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Investigation of the Isotopic Constitution of Lithium

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Investigations of the separation effects of the isotopes of lithium have been carried out by evaporation of lithium ions from a tungsten surface and by ionization of molecular beams of lithium compounds by an electron beam. In the first case two processes of ionic emission have been discovered: the first process occurs at low anode temperatures with a separation coefficient greater than for free evaporation; the second process takes place at high anode temperatures without separation of the isotopes and provides a simple and accurate method of measuring the relative abundance of the isotopes of lithium. The relative abundance of the lithium isotopes Li^7/Li^6 was found to be 12.47 ±0.02. A small separation effect of unexplained origin has been found to take place during ionization of the lithium compounds by the electron beam. By means of the method developed by the authors, the relative abundances of the lithium isotopes have been measured for several minerals.

PREVIOUS results of relative abundance measurements of lithium isotopes with mass numbers 6 and 7 show considerable spread caused by the impossibility of computing with sufficient accuracy the separation property of the ion source. Because of this, the values quoted by various authors for the relative abundance of the lithium isotopes Li^7/Li^6 range from 5 to 37. Considering the difficulty of introducing reliable corrections in the relative abundance measurements of lithium isotopes, excellent agreement may be said to exist between the early measurements of Brewer[1] and later measurements of Hintenberger[2], Inghram, Hess and Hayden[3], White and Cameron[4] and Hibbs[5]. In the published investigations of the isotopic constitution of lithium, the lithium ions were obtained by thermionic emission from hot surfaces (glass melt, Kuntzman anode, platinum surface). Ionization was also produced in a molecular vapor of lithium compounds LiCl and LiI by an electron beam.

We have measured the relative abundance of lithium isotopes utilizing various methods for ion production and making use of two-mass spectrometers built by us (predecessors of mass-spectrometers MC - 1, MC - 2 and others).

A magnetic sector field is used in the mass-spectrometers with a 60° angle of deflection and 16° 18′ beam entry and exit angles. Thereby second order geometrical aberrations in the image are reduced to zero[6,7]. The introduction of higher order focussing could increase somewhat the resolving power of the instrument, but a better reason for correcting aberrations is given next. During the course of a series of experiments an insulating layer was often formed in the ion source and on the entrance slit, somewhat deflecting the beam from its original direction, thereby worsening the image and thus the resolving power of the instrument. In the case of a field with corrected aberrations, the position of the focus and the width of resolution do not depend on small variations in the direction of the beam; thus the resolving power and the line shape depend much less upon working conditions at the ion source.

The radius of the average ionic trajectory is 200 mm; correspondingly the dispersion in the plane of the receiver,perpendicular to the beam,is 1.33 mm for a 1% mass difference. The resolving power of the mass-spectrometers that we have used is $m/\Delta m = 1000$ for a 0.1 mm wide exit slit of the ion source and 0.1 mm wide entry slit in front of the ion collector. During the course of our experiments we have used as an ion source a source of Bleakney[9] construction employed in reference 8 for gaseous ionization, or a hot anode of a form proposed by Koch[10]. A description of the latter appears below.

The ion source and the analyzer tube are pumped out by separate mercury-diffusion pumps

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

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[8] A. O. Nier, Rev. Sci. Instr. **11**, 212 (1940); **18**, 398 (1947).

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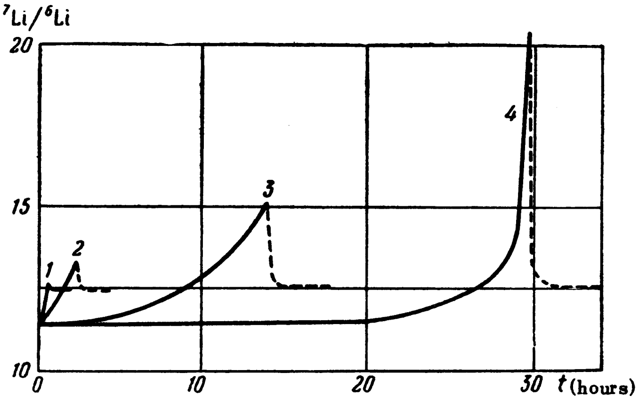
[10] J. Koch, Z. Physik **100**, 685 (1936).

which can pump 7 l/sec through a metallic trap. The tube of the mass-spectrometer is made of copper with steel end flanges and provided with metallic (copper or aluminum sheet) gaskets[11]. Electrical connections to the electrodes of the ion emitter and receiver were soldered in Kovar, so that the entire tube could be heated to 400°C and outgassed. The gaskets appear completely reliable and in some of our instruments were heated hundreds of times without need to change or tighten the bolts. We reached a final vacuum definitely below 10^{-8} mm of mercury (measured with an ionization manometer tube LM-2, by reading its ion current in the mass-spectrometer itself, and applying the proper correction for an ionization manometer at lowest pressures).

The ion source is fed by the usual electronically stabilized system. The ion accelerating potential measures 2500 V and is maintained constant. During adjustment only the magnetic field varies. The ion currents are measured with one or, when using two receivers, with two constant current amplifiers with 100% feed-back; moreover when using two amplifiers, the ratio of the ion currents could be immediately determined on a decimal voltage divider.

1. EVAPORATION OF LITHIUM IONS FROM A TUNGSTEN SURFACE

In order to obtain more reliable data about the evaporation process of lithium ions and a correct value for the relative abundance of the isotopes, we decided to study the emission process of lithium ions from the beginning of ionic emission until exhaustion of the ion source. For a hot anode we used an anode of early Koch[10] design but of simpler construction. The anode consists of a ribbon of tantalum pressed into the shape of a groove and filled with 15 mg of fine tungsten powder. This anode is carefully evacuated for several hours at a temperature of 2200° C in a special apparatus after which no trace of alkaline ion emission can be detected. During the heating process the tungsten powder is baked into a hard porous body into which the lithium salt is introduced in the form of water or alcohol solution. With the help of such an anode in the mass-spectrometer, a constant ionic current can be obtained easily and repeatedly in high vacuum. The anode is heated by a constant current from a battery. During measurements the battery is charged by a rectifier; the current through the rectifier is kept equal to the anode heating current thereby providing a constant heating current and ensuring exact measurements up to anode temperatures of 2000°C. The ion current is registered by means of a self-recording apparatus. In order to record the ion current of the lithium isotopes as a function of time, an automatically repeating recording was set up with automatic switching of the sensitivity of the recording apparatus. The method worked out for recording the ion currents of lithium isotopes is of special importance, when carrying out an isotopic analysis of small quantities of material with quickly falling ionic currents. Measurements were carried out with different quantities of LiCl (5×10^{-9}, 3×10^{-8}, 2×10^{-7} and 10^{-6} gm) as shown on the figure.



Relative abundance of lithium isotopes as a function of time during evaporation of lithium ions from the surface of tungsten powder. Original quantity of LiCl: *1* - 5×10^{-9}; *2* - 3×10^{-8}; *3* - 2×10^{-7}; *4*- 10^{-6} gm.

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[11] W. Paul, Z. Physik **124**, 244 (1948).

At the beginning, the value of the ratio Li^7/Li^6 is found to be 11.42 ±0.02 for all quantities of lithium chloride. The smaller was this quantity the faster the ratio Li^7/Li^6 grew, and the larger was this quantity the larger this ratio became; in the case of 10^{-6}g, the ratio Li^7/Li^6 grew in 30 hours to 20.60.

While the measurements were carried out the ionic current remained constant with the anode temperature increasing gradually from 800 to 1200°C. The first process of evaporation of lithium ions during which the ratio Li^7/Li^6 increases in time takes place within this temperature interval. Upon further increase in temperature the ion current falls sharply and becomes unstable. An increase of anode temperature to 1500°C does not produce a visible increase in ion current. It is therefore impossible to obatin an exact value for the ratio Li^7/Li^6 in the temperature interval 1200-1500°C. This interval is indicated on the figure by dotted lines. There is a strong impression that the material under investigation has completely disappeared.

However, upon further increase in temperature a constant ion current is observed again, and maintains itself with gradual increase in temperature to 2000°C. During this process the value of the ratio Li^7/Li^6 does not change in time and remains constant upon further increase in anode temperature until exhaustion of the anode, which takes place around 1800-2000°C. Measurement of the value of the ratio during this process yields 12.48 ±0.02.

Thus, two entirely separate processes take place during evaporation of lithium ions. During the occurrence of the first process the value of the abundance ratio of the lithium isotopes increases with time; the duration of the first process depends upon the starting quantity of lithium. During the second process the ratio Li^7/Li^6 remains constant. Since we have followed the whole evaporation process of lithium ions by means of the automatically recording potentiometer, we can compute the total ionic charge $\int i\,dt$ produced during the time T, the life of the anode. Then the ratio

$$\int_0^T i_1 dt \Big/ \int_0^T i_2 dt,$$

where i_1 is the total current of Li^7 and i_2 is the total current of Li^6, must equal the natural ratio of the lithium isotopes, independently of the isotope effect observed during the first process of evaporation of lithium ions. The use of this method for computing the relative abundance of lithium isotopes yields the value 12.47 ±0.02. Hence the value of the relative abundance of lithium isotopes obtained during the second process coincides with the true value of this ratio within limits of experimental errors.

The two processes of evaporation of lithium ions can be explained as follows. In the mass spectra, we can only observe the ions of metallic lithium; this means that dissociation of the salt takes place during the first heating of the anode. The free chlorine easily combines with tungsten and volatilizes into the vacuum. Lithium is mainly adsorbed in the form of ions and neutral atoms by the grains of the baked tungsten and a small part of lithium dissolves into the tungsten forming an alloy.

At lower anode temperatures, i.e., during the first process, ionic emission depends upon the adsorption of lithium ions by the tungsten surface. The growth of the measured ratio Li^7/Li^6 is explained by the gradual enrichment of the residue in the anode with heavier isotope, called isotope effect in free evaporation. If the evaporation of the lithium ions proceeds ideally, then the initial value of the ratio multiplied by the square root of the ratio of the masses must give the true value of the abundance ratio, in other words one must obtain a separation coefficient equal to $\sqrt{7.018/6.017} = 1.080$. The results of our measurements give for the separation coefficient the value $12.47/11.42 = 1.092 \pm 0.002$. The value thus obtained is greater than the separation coefficient predicted by the kinetic theory of gases. This means that during the first process a small effect is present in addition to the free evaporation and which further enhances the evaporation of Li^6 ions. This effect may be due to a difference in the elastic properties of the vapors of the lithium isotopes. During the first process the lithium adsorbed by the grains of tungsten is used up after a while, the ion current falls and becomes unstable. The end of stable ion emission makes it possible to reach considerably higher anode temperatures. From this moment on the second process of evaporation of lithium ions begins. In this case the ionic emission depends upon that part of the lithium which formed an alloy with the tungsten at the beginning of the heating of the anode. The relative abundance of lithium isotopes in this alloy remains normal since this part of the lithium is not exchanged with the lithium adsorbed by the grains of tungsten; it begins to evaporate with normal isotopic abundance at sufficiently high temperature, starting when the solubility of lithium in tungsten decreases with increasing temperature. The lithium which is freed upon dissolution of the alloy is vaporized and does not remain; therefore no separation effect is observed and the measured value of the abundance ration of the isotopes remains constant and is the true value.

2. THE IONIZATION OF LITHIUM COMPOUNDS WITH THE HELP OF ELECTRON BEAMS

For ideal evaporation from a surface, one might expect that the number of molecules evaporating from the surface which contain the lighter isotope is $\sqrt{M_2/M_1}$ times greater than the number of molecules containing the heavier isotope, where M_1 and M_2 are the molecular masses of the respective compounds. Because of this, the isotopic concentration within a given unit volume of atomic beam does not vary since as we just saw $\sqrt{M_2/M_1}$ more light molecules flow into this unit and similarly $\sqrt{M_2/M_1}$ more light molecules flow out of it.

It should therefore be very simple to measure the relative abundance of isotopes at the start of the evaporation process of any lithium compound or even lithium itself. In order to verify this, we prepared from lithium carbonate (supplied by the Shering-Kal'baum Co.) after additional purification by repeated recrystallization, the compounds LiF, LiCl, LiBr and LiI; moreover observations of the reaction yield made it possible to conclude that no chemical separation of isotopes had taken place. A small quantity of the compound contained in a small electrically heated platinum crucible is introduced into the ion source from which it can reach by evaporation the ionization region. The ratio Li^7/Li^6 arising upon dissociation of the halogen ions LiF^+, $LiCl^+$, $LiBr^+$ and LiI^+ is measured every time. There is superimposed upon the Li^7Cl^{37} ions a small intensity beam of CO_2^+ ions with the same mass number 44, and which cannot be corrected for; small amounts of Rb^{85} and Rb^{87} ions are also superimposed upon the Li^6Br^{79} and Li^6Br^{81} ions; one can however correct for these without serious error from the known abundance ratio of Rb. The results of these measurements reveal that within experimental accuracy (0.2%) the ratio Li^7/Li^6 is the same for all ions and equals 12.43 ±0.03. In order to settle the question of reliability of our results we measured at the same time the relative isotopic abundance of Cl and Br, for if the relative isotopic abundance of lithium varies during evaporation of the lithium halides, that of chlorine and bromine must vary in the same way. Indeed we discovered for both elements a small difference outside experimental errors, from the values we found on the very same apparatus for large quantities of the compounds in gaseous form.

	Cl^{35}/Cl^{37}	Br^{81}/Br^{79}
Evaporation of lithium compounds	0.3251	0.979
Gaseous compounds	0.3263	0.984

This difference, the reason for which we have not found, gives reasons to conjecture that the computed ratio for Li^7/Li^6 may be similarly too low. Since the difference in question is so small we can recompute the value of the ratio Li^7/Li^6 proportionally to the change in relative isotopic abundance of Cl and Br.

We find in that case

$$Li^7/Li^6 = 12.43\ \frac{0.3263}{0.3251} = 12.48 \text{ and}$$

$$Li^7/Li^6 = 12.43\ \frac{0.984}{0.979} = 12.49$$

When a few milligrams of easily vaporized salt of LiCl, LiBr, LiI are placed in the anode box and the box is heated externally, a constant ion current is produced. To obtain irreproachable data, one should use only Li^+ ions,for the presence of large quantities of heated metal of high mass number gives rise to a great many difficulties. The material vaporizing from the inner walls of the anode box recondenses on the inner walls except for a small quantity which escapes through the slit. Hence, there is no free evaporation, but a balance is established at the wall between evaporation and condensation. We found for the Li^+ ions that the ratio $Li^7/Li^6 = 12.47 \pm 0.03$, and thereby have confirmed the value computed from the first measurements.

Thus, the relative abundance of lithium isotopes obtained from ionization of LiCl and LiBr by an electron beam agrees within experimental error with the value obtained from emission of lithium ions from a hot tungsten surface.

The results of measurements of relative abundance of lithium isotopes obtained from different methods and applied to the same preparation of Li_2CO_3 supplied by Shering-Kal'baum are as follows:

Ratio of integrals of currents of lithium isotopes	12.47 ±0.02
During occurrence of the second process	12.48 ±0.02

Recomputed value:

$$12.43\,\frac{0.3263}{0.3251} = 12.48 \pm 0{,}02$$

$$12.43\,\frac{0.984}{0.978} = 12.49 \pm 0.02$$

During evaporation from anode walls 12.48 ±0.03

Average 12.48 ±0.02

Comparison of our average value for the relative abundance of lithium isotopes with values obtained by other authors,

12.53,[1]

12.4 ±0.2,[2]

12.53 ±?,[3]

12.7 ±0.07,[4]

12.46 ±?[5]

shows good agreement with the result of Hibbs[5].

Based on the results of investigations of lithium ions emission from a hot tungsten surface there emerges a simple method for obtaining the relative isotopic abundance of lithium. This method makes use of the second process of emissions of lithium ions. During this process, measurement of the ration Li^7/Li^6 gives the relative isotopic abundance of the material under investigation. During the occurrence of the second process of emission of lithium ions a stable ion current is obtained in the anode temperature interval 1600 - 2000°C; with as little as 10^{-9} gm of lithium, this process permits a determination of the relative isotopic abundance with an accuracy of 0.2%.

3. RESULTS OF MEASUREMENTS OF RELATIVE ABUNDANCE OF LITHIUM ISOTOPES IN SEVERAL MINERALS

Making use of the method worked out, the relative abundance of lithium isotopes was measured in four typical minerals bearing lithium, and in one mineral in which lithium occurs as an accidental compound in small concentration. The results that were obtained are presented in the table. There appears to be excellent agreement between the results of measurements on the four minerals and on the industrial compound; at the same time the lithium found with a concentration of 1.7×10^{-6} in pitchblend shows within experimental error a noticeable difference in isotopic ratio.

The impoverishment of the lithium isotope of mass number six found in pitchblend may be explained by the effect of neutrons appearing in the ore as a result of spontaneous uranium fission and (α, n) reactions. Calculations show that the decrease in pitchblend of the isotope Li^6 does not depend upon the effect of α-particles, but upon the action of neutrons in the reaction $Li^6(n, \alpha)H^3$.

Mineral	Source	Li^7/Li^6
Lepidolite	Village of Shrosha, Upper Imeretia Georgian SSR	12.49 ±0.02
Zinnwaldite	Ergerbirge Zinnwald, Germany	12.48 ±0.02
Spodumene	Kalbinski mountains Kazakh SSR	12.48 ±0.03
Petalite	Kalbinski mountains Kazakh SSR	12.49 ±0.02
Pitchblend	Erzgebirge Jachimov, Czechoslovakia	12.83 ±0.04
Mean value of Li_2CO_3	From all measurements on lithium obtained from Shering-Kal'baum	12.48 ±0.02

Note added in proof.- In 1955 M. Higatsberger [Acta Phys. Austria 9, 179 (1955)] published the results of his measurements on the relative isotopic abundance of lithium as 11.56 ±0.04. This value measured at the beginning of the process of ionic evaporation compares with the value obtained by Brewer for the starting value of the ratio Li^7/Li^6, 11.60. Higatsberger, like Brewer, conjectures that the evaporation of lithium ions has the character of a free evaporation, and applies a correction for the isotope effect, 11.56 × 1.080= 12.48, and computes the ratio Li^7/Li^6 to be 12.48. Higatsberger in common with other authors has not studied the process of emission of lithium ions, and apparently makes the hypothesis of free evaporation of lithium ions on the basis of Brewer's work.

In our work we first study the complete process of evaporation of lithium ions from a hot anode surface. By means of our method and without requiring any correction, the relative isotopic abundance of lithium, Li^7/Li^6, is found to be 12.47 ±0.02. The new value that we find for the separation coefficient, 1.092 ±0.002, shows that Higatsberger's correction to the ratio Li^7/Li^6 is not correct.

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