

# CHAPTER 1

## Setting the Stage

*O Unseeing Lead, would that thou hadst never appeared in the earth  
Or in the sea, or on the land, but that thou didst have thy habitation in Tartarus  
And Acheron, for out of thee arise many things pernicious to mankind*

—Timocreon of Rhodes

*All happy marriages are like one another; each unhappy marriage is unhappy in its own way.*

—Tolstoy, paraphrased

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## Introduction

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Written love stories have at least three characters: the two who love each other and the one who interprets the love story. As much as one wants the lovers to speak for themselves, the author provides a frame of reference. Many years ago I received a degree in cultural anthropology and Latin American studies and lived in a small Central Mexican town where the elders still spoke Nahuatl, the Aztec language. Later I became an environmental chemist. It was easier and more predictable, to follow the trends of chemical laws than to follow and fully understand the connections between large groups of people. When I became a chemist, I found that I could stop any conversation by announcing my profession. I was apparently perceived as some sort of computer clothed in skin. My father, trying to understand my new interests, made a remark to the effect that now I would sell out and make Agent Orange. I was now the mad scientist. Somehow my experience as a chemist set me apart from normal humanity. My experience with chemistry does not conform to either stereotype: the logical, dispassionate observer, or the venal, evil sellout. The story of lead interested me because it seemed a good way to explore the relationship between science, scientists, and the rest of humanity. How did we humans end up with the relationship we have today with lead? Why was lead so desirable that it spread throughout the world with a rapidity matched only by technologies associated with war? Were there no other technologies that could have

been used instead? Was man simply venal and lazy in his choice of lead? Or can it be postulated that the relationship between man and lead was a case of **chemical predestination**?

The intimate relationship of lead and humanity stretches through 5,000 years of history and over 7 continents. It has been most challenging to pick out a narrative thread through such temporal and spatial distances and to keep the narrative intact while examining underlying chemistry and technology. Where does a story begin? For whom is it the beginning and for whom is it the end? After some 9 years of research, I present here a “love” story framed by my particular biases. I present at each step of the way the stories of individuals in their own words or artworks. The chemistry framing the physical reality follows each collection of stories. The story of lead is exceeding diverse, like that of humanity. In some ways, however, the story of lead is shaped by its underlying chemistry. For example, over the course of human history, three separate groups of people independently discovered the art of highly articulated bronze work involving high additives of lead.

Since human stories are to be the vehicle for this environmental case history, I’ll open with a tale about Andrew Jackson.

\* \* \*

On an early autumn morning in 1805, in the backwater village of Nashville, a drama unfolded. It

originated in a horse racing bet and involved the future president of the United States, Andrew Jackson. Historian Robert V. Remini described the scene (Remini, 1981; Remini, 1984; Remini, 1988):

*“Are you ready?” asked Overton.*

*“I am ready,” replied Jackson*

*“Fere!” Cried Overton in his old-country accent.*

*Dickinson quickly raised his pistol and fired. The ball struck Jackson in the chest. As it hit, a puff of dust rose from the breast of his coat and Jackson slowly raised his left arm and placed it tightly against his throbbing chest. He stood very still, “his teeth clenched.”*

*Dickinson, horrified to see Jackson still standing, drew back a step. “Great God!” he cried, “Have I missed him?”*

*“Back to the MARK, sir!,” shouted Overton as he aimed his pistol at the dumbstruck man.*

*Dickinson regained his composure, stepped back to the mark, and waited for Jackson’s return. He was at the General’s mercy. Jackson could have been magnanimous and refused the shot or fired into the air, but he had promised to hit Dickinson and nothing could dissuade him. “I should have hit him,” he said, “if he had shot me through the brain.”*

*Slowly and deliberately Jackson raised his pistol and took aim. He squeezed the trigger. There was no explosion, only a click as the hammer stopped at half cock. The pause was an eternity. Dickinson waited. Jackson drew back the hammer, aimed again, and fired.*

*The bullet struck Dickinson just below the ribs. He reeled. His friends rushed forward and caught him as he fell. They stripped off his clothes to try to stop the flow of blood. But there was nothing they could do. The bullet had passed clean through his body, leaving a gaping hole. Charles Dickinson bled to death.*

*...The bullet Jackson took had shattered two ribs and buried itself in his chest. It could not be removed because it was lodged close to Jackson’s heart, so it remained right where it was...*

This was not the only bullet that Jackson carted around in him. In 1813 Jackson was involved in an altercation with one Thomas Benton. After threatening to horsewhip Benton, Jackson walked past the Bentons’ hotel carrying a horsewhip. On his the return trip, the Bentons were waiting. Historian Remini



**Figure 1.1:** Andrew Jackson, seventh President of the United States is thought to have suffered from lead poisoning from bullets retained in his body after fighting duels.

describes this scene as well:

*As Jackson came abreast of Thomas he suddenly turned toward him, brandished his whip, and cried, “Now, you damned rascal, I am going to punish you. Defend yourself.”*

*Benton reached into his pocket as if fumbling for a gun. Instantly the General drew his own gun and backed Thomas into the hotel. Jesse, meanwhile ducked through the barroom to a door that opened into a hallway that led to the rear porch overlooking the river. From that position he raised his pistol and fired at Jackson, hitting him the arm and shoulder with a slug and a ball. Old Hickory pitched forward, firing at Thomas as he fell. The shot missed. Thomas then fired twice at the prostrate figure, and Jesse faced forward to shoot again but was interrupted by a bystander. .... His shoulder was shattered by the slug and his arm pierced by a ball which lay embedded against the upper bone of his left arm. He soaked through two mattresses before the doctors could stanch the flow of blood. All but one physician recommended the amputation of the shattered arm.*

*“I’ll keep my arm,” ordered the General. With that, Jackson slipped into unconsciousness.*

The metal remained in his arm for nearly twenty years and was carried by him into his presidency of the United States. During that twenty year period, Jackson was plagued by ill health. The first major bout occurred in 1819. This bout was described by Remini: *“combined with the extreme fluctuations of mood that beset him—from rage over the censure ‘conspiracy’ to delirious exultation occasioned by the frenzied receptions the American people repeatedly accorded him. The rapid transitions from dejection to exhilaration may have induced a temporary emotional instability that led him to suspect*

plots and conspiracies against himself and the administration....

*“At 52, on his return to Washington he suffered a major collapse. He grew increasingly emaciated and he barely picked at his food. His chest throbbed constantly, and he brought up blood when he coughed. For a long time he needed a walking stick to steady his faltering steps.*

*“Similar ill health is recorded in Jackson’s letters. Shortly after his return to Tennessee following a brief two-month stint as Territorial Governor of Florida, Jackson suffered a severe physical breakdown. For four months, he wrote, ‘I have been oppressed with a violent cough, and costiveness.’ ...His wretched health necessarily affected his general disposition. Always sensitive, frequently petulant, constantly alert to slights, criticisms, or insults, he grew increasingly irascible as the level of pain intensified over the next five years. By 1824 his teeth were decaying very rapidly. But before they were extracted in 1828, he suffered severe tooth and jaw aches that murdered sleep and frazzled his nervous system. Thus, he sometimes lashed at his enemies with a savagery that shocked his admirers who were unaware of the degree of his misery.*

*“A constant burden for Jackson was his wretched health. Much of the winter he felt unwell and could not explain the cause. ‘I have been severely attacked with pains,’ he wrote, but the nature of the pains and their location he did not specify. Just pain. Constant pain. Almost every day he suffered excruciating headaches. ‘I shall when my head gets better write you more fully,’ he frequently scribbled at the end of his letters. In the late spring his nose became inflamed, and to make matters worse his old problem of ‘costiveness’ returned. ‘My bowels are become quite torpid,’ he told William Lewis, ‘and I have grown weary of taking medicine so frequently. I postponed it too long, having passed over three days without a passage.’ He would then resort to a high cathartic, usually Dr. Rush’s ‘Thunderbolt’ that would bring on nausea and severe diarrhea which could totally prostrate him.*

*“.... Dr. Francis May, his physician, regularly swabbed him with sugar of lead. It was widely believed at the time that sugar of lead, in addition to its astringent powers, could reduce inflammation. So Jackson both drank it and bathed in it. He took it internally to combat his supposed tuberculosis and chronic stomachaches, and externally for its antiphlogistic action. He even squirted it into his eyes when his sight began to falter.*

*“On June 8<sup>th</sup>, 1845, Andrew Jackson, son of an immigrant Irish housekeeper, teenage soldier of the American Revolution, conqueror of the Florida territories, and President of the United States, died. It has long been assumed that the immediate cause of Jackson’s death was heart failure, as evidenced by dropsy. But recently doctors have suggested that his death resulted from nephrotic kidneys caused by amyloidosis. This disease usually follows many years of infection. Certainly Jackson suffered a massive edema of the entire body during his last illness which, according to medical science, is not usual in congestive heart failure - at least not when the patient has suffered intermittent fluid retention over such a long period of time as Jackson did. Perhaps no single cause of death can ever be assigned. Jackson suffered from so many illnesses -respiratory and gastrointestinal, on top of which he regularly poisoned himself with calomel and mercury - that after a long and valiant struggle his body simply gave out.”*

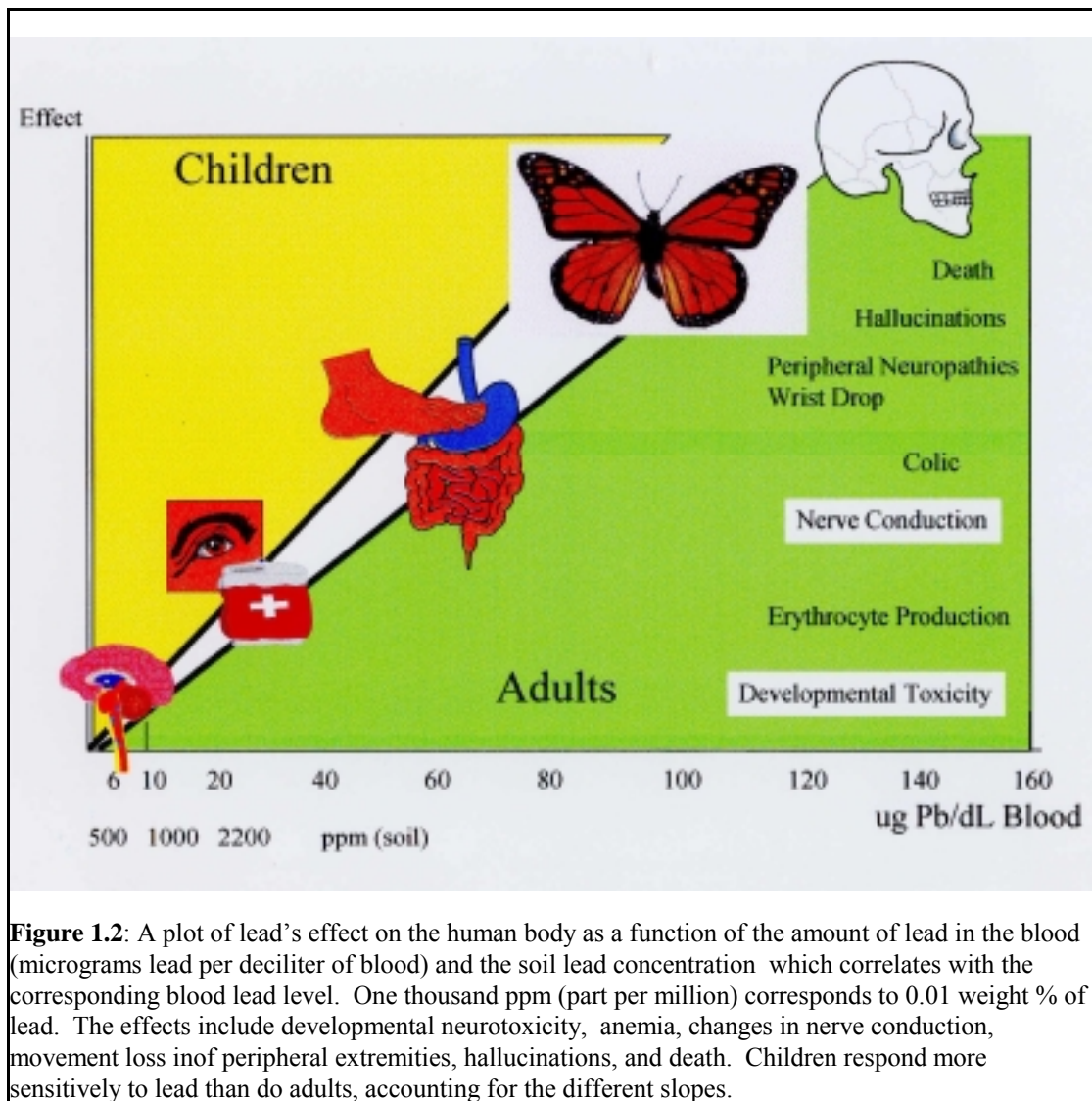
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All of Remini’s descriptions are consistent with lead poisoning. “Cositiveness” is a word for extreme cramping of the bowels: dropsy consists of fits, shaky limbs, and falling down sleeping. Additional symptoms of extreme lead poisoning are paranoia, problems with hearing, and inability to control the hands sufficiently for writing well. The lodging of the bullet within a joint where synovial fluid helped to increase the rate of dissolution is also consistent with lead poisoning. Subsequent physical evidence appears to corroborate the suspicion of lead poisoning.

In 1999, samples of Jackson’s hair were analyzed for both mercury and lead, Table G.10 (Deppisch et al., 1999). The hair of Andrew Jackson in 1815, shortly after the duels, yielded similar results to those obtained for Singaporean battery workers with elevated blood lead levels and mild symptoms of lead poisoning.

\* \* \*

As illustrated by the story of the 7<sup>th</sup> U.S. President, lead was an ordinary material used in a wide range of human activities such as warfare and medicine. It was also recognizable as a toxic material. This postscript of analytical chemistry providing physical evidence about probable cause is another important element of Jackson’s story.



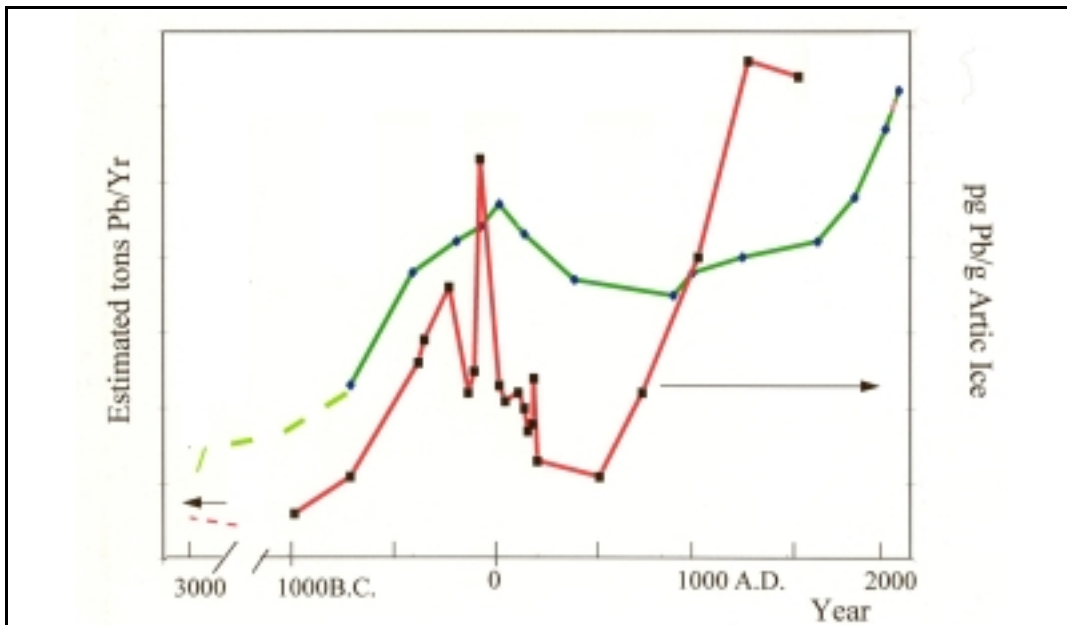
**Figure 1.2:** A plot of lead's effect on the human body as a function of the amount of lead in the blood (micrograms lead per deciliter of blood) and the soil lead concentration which correlates with the corresponding blood lead level. One thousand ppm (part per million) corresponds to 0.01 weight % of lead. The effects include developmental neurotoxicity, anemia, changes in nerve conduction, movement loss inof peripheral extremities, hallucinations, and death. Children respond more sensitively to lead than do adults, accounting for the different slopes.

Today we know that lead is a toxic poison (Figure 1.2) whose effects range from developmental neurotoxicities to death. Science has also tracked the historical deposition of lead into the Arctic ices (Figure 1.3) (Hong et al., 1994). Lead production began around 3000 B.C. and continues with some interesting peaks and valleys to modern times. Lead was one of the very first metals to be known in its pure form (Figure 1.4 and Table J.1).

Our job will be to figure out why lead was the first toxic metal used by man, why peaks and valleys occurred in its use and to find out when we became aware of its toxicity.

The early discovery of any element was made possible by six crucial factors:

1. The element must have occurred in proximity to an emerging agrarian economy which supported labor not directed at food gathering.
2. Regions of facile human migration should have experienced a **faster** rate of accumulated knowledge as well as a faster utilization of metallurgical practices.
3. The element was present in large enough **quantities** in the earth's crust to be "noticeable".
4. If the element occurred in a crystalline **form** or as a surface rock it helped in early

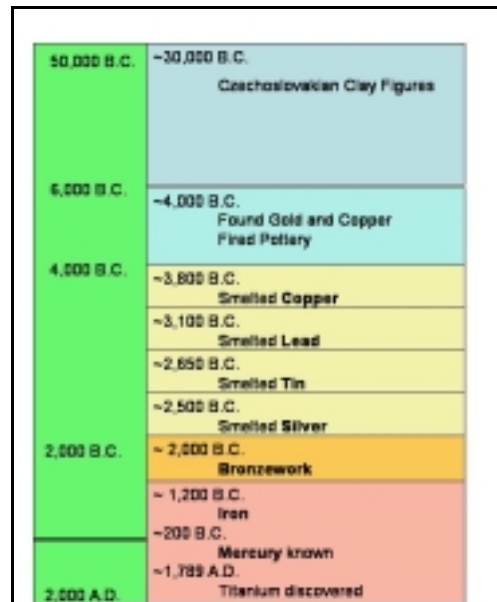


**Figure 1.3:** The estimated worldwide production of lead in tons per year is compared to the picograms ( $10^{-12}$  g Pb) of lead per gram of arctic ice with the date of the Arctic ice. Lead is first found around 3000 B.C. and became heavily utilized and dispersed by around 700-600 B.C. coinciding with the rise of Greek coinage. There was a fall lead production from 300 A.D. to about 800 A.D., then a continuous rise in deposition in the Arctic ices until the middle of the 20<sup>th</sup> century. Data source: Hong, et al, 1994.

- discovery. (An element can't help but be noticed if you stub your toe on it.)
5. The element had to have been **easily separated (melted?)** under rather primitive chemical laboratory conditions (large presence of oxygen, low temperatures).
  6. The element must have had some usable or **desirable property**. Often the desirable property was that of color. Other desirable properties were those of strength and malleability.

7. Factors 1, 2, 3, and 4 will be examined in Part I of the present chapter. Chapter 2 will examine factor 5, the separation of metals from ore, while chapter 3 will examine the manufacture of metallic objects. Chapter 4 will look at the use of lead in glazes and glass, and Chapter 5 will examine lead in pigments. Given the exploratory nature of the human animal and the physical characteristics of lead, it can be, after the fact, predicted that exploitation of lead would be among our earliest technological achievements. The use of lead in metallurgy, glazes, glass, and pigments points to a long association of the metal with humanity. This association gives rise to theories and metaphors about lead explored in Chapter 6. Chapter 7 will examine

modern technology of lead. The remainder of the book will explore lead's effects upon human history, health, and politics.



**Figure 1.4:** Time line for use and discovery of metals in the Middle East.

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## Part I: History, Art, and Technology of Lead Ores

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### MAN BEFORE LEAD

#### Location, Location, Location

Life began evolving about ~400 million years ago (mya). The mammalian species known as man achieved its nearly complete form about 5 million years ago (Time line J.2). During that entire evolutionary period, the earth surface concentration of lead was about 10 parts per million (ppm). Larger concentrations of lead, lead ore bodies, were, for the most part, locked in subterranean vaults. Where lead did hit the surface, it was generally of an insoluble or inert form. As a consequence, the biology of life has no currently known function for lead, not even as a trace element for nutrition. Worse, the biology of life has no known protective mechanism against lead.

Man could unleash lead from the subterranean ore bodies because some ore bodies were near agrarian societies capable of supporting non-hunters. The process may have been accelerated when

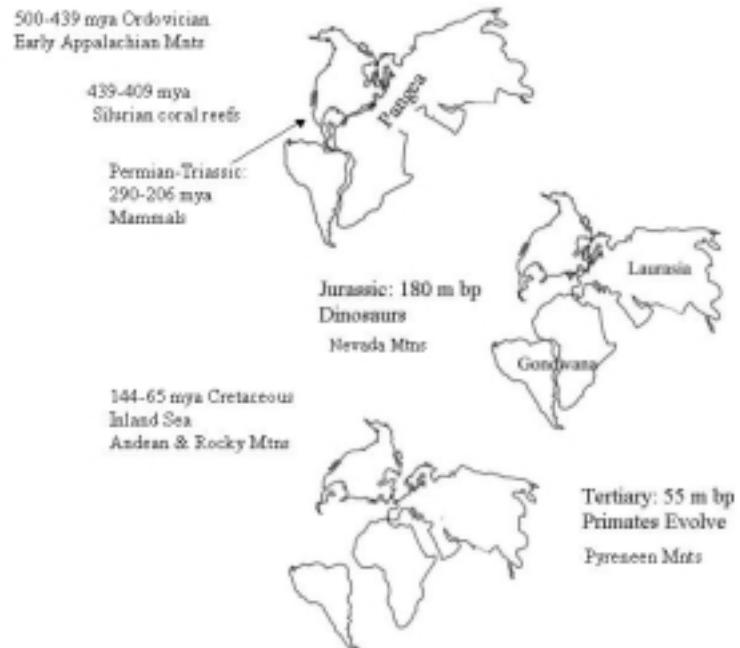
both these agrarian societies and lead ore bodies were near copper, the first metallurgically important metal.

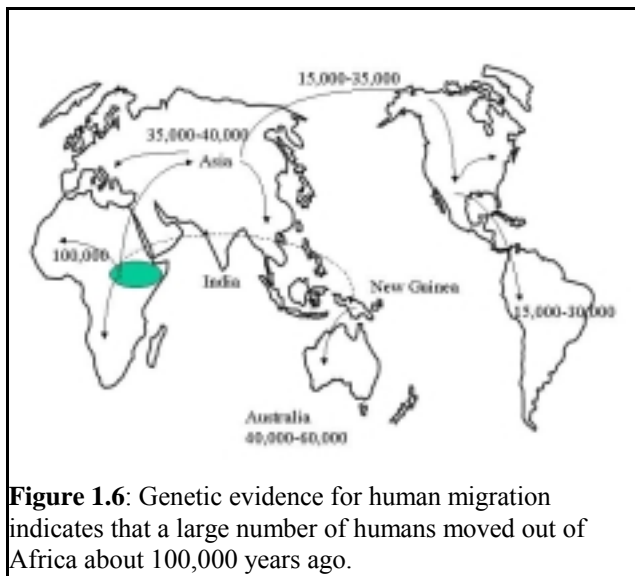
During the Pre-Cambrian period (>540 mya), the evolution of oxygen allowed for large amounts of calcite ( $\text{CaCO}_3$ ) and dolomite ( $\text{CaMgCO}_3$ ) to precipitate. Coral beds erupted during the Mississippian period (345 mya). A few lead ores were laid down in sedimentary process during this period (Evans, 1987). When the continents broke apart (Figure 1.5) and moved about the crust, these coral and carbonate beds served as the porous matrix in which later deposited metal ores could be found. Small forms of life evolved during this time period, but the explosion of large mass species occurs well after the formation of the oldest lead ore bodies.

The human path of evolution generally postdates the formation of even the newest lead ore bodies. Primates began evolving 65-55 mya on the continent of Gondwana (South America and Africa). Higher ape evolution in Africa, a region very poor in lead resources (see below), occurred after the

**Figure 1.5:**

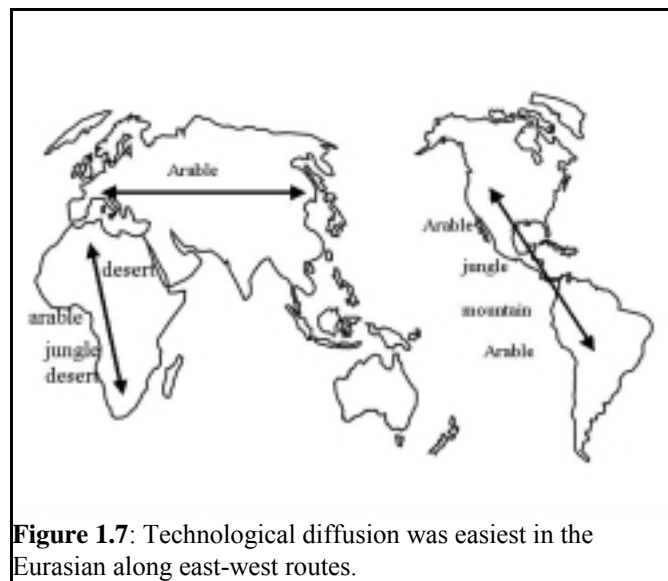
Continental drift causes mountains as well as inland seas to form where coral reefs grow. Mountain formation can be the source of energy for heating brine solutions which ultimately lead to ore body formation. Many of the ore bodies were formed before mammalian life and most were formed before human evolution.





species migrated from Africa about 200-100,000 years ago, populating China and the Mideast about 60 to 40,000 years ago. Humans moved to the New World with the Ice Age (approximately 30,000-15,000 years ago), when the ocean levels dropped due to the quantity of water stored in the glaciers. The drop of the ocean exposed a pathway across the Bering straits.

Human migrations 40,000 to 15,000 years ago were followed by the development of agrarian practices ~18,000 to 12,000 years ago. A wide variety of hypotheses have been put forward to explain the agricultural revolution. One hypothesis is that groups occupying food rich habitats became more sedentary and populous. These changes hampered their mobility and encouraged experimentation with agricultural practices.



Once agrarian practices were initiated neighboring groups could acquire agricultural technology, assuming that plants and animals were adaptable to a new region. This suggests agricultural technology would move across climatically similar regions. Most technical diffusion appears to cross east/west geography (similar latitudes) as opposed to north/south boundaries (cold/hot climate changes) Figure 1.7

Was there an abundance of lead in a form noticeable to and usable by early man in these areas? Geochemistry will answer these questions.

separation of South America and Africa. Evolution of the current human species appears to be related to *Australopithecines afarensis* (~5 mya), *Homo habilis* (2.4-1.4 mya years ago), and *Homo erectus* (~2 mya) (Feder and Park, 1998). About 500,000 years ago fire was “tamed”, i.e. used by humans.

Figure 1.6 shows a 1997 speculative map of human (*Homo sapiens*) migration, based on archaeological (bone and tool fragments) and genetic evidence. The older races have much larger amounts of genetic variation. The genetic information basically concurs with archaeological evidence indicating that the human

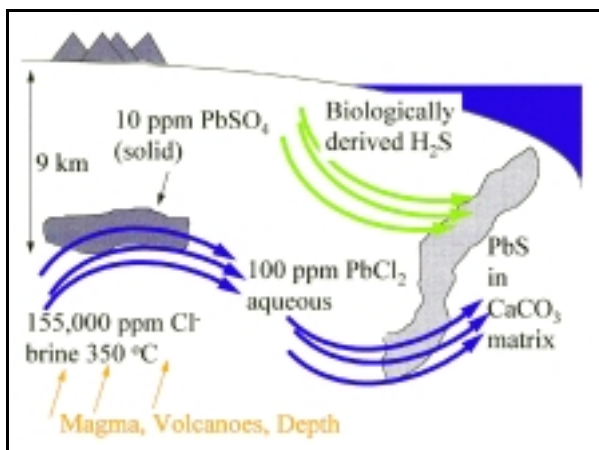
# LEAD BEFORE MAN

## Ore Formation

The previous outline of ore body formation needs to be completed. During the planetary formation process, lead, along with other elements, condensed to form the earth. The predominate form of the lead captured was lead-204. The number 204 refers to the number of neutrons and protons present in the nucleus of the lead atom. The lead so captured is thought to have spread homogeneously within the core. It was subsequently extruded to form crustal material. The result was a small amount of lead within surface rocks. These rocks spread uniformly throughout the crust. Uranium and thorium, were also extruded. With time, these decayed to lead.

When warm brine (salt water) passed over the crust, it collected and concentrated the lead by forming a water soluble lead salt, lead chloride (see Chapter 1, Part II: Chemistry). As the lead-bearing brine moved throughout the crust, it continued to collect and concentrate lead. This warm lead chloride-bearing brine encountered fractures in the crust (either due to breaks in rocks, or to porous, ancient, buried coral reefs). When this happened at the same time that it encountered a cooler sulfur containing fluid, the brine precipitated lead sulfide, or galena (Figure 1.8).

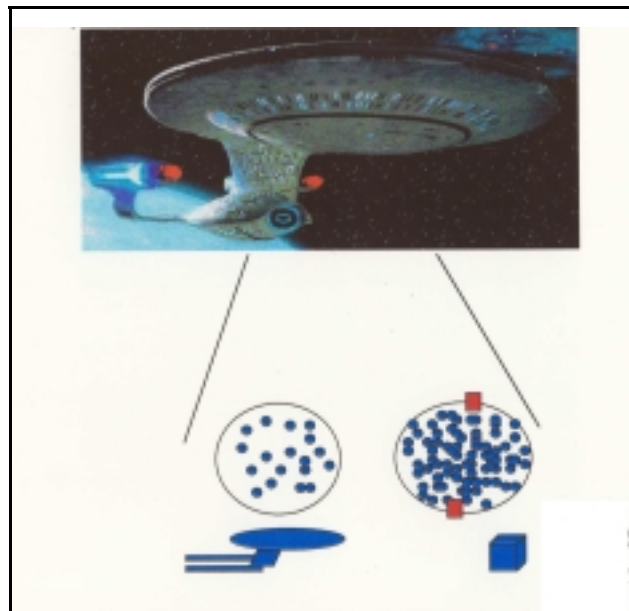
The precipitation region was therefore often associated with regions of the Earth where fractures were occurring (due to earthquakes, for example),



**Figure 1.8:** Ore formation occurs when dispersed lead (as, for example, PbSO<sub>4</sub>) is collected by hot salt water (brine). The heat comes from depth, magma, or volcanoes. The collected lead chloride precipitates in a carbonate (CaCO<sub>3</sub>) matrix derived from ancient coral beds. Precipitation occurs when the moving brine encounters a fluid high in sulfur (H<sub>2</sub>S).

where heat was available (due to earthquakes and volcanoes) and often where there were buried coral-bearing sea beds. The altered coral formed carbonates and dolomites. Both of these have a chemical form that accepts substitution of lead for calcium, thus beginning the precipitation process of the lead sulfide. These compounds “accept” lead partly because lead ion, Pb<sup>2+</sup>, masquerades as calcium ion, Ca<sup>2+</sup>, due to their similar sizes and charge. The similarity of lead and calcium ions causes the body to mistakenly adsorb lead, leading to the biological uptake of lead (Figure 1.9).

The association of lead sulfide ores with dolomitic bases that derived from the nucleation chemistry of divalent ions on the carbonates has important contemporary consequences. Most commercial antacids are mined dolomites and aluminum hydroxides. In 1986, California passed Proposition 65, which requires the governor to publish a list of toxic chemicals and their allowed limits (Wolf, 1997). If a product contains more of the toxic material



**Figure 1.9:** In the television series “Star Trek” the star ship Enterprise has long range sensors which detect various objects such as a Federation ship (left) and an enemy Borg ship (right). A tractor beam can pull the ships into dock, but only the Federation ships fit in the docking bay. Similarly, both calcium ion, Ca<sup>2+</sup>, left, and lead ion, Pb<sup>2+</sup>, have the same ionic size and charge. At a distance they can be electrostatically mistaken for each other. Lead differs from calcium by having many more electrons and by having a pair of electrons (red blocks), which can display exhibit stereochemistry. When lead ‘docks’ at an enzyme these extra electrons disrupt the enzyme function.



than allowed (i.e. more than 0.5 micrograms Pb) the amount must so be specified on the label. In April 1997, the California attorney general announced a settlement with SmithKline Beecham Consumer Healthcare, Warner-Lambert Company, American Home Products Corporation, Pharmavite Corporation, General Nutrition Corporation, Perrigo Company, Schering-Lough Health Care Products, Inc., and Twin Laboratories for their failure to divulge calcium supplement and antacid lead levels above the published allowable values. The requirement for lower lead limits requires either a dolomitic source lower in native lead or further processes to remove lead from the product. Several commercial Ca supplements have been shown to contain 0.114 to 0.259 micrograms Pb. The total amount of lead consumed could exceed 0.5 micrograms/day if several antacid tablets are taken (Wolf, 1997). On the other hand, the ability of the body to absorb lead inversely scales with calcium. Large amounts of calcium suppress adsorption of lead. Thus the actual biologically available amount of lead is to be substantially less than the total amount of lead present (Gulson et al., 2001a; Gulson et al., 2001b).

#### An Incredibly Brief Survey of Some Lead Ore



**Figure 1.10:** Separation of South America and Africa created the Benue Trough and the Amazon Rift Zone (shade) regions with lead mineralization. Source: Evans, A. M., 1987

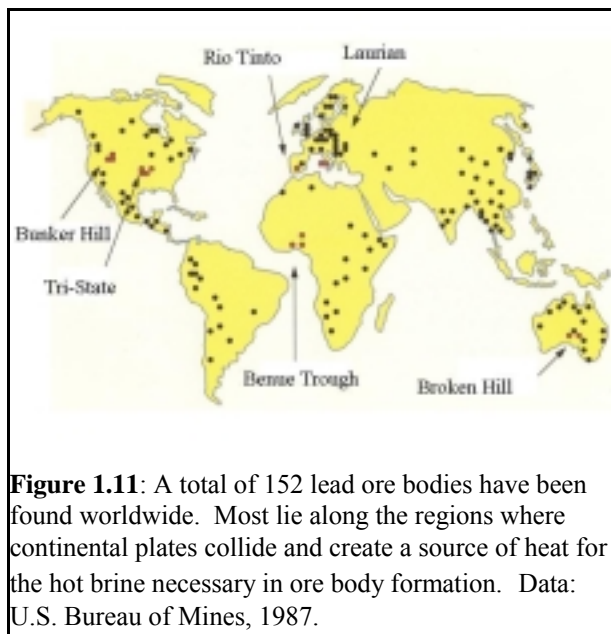
#### Bodies: Plate Tectonics

The outline of ore formation (hot brine, porous matrix, earlier marine environment) suggests that the global location of lead ore bodies has been determined by plate tectonics or the movement of crustal plates about the surface of the earth. An early single continent Gondwana existed some 520 mya. This continent broke up and eventually reformed into the super continent Pangea, about 250 mya. Pangea broke apart east/west into South America and Africa, with South America eventually colliding with North America. The motion of the plates resulted in stretching of the Pangea continents with a central subsidence (basin formation), followed by rifting (ripping apart), collisions (piling up of mountains), and the formation of subduction zones, where one plate slid beneath another. All of the processes generated enough excess energy to heat the brines necessary to concentrate the metal ions.

Separation of the plates initially stretched the continents to form subsidence zones where water could pool and concentrate and where carbonate beds could be formed. In these basins, evaporative carbonate deposits formed, serving as flat “platforms” where Pb/Zn ores were subsequently replacement-deposited. Examples of these types of ore bodies are those in Western Canada.

Continental rifts formed where plates pulled the continent of Pangea apart about 240-80 mya. Good examples are (Figure 1.10) the Benue and Amazonian Troughs, where brines circulated and deposited through evaporation to form some of the few lead deposits in western Africa and eastern South America (Evans, 1987), p. 298. The Benue Rift dates to the Mesozoic time period (Grant, 1971). The rift basin (80 km wide) was subsequently filled by sedimentary and volcanic material to a depth of 6 km. The Pb/Zn ores in the region are replacement ores (Hawkes, 1954). The host rocks are shales, limestone, sandstone, with the metal deposited from the vein wall inward (Craddock et al., 1997).

Other lead deposits occurred in regions on continental margins. As the continents separated, the passive or trailing edges served as a shelves for sedimentation and/or coral formation, resulting in carbonate regions that hosted Mississippi Valley Type (MTV) Pb/Zn ore formation. Examples of such lead ore bodies are those from the Cretaceous period in Nigeria, the Atlas Mountains in North Africa, Laisvall in Sweden, and Largentiere in France (Evans, 1987),



**Figure 1.11:** A total of 152 lead ore bodies have been found worldwide. Most lie along the regions where continental plates collide and create a source of heat for the hot brine necessary in ore body formation. Data: U.S. Bureau of Mines, 1987.

p. 303.

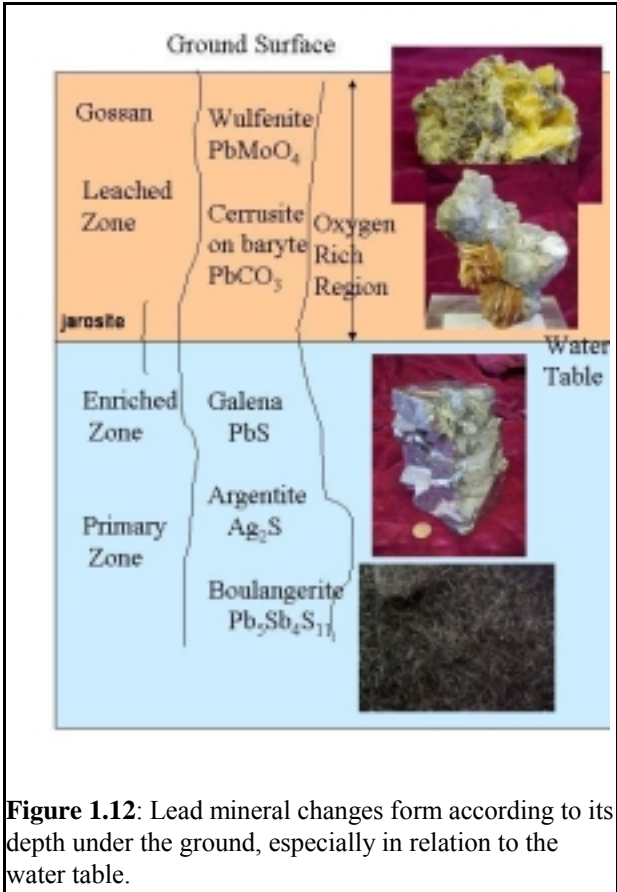
Some of the most important lead sources in the western United States derive from the leading edges of continental margins, where there is a large crust thickness due to underplating and plate convergence during the Cretaceous/Tertiary geologic period.

Other collision related lead ores were formed by the closing of a basin. This process gave rise to the lead/tin mines in Cornwall and the ore bodies in the eastern Alps, as well as those in the Red Sea.

Figure 1.11 shows a map of lead ore bodies throughout the world. Most of these ore bodies were put in place some 1,800 to 55 mya, long before primate evolution culminated in the human species. The ores are spread throughout the entire world, although Africa and the mid-Eurasian continent are lower in lead concentrates than other parts of the world. A comparison of these areas with the map of human migration and settlement shows that human agricultural settlement occurred in close proximity to metal-bearing geologic formations such as coastal mountain regions and rift remains.

**Oxidation of Ores**

It has been shown that early agricultural settlements of humans were near lead ore bodies. Was the ore noticeable (colorful, shiny?) and accessible to the early



**Figure 1.12:** Lead mineral changes form according to its depth under the ground, especially in relation to the water table.

chemist working with a simple campfire? The answer to this question depends upon the exact chemical composition of the ore, which in turn depends upon the weathering of its upper surface.

When a vein of hydrothermally deposited material is exposed to the atmosphere, further weathering takes place. A copper-sulfur ore, for example, is also rich in iron sulfides. Both the copper and iron sulfides will oxidize to form oxygen containing compounds (leading to malachite and other beautiful copper ores) and to porous ochres (iron oxides) which are yellow in color, and granular in shape. These materials are together called **gossan**. The iron oxides can be dissolved and be carried down several feet to a zone where it precipitates in a clay-rich environment. This high-clay copper ore is known as **fahl**. Similarly, a lead sulfide containing ore found at the surface of the earth's crust undergoes weathering to the mineral  $PbSO_4$ , or **anglesite**. Further weathering may result in **cerrusite**,  $PbCO_3$ . Lead and iron sulfide ore at the interface with unweathered ore high in clay is known as **jarosite**. Typically (before man was on

the scene), a lead ore body consisted of surface-oxidized ores: cerussite ( $\text{PbCO}_3$ ),

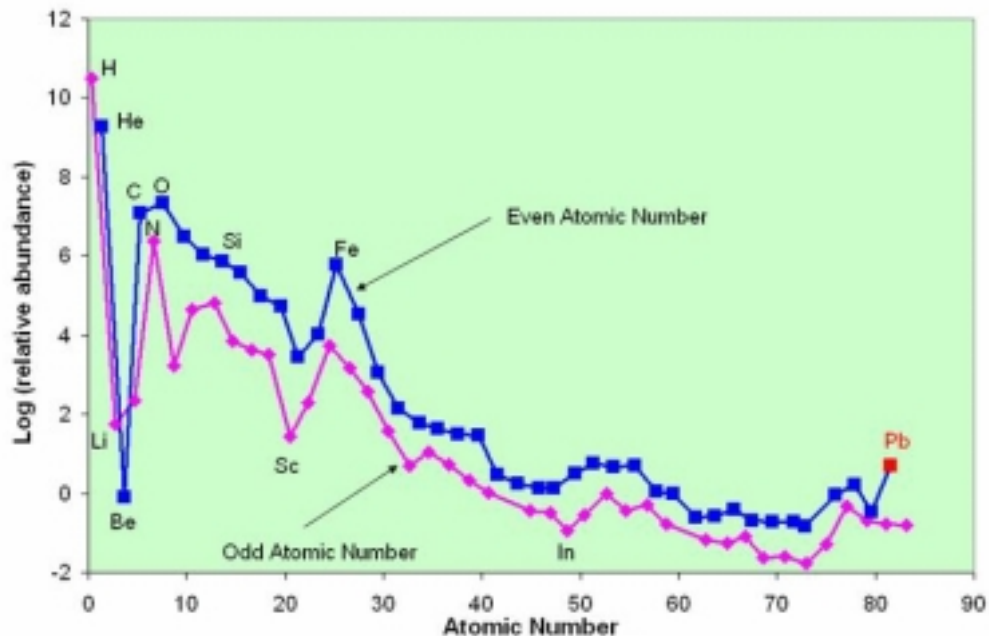
anglesite ( $\text{PbSO}_4$ ), litharge ( $\alpha\text{PbO}$ ), and massicot ( $\beta\text{PbO}$ ) below which lay plumbojarosite ( $\text{PbFe}^{3+}_6(\text{SO}_4)_2(\text{OH})_{12}$ ), then galena ( $\text{PbS}$ ) (Figure 1.12). Comparing this depth picture with the solubilities of the various minerals (Tables D.2 and D.3), it can be noted that the superficial minerals, the sulfates and carbonates, are the most soluble and that the deeper sulfide ores are more stable.

The difference in the chemistry of these minerals means that different technologies are needed to free pure lead from each ore with its specific mix of minerals. Miners distinguish between silver ores containing abundant galena and sphalerite ( $\text{ZnS}$ ) as “wet” and those with minor galena and sphalerite as “dry” ores. The technology of silver removal changes significantly when working with wet or dry ores (Cairnes, 1934). This fact had important consequences for the development of bronze technologies around the world.

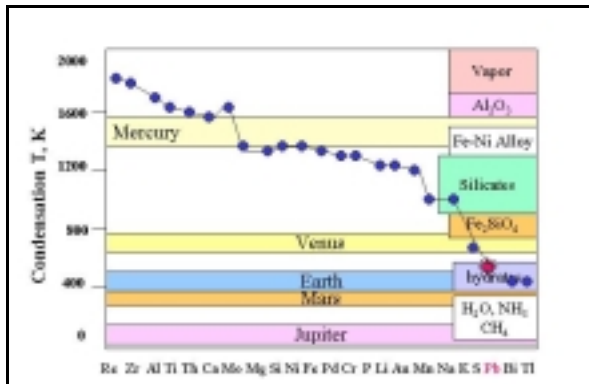
Another example of history being driven by geochemistry comes from lead ores’ association with silver as argentite ( $\text{Ag}_2\text{S}$ ). Galena ( $\text{PbS}$ ) and argentite

have similar densities ( $7.5 \text{ g/cm}^3$  and  $7.31 \text{ g/cm}^3$ , respectively). Lead is also prominently found with antimony (Sb), arsenic (As), and other trace metals. Some common minerals found mixed with lead are boulangerite ( $\text{Pb}_5\text{Sb}_4\text{S}_{11}$ ), jamesonite ( $\text{Pb}_5\text{FeSb}_6\text{S}_{14}$ ); fizelyite ( $\text{Pb}_{14}\text{Ag}_5\text{Sb}_{21}\text{S}_{48}$ ), mimetite ( $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$ ), bindheimite ( $\text{Pb}_2\text{Sb}_2\text{O}_6(\text{O},\text{OH})$ ), and other trace minerals. The other trace metals present a problem for the purification of the silver, while the presence of the antimony (Sb) results in lead slags rich in antimony. Slags represent the discarded material from mining and smelting. These facts had important consequences for the beginning of glass and pigment technologies.

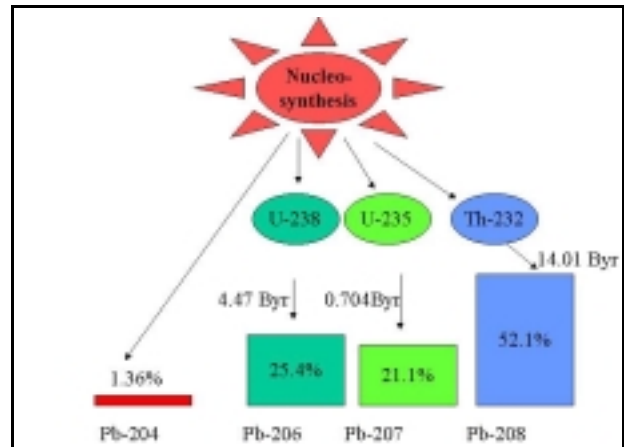
Lead minerals that are either commercially important as sources of lead or that have unique properties exploited by man are gathered into Table Appendix B.1. To summarize, chemical principles drive the formation of natural lead ore bodies. Oxidized or surface ores are limited in extent and consist of ceruse or cerussite, and occasionally litharge and massicot. Subsurface ores are more extensive and consist of galena ( $\text{PbS}$ ) and contain significant amounts of silver as  $\text{Ag}_2\text{S}$  or as  $\text{AgSbS}$  compounds.



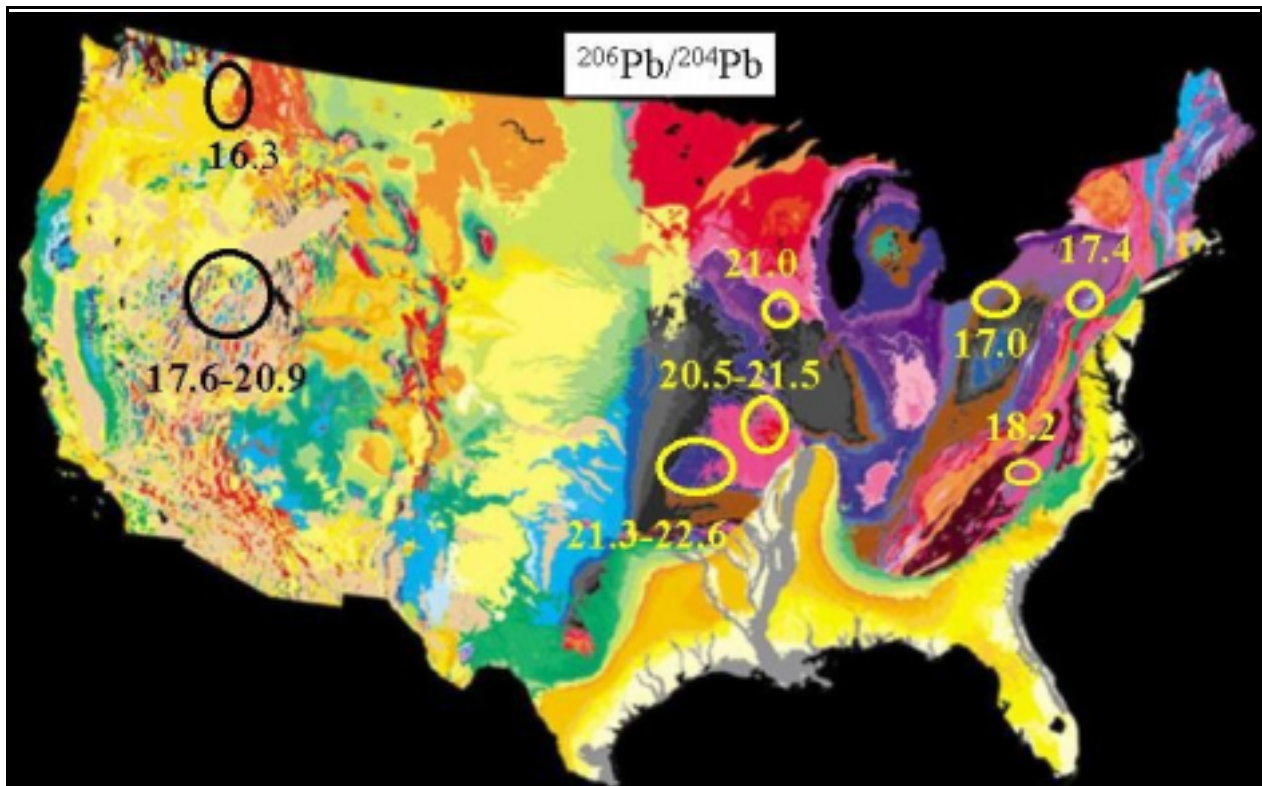
**Figure 1.13:** The abundance of a given element in the Earth’s crust is proportional to the atomic number of that element. Lead is anomalous in that it is more abundant than its atomic number would suggest. Data source: CRC Handbook of Chemistry and Physics, CRC Press, West Palm Beach, Fla.



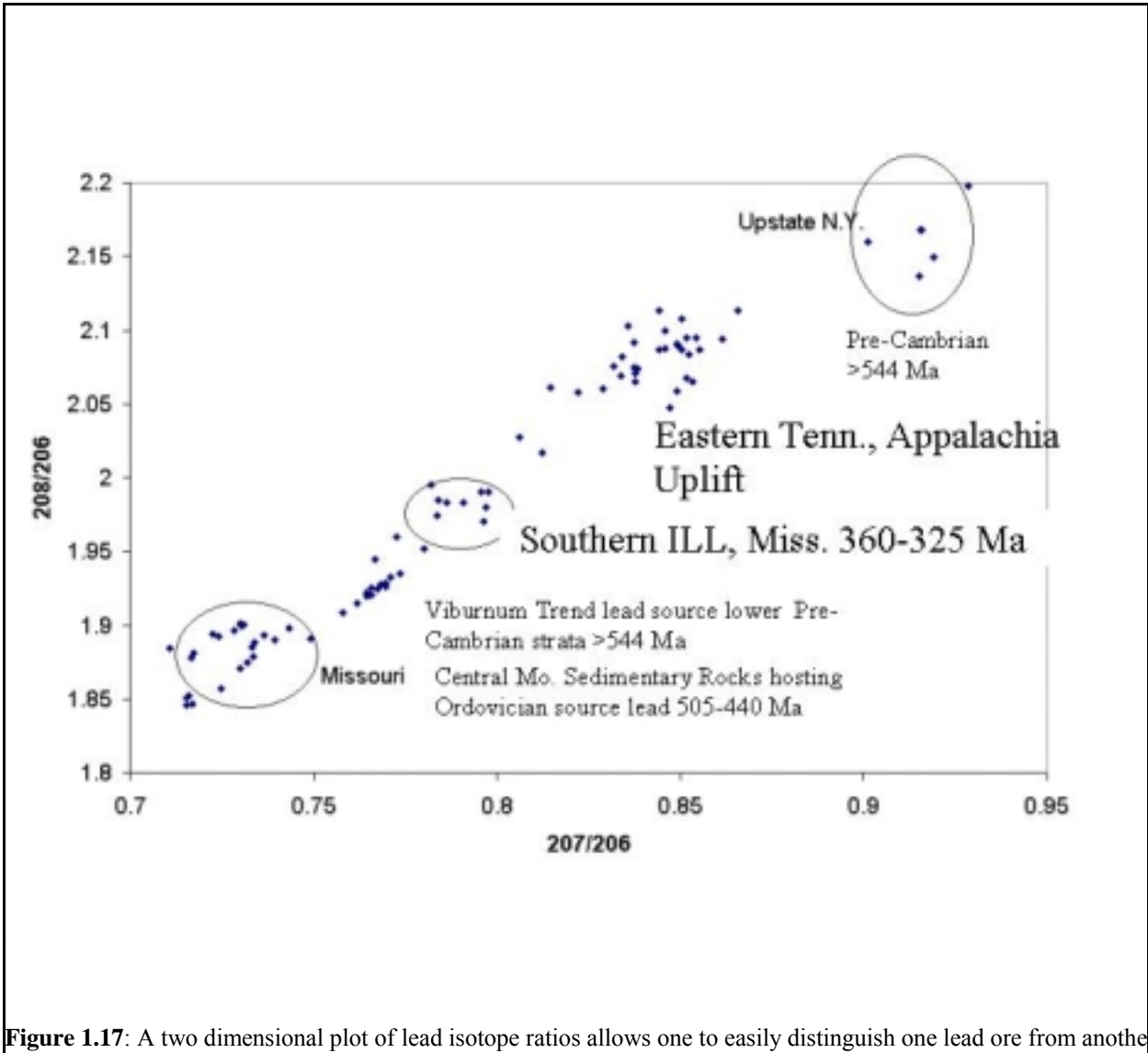
**Figure 1.14** Elements condense at different temperatures, leading to elemental segregation among the planets according to their temperature gradient away from the sun. Lead condenses at the temperature of the Earth during its formative years. Thus lead is more abundant in the Earth than in other planets of the solar system.



**Figure 1.15:** Lead consists of four isotopes whose ratios to one another vary according to the age of the ore. The ore body's isotopic ratio constitutes a "fingerprint."



**Figure 1.16:** Geologic ages of the U.S. The older areas are in the darker and pinker colors. Superimposed are isotope ratios of lead. King, P. B. and H. M. Beikman, <http://www.Ideo.columbia.edu/users/menke/envdata/quality/map>. Accessed, May 19, 2003.



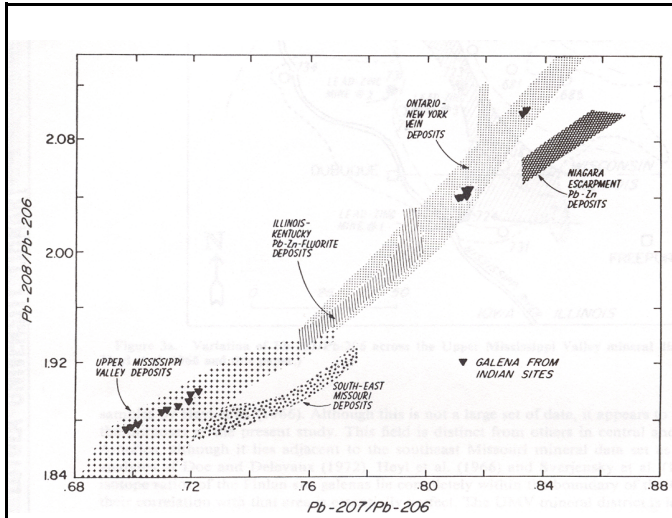
**Figure 1.17:** A two dimensional plot of lead isotope ratios allows one to easily distinguish one lead ore from another.

**Abundance and Isotope Ratios of Lead Ore Bodies**

One of the curious phenomena associated with lead is that its abundance in the earth's crust is actually larger than we would predict on the basis of nuclear synthetic reactions. Figure 1.13 shows the abundance of the various elements in the earth's crust. Note that lead, shown by its chemical symbol, Pb, is particularly abundant in comparison to its elemental near neighbors. This "over-abundance" accounts, in part, for the fact that it is a viable economic ore.

Why should lead be particularly high in abundance when its production by nuclear synthetic reactions was low?

One part of the answer lies in how lead was "sorted" from the stellar gases into the planet. The gases involved in planetary formation condensed at different temperatures as a function of their distance from the sun Figure 1.14 (Brownlee, 2000; Lunine, 1999). Lead remained gaseous at temperatures where Mercury and Venus began condensing. Its abundance is less in those planets. A second reason for lead's relatively large abundance is that part of the lead found within the Earth derives from radioactive decay of other elements (Figure 1.15). Uranium and thorium

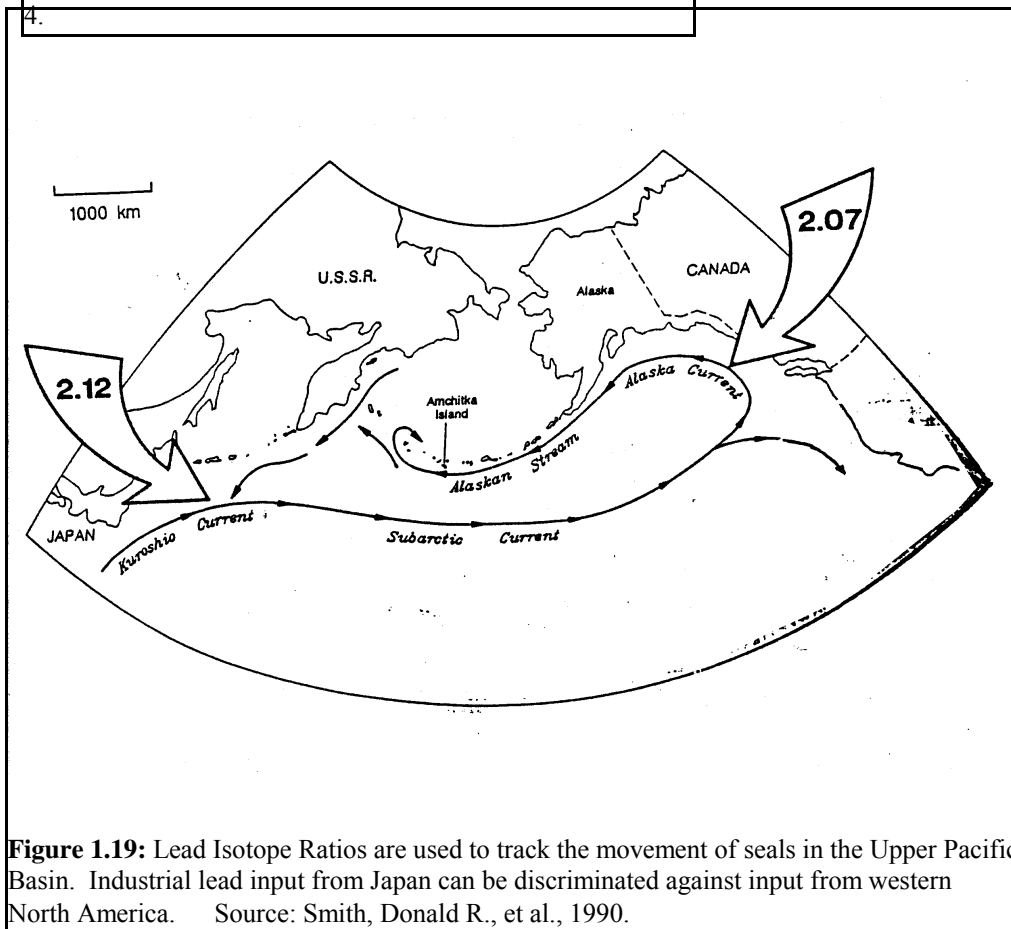


**Figure 1.18:** On the north side of Lake Ontario are various Native American camp sites. The lead found at these sites does not correspond to the lead deposits shown nearby. Farquhar, R. M. and I. R. Fletcher. *Am. Antiquity*, 1984, 49, 4.

initially present in the Earth's crust have changed over the lifetime of the earth to lead.

Lead ore bodies can be fingerprinted by the variable ratios of lead isotopes that they contain. The atomic structure of elements consists of a nucleus with protons and neutrons surrounded by a number of electrons matching the number of protons. Sometimes the number of neutral neutrons may vary, creating atoms that behave in the same chemical fashion (i.e., have the same electron configuration), but which have different masses. Lead has four common isotopes: lead-204 formed in the primordial elemental forming reactions, and lead-206, lead-207, and lead-208. These last three forms of lead result from the radioactive decay of thorium and two different isotopes of uranium (Tables B.2 and B.3).

Thorium and uranium decay at different rates to form stable lead. Because lead-containing



**Figure 1.19:** Lead Isotope Ratios are used to track the movement of seals in the Upper Pacific Basin. Industrial lead input from Japan can be discriminated against input from western North America. Source: Smith, Donald R., et al., 1990.

rocks may have different abundances of lead isotopes, lead leached by brine to form ore bodies will be highly variable. The result is an ore body “fingerprint”. If the lead in the ore body is representative of the material from which it is leached, then its isotopic composition correlates with that at the time when the lead ore body was formed (Figures 1.15 and 1.16).

The map shown in Figure 1.16 has the  $^{206}\text{Pb}/^{204}\text{Pb}$  lead isotope ratios listed. This normalization of the  $^{206}\text{Pb}$  concentration by a fixed number (like the constant concentration of  $^{204}\text{Pb}$ ) is useful in accounting for measurement errors. Since  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ , and  $^{208}\text{Pb}$  all are distinctive for a lead ore body one can make two dimensional plots which easily show variations in lead ore bodies (Figure 1.17).

Historians of lead, environmental chemists, geochemists, environmental chemists, and art historians have all made use lead’s “fingerprint” to track its motion flow of lead in the environment. A few examples follow.

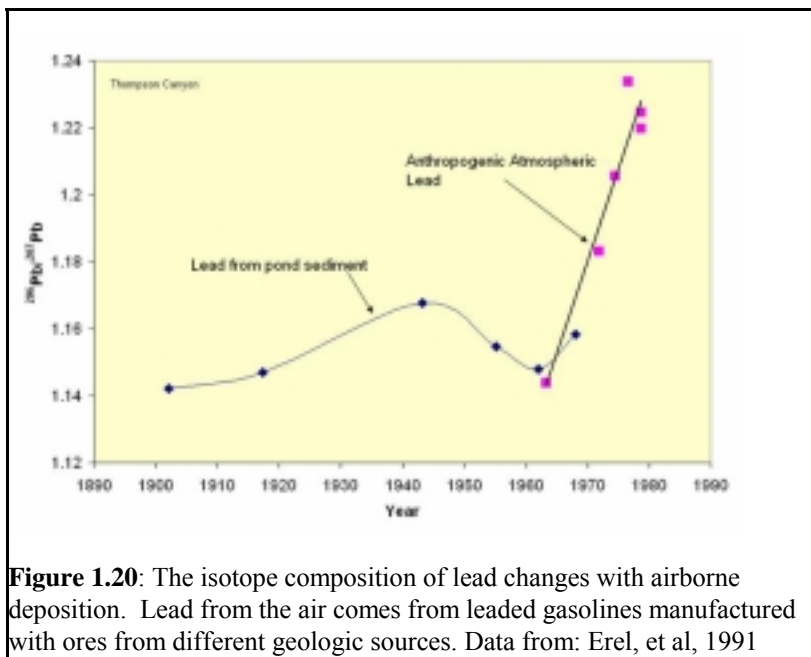
A unique isotopic ratio for lead is found in the each different ore body (Table B.4). Isotopic ratios can be used to deduce the source mineral from which lead materials and/or exposure are derived. For example, the  $^{206}\text{Pb}/^{204}\text{Pb}$  isotopic ratio can be used for prospecting in glacial till. The ratios indicate the presence of a buried ore body (Lunine, 1999), p. 116.

Isotopic ratios can be used to track the source of lead. Archaeologists have determined that trading distances for the Late Archaic Age (1,500 to 500 B.C.) in North America could be as far as 1000 km (Farquhar and Fletcher, 1984). This conclusion was reached because while most lead ore found at burial sites in Finlan, Canada near Buffalo, N.Y. matched area lead sources, some had unique isotopic ratios consistent with ores derived from western Illinois (Figure 1.16 shows where this ore body is, with a  $^{206}\text{Pb}/^{204}\text{Pb}$  ratio of 21.0).

More common archeological isotope studies involve tracing the sources of trace lead in ancient glasses - Greek (Barnes et al., 1974; Brill, 1968; Brill, 1970) (Brill, 1972; Brill and Wampler, 1967; Brill et al., 1974; Brill, 1980), Egyptian, Viking, and Anglo-Saxon (Frank, 1982) - and bronzes from such diverse

sources as the Yoruba empire of Nigeria (ca. 1200 A.D.) (Goucher et al., 1978), the Aegean, the Mediterranean (Gale, 1991; Gale, 1997; Gale and Stos-Gale, 1982; McGeehan-Liritzis and Gale, 1988), (McGeehan-Liritzis and Gale, 1988; Wagner and Gentnar, 1980), (Farquhar and Vitali, 1989), (Gale and Stos-Gale, 1982; Gale and Stos-Gale, 1989; Gale et al., 1997; Gale et al., 1999), (Stos-Gale et al., 1997; Stos-Gale et al., 1998) and China (Peng et al., 1991a), (Peng et al., 1991b). Recent studies include tracing Rio Grande Glaze and ore bodies (HabichtMauche et al., 2002).

Isotopic ratios can also be used to analyze various bone materials in order to track the introduction of industrial lead into the environment. Sources for lead within pre- and post-industrial sea otter populations has been tracked using isotopic ratios. While the total bone lead content has not statistically increased in terms of PbCa bone ratios, the source of lead has deviated from Aleutian island native minerals ( $^{208}\text{Pb}:$  $^{206}\text{Pb}/^{207}\text{Pb}:$  $^{206}\text{Pb}$  of 2.04/0.83) to industrially



**Figure 1.20:** The isotope composition of lead changes with airborne deposition. Lead from the air comes from leaded gasolines manufactured with ores from different geologic sources. Data from: Erel, et al, 1991

derived Japanese (2.12/0.86) and western United States lead (2.02/0.82) (Figure 1.19) (Smith et al., 1992; Smith et al., 1990) (Flegal et al., 1993).

Isotope ratios are used to determine the flux of gasoline-derived lead in the global environment (Moor et al., 1996), (Farmer et al., 1996), (Grouseet et al., 1994), (Weiss et al., 1999). More recently, efforts

have been made to link specific paints or gasolines to various isotopic ratios. Ores from certain mines at certain times were used primarily in the leaded gas industry, while others were used primarily in paints. Consequently, lead isotope composition might be related to a particular source (soils contaminated with auto exhaust or painted surfaces from the 1940s.) Figure 1.20 shows a plot of the variation in lead isotope ratio of airborne lead as a function of time, which is correlated to changes in the major commercial ore bodies (Erel et al., 1991). A similar change in lead in the Tokyo sediment basin in Japan has been measured (Boutron and Patterson, 1987; Croudace and Cundy, 1995; Gobeil et al., 1995; Gulson, 1996; Gulson et al., 1981; Manton, 1973; Rabinowitz, ; Rabinowitz and Wetherill, 1972; Rifkin and Harr, 1973).

Other isotope fingerprinting work has elucidated the source of lead in home dust, in transfer from maternal milk to infants, and in calcium supplements (Goldberg, 1963; Pizzolato and de Hon, 1995).(Gulson et al., 1996a; Gulson et al., 1992; Gulson et al., 1995; Gulson et al., 2001a; Gulson et al., 1998; Gulson et al., 1996b; Rabinowitz, 1995).

## SUMMARY

The human species evolved in an essentially lead-free environment. Most of the lead present was buried in subsurface deposits composed of a relatively inert (insoluble) form. As a consequence humans (and other living species) have no known use for or protection against lead. The amount of lead on the earth's crust is larger than might be predicted from stellar nuclear synthetic processes. One reason is that it was concentrated during the earth forming process and a second is that it is the "sink" for radioactive decay of uranium and thorium. Because lead has "several" parent atoms it has variable "mass" which creates a "fingerprint" for various ore bodies. The relatively low concentration of lead (as compared to the abundances of other elements in the earth crust) may be related to the fact that there is currently no known biological function for lead, making it toxic. Dispersed, small quantities of lead, were concentrated into lead ore bodies by processes associated with continental drift. Most lead in ore bodies is in the form of galena or cerrusite, both of which are attractive minerals. The chemical, or mineral form, of lead changes with depth which creates technical difficulties for miners as will be shown in Chapter 2. Lead is "married" to silver or found with silver. Because it is found with silver it was extensively mined. The effects of silver mining by the Greeks and

Romans can be seen in the lead in the Arctic ices. Lead is also found in conjunction with many other trace elements, especially with antimony. We will see that the association of lead with antimony had some unusual implications for recycling of silver mining lead by-products. Subsurface lead ore bodies are distributed widely over the surface of the earth and can be found near regions of the world that were amenable to early agriculture.



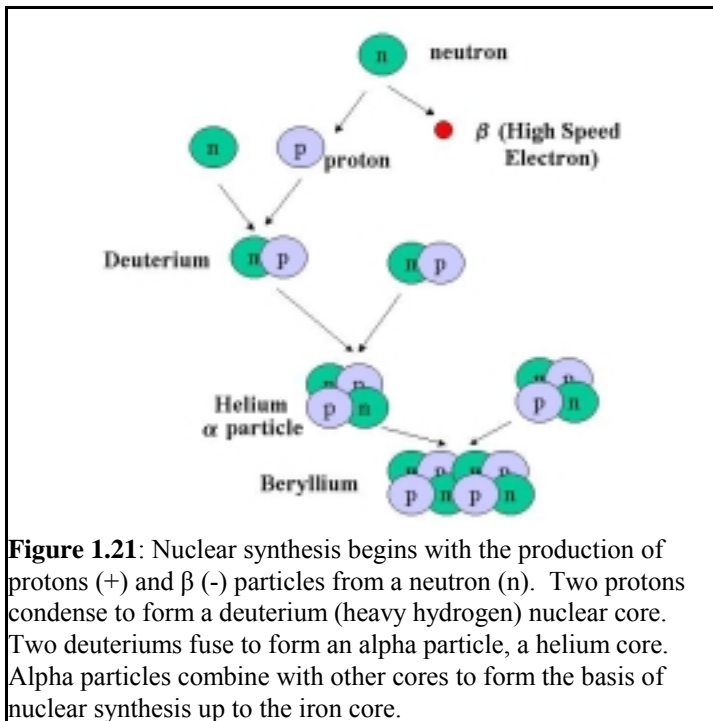
## Part II: Chemistry of Atom Formation, Planetary Formation, and Ore Body Generation

### Quantity: The Big Bang, Atom Structure and Atom Formation

Why was lead not incorporated into the structure of life? Why is there no biological use of lead, or any mechanism for reducing its toxicity? This is because lead was locked within the earth's crust and was not a commonly dispersed element. Why should this be so? The reasons have to do with the planetary formation process and its dependence chemistry and abundance.

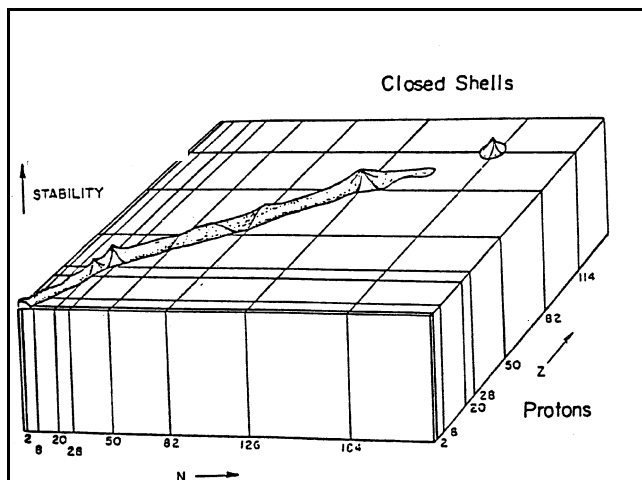
The total amount of lead in the universe, that is, lead's mass abundance, is controlled by nuclear synthetic reactions. In general, elements with lower atomic numbers are a higher percentage of the earth's mass (see Figure 1.13). In addition, elements with an even atomic number are more abundant.

These two trends, even atomic number and



**Figure 1.21:** Nuclear synthesis begins with the production of protons (+) and β (-) particles from a neutron (n). Two protons condense to form a deuterium (heavy hydrogen) nuclear core. Two deuteriums fuse to form an alpha particle, a helium core. Alpha particles combine with other cores to form the basis of nuclear synthesis up to the iron core.

	<b>Nucleosynthesis</b>	neutrons
	${}^1_0n$	↓
H burning	${}^1_0n \rightarrow {}^1_1H + {}^0_{-1}e$	proton core
	↓ 1 s	
	${}^1_1H + {}^1_0n \rightarrow {}^2_1H$	Deuterium formed
	↓ 3 min	
He burning	${}^2_1H + {}^2_1H \rightarrow {}^4_2He$	(= α particle) He, helium formed
	↓ millions yrs	
	$\alpha + \alpha \rightarrow {}^8_4Be^*$	
	${}^8_4Be^* + \alpha \rightarrow {}^{12}_6C$	
	$\alpha + {}^{12}_6C \rightarrow {}^{16}_8O$	
	C, carbon, & O, oxygen formed	
α phase	↓ more millions	
	${}^{12}_6C + {}^{12}_6C \rightarrow {}^{20}_{10}Ne + \alpha$	
	${}^{16}_8O + {}^{16}_8O \rightarrow {}^{28}_{14}Si + \alpha$	
	${}^{12}_6C + {}^{16}_8O \rightarrow {}^{24}_{12}Mg + \alpha$	
	${}^{28}_{14}Si + \alpha \rightarrow {}^{32}_{16}S$	
	${}^{32}_{16}S + \alpha \rightarrow {}^{36}_{18}Ar$	
	${}^{36}_{18}Ar + \alpha \rightarrow {}^{40}_{20}Ca$	
	${}^{40}_{20}Ca + \alpha \rightarrow {}^{44}_{22}Ti$	
	${}^{44}_{22}Ti + \alpha \rightarrow {}^{48}_{24}Cr$	
	${}^{48}_{24}Cr + \alpha \rightarrow {}^{52}_{26}Fe$	
	${}^{52}_{26}Fe + 5 {}^1_0n \rightarrow {}^{57}_{26}Fe$	Fe, iron formed
	↓ more millions, supernova	
r phase	${}^{56}_{26}Fe + 23 {}^1_0n \rightarrow {}^{79}_{26}Fe$	
	${}^{79}_{26}Fe \rightarrow {}^{79}_{27}Co + e$	etc.



**Figure 1.22:** Plot of stable elements as a function of the number of protons ( $Z$ ) and neutrons ( $n$ ). The lines represent filled  $s$ ,  $p$ , and  $d$  shells and mark the location of extra stability. Note that lead at  $Z=82$  represents an “oasis” of stability. (Sumdahl, 2000)

low atomic number, are attributed to reactions at the beginning of time (Brownlee, 2000; Viola, 1990). The primordial “sea” is thought to have consisted of neutrons,  ${}^1_0n$ , neutral charged particles in the nucleus of an atom. (See Box on preceding page labeled nucleosynthesis). The superscript, the mass number, refers to the mass (sum of positively charged particles, or protons, and neutral particles, or neutrons), while the subscript, the atomic number, refers to the number of protons in the nucleus.

The first phase of nuclear synthesis involves separation of neutrons into protons and electrons. Protons and neutrons associate to form deuterium. Deuterium nuclei fuse to form helium (an alpha,  $\alpha$ , particle). Helium fuses to form beryllium, beryllium and an alpha particle form carbon, and so forth. (Figure 1.21). As larger and larger atoms are formed by fusion, fission can occur, releasing alpha particles to create Ne, Si, and Mg, for example. With each increase in mass, the core of the atom contains larger and larger number of protons. Eventually the core becomes unstable, creating radioactive elements.

This postulated sequence of events is consistent with the fact that the relative abundance of elements is highest for the lower weight elements and is high for elements which were formed by He ( $\alpha$  particle) addition (C, O, N, Ca, Si, S, and so forth). (See the dotted line in Figure 1.13). This distribution

of elemental abundances is the reason that life is based on carbon (C), oxygen (O), and hydrogen (H), and not, as in some science fiction stories, silicon (Si) or sulfur (S).

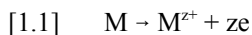
Figure 1.13 also shows that the relative abundances fluctuate greatly. To a certain extent, this fluctuation in relative abundances is related to the way in which the subatomic particles (neutrons and protons) are spatially organized. Certain nuclear configurations impart special stability. The extra stability shows up in the fluctuations in the relative abundances of the elements (Figure 1.13). The elements lithium (Li), beryllium (Be), and boron (B), have low nuclear binding energies, so they are unstable at temperatures  $>10^7$  °K. They are therefore bypassed during high temperature nuclear synthesis and have unusually low cosmic abundances.

Notice in Figure 1.13 that lead, with 82 protons in its center, represents a “blip,” or a high point where otherwise unexpected (Fergusson, 1990), p. 4. This is because Pb has a low rate of nuclear decay. Figure 1.22 shows the belt of stable nuclei which terminate near lead (Zumdahl). The stability of the nucleus, measured by the binding energy, is calculated from the mass difference between the sum of the protons and neutrons and the actual weight. From this calculation it is found that the binding energy for lead is  $4.5 \times 10^{11}$  kJ/mole (See related chemistry Example 1.2). Since lead is, at an atomic number of 82, one of the highest stable elements, it is the “sink” for the decay of radioactive materials, giving rise to its unusually high percent mass of the earth.

The increased planetary abundance of lead may be related to its accretion in stellar dust. The relative amount of lead to hydrogen found in the interstellar dust by the Hubble Space Telescope is generally less than the relative amount of lead to hydrogen found for solar system meteorites. This finding suggests that lead enriches dust particles in the interstellar space (Cardelli, 1994; Cardelli et al., 1993).

#### **After Nuclear Synthesis: Planet Formation** (Brownlee, 2000; Evans, 1987; Foster, 1983; Hess, 1989; Ringwood, 1979; Smith, 1963)

Once chemical elements are formed, they can be present in a wide number of chemical states: a plasma (an ionic gas), an atomic gas, a molecular gas, or as molecular solids. The sun is an example of a plasma which occurs at high temperatures:



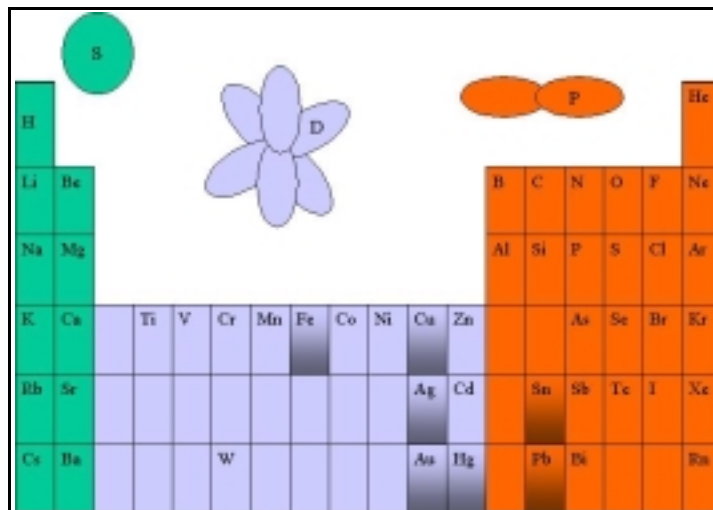
where M is an element, and z is a large number of electrons. In plasma, many of the outer electrons are stripped from the element and a free-floating sea of electrons is present. At still lower temperatures, an ionic gas forms in which the elements adopt specific cationic configurations. These configurations are driven by valence shell electron configuration, for example:



The specificity derives from the way in which electrons are added to balance the positive charge within the nucleus. Electrons are added within specific geometric orbitals, and at different radii (shells) from the center positive charge. The most common three orbitals are spherical (s), figure eight (p), and “clover leaf” (d) shaped orbitals (Figure 1.23). The reactivity of the atom will depend on how much the outermost electrons experience the positive charge of the nucleus.

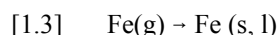
Electrons are added to or stripped from the atom in specific energies, corresponding to the different electron configurations that remain. Table B.5 shows the electron configurations of selected atoms associated with ionization. Here we see that the most stable cations are those which achieve a filled shell or orbital configuration. The ionization potentials for halogens, the group VII, seventh column elements of the periodic table (Figure 1.23), are very large. These potentials reflect the fact that as protons are added to the nucleus, the electrons added do not fully compensate for or shield the center positive charge. Thus additional electrons are held more tightly and are harder to remove. A similar set of information is contained in the electronegativities. Atoms with low electronegativity will lose electrons. Those with high electronegativity gain electrons to become anions.

At temperatures below 2000° K most elements are neutral and an atomic gas is formed. When the gas is cool enough, the density of atoms increases and atoms condense to form molecular species. These include diatomic species ( $M_{2(g)}$ ) in which electrons are shared between atoms of exactly equal electronegativities that form a covalent bond. Other early molecular species are the oxide gases ( $MO_{(g)}$ ) which are formed between elements whose electronegativities are close to oxygen. At about 1800 °K (Table B.6 and Figure 1.14) Al and Ca start to



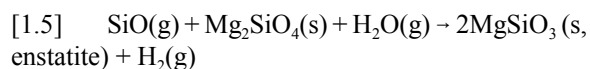
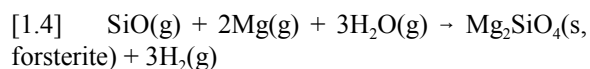
**Figure 1.23:** Periodic table of elements correlated to approximate shapes of orbitals. The shaded elements were among the first discoveries by mankind. It is important that they are grouped near the end of the “D” block and the beginning of the “P” block.

condense as cations, abstracting oxygen into Si- and Fe-poor oxides such as corundum ( $Al_2O_3$ ), spinel ( $MgAl_2O_4$ ), and perovskite ( $CaTiO_3$ ). The high-temperature stable elements are known as **refractories**, and they are often used in fire bricks. Among the refractories is the element thorium (Th), a progenitor or parent of radiogenic lead. Refractories form small aggregates which create a surface on which iron can condense (1500 °K) directly to the metal:



In the planetary forming process this results in the molten iron core, which consists of 32% of Earth’s weight.

A following temperature drop (1400 °K) can lead to the next step in planetary formation, the creation of an outer surface enriched with silicates and magnesium:



In this outer surface, pyroxene enstatite is formed. The presence of Ca in the high temperature phase also results in the formation of wollastonite ( $CaSiO_3$ ) as Ca

intercalates into the enstatite. As the gas continues to cool around the core, FeNi alloys are formed. The alloy formation results from the similar charge and radius of the elements. In this phase the mantle, which is high in magnesium and iron, is formed. A further drop in temperature enables S to react with the iron to form FeS. The drop in temperature also brings down K, Na, and Ca silicates. If the metals in these silicates can mimic the charge and ionic radius of  $Mg^{2+}$ , they can be preferentially retained in the mantle and, consequently, can be depleted in the crust (Table B.8) (Lewis, 1997; McCulloch and Bennett, 1998; O'Neill and Palme, 1998; Perkins, 1998). This apparently happened with  $Fe^{2+}$ . Material which can substitute for  $Si^{4+}$  can be preferentially pulled into the mantle also.  $Si^{4+}$  itself can not be directly mimicked but  $(Mg^{2+}Si^{4+})$  is replaced by  $(Al^{3+}Al^{3+})$  in such a way that  $Al_2O_3$  (corundum) dissolves into  $MgSiO_3$ , (enstatite).

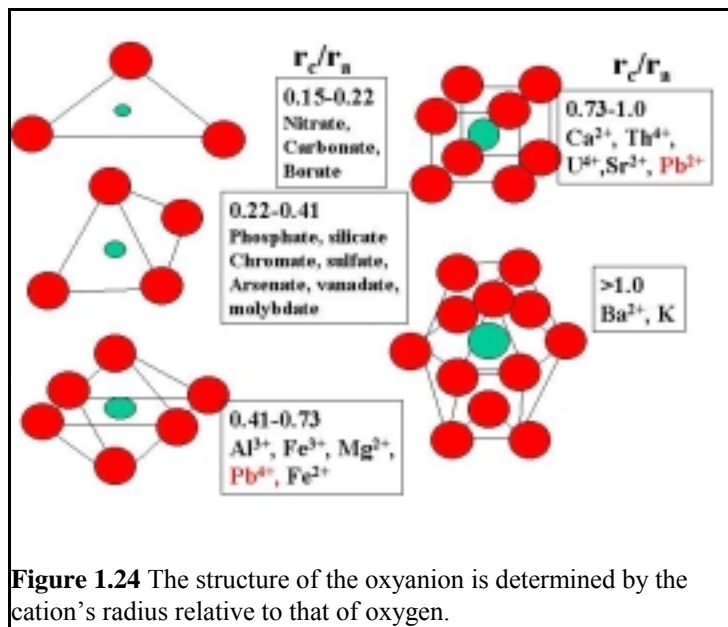
The highly volatile elements such as lead and bismuth are the last to condense. The boiling point, the condensation point for lead, and other important information about lead are shown in Table A.1.

### Common Minerals: Binding to Oxygen: Rules of Crystal Packing

As elements cool, various molecular species can form. Small cations abstract oxygen to form **oxyanions**. The size and shape of an oxyanion depends upon the size of the cation relative to that of the oxygen ion. The oxyanions are generally rather large anions. The type of structure obtained on abstraction of oxygen can be predicted from the size of cation radius to that of the oxygen anion,  $r_c/r_a$  (Table B.9 and Figure 1.24). Small cations generally have a small number of anions packed around them. Small cations such as carbon and boron can be triangular; silica is always tetrahedral; aluminum (Al) can be both tetrahedral and octahedral. Large cations, those residing deeper down or to the left on the periodic table, generally pack a larger number of cations around them. Only alkaline earths are normally cubic or dodecahedral in coordination. The packing radius ratio suggests that the oxyanions, nitrates, borates, and carbonates are triangular in shape, while silicates and sulfates are tetrahedral, along with tungstates, molybdates, chromates, phosphates, arsenates, and vanadates.

These oxyanions in turn combine with more cations to form neutral salts or crystals. The kind of crystal formed depends upon the size of the oxyanion relative to that of the cation. Many of the resulting minerals are classified by geologists on the basis of similarities in oxyanion shape. For example, geologists classify minerals in the carbonate group to include both carbonates and nitrates, since both of these anions are triangular in shape. Other similar clusters of minerals are the tungstates, molybdates, and chromates. All of these are tetrahedral and di-anionic. The phosphates, arsenates, and vanadates all tetrahedral and trivalently charged. In this classification scheme minerals belong to only a few general classes as shown in Table B.12.

The size of the resulting ionic salt is important because, in general, the larger the size, the more soluble the compound (Table D.1). Solubility is also affected



**Figure 1.24** The structure of the oxyanion is determined by the cation's radius relative to that of oxygen.

by the surface area of the fully grown crystal. The size of the crystal depends upon the rate of growth, which, in turn, is controlled by mineralization, a process that occurs upon the cooling of molten magma. The rate of cooling affects the rate of nucleation and therefore the size of the crystals obtained. High temperature melts cool slowly, allowing diffusion of atoms to the surface of the growing crystal and enlarging it. Pegmatites (quartz,  $SiO_2$ , and alkali feldspars,  $[K \text{ or } Na]AlSi_3O_8$ ) are very coarse-grained igneous rocks, whose subsurfaces cool at a lower rate. Igneous rocks

cooling on the surface have a faster rate of cooling and are generally finer in grain size.

### “Modern Ores”: Secondary Separations

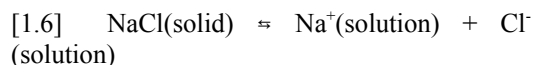
These original minerals can be solubilized and reprecipitated throughout the Earth’s crust. Low temperature crystallization is undergone by carbonates, (CaCO<sub>3</sub>, MgCO<sub>3</sub>), halides (NaCl, KCl) and sulfates (gypsum, CaSO<sub>4</sub>·2H<sub>2</sub>O), the three soluble primary anions of soluble salts (Table D.1).

Most of the more insoluble metal ores (primarily sulfides) are formed during secondary separations involving a) dissolution and leaching to concentrate metals at high temperature; b) initiation of crystallization caused by mixing, dilution, and/or temperature changes; and c) a porous soluble matrix allowing for a volume in which the metal can be precipitated (Figure 1.8).

### Dissolution and Concentration

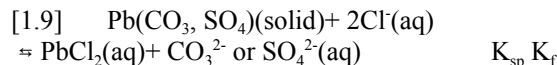
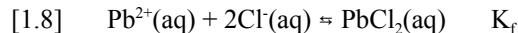
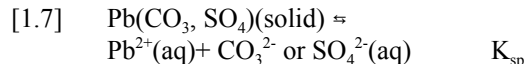
Dissolution of dispersed lead (10 ppm or parts per million) can be achieved by passing hot brine over the material. A brine is an extremely saline (salty) solution. It is more saline than the ocean, and more concentrated in chlorides than normal ocean and lake waters (Tables C.5 and C.6) (Evans, 1987; Laznicka, 1985).

In an ocean, NaCl concentration occurs by the process of evaporation and cannot reach above the level of the solubility limit set by the reaction:



The solubility reaction sets the concentration of chloride ions (Cl<sup>-</sup>) at approximately 0.5 M (see chemistry example 1.6). Because of high temperatures and pressures brine can have an enhanced concentration of chloride ions, Cl<sup>-</sup>.

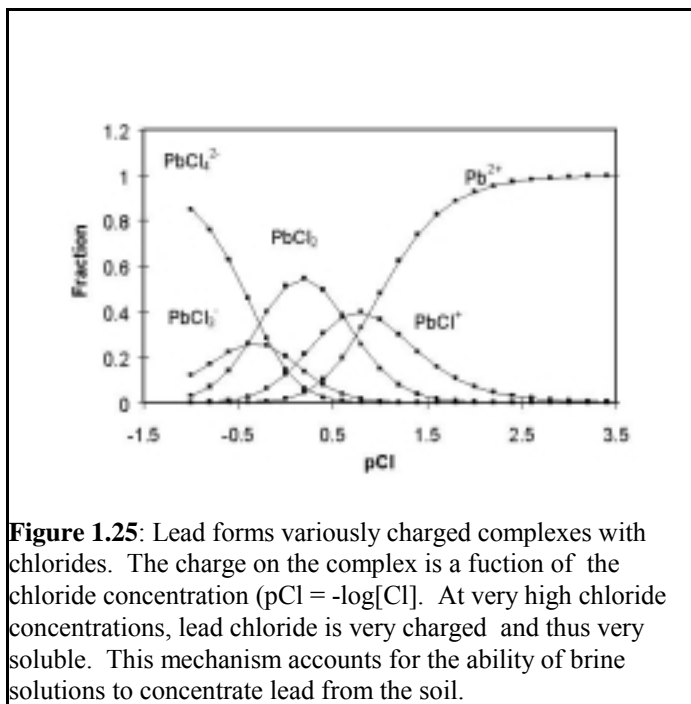
Why should the enhanced concentration of Cl<sup>-</sup> be important? The chloride ions act as ligands to bring metal ions into solution. This phenomenon is shown by the enhanced concentrations of metal ions in the brine compared to contemporary metal ion concentrations in oceans or lake waters. The overall reaction of interest is derived from the dissolution of a salt and formation of a chloride complex (Reactions 1.7 to 1.9):



Reaction [1.9] is driven to the right (towards an aqueous species) by the presence of high amounts of chloride ions, such as those existing in a brine. Many metal ions bind to Cl<sup>-</sup> in sequential steps to form a series of ionic species that remain in solution. Relative to freshwater (Tables C.5 and C.6) the ocean is high in sulfates, chlorides, and carbonates (Stumm and Morgan, 1970), p. 385. Because of the very high amount of chloride ion in the ocean, anionic chloride species form with metals there (Fergusson, 1990), p. 144. The equilibrium constants for the reaction of a variety of metals with Cl<sup>-</sup> are given in Table D.9. It is important to note that all of the chemical species shown in the table are soluble forms, not precipitates.

Figure 1.25 shows a plot of the various forms of lead as a function of the chloride concentration.

The flow of a brine solution through a 10 ppm lead-containing material can raise the value of lead in the brine to 102 ppm, leading to the concentration of lead necessary for the deposition of ore body. The lead is generally thought to be leached from three

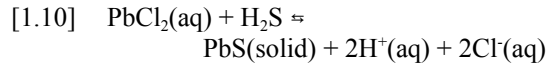


**Figure 1.25:** Lead forms variously charged complexes with chlorides. The charge on the complex is a function of the chloride concentration ( $p\text{Cl} = -\log[\text{Cl}]$ ). At very high chloride concentrations, lead chloride is very charged and thus very soluble. This mechanism accounts for the ability of brine solutions to concentrate lead from the soil.

different sources: magma, igneous rocks, or the mantle, which is high in lead and sulfides.

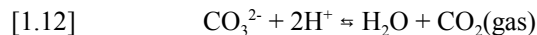
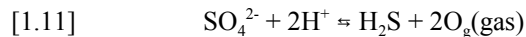
### What Drives Lead Sulfide Precipitation

To precipitate the lead, the brine reaction must be made favorable, or spontaneous:



From reaction [1.10] we can see that three different processes might drive the reaction to the right: an increase in  $\text{H}_2\text{S}$ , a removal of protons (that is, an increase in pH), or a removal of chloride ions from solution.

If the brine already contains a sulfur source, then raising the pH or removing the chloride ion concentration could initiate precipitation. The pH can be raised by boiling  $\text{SO}_4^{2-}$  or  $\text{CO}_3^{2-}$  solutions to remove oxygen and carbon dioxide gases and thus driving these reactions to the right:



Both of these reactions consume protons. Reaction [1.11] also results in the production of sulfide from sulfate, serving as a possible source for sulfide precipitation.

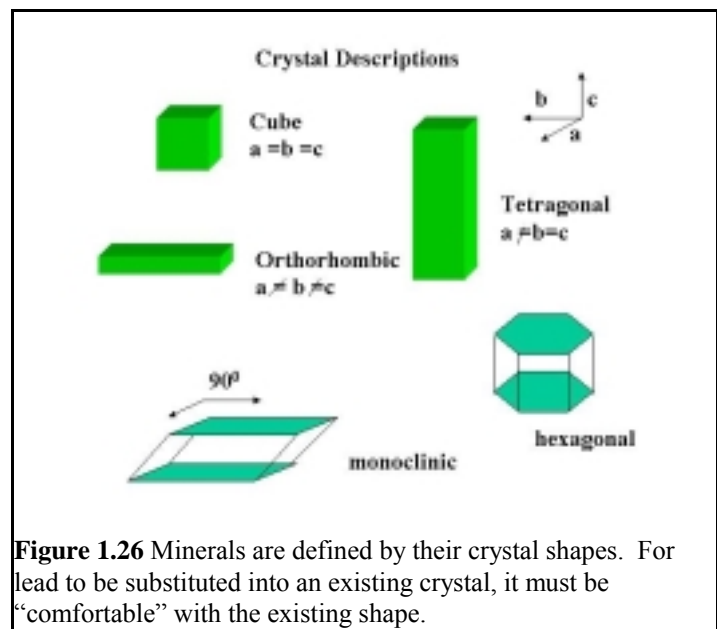
The boiling of the brine requires both a source of heat and a means to release pressure. The heat is derived from processes associated with plate tectonics, such as volcanoes, folding belts of mountains, and rift valleys (which are formed by the ripping of continents). The hot water processes (hydrothermal processes at 100-500 °C) are associated with mountain forming stresses as energy from crustal plate movement is converted into thermal energy. Ore bodies intruding into young mountainous regions generally produce the richest ore deposits. Alternatively the heat can be derived from depth and pressure, with temperatures increases at the rate of 1°C/3 km. Temperatures of 300° C could be reached by a depth of 9 km. The release of pressure must take place by means of a lower outflow pressure than inflow through a geologic formation. When pressure is released, the heated solution evaporates, leading to the

loss of steam, and other gasses. The evaporation raises the pH, helping to drive the precipitation of lead sulfides. Cooling that occurs upon boiling will also help the process (Rowan and Leach, 1989), particularly because the solubility of the lead sulfides will decrease at lower temperatures.

Both galena and argentite are less soluble at lower temperatures. As they precipitate at lower temperatures, they do not separate. Thus galena and argentite are miscible (mixable) in their molten state. Their miscibility can be predicted from their **densities**. When two components have similar densities, geologic separation through refluxing and settling is unlikely to occur. The densities of  $\text{PbS}$  and  $\text{Ag}_2\text{S}$  are 7.5 and 7.31 g/cm<sup>3</sup>, respectively. This reprecipitation of lead as a lead sulfide in the presence of silver sulfide had significant implications for the discovery and use of lead, as we will see in Chapters 2, 3, and 6.

An alternative way to explain precipitation is that the metal-bearing brine encounters less saline groundwaters that effectively dilute the chloride ion concentration and hence diminish the amount of lead chloride in solution (Reaction 1.10)

It is unlikely that either of these mechanisms completely account for lead sulfide precipitation because of the low amount of sulfide presence. A third mechanism proposes that the metal-bearing brine encounters a second fluid high in sulfur. This third mechanism is the most widely accepted one.



**Figure 1.26** Minerals are defined by their crystal shapes. For lead to be substituted into an existing crystal, it must be “comfortable” with the existing shape.

## Source of Sulfur

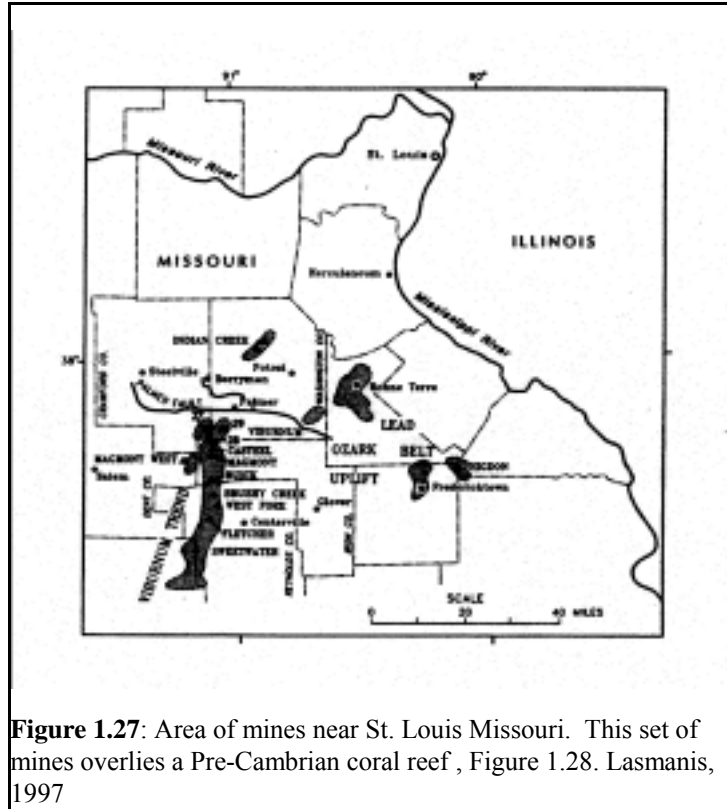
The source of sulfur in the second fluid might be either the mantle, volcanic exhalative processes, or the biological processes of many “primitive” organisms that use sulfur as an energy source instead of oxygen. (See example 1.3.) The reduction of sulfates to sulfides involves a transfer of 10 electrons. This reduction can be controlled biologically to produce energy.

The sources of sulfur may differ significantly even within the same cluster of metal sulfide deposits. Such is the case for Cierco Pb-Zn-Ag vein deposits of the Pyrene Mountains, Spain (Johnson et al., 1996). There marine sulfate was present in the shallow environment during the breakup of Pangea, and H<sub>2</sub>S formed from both rock and local bacterial sulfate reduction.

## Porous Matrix

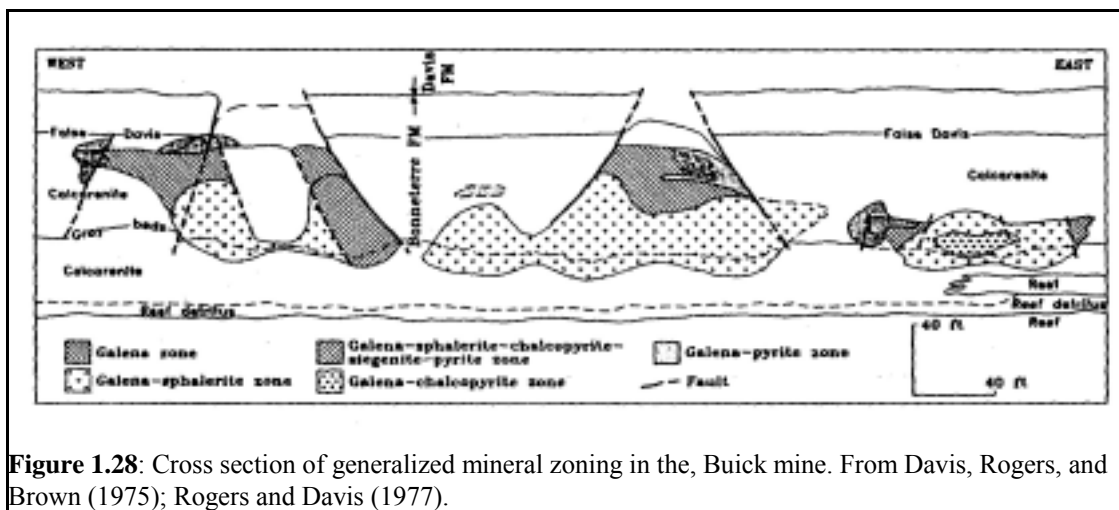
As seen from the above discussion, in order to precipitate Pb needs a site that is near a hot brine source (formed through plate tectonics) and that has a permeable layer. The permeable layer may occur either along fault lines where there are slippage planes, or through a previously formed porous bed. Lead ore bodies are often associated with Pre-Cambrian coral reefs.

Initially, the early marine life-derived carbonates were converted to dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>) with high temperature saline solutions. This conversion

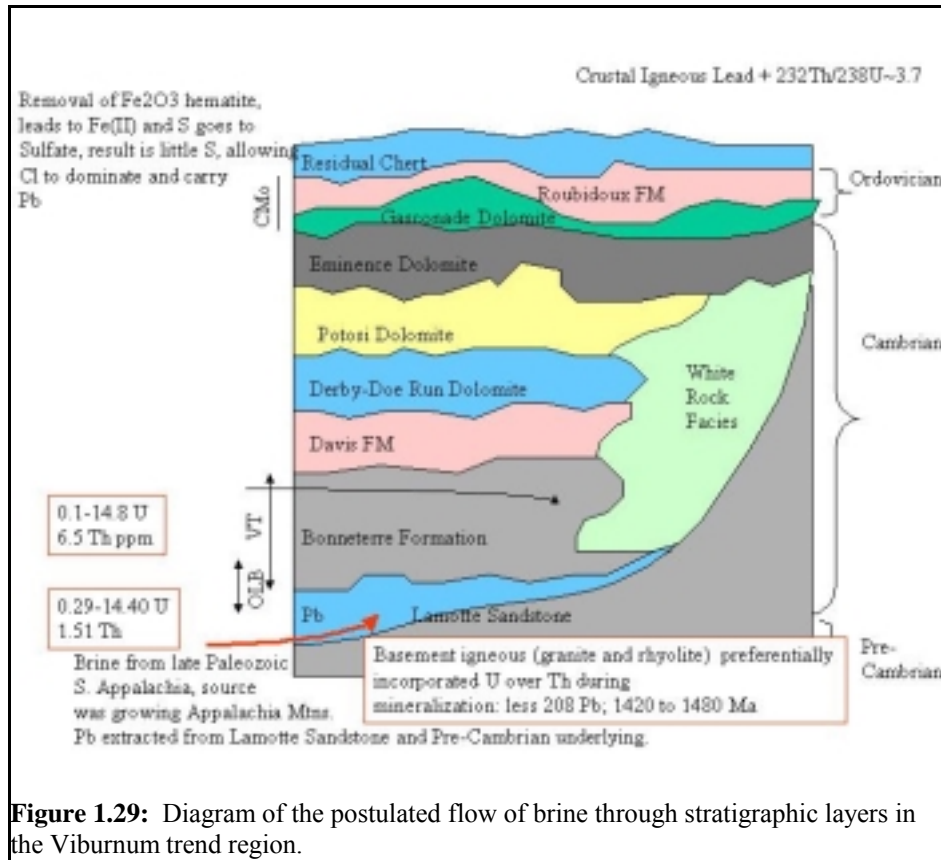


**Figure 1.27:** Area of mines near St. Louis Missouri. This set of mines overlies a Pre-Cambrian coral reef, Figure 1.28. Lasmanis, 1997

resulted in a more porous matrix allowing for transport of fluids. This conversion was followed by mineralization of sphalerite (ZnS), then calcite (CaCO<sub>3</sub>, hexagonal), and finally quartz (SiO<sub>2</sub>) (Chi and Savard, 1995). (The term hexagonal refers to the shape of the unit crystal. Unit crystals can take on a



**Figure 1.28:** Cross section of generalized mineral zoning in the, Buick mine. From Davis, Rogers, and Brown (1975); Rogers and Davis (1977).



**Figure 1.29:** Diagram of the postulated flow of brine through stratigraphic layers in the Viburnum trend region.

tetragonal, orthorhombic, hexagonal, monoclinic, or triclinic shape (Figure 1.26.)

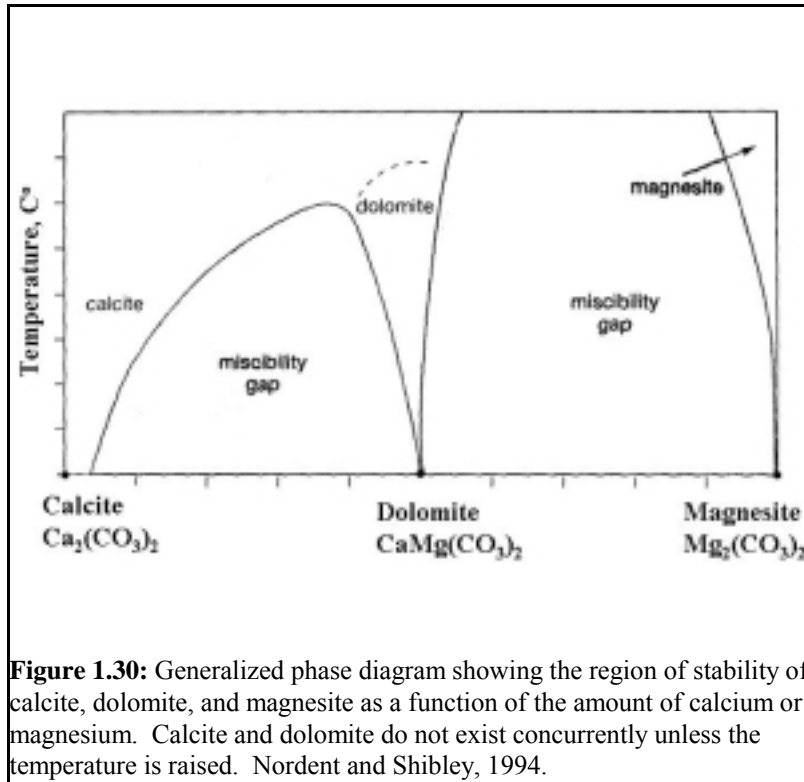
Often hydrothermal deposits of lead are found in conjunction with porous carbonate deposits that originally derived from ancient reefs whose skeletal structure was carbonate based. Consider, for examples, the Navan dolomites of Ireland associated, with Europe's largest Zn-Pb deposit (Braithwaite and Rizzi, 1997). One possible mechanism for the origin of a Mississippi Valley Type deposit in central Appalachia (U.S.) involves the rise of hot mineral-containing brine through the porous carbonate matrix, with crystallization where the brine intersected with sulfur containing over-layers (Kesler et al., 1997). Another example in the Pyrenees dates back to the breakup of the early continent Pangea. The breakup created a fault along a marine basin. The fault served as an outlet for upwardly moving thermal fluids. Deposition began with metal sulfides, then sulfates (barite, or BaSO<sub>4</sub>) and finally with calcite at the surface (CaCO<sub>3</sub>) (Johnson et al., 1996). In the Gays River ore body the porosity was initially set by aragonite (CaCO<sub>3</sub>, orthorhombic) and retained by the dolomite during

dissolution of aragonite and redeposition of dolomite in situ (Chi and Savard, 1995). A similar example of carbonate to dolomite conversion to sulfide bearing ore is given for Poland (Leach and Viets, 1993).

An important example of a similar process is that involved in the formation of the Viburnum Trend. This is a 45 mile lead belt south of St. Louis, Missouri, Figure 1.27. Its base geology is from extrusive pre-Cambrian rocks, with uplifting that influenced the formation of sedimentary rocks (Figure 1.28) (Lasmanis, 1997). Perhaps more importantly, water that presently constitutes the Gulf of Mexico extended north to this point, and the St. Francois

Mountains were islands surrounded by extensive coral reefs. Corals have carbonate skeletons. Goldhaber (1995) and coworkers suggest that the Viburnum Trend lead belt derived from the mixing of fluids traveling along three separate aquifers (Figure 1.28) (Goldhaber et al., 1995). In the late Paleozoic era, warm saline brine migrated north west from the growing Appalachian Mountains. Lead was extracted from basal rocks whose age was ~140 mya. Little H<sub>2</sub>S was present in this fluid due to sulfur oxidation by iron containing minerals. This oxidation lowered the S<sup>2-</sup> ion concentration, allowing lead to achieve very high concentrations as lead chloride in the warm brine. Lead-containing fluid in the Lamotte Sandstone was increasingly constrained by the narrowing of the sandstone belt in the vicinity of the St. Francois Mountains. This narrowing caused the fluid to move upward through more porous dolomite. At the same time, H<sub>2</sub>S or sulfur containing fluid in Bonneterre silt stone encountered narrowing of the siltstone bed, causing it, too, to move into the dolomite, resulting in the precipitation of PbS. Following this initial mineralization phase, additional sulfur- and lead-





containing fluids moving through the Bonneterre carbonate precipitated as PbS. The multiple precipitation events explain the multiple isotopic signature of the lead ore body. Above the thick reef, which has been recrystallized to dolomite, is the Bonneterre Formation of carbonate units. This porous material allowed hydrothermal waters to percolate easily (Figure 1.29). The resulting lead deposition was among the richest in the world. The source of heat for the hydrothermal process is not well known. One hypothesis is that the heat derives comes the Appalachian Mountain uplift.

Lead isotope studies of a WestShorpsire orefield in England also suggested that lead from multiple sources was tapped by a single fluid, incompletely mixed and then deposited as the ore (Haggerty et al., 1996).

It should be noted that with advances in chemical instrumentation better precision has been obtained for the lead isotope ratios. It is now apparent that the lead isotope ratio for a single ore body may vary as a function of multiple deposition steps during ore formation. Such variation within a single ore body has required geologists to determine appropriate statistical methods for spatial analysis of the ores (Gale et al., 1999; Gray et al., 1994; Shirahata et al., 1980).

The ore bodies in each of these locations all initiated with sea-floor aragonites' skeletal structure, followed by fracturing boundaries that created sites for hot brine (highly saline) fluids involved in recrystallization. Dolomites are formed in situ by replacement (space filling) hydrothermal fluids at temperatures of 95-115° C (Niew et al., 1993). Brine temperatures can reach 150 ± 20° C with 20-25 weight percent NaCl. These fluids that filled coarse dolomites served as a loci for mineralization (Nesbitt and Muehlenbachs, 1994).

The general conversion of carbonates stable at low temperature to dolomite hosts for lead precipitation involves the dissolution of aragonite with concurrent high temperature deposition from Mg-containing brine (Brand, 1994). The fundamental chemistry of carbonate to dolomite involves surface controlled nucleation kinetics (Nordeng and Sibley, 1994).

A phase diagram shows that crystal structure changes as a function of percent composition as more and more magnesium is present (Figure 1.30). The phase diagram is also temperature-dependent, as the relative stabilities of the crystals may change with temperature.

Figure 1.30 shows a phase diagram that tracks the change in the calcite (CaCO<sub>3</sub>), crystal to the dolomite (CaMgCO<sub>3</sub>) crystal as a function of the magnesium content. Although the two crystals adopt a similar packing structure, they do not coexist at low temperatures. The cause of their miscibility gap which renders them unlikely to co-exist is related to the cell dimension change that accompanies substitution of the larger Ca<sup>2+</sup> cation by the smaller Mg<sup>2+</sup> cation (Table B.15). Similar changes in crystal structure occur when lead nucleates onto the calcium matrix.

Nucleation may be driven by preferential adsorption of divalent metals (Cd<sup>2+</sup>, Sr<sup>2+</sup>, Mg<sup>2+</sup>, Ba<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>) onto specific lattice sites of aragonite and calcite (Meece and Benninger, 1993). Adsorbed lead ions generally occupy calcium sites within the calcite lattice (Cherniak, 1997; Kozar et al., 1992; Qian et al., 1994; Sturchio et al., 1997). Substitution of lead leads to a larger crystal dimension and pushes the crystal into an orthorhombic structure, similar to an expanded aragonite (CaCO<sub>3</sub>) crystal.

The deposition of lead into the crystal depends not only on adsorption to the surface, but upon diffusion into the interior of the carbonate, which results in layers of calcium depletion and lead enrichment (zoning). Calcium has been observed to have a region of depletion/concentration on the scale of  $\mu\text{m}$  to 10s of  $\mu\text{m}$  (Kozar et al., 1992). Zoning is related to the relative rate of growth of the replacing crystal vs the diffusion of the new material to the new crystal site. Replacement of the bulk calcite crystal with lead carbonate will occur when diffusion of lead within the crystal is high enough to supply the growth of the crystal. The diffusion of lead within the crystal is determined by the molecular path followed. The activation energy of lead is similar to that of strontium (Sr), but the overall diffusion coefficient is less. This implies that lead is traveling a similar path as strontium, but is held more tightly. Since both Sr and Pb have similar divalent radii, the suggestion is that the 2s electrons on lead affect its binding at each hopping site.

### Comparison of Lead to Calcium

Although lead can replace calcium in aragonite and calcite, it does differ from calcium in important ways. With the exception of chlorides and acetate, all other species of lead are also considered to be insoluble. Those anions that form insoluble salts have very high charge densities (Table D.2). The reason for lead's greater insolubility is that it is more polarizable because it resides in the nether regions of the periodic table. Furthermore, lead has an ambiguous character; it is neither quite metal nor non-metal.

The periodic table indicates that calcium has available only two possible electron configurations, leading to zero or divalent charge. Thus calcium is limited primarily to electrostatic or ionic interactions. Lead, because it lies midway across the periodic table, may not lose enough electrons to obtain the noble gas configuration. It can covalently as well as ionically bond. In covalent bonding, electrons are more or less equivalently shared by both atoms and occupy space equivalently between both atoms. Elements which covalently bond tend to be those in the same column as carbon (Si and Pb). In order to covalently bond, the 2s and 2p orbitals are mixed to obtain four equivalent new orbitals with a different geometry. These four orbitals move to occupy maximum volume resulting in a tetrahedral geometry. The covalent binding of lead with oxygen gives rise to highly insoluble species. The extremely insoluble nature of PbO is forbidden to Ca,

which can bind only by electrostatics. Tables B.1, B13 and B.14 show a list of many of the ionic compounds formed by lead, as well as some of the covalent species.

### Fingerprinting

As a result of the planetary forming processes lead that was formed in the Big Bang can be initially separated from uranium and thorium, the parents of most lead on earth. Lead generated during atom formation,  $^{204}\text{Pb}$ , condenses at a much lower temperature (496 K) and is abstracted into the siderophile (Fe-rich) and chalcophile (S-rich) phases. U and Th condense at temperatures as high as 1590° K and move to abstract oxygen because they are lithophiles in a cubic coordination environment. When the cations  $\text{U}^{4+}$  and  $\text{Th}^{4+}$  decay (Figure 1.31) to  $^{206,207,208}\text{Pb}^{4+}$ , the lead prefers an octahedral coordination environment, resulting in a less stable mineral (Table B.9).

Figure 1.32 shows the relative abundance of Th, U, and Pb in various volcanic rocks. As we proceed to the right in the figure, the melting point of the rock decreases, implying that the rock solidifies at lower temperatures. Note that Th and U show greatest preference to the low temperature forming pegmatites. Lead forms in gabbros and basalts with a higher melting point. These differences in crystallizing result in the separation of U and Th from Pb. The U and Th so isolated decay to other isotopes of lead leading to isotopically different lead ore bodies.

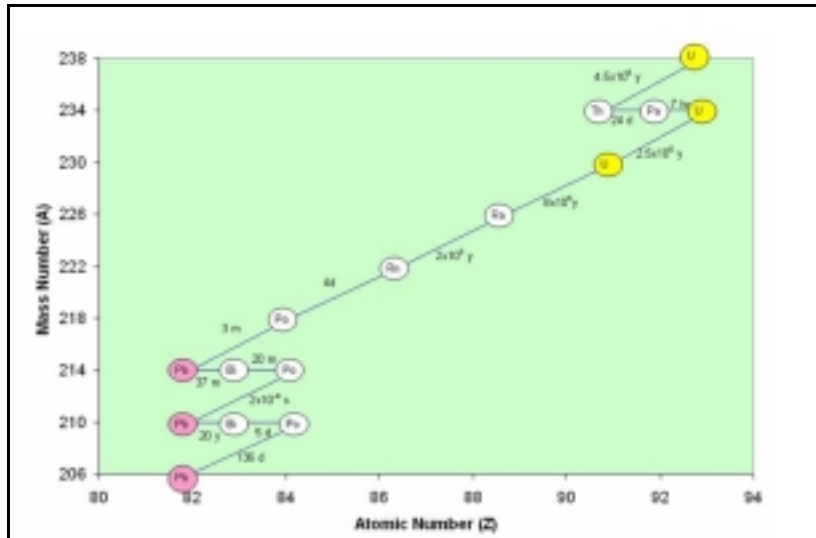
Several decay paths exist from uranium ( $^{235}\text{U}$  and  $^{238}\text{U}$ ), thorium ( $^{232}\text{Th}$ ), and plutonium ( $^{241}\text{Pu}$ ). In Figure 1.31, uranium of mass 238 and 92 protons first loses an  $\alpha$  particle to form thorium of mass 234 and a proton count of 90. It takes  $4.5 \times 10^9$  years for the initial uranium to decay to half of its original value ( $t_{1/2} = 4.5 \times 10^9$ ). The thorium formed decays, emitting a high-energy electron, a  $\beta$  particle and converting one neutron to a proton. This raises the atomic number to 91, that of Pa. A second  $\beta$  emission results in an increase in positive charge to an atomic number of 92, U with a mass of 234. Uranium of mass 234 is lost by a series of  $\alpha$  emissions until the unstable  $^{214}\text{Pb}$  is formed. Ultimately lead  $^{206}\text{Pb}$  is formed. The slowest step in the entire process is the emission of the first  $\alpha$  particle. Similar decay paths exist for  $^{235}\text{U}$  and  $^{232}\text{Th}$ . The decay of  $^{235}\text{U}$  is more rapid and nearly all of the uranium has since formed  $^{207}\text{Pb}$ . In addition,  $^{204}\text{Pb}$ , which is not a product of a decay sequence, is thought to originate from original nucleosynthetic reactions.

Several other isotopes can be created in modern nuclear experiments by  $\alpha$  ( ${}^4_2\text{He}$ ) bombardment with resulting loss of a neutron,  ${}^1_0\text{n}$ . Table B.2 shows the main progenitors of lead and their half-lives. Table B.3 shows all the known isotopes of lead (Rankama, 1965).

As Table B.3 shows, the natural abundance of lead's radioactive isotopes is low. In particular, older lead objects (for example, Roman ingots) are low in  ${}^{210}\text{Pb}$  and have been remined from sunken ships for use in physics studies where an absolute zero radiation background is required (Holden, 1991). (The half life of  ${}^{210}\text{Pb}$  is 25 years. Thus, if the source of lead is a natural, geologic, rock,  ${}^{210}\text{Pb}$  should have decayed to  ${}^{206}\text{Pb}$  by the time of mining. Modern forms of processed lead contain higher radioactivity due to contamination with manmade radioactive isotopes.)

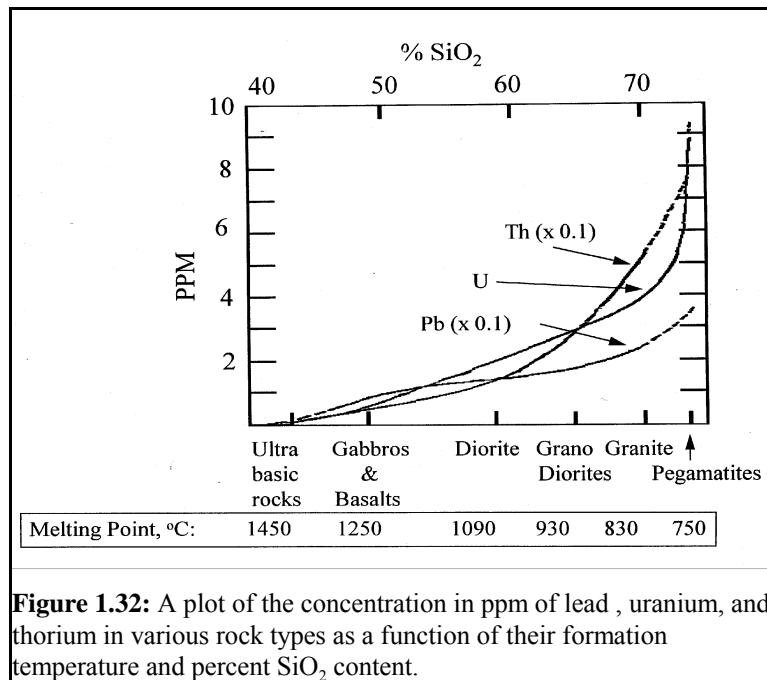
Thus far, chemical principles have shown us that two progenitors of lead, U and Th, are segregated from lead during rock formation. Consequently, under ideal circumstances, the U- and Th-containing rocks are closed systems (with no input or removal of externally derived lead). As a result, these radioisotopes decay to the more stable lead configuration, forming a new ore body that contains lead oxides with variable quantities of  ${}^{206}\text{Pb}$ ,  ${}^{207}\text{Pb}$ , and  ${}^{208}\text{Pb}$ . These quantities depend upon the original concentrations of  ${}^{235}\text{U}$ ,  ${}^{238}\text{U}$ , and  ${}^{232}\text{Th}$ ; the time since rock formation; and the decay rates of the three progenitors (Dickin, 1995), p. 105. Figure 1.16 shows the segregation pattern of lead isotopes in U.S. ore bodies, superimposed over a plot of the estimated age of the crystalline rocks (Foster, 1983; Tilton and Hart, 1963). Note in this figure that the ratio  ${}^{210}\text{Pb}/{}^{204}\text{Pb}$  is consistent with the geologic groupings.

The relative abundance of different lead isotopes can be used in various dating schemes. If the rock remains intact with no other earth-forming steps, the relative ratios of  ${}^{206}\text{Pb}/{}^{235}\text{U}$ ,  ${}^{207}\text{Pb}/{}^{238}\text{U}$ , and  ${}^{208}\text{Pb}/{}^{232}\text{Th}$  indicate the age of the rock, based on a



**Figure 1.31:** Decay sequence for Uranium -238 to Lead-206. Data Source: Rankama Kalervo, 1965.

knowledge only of the decay rates (see example 1.5) (Evans, 1987; Fergusson, 1990). A unique pattern of  ${}^{206}\text{Pb}$ ,  ${}^{207}\text{Pb}$ , and  ${}^{208}\text{Pb}$  results. This pattern aids geologists in elucidating the crustal movement and



**Figure 1.32:** A plot of the concentration in ppm of lead, uranium, and thorium in various rock types as a function of their formation temperature and percent  $\text{SiO}_2$  content.

dates of igneous formation. Each individual isotope varies in time.

The unique fingerprint patterns of the individual ore bodies can be easily cross compared to one another by plotting the ratio of isotopes  $^{208}/^{206}$  (y) vs  $^{207}/^{206}$  (x) (Figure 1.17). This plot lies along a nearly straight line which correlates with age. This time-isotope relationship derives from early geological literature (Keevil, 1939; Nier, 1939; Nier et al., 1941). See example 1.5.

U/Pb isotope dating is useful in determining a wide range of geologic processes such as the rate of soil formation from minerals and the rate of sedimentation processes. Such dating was used to determine a sedimentation rate of 50 meters/million years for the formation of sedimentary rocks in the Sidney Basin of Australia (Gulson et al., 1990). A tool useful to geologists is the amount of  $^{210}\text{Pb}$  detected.  $^{238}\text{U}$  decays through a wide variety of elements to ultimately form  $^{206}\text{Pb}$ . During this decay process radon (Rn) is formed. It has a half life of only 4 days, meaning that in four days any amount of radon decays to half of its original amount, giving off an alpha (helium) particle in the process. Radon has a closed shell configuration, meaning that chemically it is very unreactive. It exists as a noble gas and escapes into the atmosphere. There it adheres to dust particles and is redeposited in sediments, where the decay sequence continues to the next most stable element,  $^{210}\text{Pb}$ , which has a half-life of 20 years. The  $^{210}\text{Pb}$  detected in such sediments is too young to be related to geologic or historical processes; it must have been deposited in the last 20 years. It can be distinguished from other lead sources by its mass and is therefore used to track sedimentation rates.

## Chapter 1: Problem Set

1. Why are PbS and Ag<sub>2</sub>S found together in nature?
2. What other metals are found in lead ores?
3. What conditions render a metal easily found, extracted, and manipulated?
4. Is a metal in the same chemical form all the way throughout an ore body?
5. What impact would the presence of different chemical forms (if any) in an ore body have on human ability to extract ore?
6. Why is lead often found in conjunction with dolomite?
7. What does Question 6 have to do with Proposition 65 in California?
8. Where are most lead ore bodies found and why?
9. How does lead masquerade as calcium, and how does lead differ from calcium?
10. Is the abundance of lead within the earth's crust larger or smaller than expected from nuclear synthetic reactions?
11. How can the source of lead be fingerprinted?
12. What are some of the typical symptoms of lead poisoning?
13. Are children affected in the same fashion as adults by lead poisoning?

### Questions for Chemistry Afficionados

14. Give two reasons why a mystery element with mass number  $4n$  is likely to be more abundant than an element with mass number  $4n+1$ .
15. Which is more abundant, an element with mass number  $2n$  or one with  $3n$ ?
16. Using the Big Bang theory of the universe's origin explain the log decay of relative abundance of the elements.
17. Which of the following compounds would you predict to actually occur in nature? What would its charge be?
  - a) PbO<sub>6</sub>
  - b) PbO
  - c) PbO<sub>2</sub>
  - d) PbO<sub>4</sub>
18. If you have 10 grams of <sup>210</sup>Pb, how much will you have in
  - a) 20 years?
  - b) 40 years?
  - c) 80 years?

19. Why would the conversion of uraninite, UO<sub>2</sub>, to PbO<sub>2</sub> via radioactive decay result in a less stable rock, one susceptible to weathering at high temperatures?
20. Why is lead a chalcophile?
21. If you have an anion with charge/ $r^3$  of  $2.2 \times 10^{-7}$  esu/pm<sup>3</sup> is it likely to form mostly soluble or insoluble salts with Cu<sup>2+</sup>? With Pb<sup>2+</sup>?

### Suitable problems for students with more advanced chemistry

22. Calculate the age of a rock that contains <sup>238</sup>U and <sup>206</sup>Pb and has a ratio of Pb/U of 0.213. Assume that no lead was originally present in the rock and that the half lives of the intermediates are negligible, the half-life of <sup>238</sup>U is  $4.5 \times 10^9$  years and first order reaction kinetics apply.
23. A rock containing <sup>238</sup><sub>92</sub>U and <sup>206</sup><sub>82</sub>Pb had a ratio of Pb/U of 0.03. Assuming no lead was originally present and that the half lives of the intermediate nuclides are negligible, calculate the age of the rock using the half-life of <sup>238</sup><sub>92</sub>U of  $4.5 \times 10^9$  years assuming first order reaction kinetics.
24. Calculate the free energy for reduction of PbO<sub>2</sub>.
25. What is the binding energy of <sup>210</sup>Pb?
26. What is the binding energy for <sup>238</sup>U?
27. What is the solubility of Ag<sub>2</sub>S at 100C? What implications does this have for the formation of lead/silver deposits?
28. What is the K<sub>sp</sub> of lead at 70C?
29. How many grams of lead can exist in 1 liter of 50C water in the presence of PbS?
30. Calculate the temperature at which PbS is converted directly to Pb metal using the tables of enthalpies and entropies at the back of the book.

## Chapter 1: Literature Cited

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