2.2 kcal. Friedman has not examined the cause of variations in the dimer-monomer ratio between experiments and time has not permitted the writer to make such an investigation. Some attempts have been made to investigate the crystal structure with a heated diffraction camera but results were not conclusive. One gets the impression that the fused salt may exist as an amorphous and a crystalline phase and from one of these, probably the amorphous, there is a predominance of formation of the monomeric vapor.

The indications are strong that the $Li_2I^+$ ion in this system must be the parent and that reliable ratio measurements can be made only on this ion. It is formed by the dissociation of an iodine and this should not involve any discrimination because of isotope effects. The dissociation of the molecule with removal of a lithium, however, does introduce isotope effects. This is clearly demonstrated by measurement of the ratios 140/141, 133/134 and 6/7 on the same sample. Typical results of such measurements are given in the following table.

## TABLE III

### RATIOS MEASURED ON DIFFERENT IONS FROM LITHIUM IODIDE

| Relative Intensity | Ratio Measured | 6/7 | 7/6 |
|---|---|---|---|
| 100 | 140/141 | 0.07996 ± .00019 | 12.51 ± .04 |
| 44 | 133/134 | .07822 ± .00009 | 12.78 ± .02 |
| 27 | 6/7 | .07480 ± .00016 | 13.37 ± .03 |

The 156/157 ratio ($LiNaI^+$) when sodium is present agrees with the 140/141 ratio. Measurement of the 6/7 ratio may well be unreliable also for reasons of discrimination in the instrument.

For a period of several weeks it was found impossible to secure agreement between two instruments on identical material. Every possible change was made. Electrometer grid resistors, and even the electrometer panels were interchanged. Readings were made with the decade potentiometers reversed. A variety of accelerating voltages from 900 to 3000 volts was tried. Slit width at the receiver was varied. Focussing conditions were deliberately changed. The instruments were operated with and without source magnets. Measurements were made with electron energies from 20 volts to above 75 volts. The ionizing electron current was drastically altered. The instruments were operated with the electron trap both at case potential and at the +75 volts normally used. None of these changes produced any significant alteration in the 140/141 ratio. The bias was finally traced to an improperly connected battery on the secondary electron repeller plates in the collector end of the tube. This battery, normally applied -22.5 volts to the plates to prevent emission of secondary electrons. It had been connected to apply +16 volts. As soon as the plates were grounded or put at negative voltage the bias disappeared. The change from 0 volts to -45 produced no change in the ratio. No bias was observed with cadmium, lead, bromine or copper which had been measured on the same instruments. Thus, it would appear that, in spite of the high mass, the ion which contains the $Li^6$ isotope is more effective by about 2.5% in knocking out secondary electrons from the Nichrome V collector plate. A multiplication of about 50% was being obtained by the secondary emission process.

The many alterations which were made give increased confidence in the reliability of the measurements. In addition, since it had been observed in one instrument that there appeared to be other ion beams striking the slit plate, the tubes were disassembled, the exit face of the tubes beveled, and all receiver surfaces painted with Aquadag. The beams, which appeared to be both scattered positive ions and secondaries or negative ions, were eliminated for this mass range. There was no change produced in the measured ratios by these alterations and one thus has every confidence that the results have not been affected by collection of spurious or scattered beams.

At both mass positions, 133-134, and 140-141, on both instruments the valley between the two peaks being measured was consistently 0.5% or less of the height of the smaller of the two peaks. This was true when the slit was collecting 100% of a single ion beam. Pressures were below $6 \times 10^{-7}$ when readings were being taken. No effect on ratio was observed, even with pressures up to $2 \times 10^{-6}$. No shift in ratio was observed to occur with time and some of the samples investigated were sublimed for many hours.

The ion beams were brought alternately upon the receiver slit by varying the magnetic field. The voltage developed in the $4 \times 10^{10}$ ohm input resistor of the FP-54 electrometer tube was cancelled by voltage from battery operated, precision decade potentiometers. These identical units, fed from the same battery were ganged with the switch which selected scanning control A or B on the magnet supply. It was thus possible to insert automatically the proper voltage to buck out each of the two peaks. Residual galvanometer deflections were converted to potentiometer readings by interpolation factors experimentally determined after each set of ratio measurements.

It was customary to make, alternately, eleven readings of the small peak and ten of the large peak. The ratios were calculated by averaging two consecutive readings of the A peak and dividing by the intervening B peak. The ten ratios thus obtained were treated statistically as independent readings. Calculation in this manner tended to correct for time dependency of the ion currents, since in general there was a slow decrease or increase in the readings because of changes in the surface area of the sample or because of changes in the voltage on the source furnace. The 140/141 ratio is divided by two to give the 6/7 ratio.

## CHEMISTRY

The presence of a non-volatile lithium compound in the iodide is certain to lead to errors in the measured ratios. Thus, since the lithium iodide was prepared by treatment of an appropriate salt with hydriodic acid, this acid must be very thoroughly purified. Acid obtained commercially contains about 1.5% of hypophosphorous acid ($H_3PO_2$) as stabilizer. Distillation of the acid "as received" to separate it from the phosphorous compound is not entirely satisfactory. If it is done in this fashion, an inert atmosphere should be used. The most satisfactory purification scheme found was to add to the acid an amount of elemental iodine calculated to oxidize the $H_3PO_2$ to $H_3PO_4$. The acid was then refluxed. Further addition of iodine was made if necessary until a slight iodine color persisted. The acid was then distilled in all glass apparatus with a short column packed with glass beads to eliminate spray. The first and last 15% were rejected. The acid so prepared gave a very faint test for phosphoric acid indicating the presence of only a very few parts per million. The acid was stored in dark bottles out of direct light. Frequent preparations were made in order to have on hand acid which was not too heavily loaded with iodine.

Preparation of the iodide from carbonate or hydroxide is obviously very simple, involving simply addition of hydriodic acid and evaporation to dryness on a hot plate. Other salts were converted to sulfate by adding sulfuric acid and fuming off the excess. The sulfate is reduced by heating with HI and free iodine liberated. The evaporation should be repeated three times to insure decomposition of all the sulfate and removal of free sulfur.

The dry lithium iodide, probably between tri and monohydrate, could then be transferred to 5 mm o.d. quartz tubes, attached to a vacuum system and gently heated until all the water was driven off. Fusion in the water of crystallization usually occurred if the heating was done at all rapidly. The salt was heated until it refluxed and gave a quiet melt, and sealed off under vacuum. The tube was cut a few millimeters from the bottom and this capsule placed in the ion chamber.

Standard practice was to add an amount of ammonium iodide about equivalent to the lithium iodide before the final evaporation with hydriodic acid. The addition of this salt was made in order to inhibit hydrolysis. The use of fusion tubes was abandoned in favor of adding sufficient absolute ethanol or methanol to the dry iodides to make a saturated solution. Into this solution were dipped small rolls of fine nickel wire cloth of circa 180 mesh or small fragments of porous alundum. These porous substrates had been washed with hydrochloric acid and then with distilled water in a Soxhlet extractor. They were oven dried and just before use were dipped in absolute alcohol and the solvent was burned off to give additional drying and degreasing.

The sample "sponge" was warmed over a hot plate until no longer drippy, dropped into an 8 mm o.d. glass test tube and attached to the high vacuum system. It was gently warmed until the ammonium iodide had sublimed out of the sample. The samples were then thoroughly pumped and sealed off. In general an effort was made to avoid an excess of iodine in the solution for fear of reaction with the nickel. However, check samples were prepared which contained large amounts of free iodine and hydriodic acid. No significant differences were observed in the ratio measurements, even though there was good evidence of the formation of nickel iodide, since in the heating of the samples a dark sublimate of that compound appeared on the glass.

When the iodide was not immediately used it was re-evaporated with addition of a small amount of hydriodic acid before sample preparation to be sure that the samples were entirely iodide.

## Treatment of Ore Samples

Spodumenes: ($LiAlSi_2O_6$). Single crystals, or portions of single crystals were ground in a boron carbide mortar. The powder was heated in a platinum dish over a blast burner to convert the material to beta spodumene so that it would be readily attacked chemically. Sulfuric acid and 40% hydrofluoric acid were added and the silicate decomposed. The solution was evaporated under an infrared lamp and the sulfuric acid was fumed off. The cake was slurried in water and filtered. Most of the aluminum present remained as aluminum oxide. No flame test for lithium was secured from the residue. The filtrate was diluted somewhat, and ammonium hydroxide added to precipitate aluminum and iron. The solution was boiled to remove excess ammonium hydroxide and then filtered. The washed precipitate gave no test for lithium. The filtrate was evaporated and the ammonium salts fumed off. The entire sulfate residue was then converted to iodide.

Lepidolites: $K_2Li_3Al_4Si_7O_{21}(OHF)_3$. The same general treatment was used as for the spodumenes. The initial heating should not be prolonged, for fusion of the mica will occur. The crude sulfates were treated by ion exchange chromatography to separate the lithium from the large amounts of the other alkali metals present.

About 0.4 grams of the crude sulfate were dissolved in a small amount of water and charged to a column of 140-180 mesh Dowex-50 resin, 25 mm in diameter and with a resin bed 12 cm long. After charging, 50 ml of water were washed through at a rate of 2-3 ml per minute. The lithium was eluted at the same rate with 0.48 N. hydrochloric acid, care being taken to collect all of the lithium "peak" to avoid any possibility of isotope fractionation. Flame tests were used to monitor the washing of the column. The lithium solution was evaporated to dryness with a small amount of nitric and sulfuric acids and converted to iodide. The sodium was eluted from the column and discarded. The remainder of the alkali metals present were washed out with 3.5 N. acid and separately recovered as sulfates. In general potassium, rubidium and cesium were present.

Phosphates: Amblygonite ($LiAlFPO_4$), Triphylite ($LiFePO_4$), Searles Lake ($Li_2NaPO_4$). The first preparations of these materials were made by dissolving them in sulfuric or hydrochloric acid and precipitating the phosphoric acid as ferric phosphate in ammonium acetate-acetic acid buffer with addition of an excess of ferric nitrate. This is not a highly satisfactory chemical separation. The preferable approach was to dissolve a few tenths of a gram of the ore in hydrochloric acid, dilute with water to reduce the acid concentration and then to charge the sample to the Dowex-50 column. The phosphoric acid was washed out, and the lithium eluted with 0.48 N. hydrochloric acid.

## RESULTS AND DISCUSSION

The results of the measurements upon the ores thus far examined are given in table IV.

It is apparent that the ratio of the lithium isotopes varies with origin. The variation is not as great as is observed in commercial chemicals in which the 7/6 ratio varies from 12.44 for lithium carbonate from Searles Lake to 12.93 for the lithium carbonate chosen for the laboratory standard. By contrast the ores vary from 12.47 for a Kings Mountain spodumene crystal to 12.72 for the lepidolite from Nepora, P. E. A. The average of the spodumenes is 12.61 which is very close to the average of 12.63 for seven lepidolites. The phosphate minerals appear to run somewhat lower, with the amblygonite from the High Climb Mine in South Dakota being an exception.

The spodumene pseudomorph from the Helen Beryl Mine contained very little lithium. The single result obtained on this sample differs significantly from the measurements on the unaltered spodumene from the same source. Several other minerals classed as lepidolites contained so little lithium that no measurements could be made. The lepidolite from the Ingersoll mine was carried through chemistry and through ion exchange in duplicate. The agreement between the two samples is very satisfactory. The scattering of results on the phosphate minerals is believed to indicate that phosphate removal was not complete.

A few experiments were made to determine the effect of various chemical procedures on the lithium isotopic ratio. Lithium carbonate was precipitated from a lithium nitrate solution containing 35 grams per 100 grams of water. Sodium carbonate (7.35 grams) was added with stirring and the solution was digested just short of boiling for an hour and then filtered rapidly. The starting material showed a 7/6 ratio of 12.87 and the precipitated carbonate 13.07. A further treatment of the filtrate with 7.4 grams of sodium carbonate with hot digestion and rapid filtration gave a second precipitate in which the measured ratio was 13.02. Wagner, Pelz and Higatsberger (15) have recently reported changing the isotopic ratio of lithium from 12.48 to 14.03 by repetitive precipitations by addition of sodium and ammonium carbonate to a chloride solution.

An experiment was made which involved heating a solution of lithium carbonate which was saturated at room temperature. On heating, lithium carbonate was precipitated. The isotopic composition of the precipitate and of the mother liquor was determined. No significant difference was found, since the precision limits of the two determinations overlapped. However, the indicated direction of separation was the same as in the experiment involving precipitation by addition of sodium carbonate.

## TABLE IV

## ABUNDANCE OF LITHIUM ISOTOPES IN CERTAIN LITHIUM MINERALS

| Sample and Origin | $\mathrm{Li}^7/\mathrm{Li}^6$ |
|---|---|
| Spodumene, Kings Mountain, N. C.[a]<br>(Mine operated by Foote Mineral Co.) | |
| Single crystal, surface ore | 12.54 ± .03 |
| | 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]<br>Dixon County, New Mexico | |
| Single crystal | 12.60 ± .05 |
| | 12.65 ± .04 |
| | 12.57 ± .07 |
| Spodumene, Helen Beryl Mine[c],<br>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,<br>Custer County, South Dakota[c] | |
| Preparation A | 12.69 ± .02 |
| Preparation B | 12.71 ± .02 |
| Lepidolite, Spain[d] | 12.57 ± .03 |

TABLE IV - contd.

| Sample and Origin | $Li^7/Li^6$ |
|---|---|
| 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 |
| $Li_2NaPO_4$, 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 |
| Bureau of Standards, $Li_2CO_3$ | 12.48 ± .03 |
| | 12.49 ± .03 |
| | 12.51 ± .03 |
| | 12.51 ± .03 |
| Laboratory Standard, $Li_2CO_3$ - Average 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

A third precipitation experiment was made with a lithium nitrate solution containing 5 grams per 100 grams of water. To this was added 2.7 grams of ortho phosphoric acid calculated to precipitate 66% of the lithium as phosphate. The solution was made alkaline with ammonium hydroxide and digested warm. It stood overnight before filtering. Samples of solution and the precipitate were then both acidified slightly and charged into the Dowex-50 chromatographic columns, the phosphate washed out and the lithium recovered completely by eluting with 0.48 N. HCl. The isotopic ratio was determined in iodide prepared from these two samples. For the supernatant liquor two determinations gave 12.79 and 12.84 ± .03 and for the precipitate 12.89 and 12.90 ± .02. The direction of separation is the same for both the phosphate and the carbonate precipitations. This is, however, at variance with the observation that the phosphate ores in nature tend to contain a greater amount of $Li^6$ than do the silicates. Samples fused in glass consistently gave higher readings of the 7/6 ratio than those otherwise prepared, indicating that the formation of a silicate phase had selectively tied up the $Li^6$. This appears to be in direct opposition to the observations made in aqueous solution when an insoluble salt is precipitated. Further investigation is needed to clarify these observations.

In view of the demonstrated effect of precipitation on the isotopic ratio one may well ascribe the variations observed in nature to chemical effects. The writer had posed the hypothesis that the variations which Thode, et al (14) have demonstrated in boron and those which are here reported in lithium might be related to neutron exposure, since both elements possess isotopes with large capture cross sections. In pegmatites in which most of the lithium minerals occur, there is concentration of the light and heavy elements and one might expect a higher neutron incidence from $\alpha$,n reactions on light elements than would be the case in the average igneous rock. A neutron density of 608 $cm^{-2}d^{-1}$ has been demonstrated by Eugster (6) under 2100 meters of rock. The writer knows of no determination of neutron density in a pegmatite. Determinations of the $B^{10}/B^{11}$ ratio in tourmaline from pegmatites should prove interesting. This mineral carries a fair percentage of that element and has not been recently subjected to water transport as have the boron samples which Thode measured, since the latter were principally borax and boric acid. Certainly, further measurements are necessary to clarify the cause of the observed variations in both of these light elements.

The variation between individual single crystals of the Kings Mountain spodumene appears to be real. The two samples of unweathered ore were broken out of a single piece of rock, while the weathered surface ore was from a different location. As with any element in which variations are observed, different portions of a single mineral deposit should be investigated together with the surroundings if clues as to the mode of formation are to be established.

The absolute value of the natural abundance of the lithium isotopes may be open to some question. In view of the many variables which were systematically investigated in these measurements, it is difficult to see wherein the mass spectrometry may be in error. The value which one would assign would be 12.47 - 12.72, since this is the range observed in the ores investigated. The evaporites, such as the two samples from Searles Lake must be left out of consideration on account of the demonstrated effect of incomplete precipitations. In this range will fall the measurements of Hintenberger on lithium metal and on lithium chloride, after correction for free evaporation, and measurements of Inghram and of White and Cameron. The measurement of Hibbs overlaps the lower limit.

The atomic weight determination of Richards and Willard in 1910 (13) leads to a value of the ratio of 12.11 ± .20. They adopted as the purification method for their lithium salts partial precipitation of lithium fluoride by addition of ammonium fluoride. Several precipitations and washings freed the salt from other alkali metals and calcium and magnesium were then removed by several recrystallizations of perchlorate or nitrate. Such treatment would certainly alter the isotopic composition but the magnitude cannot be predicted from any experiments so far made. A recent publication by Hutchison (9) argues for a value of the ratio of 11.50 on the basis of x-ray measurements together with crystal density measurements. This value is far outside the experimental error of the work reported here and one can only wonder what might have been the history of the particular sample of lithium fluoride which was used.

## SUMMARY

1. The mass spectrometry of lithium is discussed and evidence is presented for the reliability of measurements made upon the dimer ions of masses 140 and 141 ($Li^6Li^7I^+$ and $Li^7Li^7I^+$), in contrast to measurements at 133 and 134 on the monomeric form of the vapor.

2. The preparation of lithium iodide samples is described. Both silicate and phosphate ores have been examined. Ion exchange chromatography has been used to remove phosphate, and to separate lithium from other alkali metals.

3. Variations in the 7/6 ratio in commercial chemicals has been observed to be between 12.44 and 12.93. The variation in the ores so far examined is between 12.47 and 12.72.

4. Partial precipitation of lithium as carbonate or phosphate from a nitrate or chloride solution is shown to alter the isotopic ratio. The precipitate is depleted in $Li^6$.

5. The need for further investigation to establish the geochemical significance of the observations is indicated.

## ACKNOWLEDGMENT

Many of the lithium measurements have been made by W. G. Schwab and some by J. L. Kassner, Jr. A. S. Trundle, III, assisted greatly in the construction of one of the spectrometers on which these determinations were carried out.

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