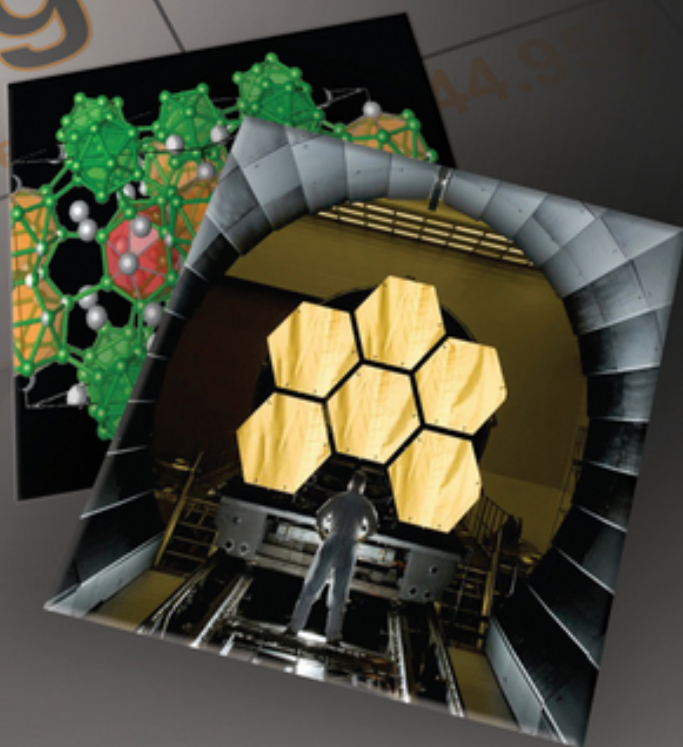


Editor
Timothy P. Hanusa

The Lightest Metals

Science and Technology
from Lithium to Calcium



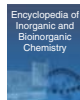
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THE LIGHTEST METALS:
Science and Technology from Lithium
to Calcium

Editor

Timothy P. Hanusa

Vanderbilt University, Nashville, TN, USA

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Contributors

- Yi An** *Texas A&M University, College Station, TX, USA*
- Cation– π Interactions
- Katsutoshi Aoki** *Tohoku University, Sendai, Japan*
- High-Pressure Synthesis of Hydrogen Storage Materials
- Merle Arrowsmith** *Universität Würzburg, Würzburg, Germany*
- Magnesium and Calcium Complexes in Homogeneous Catalysis
- David A. Atwood** *University of Kentucky, Lexington, KY, USA*
- Resource Sustainability
- Nicholas C. Boyde** *Vanderbilt University, Nashville, TN, USA*
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- Isidor Buchmann** *Cadex Electronics, Inc., Richmond, BC, Canada*
- Lithium-Ion Batteries: Fundamentals and Safety
- Elton J. Cairns** *University of California, Berkeley, CA, USA*
- Li-Ion Batteries and Beyond: Future Design Challenges
- Terence M. Civic** *Materion Inc., Mayfield Heights, OH, USA*
- Beryllium Metal Toxicology: A Current Perspective
- Peter J. Cragg** *University of Brighton, Brighton, UK*
- Ion Channels and Ionophores
- Bradley R. Cutler** *University of Illinois, Chicago, IL, USA*
Linden Oaks Medical Group at Edward/Elmhurst Healthcare, Naperville, IL, USA
- Lithium Pharmacology
- Zhili Dong** *Nanyang Technological University, Singapore*
- Processing and Applications of Transparent Ceramics
- Stephen Freeman** *Materion Inc., Mayfield Heights, OH, USA*
- Occurrence and Production of Beryllium
- Yanbing Guo** *University of Connecticut, Storrs, CT, USA*
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- Pu-Xian Gao** *University of Connecticut, Storrs, CT, USA*
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- Timothy P. Hanusa** *Vanderbilt University, Nashville, TN, USA*
- Interrelationships between the Lightest Metals
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XII CONTRIBUTORS

- Andreas Hermann** *The University of Edinburgh, Edinburgh, UK*
• Light-Element Superconductors
- Michael S. Hill** *University of Bath, Bath, UK*
• Low Oxidation State Chemistry
- Yizhong Huang** *Nanyang Technological University, Singapore*
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• Li-Ion Batteries and Beyond: Future Design Challenges
- Arnulf Jäger-Waldau** *Joint Research Centre, Ispra, Italy*
• Solar Energy and Photovoltaics
- Philip G. Janicak** *Northwestern University, Chicago, IL, USA*
Linden Oaks Medical Group at Edward/Elmhurst Healthcare, Naperville, IL, USA
• Lithium Pharmacology
- Michael J. Jaroszewicz** *University of Windsor, Windsor, ON, Canada*
• Solid-State NMR of the Light Main Group Metals
- Ling Bing Kong** *Nanyang Technological University, Singapore*
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- Deborah A. Kramer** *U.S. Geological Survey, Reston, VA, USA*
• Status as Strategic Metals
- Sven Krieck** *Friedrich Schiller University Jena, Jena, Germany*
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- Halvor Kvande** *Norwegian University of Science and Technology, Trondheim, Norway*
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- Sean Li** *The University of New South Wales, Sydney, NSW, Australia*
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- Mark R. Mason** *University of Toledo, Toledo, OH, USA*
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- Shin-ichi Orimo** *Tohoku University, Sendai, Japan*
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- Wenxiu Que** *Xi'an Jiaotong University, Xi'an, P. R. China*
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- Hiroyuki Saitoh** *Japan Atomic Energy Agency, Sayo, Japan*
• High-Pressure Synthesis of Hydrogen Storage Materials
- Robert W. Schurko** *University of Windsor, Windsor, ON, Canada*
• Solid-State NMR of the Light Main Group Metals

- Mark A. Shand** *Premier Magnesia, LLC, Arden, NC, USA*
- Occurrence of Magnesia Minerals and Production of Magnesium Chemicals and Metal
- D. W. Slocum** *Western Kentucky University, Bowling Green, KY, USA*
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- Matthias Westerhausen** *Friedrich Schiller University Jena, Jena, Germany*
- Reimagining the Grignard Reaction
- Steven E. Wheeler** *Texas A&M University, College Station, TX, USA*
- Cation- π Interactions
- Jian Zhang** *Jiangsu Normal University, Xuzhou, P. R. China*
- Processing and Applications of Transparent Ceramics
- Tianshu Zhang** *Anhui Target Advanced Ceramics Technology Co. Ltd., Hefei, P. R. China*
- Processing and Applications of Transparent Ceramics

Series Preface

The success of the *Encyclopedia of Inorganic Chemistry* (EIC), pioneered by Bruce King, the founding Editor in Chief, led to the 2012 integration of articles from the *Handbook of Metalloproteins* to create the newly launched *Encyclopedia of Inorganic and Bioinorganic Chemistry* (EIBC). This has been accompanied by a significant expansion of our Editorial Advisory Board with international representation in all areas of inorganic chemistry. It was under Bruce's successor, Bob Crabtree, that it was recognized that not everyone would necessarily need access to the full extent of EIBC. All EIBC articles are online and are searchable, but we still recognized value in more concise thematic volumes targeted to a specific area of interest. This idea encouraged us to produce a series of EIC (now EIBC) Books, focusing on topics of current interest. These will continue to appear on an approximately annual basis and will feature the leading scholars in their fields, often being guest coedited by one of these leaders. Like the Encyclopedia, we hope that EIBC Books continue to provide both the starting research student and the confirmed research worker a critical distillation of the leading concepts and provide a structured entry into the fields covered.

The EIBC Books are referred to as *spin-on* books, recognizing that all the articles in these thematic volumes are destined to become part of the online content of EIBC, usually forming a new category of articles in the EIBC topical structure. We find that this provides multiple routes to find the latest summaries of current research.

I fully recognize that this latest transformation of EIBC is built on the efforts of my predecessors, Bruce King and Bob Crabtree, my fellow editors, as well as the Wiley personnel, and, most particularly, the numerous authors of EIBC articles. It is the dedication and commitment of all these people that are responsible for the creation and production of this series and the "parent" EIBC.

Robert A. Scott
University of Georgia
Department of Chemistry

October 2015

Volume Preface

We live in a world in which uses for the “lightest metals” are ubiquitous. The seven metals with the lowest atomic number are lithium, beryllium, sodium, magnesium, aluminum, potassium, and calcium, and, apart from lithium and beryllium, are extremely common on earth. Al is the most abundant metal in the earth’s crust (over 8% by weight), and the metals Ca, Mg, Na, and K rank 5th through 8th, respectively. Although the metals themselves were not isolated until the early 19th century, their compounds have been associated with the development of civilization ever since clay pottery was first fashioned in the prehistoric past. Their critical roles in biology, building and construction materials, and electronic devices are testaments to the centrality of these metals in modern daily life. Technological advances in the 21st century have only increased their indispensability, and it is the overwhelming importance of new developments with these elements that *The Lightest Metals* was designed to showcase.

A single volume could not hope to do justice to the extensive chemistry of these elements. Therefore *The Lightest Metals* focuses on several areas of central importance, and a broader selection of topics that may be less familiar to readers. The Background section begins with an overview of the metals, a discussion of their natural abundance and historical uses, and moves on to describe issues of their production, strategic status, and sustainability. The Fundamentals section looks at the low oxidation state chemistry of the elements, metal-centered NMR (both in solution and the solid state), and the issue of cation– π interactions, important to both coordination chemistry and biology. Also included is an examination of ion channels and ionophores, and a fresh look at the controversial issue of beryllium toxicology. The Applications

section reviews new approaches to organic synthesis and catalysis using arylithium, organocalcium and organoaluminum reagents. Several chapters discuss the current state-of-the-art in lithium-ion batteries, and what enhancements or replacements might be on the horizon. Other chapters examine the high-pressure synthesis of hydrogen storage materials, transparent ceramics, light-element superconductors, and one-dimensional nanostructure-enhanced catalysis, in which the lightest metals quite literally play a supporting role — as critically important bases for catalytically active nanorods made of transition metal compounds. Developments in lithium-based therapy for the treatment of depression, and the role of the lightest metals in solar energy conversion and voltaics complete the survey of recent advances.

One of the goals of *The Lightest Metals* is to correct a common perception, even among inorganic chemists, that the light main group metals are somehow limited by their lack of available d orbitals and by their invariant oxidation states. In fact, the wealth of ways in which the metals and their compounds can serve in synthetic, structural, and mechanistic chemistry is restrained only by the imagination of the reader, an imagination that a perusal of *The Lightest Metals* is designed to stimulate.

Finally, I should note that without the unflagging support of the editorial staff at Wiley, and their expert shepherding of this project from its earliest conception, it could not have been completed; they have my profound thanks.

Timothy P. Hanusa
Vanderbilt University
Nashville, TN, USA

Periodic Table of the Elements

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Group ↑																		
Period ↓	1																	2
Atomic number ↓	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Atomic weight ↓	1.0079	4.0026	6.941	9.0122	10.811	12.0107	14.0067	15.9994	18.9984	20.179	26.9815	28.0855	30.9738	32.066	35.453	39.948	40.078	44.9559
	H	He	Li	Be	B	C	N	O	F	Ne	Zintl border →		Al	Si	P	S	Cl	Ar
	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
	Na	Mg	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
	22.9898	24.305	44.9559	47.867	50.9415	51.996	54.9380	55.845	58.933	58.693	63.546	65.409	69.723	72.64	74.9216	78.96	79.904	83.798
	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
	39.0983	40.078	44.9559	47.867	50.9415	51.996	54.9380	55.845	58.933	58.693	63.546	65.409	69.723	72.64	74.9216	78.96	79.904	83.798
	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
	85.4678	87.62	88.9059	91.224	92.9064	95.94	98.9062	101.07	102.9055	106.42	107.8682	112.41	114.818	118.710	121.760	127.60	126.9045	131.29
	55	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
	Cs	Ba	lanthanoids	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
	132.9054	137.327		178.49	180.9479	183.84	186.207	190.2	192.22	195.08	196.9665	200.59	204.3833	207.2	208.9804	(209)	(210)	(222)
	87	88	89-103	104	105	106	107	108	109	110	111	112	114	114	116	116		
	Fr	Ra	actinoids	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Fl	Fl	Lv	livermorium		
	(223)	(226.0254)		(261.1088)	(262.1141)	(266.1219)	(264.12)	(277)	(268.1388)	(271)	(272)	copernicium	flerovium	flerovium	livermorium			
	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	71	71	71
	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Lu	Lu	Lu
	lanthanum 138.9	140.12	140.9077	144.24	(147)	150.36	151.96	157.25	158.9254	162.50	164.9304	167.26	168.9342	173.04	174.967	174.967	174.967	174.967
	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	103	103	103
	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Lr	Lr	Lr
	actinium 232.0381	232.0381	231.0359	238.0289	237.0482	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(260)	(259)	(262)	(262)	(262)	(262)

Based on information from IUPAC, the International Union of Pure and Applied Chemistry (version dated 1st May 2013).
For updates to this table, see http://www.iupac.org/reports/periodic_table.

PART 1

Background

Interrelationships between the Lightest Metals

Nicholas C. Boyde and Timothy P. Hanusa

Vanderbilt University, Nashville, TN, USA

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1 INTRODUCTION

Use of the expression “the lightest metals” requires some explanation, especially because the terms “light metals” and “heavy metals”, although often encountered in chemical and engineering contexts, are not uniquely defined. Magnesium, aluminum, and titanium (and sometimes beryllium) are traditionally considered among the “light metals” in metallurgical settings, and they are indeed “light” if measured by density (grams per cubic centimeter) as compared to iron or copper (e.g., Mg is only 22% as dense as Fe). However, the use of density alone as a classifier leads to some awkward groupings. For example, yttrium has nearly the same density as titanium (both about 4.5 g cm^{-3}), and barium (3.5 g cm^{-3}) is less dense than either, but neither Y nor especially Ba is ever counted among the “light” metals [with some irony, the name *barium*, despite the element’s low density, comes from the Greek *barys*, meaning “heavy”; the heaviness refers to the oxide, BaO (5.7 g cm^{-3}), not the metal itself]. Consequently, the “lightest” metals are defined here as those pretransition metals of lowest *atomic number*; that is, lithium, beryllium, sodium, magnesium, aluminum, potassium, and calcium (atomic no. 3–20). Although they

indeed possess relatively low density, they are not a set of the least dense metals in the periodic table [elemental cesium (1.9 g cm^{-3}), e.g., is only 70% as dense as aluminum (2.7 g cm^{-3})].

Taken as a group, the “lightest metals” are among the most important elements on the Earth and are critical both to life and civilization. Much of their importance stems from their ubiquity: Al is the most abundant metal in the Earth’s crust (8.3% by weight) and is a constituent of the widely distributed aluminosilicates such as feldspars, garnets, and kaolin clays.^{1,2} The metals Ca, Mg, Na, and K constitute the fifth through eighth most abundant elements in the crust. It is perhaps not surprising that their ions (Ca^{2+} , Mg^{2+} , Na^+ , and K^+) are the most common metal species in biological systems, where they play myriad roles, from the formation of bones to conversion of solar energy through photosynthesis.^{3,4} The use of compounds of these metals has been foundational to the development of human society: limestone, marble, and concrete building materials (containing CaCO_3 , CaO , and MgO) have been associated with cultures from ancient Mesopotamia and China (e.g., in the Great Wall) to the present. The semiprecious *lapis lazuli*, a mineral whose deep blue color arises from the S_3^- ions in *lazurite*, a complex tectosilicate



Figure 1 Lapis lazuli, the mineral source of the pigment ultramarine, has been used in the arts for millennia; a polished obelisk of the material is behind the natural stone (By owner's permission)

that contains three of the lightest metals (with the formula $(\text{Na,Ca})_8[(\text{S,Cl,SO}_4,\text{OH})_2(\text{Al}_6\text{Si}_6\text{O}_{24})]$), has been mined as a gem for at least 6000 years and served as the source of the natural pigment ultramarine since the early European Middle Ages (Figure 1). In the form of *alum* ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$), aluminum has been used as a mordant in dying cloth for over two millennia.⁵ The widespread availability of aluminum metal itself at the end of the nineteenth century transformed the modern

transportation and building industries, and the aircraft and 100+-story buildings that are known today would not be possible without aluminum and its alloys. Lithium, although far less abundant than sodium or potassium, has become prominently associated with consumer electronics in the form of the lithium-ion battery, powering everything from music players, cell phones, and digital cameras to electric automobiles (see *Lithium-Ion Batteries: Fundamentals and Safety*). Beryllium, the least abundant of the “lightest” group (although about as common as arsenic), has restricted uses owing to the toxicity of its salts (see *Beryllium Metal Toxicology: A Current Perspective*), but is a component of widely used copper alloys, and, in the form of emeralds, has been treasured as a precious gemstone for millennia.

In the briefest summary, the lightest metals are all lustrous, silvery elements that, with the exception of beryllium, are relatively soft (Mohs hardness 1.5–2.75; that for Be is 5.5, about the same as molybdenum) (see Table 1). The metals are almost never found in the elemental state in nature, as they react in air, and all rapidly form an oxide coating on their surface. The oxide layer of beryllium and aluminum passivates the metals and inhibits further reaction with oxygen or water. The other metals react with water with various degrees of vigor; magnesium reacts with steam, and calcium reacts slowly with cold water. Lithium, sodium, and potassium all float on water and release hydrogen gas as they react with it; in the case of sodium or potassium, the hydrogen will often be ignited from the heat of reaction. With a few important exceptions (see *Low Oxidation State Chemistry*), the metals all display their “expected” oxidation state in compounds (e.g., +1 for Li and Na, +2 for Be and Mg, and +3 for Al).

In this article, various chemical and physical properties of both the elemental and ionic forms of the lightest

Table 1 Atomic and physical properties of the lightest metals

	Li	Be	Na	Mg	Al	K	Ca
Atomic number	3	4	11	12	13	19	20
No. of naturally occurring isotopes	2	1	1	3	1	3	6
Atomic mass (g mol^{-1})	6.94	9.01	23.00	24.31	26.98	39.10	40.08
Electron configuration	$[\text{He}]2s^1$	$[\text{He}]2s^2$	$[\text{Ne}]3s^1$	$[\text{Ne}]3s^2$	$[\text{Ne}]3s^23p^1$	$[\text{Ar}]4s^1$	$[\text{Ar}]4s^2$
Ionization energy (kJ mol^{-1})	520.2 (1st)	899.4 (1st); 1757 (2nd)	495.8 (1st)	737.7 (1st); 1451 (2nd)	577.5 (1st); 1816.7 (2nd); 2744.8 (3rd)	418.8 (1st)	589.8 (1st); 1145.4 (2nd)
Metal radius (Å)	1.52	1.12	1.86	1.60	1.43	2.27	1.97
Ionic radius (six-coordination) (Å)	0.76	0.45	1.02	0.72	0.535	1.38	1.00
E° for $\text{M}^{n+}(\text{aq}) + ne^- \rightarrow \text{M}(\text{s})$ (V)	−3.05	−1.97	−2.71	−2.36	−1.78 ($n = 3$)	−2.93	−2.84
Melting point ($^\circ\text{C}$)	181	1287	97.7	650	660	63.7	842
Boiling point ($^\circ\text{C}$)	1342	2469	883	1090	2519	759	1484
Density (20°C)	0.53	1.85	0.97	1.74	2.70	0.86	1.55
ΔH_{fus} (kJ mol^{-1})	2.93	15	2.64	8.9	10.7	2.39	8.6
ΔH_{vap} (kJ mol^{-1})	148	309	99	127	294	79	155
Electrical resistivity (20°C)/ $\mu\Omega \text{ cm}$	9.5	3.7	4.89	4.5	2.7	7.4	3.4

Data from Ref. 6.

metals are compared to each other and to the related metals and their compounds. The subject is vast, and specifics can be found in various textbooks.⁷⁻⁹ We highlight here some of the distinctive features of this special group of elements.

2 NUCLEOSYNTHESIS AND ABUNDANCE OF THE LIGHTEST METALS

Nucleosynthesis is the process by which elements in the universe heavier than hydrogen have been generated. The lightest elements are generally thought to have been produced during the “big bang”, at the start of the formation of the universe, in the process of *big bang nucleosynthesis* (BBN).^{10,11} The BBN model seeks to explain the genesis of these elements and their relative cosmic abundances. Its earliest version was developed in 1948 through the work of Alpher,¹² who suggested that all elements now present were generated in the big bang. This proposal was later shown to be incorrect; as there are no stable isotopes of mass number 5 or 8, the stepwise process of combining hydrogen with various subatomic particles to create more complex atoms cannot extend beyond lithium.

Estimates of the temperatures available in the early universe put limits on the types of reactions that can be expected to have occurred; those directly involved in the synthesis of the lightest elements in the standard model of BBN are listed in Scheme 1. With the combination of several critical nuclear cross-sections, measurements of the baryon-to-photon ratio, and the neutron lifetime ($t_{1/2} = 10.2$ min), the relative abundances of deuterium, helium, and lithium can be predicted relative to hydrogen.

To estimate the amounts of primordial lithium, measurements have been made of metal-poor “halo” stars, in which fusion has been limited; the amount of Li in these stars correlates with that of Fe, and extrapolation of the amount of Fe to zero provides an estimate for Li. The standard model of BBN predicts the observed abundance of ^4He to a high degree of accuracy, but the model overpredicts the abundance of ^7Li by a factor of 2–4, and underestimates the observed amount of ^6Li by three orders of magnitude. This has become known as the “lithium problem” (sometimes the ^7Li discrepancy is itself considered the “lithium problem”; the ^6Li anomaly is then the “second lithium problem”).^{10,11}

Some of the disagreement might be observational in nature (e.g., quantification of ^6Li in stellar atmospheres is difficult), but the problem does not seem to be dismissible purely on the basis of inadequate measurements. Recent measurements of the cross-section for equation (f) of Scheme 1 at big bang energies have refined the calculated primordial $^6\text{Li}/^7\text{Li}$ isotopic abundance ratio to $(1.5 \pm 0.3) \times 10^{-5}$, far below the detected

- (a) $p + n \rightarrow \text{D} + \gamma$
- (b) $\text{D} + p \rightarrow ^3\text{He} + \gamma$
- (c) $\text{D} + n \rightarrow ^3\text{H} + \gamma$
- (d) $^3\text{H} + p \rightarrow ^4\text{He} + \gamma$
- (e) $^3\text{He} + n \rightarrow ^4\text{He} + \gamma$
- (f) $^4\text{He} + \text{D} \rightarrow ^6\text{Li} + \gamma$
- (g) $^4\text{He} + ^3\text{H} \rightarrow ^7\text{Li} + \gamma$
- (h) $^4\text{He} + ^3\text{He} \rightarrow ^7\text{Be} + \gamma$
- (i) $e^- + ^7\text{Be} \rightarrow ^7\text{Li} + \nu e$

Scheme 1 Reaction mechanisms of the standard BBN model for the light elements (Data from Ref. 11)

levels of $^6\text{Li}/^7\text{Li} \sim 5 \times 10^{-2}$.¹³ A variety of hypotheses have been proposed to rationalize the discrepancies, including revision of the method by which primordial lithium is measured, alternate pathways of the reaction flow into and out of mass-7 nuclides, and approaches using non-standard cosmological physics.¹⁰ For example, fusion of a ^3He and a ^4He nuclei produces the short-lived ^7Be isotope ($t_{1/2} = 53$ days) ((h) in Scheme 1), which decays by electron capture to ^7Li ((i) in Scheme 1). However, under neutron bombardment, ^7Be can transform to ^7Li with ejection of a proton (i.e., $^7\text{Be} + n \rightarrow ^7\text{Li} + p$); with sufficient protons, ^7Li can be destroyed ($^7\text{Li} + p \rightarrow ^4\text{He} + ^4\text{He}$). The source of such extra neutrons may involve new physics; for example, the decay of WIMPs (weakly interacting massive particles) was at one time thought to provide the needed neutrons, but that is not now considered to be an adequate mechanism by itself.¹⁴ The decay of GeV-scale super-symmetric particles has been proposed as an alternative neutron source.¹⁵ Resolution of the lithium problem represents a vigorous area of astrophysical research.

The formation of elements heavier than lithium is believed to result primarily from cosmic ray spallation (fragmentation of heavier nuclei), nuclear fusion within stars, and supernova explosions.^{10,11} The nuclides ^9Be , ^{10}B , and ^{11}B are mostly the products of spallation. The elements beyond boron are believed to begin with the highly unstable ^8Be nucleus, formed from the fusion of two ^4He ($^4\text{He} + ^4\text{He} \rightleftharpoons ^8\text{Be}$). Although it has an extremely short lifetime ($t_{1/2} \sim 2.6 \times 10^{-16}$ s), ^8Be persists long enough that if struck by a third ^4He , an excited $^{12}\text{C}^*$ nucleus is formed, which can then decay to its ground state with the release of a 7.65 MeV γ -ray. This decay route is not common; only 4 out of 10^5 nuclei (which are in the so-called “Hoyle state”, a resonance of the $^8\text{Be} + ^4\text{He}$ group) will decay to carbon; the rest break up again into ^8Be and ^4He .¹⁶

Once carbon is formed, the heavier atoms appear through a series of reactions involving the addition or release of subatomic particles or the combination of two different elements. The isotopes ^{24}Mg , ^{40}K , and the three

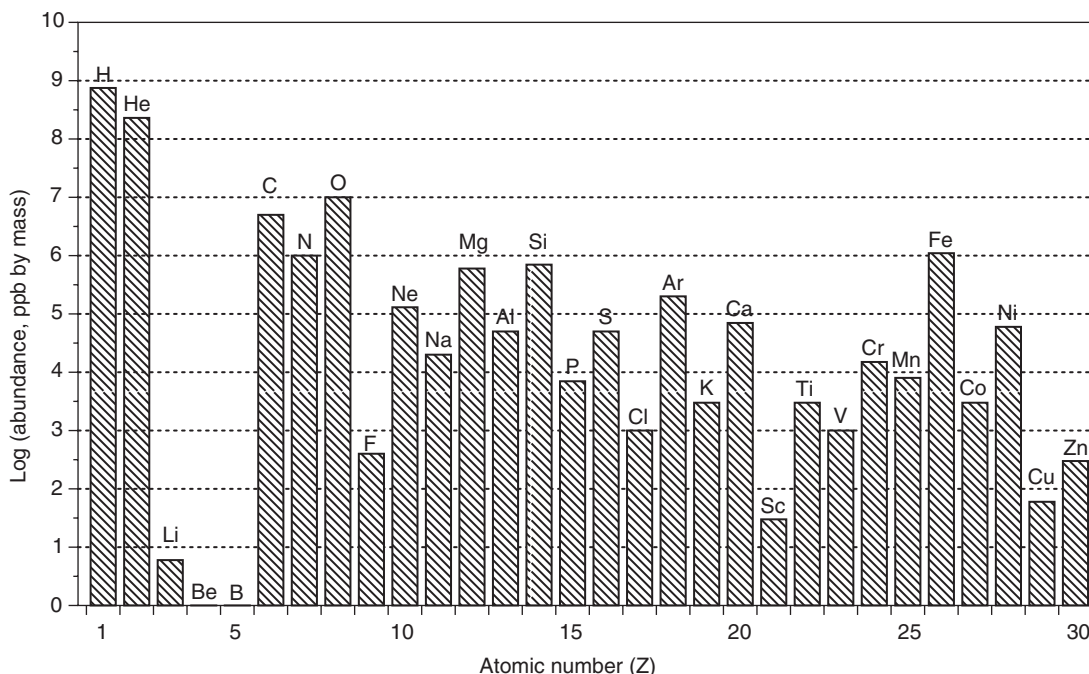


Figure 2 Log of the estimated abundances of the elements ($Z = 1-30$) in the universe; Be and B are on the order of 1 ppb (by weight) and not discernable on this graph (Data from Ref. 17)

Ca isotopes ^{40}Ca , ^{44}Ca , and ^{48}Ca all ultimately stem from combinations of alpha particles, with alpha numbers 6, 10, 10, 11, and 12, respectively. ^{24}Mg , for example, can be formed from the fusion of two ^{12}C nuclei, or ^{20}Ne and ^4He nuclei, in both cases with the emission of γ -radiation.

The effects of nucleosynthesis on the abundance of the lightest metals relative to all the elements up to $Z = 30$ (zinc) are apparent in Figure 2. The scarcity of Be (about $1 \times 10^{-7}\%$) is particularly striking; one must go to $Z = 45$ (rhodium) before comparable rarity (in ppb by mass) is found. The characteristic oscillation of abundances, in which elements of even atomic number are favored (the Oddo–Harkins rule)^{18,19} is not established until carbon, that is, after primordial nucleosynthesis finished, and element formation was confined to stellar environments.

In other contexts, such as the Earth's crust, the human body, and seawater (Table 2), the relative elemental ratios shift significantly. With respect to the Earth's crust, aluminum is now the third most abundant element (and most abundant metal); its place is taken by calcium in the human body (owing to the skeleton), and by sodium in seawater (primarily in the form of NaCl).

The high natural abundance of the lightest metals in the crust, combined with their range of oxidation states (+1 to +3) and radii (e.g., 0.59 Å for four-coordinate Li^+ to 1.51 for eight-coordinate K^+),²⁰ accounts for the enormous number of minerals in which two or



Figure 3 Tourmaline from the Himalaya Mine, Mesa Grande, California. This is an elbaite, of approximate formula $\text{Na}(\text{Li}_{0.5}\text{Al}_{0.5})_3\text{Al}_6(\text{BO}_3)_3\text{Si}_6\text{O}_{18}(\text{OH})_4$. After Arfwedson's analysis of the mineral petalite ($\text{LiAl}(\text{Si}_2\text{O}_5)_2$) in 1817, which led him to the discovery of lithium, he subsequently found the same oxide in spodumene ($\text{LiAl}(\text{SiO}_3)_2$) and elbaite.²¹ (By owner's permission)

three of them appear together; such is the case, for example, with tourmalines, which are cyclosilicates that incorporate various combinations of Ca, Na, K, Al, Li, and Mg ions (Figure 3). Even four or five of the seven lightest metals can be simultaneously present in

Table 2 Abundance of the lightest metals in various contexts

Element	Abundance				
	ppb by weight (Earth's crust)	ppb by weight (universe)	Relative abundance in the Earth's crust (oxygen = 1)	ppb in human body	ppb in seawater
Li	17 000	6	33	30	180
Be	1900	1	48	0.4	0.0006
Na	23 00 000	20 000	6	1 00 000	11 50 000
Mg	29 00 000	6 00 000	8	2 70 000	1 26 000
Al	82 00 000	50 000	3	900	5
K	15 00 000	3000	7	2 00 000	416 000
Ca	50 00 000	70 000	5	14 00 000	4220

Data from Refs. 7 and 9.

some minerals, such as in the olive green *swinefordite*, a lithium-rich smectite clay with the empirical formula $\text{LiCa}_{0.5}\text{Na}_{0.1}\text{Al}_{1.5}\text{Mg}_{0.5}\text{Si}_3\text{O}_{10}(\text{OH})_{1.5}\text{F}_{0.5}\cdot 2(\text{H}_2\text{O})$.²²

The high abundance of sodium, potassium, and magnesium in seawater contributes to the distinctiveness of their isolation processes, discussed in the following section. Lithium not only is isolated from certain brines, but also is mined from conventional ores; aluminum and beryllium are isolated exclusively from ores (most commonly bauxite and bertrandite, respectively).

3 DISCOVERY, INITIAL ISOLATION, AND COMMERCIAL PRODUCTION

The lightest metals very rarely occur in their elemental state in nature (an exception is native aluminum, which occasionally is found in the low oxygen environments in certain volcanoes, and has been identified in the bacteria-rich cold seeps in the North China Sea).²³ They are all commercially produced through electrolysis of their molten salts, although magnesium is also isolated through a silicothermal process. Brief histories and details of the isolation of each of the metals will be described here, although further details for selected metals can be found in other sources, where noted.

3.1 Alkali Metals

Compounds containing alkali metals have been known and used for thousands of years. Most prominent of course is table salt (NaCl), which although abundant in seawater (about 3%), can be a rarity in locations far from an ocean [the suggestion that the Latin word *salarium* (salary) comes directly from *salarium* (salt)—Pliny the Elder proposed it in the first century—is, however, not well founded. In the late Republican and Imperial periods, soldiers were paid in specie coin; there is no hard evidence that soldiers from before that time were actually paid in salt²⁴].

Sodium carbonate in the form of *natron* (a mixture of the carbonate and bicarbonate) was used as a desiccant in Egyptian mummification²⁵ and to prepare the pigment Egyptian blue.²⁶ Various potassium compounds under the umbrella term *potash* (principally the chloride, carbonate, and later the hydroxide, known as *caustic potash*) were used in glass and soap manufacture and textile bleaching. The term *alkali* itself is derived from the Arabic *al-qaliy* (“burnt ashes”) and has become synonymous with basic compounds. Lithium, sodium, and potassium are used in elemental form in academic and industrial work, but the most commonly encountered forms are metal salts and oxides.

3.1.1 Lithium

The name lithium has Greek origins from *lithos*, meaning stone. The name reflects the original discovery of lithium from the mineral petalite ($\text{LiAl}(\text{Si}_2\text{O}_5)_2$), rather than from the botanical sources from which sodium and potassium had been identified. In 1817, the Swedish chemist Johan August Arfwedson (1792–1841) determined that petalite contained an unknown element, but he did not isolate the metal. That was accomplished the following year independently by Humphrey Davy (1778–1829) and William Thomas Brande (1788–1866) through electrolysis of lithium carbonate and oxide, respectively.²⁷

The source of lithium has historically been both continental brines and hard rock minerals, although it has become more time, energy, and cost effective to isolate lithium carbonate from brines instead of solid minerals.^{6,28} To produce elemental lithium, the carbonate is converted to the chloride, which is then subject to molten salt electrolysis, using a mixture of LiCl and KCl to separate the lithium. KCl is added to reduce the melting point of LiCl , which lowers the overall energy usage. LiCl and KCl alone melt at 610 and 772 °C, respectively; the eutectic point of LiCl – KCl is 350 °C at 42 mol% KCl . Nevertheless, the electrolysis is typically carried out at temperatures of

400 °C or higher, where a larger percentage of LiCl can be used; the energy consumption is 35 kWh kg⁻¹. The current production model for lithium is focused on lithium carbonate, chloride, and hydroxide, lithium metal, and organolithium compounds.²⁸ Elemental lithium is used in academic research, and lithium compounds are extensively used for batteries (see *Lithium-Ion Batteries: Fundamentals and Safety; High-Pressure Synthesis of Hydrogen Storage Materials*) and organic synthesis (see *Aryllithiums and Heteroaryllithiums: Generation and Reactivity*); lithium carbonate is used in pharmaceuticals (see *Lithium Pharmacology*).

3.1.2 Sodium

The symbol for sodium (Na) comes from Latin *natrium*, derived from *natron*, the naturally occurring mixture of sodium carbonate and bicarbonate used since the times of the ancient Egyptians (the Egyptian word is *ntr*). The name sodium comes from “soda” or “sodanum” (principally sodium carbonate), which was long known as a headache remedy; the name may ultimately stem from the Arabic *suwwad* (“saltwort”), a plant from whose ashes the carbonate was obtained. Sodium is a very common element, with large amounts in the crust and in seawater. Sodium was first isolated in 1807 by Humphrey Davy through electrolysis of molten sodium hydroxide.²⁷

Sodium metal is generally produced today from electrolysis of sodium chloride. This method uses the addition of CaCl₂ to reduce the melting point of NaCl (40% NaCl, 60% CaCl₂ in a reaction conducted at 580 °C);⁶ the higher electronegativity of calcium prevents its deposition on the electrode. Sodium metal is used on the tonnage scale to produce sodium hydride by direct hydrogenation, which in turn is used to produce sodium borohydride by the Schlesinger process ($\text{B}(\text{OCH}_3)_3 + 4 \text{NaH} \rightarrow \text{NaBH}_4 + 3 \text{NaOCH}_3$); the latter is employed as a reducing agent in organic synthesis for bleaching wood pulp and textiles, and in metal plating. Soda ash (Na₂CO₃) is refined from the mineral *trona* (Na₃(CO₃)(HCO₃)·2H₂O) and from brine sources.²⁹ Other commonly used sodium products include sodium bicarbonate, sodium borate (borax), and sodium sulfate; the low melting point of the latter’s hydrate (Na₂SO₄·10H₂O, m.p. 32 °C) and its high heat of fusion (82 kJ mol⁻¹) have attracted interest in its use as a medium for solar thermal energy storage.³⁰

3.1.3 Potassium

Potassium has the chemical symbol K, which comes from Latin *kalium*, meaning “potash”, the historically common source of potassium. “Pot-ashes”, as the original name suggests, refers to the water-soluble compounds (chiefly K₂CO₃) obtained by soaking burnt wood ashes in water and evaporating the extracts in iron pots. Potassium was isolated by Humphrey Davy in 1807

by electrolysis of the hydroxide. As with other elements, potassium compounds had been known long before the element was available.²⁷

Potassium salts are common in lakebeds and on the seabed, which make collection relatively easy and cost efficient.³¹ The term potash is still used for several potassium compounds that are mined around the world. The chloride is produced in the largest amount and finds its chief use in fertilizers. The pure metal is isolated through electrolysis. Electrolysis of KOH is the common method, but a thermal reaction of KCl and Na will also result in NaCl and K, or the alloy NaK depending on the time and sodium amount used. NaK will be discussed further in Section 7.

3.2 Alkaline-Earth Metals

Before the nineteenth century, nonmetallic materials that were insoluble in water (although they might react with them) and not affected by fire were commonly known as *earths*. Those earths, such as lime, that resembled the water-soluble alkalies (i.e., soda ash and potash) were designated *alkaline earths*. Alkaline earths were thus distinguished from the alkalies and from other earths, such as alumina and the rare earths (lanthanides). Through the work of Lavoisier and others, by the early 1800s it became apparent that the earths, formerly considered to be elements, were in fact oxides. The metals whose oxides make up the alkaline earths then came to be known as the alkaline-earth metals, and have been classified in Group 2 of the periodic table from the time of Mendeleev’s version of 1870.³²

3.2.1 Beryllium

Beryl and emeralds have been known since antiquity; the word “beryl” stems from the Latin *beryllus*, in turn derived from the Greek *beryllos*, and possibly from the Indian Prakrit *veruliya* and ultimately the Sanskrit *vaidurya* (which referred to the blue-green variety of beryl). “Emerald” is a term of Greek origin, *smaragdus* (a “green gem”), and entered Latin as *smaragdus*. It went through various transformations in Medieval Latin and Old French, including “esmaraldus”, “esmeraude”, and “emeraude” before emerging in English as “emerald” in the sixteenth century. The fact that both stones could be found with similar colors and hardness did not escape notice in antiquity. In his first century AD treatise *Historia Naturalis* (Book 37, Chap. 20), Pliny the Elder comments: “Beryls, it is thought, are of the same nature as the smaragdus, or at least closely analogous.”

Acting on a comment from the mineralogist René-Just Haüy (1743–1822), who had noted the morphological similarities between emerald and beryl, the French chemist Nicolas-Louis Vauquelin (1763–1829) analyzed a Peruvian

emerald and a beryl from Limoges, France, to establish their identities. Vauquelin demonstrated in 1798 that both minerals comprised not only alumina and silica but also a previously unrecognized earth, eventually named *beryllia*, which had similarities to alumina (e.g., both dissolved in alkali), but generated a precipitate on continued boiling, something that did not occur with alumina. Both beryl and emerald are approximately represented by the formula $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$; the green color of emeralds arises from the presence of about 2% Cr. The metal was isolated (1828) independently by the German chemist, Friedrich Wöhler (1800–1882), and the French chemist, Antoine Bussy (1794–1882), by the reduction of its chloride with potassium. It might be noted that beryllia was originally called *glucina* (Greek *glykys*, sweet) because of its sweet taste. (This etymological root is retained in France, where the element beryllium is also known as glucinium; this was an accepted alternative name internationally, with the symbol Gl, until 1957.)

There are two primary minerals that are of commercial importance for the production of beryllium. The first is bertrandite ($\text{Be}_4\text{Si}_2\text{O}_7(\text{OH})_2$), which is ideally 15% beryllium by mass, but typical ores of bertrandite contain only about 1% beryllium.³³ The second source is beryl, which contains about 5% beryllium. The primary product of beryllium ore processing is beryllium hydroxide, which is usually converted to the sulfate, then to the fluoride or chloride, and either chemically or electrochemically reduced to the metal.³³ Details of the process can be found elsewhere (see *Occurrence and Production of Beryllium*).

3.2.2 Magnesium

Magnesia (the name likely stems from Magnesia, a district of Thessaly in Greece), the oxide of magnesium, was shown to be an alkaline earth different from lime by the Scottish chemist Joseph Black in 1755; magnesia produced a soluble sulfate, whereas that derived from lime was insoluble.

Magnesium was isolated as an impure metal by Humphry Davy in 1808 by means of the electrolytic method he had previously used for isolating the alkali metals potassium and sodium. This process used a mixture of MgO and HgO that was then electrolyzed; heating the resulting mixture vaporized the mercury, leaving the magnesium. Magnesium hydroxide, $\text{Mg}(\text{OH})_2$, is produced in large quantities from seawater by the addition of lime (calcium hydroxide). It is the primary raw material in the production of magnesium metal; converted to the chloride (MgCl_2), the molten salt is then electrolyzed. A significant fraction of elemental magnesium is commercially produced by the direct reduction of its compounds with suitable reducing agents, for example, from the reaction of magnesium oxide or calcined dolomite with ferrosilicon (the Pidgeon process).³⁴ Details of these processes can be

found elsewhere (see *Occurrence of Magnesia Minerals and Production of Magnesium Chemicals and Metal*).

3.2.3 Calcium

Calcium is ubiquitous in the Earth's crust and the mineral forms are easily mined. Calcium carbonate is the most common form of calcium in nature and occurs as limestone, marble, and chalk. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was the form most used by the ancient Egyptians, Greeks, and Romans (as plaster). The long-standing use of *lime mortar* [a mixture of slaked lime ($\text{Ca}(\text{OH})_2$), sand, and water] allows for the radiodating of ancient buildings. As such mortar cures, it absorbs CO_2 from the atmosphere in its conversion to the carbonate, enabling ^{14}C dating using AMS (accelerator mass spectrometry). In some cases, such testing has confirmed traditional dates of construction (e.g., mortar from the Roman Colosseum has been radiodated to 45–80 AD, whereas historical sources place its erection from 70 to 80 AD). The method has also supplied dates where historical records are lacking, as in determining that a stone tower located in Newport, Rhode Island (Figure 4), is the remains of a Colonial-era windmill and not a relic built by Vikings sometime after 1000 AD, as some had argued.³⁵

The first recognized alkaline earth was lime (the oxide, CaO); the metal itself was isolated (1808) by Humphry Davy after distilling mercury from an amalgam formed by electrolyzing a mixture of lime and mercuric oxide. The name for the element was taken from the Latin word for lime or limestone, *calx*.



Figure 4 The Newport tower has been radiodated from its mortar to the late seventeenth century, confirming a Colonial-era construction (By owner's permission)