REDISCOVERY OF THE ELEMENTS — A HISTORICAL SKETCH OF THE DISCOVERIES

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INTRODUCTION

For over five millennia the mysterious transmutation of substances into new ones — the enigmatic metamorphosis of sand and clay into glass and pottery, the mutation of larvae into flies, the basic riddle of life itself — suggested to the human mind that deep-seated principles were responsible. Beginning with recorded history, the ancient Egyptians were deeply preoccupied with life and death and sought answers through medications, pharmaceutical preparations, and incantations.

The ancient Greeks were the first to address the question of what these principles might be. Water was the obvious basic essence, and Aristotle expanded the Greek philosophy to encompass a obscure mixture of four elements — fire, earth, water, and air — as being responsible for the makeup of all materials of the earth. As late as 1777, scientific texts embraced these four elements, even though a over-whelming body of evidence pointed out many contradictions. It was taking thousands of years for mankind to evolve his thinking from *Principles* — which were ethereal notions describing the perceptions of this material world — to *Elements* — real, concrete basic stuff of this universe.

The alchemists, who devoted untold grueling hours to transmute metals into gold, believed that in addition to the four Aristotelian elements, two principles gave rise to all natural substances: mercury and sulfur. The progenitor of this theory was the Arabian alchemist Geber. A thousand years ago he explained that mercury could contribute "fluidity," and sulfur "combustibility"; later alchemists — principally Paracelsus — added salt, which would confer "fixity."

Robert Boyle, best known for his "Boyle's Law," in the 1600s discussed in "The Sceptical Chymist" the standards by which a substance could be adjudged as an element. He realized that Aristotle's four elements and the alchemists' three principles could not be correct, because they were never proven to compose, nor could they be extracted from, any other substances. He expounded:

"I now mean by Elements, as those Chymists that speak plainest do by their

Principles, certain Primitive and Simple, or perfectly unmingled bodies; which not being made up of any other bodies, or of one another, are the Ingredients of which all those call'd perfectly mixt Bodies are immediately compounded, and into which they are ultimately resolved: now whether there be any one such body to be constantly met with in all, and each, of those that are said to be Elemented bodies, is the thing I now question."

In other words, if something was an element, then it must be proven by experiment to be separable as basic material which could not reduced to any more fundamental stuff. Since this decisive experiment was sorely lacking, the "chymist" had no recourse but to rely on the old theories. He was still stumbling over the basic flaw — he could not abandon the outmoded concept that elements were Aristotelian *principles* reflecting essences immediately manifest to the eye and other senses. He had merely renamed the old principles — the Aristotelian "hotness" had simply evolved to alchemical "combustibility."

The truth was much more subtle — and surprisingly simple. True elements were commonly *ingredients* to worldly materials. Only rarely did an element present itself in simple form in nature — such as gold. It was like trying to identify the flour, sugar, salt, lard, and eggs that went into the baking of a cake from the smells emanating from the final concoction, often when one had never seen these original ingredients! More commonly, an element was in combined form in nature, and the extraction of these *material* elements eluded the scientist. The modern recognition of element had to await a true genius who could wonder about the original recipe of the Cosmic Baker.

The giant step in this evolution of thought — from philosophical Principle to materialistic Element — was made by Lavoisier, who in his Treatise of 1789 realized that since water was manufactured by the combination of "inflammable gas" (hydrogen) and "vital air" (oxygen), then water must be a *compound*. From this remarkable intuition all else followed. Lavoisier listed 31 materials which he proposed — correctly — were the true elements, including sulfur, iron, carbon, copper, molybdenum, etc. Recognizing that "inflammable air" and "vital air" were elements, he dubbed them with the names by which we know them today. He even recognized that "radical muriatique" (chlorine), "radical fluorique" (fluorine) and others which had not been yet prepared in the elemental form were also elements. Lavoisier had peeked beyond the dining room into the kitchen.

Lavoisier's insight opened the cupboard doors, out of which tumbled a myriad of wondrous oils, sugars, and spices. Excitement grew in the scientific community as, one by one, new condiments were discovered pell-mell in this pantry. By the middle of the nineteenth century it was recognized that the cabinet was even organized in tidy shelves and bins, and soon Mendeleev was even predicting new flavorings not yet tasted or dreamed of!

By the early twentieth century, ninety-two continuous cubicles had recognized, each with an identified staple, and the scientists had cooked up thousands of new culinary formulations. But the cuisine did not stop there! The nuclear chemist synthesized new makings, new racks were built in the pantry, and eventually the list of condiments expanded to over one hundred.

This, then, is the story of how that kitchen was explored. . . .

1. THE ANCIENTS
(prehistoric times-500 A.D.)

The Story of the Elements begins with Stone Age Man, who had discovered how to prepare tools out of wood, bone, and rocks. He discovered that wood was good for preparing pliable implements, such as shafts and spears. Bone was excellent for fine instruments such as needles. Rocks could be used for kitchen utensils (for example bowls, typically from rough igneous stones), and for tools and weapons (such as scrapers and spearheads, usually flint). These materials were effective but all suffered from their tendency to splinter or break — they were all brittle. Man eventually stumbled upon *metals* which had unique properties — they were simultaneously malleable and strong — they could be used for tools and weapons, could be prepared under heat, and were not brittle.

Well over ten thousand years ago metals were adopted by Man. The ancients recognized that metals were very special and they attributed these metals with special magical properties and spirits. The discovery of *metals* was so important that the anthropologists differentiate the "Stone Age" from the subsequent "Bronze Age" and "Iron Age."

Seven metals were known to the ancients — gold, copper, tin, lead, silver, iron, and mercury. The first metal to be discovered was probably gold, because of its beauty and its resistance to corrosion, and was adopted for jewelry and ornaments. The first metal of practical use was copper, perhaps 10,000 B.C., which could be beaten into tools and ornaments. Elemental copper was occasionally found in the form of nuggets, and later (roughly 5000 B.C.) could be smelted from ores. About 3000 B.C., it was found that when copper was mixed with tin a harder, more durable metal could be formed — bronze. However, tin was originally scarce, and tin sources were sought out and developed. Lead was soon discovered — as a softer and heavier metal, it could be used as weights, water pipes, writing tablets, and coins. Silver was usually found in nature in compounds (such as silver sulfide); for a while metallic silver was actually more expensive than gold until effective smelting methods were discovered. The discovery of iron was delayed because of its corrosion and the difficulty of smelting it. About 1500 B.C., the beginning of the Iron Age, the Hittites developed effective procedures for extracting iron. Mercury was easily obtained from its ore by mere heating — sometimes mercury "sweat" could be seen on cinnabar. Nevertheless, it was more casually mentioned in ancient literature since it not utilized in tools and implements; it was used in more esoteric applications, such as "medicines."

The Old Testament mentions six metals. As early as about 1200 B.C. (*Numbers* **31**:22) reference is made to firing gold, silver, bronze (copper), iron, tin, and lead. In *Ezekiel* **27**:12-13, dated about 600 B.C., Spain is mentioned as a rich source of silver, iron, tin, and lead; and Greece is described as a provider of bronze.

Ancient civilization, which had developed a sophisticated technology of materials, attributed Gods as being responsible for the special properties of metals. Since there were seven metals known to the ancients, and since there were seven heavenly bodies, it was apparent that each of these heavenly bodies was associated with one of these metals. Since each of these heavenly bodies was a God with a distinct temperament, they found that each of these elements was clearly connected with one of these personalities:

Gold — the Sun, or Sol, with his

golden radiance

Silver — the Moon or Luna, with her soft light

Quicksilver — Mercury, the rapid Messenger of the Gods

Copper — Venus, with her beauty

Iron — Mars, the God of War

Tin — Jupiter, the Supreme God

Lead — Saturn, the God of Old Age and Heavy Dullness

The Greeks, with their insatiable curiosity and drive for reason and logic, attempted to explain the universe in terms of "Principles." It was obvious to them that the most common and important "principle" — which is found in rivers, lakes and oceans, which falls out of the sky, and which we must drink to survive — is water. Hence, water was recognized as the first element.

Aristotle, who codified most of the ancient information which was embraced by the educated persons of the world for hundreds of years, even into the Renaissance, stated that there were *four* elements — not only water, but also fire, earth, and air. He reasoned that these four principles could explain all materials we see. These four elements could blend in various proportions to give rise to any property one could want: water with its wetness and coolness, earth with its dryness and coolness, fire with its dryness and its hotness, and air with its wetness and its hotness, could produce all the rocks, wood, organisms, etc., that we observe in the world.

The ancient Greeks, with their penchant for harmony and mathematics, further ascribed each of these "Principles" or "Elements" with one of the regular polyhedrons, known as the "Platonic solids." Hence, earth was a chunky cube, air was a multifaceted octahedron, fire was a pointy tetrahedron, and water was a smooth icosahedron. The remaining Platonic solid, the dodecahedron, represented the universe or the "cosmos."

The view that the earth was composed of these four elements persisted into the 18th century. Indeed, in a leading encyclopedia of the day — under "Element" in *A Dictionary of Chemistry*, by P. J. Macquer, published in 1777 — the following entry is made:

"Those bodies are called by chemists *elements*, which are so simple, that they cannot be by any known method be decomposed, or even altered; and which also enter as principles, or constituent parts, into the combination of other bodies, which are therefore called compound bodies.

"The bodies in which this simplicity has been observed are fire, air, water, and the purest earth; for by the most complete and accurate analyses which have been made, nothing has been ever ultimately produced but some one, or more, of these four substances, according to the nature of the decomposed bodies.

"These substances, although reputed simple, may possibly not be so, and may even result from the union of several other more simple substances: but as experience teaches us nothing on this subject, we may without inconvenience, and we ought to consider, in chemistry, fire, air, water, and earth, as simple bodies; because they really act as such in all chemical operations."

Modern chemistry could not emerge until these ancient philosophies and superstitions of principles, essences, and spirits were replaced by more practical schemes. But these old thoughts could not be abandoned until they were thoroughly tried out in real-world situations (*i.e.*, by experimentation). This exhaustive examination was performed by the alchemists and belongs in the next chapter.

Gold

Au 79
[Anglo-Saxon *gold*, L. *aurum*]
Known to ancients
mp 1064°; bp 2808°; sp gr 19.3

Gold artifacts are known from all ancient cultures. A major quest for millennia has been the search for the philosopher's stone, the method by which base metals can be transmuted into gold. To alchemists the symbol of gold was the sun.

Gold, the most beautiful metal, has been known and valued since ancient times. In bulk gold has the familiar yellow color, but when finely divided may be dark. Gold is the most malleable and ductile of all metals — 1 gram can be beaten to a one-square meter sheet, where the gold is 50 nm (50 x 10^{-9} m) thick. Gold is soft and is usually alloyed to give it hardness. It is an excellent conductor of electricity and heat. Unaffected by air and reagents, it can be used as connector contacts. It has been used in coinage, and is used in jewelry, decoration, dental work and for plating. Gold can be dissolved by *aqua regia* — 3:1 hydrochloric acid:nitric acid.

Silver

Ag 47
[Anglo-Saxon *siolfur*, L. *argentum*]
Known since ancient times
mp 961.9°; bp 2212°; sp gr 10.50

Silver has been known since ancient times. It rarely occurs uncombined; in ancient Egypt it was more expensive than gold. The art of refining silver soon was developed; Isaiah described the process by adding a base metal which was oxidized, leaving a regulus of metallic silver. To the alchemists silver was the symbol of Diana (the Moon).

Silver is a little harder than gold, and is extremely ductile and malleable. Silver has the highest electrical and thermal conductivity of all metals. It is stable in air, but tarnishes in the presence of sulfur compounds (to form black Ag_2S). Sterling silver (92.5% silver) is used in jewelry and silverware. Silver is extremely important in photography; is used in dental alloys, soldering and brazing alloys, and arc-resistant electrical contacts. Silver is the best reflector of light known, but can tarnish and loses its reflectance. Silver iodide has been used in seeding clouds to produce rain. Silver has been used in coinage for millennia — old silver dollars are 90% silver and 10% copper.

Copper

Cu 29
[L. *cuprum*, Cyprus]
Prehistoric
mp 1083°; bp 2567°; sp gr 8.96

Copper artifacts date back for ten thousand years. Alloys of copper — brass and bronze — are sometimes historically confused with copper. To the alchemists copper was the symbol of Venus.

Copper is an excellent conductor of electricity (second only to silver); hence, the electrical industry is one of the greatest uses of this element. The alloys of copper — brass (copper and zinc) and bronze (copper and tin) have been known since historic times and are still important. The sulfate ($CuSO_4$, blue vitriol) is used as an agricultural poison and as an algicide. Fehling's solution (copper tartrate) is used in analytical chemistry as a test for sugar.

Mercury

Hg 80

[Planet *Mercury*, Gr. *hydrargyrum*, liquid silver]

Known to ancients

mp -38.8°; bp 356.7°; sp gr 13.55

Mercury was known to the ancient Chinese and Egyptians, and Pliny describes its preparation. Mercury was the alchemist symbol for the planet Mercury. To the alchemists, mercury (the principle of fluidity) and sulfur (the principle of combustibility) were responsible for the evolution of all metals. A continuous quest for the alchemists was the conversion of silver, mercury, and other metals into gold. With the true understanding of the elements, it was concluded that transmutation into gold by fire and flask was impossible.

Mercury, also known as *quicksilver*, is the only common metal which is liquid at ordinary temperatures, and has the lowest melting point of all the metallic elements. Mercury is a poor conductor of heat, but a fair conductor of electricity — and thus can be used in mercury switches. Mercury forms alloys ("amalgams") easily with many metals. It is used extensively in laboratory instruments, such as thermometers, barometers, and diffusion pumps. It is used in mercury-vapor lamps. Mercury fulminate, $Hg(ONC)_2$, is a detonator in explosives.

Lead

Pb 82

[Anglo-Saxon *lead*, L. *plumbum*]

Known to the ancients

mp 327.5°; bp 1740°; sp gr 11.35

Lead is mentioned in the Old Testament. Lead ores are common in nature, and are easily smelted. The Romans used lead for plumbing, writing tablets, coins, and cooking utensils (which caused lead poisoning). Lead pipes fashioned by the Romans 2000 years ago still function. To the alchemists, lead was the oldest metal, associated with Saturn. The "philosopher's stone" was sought by the alchemists to convert lead and other base metals to gold.

Lead is principally used in storage batteries. It is also used in ammunition, plumbing, lead tetraethyl, and X-ray radiation shields. Lead oxide is used in crystal glass and flint glass. Lead is a cumulative poison and poses a health hazard, notably in older outdoor white paints.

Iron

Fe 26

[Anglo-Saxon, *iron*, L. *ferrum*]

Prehistoric

mp 1535°; bp 2750°; sp gr 7.87

Iron articles and implements have been fashioned for perhaps five millennia. Iron is extensively mentioned in the Bible. To the alchemists iron was the symbol of Mars.

Iron — used in the production of steels — is the cheapest, most abundant, most useful, and most important of all metals. The pure metal itself is utilized sparingly; usually iron is alloyed with carbon or other metals. The core of the earth is largely composed of iron. Iron is a critical component in life, appearing in hemoglobin as the red pigment and the coordinating agent for oxygen.

Tin

Sn 50
[Anglo-Saxon *tin*, L. *stannum*]
Known to the ancients
mp 243.0°; bp 2270°; sp gr 7.31

Tin was known to the ancients, who used it in bronze. The Romans distinguished "plumbum album" (tin) from "plumbum nigrum" (lead), and mentioned tin's use as a coating for copper vessels. The alchemists associated tin with Jupiter. Tin dishes have been used in Europe for hundreds of years. Tin was mined by the Incas and later by the Spaniards in Bolivia.

Alloys of tin are quite important, including solders (tin-lead), pewter (tin-antimony), and bronze (copper-tin). Tin-plating over steel cans provide "tin cans."

Sulfur

S 16
[L. *sulphurium*]
Known to the ancients
mp (rhombic) 112.8°, (monoclinic) 119.0°;
bp 444.7°;
sp gr (rhombic) 2.07, (monoclinic) 1.96

Sulfur is known in the Bible as brimstone. The ancient Greeks used burning sulfur as a fumigant. Pliny described in detail the Italian and Sicilian deposits during the Roman Empire, and described sulfur's medicinal purposes, bleaching of cloth, sulfur matches, and lamp wicks. Sulfur was incorporated into gunpowder in the Middle Ages.

Sulfur occurs in elemental form and in combination (as sulfides and sulfates) in nature. This element is exemplary of a *nonmetal*, which does not conduct electricity or heat, does not have a metallic luster, and crumbles or shatters easily. Sulfur is used to manufacture gunpowder, vulcanized rubber, sulfuric acid, and paper. Sulfur is essential for life — as a minor constituent of proteins and skeletal minerals.

Carbon

C 6
[L. *carbo*, charcoal]
Prehistoric
mp 3550°; bp (sublimes) 3367°;
sp gr (graph) ~ 2.0, sp gr (diam) 3.1-3.5

Three forms of carbon — diamonds, graphite, and charcoal — have been known in nature for millennia, but only two hundred years ago were they recognized as common material, all yielding carbon dioxide when burned. In 1985 another form of carbon was found in the soot of electrically evaporated graphite. In this new form, carbon atoms form C_{60} molecular clusters shaped like soccer balls. This molecular form is called "buckminster-fullerene" after the designer of the geodesic dome. It is possible to place another atom inside a "buckyball," leading to unique properties.

Diamond is one of the hardest substances known, while graphite is one of the softest. Carbon is the base of organic compounds and is found in more than a million different compounds. Important compounds include carbon dioxide, methane, and carbonates. Carbon-14, with a half-life of 5730 years, is used to date wood and archeological specimens.

In ancient and medieval days graphite was confused with lead (Pb) and molybdenite

(MoS_2) — all being gray, soft, and slippery. All three were commonly given the collective name of "plumbago." The first person to distinguish clearly among these different substances was Scheele in 1779.

It was not recognized until the the late 1700s that charcoal and diamond were related chemically, when Lavoisier in 1784 showed that either diamond or charcoal could be burned to give the same product, carbon dioxide. Nevertheless, it was not yet recognized that diamond and charcoal were forms of the same material; instead, it was believed by some that graphite was "partially oxidized" carbon. Not until 1796 did Smithson Tennant find that carbon and diamond were the same material by demonstrating that equal amounts of carbon and diamond burn to give equal amounts of carbon dioxide.

2. THE ALCHEMISTS
(500-1700 A.D.)

During the Dark Ages, the bright light of chemistry was sustained by the Arabians. The classical Greek texts in mathematics, astronomy, and medicine had been translated into Arabian by about 850 A.D. A huge amount of experimental data was being accumulated not only for metals, but also for acids and bases, salts, organics, and other chemicals. Foremost of the Arabian chemists was Geber, who raised experimental science to a new level with extensive documentation and new textbooks. This Arabian wealth of information slowly migrated into Europe. Known by its Arabian name — "al kimiya," i.e., "the chemistry" — practitioners of this art became known as "alchemists."

The Medieval alchemists were accumulating a wealth of information on the mysteries of "transmutational" changes, and were making attempts to interpret their observations and their hopes. They observed that substances were continuously changing from one from to another. Deep in the earth, they believed, the metals slowly evolved to a higher form. Lead would slowly transform into iron, then into copper, thence to silver, and finally to gold. Indeed, if one dug into the ground and found a baser metal, such as iron, then it was natural to remark, "The metal was dug up too soon. Cover it up and let it continue to grow and mature." Unfortunately, it was thought, the earth took too long to change iron into gold, and only a future generation could benefit from this transformation.

Since all substances contained principles, if one could only understand and direct these principles, then he could produce more precious materials. If only one could discover a catalyst to rapidly effect this transformation, it would be glorious indeed! Such a catalyst, called "the philosopher's stone," would enable one to produce gold in large quantities. Thus was born the "Alchemist," who spent thousands of toiling hours trying to unlock these secrets of the philosopher's stone.

The Alchemists developed a theoretical basis for their work and findings. They believed that all metals were formed from two principles — mercury and sulphur. The mercury, with its essential property of fluidity and fusibility, gave rise to the malleability of metals. The sulphur, with its essential property of combustibility, contributed body and calcination (rusting). It made sense that the most perfect of metals — gold — was produced from mercury and sulphur, because the sulphur would impart the yellow color to the mercury to produce the beautiful lustrous metal. If only the Alchemist could combine mercury and sulphur in the correct proportions, with the philosopher's stone as a catalyst, he would produce gold in prodigious quantities.

As the Alchemists toiled countless hours over the furnace, they stumbled upon several new substances, which today we recognize as elements, but at the time were characterized as strange blends of the principles of fire, earth, water, and air, and of mercury, sulphur, and salt. Phosphorus was isolated from urine, and was named as such because it literally glowed in the dark. Antimony was recognized as a new substance; it actually had been mentioned in the Bible as "stibic stone," used as a black mascara. Zinc was used in medical preparations, known primarily in calamine and also recognized as an ingredient in brass. Bismuth was discovered more recently; as a heavy, malleable metal, it was used in metallic woodwork trim; and with its low melting point it could be used in casting printing type.

Although Paracelsus is recognized as the discoverer of arsenic, it had been known in the form of its compounds since ancient days; Pliny the Elder described its use in yellow cosmetics and medicines (even though it is a poison!).

The alchemists were responsible for the genesis of modern chemistry. They developed as a subculture in medieval Christianity, and unwittingly paved the way for this science by making three distinct contributions: (1) experimentation itself, involving the ancient chemical processes of distillation, precipitation, decrepitation, calcining, etc.; (2) a basis of Greek logic and harmony, providing the faith that logic and reasoning could arrive at a final answer, even when the truth was not intuitively obvious; and (3) a faith in God, with the belief that He had created a harmonious world with Perfection as the ultimate goal and which, excepting miracles, functioned through orderly processes , eventually to be known by the Natural Philosopher as "scientific laws." Chemistry, as with all the sciences, depended upon these three factors for its development.

The Moslem culture had invaded Spain, and the ideas of Geber (experimentation) and of Aristotle (logic) invaded the minds of the Medieval Europeans, much to the dismay of the Catholic Church, who viewed these inquiries as a threat to its ultimate authority. The successive waves of translations from the Arabic and Greek spread across Europe and threatened the Christian philosophy unless Christendom could construct a counterphilosophy.

Meanwhile, Charlemagne had directed cathedrals and monasteries to establish schools where clergy and laity might learn to read and write, and later to study grammar, music, and arithmetic. This idea spread and developed until Universities were common, teaching a liberals arts curriculum of the "trivium" — grammar, rhetoric, and logic — and then the "quadrivium" — arithmetic, geometry, music, and astronomy. Since the culture of the church was responsible for the University, and since knowledge threatened the faith of the church, the role of the University became to establish the Biblical Truth by using Aristotelian logic and knowledge.

A common teaching technique of the University was by means of *disputations* among the teachers, students, and visitors. A question was stated and argued by Biblical quotations and Aristotelian certitudes, and the negative was given and defended in kind. This back-and-forth discussion formed debates, sharpened the mind, and expanded the mental arena that could be explored.

From this culture came the most famous of the Medieval scientists, Roger Bacon. Although he reduced science and philosophy to the role of servants to theology, nevertheless he appealed to the Pope and the Clergy that science should be a necessary part of education, since science reveals the glory of the Creator in His Creation and His Works. Most importantly, Bacon introduced the *inductive method* to science. Others had argued that the only real proof is *deductive* and *a priori*: Effects must follow from the Cause, and since the Cause is known from the Scriptures and from Aristotelian knowledge, one can merely argue from them — the specific must follow from the general. Bacon, on the other hand, pled that science must use experiment as its method, since it cannot reach its conclusions until explained mathematically. In other words, the description of natural law must be induced from many examples — the general can follow from the specific. He graphically illustrated his point by stating, "The most rigorous conclusions of logic leave us uncertain until they are confirmed by experience; only when we are singed are we convinced that a fire is hot and can burn us." This breakthrough led the way for the experimental method, the foundation of modern science. Finally philosophy could break the shackles of Aristotelian philosophy, which held that all could be deduced from previous writings and observations with no need for further inquiry. The "official" explanations could now be questioned.

But while all of this philosophizing was taking place, everyday life must carry on. That is, technology was evolving. That new topic will be the basis of the next chapter.

Phosphorus

P 15 30.97376
[Gr. *phosphoros*, light bearing]
Discovered 1669
mp (white) 280°; sp gr (white) 1.82,
(red) 2.20

Hennig Brand, a seventeenth century alchemist and physician of Hamburg, learned how to extract from urine a waxy, white substance that glowed in the dark. Soon the secret recipe was out, and many chemists were preparing the mysterious substance, studying it, and displaying it in public and in regal court. Soon phosphorus was found not only in urine, but in other animal and vegetable matter; in the 1700s bones were discovered to consist of "lime saturated with phosphoric acid." Before the true nature of combustion was understood, phosphorus was considered an "escape of phlogiston." It was observed that white phosphorus, when exposed to light, is transformed into red phosphorus. Berzelius showed the two forms were modifications of the same element. In the 1800s phosphorus was used in matches.

Another less common form of phosphorus — "black phosphorus" — is known, which resembles graphite. The molecular structure of white phosphorus is individual tetrahedra of P_4 units; that of red phosphorus is cross-linked tetrahedra; that of black phosphorus is hexagonal sheets (like graphite).

Phosphorus is found in minerals in the form of phosphates, and in living systems in protoplasm (in nucleic acids) and bones (as hydroxyapatite). White phosphorus ignites spontaneously in the air and is stored under water, but red phosphorus is safer. Phosphates are extensively used as fertilizers in agriculture and horticulture. Monosodium phosphate is used in baking powder. Phosphorus is used in the production of bronze and other metals. Trisodium phosphate is used as a cleaning agent, water softener, and corrosion inhibitor.

Arsenic

As 33 74.9216
[Gr. *arsenikon*, yellow orpiment]
Known to ancients; element discovered 1250
mp 817° (28 atm); sublimes 613°;
sp gr 5.73

Arsenic was known to the ancients as orpiment, a yellow pigment (arsenic sulfide). Albert the Great was probably the first to isolate the element, by heating orpiment with soap (ca. 1250).

Arsenic is found in nature commonly associated with sulfides of metals. When heated, arsenic forms arsenic oxide (As_2O_3), which smells like garlic. Arsenic and its compounds are highly poisonous and have been used as agricultural insecticides. Arsenic is used in the semiconductor industry.

Antimony

Sb 51 121.76
[Gr. *anti-monos*, not alone]
Known to ancients;
element known to alchemists
mp 630.7°; bp 1950°; sp gr 6.69

Antimony was known to the ancients in the form of its sulfide, a black eye paint used in the characteristic Egyptian portraits with cat-like eyes. In the Bible, Jezebel paints her face with "stibic stone" (antimony sulfide). It is not clear whether the ancients knew metallic antimony, but the alchemists were very familiar with it — Georgius Agricola mentions an alloy with tin in printer's type.

In nature, antimony can be found with sulfides and arsenides. Antimony is used in the semiconductor industry. As an alloying agent, antimony is used to harden lead. Pewter is a tin alloyed usually with antimony.

Zinc

Zn 30 65.39
[Ger. *Zink*]
Known to ancients in brass; discovered as metal in the Middle Ages
mp 419.6°; bp 907°; sp gr 7.13

Zinc compounds have been used for centuries for medicinal purposes — Pliny described how they were used for healing wounds and sore eyes. In the Middle Ages Marco Polo reported tutty (zinc oxide) manufacture in Persia. Brass, an alloy of copper and zinc, has been produced for centuries. Probably zinc has been prepared in isolation from time to time, but the first authentic report of elemental zinc was in the sixteenth century, when zinc was imported from China. Soon zinc was being smelted in Europe. In 1695 Wilhelm Homberg guessed, and in 1735 Johann and Georg Stahl confirmed, that calamine consisted of an "ore of zinc." By the end of the 1700s zinc was recognized as an element.

Zinc is extensively used in alloys: brass, nickel, silver (industrial and restaurant kitchen sinks), solder, die castings, etc. Zinc is plated onto iron to "galvanize" and to prevent corrosion. Zinc oxide (white) is used in paints, rubber products, cosmetics, pharmaceuticals, soaps, textiles, etc. Zinc sulfide is used to make luminous dials, X-ray and TV screens, and fluorescent lights.

Bismuth

Bi 83 208.9804
[Ger. *Weisse Masse*, white mass]
Known in the Middle Ages
mp 271.3°; bp 1560°; sp gr 9.75

Bismuth dates back to the 1400s, when it was used as trim in woodwork. Because of its low melting point, it was employed (1450) in casting type for printing presses. Agricola recognized bismuth, which was being procured from mines near Schneeberg, Germany, as a metal separate from lead — at this time most miners believed there were three kinds of lead (tin, lead, and bismuth), and that bismuth had advanced the furthest in the transmutation of lead into silver. By the early 1700s bismuth was recognized as a specific metal.

With a low melting point, bismuth is used in low-melting alloys for safety devices in fire detection and extinguishing systems. Bismuth is the most diamagnetic of all the metals, has a lower thermal conductivity (except mercury), and has the highest Hall effect (increase in electrical resistance in a magnetic field).

The Medieval source for zinc was mostly calamine, a general term for zinc carbonates and silicates. In modern times, when this "useful" ore of zinc was no longer readily available, zinc sulfide (sphalerite) has been exploited. Typical impurities in zinc include gallium, indium, and cadmium, often are prepared as byproducts of zinc manufacture.

In ancient times elemental zinc was not observed because it is volatile and evaporates in a hot fire.

3. THE MINERS
(1500-1800 A.D.)

Modern science depends upon both theory (that is, basic science) and technology (practical applications). Likewise, progress during the Middle Ages depended upon both theory and technology. As the Alchemists were plodding along with their secret recipes and cryptic writings, the practical miners were advancing their techniques for extracting the metals from the ores for spears, plowshares, and ornaments.

A marvelous volume was produced by Georgius Agricola toward the end of this period. This work, entitled *De Re Metallica* ("About Metal") described the complete production of metals from ores, including prospecting, mining, smelting, and assaying. This 650-page book includes spectacular woodcuts which meticulously describe the methods of the time. Originally written in Latin, *De Re Metallica* was translated into English by Herbert Hoover (who before his Presidency had earlier been a mining engineer) and his wife Lou Henry Hoover.

Different methodologies were used for different metals and different ores. Mercury, for example, was produced by merely heating the ores. Indeed, cinnabar and other mercury ores commonly show a metallic "sweat" in nature. Other metals, such as lead, required a more elaborate scheme of roasting litharge and other lead ores. Iron, the most difficult of the ancient metals to smelt, required special reducing conditions and a hotter temperature.

The mines of these times were dark and spooky places. Illumination was provided by flame and was meager. Every corner of the mine was shadowy and hid mischievous gnomes and goblins who caused havoc with the mining and smelting process. In church the miners and their families would pray for safety and protection from these evil spirits.

Brandt in 1737 was able to isolate a metal as an impurity from Scandinavian ores and was able to show that this new substance was the cause of the difficulty in smelting copper and iron ores. He named this metal after the German "Kobold" — gnome — and thereby discovered cobalt. Cobalt had actually been known for hundreds of years as a blue compound, used in glass — known today as "cobalt glass." Cronsted, a Swedish mineralogist, likewise investigated the "green ores" of the Scandinavian mines and was able to isolate another of these troublesome impurities. He named the new metal "nickel" after the German "Kupfernickel," another one of the meddling "devils" in the smelting process ("nickel" means "Satan").

One by one several other metals were discovered during this period. Gahn found manganese in pyrolusite (manganeseoxide), which was used to decolorize glass. The de Elhuyar brothers in their Basque seminary in Spain isolated tungsten in wolframite (iron tungstate), named after the "tung stens" or "heavy stones" of Scandinavia. Charles Hatchett, an English chemist, discovered niobium from a sample of columbite (calcium niobate) discovered in New England. This metal, originally named "columbite" was confused with the very chemically similar tantalum (discovered by Ekeberg) in subsequent years and was formally named by Heinrich Rose as "niobium." Vauquelin, a French mineralogist, discovered chromium in "red lead from Siberia" (crocoite, lead chromate), an unusual mineral found in the gold mines of the Ural Mountains. Stromeyer, a German pharmacist, was curious about a yellow impurity in a medical zinc (calamine) preparation and found cadmium. Andrés del Río, a professor of mineralogy at the School of Mines in Mexico, isolated a new metal he named “erythronium” in “brown lead from Zimapán, Mexico” (vanadinite, lead vanadate chloride). Owing to Old World arrogance, del Río was refused recognition of this metal, which was “rediscovered” by Sefström in Sweden. Sefström named the metal “vanadium,” but recognized his material was identical to del Río’s erythronium. Tellurium and selenium were isolated from the dregs of sulfuric acid vats, by von Reichenstein and Berzelius, respectively. These two elements were later traced to the pyrites (sulfides) of the ores of more common metals. Yttrium was isolated by Gadolin from a strange black ore (gadolinite, a rare earth calcium silicate) from Ytterby, Sweden. Molybdenum was extracted from molybdenite (molybdenum sulfide) by Scheele by the reaction of the ore with nitric acid, then charcoal. Titanium was discovered in “magnetic black sand” in Cornwall, England by Reverend Gregor. Slowly the list of metals was growing, and each was recognized as unique.

Somebody had to make sense out of this hodgepodge of metals! Technology had far outstripped theory. Obviously the alchemist’s doctrine of a mingling of mercury and sulfur was woefully inadequate to explain the riches spewing from the mines and hillsides of Sweden, England, Transylvania, Mexico, and the U.S. Meanwhile, the Universities were questioning the basic tenets of Aristotle. The time was ripe for a profound change in philosophy and a recantation of two thousand years of pedagogical dogma. The next chapter tells this story.

Cobalt

Co 27 58.9332
[Ger. *Kobold*, goblin]
Ores known for centuries, metal isolated 1735
mp 1495°; bp 2870°; sp gr 8.9

In the 1400s an annoying mineral was found in the mines of Saxony and Bohemia. This mineral was difficult to remove during the smelting, and arsenic in it was unhealthy. This mineral was called “cobalt” from the German *Kobold* meaning subterranean gnome, which according to local myth caused miners mischief and endless trouble. By the 1500s it was realized that this mineral could produce beautiful blue glass. Georg Brandt prepared a blue pigment from an ore from Riddarthytta, Sweden, and by 1735 he had prepared the metal. The similarity of iron, nickel, copper, and cobalt ores, and the confusing mix of their reduced metals and arsenic made it difficult to establish conclusively the elemental nature of cobalt until the late 1700s.

Cobalt, when alloyed with iron and nickel, produces Alnico, an alloy of high magnetic strength. Salts of cobalt have been used since historic times to produce the blue colors in porcelain and glass. The transition $CoCl_2{\cdot}6H_2O$ (pink) $\rightleftharpoons$ $CoCl_2$ (blue) + $6H_2O$ is utilized in invisible ink and in humidity indicators.

Nickel

Ni 28 58.693
[Ger. *Nickel*, Satan]
Ore known for centuries, metal isolated 1751
mp 1453°; bp 2732°; sp gr 8.90

The history of nickel is similar to that of cobalt. In Germany a reddish-brown ore with green spots was used to color glass green. The miners called the mineral *Kupfernickel*, meaning copper devil or “fake copper.” J. H. Linck stated in 1726 that since the ore gives green solutions, it must be a cobalt ore containing copper (even though no one had ever extracted from it!). The miners sometimes described the mineral as “cobalt which has lost its soul.” Axel Cronstedt in 1751 investigated a mineral from a mine at Los, Hälsingland, Sweden. He calcined (oxidized) the greenish coating of this mineral and reduced the product with charcoal to metallic nickel. Cronstedt immediately claimed the new metal to be an element, but the elemental nature of nickel was doubted by some until the latter 1700s, because of confusing mixes of ores in nature.

Nickel is used in stainless steels and other corrosion-resistant alloys such as Hastelloy; copper-nickel alloys are used in desalination plants. Nickel is now the predominant metal in coinage. It is used in armor plate and burglar-proof safes and vaults. Nickel plating is common in consumer steel products, such as office supplies. Nickel powder is used as a catalyst in hydrogenating vegetable oils. Nickel, as the second most common constituent in iron meteorites, is used as a criterion for identifying them.

Manganese

Mn 25 54.9380
[L. *magnes*, magnet]
Oxide known for centuries,
metal isolated 1774
mp 1244°; bp 1962°; sp gr 7.30

Pyrolusite had been used for centuries to color glass a beautiful violet. The mineral was known by the names “black magnesia” and “manganese.” Johan Gahn in 1774 prepared metallic manganese by heating pyrolusite (manganese oxide) and charcoal.

Manganese improves the manufacturing qualities and the strength of steel. The dioxide is used in dry cells, and decolorizes green glass (caused iron impurities). Manganese is the trace impurity producing the lavender color of amethyst. Permanganate (MnO_4^{-1}) is an excellent oxidizing agent, used in analytical chemistry and in medicine. Manganese nodules recently discovered on the floor of the ocean may be a future rich source of this element.

Tungsten (Wolfram)

W 74 183.84
[Swed. *tung sten*, heavy stone, Ger.
Wolfrahm, wolf froth]
Discovered 1781, metal isolated 1783
mp 3410; bp 5660°; sp gr 19.3

In 1781 Scheele dissolved a mineral from Sweden called *tungsten* (now known as scheelite) in nitric acid and discovered an acid similar to molybdic acid, which he called *terra ponderosa molybdænata* (tungstic acid). Two years later the de Elhuyar brothers extracted from wolfram (wolframite) the same acid and prepared a metallic sample by heating with charcoal. The source of the word “Wolfrahm” is derived from the interference of the ore with the smelting of tin — it supposedly “devoured” the tin.

Tungsten has the highest melting point and the lowest vapor pressure of all metals, and at temperatures above 1650° the highest tensile strength. It is used as filaments in electric lamps and electron and television tubes; for electrical contacts in automobile distributors; and X-ray targets and heating elements. Tungsten is used in high-speed tool steels and Hastelloy, and tungsten carbide in metal-working activities. The coefficient of expansion is the same as borosilicate glass, and is used for glass-to-metal seals.

Niobium

Nb 41 92.9064
[*Niobe*, daughter of Tantalus]
Discovered 1801, metal isolated 1864
mp 2468°; bp 4742°; sp gr 8.57

Charles Hatchett, a wealthy chemist in London, while rearranging specimens at British Museum discovered a curious heavy black stone, labeled as an "iron ore from Mr. Winthrop of Massachusetts." The sample of "columbite," as it became known, yielded in 1801 a brown precipitate which Hatchett identified as a derivative of a new metal, dubbed *columbium*. Hatchett never succeeded in isolating the elemental form; in 1864 C. W. Blomstrand reduced the chloride with hydrogen to produce the metal. Attempts to find the original source of the "Columbian mineral" were unsuccessful, and some Continental chemists (Berzelius) even doubted the authenticity of the American origin; more recent work has confirmed the sample's origin was Connecticut. The name *columbium* was used by the English and Americans, although Berzelius opposed this use and preferred *niobium* (which had been given by Heinrich Rose). The International Union of Pure and Applied Chemistry in 1950 officially adopted the name "niobium," although it is still known among metallurgists and U.S. producers as "columbium," with the symbol "Cb."

Niobium has been extensively used in advanced frame systems in aviation and space technologies. It is used in arc-welding rods for stainless steel.

Tantalum

Ta 73 180.9479
[Gr. *Tantalos*, bearer, sufferer]
Discovered 1802
mp 2996°; bp 5425°; sp gr 16.65

In 1802 Anders Ekeberg, Professor of Uppsala, isolated a new metal from both yttrotantalite collected at Ytterby, Sweden, and tantalite from Kimito, Åbo, Finland. He named the new metal *tantalum* because of the tantalizing efforts in isolating it. Wollaston thought niobium and tantalum were identical, but later work by Heinrich Rose (1846) and Jean-Charles de Marignac (1866), on the basis of the niobic and tantalic acids, proved the two metals were indeed separate and distinct. Tantalum occurs with niobium in nature, and is separated from this element with difficulty. Tantalum is virtually immune to chemical attack at ordinary temperatures and is excellent in anti-corrosive applications. The melting point is exceeded only by tungsten and rhenium. Tantalum can be drawn into a fine wire, and was originally used in electric light bulbs until tungsten replaced it; now tantalum is used as a filament for evaporating metals. Most of tantalum's use is in electronic components, mainly capacitors. The second most common use is tantalum carbide, used in cutting tools and dies. Alloys with tungsten, titanium, and niobium have high melting points and high strength, and are used in the aircraft and missile industry, nuclear reactors, and chemical process equipment — such as a "patch" in a boiler perforation. Since tantalum is not irritating to the body, it is used in surgical equipment and artificial joints in the body. Tantalum oxide is used in high refractive glass for camera lenses.

Chromium

Cr 24 51.996
[Gr. *chroma*, color]
Discovered 1797, metal isolated 1798
mp 1857°; bp 2672°; sp gr 7.20

Nicolas-Louis Vauquelin studied red lead from Siberia (crocoite) and concluded it contained a new element (1797). The following year he obtained the metal by reacting the oxide with charcoal. Because of the many colors of its compounds, he called it *chromium*.

Chromium is used, with iron and nickel, to manufacture stainless steels. As chrome plating, it can be used to produce a hard, beautiful surface. Chromium gives emerald its green color, and ruby its red color. The yellow dichromates ($Cr_2O_7^{-2}$) are used as oxidizing agents in analytical chemistry and in tanning leather. Chromium compounds are used in the textile industry as mordants, and for anodizing aluminum (forming a very thin protective oxidized coating).

Cadmium

Cd 48 112.41
[L. *cadmia*, calamine]
Discovered 1817
mp 320.9°; bp 765°; sp gr 8.65

Friedrich Stromeyer, inspector-general of apothecaries in Hanover, on an inspection trip in 1817 noticed that a certain medical preparation contained zinc carbonate instead of the specified zinc oxide. Upon questioning, the director of the pharmaceutical firm explained that when the carbonate was calcined to produce the oxide, instead of remaining white, it assumed a displeasing ocher color; hence, this step was omitted. Iron, the immediate suspect for the yellow contamination, was shown to be absent. Curious, Stromeyer dissolved the zinc carbonate in ammonium carbonate; the residue he ignited to a brown oxide. Upon reaction with charcoal, a bluish gray metal was obtained. He named the element *cadmium*, from *cadmium fornacum* ("furnace calamine").

Cadmium occurs most often in zinc ores, and is similar to zinc in many respects — for example, as a protective electroplated coating on steel agents, its greatest use. It is used in bearing alloys with low coefficients of friction and resistance to fatigue. It is used in solders and Ni-Cd batteries. Its compounds are used in blue and green phosphors in television tubes, and as a yellow pigment (CDs). Vincent van Gogh used yellow cadmium paints (cadmium sulfide is yellow, while most other transition metal sulfides are black).

Vanadium

V 23 50.9415
Discovered 1801, metal isolated 1869
[Scandinavian goddess, *Vanadis*]
mp 1890°; bp 3380°; sp gr 6.11

Andrés Manuel del Río, a native of Madrid who took a position at the School of Mines in Mexico, studied a specimen of "brown lead from Zimapán" and concluded it contained a new element, which he named "erythronium" (1801). The initial report of his discovery was doubted in Europe, because the element's properties were similar to those of recently discovered chromium. Losing confidence in his discovery, del Río dropped his claims. His specimen which was transported to Europe is presently exhibited in the Berlin *Museum für Naturkunde* (Natural History Museum), accompanied by the lengthy descriptor written by the naturalist Alexander Humboldt: "Brown lead ore from the veins of Zimapán. Lead chromate. M. del Río thought he had a new metal in it, later he realized it was ordinary chromium." In 1831 Nils Sefström discovered a new element in iron from the Taberg mine in Småland, Sweden,which he called *vanadium*. Wöhler the same year analyzed the "brown lead from Zimapán" and concluded that del Río had been correct in his original assessment, and that his erythronium was identical to Sefström's vanadium. The mineral is now known as vanadinite. Roscoe in 1869 prepared metallic vanadium by reducing vanadium trichloride with hydrogen.

Most of the vanadium is used as an additive in rust resistant and tool steels — a tough alloy utilized in armor plate, axle rods, piston rods, and axles. Vanadium is also used in superconductive magnets. Vanadium pentoxide is used in ceramics and as a catalyst.

Selenium

Se 34 78.96
[Gr. *Selene*, moon]
Discovered 1817
mp 217°; bp 685°; sp gr 4.79

In 1817 Berzelius observed a red mass at the bottom of a vat of a sulfuric acid plant at Falun Mine, Sweden. He originally thought he had prepared tellurium (discovered 35 years earlier), but the strong odor of "decaying radishes" aroused his suspicion. Careful experiments resulted in the preparation of a new element, recognized to be the cause of the strange odor, which he named *selenium* in analogy with tellurium. In 1820 Gmelin in Bohemia prepared pure selenium from fuming sulfuric acid and demonstrated the element originally came from bits of pyrite.

Selenium manifests photovoltaic action (light is converted directly into electricity) and photoconductive action (electrical resistance decreases with increased illumination). Hence, selenium is used in photocells, exposure meters, and solar cells; the drum in photocopy machines is coated with selenium. Selenium can convert alternating current (ac) to direct current (dc) and is used in rectifiers. Selenium occurs in some soils in sufficient amounts to poison animals feeding on plants.

Tellurium

Te 52 127.60
[L. *tellus*, earth]
Discovered 1782
mp 449.5°; bp 989.8°; sp gr 6.24

In the 1700s certain gold ores in Transylvania proved difficult to assay and were considered "unripe gold" (an alchemist term for impure gold). Müller von Reichenstein, a mining commissioner in this region, after three years of testing concluded that the ores contained an unknown new metal which imparted a red color to sulfuric acid, and which reprecipitated as a black solid when diluted with water (1782). He published in an obscure journal, of which only two volumes were printed (*Physikalische Arbeiten der einträchtigen Freunde in Wien — "Work in physics by harmonious friends in Vienna"*). Desiring verification of a new metal, he submitted a sample to Klaproth, the leading analytical chemist of Germany. In 1798 Klaproth reported the new discovery before the Academy of Sciences in Berlin, naming the element *tellurium* and giving credit for the discovery to Müller von Reichenstein. The

Hungarian Paul Kitaibel, who independently discovered tellurium several years later in his home country, is sometimes considered a co-discoverer of tellurium.

Tellurium is used as a basic ingredient in blasting caps and in ceramics. It improves the machinability of copper and stainless steel, and added to lead it decreases the corrosive action of sulfuric acid.

Yttrium

Y 39 88.9059
[*Ytterby*, village in Sweden]
Discovery: oxide 1794; crude metal 1828; pure metal 1953
mp 1522°; bp 3338°; sp gr 4.47

The chemistry of the rare earths began with *gadolinite* in 1787 (then called *ytterbite*), when Lieutenant Karl Axel Arrhenius, Swedish mineralogist, collected a black rock at a fluorspar mine near Ytterby, Sweden, just north of Stockholm. The mineral "resembled coal" and because of its weight was suspected to contain tungsten. Johan Gadolin, at the University of Åbo, Finland, investigated the mineral in 1794 and was successful in separating a "white earth," which was named *yttria* from the quarry where the mineral was found. This Ytterby site was soon to become famous for its strange and intriguing rare earth minerals. In 1828 Wöhler obtained the metallic element by reducing the yttrium chloride with potassium.

Since yttrium behaves like a rare earth, it is sometimes considered "out of place" in the Periodic Table, the other rare earths being the fiften elements 57-71 (lanthanum-lutetium). The largest use of yttrium is in the form of its oxide, which is used to make YVO_4-europium and Y_2O_3-europium phosphors to produce the red color in television. Yttrium oxide is also used to produce yttrium-iron garnets, excellent microwave filters and transmitters of acoustic energy. Yttrium is also used in laser systems and as a catalyst for ethylene polymerization.

Molybdenum

Mo 42 95.94
[Gr. *molybdos*, lead]
Ores known for centuries, element recognized 1778, metal isolated 1781
mp 2617°; bp 4612°; sp gr 10.22

Molybdän, or *molybdæna*, was the name for a soft, black graphite-like mineral now known as "molybdenite" (MoS_2). To the German-speaking population it was known as *Wasserbley* ("water-lead"). Although Johann Pott recognized it was not a lead compound, he confused it with graphite (*Reissbley*), and believed it consisted of lime, iron, and sulfuric acid. In 1778 Scheele investigated the mineral and demonstrated that graphite and molybdæna were two entirely different substances — nitric acid had no effect on graphite, but reacted with molybdæna to produce a white solid he called molybdic acid. He suggested it contained a new metal, and three years later with Peter Hjelm's furnace they fired the molybdic acid with charcoal to produce the metal *molybdenum*.

Molybdenum has the third highest melting point among the common elements (tungsten and tantalum being 1st and 2nd). It is a valuable alloying metal to harden and toughen steels, and improves the strength of steel at high temperatures. Almost all ultra-high strength steels contain molybdenum in amounts up to 8%. Molybdenum is also a catalyst in petroleum refining.

Titanium

Ti 22 47.867
[Gr. *Titans*, the first Sons of the Earth]
Discovered 1791, metal isolated 1887
mp 1660°; bp 3287°; sp gr 4.54

Two hundred years ago Reverend William Gregor collected some black sand from his parish in Menachan Valley, Creed, Cornwall, England. He called the substance "menachanite" (now known as ilmenite). From this mineral he prepared a "reddish brown calx" (1791). Meanwhile, Klaproth in 1795 discovered a new oxide from red schorl (rutile, TiO_2) from Boinik, Hungary. This substance, which he called "oxyd of titanium," bore a close resemblance to Gregor's, which he investigated. After he analyzed an authentic menachanite sample, he concluded they were the same, and gave credit to Gregor for the discovery of the element, but retained his name of *titanium*. In 1887 Lars Nilson prepared the metal by reducing titanium tetrachloride with sodium.

Titanium is almost always found in igneous rocks. Some rocks from the moon also showed large amounts of TiO_2. Titanium has both a low density and a high strength. It is easily fashioned metallurgically, can withstand extremes of temperature, and resists corrosion — thus, it is ideal for aircraft and missiles, and for propeller shafts and other parts of ships exposed to sea water. Titanium is as strong as steel, but is almost one-half as light. Star sapphires and rubies exhibit asterism because of TiO_2. Titanium dioxide, as a white base, is used in house and artist's paint — the largest use of the element.

Many ores are sulfides, formed in hydrothermal vents in the earth's crust. These sulfides are precipitated from aqueous solutions in fracture zones located in batholiths, huge pockets of molten igneous rocks. As the batholith cools, silicates crystallize in a standard sequence starting with olivines (peridot) and feldspars and ending with mica and quartz. Remaining is a pressure cooker aqueous solution of sulfur, arsenic, antimony, lead, copper, tin, and other transition metals. As the solid batholith cools further and fractures, the hot solution vents upward to cooler and lower pressure regions, where many minerals crystallize, often in exquisite forms and lovely colors.

The most common sulfide is pyrite, FeS_2*, called such because it gives off sparks when struck. Pyrite is also known as "fool's gold," but it is easily distinguished from gold, since it is harder and more brittle. Copper frequently forms bornite,* Cu_5FeS_4*, also known as "pea-cock ore" because of its avian iridescence. Cobalt is often found in cobaltite, CoAsS, a bright metallic steel-gray mixed sulfide. Galena (PbS), a dark lead gray mineral, is the most common ore of lead. When galena has inclusions of acanthite,* Ag_2S*, it is called "argentiferous" and is mined for the silver. When acanthite crystals grow to observable sizes, their intricate shapes well describe the name — "thorn" in Greek. The most common ore of nickel, pentalandite,* $(Fe,Ni)_9S_8$*, is a light bronze yellow. Molybdenite,* MoS_2*, is the major ore of molybdenum. Molybdenite is a soft, greasy black mineral that closely resem-bles graphite (in fact, it was confused with graphite until Scheele's work). Most of these sulfides are metallic in appearance, and are either dark, silvery, or bronze. A notable exception is mercury — cinnabar, HgS, is a stunning vermillion mineral. The very rare greenockite, CdS, is a sulphur yellow. Orpiment,* As_2S_3*, well know to the ancients, is also bright yellow. Sphalerite, ZnS, is the most common* *ore of zinc. Although white when pure, sphalerite often is colored to beautiful hues. A burgundy form, ruby sphalerite” from the Tri-State area (Missouri-Oklahoma-Kansas), furnished small but critical amounts of germanium and gallium during World War II. Cadmium also is commonly mixed with sphalerite and other zinc compounds, and is a byproduct of zinc production.*

Transition metals are also found in other forms. The most common ore of iron is the red hematite, Fe_2O_3. Copper is found as the sulfide (chalcopyrite, $CuFeS_2$), oxide (cuprite, Cu_2O), and the carbonates (malachite and azurite, $Cu_2(CO_3)_2(OH)_2$ and $Cu_3(CO_3)_2(OH)_2$, respectively). Malachite and azurite are the royal green and blue ores of copper. Malachite is fashioned into elegant ornaments, jewelry, and boxes. Tin is found as cassiterite, SnO_2, a brownish adamantine mineral. Titanium is most frequently seen in ilmenite, $FeTiO_3$, a black spar that frequently powders into “magnetic black sand.” Pyrolusite, MnO_2, is the main ore of manganese, an amorphous black mineral. Niobium and tantalum are seen in columbite/tantalite, $(Fe,Mn)(Nb,Ta)_2O_6$, pyrochlore, $(Na,Ca)_2Nb_2O_6(OH,F) \bullet nH_2O$, and samarskite, $(Y,Fe,U)(Nb,Ta)O_4$, all dense, dark minerals. Tungsten is mixed with other minerals but occasionally crystallizes out as scheelite, $CaWO_4$, a heavy, white octahedral crystal that fluoresces a dazzling blue-white under an ultraviolet lamp. Scheelite can be distinguished from the associated powellite, $CaMoO_4$, from the latter’s custard-yellow fluorescence. Vanadium is commonly found in vanadinite, $Pb_5(VO_4)_3Cl$, a pretty red-brown mineral. Chromium, although forming resplendent red crocoite crystals, $PbCrO_4$, mostly occurs in the dull black mineral chromite, $FeCr_2O_4$.

Selenium and tellurium are found as selenides and tellurides of copper, lead, and other metals. Tellurium forms interesting minerals with gold and silver, such as calaverite, Au_2Te_4, and sylvanite, $AgAuTe_4$. These were the principal gold ores during the gold rush in Cripple Creek, Colorado, forming stunning silvery blades and prisms.

Yttrium is mainly found in rare earth minerals, such as samarskite (see above), gadolinite, $(Ce,La,Nd,Y)_2FeBe_2Si_2O_{10}$, and euxenite, $(Y,Ca,Ce)(Nb,Ta,Ti)_2O_6$. These minerals will be seen again in Chapter 11, as a general source of the rare earths.

The ancient miners had good cause to be confused, because nickel and cobalt ores that appeared like copper ores did indeed give them cause to think that gnomes were busy in their mischievous ways. Niccolite, (NiAs, also known as nickeline) is a pale copper-red color; it alters with time (oxidizes) to annabergite, $Ni_3(AsO_4)2 \bullet 8H_2O$, of an apple-green color. This transformation from red to green color precisely mirrors the behavior of copper. The Statue of Liberty, for example, is constructed of copper but with age acquires a pretty green patina of malachite, $Cu_2(CO_3)_2(OH)_2$. Like-wise, the similar appearances of “cobalt blue” and azurite, $Cu_3(CO_3)_2(OH)_2$), were equally mystifying to the ancient miners.

4. LAVOISIER AND PHLOGISTON

(1750-1800 A.D.)

The stage was now set for a giant leap in the understanding of chemistry. A vast amount of knowledge had been accumulated during the previous several thousand years. Man understood how to process ceramics, glass, and metals. In the previous several hundred years new compounds and acids had been discovered; the technology of ceramics, glass, and metals had advanced greatly; gunpowder had been discovered and utilized in peace and in warfare; physics had exploded with a new understanding of the laws of motion; electricity had been discovered; and the center of the universe was no longer the earth, but the sun. However, the four basic elements were still considered to be fire, earth, water, and air. Since chemistry involves invisible atoms (not yet hypothesized, except briefly by the Greek Democritus), the basic understanding of chemical processes would be difficult. It would take a great genius to take that great leap from archaic thinking to a new theory of chemical processes.

Ironically, this great leap involved not traditional substances — metals, sulphur, charcoal, salts and acids — but instead revolved about the investigation of the three gases nitrogen, oxygen, and hydrogen. Lavoisier, a French tax collector and part-time chemist, was able to piece together all the fragmentary information to arrive at a new view of the universe that allowed the birth of a new view of chemistry. Indeed, Lavoisier is called the Father of Modern Chemistry.

Lavoisier's work was founded on a theory proposed a hundred years before his time. In the 1600s Becher founded, and Stahl elaborated, the so-called phlogiston theory, suggested to explain the overall observations of combustion (burning), calxing (rusting), and respiration (animal breathing). Although this theory is now considered crude and far off the mark, it was one of the most important advances in chemistry because it allowed for the first time a *theory that allowed predictions and therefore could be tested.* As any modern scientist knows, the progress of science rests upon the proposal of theories that predict and can therefore be tested, validated, refined, or discarded.

Stahl proposed that the three processes of combustion, calxing, and respiration together reflected Nature's management of a universal principle called "phlogiston" (Greek "inflammable" principle). According to this theory, when a material burns (combusts), phlogiston is emanated and is released into the atmosphere. One can actually "see" and "hear" the release of phlogiston during, for example, the burning of wood, as heat waves are observed and the hissing of escaping phlogiston is detected. Whereas the ancients believed that fire ascended into the empyreum, Stahl believed that the phlogiston combined with the atmosphere. Plants then could absorb the phlogiston into their organic material to produce "phlogisticated" substances which animals could then eat. As the animals respired, the foods released their phlogiston back into the atmosphere. Thus was observed a continuous cycle, with phlogiston flowing from fires and animals into the atmosphere, where plants could produce "rephlogisticated" material. Meanwhile, metals were observed to calcine to produce a calx (red-brown in the case of iron, but different colors for different metals, such as white for antimony or black for manganese). This calcining phenomenon was explained by the same process: metals would release phlogiston to the atmosphere (today we know this process as "oxidation," but remember, "oxidize" was not known as a word yet, because "oxygen" had not been identified). The calx could be "rephlogisticated" by reaction with charcoal to regenerate the metal. Obviously, Stahl said, charcoal was very rich in phlogiston, which made sense since charcoal comes from plants (wood).

Although wood and other combustible materials lost weight during burning, metals when calcined mysteriously *gained* weight. The former observation — that wood disappeared upon burning — was easily explained by simply assuming the products of burning disappeared into the atmosphere. The gain of weight of metals, however, was more difficult to explain. Since metals *gained* weight when they *lost* phlogiston, then it followed that phlogiston must have *negative* weight! That is, the prediction was made that phlogiston had anti-gravity.

"Phlogisticated" air was first characterized by Daniel Rutherford (not to be confused with Ernest Rutherford, who investigated the structure of the atom more than a century later). Rutherford prepared "phlogisticated air" by burning a candle, calcining a metal, and by collecting the respiration gases of a mouse. He showed that all of these gases behaved similarly. For example, after the mouse died in a closed container (it usually took about fifteen minutes), Rutherford showed that this "dead mouse gas" would not support the combustion of a candle nor the calcining of metal. Likewise, the air produced from a calcined metal or a burned candle would not support a mouse for the full fifteen minutes. Hence, Rutherford had shown that "Stahl was correct": The air from the three processes of combustion, calcining, and respiration were indeed the same, and hence this air must be "phlogisticated air."

The next step was to prepare "dephlogisticated air." Priestley and Scheele were independently able to produce this air. Although Priestley is generally credited with the discovery (because his publications appeared first), Scheele performed more precise experiments and actually made the discovery earlier.

Scheele heated a calx (mercuric oxide) and collected the resulting gas in a bladder (balloons had not yet been invented). He called his product "Feuerluft" (fire air). Priestley called his gas, produced in a similar fashion, "dephlogisticated air." Scheele proposed a balanced equation for the process which was consistent with Stahl's phlogiston theory:

$$\text{calx of mercury} \;+\; (\phi + \text{fire air}) \;\rightarrow$$

[heat]

$$(\text{calx of mercury} + \phi) \;+\; \text{fire air}$$

[mercury]

It only remained for phlogiston itself to be found. This "discovery" was made by Cavendish, an eccentric millionaire who performed experiments in laboratories he set up in his mansions. Shy and retiring, Cavendish rarely showed himself in public; but his lectures were brilliant and reflected extremely careful and meticulous work. His retiring ways were so extreme that he fired a servant who ventured to speak with him rather than communicate by his preferred method of writing notes and shoving them under the door. He never posed for a portrait and only one quick sketch of him exists.

Cavendish's experimentation involved the addition of Mars (iron) to oil of vitriol (sulfuric acid) to produce a gas which he collected in a bladder. He observed that the bladder floated in the air, and thus he must have phlogiston, which was predicted to have negative weight! This trapped air was shown to be quite combustible and accordingly was termed "inflammable air." It made perfect sense that phlogiston itself should be so reactive. He even wrote a balanced equation to show the chemical combinations of all the materials involved:

$$\underset{\textbf{[metal]}}{(\text{calx} + \phi)} + \text{acid} \rightarrow \underset{\textbf{[salt]}}{(\text{calx} + \text{acid})} + \underset{\textbf{[inflammable air]}}{\phi}$$

It would appear that Stahl's theory of phlogiston had been fully vindicated — the equations appeared to accurately describe chemical behavior in accordance with Stahl's interpretation of nature. Additional cases abounded: for example, one could predict that sulphur was a combination of oil of vitriol (sulfuric acid) and phlogiston by the following reasoning: Since liver of sulphur (potassium sulfide) could be made by heating potash (potassium hydroxide) with sulfur; and since liver of sulphur could also be produced by heating vitriolated tartar (potassium sulfate) with charcoal (rich in phlogiston), then:

$$(\text{sulphur} + \text{potash}) \rightarrow (\text{oil of vitriol} + \text{potash}) + \text{phlogiston}$$

And by subtracting potash from both sides of the equation, we conclude that

$$\text{sulphur} = \text{oil of vitriol} + \text{phlogiston}.$$

Hence, it was reasoned, sulfur must be a compound — and it was believed that quite possibly oil of vitriol (sulfuric acid) was an element!

By now a student of chemistry would recognize a thread of truth throughout all of these theories, observations, and conclusions, but would also perceive that everything seemed to be backwards. But hindsight is powerful, and it took a powerful genius to figure out what was actually happening. This master, Lavoisier, boldly made the prediction: If Stahl were correct, then dephlogisticated air (oxygen) would react with phlogiston (hydrogen) to produce phlogisticated air (nitrogen). To test this prediction, Lavoisier assembled an apparatus that contained dephlogisticated air and phlogiston that could be reacted with a spark. He passed a charge through the arc and witnessed a mighty explosion. He had fashioned strong glass walls to withstand the force of the reaction. Upon carefully inspecting the contents, he observed not phlogisticated air (nitrogen) as the product but *water*!

In every science, there has been a event that signaled the evolution from a primitive faith to a true modern science. In biology this event was Darwin's theory that all species were created by natural mutation and selection; ever since, "no thing in biology makes sense without evolution." In physics perhaps this milestone was laid by Galileo, who observed that all objects fell at the same rate and showed that all physical phenomena obeyed mathematical laws. In astronomy this turning point was founded by Copernicus, who postulated the heliocentric theory. In geology it was the understanding that earthquakes were caused by natural events in Terra instead of by the rage of God; in bacteriology it was that microscopic living beings caused diseases instead of humors and evil spirits. And in chemistry it was the Lavoisier's insight that water was a compound, and therefore the "inflammable air" (which had been supposed by others to be phlogiston) and the "dephlogisticated air" or "vital force" were actually *elements*. In fact, Lavoisier gave names to these two elements, calling the first "hydrogen" ("water-former") and the later "oxygen" ("acid-former"). Hence, phosphorus was no longer "the fatty part of urine concreted to a very combustible earth" but was an *element*. With this keen perception, Lavoisier went on to identify thirty-one substances as elements. Incredibly, he recognized chlorine ("muriatic radical") and fluorine ("fluoric radical") were elemental, even though the elemental substances themselves *had never been isolated* (only salts)! He continued to realize that other elements must exist from their compounds: boron (from borax and similar compounds), silicon (from quartz and glass), magnesium (from Epsom salt), calcium (from limestone), and aluminum (from clays) — when none of these elements had ever been isolated in its elemental form! This was insight of a staggering degree.

These are the elements Lavoisier recognized:

Oxygen
Hydrogen
Phosphorus
Chlorine
Boron
Silver
Bismuth
Copper
Iron
Mercury
Nickel
Platinum
Tungsten
Calcium
Barium
Silicon
Nitrogen
Sulfur
Carbon
Fluorine
Antimony
Arsenic
Cobalt
Tin
Manganese
Molybdenum
Gold
Lead
Zinc
Magnesium
Aluminum

And Lavoisier did not stop there! He went on to understand, since compounds were combinations of these elements, that they could be named on this basis. Thus it became understood that the "fixed air" of Black was actually an oxide of carbon, and the white "flowers of zinc" which grew from the gray metal was "zinc oxide." Thus, Lavoisier revolutionized chemistry not only by recognizing the true elements, but by also completely transforming the vocabulary.

The understanding that compounds were composed of distinct contributions of elements also greatly simplified the great confusion created by many names for the same substance. For example, the "fixed air" (oxide of carbon) had been observed under various circumstances and experiments and had been cataloged by a bewildering array of different names, including: aërial acid, Mephitic air, air surabaondante, gas sylvestre, mineral spirit, mineral elastic spirit, choke-damp, acid crayeux (chalky acid), "the poisonous gas that extinguishes a candle flame," "gas forming in cellars, especially from fermenting wine," and so on.

Interestingly, Lavoisier identified "heat" and "light" as elements. At the time it was natural, because these "substances" were observed to evolve from other substances. For example, when a cannon was bored, "heat" wasreleased from the iron. It was left to Count Rumford (who married Lavoisier's widow when he was guillotined during the French Revolution) to understand the true nature of heat.

Lavoisier was a tax collector for King Louis XVI and was well versed in accounting. He was keen on "balancing of the ledger." This view led him to understand that in all chemical reactions, there must be neither a net gain nor a net loss. Lavoisier thus embraced the concept of "The Conservation of Mass," the basis for balancing equations.

The execution of Lavoisier was indeed tragic. Being a government employee by vocation, he had been caught up in political events. "It required but a moment to cut off his head and perhaps a hundred years will not suffice to produce another like it."

— *Comte de Joseph- Louis Lagrange.*

Nitrogen

N 7 14.0067
[Gr. *nitron-genes*, niter-forming]
Discovered 1772
<u>mp</u> -209.9°; <u>bp</u> 195.8°; <u>density</u> 1.25 g/L

For half a millennium it has been known that air has two major constituents. Leonardo da Vinci himself described these two gases, one that supported flame and animals, and the other that did not. Scheele called these two gases “fire air” and “vitiated air.” Daniel Rutherford, uncle of Sir Walter Scott, first isolated nitrogen and announced its discovery in a doctor’s dissertation. In 1772 he prepared nitrogen by means of a mouse confined in a container of atmosphere until it suffocated. After removing the “mephitic air” (carbon dioxide) with caustic potash, he had remaining “noxious air” (nitrogen), which was unwhole-some because it was “atmospheric air saturated with phlogiston.” After Cavendish prepared niter (sodium nitrate) by sparking the gas in the presence of oxygen and caustic soda, the name *nitrogen* was suggested. Lavoisier (1789) considered the substance an element and called it *azote* (“without life”). In German it was named *Stickstoff* (choke-damp). Curiously, the elemental nature of nitrogen was questioned for years — even by Sir Humphry Davy, who tried to decompose it in the early 1800s.

Nitrogen is the principal constituent of the atmosphere (N_2). Nitrogen is important in foods, poisons, fertilizers, and explosives. Nitrogen can exist in many oxidation states, giving rise to N_2O, NO, NO_2, N_2O_3, N_2O_5, NH_3, and others. In certain desert areas of the world nitrogen is found in the form of nitrates. The largest consumer of nitrogen is the ammonia industry.

Oxygen

O 8 15.9994
[Gr. *oxys-genes*, acid-former]
Discovered 1774 independently
by Priestley and Scheele
<u>mp</u> -218.4°; <u>bp</u> -183.0°; <u>density</u> 1.43 g/L

Five centuries ago, Leonardo da Vinci was the first to recognize that air consisted of two major components. However, the concept that flammable materials directly *reacted* with one of these atmospheric constituents was delayed by the concept of *phlogiston* (φλογιστὸν), formulated by Becher and Stahl in the late 1600s. They maintained phlogiston was a volatile constituent of flammable matter released by combustion. Hence, Priestley called the gas “dephlogisticated air” that he obtained in 1774 when he heated oxide of mercury to obtain the metals (i.e., he interpreted the phlogiston to be reuniting with the metals). Lavoisier, noticing that metals *gained* mass during calcination, asserted the gas couldn’t be losing any constituents such as “phlogiston.” Instead, a substance from the air was *combining* with the metal during calcination. Through very careful experimentation Lavoisier unequivocally disproved the phlogiston theory by defining the true nature of com-bustion. He recognized the active atmospheric principle as an element and named it *oxygène*.

Oxygen (O_2) is the most common element in the earth’s crust, constituting 50% of the sand, clay, limestone, and igneous rocks. Oxygen is the second most common element in the atmosphere (O_2) and the most common element in the oceans (H_2O). This element is very reactive and can combine with most elements, forming a countless number of mineral and biological compounds. It is essential for respiration in plants and animals and atmospheric combustion.

Hydrogen

H 1 1.0079
[Gr. *hydro-genes*, water-former]
Discovered 1766
mp -259.3°; bp -252.9°; density 0.0899 g/L

Hydrogen had been observed several times before its "discovery" in 1766. Robert Boyle in 1671 observed that Mars (iron) in acid produced an "inflammable stinking smoke." In the latter 1600s, Johann J. Becher and Georg E. Stahl proposed a theory of combustion that chemists accepted for a hundred years. According to this theory, all combustible materials contain a substance, phlogiston (φλογιστὸν), which escapes in the form of a flame while burning; a metal consisted of its calx (oxide) and phlogiston. Observations of hydrogen were generally interpreted as the release of this principle; M. V. Lomonosov in Russia reacted metals with acids and observed an "inflammable vapor" which "could be nothing else but phlogiston" (1745). The first person to make a careful study of this inflammable gas was Henry Cavendish, an eccentric English millionaire (1766). He collected hydrogen over mercury and distinguished it from other gases. He described the properties of hydrogen and methods of collection from different sources. Mistakenly, he thought hydrogen was derived from the metal rather than from the acid. He was the first to discover as an observable *fact* that hydrogen and oxygen can be completely converted to their own weight of water — from this he concluded that hydrogen was a compound of phlogiston and water. (Lavoisier's quantitative analysis of water was more precise). He was aware of, but rejected, Lavoisier's interpretation of combustion. Lavoisier in his brilliant contribution (*Traité Élémentaire de Chimie*, 1789) correctly interpreted water not as an element, but as a compound, and hydrogen as an element, and its combustion as its reaction with oxygen. Cavendish called hydrogen the "inflammable air"; Lavoisier gave it the modern name, *hydrogène*.

Hydrogen is the most abundant element in the universe, although limited in quantity on the planet earth, mostly in the form of water (H_2O). Ordinarily a gas (H_2), hydrogen is converted to a solid metallic form under the intense pressure in the core of the giant planets. Hydrogen is the lightest gas, but is vigorously combustible, leading to tragedies such as Zeppelin *Hindenburg*. Hydrogen ions are the active principle in acids (H^+). Most of the commercially produced hydrogen is used in the Haber process for manufacturing ammonia ($3H_2 + N_2 \rightarrow 2NH_3$). A great deal of hydrogen is also used in the food industry to hydrogenate oils.

Lavoisier's laboratory was located in Le Petit Arsenal, near the Bastille in Paris, France. Neither the Bastille, the Arsenal, or Lavoisier's laboratory still exist. Only a plaque presently exists on the wall of a modern building,

"Ici se trouvait
l'Hotel de la Regie des Poudres
ou travilla et habita de 1776 à 1792
Antoinne-Laurent Lavoisier
Régisseur des Poudres et Salpêtre
qui y installa son laboratoire de chimie"

"Here was located
the Hotel of the regulation of (gun) powder
where from 1776 to 1792
Antoine-Laurent Lavoisier worked and lived
Registrar of powder and saltpeter
who there established his laboratory of chemistry"

A wonderful exhibit of Lavoisier's apparatus exists in the Musée des arts et métier (Museum of arts and measurement) on the Right Bank of the Seine. The exhibit includes some of his delicate equipment with which he carefully weighed specific amounts of hydrogen and oxygen and the spark flask which produced the water. This equipment was state-of-the-art apparatus of the day, without which Lavoisier could not have quantitatively studied the basic reaction of:

hydrogen + oxygen → water.

Lavoisier was an unique individual who could combine both abstract and descriptive chemistry to arrive at fundamental truths. His vocation as a tax collector trained him to quantitate and expect conservation of mass — "The ledger must balance; what goes in must come out; there must be no loss in either an accountant's books or in a chemist's laboratory." His avocation as a lover of science and dreamer allowed him to make the leap of genius to recognize the true elements.

The "French chemistry" was quickly accepted in Lavoisier's homeland but was bitterly resisted in Stahl's home country of Germany. Thomas Thomson of the University of Edinburgh was one of the first in the British Isles to embrace the "anti-phlogistic theory." It was many years before the chemical world generally rejected the phlogiston theory which had held sway for a hundred years.

5. HALOGENS FROM SALTS (1740-1890)

During the age of alchemists, there was frequent opportunity for fraud. Many a trickster could exploit the greed of the public by perpetuating hoaxes, typically the creation of gold. A notable exception to the chicanery was the early sixteenth century alchemist Theophrastus Bombastus von Hohenheim, better known as Paracelsus. Determined to break from the superstitions of the past, he promoted logical explanations and true cures. For example, he explained that miners suffering from lung disease were afflicted with ore dust rather than being besieged by evil spirits. His most famous contribution was the discovery of mercury compounds, which he promoted as a cure for syphilis which was sweeping across Europe. These mercury compounds were used as effective agents until the twentieth century.

Trying to make sense out of old explanations, Paracelsus accepted the idea of mercury as the principle of fusibility and sulphur as the principle of combustibility, but he reasoned that there must exist another principle of fixity and incombustibility — salt. When these three principles are present in the human body in the correct proportions, health is experienced. Disease is thus caused by an imbalance of these three principles (and not by evil spirits). Paracelsus anticipated by several centuries the three classes of compounds: alloys (metals bonding with metals), covalent compounds (nonmetals bonding with nonmetals), and salts (metals bonding with nonmetals). Paracelsus analyzed metals and their calxes (rusts, or oxides), and first used the term "reduce" when a calx was reverted back to the metal.

Johann Rudolph Glauber was an early seventeenth century self-educated German chemist who made a particularly avid study of salts. His interest in salts began when he cured himself by drinking the water of a mineral spring. He investigated the water and found a salt he called "Sal mirabile" ("wonderful salt"), named after him as "Glauber's salt," or sodium sulphate. Glauber's descriptions of acids, which were prepared from salts, were superb. He recounted the preparation of hydrochloric acid, nitric acid, and sulphuric acid by several methods, some of which are used in the teaching laboratory today. Hydrochloric acid — termed in his day as "spiritus salus," or "spirit of salt" — could be prepared by the distillation of common salt with oil of vitriol (sulphuric acid). Nitric acid ("spiritus fortis," or "strong spirit") could likewise be made from saltpetre and oil of vitriol. Oil of vitriol in turn was generated from heating wet green vitriol (iron sulfate) or alum (aluminum sulfate). These distillations were prepared in Glauber's own invention, a huge retort called the "Iron Man."

Chlorine. Scheele, the codiscoverer of oxygen, in 1774 reacted spiritus salus (hydrochloric acid) with pyrolusite (manganese dioxide) to form a suffocating gas. Under the philosophical spell of Stahl, he interpreted his observations as the pyrolusite extracting phlogiston from the acid to form "dephlogisticated muriatic (marine) acid." Scheele noticed that this gas bleached flowers and reacted with metals.

There exists a rule in science labeled "Occam's razor" which is commonly used to make decisions when a choice is to be made between two theories. Named after William of Occam, this tenet holds that in lieu of hard evidence to the contrary, the simplest theory should be selected. The current belief at the end of the sixteenth century was that oxygen existed in all acids (indeed, Lavoisier had named "oxygen" as an "acid-former"), and subsequent interpretations of this mysterious substance mainly included a composition of oxygen and hydrochloric acid. By 1807 Sir Humphry Davy chose the simplest view that chlorine must be elemental, and he named it (after its yellow-green color). Acceptance of the elemental nature of chlorine was not immediately universal, even though attempts to decompose chlorine by heating with dry charcoal were unsuccessful. However, after iodine and bromine were discovered and were shown to be irreducible, "oxidized muriatic acid" as a term for HCl was abandoned.

Iodine. The next halogen that was isolated in the elemental state was iodine — and quite by accident. Never suspected before, iodine was produced by Bernard Courtois in 1811 when he treated seaweed with sulfuric acid. Courtois was involved in the production of sodium and potassium compounds from seaweed. This abundant commodity along the French seashore was reduced to ashes by burning and was subsequently leached to form a brine which was allowed to evaporate. First sodium chloride, and then potassium chloride, were selectively precipitated. To destroy and remove some of the undesired by-products (mainly sulfur compounds) of the mother liquor, Courtois added sulfuric acid. One day he added too much, and to his surprise lovely violet clouds arose with a chlorine-like odor. These colored clouds condensed on cool objects to form beautiful dark violet crystals with a metal-like luster. Courtois characterized this substance, noticed it did not compose with heat, and suspected it was an element. Davy proved its elemental nature by demonstrating that it could not be altered by passage over a red-hot carbon filament.

Bromine. Balard, a pharmacist in Montpellier, France, discovered bromine. While investigating mother liquor from a salt marsh near his home, he noticed the liquor become brown when treated with chlorine. He isolated this brown substance by distillation from potassium bromide, sulfuric acid, and manganese dioxide. Rapid progress on bromine was made, because it was recognized as being similar to chlorine and iodine. Indeed, it was realized that "bromine finds its place between chlorine and iodine," thus anticipating periodic behavior of the elements by a quarter of a century.

Balard wanted to name the substance "muride" (after "sea") but the scientific community preferred "bromine" ("stench"). Other scientists had isolated bromine but had missed the "discovery" because they identified it as "iodine chloride."

Several researchers of the time also observed bromine compounds in certain Mediterranean mollusks. Indeed, Tyrian (or Royal) Purple, a beautiful, expensive dye, had been extracted from the straight-spined Murex since ancient times. It is now known that this dye is 6,6'-dibromoindigo.

Fluorine. Fluorine compounds have been used for hundreds of years; Agricola described how fluorspar (calcium fluoride) could be used as a flux for smelting. "Acid of fluorspar" (hydrofluoric acid), produced by the action of sulfuric acid on fluorspar, was found to etch glass. Soon this method was preferred to create intricate designs on glassware over the more time-consuming procedure of scratching with a diamond tip.

During the 1700s much confusion existed concerning the nature of "acid of fluorspar," principally because it dissolved the glass containers that held it, producing a white precipitate (silicates). After it was shown that the acid in lead or gold-lined vessels did not produce such a white precipitate, analysis of the acid could proceed without misinterpretation. The acid created much interest, and many investigators suffered grievously from its harmful effects on the body, and some even died. Nevertheless, research was pursued relentlessly. After hydrochloric acid, hydrobromic acid, and hydroiodic acid were shown to be simple (without oxygen), and that chlorine, bromine, and iodine were recognized as elements, it was assumed that the acid of fluorspar was likewise a simple acid, hydrofluoric acid, and that a simple element fluorine might be produced. Since fluorine must be very reactive (even more so than chlorine!), then electrolysis was chosen as the method of preparation. The problem was to utilize a solution that was conductive and yet held no water — because electrolysis of an aqueous solution would merely break down water into hydrogen and oxygen.

The seemingly impossible task of the electrolysis of hydrofluoric acid was finally accomplished by Henri Moissan in Paris. In 1886 he electrolyzed a solution of dry potassium fluoride and anhydrous hydrogen fluoride, using platinum-iridium electrodes sealed into a platinum U-tube sealed off with fluorspar caps, with the entire apparatus cooled to −23° (using methyl chloride as the refrigerant). At the anode a gas was produced that immediately burst silicon into flame. The most reactive nonmetal had finally been isolated.

Moissan's method of electrolyzing salts to form fluorine was based upon Sir Humphry Davy's technique developed many years before for the reactive metals. The story of Davy's voltaic pile follows in the next chapter.

Fluorine

F 9 18.998403
[L. *fluere*, flow]
Hydrofluoric acid known since 1700s,
element isolated 1886
<u>mp</u> -219.6°; <u>bp</u> -188.1°; <u>density</u> 1.70 g/L

Fluorspar (CaF_2) has been known since the 1500s. In 1670 the glass cutters of Nuremberg discovered that fluorspar when treated with acids etched glass. Various investigators who studied this "acid of fluorspar" (hydrofluoric acid, which is extremely poisonous) became ill and some even died. Henri Moissan prepared elemental fluorine itself in 1886 by electrolyzing a KF-HF melt chilled to -23°. At the anode fluorine was produced, identified by bursting a piece of silicon into flame. Since Moissan could not use glass, which would react with fluorine, he fashioned fluorite (CaF_2) plugs, connectors, containers, and windows for his apparatus.

Fluorine (F_2) is the most reactive and corrosive of the oxidizers. Metals, carbon, and even water burn in fluorine with a bright flame. Fluorine is used in producing fluorochemicals and freons (chlorofluorocarbons, CFCs), high-temperature plastics, and etched glass products. Fluoride in drinking water and toothpaste helps prevent dental caries, but an excess of fluoride is toxic.

Chlorine

Cl 17 35.453
[Gr. *chloros*, greenish yellow]
Discovered 1774
<u>mp</u> -101.0°; <u>bp</u> -34.6°; <u>density</u> 3.21 g/L

Scheele in 1774 reacted pyrolusite (MnO_2) with "spiritus salis" (HCl) to produce a gas with a suffocating odor, which he called "dephlogisticated muriatic acid" (Cl_2).

Lavoisier thought all acids contained oxygen, and it was natural to think of the gas as a loose compound of hydrochloric acid and oxygen. However, in 1807 Davy chose the simpler interpretation — a "simple" substance, and he named it *chlorine*. This explanation was gradually accepted; and after iodine was discovered and characterized by the early 1800s, chlorine was universally accepted as an element.

Chlorine (Cl_2) is used world-wide to render water safe for drinking. It is used in the production of paper, textiles, petroleum products, medicines, insecticides, solvents, paints, and plastics. It is used as a bleach and disin-fectant. Chlorine is toxic and was used as a poison gas in World War I.

Bromine

Br 35 79.904
[Gr. *bromos*, stench]
Discovered 1826
mp -7.2°; bp 58.8°; sp gr 3.12

Balard reacted Montpellier, France, brines with chlorine and prepared a dark red liquid. After his presentation to the French academy, this material was rapidly accepted as a "simple body" (element). Other chemists had just missed the discovery — Liebig, for example, had a bottle of bromine that he had labeled "liquid iodine chloride." Chagrinned, Liebig placed the bottle in his "cupboard of mistakes."

Bromine (Br_2) is the only liquid nonmetallic element. It is found in brine mixtures. When not sealed, thick red-brown fumes are given off that have a choking odor. It is used in making fumigants, flameproofing agents, and organic bromides for photography. Previously, bromine was used in the production of ethylene dibromide, a lead (Pb) scavenger used in making gasoline antiknock compounds (today, only non-leaded gasoline is sold for automobiles, owing to the toxic effects of lead).

Iodine

I 53 126.9045
[Gr. *iodes*, violet]
Discovered 1811
mp 113.5°; bp 184.4°; sp gr 4.93

Bernard Courtois discovered iodine when he added an excess of sulfuric acid to a concentrate from marine algae; beautiful violet clouds effused and condensed on cold glass to form dark crystals with a strange metallic-like luster. Davy showed in 1814 that these dark crystals were an element, because they could not be decomposed by a red-hot carbon filament.

Iodine is found in the ocean where it is assimilated by seaweeds. Iodine is principally extracted from salt brines and Chilean saltpeter, where it exists in the form of iodates. Lack of iodine is the cause of goiter, and "iodized salt" contains a small amount of iodide for this purpose. Iodine is used as an antiseptic in medicine. The black solid sublimes at room temperature to produce a violet gas that is irritating to the eyes, nose, and throat.

Brines, formed by the evaporation of sea water, are composed mostly of sodium chloride (halite, NaCl), although bands of potassium chloride (sylvite, KCl) also occur. Halite is named for the Greek "hals," salt. Sylvite is named for "Sal digestivus Sylvii," or *digestive salt of Francis Sylvius de le Boë, a Dutch physician of Leyden. Sylvite is much less common in nature than is halite, because most of the potassium is locked up in the earth's crust in clays and feldspars.*

It is sometimes difficult to distinguish halite and sylite in the field, because they can assume similar crystalline habits (cubes). Sylvite is a little more astringent to the tongue (and tastes like "low sodium salt" available at food markets), but this test is too subtle to be a reliable indicator. The two minerals, however, can be distinguished by testing with a sodium tetraphenylborate ($NaB(C_6H_5)_4$) *solution. A distilled water washing of the mineral, of only a few milliliters, is dropped into a test solution. Halite produces no change; sylvite causes the formation of a cloudy precipitate from insoluble potassium tetraphenylborate.*

Even though bromide and iodide exist in marine water, they do not crystallize out as alkali halides; instead in nature they appear mainly as the silver halides — bromargyrite (AgBr) and iodargyrite (AgI). Both minerals were discovered in Mexico.

Fluorides as minerals are almost exclusively in the form of fluorite (CaF_2)*, which commonly forms beautiful cubic and octahedral crystals of green, yellow, purple, and blue. The term "fluorescence" — emission of a light stimulated by incident light (typically, brilliant colored light produced by ultraviolet light or "black light") — originates from certain English fluorspars (the old name for fluorite) which glowed when exposed to daylight.*

Sal ammoniac (NH_4Cl) *is formed near volcanic fumaroles; it was named for the salt of Ammon, near the Oracle of Ammon in Egypt, where it was prepared by the Arabians. This temple was made famous by Alexander the Great, who was crowned a Pharoah there. Many of the coins of Alexander the Great show him with the horns of Ammon — Egyptian religion frequently portrayed Ammon as a ram. The "volatile alkali" which was produced by reacting sal ammoniac with lime was to become known as "ammonia."*

Sal ammoniac is also found as masses of icy dagger-like crystals, formed as a sublimate from burning coal seams. Burning coal mines are also the home of other exotic minerals, such as SeO_2 *(downyite) and* As_2O_3 *(arsenolite). Downyite is so hygroscopic that it quickly absorbs atmospheric moisture and dissolves to droplets of selenous acid.*

The "sal mirabile" that Glauber discovered, $Na_2SO_4 \bullet 10H_2O$*, is found in nature on rare occasions. It crystallizes out of salt lakes during winter due to decreasing solubility at low temperatures. Its name is "mirabilite." There also exists a mineral bearing his name, "glauberite,"* $Na_2Ca(SO_4)_2$*, which forms as a marine evaporite.*

Probably the most bizarre formula for a halide is $KNa_{22}(SO_4)_9(CO_3)_2Cl$*, for hanksite. This mineral looks like multifaceted lemon drops and is found at Searles Lake, California. The local populace collects them by dyna-miting the mud flats of the lake and collecting the strewn gems in buckets.*

6. HUMPHRY DAVY AND THE VOLTAIC PILE
(1800-1855)

The distinction between soda and potash was not made easily. Only gradually was it recognized that there was a difference between "plant alkali" (potash), obtained from the ashes of plants, and "mineral alkali" (soda), found in salt flats and evaporated seawater. In 1683 Johnan Bohn prepared "cubic saltpetre" (sodium nitrate) from a mixture of salt and nitric acid, which he recognized as different from the ordinary saltpetre (potassium nitrate) by the shape of its crystals and its taste. Stahl himself distinguished between natural alkali (soda) and artificial alkali (potash) in 1702. Several other investigators continued to characterize the two alkalis, with the most definite account by Marggraf in 1759 who prepare very pure samples of "cubic saltpetre" and "prismatic saltpetre" from which he made gunpowder (from sulfur, charcoal, and saltpetre). The "cubic saltpetre gunpowder" flashed yellow and the "prismatic saltpetre gunpowder" flashed blue. But the true nature of the two alkalis remained unknown.

With Lavoisier's amazing insight, it may seem strange that he did not include sodium and potassium in his list of the elements. He explained that he did not include the "fixed alkalis" in his list of thirty-three substances because he believed they were compounds, although the "nature of the principles which enter into their composition is still unknown." We may pardon this error when we realize that the alkali metals did appear to be unique. He even suspected that they might contain nitrogen, since it had been shown that ammonium contained that element. It remained for Sir Humphry Davy, at the beginning of the nineteenth century, to decompose soda and potash to the elemental substances.

Davy was well educated and became a lecturer and director of the laboratory at the Royal Institution at London. He became interested in electrochemistry and tried to electrolytically decompose the caustic alkalis with a voltaic pile (the original name for a chemical battery, invented by Volta). First attempts accomplished nothing but decomposing the water of the aqueous solutions. Recognizing his mistake, he fused anhydrous potash itself, and to his great delight observed flames at the cathode. Upon closer examination metallic globules, appearing like quicksilver, were being generated at this negative pole which quickly burst into flame. Able to collect a few of these globules, he observed that when tossed into water they raced about swiftly and burst into a beautiful lavender light. Davy continued his investigation and found the flames were caused by the ignition of hydrogen which was being generated upon contact with moisture. He named this element *potassium* after potash. According to witnesses, upon his discovery Davy danced about the laboratory with ecstatic joy.

Davy immediately turned to soda, but found it could be generated only with "greater intensity of action in the batteries," (i.e., greater voltage). He named this new element *sodium* after soda, only a few days after the discovery of potassium.

Many chemists believed that these "elemental metals" sodium and potassium were in fact compounds made up of the alkalis + hydrogen. This hypothesis appeared to be reasonable, since ammonium was ammonia + hydrogen. However, it was promptly shown that no hydrogen could be evolved from the metal itself, and the elemental nature of sodium and potassium was universally accepted.

Flushed with success, Davy turned to the alkaline earths. Compounds of calcium had figured prominently in the technology of the ancients. The ancient Romans understood that limestone (calcium carbonate) when heated in a kiln produced lime (calcium oxide), which served as excellent mortar. The explanation was that "water had boiled out of the limestone," not correct but consistent with the observation that weight was lost in the process. Another compound of calcium, gypsum (calcium sulfate) when heated produced another form of mortar used in Egypt. This mortar, which *had* lost water, was later called Plaster of Paris. Later explanations of this slaking of lime included the interpretation that limestone and baryta were elements, although Lavoisier correctly believed they were oxides of elements not yet prepared. Methods then available which were employed to provide the metallic elements by reduction of the oxides — principally heating with charcoal — were not powerful enough, and the preparation of the metallic elements had to await the electrolysis technique of Davy.

In the 1750s, the work of Joseph Black, a professor of chemistry at Edinburgh, Scotland, was pivotal in elucidating the true nature of the slaking (calcining) process). Black investigated both lime and *magnesia alba*, a medicine sold in Rome. He determined that the loss of weight during the calcining process was due to a compound he called "fixed air" (carbon dioxide). This air could be "fixed" (made solid) by reacting again with the metal oxide. Working principally with calcium and magnesium compounds, Black showed that:

limestone = quickline + fixed air, i.e.,
$CaCO_3 \rightarrow CaO + CO_2$

magnesia alba = calcined magnesia + fixed air, i.e.,
$MgCO_3 \rightarrow MgO + CO_2$

limestone + acid = calcium salt + fixed air, i.e.,
$CaCO_3 + 2H^+ \rightarrow Ca^{+2} + H_2O + CO_2$

magnesia alba + acid = magnesia salt + fixed air, i.e.,
$MgCO_3 + 2H^+ \rightarrow Mg^{+2} + H_2O + CO_2$

At that time it was believed that the calcining of all mild alkalis (carbonates of the alkali metals) involved the combination with "an acrid principle" from the fire to form the caustic alkalis (oxides or hydroxides of the alkali metals). Black showed the true nature of this process by demonstrating that:

quicklime + mild alkali = limestone + caustic alkali, i.e.,
$CaO + Na_2CO_3 \rightarrow CaCO_3 + Na_2O$

Black came close to suggesting the atomic theory of gases by suggesting that the fixed air was dispersed through the atmosphere in the form of an "extremely subtile powder." Black continued his studies to show that fermentation and combustion evolve fixed air by mixing this air with lime water, producing the milky product of precipitated lime (calcium carbonate). This test of identifying carbon dioxide exists to this day in the laboratory.

Yet another alkaline earth oxide — baryta — had been produced Scheele in 1774. This earth, named because of its heaviness, had been first observed in "Bologna stone," discovered in the 1600s by Vincenzo Casciarolo, a shoemaker and alchemist in Bologna. This stone phosphoresced when mixed with a combustible substance and heated.

Meanwhile, a mineral from Strontian, Argyleshire, Scotland was analyzed by Crawford and Hope, both of whom concluded in the late 1700s that an earth was present that was intermediate between calcium and barium.

The stage was now set for Davy to demonstrate that his method for potassium and sodium could be used as a general procedure. One by one he decomposed salts of calcium, magnesium, strontium, and barium by a special recipe he developed (and suggested by Berzelius, who had already experimented with voltaic cells): he electrolyzed a mixture of moist alkaline earth oxide and mercury oxide to produce the amalgamated metal. The free metal was then prepared by volatilizing the mercury by heating. Davy produced each of these metals in 1808.

The sample of magnesium that Davy prepared was very small — it was not until 1831 that Bussy prepared magnesium in substantial amounts not by electrolyzing the salts, but by reacting the salts with metallic potassium.

Another element that caused Davy difficulty was lithium. Lithium had been known only for a short period of time — the presence of this element was not suspected until the early 1800s when Arfwedson (in Berzelius' laboratory) analyzed petalite ($LiAlSi_4O_{10}$) and found a difference between the observed and calculated total weight. Too small to be accounted for by sodium, the discrepency was explained by the presence of a new, lighter alkali (in 1818). Several investigators, including Davy, promptly tried to decompose the alkali salt by electrolysis, but only minute and impure samples could be obtained. Only in 1855 could sufficient quantities of pure lithium be prepared, from pure lithium chloride by Bunsen and Matthiessen in Germany using a powerful battery bank.

These metals of Davy were used to isolate a whole new series of elements which could not be obtained by direct electrolysis — but the story of this new group of elements will wait until the next chapter.

Lithium

Li 3 6.941
[Gr. *lithos*, stone]
Discovered 1817, element isolated 1855
mp 180.5°; bp 3402°; sp gr 0.53

At the end of the eighteenth century de Andrada collected two minerals in Scandinavia which he named petalite and spodumene. Although several chemists analyzed these minerals, including Vauquelin (who had recognized beryllia), none correctly interpreted the puzzling "loss of weight." Johan Arfwedson repeated meticulous analyses on the minerals in 1817 and concluded that a new, very light, alkali metal must be constituting the difference. In 1855 R. Bunsen and A. Matthiesen isolated the metallic element by electrolyzing lithium chloride.

Lithium is lightest of all the metals, with one-half the density of water. Lithium reacts with water, but not as vigorously as sodium. Like the other alkali metals, lithium can be cut easily with a knife, and the freshly exposed surface rapidly tarnishes in the air. Lithium is used in light-weight structural alloys and in batteries. With the highest specific heat of any solid element, this element is used in heat transfer applications. Lithium carbonate is used in the treatment of manic-depressive psychoses.

Sodium

Na 11 22.98977

[Eng. *soda*, L. *natrium*]

Sodium compounds known to ancients,

element isolated 1807

mp 97.8°; bp 882.9°; sp gr 0.97

Until the 1700s, chemists did not differentiate "mineral" or "natural" alkali (Na_2CO_3) found in shallow mines and "vegetable" or "artificial" alkali (K_2CO_3) collected by leeching water through wood ashes. In 1702 Stahl distinguished between the "natural and artificial alkalies" by the difference in crystalline forms of their salts. In 1759 Marggraf distinguished the two alkalis in a dazzling experiment — cubic saltpeter ($NaNO_3$) gave a yellow flash in gunpowder and prismatic saltpeter (KNO_3) gave a blue flash. In 1807, Sir Humphrey Davy prepared the metals through electrolysis of the molten caustic soda and potash (the hydroxides) and named the elements *sodium* and *potassium*.

Sodium metal reacts rapidly with water, frequently igniting the evolving hydrogen to form a yellow flame. Sodium forms soluble salts with virtually all the anions, organic as well as inorganic, and is important to animal nutrition. The most common compound is sodium chloride (table salt).

Potassium

K 19 39.0983

[Eng. *potash*, pot ashes; L. *kalium*]

Potassium compounds to ancients,

element isolated 1807

mp 63.2°; bp 760°; sp gr 0.86

In his list of elements Lavoisier listed thirty-three substances, but did not include potash and soda — he considered these as "evidently compound." Sir Humphrey Davy's electrolysis experiments demonstrated that the principles of potash and soda were indeed elements. The methods developed by Davy allowed the production of potassium and sodium for further chemical procedures which required strong reductive conditions, resulting in the discovery of even more elements.

Potassium and sodium are essential to nerve transmission; potassium is the universal cation found in both plants and animals, as the principal salt in extracellular fluids, and is used in fertilizers. This element ignites spontaneously in water with a violet flame.

Magnesium

Mg 12 24.305

[*Magnesia*, district in Thessaly, Greece]

Magnesia know to ancients,

element isolated 1808

mp 648.8°; bp 1090°; sp gr 1.74

In the early 1600s certain wells in Epsom, England, delivered water so bitter that the cows would not drink it — but it was discovered that the water could heal wounds. In a few decades Epsom became a fashionable spa for Europe. Thus was created "Epsom salts" ($MgSO_4$) which eventually became a world-wide health remedy. Magnesia had been known since ancient times — it is mentioned in a treatise by Hippocrates. During the early eighteenth century, a panacea called *magnesia alba* (magnesium oxide) was sold in Rome, and was identified as the earth obtained from Epsom salts. In 1755 Dr. Joseph Black showed that magnesia is entirely different from lime (CaO). Davy prepared a sample of the metallic element by means of his voltaic pile in 1808. For his research Black is considered by some to be the proper "discoverer" of magnesium.

Magnesium is a fairly tough metal and can be used as a structural material; one-third as light as aluminum, it is essential for airplane and missile construction. However, it can burn with a blinding white flame, and is used in flashlight photography and pyrotechnics. The hydroxide $Mg(OH)_2$ is used in medicine (milk of magnesia). Magnesium is critical to photosynthesis, because chlorophyll is a porphyrin (a heme-like molecule) with a centered magnesium atom.

Calcium

Ca 20 40.078
[L. *calx*, lime]
Lime known to ancients,
element isolated 1808
mp 839°; bp 1484°; sp gr 1.55

Limestone (calcium carbonate, $CaCO_3$) and gypsum (hydrated calcium sulfate, $CaSO_4•2H_2O$), the principal minerals of calcium, have been known and utilized since ancient times for plasters and cements. When gypsum is heated, the dehydrated powder (Plaster of Paris, $CaSO_4•½H_2O$) can be mixed with water to produce plaster, which sets to generate the original hydrated sulfate. When limestone is heated, carbon dioxide is liberated to give calcium oxide. Addition of water gives slaked lime, calcium hydroxide, which can be molded until hardening takes place by reaction with atmospheric carbon dioxide to produce the original calcium carbonate. This slaked lime was used to cement together sand and stone into a primitive concrete. The Romans discovered that burning a mixture of limestone and silica dramatically improved the material. In 1824 the patent issued for Portland cement was only a refinement of this ancient technology. Davy in 1808 prepared the elemental calcium with his voltaic pile.

Calcium exists abundantly in bones, teeth, shells, coral, and limestone. In the form of carbonate, this element causes hardness in water and produces cave formations.

Strontium

Sr 38 87.62
[*Strontian*, town in Scotland, source of
original strontianite]
Recognized as element 1790,
element isolated 1808
mp 769°; bp 1384°; sp gr 2.54

Dr. Adair Crawford analyzed a mineral specimen collected at Strontian, Scotland, which supposedly was a mixture of "calcareous and ponderous spars" ($CaCO_3$ and $BaCO_3$). He recognized the existence of an earth with chemical properties quite different from calcium or barium. The next year it was shown that the spectrum also was different — strontia produced a "candle red" color, while calcium produced red, and barium green. In 1808 Davy isolated the element in the manner as for calcium and barium.

The salts of strontium produce a brilliant crimson flame used in pyrotechnics. Strontium-90, with a half-life of 28 years, is a component of nuclear fallout and can potentially be a health problem by incorporation in bones. Uses of strontium are similar to those of barium and calcium, but are limited because of the much greater cost.

Barium

Ba 56 137.33
[Gr. *barys*, heavy]
Baryta discovered 1774,
element isolated 1808
mp 725°; bp 1640°; sp gr 3.5

In the early 1600s Vincenzo Casciarolo, a shoemaker and alchemist in Bologna, reported that when heavy spar (barite) is mixed with a combustible substance and heated red-hot, the resulting "Bologna stone" became phosphorescent. Marggraf found the stone to be a sulphate, but believed it had lime (CaO) as a base. Scheele and Gahn in 1774 concluded that the earth instead was a new principle, called baryta or "earth of heavy spar." Davy prepared the metallic element in 1808 with his voltaic pile.

Water-soluble barium salts are poisonous, but barium sulfate is insoluble and is used as a "barium cocktail" allowing X-ray images of the otherwise invisible digestive tract. Barium sulfate is also used as a white pigment in paint (*blanc fixe*). The metal is used as a "getter" in vacuum tubes.

Limestone beds were laid down by invertebrates and algae in the ocean millions of years ago. The mineral in limestone is calcite, a rhombohedral form of calcium carbonate, $CaCO_3$*. Iceland spar, a form of calcite, exhibits double refraction. Calcite is the most common carbonate in nature.*

The original shells of mollusks and corals actually are not calcite, but aragonite, an orthorhombic form of $CaCO_3$*. Aragonite over the eons slowly transforms into the more thermodynamically stable calcite. The crystalline form of aragonite is typically hexagonal prisms.*

The famous Dolomite Alps of northern Italy are composed of dolomite (magnesian limestone) with the formula $CaMg(CO_3)_2$*. Dolomite is common in nature but is difficult to produce in the laboratory; special geological conditions are needed with the correct temperatures and pressures to form this precise 1:1 stoichiometry of calcium and magnesium.*

7. USING DAVY'S METALS (1800-1890)

Davy's discovery of preparing elements electrolytically opened up a whole realm of possibilities — metals which had been hidden up in combined form in the earth's crust now could be isolated and their unusual chemical and physical properties could be explored. Optimistic about unlocking the mysteries of the remaining elements of the Periodic Table, Davy attempted to purify many additional metals. However, there were unexpected difficulties — for example, aluminum and silicon were too tightly bound in their polymeric oxides, the feldspars and clays of the earth. Additional techniques needed to be developed, many of which utilized Davy's very reactive metals.

Boron. Borax ($Na_2B_4O_5(OH)_4 \bullet 8H_2O$) was known by the ancient name of "tincal." Obtained originally from the Far East, it was found to be a very efficient flux in the blowpipe analysis of minerals. Boric acid itself (H_3BO_3), first prepared in 1702 by Willem Homberg, was rapidly recognized as a "sedative salt" for various ailments. By the middle 1700s borax was recognized as a compound of "sedative salt" and "soda," and despite the similarity of compounds of aluminum and boron, the two were acknowledged as separate. Lavoisier recognized boron as an element.

Davy was not able to prepare the metal by electrolysis, but he was able to prepare the element by reacting boric acid with potassium in 1808. Simultaneously, across the English Channel, Gay-Lussac and Thenard isolated boron using the same method. By now it was being recognized that the reaction of a compound with hot potassium in some instances were cleaner and preferable to Davy's voltaic pile, and this technique was adapted to many additional elements.

Silicon. The two most common elements in the earth's crust — silicon and oxygen — constitute quartz, silicon dioxide. The use of quartz in the manufacture of glass was a sophisticated art even with the ancient Egyptians. However, the exact nature of quartz was not well understood for centuries — Palissy thought that "rock crystal" had been precipitated from water "like saltpetre," but since the crystal could not be redissolved, the prevalent explanation was that it was water that had been "frozen very hard." A century later Boyle showed this could not be, since quartz was much heavier than ice. (Today we know that quartz is indeed precipitated from geothermal aqueous solutions). Lavoisier's brilliant mind understood that quartz must contain a basic element which was named after "silex," Latin for "flint."

When Davy was not able to isolate silicon by his atomic pile, he attempted to prepare the element by passing potassium vapor over hot silica (silicon dioxide), and even this failed. Berzelius heated potassium fluosilicate (K_2SiF_6) with potassium and obtained a brown mass in 1824 which he purified by washing with excess water. Pure, crystalline silicon was prepared by Deville of Paris in 1854 along with his experiments on aluminum.

Aluminum. Alum (potassium aluminum sulfate) had been used for centuries as a mordant in the dye industry. Early scientists believed that alum contained lime, but Lavoisier recognized that a separate element was present. As with silicon, aluminum could not be separated electrolytically, but Ørsted in 1825, and Wöhler in 1827 were able to isolate it by reacting metallic potassium with aluminum chloride. Wöhler found that when he conducted the reaction in platinum crucibles the aluminum reacted with the platinum, and so he resorted to porcelain crucibles.

Deville was able to prepare very pure aluminum by developing a procedure of passing aluminum chloride vapor over molten sodium. It was later found that the reaction proceeds more cleanly and easily with sodium aluminum chloride, which acts as a flux for the process. Deville was under the employ of Napoleon III, and was able to prepare silverware for the emperor, who prized his collection and saved it for use at banquets by the most important of guests (silver was for the "second-rate" visitors). Hence, aluminum was called the "silver from clay." In 1884 the Washington Monument was capped with a solid aluminum tip, since the metal was so "valuable and precious."

The breakthrough to the production of this element, which is so abundant in the earth's crust, was found simultaneously by Charles Hall, an American chemist who discovered this process when only a student at Oberlin College, and Paul Héroult in Gentilly, France (a suburb of Paris). The method, known today as the Hall-Héroult process, utilized the electrolysis of cryolite (Na_3AlF_6). This electrolysis proceeds similarly to that of silicon, where the complex fluosalt functioned as a flux for the process. Cryolite — which was named because it melted easily, "like frozen brine" — had been discovered in Greenland in 1872.

Beryllium. In Roman times beryl and emerald were suspected to be closely related. Haüy of the École des mines in Paris recognized that the two had identical crystalline structures, and he asked Vauquelin to analyze the two minerals chemically. Vauquelin in 1798 found each contained silica, alumina, and a new substance he named "glucina" on the basis of the sweet taste of its salts (emerald/beryl is a beryllium aluminum silicate). Since yttria forms sweet salts as well, to avoid ambiguity "beryllia" was accepted as the official name.

Wöhler prepared metallic beryllium in 1828 in the same manner as for aluminum (by reaction of beryllium chloride with potassium).

Beryllium is now know to be very poisonous, and extreme precautions must be taken during milling or sawing of the metal or its compounds to avoid exposure to its dust. Salts as well are poisonous — which thankfully did not lead to the demise of the early chemists who customarily tasted chemicals.

Zirconium. Zirconium is the basis of an ancient gemstone, just as is beryllium. Zircon ($ZrSiO_4$) has been called historically by various names, including jacinth and hyacinth. Because of chemical similarities of zirconium and aluminum, early chemical examinations suggested "silica and alumina" were the basic components of zircon. Klaproth first recognized the new earth in 1789. Davy attempted to isolate this metal, but was unsuccessful. Berzelius isolated the metal in 1824 by reacting potassium and potassium zirconium fluoride.

Silicon

Si 14 28.0855
[L. *silex*, flint]
Quartz known to ancients,
element isolated 1824
mp 1410°; bp 2355°; sp gr 2.33

Since prehistoric times, rock crystal (silica, SiO_2) has been used in the manufacture of jewelry, vases, and glassware. Sir Humphry Davy, who broke down so many compounds to produce elements with his voltaic pile, could not decompose silica and believed it was not an element. Berzelius prepared elemental silicon in 1824 by heating potassium fluosilicate with excess potassium.

As the second most common element, silicon is found in a remarkable variety of minerals and can be used to produce a very great number of useful materials, including refined element for transistors, silicates in glasses and ceramics, and silicones in thermally resistant polymers. Ordinary beach sand is quartz, silicon dioxide. Diatoms in water use silica from the water to build up their cell walls.

Aluminum

Al 13 26.98154
[L. *alumen*, alum]
Alum known to ancients,
element isolated 1825
<u>mp</u> 660.4°; <u>bp</u> 2467°; <u>sp gr</u> 2.70

The ancient Greeks and Romans used alum (various aluminum sulfates) in medicine and as a mordant (fixer) in dyeing cloth. In the Middle Ages and Renaissance an active alum industry was thriving. Marggraf in 1754 was the first to recognize that the earth in alum must be different from that in limestone, and he demonstrated the presence of this alumina in clay. Davy, who had been so successful in separating other metals by means of his voltaic pile, could not isolate the element. Ørsted in 1825 and Wöhler in 1827 reacted aluminum chloride (prepared by passing chlorine over a mixture of alumina and charcoal) with potassium to make powdered aluminum. By 1845 Wöhler was able to melt the powder to a metallic ingot. Commercial production of aluminum was made feasible by the discovery of Hall in 1886 that alumina dissolved in cryolite (Na_3AlF_6) could be electrolyzed to produce pure aluminum in quantity.

Aluminum is the most abundant metal on earth, but was discovered only recently owing to the difficulty in extraction from aluminum ores. Today metallic aluminum is inexpensively produced by electrolysis of an artificial mixture of sodium, aluminum, and calcium fluorides. Aluminum is used in scores of industrial and domestic applications where a cheap, light-weight, easily fashioned structural material is needed. The oxide layer that forms on aluminum forms a protective coating, and aluminum is ideal as a reflective material on telescope mirrors.

Beryllium

Be 4 9.01218
[Gr. *beryllos*, beryl]
Beryl known to ancients, beryllia recognized
in 1798, element isolated 1828
<u>mp</u> 1278°; <u>bp</u> 2970°; <u>sp gr</u> 1.85

Until 1798, it was not realized that emerald and beryl were the same mineral. Haüy, who founded the atomic basis for crystallography, had seen identical crystal patterns for each, and at his suggestion Vauquelin analyzed the two. He isolated the same earth (oxide) from both minerals, thus establishing a new element existed as the basis for each. The new element was first prepared in 1828 by Wöhler and Bussy by the action of potassium on beryllium chloride. Vauquelin had suggested that the new element be named *glucina* because its compounds are sweet. This habit of testing beryllium compounds by taste was discontinued when it was learned that these compounds were poisonous. Since yttrium salts also were reported to be sweet, Klaproth suggested the name *beryllium* instead of glucinum.

Beryllium has one of the highest melting points of the light metals (1278°). Beryllium resists attack by nitric acid and can be used as a structural material. It is used as an alloying agent to produce beryllium copper which has excellent spring characteristics. The oxide, beryllia, has a surprisingly high thermal conductivity for an insulator. Beryllium and its salts are very toxic and care must be taken not to inhale beryllium or beryllia dust.

Boron

B 5 10.81

[Ar. *Buraq*, borax]

Borax known for centuries,
element isolated 1808

mp 2079°; bp (sublimes) 2550°; sp gr 2.34

Samples of borax ($Na_2B_4O_7$), called tincal, arrived from the East Indies during the Renaissance. It was used in the purification and fusion of metals. Boric acid (H_3BO_3) was prepared in 1702 by Wilhelm Homberg and was originally called "sedative salt" before it was recognized as a weak acid. In 1808 the composition of boric acid was ascertained by Sir Humphrey Davy in England and by Gay-Lussac and Thenard in France, when it was reduced by metallic potassium. The French and the British chemists originally called the new element *bore* and *boracium*, respectively.

Boron is found in nature in the form of borates. Boric acid is so weak that it can be used to wash out the eyes. Borax is used as a cleansing flux in welding and as a water softener in detergents. Boron is an extremely hard crystal, nearly as hard as diamond but too brittle to be useful. Boron filaments are high-strength, light-weight fibers used in aerospace composite materials.

Zirconium

Zr 40 91.224

[*Zircon*, gemstone]

Zircon known to ancients, oxide discovered
1789, metal isolated 1824

mp 1852°; bp 4377°; sp gr 6.51

Jargon and hyacinth (zircon, $ZrSiO_4$) have been prized as precious stones for centuries. The presence of an unknown element was not suspected, owing to the similarity of zirconia to alumina. It took the craft of Klaproth to recognize the new earth, who in 1789 analyzed the mineral correctly for the first time, reporting 25% silica and 70% "jargonia" (zirconia). Davy attempted to decompose zirconia, but was unsuccessful. Berzelius in 1824 obtained the metal by reacting zirconium fluoride with potassium.

Zirconium is mostly used in commercial nuclear power plants — with a low absorption cross section for neutrons and with a high resistance to deterioration, it can be used to clad radioactive fuel elements. Zirconium is also used where corrosive-resistant materials are needed, such as surgical instruments, photoflash bulbs, and explosive primers. Zirconia (ZrO_2) can withstand heat shock and can be used to line metallurgical furnaces and as a refractory material in the glass and ceramics industries. Lunar rocks have shown a surprisingly high content of zirconia.

Careful analytical work in the laboratory was becoming increasingly important in the advancement of chemistry. In the 1700s there had been much sloppy *analysis which could be characterized as "semiquantitative" at best. Whenever there had been a disparity between observed and predicted values (when the total weight did not add up to 100%), it would be easy for an "unaccountable loss" to be dismissed as "experimental error." Undoubtedly many discoveries had been missed this way.*

Around 1800 Vauquelin of Paris and Klaproth of Berlin were recognized as the best analytical chemists of the day, and these skilled scientists were often consulted by others not so skilled in this art. The meticulous care of these two chemists led to Vauquelin's observation of the small discrepancy in the analysis of beryl that led to his discovery of beryllium, and likewise to Klaproth's careful work that allowed him to recognize that the earth in zircon was different from aluminum. It is to the credit of these professional scientists that routinely they gave the credit of "original discovery" to others who had performed the initial, and even inconclusive, work.

A few decades later Berzelius of Sweden lifted analytical chemistry to new heights. In his laboratory he carried out the painstaking analysis of hundreds of substances to define an accurate listing of atomic weights, necessary to develop a Periodic Table in the mid-1800s. Adhering to the demanding standards of Berzelius' laboratory, his assistant Arfwedson discovered the lightest metal lithium by refusing to ignore a few percent discrepancy in total weight of the Swedish minerals, petalite and spodumene, that he analyzed.

8. PLATINUM AND THE NOBLE METALS (1740-1850)

Platinum exists in native (elemental) form in nature, just as gold, and yet platinum was not discovered until about five hundred years ago. Modern scientists have often speculated why platinum had not been discovered until comparatively recent times — they thought perhaps references to platinum could be ascribed to ancient alloys. Hence, the Greeks' "electrum" or the alchemists' "augmentation of gold" might refer to the addition of small amounts of platinum. However, no definite older reference is certain, except perhaps for a random discovery of platinum alloys in ancient civilizations (e.g., trim from caskets of Pharaohs).

Don Antonio de Ulloa, a Spanish scientist and explorer, gave a description of a new metal during his voyages to South America during 1735-36. While making astronomical measurements and tours of tropical plantations, he observed nuggets of this white metal which interfered with the gold mining near Chocó, Colombia. The new metal was hard and could not be as easily worked as gold, it could not be separated easily, and it could not even be melted by conventional means, as could gold and silver. This account of de Ulloa was published in 1748.

Two years later Watson and Brownrigg contributed to *Philosophical Transactions* a detailed description of this metal and marveled that this "platina" (Spanish for "silver") should have been unknown for so long. "Gold is usually esteemed as the most ponderous of bodies. . ." and yet this new metalline substance was "specifically heavier."

Since platinum could be used to alloy gold (thus "debasing" it), the Spanish government ordered all platinum "to be thrown into the river"! However, sizeable quantities of platinum accumulated in the laboratories of Europe as the scientists became strongly interested in this refractory metal. Finally a method was found by Achard for fusing it — implements of platinum, such as crucibles, could be produced by molding a platinum-arsenic alloy and then heating to expel the arsenic. Priestley suggested that platinum might be fused with "dephlogisticated air" (oxygen) instead of ordinary air, and by 1801 Robert Hare (University of Pennsylvania) had melted platinum with his newly invented oxy-hydrogen blowpipe. Later Hare's student Joachim Bishop founded the American platinum refining industry, but the prolific research on platinum did not commence, because of the difficulty of working with it, until Wollaston conducted his famous experiments.

William H. Wollaston was a British physician who retired to devote his full time to chemical research. He found a method of producing malleable platinum that could be fashioned into implements — in fact, it was this discovery that allowed Wollaston to retire from his medical profession at 34 years of age, in 1800. His method involved dissolving platinum in *aqua regia* with a specific composition, then reprecipitating the platinum by the careful addition and removal of ammonia. The result was a fine "sponge" powder that could be compressed and heated in a mold. This method of fashioning objects from powdered metal anticipated the modern methods of sintered metals, by which articles of high-melting metals could be manufactured from powders.

Well into the 1800s, platinum was considered an exclusive product of South America. However, in 1819 white nuggets were observed in the gold placers on the Siberian Urals, south of Ekaterinburg (where chromium had been discovered some twenty years before). Although Wollaston did not disclose his secret procedure for processing platinum until 1826, Russian metallurgists at St. Petersburg had devised a similar process two years before, and prodigious quantities of platinum were soon available from Russia. For about twenty years Russia minted several coins of various ruble denominations.

Other metals from platinum — palladium and rhodium. Wollaston in his famed experiments found additional elements in the platinum family. These elements were less common components in the platinum he had been investigating.

The first additional noble metal that Wollaston isolated was palladium (in 1803). This he isolated from a concentrated solution of *aqua regia* solution of platinum, by adding mercuric cyanide to form a yellow precipitate (palladious cyanide). The metal was easily produced from this precipitate by heating with sulfur and borax. Wollaston named this element in honor of the recently discovered asteroid Pallas. Rapidly it was discovered that gold, as well, from South America contained palladium — indeed, "brittle gold" had at first been refused by the Mint of England until it was ascertained that the culprit was palladium, which could be extracted out by simple procedures. Gold-palladium alloys were recommended for scientific and astronomical instruments, and for metal used by dentists.

The second metal of the platinum family that Wollaston discovered was rhodium. By now he had perfected his procedure by dissolving platinum in *aqua regia*; then by adding ammonia precipitating the platinum in the form of ammonium chloroplatinate; then by precipitating the palladium by adding mercuric cyanide; then by collecting the filtrate and evaporating to dryness to produce a beautiful red powder (sodium rhodium chloride). The element was produced easily by reduction with hydrogen gas and washing out the sodium chloride.

Undissolved metals in aqua regia — iridium and osmium. Smithson Tennant discovered two additional noble metals which did *not* dissolve in aqua regia. When platinum had been dissolved in *aqua regia*, a black residue remained which had been assumed to be graphite. However, Tennant in 1803 further investigated this powder and was able to separate two new metals: one that imparted a red color to ammoniacal platinum solution (iridium) and another whose oxide was volatile and which had a vile odor (osmium). The black residue was thus named *osmiridium*. (Fourcroy and Vauquelin are sometimes considered independent discoverers of iridium even though they never distinguished it from osmium).

Tennant and Wollaston were quite friendly with one another throughout their respective careers, and even vacationed together in Northern Ireland. Indeed, their close association began at an early age — Wollaston had been Tennant's assistant who conducted a diamond-combustion experiment which proved that diamond was carbon.

Ruthenium. Various scientists had subsequently investigated platinum ores and could find nothing definite in addition to platinum, palladium, rhodium, osmium, and iridium. Sniadecki had studied 400 grams of crude platinum ores in 1807 and believed he had isolated a new metal he named *vestium* (in honor of the asteroid Vesta). Although it appeared that he in fact had isolated a new element, a commission in Paris could not repeat the isolation with their sample of platinum ore, and recent investigations have shown his claim was incorrect.

Later in 1828, Osann claimed the discovery of several new metals in crude platinum. However, he was never able to characterize a new element, and it is clear that his "discoveries" were impure mixtures, some of which *may* have contained some ruthenium.

It remained for Karl Klaus to make a careful study of Osann's work, which he repeated and further investigated. With 18 pounds of platinum residues from the Treasury of Russia, after extensive chemical treatment he was able to isolated six grains of the new metal from the portion of metal not soluble in *aqua regia*. Klaus then investigated the osmiridium from American ores and found about 1% ruthenium.

Form of noble metals in platinum. At the time of their discovery, the noble metals palladium, iridium, osmium, and ruthenium were assumed to be in the form of platinum alloys dispersed evenly through the platinum. It is now known that these noble elements occur in the form of microscopic inclusions with specific compound formulas. Examples of such com-pounds include:

Osmiridium (Ir,Os)
Ruthenosmiridium (Ir,Os,Ru)
Iridosmine (Os,Ir)
Platiniridium (Ir,Pt)

Occasionally these inclusion compounds have been dislodged from the mother lode and are found as silvery flecks in stream beds and can be panned like gold. Famous sites noted for these rich streams include Alaska and Tasmania.

The platinum metals can also be found as sulfides, selenides, tellurides, arsenides, stannides, antimonides, and plumbides. Mineralogists typically sell specimens of these alloys in platinum cross sections with the inclusions located by scanning electron microscopy (SEM) and the formulas identified by energy dispersive X-ray (EDX). These inclusions can vary in size from a micrometer upwards. Examples include:

Atokite ($(Pd,Pt)_3Sn$)
Bowieite ($(Rh,Ir,Pt)_2S_3$)
Erlichmanite (OsS_2)
Iridarsenite ($(Ir,Ru)As_2$)
Palladoarsenide (Pd_2As)
Palladseite ($Pd_{17}Se_{15}$)
Plumbopalladinite (Pd_3Pb_2)
Rhodplumsite ($Pb_2Rh_3S_2$)
Sperrylite ($PtAs_2$)

Compositions of "platinum nuggets" can vary widely and are probably the cause of inconsistent and irreproducible observations, notably during the search for ruthenium. Very early claims that platinum was merely an alloy of iron undoubtedly derive from the fact that platinum nuggets generally contain iron, commonly about 5%.

Platinum

Pt 78 195.08
[Sp. *platina*, silver]
Used by pre-Columbia Indians,
"discovered" 1735
mp 1772°; bp 3827°; sp gr 21.45

The pre-Columbian Indians of Ecuador had discovered platinum and manufactured artifacts of platinum-gold alloy. Don Antonio de Ulloa on a voyage to the New World from Spain in 1735 rendered a clear description of the metal from Chocó, Columbia; and Charles Wood in 1741 returned a sample to the New World from Columbia. During the second half of the eighteenth century there was a great deal of research in the New World on platinum; its chemical inertness rendered it ideal for crucibles and other utensils. In 1819 a white metal was discovered in the gold placers on the Siberian slopes of the Urals. Three years later it was identified as platinum.

The first commercially profitable deposit of platinum in the Urals was discovered in 1824, which began Russia's platinum industry.

Platinum has a expansion coefficient the same as glass, and is used to make sealed electrodes in glass assemblies. Platinum does not oxidize in air at any temperature, and is used in jewelry, wire, laboratory ware, electrical contacts, and in dentistry. Since it can perform at high temperatures, it is used for coating missile cones and jet engine nozzles. Powdered platinum is an excellent catalyst for producing sulfuric acid, cracking petroleum products, fuel cells, and anti-pollution devices for automobiles.

Palladium

Pd 46 106.42
[Gr. *Pallas*, goddess of wisdom]
Discovered 1803
mp 1554°; bp 2970°; sp gr 12.02

Brazilian miners in the early 1700s recognized a natural alloy they called *ouro branco* (white gold), which was probably a gold-palladium alloy. One hundred years later, in 1803, W. H. Wollaston separated palladium from platinum by dissolving the crude platinum in *aqua regia* and precipitating the palladium as the yellow palladious cyanide. By heating the yellow precipitate with sulfur and borax he obtained a button of the new metal which he named *palladium* from the recently discovered asteroid *Pallas*. Five years later he reported the presence of grains of native palladium and platinum in Brazilian gold ore. Today palladium-rich specimens of gold can still be found in the Minas Gerais state (southeastern part) state of Brazil.

Palladium can absorb 900 times its own volume of hydrogen; hydrogen diffuses through heated palladium and is used to purify the gas. Powdered palladium is an excellent catalyst for hydrogenation and dehydrogenation reactions of organic compounds. White gold is alloy of gold with palladium added. Palladium can be beaten into a leaf 0.1 µm thick. Palladium is used in dentistry, watchmaking, and surgical instruments.

Rhodium

Rh 45 102.9055
[Gr. *rhodon*, rose]
Discovered 1804
mp 1966°; bp 3727°; sp gr 12.41

W. H. Wollaston discovered rhodium in 1804 from a sample of crude platinum ore originating from South America (the Russian platinum ores had not yet been discovered). He dissolved the crude platinum in *aqua regia*, and precipitated the platinum as the ammonium chloroplatinate by adding ammonium chloride, and then precipitated the palladium by adding cyanide. The filtrate yielded a dark red powder — the complex chloride salt of sodium and of a new metal he called *rhodium*. The salt (sodium hexachlororhodate hydrate, $Na_3RhCl_6 \bullet 18H_2O$) was easily reduced with hydrogen to give the metal.

Rhodium is mostly utilized as an alloying agent to harden platinum and palladium — used in thermocouple elements, electrodes for aircraft spark plugs, and laboratory crucibles. Rhodium has a low electrical resistance, a low contact resistance, and high resistance to corrosion, and is used in electrical contacts. Plated rhodium is very hard and is used for optical instruments.

Iridium

Ir 77 192.22
[L. *iris*, rainbow]
Discovered 1803
<u>mp</u> 2410°; <u>bp</u> 4130°; <u>sp gr</u> 22.42

Smithson Tennant in 1803 discovered that when crude platinum is dissolved in *aqua regia*, a black powder with a metallic luster remained. By alternate action of acid and alkali, he was able to separate this powder into two fractions. One metal he named *iridium*, because of the variable colors of its salts. (Fourcroy and Vauquelin are sometimes given credit for the independent discovery of iridium; they found same crude residue but did not adequately characterize nor purify it. Descotils also had noticed a red precipitate while studying platinum salts, apparently an iridium complex).

Iridium is hard and brittle, difficult to machine or work, but is the most corrosion-resistant metal known — it is not attacked even by aqua regia. Iridium is used for making high temperature crucibles and electrical contacts. It is used as a hardening agent for platinum. With osmium, it is used for pen tips and compass bearings. Iridium is used as a tracer for the geological K-T boundary (from a meteorite that caused the extinction of the dinosaurs). Iridium and osmium have the highest specific gravities of all the elements.

Osmium

Os 76 190.23
[Gr. *osme*, odor]
Discovered 1803
<u>mp</u> 3045°; <u>bp</u> 5027°; <u>sp gr</u> 22.57

The other metal Tennant isolated in 1803 was named *osmium*, because of its odor.

Osmium is difficult to fabricate in coherent form and is usually found in the powdered state. The metal is used to produce very hard alloys with other metals of the platinum group to produce fountain pen tips, instrument pivots, phonograph needles, and electrical contacts. The tetroxide (OsO_4) is volatile, has a strong odor, is toxic, and is very damaging to the eyes. Osmium is the heaviest element, only very slightly more dense than iridium.

Ruthenium

Ru 44 101.07
[L. *Ruthenia*, Russia]
Discovered 1828, metal isolated 1844
<u>mp</u> 2310°; <u>bp</u> 3900°; <u>sp gr</u> 12.41

Ever since platinum was introduced into the New World in the 1700s, it was zealously investigated in an attempt to discover new elements; in the early 1800s four elements — iridium, osmium, palladium, and rhodium — were separated from platinum. In 1807 Sniadecki reported a new metal which could not be confirmed and is now discredited.

Twenty years later platinum was discovered in Russia, and in 1828 Berzelius and Osann investigated platinum ore from the Ural Mountains. Berzelius found evidence only of the four elements recently discovered, while Osann prematurely reported the presence of three new metals, which he named pluranium, polinium, and ruthenium.

Karl Klaus in 1844 showed that Osann's compounds were mostly crude oxide mixtures of silicon, titanium, iron, and zirconia. From eighteen pounds of crude platinum residues Klaus received from the Secretary of the Treasury in St. Petersburg, Russia, he obtained six grams of ruthenium from the portion not soluble in *aqua regia.* In recognition of Osann's work, Klaus retained the name *ruthenium*.

Ruthenium does not tarnish at room temperatures, and is not attacked by hot acids or by *aqua regia.* It is utilized as a hardener for platinum and palladium, used to make electrical contacts for severe wear resistance. The corrosion resistance of titanium is increased a hundredfold by the addition of only 0.1% ruthenium. Used as a catalyst to split hydrogen sulfide, ruthenium oxide may be used to remove H_2S from oil refining and other industrial processes.

Today it is difficult for a chemist to understand the arduous task in the late 17th and early 18th centuries to procure adequate laboratory facilities. Although in Paris there were some public laboratories that were the envy of Europe, in other countries the experimenter usually set up his laboratory in his own home and even taught classes there. Wollaston produced his malleable platinum in his house laboratory on Cecil Street near the Thames in London; his later discoveries of palladium and rhodium were performed in his home laboratory on Buckingham Street. Smitihson Tennant discovered osmium and iridium in The Temple, an "apartment complex" and his home, near the Thames. Dalton, based out of his apartment in Manchester, conducted his studies on meteorology and marsh gas. Priestley carried out his research in his personal home laboratories in Leeds, Birmingham, and later in Northumberland, Pennsylvania. He discovered oxygen in the private laboratory of Lord Shelburne in Bowood, England. Cavendish was able to perform his sophisticated experiments in his mansion laboratories that he financed from his family inheritance. Berzelius completed his meticulous atomic weight determinations in his old house, "German Baker's House" in Stockholm, Sweden. Scheele discovered chlorine, molybdenum, and tungsten in his home apothecaries in Uppsala and Köping, Sweden. Klaproth discovered zirconium and uranium in his apothecary laboratory in Berlin.

A handful of public laboratories during this time included the Royal Institution in London, where Davy isolated the reactive alkali and alkaline earth metals; the University of Edinburgh where Black and Rutherford investigated fixed air and nitrogen; the Berlin Academy where Marggraf performed his research on alkalis, clays, and sugar beets; the École Polytechnique in Paris, where Vauquelin conducted his research on beryllium and chromium; and Lavoisier's laboratory in Le Petit Arsenal in Paris, where he studied explosives, combustion, and respiration.

By the middle 1800s laboratories had been established in many more universities. However, even as late as 1860 Crookes discovered thallium in a laboratory on his parents' farm in Brook Green, near London; Boisbaudran in 1875 discovered gallium in the laboratory in his family's home in the wine country of Cognac, France; Marignac found samarium and gadolinium in the home laboratory on Rue Senebier in Geneva, Switzerland, in 1880; and in 1901 Demarçay discovered europium in his personal laboratory on Boulevard Berthier, Paris.

9. THE PERIODIC TABLE (1870-1890)

In 1789 Lavoisier turned the concept of "element" on its head when he proposed that water was a *compound* and that hydrogen, oxygen, carbon, sulfur, iron, copper, and 25 other substances were the true *elements*. At this time the listed elements appeared to be a medley of metals, nonmetals, and gases. But scientists are forever searching for order and patterns, and as additional elements were discovered, trends were observed. Döbereiner in 1829 noticed that there were several "triads" in which the middle element (whose atomic weight lay between the other two elements) had chemical and physical properties which likewise were an average of the other two elements — for example, he pointed out that the equivalent of strontium (42.5) was the arithmetic mean of calcium (20) and barium (65), and all had similar chemical properties.

This pattern that Döbereiner observed depended upon the idea of atomic weight — a concept for which John Dalton was principally responsible. Dalton showed how atomic theory could be used to explain the specific weight ratios in chemical combinations. The first known atomic weights were listed by Dalton in his notebook in 1805:

hydrogen	1	carbon	4.5
oxygen	5.66	sulphur	17
azot (nitrogen)	4		

These values appear strange to the modern chemist — oxygen should be more nearly double the figure given by Dalton. However, these atomic weights did not take into consideration valence, or combining power — Dalton believed that water was composed of one atom of hydrogen and one atom of oxygen. These listed values delivered a powerful concept: Dalton substances made up of "ultimate particles" (i.e., molecules) and "ultimate atoms," and he believed that the "specific gravity" (i.e., weight of an atom) was constant for a given atom (element).

By 1810 his atomic weights had been expanded to include 36 elements:

hydrogen	1	arsenic	42
azote	5	cobalt	55
carbon	5.4	manganese	40
oxygen	7	uranium	60
sulphur	13	tungsten	56
phosphorus	9	titanium	40
gold	140	cerium	45
platina	100	potash	42
silver	100	soda	28
mercury	167	lime	24
copper	56	magnesia	17
iron	50	barytes	68
nickel	50	strontites	46
tin	50	alumine	15
lead	95	silex	45
zinc	56	yttria	53
bismuth	68	glucine	30
antimony	40	zircone	45

These atomic weights were crude, but they were crucial to develop the concept that the organization of elements could depend upon *numbers*.

Dalton was colorblind and would sometimes appear at meetings with gaudy red socks. He discovered this malady in himself and described the phenomenon — today "daltonism" is a synonym for red-green colorblindness.

The atomic weights were refined by other investigators, and by 1826 Berzelius had published a fairly accurate list of the atomic weights of 28 elements. By this date, Avogadro had shown that *two* volumes of hydrogen unite with *one* volume of oxygen, and therefore that water is composed of *two* atoms of hydrogen and *one* atom of oxygen. This recognition doubled many of the atomic weights. Hence, on the basis that hydrogen =

1.000, then oxygen = 16.026, sulfur = 32.24, and so on.

By 1862 de Chancourtois had devised a "telluric screw (helix)" on which he plotted atomic weights as the ordinates and traced a spiral at 45° in sixteen equal portions (arbitrarily chosen on the basis that oxygen's atomic weight = 16). As the trace spiraled around the cylinder, elements appeared on vertical lines that had similar properties, such as lithium, sodium, and potassium; and oxygen, sulfur, selenium, and tellurium. de Chancourtois hypothesized that "the properties of substances are the properties of numbers." Unfortunately, his contribution was not immediately appreciated and was not published in the prominent journals.

An analogous approach was taken by Newlands, who in 1864 discovered the "Law of Octaves" — after each series of eight elements, similar properties (both chemical and physical) repeated. Newlands proceeded to organize the elements in families and periods. For this brilliant insight Newlands was met with derision; one jokester even suggested that elements might well be organized by the initials of their names! The Chemical Society declined to publish his work, but later recognized their error and awarded him a Davy Metal in 1887.

The honor of discovering the periodic behavior of the elements was shared by Dimitri Mendeleev and Lothar Meyer in 1869. By now 56 elements were known, and Meyer plotted atomic weight vs atomic volume to show periodicity with six sections — with increments of 16 units in the second and third series and increments of about 46 units in the fourth and fifth sections. Meyer proceeded to show similar behavior of melting points, volatility, malleability, brittleness, and electrochemical behavior.

Mendeleev's approach was to arrange the elements in a table reflecting periodic behavior of the chemistry in a more descriptive manner. Mendeleev's approach proved to be more useful, because it could be generalized — and, as Mendeleev pointed out, it even *predicted* new elements! Mendeleev himself stated, "Each law of natural science is of particular value scientifically only when it is possible to draw from it practical consequences. . . . especially, which permit making predictions that can be confirmed by experiment." Scarcely half a generation later, his words would be powerfully borne out.

The table published in 1871 by Mendeleev arranges the elements on the basis of the chemistry of the elements known at that time (see Figure 1, page 95). Mendeleev was so convinced of the reality and truth of this arrangement that he corrected the valence of beryllium from 3 (as fixed by Berzelius, who claimed beryllia had the formula Be_2O_3) to 2, to give the correct formula as BeO. He further assumed (correctly) that the oxide of indium was In_2O_3 and that the oxide of uranium was UO_3.

Even though Meyer admitted that Mendeleev's approach was more powerful, Mendeleev allowed equal claim of the discovery. As both were presented with the Davy Medal in 1882, Mendeleev simply rose and bowed, not feeling comfortable with addressing the audience in English. Meyer then stood and gave the unpretentious words, "I am not Mendeleev. I am Lothar Meyer." The audience gave a standing, deafening ovation for both scientists.

Mendeleev's predictions realized! Mendeleev had been so bold as to predict not only the *existence* of new elements — "eka-boron," "eka-aluminum," and "eka-silicon" — but also the *properties* of each. Before 15 years had passed, these elements had been discovered, with an uncanny agreement of predicted atomic weights, physical properties, and chemical reactivities.

Gallium (Mendeleev's predicted eka-aluminum) was discovered by Boisbaudran, who used spectroscopy to ferret out a trace metal in the zinc mines of southern France. For this analysis Boisbaudran had developed methods of spectroscopic analysis, and his contributions rank him with Bunsen, Kirchhoff, and Crooks as one of the founders of spectroscopy (see Chapter 10). He reasoned that since most minerals had now been completely analyzed, there was little hope of finding a new mineral whose principal constituent was one of the undiscovered elements. Therefore, he concluded, the undiscovered elements would be in trace amounts, and might be best detected by spectroscopic analysis. He had already analyzed aluminum and indium spectra and expected spectral lines between the two.

Boisbaudran in 1875 processed several hundred kilograms of "la blende" (zinc blende, or zinc sulfide) from the Pyrénée Mountain region of southern France and followed the extraction and separation of the desired gallium fraction by observation of a new violet line at 417 nm. The gallium hydroxide he thus obtained was electrolyzed to produce a gram of gallium metal.

Scandium (eka-boron) was discovered by Nilson, in conjunction with his studies of the rare earth elements (see Chapter 11). He was analyzing a sample of Scandinavian euxenite (a mixed calcium-rare earth titanate-niobate-tantalate), named for its rare components ("good stranger"), and upon separating some ytterbia also obtained an unknown earth whose properties coincided precisely with those predicted by Mendeleev.

Germanium was discovered by Winkler at the Freiberg Mining School, in a new sulfide mineral found in the Himmelfürst Mine nearby. The new mineral, called argyrodite (Ag_8GeS_6), was analyzed and proved to contain silver and sulfur totaling to 93%. Winkler was able to isolate the new element in 1886, which he named in honor of his country. At first Winkler thought he had isolated "eka-stibium" (between antimony and arsensic), and Mendeleev thought perhaps the element was "eka-cadmium" (between cadmium and mercury). However, as enough material had been isolated for determination of its properties, it became clear that the new element was indeed "eka-silicon" (between silicon and tin).

The behavior of germanium surprised Winkler, who thought it should combine with oxygen and be present with titanium and zirconium minerals. This expectation depended upon the view of the Periodic Table at the time, where the transition metals were not yet recognized as a distinct class, and where carbon, silicon, titanium, germanium, zirconium, and tin were all lumped into the same family.

Huge reserves of germanium were eventually found in the TriState area of the United States (Missouri-Kansas-Oklahoma), which were a byproduct (along with gallium) of zinc production in the local mines. When germanium was recognized as a critical war material, this "useless" substance came into great demand, and for a while this area was the only source of material for semiconductor devices.

Filling in the rare earth gap. After two decades, Mendeleev's Periodic Table (see Figure 2, page 96) still afforded the basic structure for the organization of the elements, but the elements in the atomic weight range of 140-180 (the rare earths) were troublesome. Trends in this range made little sense — at first, Mendeleev thought he had correctly placed didymium (actually a mixture of two rare earths), cerium, erbium, and lanthanum, but with the discovery of further rare earths he gave up and left them out. A further difficulty was found when Brauner discovered (in 1889) the true atomic weight of tellurium was 127.6, actually *greater* than that of iodine. Mendeleev assumed the value was incorrect — but chemical periodicity by now was deeply set in the minds of chemists, and it was becoming accepted that atomic weight was obviously not the *ultimate* criterion for periodicity.

In Mendeleev's last Periodic Table, presented in 1902 (see Figure 3, page 97), he had added a column of inert gases (see Chapter 12), but he avoided the rare earths. Brauner was more ambitious. An attempt by him to create order was noble but artificial (see Figure 4, page 98). One of the difficulties in understanding the gaps in the table was that it was not known how many elements *should* exist between barium and tantalum. This important bit of information was not learned until Moseley's X-ray work which defined atomic numbers (see Chapter 14). Another problem — the rare earths — had to await Bohr's theoretical work in 1922 (see Chapter 14) which allowed the organization of the Periodic Table into s, d, p, and f blocks. The work of Moseley and Bohr then allowed a Periodic Table which is essentially the same as today's (see Figure 5, page 99).

Thus, Mendeleev had in a short moment in 1869 captured the extent to which chemical theory could be driven: the chemical elements could be organized according to their chemical behavior, but vagaries existed and a motley collection of rare earths defied explanation despite almost forty more years of toil by the famous Russian scientist.

Gallium

Ga 31 69.723
[L. *Gallia*, France]
Discovered 1875
mp 29.8°; bp 2403°; sp gr 5.90

Mendeleev had predicted "eka-aluminum" to lie below aluminum in the Periodic Table. In 1875 Lecoq de Boisbaudran found this element in sphalerite (zinc sulfide) by methodically concentrating a fraction which exhibited new spectral lines.

Gallium is one of three metallic elements with a melting point near or below room temperature (30° C). Gallium cannot be stored in glass containers, because it expands when freezing and cracks the glass. Gallium is an extensively *dispersed* element in nature, and minerals with specific stoichiometries are rare. Instead, most of the gallium is found in trace quantities beside other elements, and is recovered as a byproduct of other refinery productions, notably zinc. Gallium is used in semiconductors; gallium arsenide can convert electricity directly into coherent light.

Scandium

Sc 21 44.9559
[L. *Scandia*, Scandinavia]
Discovery: 1879; crude metal 1937;
pure metal 1960
mp 1541°; bp 2836°; sp gr 2.99

Mendeleev had predicted the existence of "eka-boron" between calcium and titanium. Lars Fredrik Nilson stumbled upon this element while examining an extract of erbia from euxenite and gadolinite. Following Marignac's procedure, he obtained some pure ytterbia, and in addition a feebly basic unknown earth. This earth's properties corresponded to those anticipated by Mendeleev, and was rapidly accepted as the sought eka-boron. The metallic element was first prepared in 1937 by Fischer, Brunger, and Grieneisen.

Scandium is expensive and rare; it exists in higher levels in the sun than on earth. The first pound of this metal was obtained in 1960. Scandium iodide added to mercury vapor lamps produces a bright light source resembling sunlight.

Germanium

Ge 32 72.61
[L. *Germania*, Germany]
Discovered 1886
mp 937.4°; bp 2830°; sp gr 5.32

Mendeleev had predicted "eka-silicon" to fill a gap between silicon and tin in the Periodic Table. Clemens Winkler discovered this prophesied element by investigating argyrodite, a mineral from the Himmelfürst mine near Freiberg, Germany. When his routine analysis did not account for all the elements, he concluded that the ore must contain an unknown element. In 1886 he succeed in isolating the sulfide, and then the element itself. Winkler named the element *germanium*. Comparison of its properties with Mendeleev's published prophesying data gave convincing proof his new element was indeed eka-silicon.

Germanium is used as a semiconductor material. The first transistor was prepared from germanium in 1947 at Bell Laboratories. Transparent to infrared light, germanium and its oxide are used in optical equipment such as sensitive infrared detectors. With a high index of refraction, germanium is used in wide-angle camera lenses and microscope objectives.

The Periodic Table was developed from chemical behavior of the elements, which exhibits useful and consistent trends. Physical behavior is a different story. Melting points, for example, decrease down the alkali metal family but increase down the halogens. The three metals with low melting points (cesium, gallium, and mercury) are not grouped together but are scattered about the Periodic Table. Transition elements (in the d-block) tend to have interesting and color and magnetic properties. Metal ions that have empty d subshells (such as Sc^{+3} *or* Ti^{+4}*) or filled d subshells (such as* Zn^{+2}*) are colorless. The colored ions include* Mn^{+2} *(pink),* Cr^{+6} *(yellow/orange),* Cr^{+3} *(green),* Fe^{+3} *(red),* Fe^{+2} *(green),* Ni^{+2} *(green), and* Cu^{+2} *(blue). Often the hydrated and anhydrous species are colored differently (such as* $Co(H_2O)_6^{+2}$*, pink,* Co^{+2}*, blue).*

The middle of the first d-block includes ferromagnetic elements (iron, cobalt and nickel), but not the second and third d-blocks. There exists one more ferromagnetic metal, in the middle of the lanthanides (f-block) — gadolinium (which loses its magnetism at 16°).

10. THE BUNSEN BURNER SHOWS ITS COLORS

(1860-1863)

The alchemists had known since the 1500s that heated substances imparted various colors to a flame. In the 1700s Marggraf demonstrated that sodium salts could be differentiated from potassium salts by the former's yellow color and the latter's purple hue. Fraunhofer in 1818 invented the spectroscope which allowed the observation of different light wavelengths (colors) and the exact measurement of these wavelengths. Careful observation allowed Talbot in 1834 to differentiate lithium from strontium, even though each both gave red flames (lithium is carmine; strontium is scarlet). Soon it was recognized that each element exhibited its own unique spectrum: David Alter in 1854 unequivocally stated that each element had a characteristic independent spectrum, and an alloy of two metals in an electric spark would exhibit the spectral lines of each. Alter had the foresight to predict that spectroscopic analysis would even someday be used to identify the elements in stars.

In 1859 Robert Bunsen and Gustav Kirchhoff invented the flame spectroscope, an instrument that allowed the identification of elements by their emission spectra. This instrument consisted of three parts: (1) a flame and collimator which would allow light in a narrow band from the incandescent sample; (2) a prism which could be rotated to admit and pass on various wavelengths of light; and (3) a telescope to observe the color being emitted by the glowing sample. This optical instrument allowed the very precise measurement of wavelengths of light that were being emitted by samples heated to incandescence in the flame. Bunsen, the perfecter of the Bunsen burner, and Kirchhoff were professors at Heidelberg University, and together they founded the science of spectroscopic analysis.

Bunsen and Kirchhoff in 1860 studied a concentrate of mineral water (from Bad Dürkheim) using their spectroscope. The usual lines could be observed of sodium, potassium, lithium, calcium, and strontium. However, two new blue lines were observed, which they attributed to a new element and which they named *cesium* from the color. A few months later they observed new deep red spectral lines of a new element they named *rubidium*. The elements themselves were isolated in the same laboratory from lepidolite (an attractive lavender mica) in 1862 (by Bunsen) and 1882 (by Setterberg), respectively.

Sir William Crooks, who shared with Bunsen, Kirchhoff, and Boisbaudran the honor of establishing the science of spectral analysis, was studying some waste from a sulfuric acid plant in the Harz Mountains, central Germany. Analyzing the residues for selenium and tellurium, he observed a new intense green line, which he attributed to a new element he named *thallium* for "green branch."

To isolate a sample of thallium, Lamy in 1873 extracted the sulfuric acid prepared from burned pyrites (sulfide ores). He studied thallium compounds extensively and discovered they were extremely poisonous.

The codiscoverers of indium were Reich and his assistant Richter at the Freiberg Mining School. Reich published the results jointly with Richter, but later regretted this decision, because Richter attempted to claim full credit for the discovery.

In 1863 Reich began a search for thallium in zinc ores from the Himmelfürst Mine. It will be recalled (Chapter 9) that germanium was discovered at this famous school and mine. Reich wanted to conduct a spectroscopic analysis, but he was colorblind and preferred to entrust the examination to his assistant Richter. Upon placing a platinum loop of zinc blende ore in a flame, Richter observed an intense indigo color which was obvious even without a spectroscope. The new element was named *indium*.

Reich and Richter were able to easily prepare the elemental metal by reduction of the oxide with charcoal. They found that this metal was admixtured with zinc prepared from the Mine and could be isolated more easily from the zinc itself than from the ore.

Generally indium is found in geologically old zinc blendes, whereas newer geological formations are more likely to hold germanium and gallium.

With the new spectroscopic method, an invaluable tool was now available to find a wide array of new elements. In fact, this technique was responsible for the discovery of a new entire family of elements (the inert gases). This story is told in Chapter 12.

Cesium

Cs 55 132.9054
[L. *caesius*, sky blue,
from lines in spectrum]
Discovered 1860, element isolated 1882
mp 28.4°, bp 669.3°; sp gr 1.87

Bunsen and Kirchhoff in 1860 analyzed by flame spectroscopy the mineral water of Bad Dürkheim, Germany, and observed two new blue lines which they attributed to a new element they named *cesium*. Carl Setterberg separated the metallic element electrolytically in Bunsen's laboratory from cesium salts in 1882. The most cesium-rich mineral at that time was pollucite, a cesium-sodium silicate, from the Island of Elba, off the coast of Italy.

Cesium is the most reactive metallic element, exploding violently with water. Cesium is used as a "getter" in electron tubes, scavenging residual oxygen. With the second lowest melting point of all the metals (28° C), cesium is a liquid in a warm room. This element is used as an atomic clock, accurate to 5 seconds in 300 years.

Rubidium

Rb 37 85.4678
[L. *rubidus*, deepest-red,
from lines in spectrum]
Discovered 1861, element isolated 1863
mp 38.8°; bp 686°; sp gr 1.53

Robert Bunsen and G. R. Kirchhoff in 1861 detected the element *rubidium* by its red spectral lines in Dürkheim spring water. Two years later they chemically separated the element from lepidolite (a mica, a mixed potassium alkali aluminum silicate) from Czechoslovakia, using the common method at that time for the preparation of metallic potassium. (This procedure involved heating to redness in an iron retort a mixture of charcoal and potassium tartrate or carbonate, yielding carbon monoxide and the potassium which was distilled directly into oil. This same procedure worked well for rubidium carbonate, but not for cesium carbonate). The burner which issued a colorless flame, which Bunsen had designed in 1854-55, made this discovery possible.

Rubidium ignites spontaneously in air. With a melting point of 39° C, rubidium would melt on a hot sidewalk. Rubidium is used in photoelectrical cells. This element is dispersed through nature, mixing with the other alkali metals, and does not form compounds with specific stoichiometries. Small quantities of rubidium are found in certain foods, including coffee and tea; trace quantities may be required by living systems.

Indium

In 49 114.82
[from indigo spectroscopic line]
Discovered 1863
mp 156.6°; bp 2080°; sp gr 4.93

Searching for thallium in some Freiberg, Germany, zinc ores, Reich and Richter observed an intense blue color when a sample of zinc blende (zinc sulfide) was heated in a Bunsen burner (1863). These lines did not coincide with those of cesium, and the blue color was attributed to an new element named from the indigo spectral color. They found the new element was infused with zinc metal smelted from the ore, and discovered how to isolate it. Until 1924, a gram constituted the world's supply of elemental indium.

Indium is a dispersed element in nature, procured principally from zinc ores. Indium is used to make low-melting alloys; indium is particularly important in the production of optical devices that require a glass-to-metal seal.

Thallium

Tl 81 204.383
[Gr. *thallos*, green twig,
from lines in spectrum]
Discovered 1861
mp 303.5°; bp 1457°; sp gr 11.85

Examining some residues from a sulfuric acid plant in the Harz Mountains, Germany, Sir William Crookes observed a bright green line in the spectroscope mixed with the familiar bands of selenium (1861). He christened this element *thallium* for its spectroscopic line. Lamy prepared an ingot of thallium that he presented the following year to the Académie des Sciences.

Thallium, whose oxide spalls off, does not form a protective oxide coating as do other elements such as aluminum and copper. Because of its tendency to crumble into crumbs of black corrosion over a period of years, thallium as a metal has no commercial application. Soluble thallium salts are poisonous; tasteless and odorless, they were formerly used as rodenticides and insecticides. Thallium bromide-iodide crystals are used in infrared optics.

From Agricola's time until the 1800s, chemistry and mineralogy were united disciplines. In fact, many of the chemists of these times were also mineralogists who were making their chemical discoveries through the analysis of ores. Today several excellent mineralogical collections of historical value may be viewed at famous museums, such as the Musée de Minéralogie at the École des Mines in Paris and the Werner Museum at Technische Universität Bergakademie Freiberg, Germany, where several elements were discovered.

Lepidolite, which figured in the history of the alkali metals rubidium and cesium, is a form of mica. Mica is a flaky mineral, made up of an intricate aluminum silicate molecular network interspersed with alkali ions. In micas the alkali ion is locked up chemically (usually in a cage structure) and cannot be extracted easily in aqueous solution, as it can from alkali halides such as halite or sylvite. Lepidolite, a pretty lavender form of mica, has the formula $K(Li,Al)_3[AlSiO_3O_{10}](F,OH)_2$ *where rubidium and cesium can replace in* *potassium ions to the extent of a few percent. Commonly lepidolite is mined for its lithium content.*

The richest source for cesium is pollucite, a zeolite first found on Elba, an island off the northwest coast of Italy, in 1846. Pollucite has the formula $CsNaAl_2Si_4O_{12}\bullet H_2O$*. Zeolites are hydrated aluminum silicates which can be repeatedly hydrated and dehydrated without losing their structure.*

When pollucite was first investigated by Plattner at the Freiberg Mining School in 1848, he was puzzled by the anomalous alkali content of the mineral — he had mistaken the cesium for potassium. Plattner was an expert in blowpipe analysis, but his analytical skills were of no avail to solve the problem since no alkali metals beyond potassium were yet known. With little material to work with, and with spectroscopic analysis yet not developed, his problem was not solved until 1864 (four years after the discovery of cesium) when the French mineralogist Félix Pisani explained the discrepancy.

Although the thallium discovered by Crookes was reported in the literature to be taken from the sludge from a sulfuric acid manufactory in Tilkerode, this is in error — there was no such manufactory in Tilkerode at this time, but in Oker, on the other (west) side of the Harz Mountains. Instead, Tilkerode was the source of the ore (which was transported to Oker). Today Tilkerode is well known to mineralogists as a rich source of thallium compounds. The error apparently was made inadvertently by A. W. Hofmann, founder of the Royal College of Chemistry in London, who furnished the material to Crookes (a student at the school at that time) and who apparently was misinformed of the source of the material that Crookes analyzed.

11. THE RARE EARTHS (1800-1910)

The separation and identification of the rare earth elements tested the skills and patience of the best chemists of the nineteenth century. The first hint of the riches of this group of elements lay in a black mineral found in the Ytterby Mine, near Stockholm. This heavy rock, first called "ytterbite," was discovered by Lieutenant Carl Axel Arrhenius, a Swedish chemist and mineralogist.

In 1794 Johan Gadolin, professor of chemistry at the University of Åbo, Finland, made an exhaustive analysis of the new mineral and found silica, glucina (beryllia), iron, and a new "earth" (oxide of an element) he named yttria. Ytterbite is now known as "gadolinite" (a mixed rare-earth mineral with the formula $RE_2FeBe_2Si_2O_{10}$, where RE= Y, Ce, and other rare earths).

Another heavy mineral was found in the Bastnäs Mine at Riddarhyttan, Vestmanland, Sweden, by Cronstedt as "the heavy stone of Bastnäs." Scheele and de Elhuyar studied this mineral, expecting to find tungsten, but found none. Berzlius, Klaproth, and Hisinger all examined this mineral, searching for yttria, since they reasoned that previous investigators, not aware of this new element, might have missed it. Instead, they discovered a new earth in 1803 which was named cerium after the asteroid recently discovered (Ceres). The mineral, named "cerite," is now known to have the formula $(Ce,Ca)_{10}(SiO_4)_6(OH,F)_5$, but as with all rare earth minerals can be admixtured with these scarcer elements. Soon cerium was discovered in additional minerals: allanite from Greenland, $(Ce,Ca,Y)_2(Al,Fe)_3(SiO_4)_3(OH)$, and yttrocerite from Sweden, $(Ca,Y,Ce)F_2$.

The two new earths yttria and ceria proved to be composed of perplexing mixtures of yet further elements. The first hint of this complexity was gained by Carl Gustav Mosander, one of Berzelius's assistants. Mosander in 1839 treated cerium salts in nitric acid; the cerium oxide remained insoluble while in the extract a new earth was found. He named this new substance *lanthana*, meaning "hidden." The same year Axel Erdmann, one of Sefström's students, found lanthana in a new Norwegian mineral, named "mosandrite" (a mixed calcium-cerium titanium-silicate). Friedrich Wöhler, one of Mosander's closest friends, kept nagging Mosander to publish his work on lanthana, but Mosander hesitated. Soon the reason for the delay became apparent when in 1841 when a new brown earth (pure ceria and lanthana were both white) was extracted from lanthana. This new earth was named "didymia," named so because it was an "inseparable twin brother of lanthana." The new earth imitated the properties of cerium and lanthanum salts so closely that only with repeated crystallizations could it be separated.

Mosander then turned to yttria, which he likewise showed in 1843 was composed of yet two additional substances by fractional precipitation with ammonium hydroxide: erbia (rose-colored) and terbia (whitish).

Mosander's experiments were only the beginning — other chemists proved that yttria and ceria held twelve additional rare earths! Yttria yielded the "heavy rare earths": terbia, erbia, gadolinia, ytterbia, dysprosia, holmia, thulia, lutetia. Ceria surrendered the "light rare earths": samaria, europia, praseodymia, and neodymia.

In 1878 Marignac separated ytterbia from erbia. Nilson (see Chapter 9) then separated scandia from ytterbia in 1879. The erbia fraction proved to also hold holmia and thulia (Cleve, 1879), and the holmia further gave dysprosia (Boisbaudran, 1886). The didymia of Mosander further gave samaria (Boisbaudran, 1879), and yet again gadolinia (Boisbaudran, 1886). Although Boisbaudran named gadolinia, it was identical to a rare earth that Marignac in 1880 had discovered in samarskite (Marignac gave his consent for this name). Boisbaudran's didymia was then separated into praseodymia and neodymia (Welsbach, 1885). Europa was extracted from samaria (Demarçay, 1901). Finally, lutetium was separated from ytterbia (1907). Credit for this last discovery is shared by Georges Urbain of Paris (who gave it the accepted name), Auer von Welsbach (who named it cassiopeium), and Charles James of New Hampshire (who had prepared a large amount of pure lutetium at the time of Urbain's announcement).

Because of their separation difficulties, the rare earths were originally thought to be quite rare indeed — but in fact are as common as mercury or lead, which have been known for centuries. Thulium, the least common rare earth, is actually more common than gold. In nature rare earths are dispersed — while such elements as mercury, lead, and gold have been concentrated, giving the false appearance of greater abundance. Such properties as melting points of the metallic rare earths and their oxides had to await isolation of pure material. In most cases this was not possible, owing to their very similar chemical behavior. Most rare earths were not isolated in pure form until the 1950s, when ion-exchange separation and metallographic reduction techniques were developed by Frank Spedding at Iowa State University.

The major question concening the rare earths facing the chemists of the eartly twentieth century was: Exactly how many rare earths were there? Chemists wondered how many more elements would be separated from the score of variably colored oxides already known. The definitive answer to this question would have to wait until Moseley's X-ray work (Chapter 14).

A descriptive flow chart of the separation and discoveries of the rare earths is presented in Figure 6, page 100.

Yttrium

(See page 20)

Cerium

Ce 58

[L. *Ceres*, goddess of agriculture]

Discovery: oxide 1803; impure metal 1875; pure metal (>99%) 1944

mp 798°; bp 3443°; sp gr 6.77

Wilhelm Hisinger, Swedish mineralogist and geologist, was owner of the famous Riddarhyttan property, where the Bastnäs mine yielded a curious mineral called cerite. Because of its high density, it was called "the tungsten (heavy stone) of Bastnäs." Klaproth, Hisinger, and Berzelius in 1803 investigated cerite, searching for yttria. Instead, they found a new element, which was named *cerium* in recognition of Ceres (the first asteroid, discovered two years previously). W. F. Hillebrand and T. H. Norton prepared the metal in 1875 by electrolyzing molten cerous chloride.

Cerium is the most abundant rare earth, and the second most reactive rare earth; it slowly decomposes in cold water. Cerium is the main constituent of "misch metal," a pyrophoric alloy which when struck liberates showers of sparks — and thus is used in automatic gas-lighters and cigarette lighter flints (Misch metal is a mixture of light rare earths, with typical ratios of 50:25:18:5:2 Ce:La:Nd:Pr:other). The white oxide CeO_2 is used in incandescent gas mantles and a hydrocarbon catalyst in self-cleaning ovens. Cerium oxide is replacing rouge as a polishing agent for lenses and television faceplates, because it is much faster. Cerium, as well as other rare earths, is used as a molecular sieve catalyst in petroleum refining.

Lanthanum

La 57
[Gr. *lanthanein*, to be hidden]
Discovery: oxide 1839; crude metal 1875; pure metal 1952
mp 918°; bp 3464°; sp gr 6.14

Carl Mosander, one of Berzelius' assistants, first recognized the complexity of the rare earths. He was the first to show that Klaproth's ceria and Gadolin's yttria actually held additional rare earths. The first "hidden" rare earth (*lanthana*) was separated from ceria in 1839 by extraction with dilute nitric acid. In the same year, Axel Erdmann, one of Sefström's assistants, discovered lanthana in a new Norwegian mineral, named "mosandrite." Since lanthanum behaves as a rare earth, it could not be prepared in pure form until rare earth separation techniques were developed.

Lanthanum is used in carbon lighting applications, particularly by the motion picture industry. Lanthanum oxide (La_2O_3) increases the resistance of glass to alkalis, used in special optical glasses. Lanthanum is one of the more reactive rare earth elements, combining directly with carbon, nitrogen, boron, selenium, silicon, phosphorus, sulfur, and the halogens; thus, lanthanum is an effective scavenger for gases in molten metals and their refining. Metallic lanthanum oxidizes rapidly in air to give a white oxide. The greatest use of lanthanum (mixed with other rare earths) is for molecular-sieve catalysts for cracking petroleum. Misch metal, used in cigarette lighter flints, is composed of 25% lanthanum.

Praseodymium

Pr 59
[Gr. *prasios-didymos*, green-twin]
Discovery: oxide 1885; impure metal 1931; pure metal 1952
mp 931°; bp 3520°; sp gr 6.77

Ceria and yttria, the first two rare earth oxides prepared, proved to consist of a bewildering array of no less than thirteen additional rare earths. The first to tackle this complex problem was Carl Gustav Mosander, one of Berzelius's assistants. First, in 1839 he extracted lanthana from ceria. Then, in 1841 he further treated lanthana with dilute nitric acid and extracted a new brown oxide, which he named *didymium* because it was a "twin brother of lanthanum." Mosander carefully showed that the original pastels of yttric and cerous salts were in fact due to contamination of didymium salts. Many thought didymium was again simply a mixture of rare earths. In 1882 Brauner spectroscopically examined didymia and saw absorption bands from two elements. Welsbach separated the two in 1885, which he named *praseodymia* (green dymia, the color of the oxide) and *neodymia* (new dymia).

There actually exist two common oxides of praseodymium: Pr_6O_{11}, the common oxide which is black; and Pr_2O_3, the green oxide which forms initially on oxidizing praseodymium. This latter green oxide is the one Welsbach noted. The black oxide was originally thought to have the formula PrO_2.

Praseodymium is used in misch metal and in carbon arcs. Didymium (praseodymium and neodymium) is used to color welder's and glassmaker's goggles. The resulting lenses filter out the yellow light of glass very efficiently.

Neodymium

Nd 60
[Gr. *neos-didymos*, new-twin]
Discovery: oxide 1885; impure metal 1925;
pure metal 1944
mp 1021°; bp 3074°; sp gr 7.01

Neodymium was the other component of Mosander's didymia. Both praseodymium and neodymium have never been resolved into further oxides.

Neodymium is used in misch metal and in didymium. Neodymium colors glass delicate shades of pure violet through wine-red to warm gray. Light transmitted through this glass shows very sharp absorption bands and is used to calibrate spectral lines in astronomical studies. A neodymium-iron-boron compound ($Nd_2Fe_{14}B$), exhibiting a energy product of 50 megagauss-oersteds, exceeds the well-known samarium-cobalt magnets in strength; these Nd-Fe-B magnets are now commercially available and serve as incredibly strong refrigerator magnets. Neodymium and praseodymium are the third and fourth most reactive rare earths; they give oxides which spall off, exposing more metal. The oxide of neodymium, Nd_2O_3, is light blue.

Samarium

Sm 62
[*Samarskite*, a mineral]
Discovery: oxide 1879; crude metal 1937;
pure metal 1953
mp 1074°; bp 1794°; sp gr 7.52

Lecoq de Boisbaudran, believing in 1879 that Mosander's didymia was not one oxide, added sodium hydroxide, and another earth precipitated before the didymia. He named the earth *samaria* after samarskite, named after Colonel Samarski, a Russian mine official. Samarskite, studied by J. Lawrence Smith, was proving to hold several rare earths.

Samarium is used in misch metal and in carbon-arc lighting. $SmCo_5$ has been used to make a new permanent magnet, which until recently, was the strongest known — over 25 megagauss-oersteds. Samarium oxide (Sm_2O_3, off-white in color) is used in optical glass to absorb infrared, and can act as sensitizers for phosphors excited in the infrared. Samarium oxide is a catalyst in the dehydration and dehydrogenation of ethyl alcohol.

Europium

Eu 63
[*Europe*]
Discovery: oxide 1901; crude metal 1937;
pure metal 1953
bp 822°; bp 1527°; sp gr 5.24

Eugène-Anatole Demarçay, through a laborious sequence of crystallizations of samarium magnesium nitrate, in 1901, was able to separate a new earth. He named the new element *europium*.

Europium is the most reactive of the rare earths. It oxidizes rapidly in air and resembles calcium in its reaction with water. Europium can ignite if scratched with a knife. Europium oxide (Eu_2O_3, white in color) is extensively used as the red phosphor in color television tubes. The oxide fluoresces intense red in ultraviolet light.

Gadolinium

Gd 64

[*Gadolinite*, a mineral]

Discovery: oxide 1880; crude metal 1935; pure metal 1944

mp 1313°, bp 3273°; sp gr 7.90

Boisbaudran, after discovering samarium, isolated yet another earth from didymia in 1886. This was identical to the rare earth which Marignac had separated from samarskite in 1880. Samarskite is a radioactive, glassy-black, brittle mineral with the formula $(Y,U,Fe)_3(Nb,Ta,Ti)O_5O_{16}$, where Y can be other heavy rare earths. Marignac consented to Boisbaudran's suggested name of *gadolinium*, after the mineral gadolinite, which has the formula $RE_2FeBe_2Si_2O_{10}$, and which was the original mineral analyzed by Gadolin.

Gadolinium is the "transition" element between the heavy and the light rare earths. Indeed, "gadolinite" is a very appropriate name for the mineral which can contain both heavy and light rare earths. The oxide Gd_2O_3 is white.

Gadolinium has the highest thermal neutron capture cross section of any known element, and therefore is used as shielding for nuclear reactors and neutron radiography. Gadolinium has been used in making gadolinium yttrium garnets, used in microwave applications. It has used in making phosphors for color television tubes.

Gadolinium is unique for its high magnetic moment and its Curie temperature (at which ferromagnetism disappears) at room temperature. An interesting demonstration of its Curie temperature involves placing an ingot of gadolinium (warmed in hot water) onto an ice cube next to a magnet; suddenly the metal will snap to the magnet as the temperature of the ingot passes below the Curie temperature (the other ferromagnetic elements at room temperature are iron, cobalt, and nickel; their Curie temperatures are much higher).

Terbium

Tb 65

[*Ytterby*, Sweden]

Discovery: oxide 1842; crude metal 1937; pure metal 1953

mp 1356°; bp 3230°; sp gr 8.23

Mosander, who had shown ceria was composed of additional rare earths, studied yttria in the same manner. He separated out two additional earths in 1842, which he named *erbia* (yellow) and *terbia* (rose). This work was confirmed by Delafontaine, Marignac, Smith, Cleve, and Boisbaudran. For some reason the names erbia and terbia were interchanged, so that the *yellow* earth now is *terbia.*

Terbium oxide (Tb_4O_7, chocolate-brown in color) can be used as an activator for green phosphors in color television tubes. Sodium terbium borate is used as a laser material.

Dysprosium

Dy 66
[Gr. *hard to reach*]
Discovery: oxide 1886; crude metal 1937;
pure metal 1952
mp 1412°; bp 2567°; sp gr 8.55

In 1886 Lecoq de Boisbaudran separated yet another rare earth from holmia — *dysprosium* — by fractional crystallization, first with ammonium hydroxide and then with potassium sulfate. He found the following fractions in this order: terbia, dysprosia, holmia, and erbia. Never having much material to work with, Boisbaudran did most of his research on the mantle of his fireplace!

Dysprosium has found limited use in laser materials. Its high thermal neutron absorption cross-section and high melting point suggest nuclear applications. The oxide Dy_2O_3 is white.

Holmium

Ho 67
[L. *Holmia*, Stockholm]
Discovery: oxide 1879; crude metal 1939;
pure metal 1953
mp 1470°, bp 2700°; sp gr 8.80

The erbia remaining after the removal of ytterbia was still further fractionated in 1879 by Per T. Cleve, who obtained two additional rare earths: *holmia* (named for his native city) and thulia.

Holmium has found few uses. It has unusual magnetic properties. The oxide Ho_2O_3 is yellow.

Erbium

Er 68
[*Ytterby*, Sweden]
Discovery: oxide 1842; crude metal 1934;
pure metal 1953
mp 1529°; bp 2868°; sp gr 9.07

Erbium is the sister rare earth to terbium, both of which Mosander isolated from yttria in 1842. Subsequently, erbium was isolated into five additional rare earths, plus scandium!

Erbium added to vanadium lowers the hardness and improves workability. Erbium oxide (Er_2O_3, pink in color) has been used as a fast pigment in glass and enamel, and is the best pink colorant for ceramics.

Thulium

Tm 69
[*Thule*, Scandinavia]
Discovery: oxide 1879; crude metal 1937;
pure metal 1953
mp 1545°; bp 1950°; sp gr 9.32

Thulia was the second rare earth, in addition to holmia, that Cleve isolated from erbia.

Thulium is the rarest of the rare earths — only a few years ago, it was not obtainable at any price. The oxide Tl_2O_3 is white.

Ytterbium

Yb 70

[*Ytterby*, Sweden]

Discovery: oxide 1878; crude metal 1937; pure metal 1953

mp 818°; bp 1196°; sp gr 6.90

Marignac in 1878 isolated an additional earth from erbia. This earth was prepared by extracting erbia with water — for the rose fraction he retained the name erbia, and for the colorless fraction he gave the name *ytterbia.*

Ytterbium can be used to improve the mechanical properties of steel. The oxide Yb_2O_3 is white.

Lutetium

Lu 71

[*Lutetia*, ancient name for Paris]

Discovery: oxide 1907; crude metal 1937; pure metal 1952

mp 1663°; bp 3402°; sp gr 9.84

The last natural rare earth to be discovered was *lutetium*, obtained by Georges Urbain in 1907 by fractional crystallization of ytterbium nitrate from nitric acid. Ytterbium and lutetium were identical with "aldebaranium" and "cassiopeium," respectively, discovered independently by Auer von Welsbach. The credit of discovery of lutetium is also shared with Charles James of New Hampshire who had prepared a large amount of lutetium by the time or Urbain's announcement.

Lutetium is one of the most difficult rare earths to isolate. Possible future uses include catalysts for cracking, alkylation, hydrogen-ation, and polymerization. The oxide Lu_2O_3 is white. Lutetium tantalate ($LuTaO_4$, with a specific gravity of 9.75), is the heaviest white substance known.

Chemically, the "rare earths" include not only the "lanthanides" (elements cerium at. no. 58 → lutetium at. no. 71) but also yttrium (39) and lanthanum (57) of the transition 3B group.

The lanthanides at the bottom of the Periodic Table are divided into the "light" rare earths, behaving like cerium (left half), and the "heavy" rare earths, behaving like yttrium (right half). This difference of "weight" is due to the lanthanide contraction, which reduces the size of the atoms as one progresses to the right across the lanthanides.

The lanthanides share a valence of 3 and have a strong affinity for oxygen.

Mixed rare-earth fluorides are burned in carbon electrodes to create the intense sunlike illumination used by motion picture projectors and searchlights.

Europium, gadolinium, dysprosium, samarium, and erbium have the highest thermal neutron absorption properties in the elements; yttrium by contrast is almost transparent to thermal neutrons and is stable in the presence of liquid uranium.

Four elements are named from the famed mine in Ytterby — not only the original yttrium, but also erbium, terbium, and ytterbium.

Two principal sources currently exist for the production of the rare earths: California and China. The American source, a strip mine at Mountain Pass, California, principally affords the lighter rare earths, while the Oriental source contains more of the heavier rare earths.

12. THE INERT GASES
(1894-1898)

Because of his experimental skill and careful measurements, Cavendish in 1785 had actually discovered the first inert gas — argon. He described how he passed an electric spark through a mixture of "dephlogisticated air" (oxygen) and "phlogisticated air" (nitrogen) to form niter, and he found that part of the "phlogisticated air" failed to react and remained as a gaseous residue. His precise measurements even allowed him to quantitate the residue: 1/120 of the atmosphere. This keen observation lay dormant for a century until Lord Raleigh began his experiments on the atmosphere in 1882.

John William Strutt, Lord Raleigh, was professor of physics at the Cavendish Laboratory at Cambridge University. He was engaged in the study of the molar volumes of gases, and accordingly had need to measure very accurately the densities of hydrogen, oxygen, and nitrogen. Although he obtained consistent results for the first two gases, the values he obtained for nitrogen varied depending upon the source. The value for nitrogen he obtained from ammonia was about ½% lower than that obtained from the atmosphere. Deeply puzzled, he even wrote *Nature*, asking the readers for any possible explanations. Possible reasons included contamination with oxygen or hydrogen, or even an allotropic form of nitrogen N_3, analogous to ozone O_3. He turned to the experimental abilities of Sir William Ramsay.

Ramsay passed atmospheric nitrogen over incandescent magnesium (to form magnesium nitride) repeatedly until a consistent volume of residual gas remained (1/80 of the original volume). Both Ramsay and Raleigh believed this might possibly be a modification of nitrogen, but its spectrum showed red and green lines never before observed. Crooks himself performed a thorough study of the gas and established that it was not any form of nitrogen.

Finally Ramsay and Raleigh stumbled onto the truth: Ramsay in a letter to Raleigh in 1894 asked, "Has it occurred to you that there is room for gaseous elements at the end of the first column of the Periodic Table?" They concluded that they had isolated a new, inert elemental gas. They announced their discovery the same year at a meeting of the British Association, and named the element at the suggestion of the Chairman — *argon* for the *lazy one*. Boisbaudran predicted that argon might belong to a whole new family of inert elements, and he even suggested atomic weights that foretold neon, krypton, and xenon. Argon constituted about 1% of the atmosphere. No wonder Cavendish had found a respectable residue that would not react!

Actually, argon had not been the first inert gas observed spectroscopically. In 1868 Janssen had traveled to India to make a spectroscopic study of the sun's chromosphere during a total eclipse. He saw an intense yellow line which was shifted from the familiar D-line of sodium. The English astronomer Lockyer proposed that a new element had been detected, which he named *helium*. So far away, there seemed no way to confirm a hypothetical element on the sun, and many spectroscopists scorned the idea. However, John W. Draper, first president of the American Chemical Society, was more visionary: "Helium. . . seems trembling with excitement to tell its story. . . . And if this be the case with the sun, what shall we say of the magnificent hosts of the stars? May not every one of them have special elements of its own?"

Ramsay in 1895 heated a sample of

cleveite (a rare earth-uranium ore, named for Per Theodor Cleve) and obtained a gas whose spectral lines suggested a mixture of nitrogen, argon, and something else. Ramsay was thinking the spectrum might be "krypton" — a hypothetical heavier analogue of argon. He wrote about his puzzlement in a letter to his wife, Lady Ramsay: "I bottled the new gas in a vacuum tube, and arranged so that I could see its spectrum and that of argon in the same spectroscope at the same time. There is argon in the gas, but there was a magnificent yellow line, brilliantly bright, not coincident with, but very close to, the sodium yellow line. I was puzzled, but began to smell a rat."

Preferring the superior instrumentation of Lockyer and Crookes, he sent the gas to them for spectroscopic analysis. Sir William Crooks soon telegraphed back the electric news: the spectrum was identical to that of the "helium" of the sun!

The search was on for respectable quantities of helium. Italy was considered a likely spot, especially in the gaseous emanations of volcanoes. Scientists plodded through the mountains of Italy, on horseback, on mule, and on foot — but helium was discovered only in minute quantities. "It is among the rarest of elements," declared Winkler.

A few years later huge quantities of helium were found in gas wells in the Southwest United States. The first source was in Dexter, Kansas, in 1903, and was discovered in a comical way — a dedication ceremony was planned where gas from the first well in this community would be lit, but the tapped portion would not support combustion and extinguished all flames. A sample sent to the University of Kansas proved the presence of helium. Because of the rich source of helium in the United States, it has been extensively used for filling balloons and dirigibles. Europe, being much poorer in the gas, had to make painful decisions regarding the inflation of dirigibles — leading to the use of hydrogen and the subsequent fiery tragedy of the *Hindenburg* during an attempted landing at Lakehurst NJ, in 1937 (for an explanation of the cause of this tragedy, see page 72).

With two inert gases on record, the chase was on for further members of this family. Ramsay continued his search, now with his assistant Morris Travers. They first tried to find new gases by heating rare minerals. Soon they conceded defeat, and returned to the atmosphere.

In 1898, boiling away liquid air, they saved the residues whose spectrum exhibited a new green lines that did not coincide with any of argon, helium, mercury, or hydrogen. They determined the density and realized the gas fit between bromine and rubidium of the Periodic Table. In their excitement they worked late into the night and almost forgot Travers' examination for his doctorate which had been scheduled for the next day! They called the new gas *krypton* ("hidden").

Ramsay and Travers realized there was room in the Periodic Table for a lighter gas, and they searched in the more volatile component. When the scientific pair boiled off liquefied argon, the first fraction was collected and gave a brilliant red spectrum. Its new spectrum immediately convinced them it must be a new gas. Travers later exclaimed, "The blaze of crimson light from the tube told its own story, and it was a sight to dwell upon and never to forget. It was worth the struggle of the previous two years. . . ." This new "blaze of crimson" was *neon* ("new," named by Sir William's son), now familiar at night in any city.

After obtaining a new liquid-air machine, Ramsay and Travers prepared larger quantities of neon and krypton. By repeated fractionation of krypton, a yet heavier gas was sequestered which gave a beautiful blue glow. They named this gas *xenon* ("stranger"). Soon the vacuum tube industry would use large quantities of this gas, giving the faint blue glow familiar to those working with vacuum tube electronics.

Hence, in the space of half a decade, a complete new family of the Periodic Table was developed. Only one more inert gas was to be discovered, radon (see Chapter 13).

Helium

He 2 4.00260
[Gr. *helios*, sun]
Discovered spectroscopically in the sun
1868, collected terrestrially 1895
mp <172.2°; bp -268.9°;
density 0.178 g/L

Helium was discovered in 1868 by the French astronomer Pierre-Jules-César Janssen. During an eclipse of the sun in India he observed an unfamiliar yellow line in the spectrum of the sun's chromosphere. Sir Norman Lockyer had observed the line himself in his home observatory in northern London, which he dubbed D3, to distinguish it from the D1 and D2 double lines of sodium. He confirmed the line did not belong to any known element; he named it *helium*. Most spectroscopists doubted the existence of Lockyer's helium and some even ridiculed it.

In 1895 Sir William Ramsay collected some gas from cleveite, which he sent to Lockyer. Lockyer excitedly and promptly confirmed that the new gas gave an identical yellow line. The ultimate confirmation came from Crookes home laboratory in London, where he had set up a sophisticated spectroscopic system. Crookes made the announcement in his own weekly journal, the *Chemical News*.

Soon helium was discovered in the atmosphere in minute amounts, and in 1903 helium was discovered in a gas well in Kansas. Since then huge reserves have been discovered in wells in Texas, Oklahoma, and Kansas.

Helium is the second most abundant element in the universe, although scarce on earth. The boiling point of helium is close to absolute zero. Helium is the only liquid that cannot be solidified by simply lowering the temperature; the pressure must also be increased. Helium is used for filling balloons, since it is much safer than hydrogen. Helium is used in breathing mixtures for divers, because it has a low solubility in the blood. Liquid helium is used in cryogenic research.

Neon

Ne 10 20.180
[Gr. *neos*, new]
Discovered 1898
mp -248.7°; bp -246.0°;
density 0.900 g/L

With the recent discoveries of helium and argon, Sir William Ramsay and Morris W. Travers became fascinated with the possibility of discovering further inert gases. In a series of rapid, simple, but elegant experiments, they isolated in 1898 three additional inert gases from the atmosphere. The lightest was collected in the first fraction obtained by distilling off a sample of solid argon. Spectroscopically, the gas exhibited many, brilliant lines in the red. They named the gas *neon*.

Neon is prepared by the liquefaction of air. It is used in the common advertising signs, glowing reddish orange. Of all the inert gases, the electrical discharge of neon is the most intense.

Argon

Ar 18 39.948
[Gr. *argos*, lazy]
Discovered 1894
mp -189.2°; bp -185.7°
density 1.78 g/L

John William Strutt (the Third Lord Raleigh) and William Ramsay passed nitrogen over red-hot magnesium and found it would not be completely absorbed. They suspected a modification of nitrogen (perhaps analogous to ozone, O_3, for oxygen), but examining the spectrum, they observed new red and green bands. They concluded they had a new gas — the first inert gas — and that there must be an entirely new family in the Periodic Table. The chairman of the British Association, where they delivered their paper, suggested the name *argon, the lazy one*. Interestingly, Cavendish a century before had noticed an inert portion of the atmosphere, which undoubtedly was argon. With the discovery of argon, the hunt was on for further “lazy gases.”

Argon is the third most common gas in the atmosphere, constituting about 1%. It is prepared commercially in bulk quantities by fractionation of liquid air. It is used in electric light bulbs and in fluorescent tubes, and as an inert gas in welding and cutting and other metallic processes. In chemical research it is used as an inert atmosphere in situations where the cheaper nitrogen would react, such as in arc welding and cutting; the production of titanium, magnesium, and other reactive metals; and growing silicon and germanium crystals.

Krypton

Kr 36 83.80
[Gr. *kryptos*, hidden]
Discovered 1898
mp -156.6°; bp -152.3°;
density 3.73 g/L

Ramsay and Travers evaporated a sample of liquid air and collected the residual gas. They observed a brilliant green line in the spectrum never before observed. They determined the density and concluded the gas belonged between bromine and rubidium in the Periodic Table. They named the gas *krypton*.

Krypton exists in the atmosphere to the extent about 1 ppm. Its use is limited because of its high cost — but it is ideal in high intensity lamps, such as airport approach landing systems, because of the white color of the brilliant light.

Xenon

Xe 54 131.29
[Gr. *xenon*, stranger]
Discovered 1898
mp -111.9°; bp -107.1°;
density 5.89 g/L

By repeated fractionation of krypton, Ramsay and Travers separated a still heavier gas which they named *xenon*. Spectroscopically, it exhibited a beautiful blue glow.

Xenon exists in the atmosphere to the extent of about 0.05 ppm. The gas is used in electron tubes, stroboscopic lamps, and lasers. Although a member of the “inert gases,” xenon forms some exotic compounds with reactive elements, such as XeF_4.

Radon

(See Chapter 13, page 77)

Recent research has suggested that the Hindenburg dirigible caught fire not because the hydrogen was sparked by lightning, but because a flammable varnish with powdered aluminum was ignited by static discharge. Recent engineering advances suggest that hydrogen may be handled and stored safely, and may become a very economical fuel in the future.

By the time of Ramsay, spectral analysis had come a long way. Bunsen and Kirchhoff had developed the method of spectroscopy to discover cesium and rubidium. Later, Boisbaudran studied the rare earths and discovered two of them and had confirmed several others; other investigators were using spectral analysis routinely and were using it to make various claims with the rare earths. Reich and Richter would use the method to discover indium; and Crookes to detect thallium. This method in the right hands could be used to analyze mixtures confusing mixtures — Demarçay, the discoverer of europium, would become famous in Paris with his laboratory on Berthoud Boulevard. "Là, et là seulement, un spectre compliqué se lisait comme une partition d'opéra." ("There, and there only, could a complex spectrum be read like the score of an opera.") Later Demarçay would help the Curies with their discovery of minute quantities of radium.

Nine years after the invention of the spectroscope by Bunsen and Kirchhoff, helium was discovered in the sun. Originally confused with sodium, the yellow line of helium was noticeably different not only because its position was not the same, but also because sodium's yellow line was actually a double line separated by 0.6 nanometer. Scientists who doubted the proof of a new element gave suggested explanations that the line was actually due to a weak line in hydrogen that was apparent in a huge reservoir of hydrogen such as the sun; or that the spectra of elements might appear differently in the extreme temperature, pressure, or magnetic conditions of the sun.

Across the main street (Hauptstraße) from a statue of Bunsen in the Altstadt (Old Town) of Heidelberg, Germany, on a plaque mounted on an old building, reads:

> *"In diesem Hause hat Kirchhoff 1859 seine mit Bunsen begründete Spectralanalyse auf Sonne und Gestirne gewandt und damit die Chemie des Weltalls erschlossen."*

("In this building in 1859 Kirchoff applied his spectral analysis, that he had established with Bunsen, to the sun and the stars and thereby unlocked the chemistry of the cosmos.")

13. THE RADIOACTIVE ELEMENTS
(1890-1920)

Pitchblende, composed mostly of uranous (UO_2) as well as uranic oxide (UO_3) and compounds of other elements, is the most commonly known and richest ore of uranium. However, uranium was actually discovered in secondary minerals, which are more soluble and manageable in chemical analyses (secondary minerals are formed by leaching of major minerals by water). In 1789 Martin Klaproth discovered uranium in *Grüneruranglimmer* ("green uranium mica") and *Uranocher* ("uranium ocher") — present-day *torbernite* ($Cu(UO_2)_2(PO_4)_2 \bullet 11H_2O$) and *gummite* (yellow mixed uranium oxides of indefinite composition). He named the element after the new planet which Sir William Herschel had recently discovered. By reacting uranium ore residues with charcoal, Klaproth obtained a black substance which he presumed was the element, but which was actually the oxide (uranous oxide, UO_2, no more than purified pitchblende itself). Since uranic oxide cannot be reduced with hydrogen or carbon, no one suspected anything other than the element form was obtained until Peligot in 1841 treated uranium chloride with potassium, in the manner developed by Davy. Peligot obtained a black powder — elemental uranium — quite unlike the original material.

Berzelius in his investigations of the rare earths investigated a mineral in 1828 which appeared like gadolinite, but which proved to be a silicate of a new metal. Berzelius named the new metal *thorite* ($ThSiO_4$) and the element thorium. He prepared a sample of the metallic thorium by heating a preparation of potassium and potassium thorium fluoride. He prepared a sample of the metallic thorium by heating a preparation of potassium and potassium thorium fluoride.

Uranium and thorium were known many years before radioactivity was discovered by Antoine-Henri Becquerel, who noticed in 1896 that uranium salts could expose photographic plates, even when protected by opaque black paper. A faster method for detecting radioactivity was the electroscope, a device where two hanging gold leaves repel each other when in contact with an ionizing source, but this method did not allow good quantitative measurements.

Continuing the work of Becquerel, the persons most responsible for understanding the phenomenon of radioactivity were Pierre and Marie Sklodowska Curie. To carry out their famous studies, a reliable method was required for sophisticated radioactivity measurements. The ingenious Pierre Curie devised an apparatus assembled from an ionization chamber, an electrometer, and a piezoelectric quartz sensor which allowed quantitative measurements (the principles of piezoelectricity had been established previously by him and his brother Jacques). Marie was the patient operator of Pierre's device as she studied all known elements, all borrowed from nearby museums.

Marie found by 1898 that uranium and thorium were the only known elements which were radioactive. However, she noticed that the pitchblende and certain other radioactive minerals were more radioactive than uranium itself, and since the main constituents of the ore were known, the responsible radioactive agent (presumably in small quantities) must be quite active indeed.

Careful chemical separations gave a bismuth fraction and a barium fraction, both of which were intensely radioactive. Polonium was in the first fraction and radium in the second fraction; on the basis of their radioactivity alone these elements were announced in 1898.. To obtain weighable amounts of these two elements, several tons of residues were obtained from the Joachimsthal Mine, Czechoslovakia. These residues were processed in the famous "Shed" at the École Supérieure in Paris over a period of years, a miserable shack which had once been used for the dissection of corpses by Medical School students. Only after they became famous — and won the Nobel Prize! — were Marie and Pierre Curie furnished modern laboratory facilities.

Subjecting the barium salts to spectroscopic analysis (by Demarçay), new lines were detected. After laborious fractionations of the barium chloride, the least soluble part proved to be the most radioactive and exhibited the strongest of these new spectroscopic lines. As the scientific pair finally isolated the white radium chloride salt, they were thunderstruck to observe that it glowed in the dark! At night their laboratory exhibited a soft incandescence, with bottles, capsules, and tubes glowing like "fairy lights." After the tragic death of Pierre in 1906, André Debierne, a close friend, isolated a sample of the shining white metal in 1910.

The radioactive decay of uranium and thorium gives a sequence of many elements of varying weights, and it soon became clear that different isotopes of the same element could have different levels of radioactivity. With each new discovery there was confusion whether a new element had been discovered, or merely a new isotope of an old element. New names were assigned to new discoveries: uranium X_1, uranium X_2, brevium (named for its short half life), ionium, niton, emanium, radium D, E, or F, etc. Sometimes new names were assigned to old discoveries, for example, radium F was actually polonium. After several years sense was made of the tangle, and frequently more than one research group has been given credit for the independent discovery of an element, each of whom arrived at the finding of a particular isotope by a different route.

The first element in this series of decay products was discovered in 1899 by Debierne, who found it in the rare earth fraction of pitchblende. This element was named *actinium*.

Next, the Curies had noticed that when air comes in contact with radium, it becomes radioactive. Dorn in 1900 showed this was due to a radioactive emanation. Rutherford and Soddy had observed this same radioactive gas emanating from thorium the previous year. Rutherford and Soddy then proceeded to prove the existence of this gas in 1902 by liquefying it. This radioactive gas, eventually named *radon*, was thus verified as the heaviest gas known when in 1910 Ramsay determined the density.

If pitchblende is treated with hot concentrated nitric acid to remove radium and other radioactive components, the insoluble residue remaining contains yet another radioactive substance. Hahn and Meitner isolated this material in 1917 which they called *protoactinium* (later shortened to *protactinium*). Credited with independent discovery of this element are Kasimir Fajans and O. H. Göhring in 1913 (named "brevium," or "uranium X_2"), and Frederick Soddy, John A. Cranston, and Alexander Fleck in 1917 (named by the discoverers, "eka-tantalum").

"The stately procession of element evolution." Soddy showed that when a radioactive element emits an α-particle (a helium nucleus) the element shifts two spaces to the left in the Periodic Table (loses an atomic number of 2), while loss of a β-particle (an electron) shifts the element one space to the right (atomic number increases by 1). The confusing array of various radioactive elements was caused by this "stately procession of element evolution" as an atom lost α-particles and β-particles in a specific zigzag sequence to eventually end up as stable lead (Pb). The complete sequence of radioactive evolution was worked out by Soddy and others, including Russell, Fajans, and Fleck. A mineral that has lain undisturbed for millions of years is able to establish a steady-state concentration of all of these elements and isotopes, and this explains why the pitchblende that the Curies investigated contained these trace radioactive elements. The known sequences for the common radioactive elements — U-238 (99.27%), U-235 (0.72%), and Th-232 (100%), are given on pages 79-80.

Nobel prize. In 1903 Pierre and Marie Curie, and Becquerel, were awarded the Nobel Prize in Physics. Tragedy struck three years later when Pierre Curie was killed while struck by a heavy vehicle in Paris. After struggling through her grief, Marie Curie accepted a professorship at the University of Paris, and with André Debierne as an assistant, she directed the research in radioactivity. In 1911 she was awarded the Nobel Prize in Chemistry — and thus was the first person to receive the Nobel Prize twice (as well as the first woman to win the Prize).

Uranium

U 92 238.0289
[Planet *Uranus*]
Discovered 1789, metal isolated 1841
mp 1132.3°; bp 3818°; sp gr 18.9

The use of uranium oxide can be dated back to 79 A.D. — it was incorporated in a glass mosaic mural in the Imperial Roman Villa on Cape Posilipo, Bay of Naples. Martin H. Klaproth in 1789 was the first to recognize uranium as a new element; he isolated black UO_2 from secondary uranium minerals (*torbernite*, $Cu(UO_2)_2(PO_4)_2{\bullet}11H_2O$), and *gummite* (mixed uranium oxides). Klaproth named the new element *uranium*, from the planet discovered by Herschel eight years earlier.

Uranium figured prominently in the discovery of *radioactivity* — Henri Becquerel in 1896 observed that a sample of potassium uranyl sulfate exposed a photograph plate protected from light. He described these "uranium rays" as passing through paper or sheets of metal "opaque to ordinary light." Peligot obtained the metal in 1841 by reacting uranium tetrachloride with potassium.

Uranium is extremely important as a nuclear fuel — one pound has the fuel equivalent of 1500 tons of coal. Nuclear fuels can be used to generate electrical power, make new isotopes, or produce explosives. The main isotope is U-238 (99.28%, with a half-life of 4.5×10^9 years), which is used to calculate the age of rocks. The uncommon isotope is U-235 (0.71%, with a half-life of 7.1×10^8 years), which is fissionable with slow neutrons and can sustain a chain-reaction in a reactor containing a moderator such as heavy water. Depleted uranium, with the U-235 content lowered to 0.2%, is used in inertial guidance devices, ballast for missiles, and as shielding material. Uranium compounds are typically yellow and are used in glazes and glass. The well-known Fiestaware is pigmented red by oxidized uranium.

Thorium

Th 90 232.0381
[*Thor*, Scandinavian god of war]
Discovered 1828
mp 1750°; bp 3800°; sp gr 11.72

Berzelius investigated a mineral in 1828 sent to him from Langesund Fjord, Norway and found it to be a silicate of a new metal. He called the mineral thorite and the element *thorium*. He isolated a specimen of the metal by reacting potassium thorium fluoride with metallic potassium. The radioactivity of thorium was announced by G. C. Schmidt and Marie Curie in 1898.

Thorium is more abundant than uranium — there is probably more energy available from thorium than from both uranium and fossil fuels. However, thorium reactors are not expected to become commercially significant for several years. Thorium oxide melts at 3300°, the highest of the elemental oxides. Until recently, the main present use of thorium (along with a minor amount of cerium) has been the manufacture of the Welsbach mantle (the trademark for gas mantles) using the oxides impregnated in a gauze in a portable lamp. Thorium oxide is used as a catalyst in the oxidation of ammonia to nitric acid, in cracking petroleum, and the manufacture of sulfuric acid. Naturally-occurring thorium, with a half life of 1.4 x 10^{10} years, disintegrates producing radon-220.

Radium

Ra 88 226.0254
[L. *radius*, ray]
Discovered 1898, metal isolated 1911
mp 700°; bp 1140°; sp gr ~5

In studies of barium chloride, Pierre and Marie Curie noticed that the barium fraction was particularly radioactive, and concluded a new element was present (1898). Over a period of several years, the unknown was concentrated through repeated concentrations. Eventually, an observable amount of chloride salt of the element was obtained — which was so radioactive that it glowed in the dark! The Curies named the new element *radium*. Pierre Curie was killed in a street accident in 1906 and Marie continued the research alone. By 1910 she had prepared a gram of radium chloride, and the next year isolated the metal by electrolysis of the chloride salt. For her elegant investigations in radioactive substances, Marie Curie won *two* Nobel Prizes (one shared in Physics with her husband and Becquerel, the other Prize alone in Chemistry).

Radium is used in self-luminous paints, neutron sources, and medical applications. The *curie* (*Ci*) is defined as that amount of radioactivity having the same disintegration rate as 1 gram of Ra^{226} — 3.17 × 10^{10} disintegrations per second. One gram of radium produces about 0.0001 milliliter of radon gas per day. The half-life of Ra-226, resulting in a decay sequence from U-238, is 1600 years. The general problem of radium poisoning was dramatized by a number of women, who during the World War I had made luminous dials. They were wetting the tips of their brushes with their lips — and accumulated an excess of radium in their bodies; 24 died of sarcoma or anemia.

Polonium

Po 84 (209)
[*Poland*]
Discovered 1898, metal isolated 1902
mp 254°; bp 962°; sp gr 9.3

Polonium, discovered in the bismuth fraction separated from pitchblende, was the first element Marie Curie discovered while searching for the cause of unexpected radioactivity in pitchblende — the level of activity was greater than that expected from the uranium and thorium content alone. Dr. Willy Marckwald of Berlin precipitated a deposit of the metal four years later.

Polonium results from the radioactive decay of uranium and thorium. Polonium-210 has a half-life of 138.4 days. Gram quantities can be prepared, but the material is *extremely* radioactive — half a gram of metal spontaneously heats up to 500°! A milligram of polonium emits as many α-particles as 5 grams of radium. A ton of uranium ore contains about 100 µg of polonium. Polonium-210 is used commercially as an α-particle source, and on static brushes for removing dust from photographic films.

Other radioactive elements in nature

In any uranium or thorium ore, in addition to radium and polonium, there exist several other elements that are produced by radioactive sequences that culminate in inert lead (see pages 79-80 for these sequences). Since these elements are short-lived, they exist in trace quantities only in nature. They are virtually impossible (and illegal!) to acquire in any observable quantities. Some of these elements were actually first discovered by their artificially creation, and therefore technically speaking should belong in chapter 15, but all are included here because they *do* occur in nature.

Astatine

At 85 (210)
[Gr. *astatos*, unstable]
Discovered 1940
mp 302°; bp 337°

Corson, Mackenzie, and Segrè synthesized this element in 1940 by bombarding bismuth with alpha particles. Since the naturally occurring isotopes of astatine all have half-lives less than a minute, only minute traces exist in nature — the total amount of astatine in the earth's crust is estimated at less than one ounce.

Radon

Rn 86 (222)
[from *radium*]
Discovered 1900
mp −71°; bp −61.8°; density 0.00973 g/L

Dorn observed emanation from radium in 1900, but did not understand its nature (in fact, Rutherford gave it the name *radium emanation*, contrary to various claims in the literature that others gave it this name). Rutherford and Soddy discovered the cause of the emanation was a gas, characterized the gas, were able to liquefy it, and were the first to recognize it as an element and as a decay product of radium. They also had previously discovered the gas as an emanation product of thorium. Ramsay in 1908 measured its density and determined it as the heaviest gas known.

Radon is a radioactive, chemically inert gas, which is produced naturally from radium (Ra-222) and thorium (Ra-220). One gram of radium produces 0.0001 mL of radon gas per day. Rn-222, the longest-lived isotope, has a half-life of 3.82 days. As for xenon, radon can form a limited number of compounds with electronegative elements, e.g., radon fluoride. Radon is used in hospitals for application to patients. Radon collects in basements and can constitute a health hazard.

The name for radon has variously been radium emanation, niton (the 226 isotope, half-life 3.82 days) actinon, (the 219 isotope, half-life 3.96 seconds, originating from actinium), and thoron (the 220 isotope, half-life 55.6 seconds, produced by thorium).

Francium

Fr 87 (223)
[*France*, site of Curie Institute]
Discovered 1939
mp 27°; bp 677°

In 1939 Mlle. Marguerite Perey of the Curie Institute of Paris discovered francium as an α-decay product of actinium. The longest-lived isotope has a half-life of 22 minutes. The total amount of francium in the earth's crust is estimated at less than an ounce.

Actinium

Ac 89 227.0278
[Gr. *aktinos*, beam or ray]
Discovered 1899
mp 1050°; bp 3200°; sp. gr. 10.07

This element was discovered by Debierne in 1899; then by Giesel in 1902. Actinium-227 is a decay product of U-235, with a half-life of 21.6 years. It is 150 times as active as radium.

Protactinium

Pa 91 231.0359
[Gr. *protos*, first (member
of the actinium series)]
Discovered 1918
mp 931°; bp 3520°; sp. gr. 6.77

Hahn and Meitner isolated samples of this element from pitchblende after the other radioactive materials and tantalum (which chemically resembles protactinium) were separated. Credited with independent discovery of this element are Kasimir Fajans and O. H. Göhring in 1913 ("brevium," or "uranium X_2"), and Frederick Soddy, John A. Cranston, and Alexander Fleck in 1917 ("eka-tantalum"). In 1927 two milligrams of protactinium oxide (Pa_2O_5) were prepared by A. V. Grosse, and he reduced the metal element from the oxide in 1934. Protactinium-234 is a decay product in the U-238 series, with a half-life of 6.7 hours; At-231 is a decay product in the U-235 series, with a half-life of 32,700 years.

Radioactive elements in an ore sample

In a rich sample of pitchblende, the following elements are calculated to be present in the following approximate amounts:

Uranium-238	~10 grams
Uranium-235	~70 milligrams (7×10^{-2} gram)
Uranium-234	~0.5 milligram (5×10^{-4} gram)
Polonium-210	~1 nanogram (1×10^{-9} gram)
Radium-226	~3 micrograms (3×10^{-6} gram)
Actinium-227	~2 nanograms (2×10^{-9} gram)
Protactinium-231	~3 micrograms (3×10^{-6} gram)
Radon-222	~2×10^{-11} gram
Astatine-218 and -219	~10^{-20} gram (~1 atom)
Francium-223	~10^{-20} gram (~1 atom)

Although most discoveries of radioactive elements have been performed through the analysis of pitchblende (uraninite, UO_2), the first discoveries by Klaproth were made on secondary uranium minerals, which he found must easier to dissolve for analysis. These secondary minerals (commonly +6 oxidation state) result from long-term oxidation and weathering of uraninite (+4 oxidation state).

After Klaproth characterized uranium, miners called pitchblende "Pechuran," or "bad-luck uranium," because it did not contain any of their precious silver. Klaproth performed subsequent work on pitchblende, which had previous been considered to be an ore of zinc and iron. He dissolved pitchblende in nitric acid and observed a yellow precipitate when he added potash. This yellow solid was uranium oxide with an oxidation state greater than +4. He reacted this yellow solid with charcoal to produce black UO_2, where the oxidation state of uranium is +4. Klaproth therefore had a pure form of uranous oxide, UO_2. This was erroneously considered to be the element, because it could not be easily reduced. The metallic element itself was not produced until half a century later when Eugène Peligot of Paris reacted uranium tetra-chloride with potassium.

A number of beautiful secondary uranium minerals exist, which vary from canary yellow to malachite green. Examples are:

Torbernite ($Cu(UO_2)_2(PO_4)_2 \bullet 11H_2O$), green mica-like flaky crystals (the compound originally studied by Klaproth);

Autunite ($Ca(UO_2)_2(PO_4)_2 \bullet 10\text{-}12H_2O$), yellowish-green crystalline scales which fluor-esce brilliant green;

Soddyite ($(UO_2)_2SiO_4 \bullet H_2O$), amber-yellow resinous crystals, named for Frederick Soddy;

Curite ($Pb_2U_5O_{17} \bullet 4H_2O$), orange-red or vermillion prisms, named for Pierre Curie;

Sklodowskite, lemon-yellow fibrous nee-dles ($Mg(H_3O)_2(UO_2SiO_4)_2 \bullet 4H_2O$), named for Marie Sklowdowska Curie.

A great deal of the internal heat generated in the earth is due to thorium and uranium through radioactive decay. Before this source of heat was known, the age of the earth was reckoned to be much younger than its actual 4.6×10^9 years, since obviously "it had not had much time to cool off since its origin." Rutherford was the first to point out that radioactive decay would be an important source of dating the earth and minerals.

Radioactive sequences for U-238, U-235, and Th-232

(Figures presented on pages101-104)

A sample of a radioactive element, if allowed to stand over a period of time, can attain a state of equilibrium, where all the products in the sequence remain in constant proportion. For this state of equilibrium to exist, the parent element must have a much longer half-life than any of the radionuclides in the series, and at least ten half-lives of the longest-lived nuclide in the subsequent sequence must have expired.

Radioactive sequence for for U-238

Radioactive decay series originating from uranium-238. Half-lives are shown for each isotope. The natural abundance of uranium-238 in the earth's crust is 99.27%.

U-238 (4.47x10^{9} yr) emits α to give
Th-234 (24.1 day) emits β to give
Pa-234m* (1.17 min) emits β to give
U-234 (2.47x10^{5} yr) emits α to give
Th-230 (7.54x10^{4} yr) emits α to give
Ra-226 (1600 yr) emits α to give
Rn-222 (3.824 day) emits α to give
Po-218 (3.10 min) emits α to give
Pb-214 (27 min) emits β to give
Bi-214 (19.9 min) emits β to give
Po-214 (163.7 μsec) emits α to give
Pb-210 (22.3 yr) emits β to give
Bi-210 (5.01 day) emits β to give
Po-210 (138.8 day) emits α gives
Pb-206 (stable)
*(Pa-234m is the metastable form. See caption to Figure 7).

Radioactive sequence for U-235

Radioactive decay series originating from uranium-235. Half-lives are shown for each isotope. The natural abundance of uranium-235 in the earth's crust is 0.72%. Note that there are two decay routes for Ac-227, which after two steps by either route produces Ra-223.

U-235 (7.04x10^{8} yr) emits α to give
Th-231 (1.063 day) emits β to give
Pa-231 (3.28x10^{4} yr) emits α to give
(route 1)
Ac-227 (21.77 yr) (98.62%) emits β to give
Th-227 (18.72 day) emits α to give
Ra-223 (11.435 day) emits α to give
Rn-219 (3.96 sec) emits α to give
Po-215 (1.780 msec) emits α to give
Pb-211 (27 min) emits β to give
Bi-211 (2.14 min) emits α to give
Tl-207 (4.77 min) emits β to give
Pb-207 (stable)
(route 2)
Ac-227 (21.77 yr) (1.38%) also emits α to give
Fr-223 (21.8 min) emits β to give
Ra-223 (11.435 day)
and so on in the sequence immediately above.

Note: "Enriched uranium" is uranium which is enriched with the isotope U-235.

Radioactive sequence for Th-232

Radioactive decay series originating from thorium-232. Half-lives are shown for each isotope. The natural abundance of thorium-232 in the earth's crust is 100%. Note that there are two decay routes for Bi-212.

Th-232 (1.40x10^{10} yr) emits α to give
Ra-228 (5.76 yr) emits β to give
Ac-228 (6.15 hr) emits β to give
Th-228 (1.913 yr) emits α to give
Ra-224 (3.66 day) emits α to give
Rn-220 (55.61 sec) emits α to give
Po-216 (0.145 sec) emits α to give
Pb-212 (10.64 hr) emits β to give
(route 1)
Bi-212 (1.009 hr)(64.07%) emits β to give
Po-212 (0.298 μsec) emits α to give
Pb-208 (stable)
(route 2)
Bi-212 (1.009 hr) (35.93%) emits α to give
Tl-208 (3.053 min) emits β to give
Pb-208 (stable)

Descriptive flow charts for these radioactive sequences are presented in Figures 7-10 on pages 101-104.

14. MOSELEY AND ATOMIC NUMBERS (1910-1925)

Mendeleev's insight that the Periodic Table should be based on chemistry rather than atomic weight was accurate prophesy — tellurium has a higher atomic weight than iodine; argon has a higher atomic weight than potassium; cobalt and nickel, and thorium and protactinium have similar discrepancies; and the radioactive elements have very confusing and variable atomic weights. But then the question remains, is there a numerical basis of the Periodic Table at all? Is there indeed any meaning to the "ordinal number" or "number of the element" that the Periodic Table appeared to suggest? Henry Moseley gave a definite "yes" to this query — the Periodic Table should be based on an "atomic number," a variable that could be defined on the basis of X-rays of the elements.

Moseley, a lecturer and then researcher at the University of Manchester and later at Oxford University, was fascinated with Max von Laue's recent discovery that the lattice of atoms in a crystal would diffract X-rays. In this method, X-rays are generated by bombarding a metal with cathode rays (electrons), and various metals emit X-rays of different frequencies. Curious as to what the relationship was between an element and the frequency of the X-rays radiated, Moseley conducted a thorough investigation of all known elements, and he plotted the X-ray frequencies against the atomic number. A simple and yet elegant relationship emerged: of a given element, the square root of the X-ray frequency is directly proportional to the atomic number:

$$\sqrt{\frac{\nu}{\frac{3}{4}\nu_0}} = N - 1$$

where

N= the atomic number of the element;
$\nu = 1/\lambda$ = the observed wavenumber of the X-ray line (the K_α line);
ν_0 =a constant (the Rydberg constant).

Moseley had borrowed this constant from the work of J. Rydberg, who had found in 1890 that the wavenumber $\nu = 1/\lambda$ could be related to the emission spectra of the hydrogen atom in the Balmer series, giving rise to the constant that bears his name. This new, extremely powerful method of Moseley immediately foretold exactly how many elements should exist, and thus how many were left to be discovered. Professor Urbain, who had worked *twenty years* on the rare earths, visited Moseley in Oxford and in only *a few days* confirmed his values for the atomic numbers for erbium, thulium, ytterbium, and lutetium!

Now a systematic Periodic Table could truly be devised. It was now obvious that seven missing elements would be found in precisely numbered positions (through uranium, or atomic number 92). Furthermore, although it was not clear just what was going on in the rare earths, nevertheless it was clear that elements 61 and 72 were to be discovered. Urbain had searched diligently with Moseley for these two elements in his rare earth mixtures, but found no trace.

Hafnium. On the basis of Moseley's work there clearly existed an element below zirconium. Urbain had previously believed that he had seen evidence for this element 72 in an arc spectrum of a rare earth mixture, and he had even given a name to the element —

celtium. However, a visit to Moseley and his apparatus in Oxford resulted in no indication that there was any element 72 whatsoever. After World War I, Urbain continued to search in the rare earth residues but could never find anything encouraging. The reason for his failure was that he was looking in the wrong place, as became clear from Niels Bohr's work.

Bohr had been elucidating the meaning of the Periodic Table in terms of atomic structure. He was able to explain the anomalous behavior of the rare earths and why they lay in a group all by themselves. Bohr, adopting Planck's quantum theory, developed a structure for the atom where the electrons lay in specific orbits. He arrived at a scheme for this internal structure of the atom that corresponded with the Periodic Table. Thus, he assigned inner electrons (d-electrons) to the transition elements and another group of deeper electrons (f-electrons) to the rare earths. Bohr understood that during the building up of these deeper electron orbitals, a separate class should exist similar to lanthanum (element 57), but that after the completion of deeper electron layers the elements should continue in the normal manner. Previously, scientists had assumed 72 would behave like 71 (lutetium), but Bohr said element 72 should behave not like the rare earths but like zirconium.

Taking the hint of Bohr, Dirk Coster and George de Hevesy working in Bohr's laboratory made a thorough search in Norwegian zircon and other minerals and found the new element in 1923. To their surprise, this new element hafnium behaved almost exactly like zirconium, and thus could be separated only with difficulty. In fact, previous "pure" zirconium samples were found to contain substantial amounts of hafnium (sometimes as much as 5%!). Subsequent study showed that because of the lanthanide contraction, hafnium and zirconium had almost identical atomic volumes, thus explaining the similar behavior.

Modern methods are capable of ferreting out minor amounts of hafnium. EDX spectra can be obtained fairly quickly and are used extensively by mineralogists by determine the chemical composition of specimens. With proper equipment the composition of minute samples (a micrometer or less in diameter) can be ascertained, which has been used a great deal with platinum group compounds. Some zircons, particularly the gem-like specimens, can contain relatively pure zirconium. Other forms of zircon can contain substantial amounts of hafnium. The extreme composition of 100% hafnium, called "hafnon" with an ideal formula of $HfSiO_4$, has never been seen in nature, but reputedly has been closely approached in rare cases (99%).

Rhenium. At the beginning of the twentieth century manganese had no other members in its periodic column. Thinking that element 75 might have similar properties of manganese, Noddack, Tacke, and Berg carried out a 100,000-fold concentration in gadolinite, and by a careful inspection of the X-ray lines found the new element in 1925, which they named *rhenium* from the German Rhine River. By processing 660 kilograms of molybdenite, a gram of rhenium was prepared in 1928.

By the X-ray technique this scientific group also thought they had discovered element 43, directly above rhenium in the Periodic Table. They dubbed this element "masurium." This claim has not been verified.

"Scientifically precise Periodic Table." By 1925 the Periodic Table showed that (through uranium) only four elements remained to be discovered. These elements had to await artificial synthetic techniques (see next chapter).

The elements 90-92 (thorium, protactinium, uranium) were placed in the groups of titanium, vanadium, and chromium — but it became clear later (see next chapter) that 90-92 should lie in a row analogous to the rare earths, directly below the lanthanides.

When Great Britain entered World War I, Moseley promptly and patriotically entered the military service. He was killed while engaged on the Turkish front, at the age of 27. No brilliant scientist has undergone a more premature, tragic end. Because of Moseley's insight, as Urbain stated, Mendeleev's romantic classification had been substituted by a "scientifically precise Periodic Table."

Hafnium

Hf 72 178.49
[L. *Hafinia*, Copenhagen]
Discovered 1923, metal isolated 1925
mp 2227°; bp 4602°; sp gr 13.31

In 1914 Henry Moseley suggested that, within the limits of his X-ray technique, (elements 13-79, aluminum-gold), he could predict the lines for the missing elements (43, 61, 72, 75). Niels Bohr suggested that element 72 would have properties similar to those of zirconium. Dirk Coster and George de Hevesy thus investigated zirconium minerals, and were amazed to find substantial amounts of element 72 in all zirconium preparations (1-5%), even those which had previously been thought to be pure. They named the element *hafnium* for Copenhagen, the city in which the research was conducted. Hafnium had been overlooked not because of its rarity, but because of its remarkable similarity to zirconium — the separation of zirconium and hafnium is even more difficult than that of niobium and tantalum. George de Hevesy and Thal Jantzen separated hafnium from zirconium by repeated recrystallization of the ammonium or potassium fluorides. The metal was prepared by A. E. van Arkel and J. H. de Boer in 1925 at Philips NatLab (Physics Laboratory) in Eindhoven, Netherlands, by passing the tetraiodide over a heated tungsten filament.

Hafnium is almost chemically identical to zirconium; however, hafnium has twice the density. Generally found in zirconium minerals, these two metals are extremely difficult to separate. Hafnium has a good absorption cross section for thermal neutrons (600 times that of zirconium) and is used in reactor control rods, commonly in submarines. Hafnium carbide and nitrides are excellent refractories.

Rhenium

Re 75 178.49
[L. *Rhenus*, Rhine]
Discovered 1925, metal isolated 1928
mp 3180°; bp 5627°; sp gr 21.01

By a 100,000-fold concentration in gadolinite, the German scientists Walter Noddack, Ida Tacke, and Otto Berg detected element 75 in Berlin at the Physikalisches-Technisches Reichsanstalt by Moseley's brand-new X-ray techniques. Three years later they were able to isolate a gram of the element by processing 660 kilograms of molybdenite. They named the element *rhenium* in honor of the German Rhine River.

Rhenium has a melting point exceeded only by tungsten and carbon, and is used for filaments in ion gauges. Rhenium withstands arc corrosion and is used for electrical contacts. Thermocouples of Re-W can measure temperatures to 2200°, and rhenium wire is used in photoflash lamps.

The reason for the remarkable similarity between zirconium and hafnium is the "lanthanide contraction" — the filling of the 4f orbitals through the lanthanide elements between lanthanum (57) and hafnium (72). Through this series, there is a steady increase of the effective nuclear charge, producing a decrease in size. Thus, the third transition elements are remarkably similar to the respective second series elements, particularly at the beginning of the series, where atomic sizes are almost identical: zirconium and hafnium. Similarly, in the next family, niobium and tantalum were confused for many years — Wollaston even thought the two elements were identical (see page 14 where recently discovered tantalum was thought merely to be niobium).

The power of Bohr's insight was borne out when virtually overnight it became clear that the search for element 72 in rare earth compounds was in vain. Upon Bohr's recommendation, Hevesy turned to the Copenhagen Geology Museum for a sample of alvite to analyze (a type of zirconium) — and the rest is history.

15. THE ARTIFICIAL ELEMENTS
(1935-present)

By 1925, despite a tremendous amount of searching, four elements escaped detection — elements 43, 61, 85, and 87 — and apparently uranium — 92 — was the end of the list. A pair of claims had been made to fill in the gaps but were withdrawn. The same scientists who discovered rhenium — Noddack, Tacke, and Berg in 1925 — also believed they observed X-ray lines for element 43, which they named *masurium* (named for Masuria, a region in East Prussia, now Northeast Poland), but this announcement could not be confirmed. A continuing debate to this day — on which several articles have been written, both pro and con — is whether Noddack, Tacke, and Berg in 1925 with their equipment could have detected the X-ray lines for masurium (technetium) and whether in fact they did observe the element.

In 1926 J. A. Harris and B. S. Hopkins concentrated mozanite sands which gave X-ray lines which they claimed were element **61**, and they it named it *illinium*. Meanwhile, Luigi Rolla and L. Fernandes claimed they had detected element 61, which they named *florentium*.

Fred Allison claimed he had discovered element **85**, which he named *alabamine*.

Several investigators asserted they had found element **87**, which was given the various names *russium*, *alcalinium*, *virginium*, and *moldavium*.

But none of these discoveries could be verified. After the elements had finally been prepared artificially, it was realized that they were not found because they were very short-lived, radioactive substances, never to accumulate in appreciable quantities in nature.

The key to discovering the remaining four elements was found in the artificial transmutation of elements. Lord Rutherford, in 1919, had shown that nitrogen-14, when bombarded with highly energetic helium atoms, would transmute into oxygen-17:

$$^{14}_{7}\mathrm{N} + ^{4}_{2}\mathrm{He} \rightarrow ^{17}_{8}\mathrm{O}$$

In 1930 W. Bothe and H. Becker saw a very hard radiation produced by bombarding beryllium with helium atoms. Jean-Frédéric Joliot and Irène Joliot-Curie (the daughter of Pierre and Marie Curie) and Professor James Chadwick showed that a *neutron* was produced in this reaction:

$$^{9}_{4}\mathrm{Be} + ^{4}_{2}\mathrm{He} \rightarrow ^{12}_{6}\mathrm{C} + ^{1}_{0}n + \gamma$$

(gamma rays)

M. and Mme. Joliot-Curie discovered many kinds of transmutations and found that some artificially produced elements are radioactive, and thus they synthesized isotopes which had not been previously known. For example, the reaction of boron-10 with helium gave nitrogen-13, which decayed with a half-life of 14 minutes:

$$^{10}_{5}\mathrm{B} + ^{4}_{2}\mathrm{He} \rightarrow ^{13}_{7}\mathrm{N}$$

$$^{13}_{7}\mathrm{N} \rightarrow ^{13}_{6}\mathrm{C} + ^{0}_{+1}e$$

($^{0}_{+1}e$ is a positively charged electron, or positron)

By 1940, 330 artificial isotopes had been described, which included isotopes of every known element in the range 1-85, as well as thorium and uranium.

This new technique of M. and Mme. Joliot-Curie was used by other investigators to synthesize the four remaining elements: numbers 43, 61, 85, and 87.

Element 43. A long-standing mystery

was element 43. Why should an element with such a low atomic number be so elusive? In 1936 Segrè analyzed a sample of molybdenum that had been bombarded by deuterons by Ernest Lawrence in his cyclotron in Berkeley which had been sent to his laboratory in Italy. By extracting the treated molybdenum with ammonium hydroxide-hydrogen peroxide, he was able to isolate a radioactive portion which was approximately 10^{-10} gram of the new element, named technetium:

$$_{42}\mathrm{Mo} + {}^{2}_{1}\mathrm{H} \rightarrow {}_{43}\mathrm{Tc} + {}^{1}_{0}n$$

Larger quantities of technetium were subsequently available by bombardment of molybdenum with neutrons and niobium with helium ions. Technetium was also detected in fission products from uranium. All isotopes of technetium proved to be radioactive. The longest-lived isotope, Tc-98, has a half-life of 4,200,000 years.

The instability of technetium permitted development of theories regarding the structure of the nucleus. It became apparent that the construction of the nucleus has "shells" as do the electrons of an atom, and various combinations of protons and neutrons would allow predictable stabilities. The number of protons was particularly important — an even number of protons tended to promote stability; an odd number of protons would not be so favorable. Indeed, all four of the remaining elements had odd atomic numbers.

Element 87. Discovery of element-87 was made by Mlle. Marguerite Perey at the Curie Institute of Paris in 1939. She showed that actinium-227 decayed to give an element she named *francium*. Ordinarily actinium-227 decays by β-decay to give thorium-227 (see radioactive sequence on page 80). However, about 1% of the actinium decays by α-emission to give a new element she called *francium*:

$$^{227}_{89}\mathrm{Ac} + \rightarrow {}^{223}_{87}\mathrm{Fr} + {}^{4}_{2}\mathrm{He}$$

The chemistry showed the properties were that of an alkali metal. Chemical separations, which involved precipitations by ammonium bisulfates, tartrates, or chromates, had to be performed very rapidly, because the half-life of the longest-lived isotope of francium is about 20 minutes!

Element 85. Segrè, who had moved to the University of California at Berkeley, was involved with Dr. R. Corson and K. R. Mackenzie in the discovery of element-85. Bombardment of bismuth with α-particles produced this element, named *astatine*, in 1940.

$$^{209}_{83}\mathrm{Bi} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{211}_{85}\mathrm{At} + 2\,{}^{1}_{0}\mathrm{n}$$

The longest-lived isotope is At-211, with a half-life of 7.21 hours.

Element 61. Attention was next turned to the missing rare earth element. Fission products from an atomic pile at Oak Ridge, Tennessee, containing uranium contained, among other elements, rare earths from lanthanum through europium. Using the ion-exchange techniques developed by Spedding (see Chapter 11, page 62), milligram quantities of the new element 61 were isolated in 1945 by J. A. Marinsky and L. E. Glendenin at Oak Ridge National Laboratory, in the group of Charles D. Coryell. All isotopes of this element, named *promethium*, proved to be radioactive. The longest-lived isotope, Pm-145, has a half-life of 17.7 years.

Source of heavy elements. The vast majority of material in the universe is hydrogen and helium. "Heavy elements" — elements beyond hydrogen and helium — are created mostly in supernovae. The heavy elements in the earth's crust originated from the primordial material from a supernova captured by the sun and as the planets formed. Hence, during the beginning of the solar system, significant quantities of transuranium elements undoubtedly existed — even above 92 — but decayed until only elements 1-92 remained. Hence, all elements beyond uranium on earth are artificial.

Actually, there is evidence that small, but significant, amounts of neptunium (93) and plutonium (94) have been synthesized in natural atomic piles in the earth's crust at a much earlier age (millions of years ago) when the amount of U-235 was greater and could concentrate to critical levels. Ever since atomic fission was discovered, the detonation of atomic and hydrogen bombs have created elements beyond uranium in trace quantities in the earth's atmosphere and crust.

With the understanding that artificial elements could be synthesized, Glenn Seaborg at the University of California at Berkeley embarked on a journey beyond uranium: the transuranium elements. Plutonium was originally created in 1940 and was produced in the wartime economy in a race to ensure the U.S. attained the atomic bomb before Germany. Through the following years Seaborg and Ghiorso stepped through several elements, and later groups in Russia and Germany have continued the climb. Today the list extends beyond 100, with ever-increasing instability.

This quest for elements of higher atomic number seems more and more elusive — but there is a reason to explore the further regions. Glenn Seaborg suggested that there should be an "Isle of Stability," perhaps around atomic number 125, and observation of an element of this size would be of great theoretical interest. Current theory suggests that perhaps an element with 114 and 184 neutrons would have surprising stability.

With the increasing atomic number of the elements with their shorter lives — shrinking to milliseconds in some instances — naming a compound seemed to some as contrived, and Glenn Seaborg himself suggested that starting with atomic number 104, the name of the element should simply reflect the atomic number. Element-104 would be "unnilquaddium," element-105 would be "unnilquinnium," etc. However, the tendency to derive names for *all* elements continued, even for elements 104 and above. It is ironic that Seaborg himself has been thus honored (element-106 = "seaborgium"). Indeed, he is the first person for whom an element has been named during his lifetime.

It would be desirable to extend UNT's collection of elements beyond 92. Unfortunately, the public exhibition of elements beyond uranium is against National Regulations, and display of transuranium elements are not possible in a university course. Therefore, the descriptive story of the elements comes to an appropriate end with uranium, element-92. In the following short summaries of each artificial element, a full portrait is given, as in previous chapters, for those artificial elements embraced through 92. A shorter description is given for the transuranium elements.

It is to be stressed that particularly for the higher elements, all reports mandate verification and reproducibility. Sometimes only one atom has been observed in an experiment! Indeed, sometimes certain claims may be retracted. For example, an announcement in 1999 by the California group that they had observed Elements 116 and 118 was later recanted..

Technetium

Tc 43 (99)
[Gr. *technetos*, artificial]
Prepared 1937, metal isolated 1952
mp 2172°; bp 4877°; sp gr 11.50

By 1937 all attempts to discover elements 43, 61, 85, and 87 had failed. Number 43 was particularly intriguing, since it was such a low atomic number. Ernest Lawrence sent to Segré and C. Perrier at Palermo a sample of molybdenum which had been bombarded in the cyclotron for months with a deuterium beam. It was found (1937) that a new element could be extracted in small amounts (estimated at 10^{-10} gram) with ammonium hydroxide-hydrogen peroxide. Soon other methods were developed to prepare larger amounts of the element. All isotopes were found to be radioactive and unstable. At Oak Ridge National Laboratory, the reduction of the technate with hydrogen gave the metal which tarnished slowly in moist air (1952). Although technetium has not been found on earth, its spectral lines are observed in older stars (though not in the sun). Astronomers believe that technetium is formed continuously in the later stages of a star, and that the sun is too young for this to occur.

Technetium, not occurring in nature, was the first element to be produced artificially. All isotopes of technetium are radioactive. Technetium is not generally available for consumer applications, although Tc-99m is widely used for biological tracer studies. The "m" represents "metastable" — the isotope decays with a 6-hour half-life with the emission of only gamma-rays. Mapping blood circulatory systems is particularly effective with Tc-99m.

Promethium

Pm 61 (145)
[*Promethus*]
Prepared 1945, metal isolated 1963
mp 1042°; bp 3000°; sp gr 7.26

In 1945 J. A. Marinsky, L. E. Glendenin, and C. D. Coryell at Oak Ridge National Laboratory obtained a mixture of fission products of uranium; by using ion-exchange chromatography on Amberlite resin they were able isolate element 61 in milligram quantities. This ion-exchange technique had been developed for the transuranium elements and was the same method utilized for separation of the rare earths (see Chapter 11). They named the element *promethium* after Prometheus, the Titan who stole fire from heaven for use on earth — symbolizing the awesomeness of nuclear power. In 1963 Fritz Weigel obtained the metallic element by heating promethium trifluoride with lithium in a tantalum crucible.

Promethium, never found naturally on earth, has been observed in stars. The longest-lived isotope of promethium is Pm-145, with a half-life of only 17.7 years. Research is being conducted to explore its use in a nuclear-powered battery.

Francium and Astatine

(See Chapter 13, pages 77-78)

Transuranium elements

The three main players of the Transuranium Game have been the University of California-Berkeley; GSI (Gesellschaft für Schwerionenforschung), Darmstadt (near Frankfort), Germany; and the Joint Institute for Nuclear Research, Dubna (near Moscow), Russia. The leaders of the American effort have been Glenn Seaborg and Albert Ghiorso. G. N. Flerov has headed the Russian development. At G.S.I. in Darmstadt, Matthias Schädel has been particularly successful in conducting *chemical* reactions including *analytical separations* with heavy elements, notably seaborgium (they must be done rapidly, in a matter of seconds!).

Over the past half century each of the three research groups has adopted a particular approach that appears to be successful with a particular group of elements. The Berkeley approach — to bombard elements with highly energetic light particles to create a new, fused species — worked for the first few decades. However, the resulting particles were so energetic that they tended to fission rather than relax into a stable state, and the effort stalled after a dozen elements or so. The German approach was to accelerate heavier particles to bombard light targets, resulting in fused products with lower excitation energies. This process is known as "cold fusion" (not to be confused with the discredited reaction occurring at conventional laboratory temperatures). The Russian group has adopted the same approach.

Here is a listing of the transuranium elements. Sometimes elements beyond 100 are called "transfermium." Above lawrencium (103), the last actinide, the elements are called "superheavy." Above 110, the elements are of great theoretical interest because some of them *might* be surprisingly stable — if only one can discover a way to synthesize them. These stable elements would lie in a theoretical "Isle of Stability" in a sea of uncharted waters.

Neptunium Np 93 237.048

[*Neptune*] Discovered 1940 mp 640°; bp 3902°; sp gr 20.45

Neptunium was the first artificially synthesized transuranium element, prepared in 1940 by bombarding uranium-239 with neutrons, by E. M. McMillan and P. H. Abelson. Np-237 can be prepared in large (gram) quantities as a byproduct of nuclear reactors. Longest-lived isotope: Np-237, with a half-life of 2.14×10^6 years.

Plutonium Pu 94 (244)

[*Pluto*] Discovered 1940 mp 641°; bp 3232°; sp gr 19.8

Plutonium was prepared in 1940 by bombarding uranium with deuterons by Seaborg, McMillan, Kennedy, and Wahl. Plutonium is now prepared in kilogram quantities. Plutonium was used in the atomic bomb at Nagasaki (uranium-235 was used at Hiroshima). Plutonium is a very dangerous radiological hazard. Longest-lived isotope: Pu-244, with a half-life of 8.0×10^7 years.

Americium Am 95 (243)

[*America*] Discovered 1944 mp 944°; bp 2607°; sp gr 13.6

Americium was produced in 1944 by Seaborg, James, Morgan, and Ghiorso by reacting plutonium with neutrons, and is now prepared in large quantities by the natural decay of plutonium. Americium is used as the radioactive agent in smoke detectors. Longest-lived isotope: Am-243, with a half-life of 7370 years.

Curium Cm 96 (247)

[*Curie*] Discovered 1944 mp 1340°; sp gr 13.5

Curium was produced in 1944 by Seaborg, James, and Ghiorso by bombardment of plutonium with helium. Longest-lived isotope: Cm-247, with a half-live of 1.56×10^7 years.

Berkelium Bk 97 (247)

[*Berkeley*, site of transuranium discoveries] Discovered 1949

Berkelium was produced in 1949 by Seaborg, Thompson, and Ghiorso by reacting americium with alpha particles. Longest-lived isotope: Bk-247, with a half-life of 1400 years.

Californium Cf 98 (251)

[*California*, site of Berkeley laboratories] Discovered 1950

Californium was produced by Seaborg, Thompson, Ghiorso, and Street by bombarding curium with helium. Longest-lived isotope: Cf-251, with a half-live of 900 years.

Einsteinium Es 99 (254)

[Albert *Einstein*] Discovered 1952

Einsteinium was detected in the debris from the first hydrogen bomb by Ghiorso and others. Longest-lived isotope: Es-252, with a half-life of 1.29 years.

Fermium Fm 100 (257)

[Enrico *Fermi*, discoverer of chain reaction] Discovered 1952

Fermium was detected in the debris from the first hydrogen bomb by Ghiorso and others. Longest-lived isotope: Fm-237, with a half-life of 110.5 days.

Mendelevium Md 101 (260)

[Dimitri *Mendeleev*] Discovered 1955

Mendelevium was synthesized by Seaborg, Thompson, Ghiorso, and street by bombarding einsteinium with alpha particles. Longest-lived isotope: Md-258, with a half-life of 51.5 days.

Nobelium No 102 (259)

[Alfred *Nobel*] Discovered 1958

Nobelium was produced by bombarding curium with carbon by Seaborg, Ghiorso, Sikkeland, and Walton. Longest-lived isotope: No-255, with a half-life of 3.1 minutes.

Lawrencium Lr 103 (262)

[Ernest *Lawrence*, inventor of the cyclotron] Discovered 1961

Lawrencium was produced by Ghiorso, Sikkeland, Larsh, and Latimer by bombarding californium with boron atoms. Longest-lived isotope: Lr-256, with a half-life of 28 seconds.

Rutherfordium Rf 104 (261)

[Ernest *Rutherford*, discoverer of artificial trans-mutation] Discovered 1969

Rutherford was synthesized by Ghiorso and others by bombarding californium with carbon. Longest-lived isotope: Rf-257, with a half-life of 4.7 seconds.

Dubnium Db 105 (262)

[*Dubna*, Russia, site of Joint Institute for Nuclear Research] Discovered 1970

Dubnium was synthesized by Ghiorso and others by bombarding californium with nitrogen. Longest-lived isotope: Db-262, with a half-life of 34 seconds.

Seaborgium Sg 106 (263)

[Glenn *Seaborg*, discoverer of transuranium elements] <u>Discovered</u> 1974

Seaborgium was the first element named after a living person. It was produced by bombarding californium with oxygen, independently announced by workers at the Dubna, U.S.S.R. Institute and by the Lawrence Liver-more Laboratories. Longest-lived isotope: Sg-263, with a half-life of 0.8 second.

Bohrium Bh 107 (262)

[Niels *Bohr*, interpreted atomic structure of the atom] <u>Discovered</u> 1976

Bohrium was produced by bombarding bismuth with chromium in Germany. Longest-lived isotope? Bh-262, with a half-life of 0.1 second, has been observed. In the decay series of Element 111, Bh-264 with a half-life of 1.4 seconds was observed.

Hassium Hs 108 (265)

[Latin *Hassia*, Hessen, German state where the Gesellschaft für Schwerionenforschung, GSI, is located, in Darmstadt] <u>Discovered</u> 1984

Hassium was synthesized by bombarding lead with iron at GSI. Longest-lived isotope? Hs-265, with a half-life of 2 milliseconds, has been observed. In the decay series of Element 112, Hs-269 with a half-life of 9.3 seconds was observed.

Meitnerium Mt 109 (266)

[Lise *Meitner*, codiscoverer of fission, Fig. 87] <u>Discovered</u> 1982

Meitnerium was synthesized by bombarding bismuth with iron at GSI. Longest-lived isotope? Mt-266 has been observed with a half-life of 3.4 milliseconds. In the decay series of Element 111, Mt-268, with a half-life of 72 milliseconds was observed.

Darmstadtium Ds 110

[Darmstadt] <u>Discovered</u> 1994

This element was synthesized in Germany by bombarding bismuth with cobalt. Longest-lived isotope ? The half-life of the 269 isotope was 170 microseconds.

Roentgenium Rg 111

[Roentgen, discoverer of X-rays] <u>Discovered</u> 1994

This element was synthesized in Germany by bombarding bismuth with nickel. Longest-lived isotope? The half-life of the 272 was 2042 microseconds.

Element 112 112 <u>Discovered</u> 1996

This element was synthesized in Germany by bombarding bismuth with zinc. Longest-lived isotope? The half-life of the 277 isotope was 240 microseconds.

Element 113 113 <u>Discovered</u> 2003

This element was produced in the decay sequence of element 115 (see below). Longest-lived isotope? The half-life of the 284 isotope was 1.2 seconds.

Element 114 114 <u>Discovered</u> 1998

This element has been claimed by the Russian research group by bombarding plutonium with calcium. Only one atom was detected. The half-life of the 291 isotope was an incredibly long 30.4 seconds, decaying to element-112, which in turn decayed in 15.4 minutes to element-110, which decayed in 1.6 minutes to element-108. Element-108, far from the island of stability, fissioned spontaneously. Another claim by the Russian group for Element 114 involved the 287 isotope, which had a half-life of 5 seconds, which decayed to Element 112 (isotope 283) which did not decay for several minutes.

Element 115 115 Discovered 2003

This element was synthesized in Dubna by bombarding americium with calcium. Longest-lived isotope? The half-life of the 288 isotope was 100 milliseconds.

Element 116 116 Discovered 2000

The Russian group claimed this element by bombarding curium with calcium. Isotope 292 decayed with a half-life of 50 milliseconds.

Element 118 118 Discovered 2006

This element was synthesized in Dubna by bombarding californium with calcium. Isotope 294 decayed with a half-life of 0.89 millisecond.

This list is to be continued (and must be verified!). . . .

Chemical Research on Transactinides. Despite the short lives and scarcity of the transfermium elements, some research has been performed to determine their chemical behavior. These impressive experiments (performed by GSI in Darmstadt) involve repetitive, short chemical experiments (less than 60 seconds long) that determine oxidation states, types of compounds formed, liquid chromatography behavior, and gas chromatography patterns. The transfermium element is detected on an atom-by-atom basis from its radioactivity. The GSI group has been concentrating particularly on the superheavy elements, the transactinides above lawrencium (103), the last element in the second f-row series of the Periodic Table.

The GSI group has been exploring the question: Should the superheavy elements be placed with the transition (d-block) elements? That is, should rutherfordium (104) be located below hafnium, dubnium (105) below tantalum, seaborgium (106) below tungsten, bohrium (107) below rhenium, and hassnium (108) below osmium? The GSI research has shown that there are disparities, but that nevertheless the transactinides may indeed closely resemble homologs in the respective chemical families. Seaborgium, for example, behaves quite like molybdenum and tungsten, with the volatile oxydichloride SgO_2Cl_2 *detected and ionic complexes (hydroxides and oxyfluorides) of hexavalent seaborgium in a liquid chromatography analyte. Thus, seaborgium fits well enough in its group to reaffirm the validity of the Periodic Table for the elements in the fourth d-row. Likewise, for the next element (107) the volatility of bohrium oxychloride,* BhO_3Cl*, fits well into the sequence* TcO_3Cl *and* ReO_3Cl*. Incredibly, the GSI group has extended studies as high as hassium (108), which falls below osmium in the Periodic Table. Indeed, the property that earmarks osmium (the volatility of its tetroxide), may be reflected to a certain extent in the chemistry of hassium oxide (*HsO_4*).*

It appears that there exists an "actinide contraction" just as there is a "lanthanide contraction," but relativistic effects lead to divergences for rutherfordium (104) and dubnium (105). For example, the ionic radius of tetravalent rutherfordium is much larger than those for tetravalent zirconium and hafnium (see page 84 where the radius of zirconium and hafnium atoms are almost identical). Rutherfordium forms fluoride complexes like zirconium and *hafnium, but the chemistry is not the same. Hence, if the chemistry were known only as far as rutherfordium (104), it would be difficult to say if the transactinides were "well-behaved" and should lie below hafnium, tantalum, tungsten, rhenium, and osmium in the Periodic Table. Fortunately, GSI has given to us a clearer picture of the chemistry of the transactinides and has located their proper place in the Periodic Table, just as Seaborg originally did for the actinides themselves.*

How Large Will the Periodic Table Grow? Although initial attempts to produce transuranium elements have been successful, the undertaking of the synthesis of higher elements — the "superheavy elements" — has proven to be challenging indeed. Two major problems are: insufficient neutrons and the natural repulsion of nuclei. The Darmstadt group has attempted to overcome the first problem with neutron-rich isotopes, but these are sometimes difficult to synthesize in sufficient quantity. There is no obvious way to solve the second problem. Yet, the search continues, if only to test the theoretical "Isle of Stability" — perhaps with an atomic number of 114 and a neutron number of 184 — that has been predicted by several scientists.

In nature, synthesis of heavier atoms requires a high flux of neutrons. This condition did not exist during the "Big Bang" and only light elements were formed at the creation of the universe — mostly hydrogen and helium. The interior of stars can produce medium elements. Heavy elements are created in the "r-process" of supernovae explosions where an incredible fury of neutrons is created. Hence, we on earth can thank some past supernova, somewhere and sometime in the past, for the supply of our thorium, uranium, and other heavy elements on Earth. Some models place this supernova about 5 billion (5 × 10^9) years) ago.

In addition to our terrestrial thorium and uranium, our ancient mother supernova also produced plutonium, americium, curium, einsteinium, etc., which have all disappeared since the creation of the earth 4.6 billion (4.6 × 10^9) years ago. Most probably the supernova also produced atomic numbers above 100 — but just how far above? If there is an "Isle of Stability," then why don't we see evidence of superheavy elements in nature? Is it because the "r-process"does not produce them, or because they are simply not stable enough?

Some scientists believe that if we were able to synthesize a nucleus with the correct proton number and neutron number, we might have an element with incredibly long half-lives, years or even thousands of years in magnitude! The problem, of course, is finding a way to load up a nucleus with a sufficiently large number of neutrons while keeping the nucleus thermally relaxed.

EPILOGUE

During the past several thousand years scientists have worked on a labor of love to present a portrait of the fundamental stuff of our chemical world. Each brush stroke has contributed to allow a fuller understanding of how our universe is made up. We know that all matter is made up of atoms — the word is taken from the Greek *atomos* for "indivisible" — and we have arrived at our quest of comprehending how these atoms assemble and rearrange to transform substances into others. Our heritage is rich, and we see far.

Now scientists are telling us that the atoms themselves are made up of yet smaller particles — quarks. The recent discovery of the "top" quark completes for the nuclear scientists an orderly collection of these curiosities. They tell us that unlocking the secretsof these particles may explain the very creation of the universe itself. It appears that the portrait is not yet finished.

All of this is driven by curiosity of Man to answer the physical riddles of the Universe. The same inquisitiveness that drove the alchemist to toil over his crucible, the miner to pick up a nugget here and there and wonder what this new glistening rock really was, the nuclear chemist to split the atom — is reflected in the modern scientists as he ponders over sprays of exotic particles that spew from collisions of relativistic leptons and baryons. It is as if we are now analyzing the condiments in the kitchen itself, tearing each spice apart into its constituent flavors. Scientists are suggesting that they may even tackle the question of why matter exists at all. This universe is indeed full of wonders.

PERIODIC TABLE OF THE ELEMENTS

(Mendeleev, 1871)

Row	1 R_2O	2 RO	3 R_2O_3	4 RO_2 RH_4	5 R_2O_5 RH_3	6 RO_3 RH_2	7 R_2O_7 RH	8 RO_4		
1	H (1)									
2	Li (7)	Be (9.4)	B (11)	C (12)	N (14)	O (16)	F (19)			
3	Na (23)	Mg (24)	Al (27.3)	Si (28)	P (31)	S (32)	Cl (35.5)			
4	K (39)	Ca (40)	“eka-B”	Ti (48)	V (51)	Cr (52)	Mn (55)	Fe (56)	Co (59)	Ni (59)
5	Cu (63)	Zn (65)	“eka-Al”	“eka-Si”	As (75)	Se (78)	Br (80)			
6	Rb (85)	Sr (87)	Y (88)	Zr (90)	Nb (94)	Mo (96)	(100?)	Ru (104)	Rh (104)	Pd (106)
7	Ag (108)	Cd (112)	In (113)	Sn (118)	Sb (122)	Te (125)	I (127)			
8	Cs (133)	Ba (137)	Di (138)	Ce (140)						
9										
10			Er (178)	La (180)	Ta (182)	W (184)		Os (195)	Ir (197)	Pt (198)
11	Au (199)	Hg (200)	Tl (204)	Pb (207)	Bi (208)					
12				Th (231)		U (240)				

Figure 1. Mendeleev’s Periodic Table, 1871. In constructing this table, Mendeleev assumed that the oxide of beryllium was BeO, the oxide of indium was In_2O_3, and the oxide of uranium was UO_3. The elements that are misplaced are underlined. “Di” was the symbol for didymium, which was later shown to be a mixture of rare earths. Mendeleev boldly predicted at least three new elements with specific properties: eka-boron, eka aluminum, and eka-silicon. These elements were discovered less than twenty years later (see Figure 2, page 96).

PERIODIC TABLE OF THE ELEMENTS

(Mendeleev, 1891)

1	2	3	4	5	6	7	8			1	2	3	4	5	6	7
R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7				R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7
										H (1)						
Li (7)	Be (9)	B (11)	C (12)	N (14)	O (16)	F (19)				Na (23)	Mg (24)	Al (27)	Si (28)	P (31)	S (32)	Cl (35.5)
K (39)	Ca (40)	Sc (44)	Ti (48)	V (51)	Cr (52)	Mn (55)	Fe (56)	Co (58.5)	Ni (59)	Cu (63)	Zn (65)	Ga (70)	Ge (72)	As (75)	Se (79)	Br (80)
Rb (85)	Sr (87)	Y (89)	Zr (90)	Nb (94)	Mo (96)		Ru (103)	Rh (104)	Pd (106)	Ag (108)	Cd (112)	In (113)	Sn (118)	Sb (120)	Te (125)	I (127)
Cs (133)	Ba (137)	La (138)	Ce (140)													
		Yb (173)		Ta (182)	W (184)		Os (191)	Ir (193)	Pt (196)	Au (198)	Hg (200)	Tl (294)	Pb (206)	Bi (208)		
			Th (232)		U (240)											

Figure 2. Mendeleev's Periodic Table, 1891, twenty years after his original table. Also known in 1891 were erbium, terbium, holmium, thulium, samarium, gadolinium, praseodymium, neodymium, and dysprosium — but no one knew how to fit them into the table. Another difficulty had been discovered: Brauner found an accurate atomic weight of tellurium as 127.6, not the previously accepted value of 125 — greater than that of iodine. Nevertheless, in the table above, Mendeleev continued to fix tellurium's weight at 125 in order to maintain a smoothly increasing atomic weight trend through the table. Mendeleev was correct in his placement of tellurium, but incorrect in thinking that its atomic weight was lower than that of iodine.

PERIODIC TABLE OF THE ELEMENTS
(Mendeleev, 1902)

Row	0 R	1 R_2O	2 RO	3 R_2O_3	4 RO_2 RH_4	5 R_2O_5 RH_3	6 RO_3 RH_2	7 R_2O_7 RH	8 RO_4		
1		H 1.008									
2	He 4.0	Li 7.03	Be 9.1	B 11.0	C 12..0	N 14.0	O 16.0	F 19.0			
3	Ne 19.9	Na 23.0	Mg 24.3	Al 27.0	Si 28.4	P 31.0	S 32..0	Cl 35.4			
4	Ar 38	K 39.1	Ca 40.1	Sc 44.1	Ti 48.1	V 51.4	Cr 52.1	Mn 55.0	Fe 55.9	Co 59	Ni 59
5		Cu 63.6	Zn 65.4	Ga 70	Ge 72.3	As 75	Se 79	Br 79.9			
6	Kr 81.8	Rb 85.4	Sr 87.6	Y 89.0	Zr 90.6	Nb 94.0	Mo 96.0		Ru 101.7	Rh 103.0	Pd 106.5
7		Ag 107.9	Cd 112.4	In 114.0	Sn 119.0	Sb 120.0	Te 127	I 127			
8	Xe 128	Cs 132.9	Ba 137.4	La 139	Ce 140						
9											
10				Yb 173		Ta 183	W 184		Os 191	Ir 193	Pt 194.9
11		Au 197.2	Hg 200.0	Tl 204.1	Pb 206.9	Bi 208					
12			Ra 224		Th 232		U 239				

Figure 3. Mendeleev’s last Periodic Table, 1902, four years before his death. During Mendeleev's funeral procession, mourners carried not crosses but Periodic Tables! The power of his table is obvious here, as it will accommodate an entire new family (the inert gases, discovered during the 1890s). In this table Mendeleev conceded tellurium's higher value, but he stubbornly did not allow its value to surpass that of iodine. The following elements, known at the time, were not included: Er, Tb, Ho, Tm, Sm, Gd, Pr, Nd, Dy, Eu, Po, Ac, Rn.

PERIODIC TABLE OF THE ELEMENTS

(Brauner, 1902)

Row	0	1	2	3	4	5	6	7	8		
1		H (1)									
2	He (4)	Li (7)	Be (9)	B (11)	C (12)	N (14)	O (16)	F (19)			
3	Ne (20)	Na (23)	Mg (24)	Al (27)	Si (28)	P (31)	S (32)	Cl (35.5)			
4	Ar (40)	K (39)	Ca (40)	Sc (44)	Ti (48)	V (51)	Cr (52)	Mn (55)	Fe (56)	Co (59)	Ni (59)
5		Cu (63)	Zn (65)	Ga (70)	Ge (72)	As (75)	Se (78)	Br (80)			
6	Kr (82)	Rb (85)	Sr (87)	Y (89)	Zr (90)	Nb (94)	Mo (96)	(100)	Ru (102)	Rh (103)	Pd (106)
7		Ag (108)	Cd (112)	In (114)	Sn (119)	Sb (120)	Te (128)	I (127)			
8	Xe (128)	Cs (133)	Ba (137)	La (139)	Ce (140)	Pr (141)	Nd (144)	(145)			
					(147)	Sm (148)	Eu (151)	(152)			
					(155)	Gd (156)	(159)	(160)			
					Tb (163)	Ho (165)	Er (166)	(167)			
					Tm (171)	Yb (173)	(176)				
					(178)	Ta (182)	W (184)	(190)	Os (191)	Ir (193)	Pt (195)
9		Au (197)	Hg (200)	Tl (204)	Pb (207)	Bi (209)	(212)	(214)			
10	(218)	(220)	Ra (225)	(230)	Th (233)	(235)	U (239)				

Figure 4. Brauner's Periodic Table of the elements, 1902. By this date a whole new family had been recognized — the inert gases. Brauner bravely included a number of rare earths in an arbitrary, but imaginative design. Elements known but not included in the table are dysprosium, polonium, actinium, and radon. In this scheme he predicts 98 elements through uranium (6 too many!). Sense could not be made of the Periodic Table until Bohr's understanding of s, p, d, and f block elements (see Figure 5, page 99).

PERIODIC TABLE OF THE ELEMENTS

(1925)

1A	2A	3B	4B	5B	6B	7B		8B		1B	2B	3A	4A	5A	6A	7A	8A
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	43	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	85	Rn
87	Ra	Ac	Th	Pa	U												

*Rare earths	Ce	Pr	Nd	61	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

Figure 5. Periodic table of the elements, 1925, after Moseley had defined atomic number in terms of his X-ray data, and Bohr had explained the behavior of transition elements and rare-earth elements in 1922. Hafnium was discovered in zirconium ore after Bohr's suggestion that the missing element would behave more like zirconium than like a rare earth element. Rhenium was discovered from platinum ores. "Masurium" (eka-manganese, 43) and "illinium" (the missing rare earth, 61) were announced but later discredited.

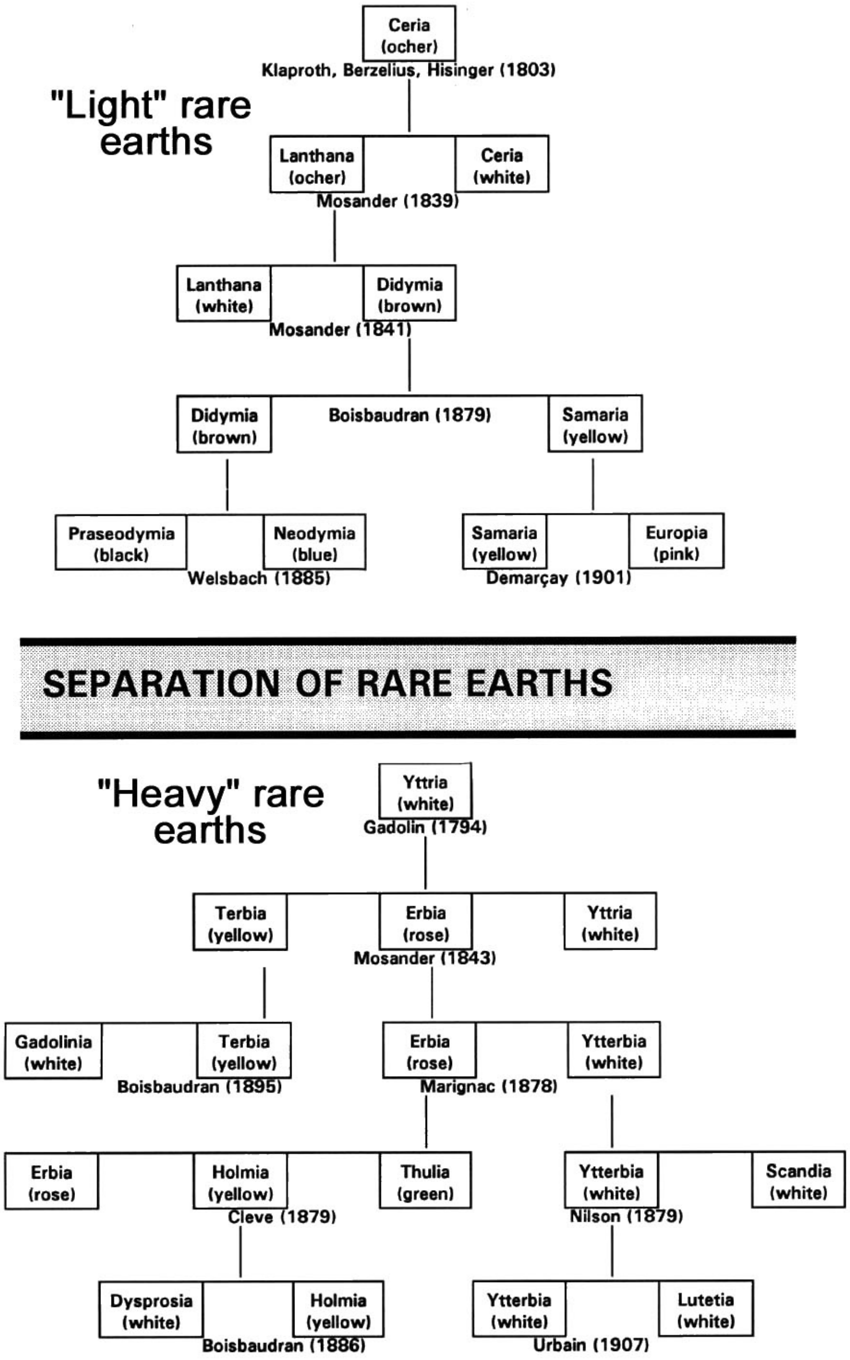

Figure 6. Flowchart of the historical chemical separation of the rare earth elements. The rare earths are broadly separated into the "light" rare earths (top half of figure) and the "heavy" rare earths (bottom half of figure). The difference of the two groups is due to the lanthanide contraction, which causes the atomic radii of elements of the first half of the f-block of the Periodic Table to larger (with a radius closer to that of cerium) and thus heavier (larger atomic density); and which causes the atomic radii of elements of the second half of the f-block of the Periodic Table to be smaller (with a radius closer to that of yttrium) and thus lighter. In nature, the rare earths tend to be found with either the common "light" rare earth (cerium) or the common "heavy" rare earth (yttrium), according to the respective atomic radii.

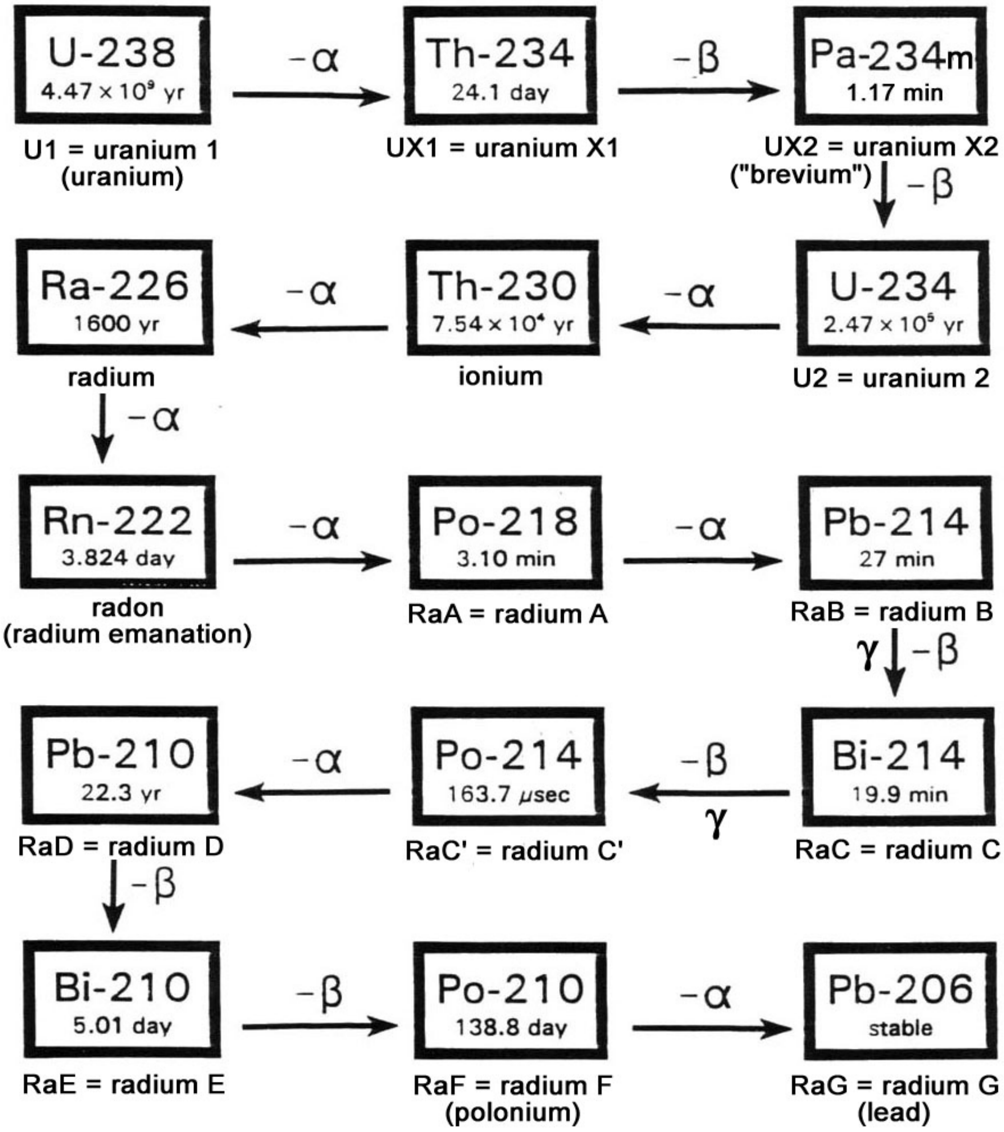

Figure 7. Radioactive decay series originating from uranium-238. Half-lives are shown for each isotope. The natural abundance of uranium-238 in the earth's crust is 99.27%. The original names given during the discovery of the radioelements (1900-1918) are listed below the respective boxes. This sequence gives rise to the radium and polonium discovered by the Curies. This sequence also is responsible for the isotope of radon with the longest half-life. Pa-234m is the metastable isotope of protactinium-234, which was the "brevium" discovered by Fajans and Göhring in 1913 (the ground state Pa-234, which is produced by an isomeric transition process to the extent of 0.16% from "brevium," has a half-life of 6.70 hr and also proceeds to U2; historically this isomeric ground state of Pa-234, discovered in 1921, was called "UZ").

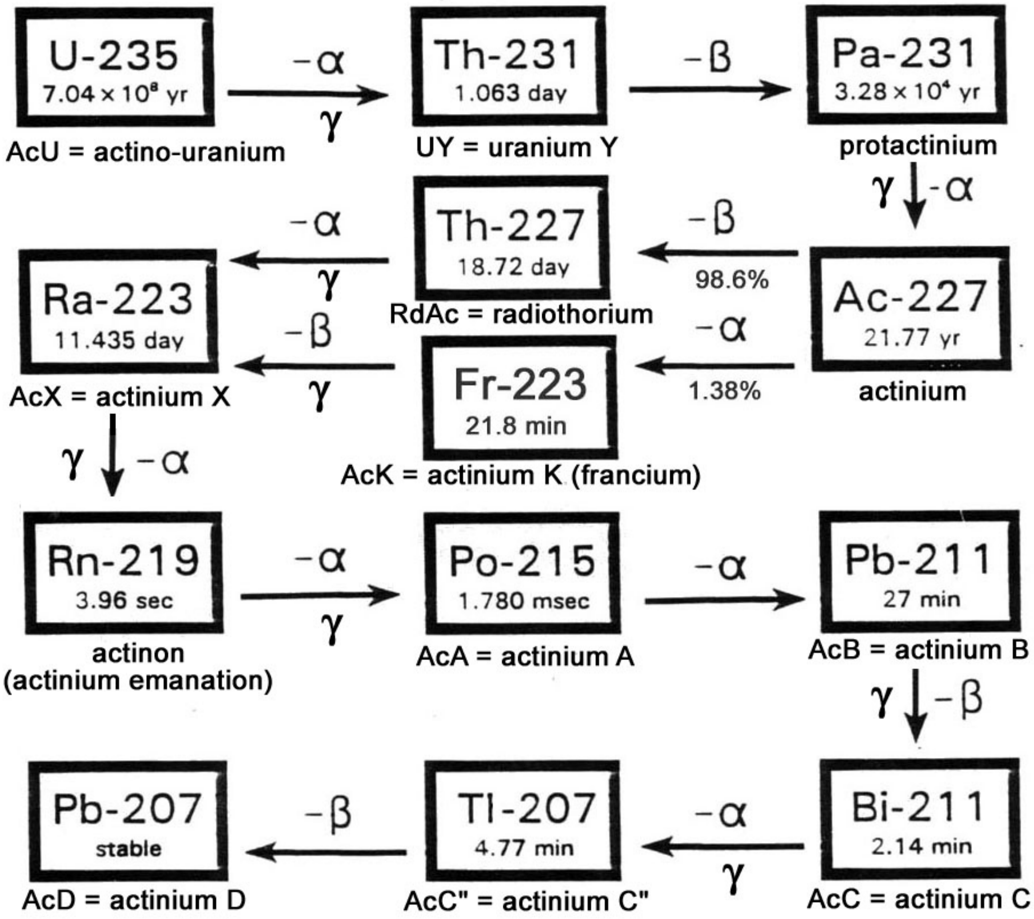

Figure 8.Radioactive decay series originating from uranium-235. Half-lives are shown for each isotope. The natural abundance of uranium-235 in the earth's crust is 0.72%. The original names given during the discovery of the radioelements (1900-1918) are listed below the respective boxes (but actinium K was not indisputably discovered until 1939). Originally, this series was known as the actinium sequence before it was understood that it arose from an isotope of uranium; Rutherford provisionally called this isotope "actino-uranium" in 1929. This sequence gives rise to the francium discovered by Perey; and to the actinium discovered by Debierne; and to the protactinium discovered and prepared in 1918 independently by Hahn and Meitner, and by Soddy and Cranston, and named by Hahn and Meitner (see "brevium," the short-lived isotope of protactinium discovered in 1913, in Figure 7).

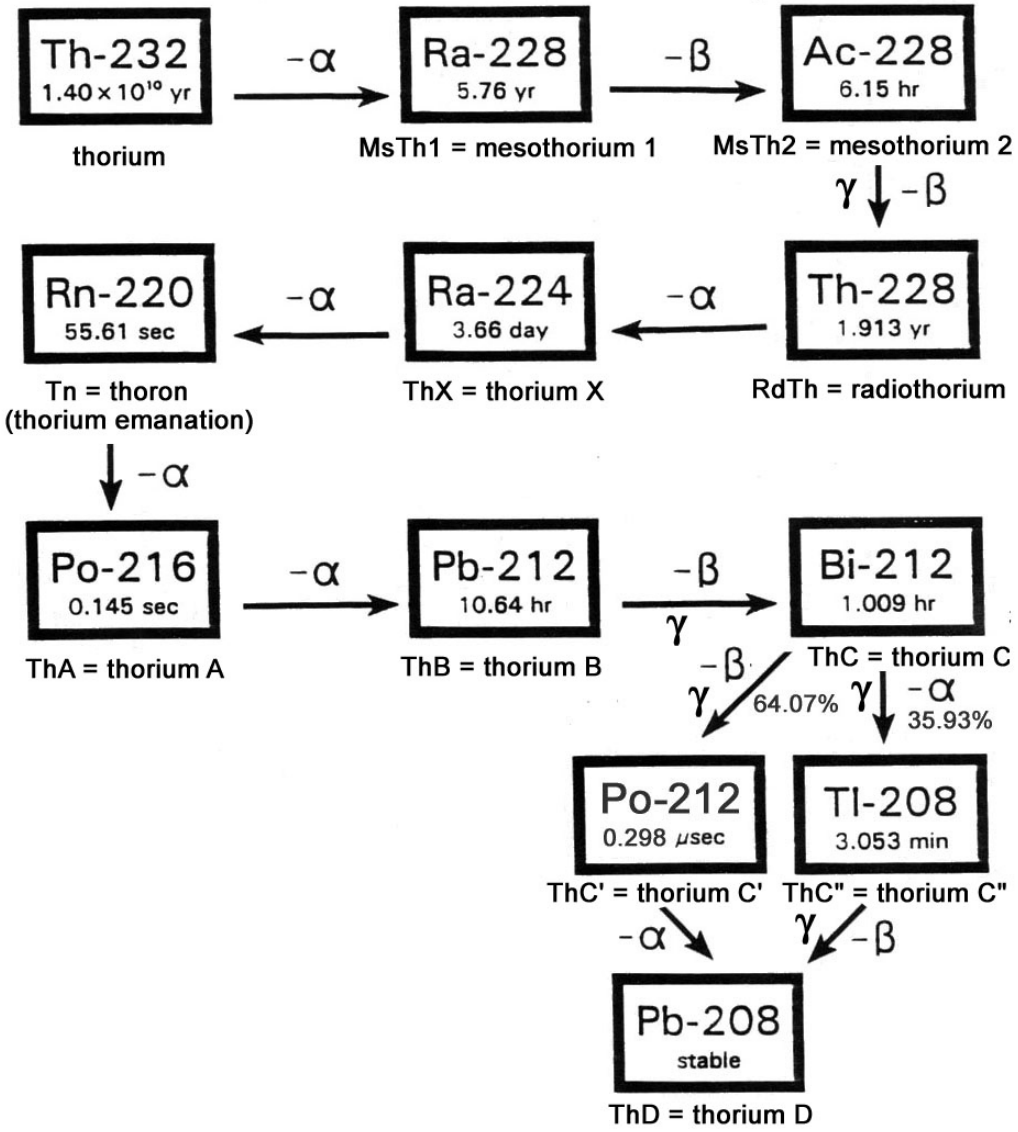

Figure 9. Radioactive decay series originating from thorium-232. Half-lives are shown for each isotope. The natural abundance of thorium-232 in the earth's crust is 100%. Even though thorium-232 has a long half-life, there are no more long-lived members in this series, and once an atom of thorium decays it rapidly cascades to stable lead. The original names given during the discovery of the radioelements (1900-1918) are listed below the respective boxes. Rutherford and Soddy made their original radon investigations on thorium emanation (radon-220) produced in this sequence — a challenging problem considering the short half-life (less than a minute). Their study of thorium emanation allowed the first recognition of natural transmutation of elements as a fact.

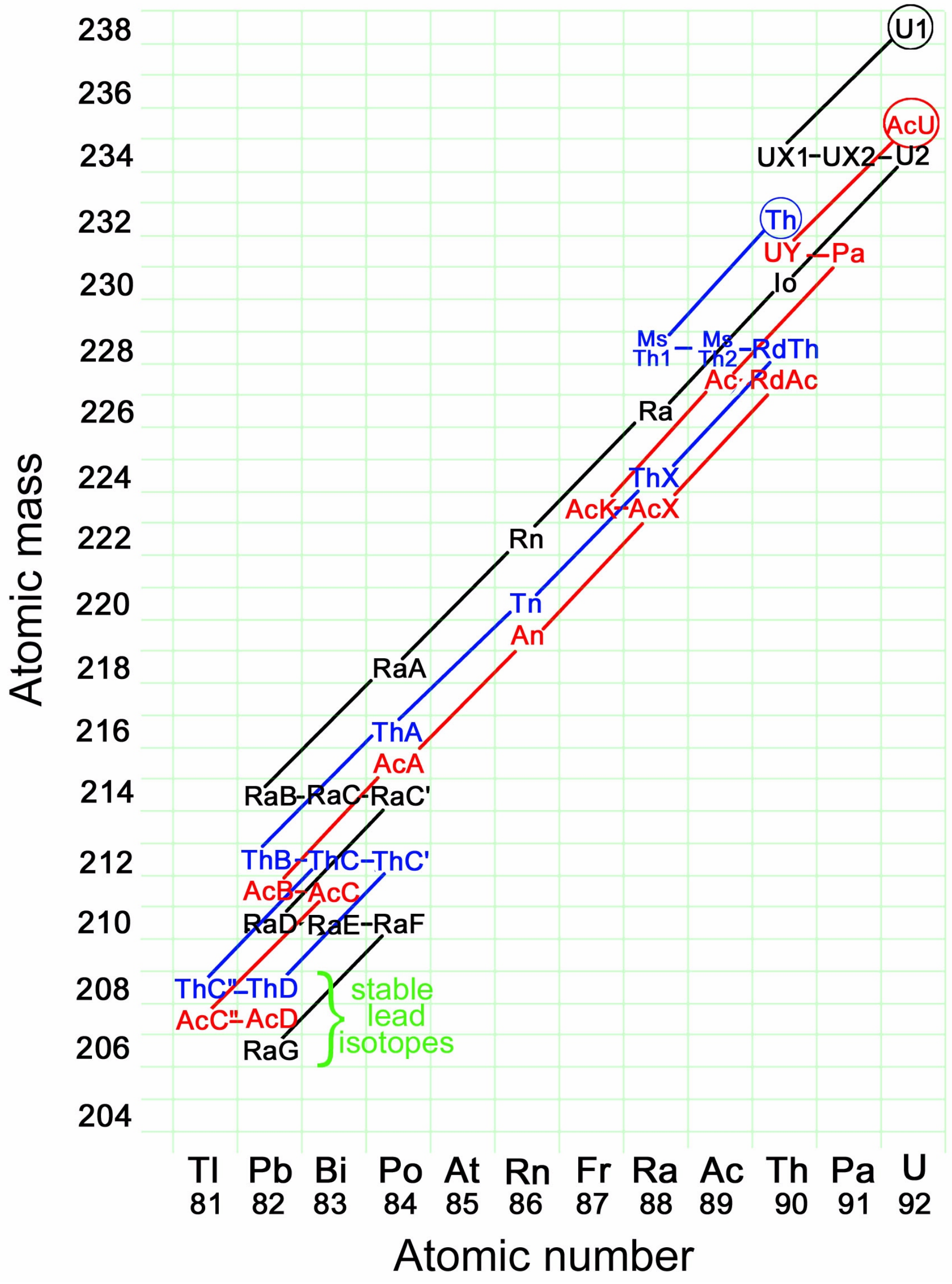

Figure 10. Composite graph of displacement laws, integrating Figures 7-9. The uranium-238 (U1) decay sequence is coded in black; uranium-235 (AcU) in red; thorium-232 (Th) in blue. Each alpha decay moves an atom left (two units) and down (four units); each beta decay right (one unit). Lack of atomic mass data originally prevented one from knowing just where on the vertical scale the actinium sequence (red) lay, and furthermore it was believed (incorrectly) that this sequence branched off the main uranium sequence (black). However, mass spectral data in 1929 by Aston allowed Rutherford to identify actino-uranium with a mass of 235, which precisely anchored the actinium sequence and identified it as an independent scheme. Notice that there is no astatine (At) in these natural sequences; this element was not discovered until 1940 when it was artificially synthesized. See note about UZ (isomeric form of UX2) in caption for Figure 7.