6. Isotope Geochemistry

6.1 Introduction

Isotopes were first discovered by F. Soddy in 1913 and since that time their study has become one of the most important and powerful tools in geochemistry. *Isotopes* are defined as atoms of the same atomic number, but with different atomic masses. The differing mass is due to a different number of neutrons in the nucleus. Some elements have only one isotope, while others have two and some have as many as eight. Isotopes are denoted by ^{41}K where the number 41 equals the protons plus neutrons, in this case 19 protons and 22 neutrons. All isotopes of the same element have similar chemical and physical properties resulting from the same number of protons and electrons. However, for elements of lower atomic mass there can be significant differences in properties due to the large proportional differences in mass. The atomic weight given on periodic tables is the average of all isotopic weights corrected for abundance (39.102 for K of which 93.1% is ^{39}K, 0.01% is ^{40}K, and 6.9% is ^{41}K).

Isotopic variations may be divided into two major groups: (a) those due to radioactive decay of unstable nuclides, which causes variations in the isotopic composition of the stable daughter products, and (b) those due to variations in nonradiogenic isotopes most often produced by exchange reactions, kinetic reactions in biological systems, or physical-chemical processes such as evaporation or diffusion. Radiogenic isotopes most often studied are those of argon, strontium, lead and neodymium. These elements may show significant variations due to the length of time their parent radioactive nuclides have had to decay and the original concentrations of the parent and daughter nuclides. Strontium isotopes have proven to be a particularly useful tracer to indicate whether the magma that formed an igneous rock originated in the mantle or crust. Stable isotopic variations are most pronounced in the low atomic weight elements hydrogen, carbon, oxygen and sulfur. Stable isotope variations occur and are most easily detected when the relative mass differences between the isotopes are significant, such as ^{1}H and ^{2}H, or ^{12}C and ^{13}C with mass differences of 100% and 8% respectively. Also, as temperature increases the degree of fractionation (separation) of the isotopes decreases. Thus, stable isotope studies have found more application in near surface sedimentary or low temperature environments than in magmatic environments.

6.2. Radioactive Isotopes

During radioactive decay three types of radiation can/may be produced:

1) *alpha particles* (helium nuclei) – results from the loss of two protons and two neutrons from the nucleus. Causes a reduction by two in the atomic number and 4 in the mass.

2) *beta particles* (electrons) – can occur in two directions, as electron capture by the nucleus or electron emission from the nucleus (ex. neutron $\rightarrow$ proton + electron. The result can be either a gain or loss of one in the atomic number with no change in mass.

3) *gamma radiation* (X-rays) – although detectable and harmful, of no value to the geologic application of radioactive isotopes as there is no mass change.

During the decay process the original unstable radioactive isotope is termed the **parent** and the newly formed decay product is the **daughter**.

In order to apply the decay process to the determination of an age for a rock it is necessary to make three assumptions:

- the decay rate is a constant;

- the rate at which decay occurs is unaffected by physical changes (e.g., T & P);

- when the radioactive element is trapped in a crystallizing mineral the daughter and parent will not be separated by normal physical processes.

Then by measuring the concentration of the parent and daughter and knowing the rate of decay we can calculate when the mineral or rock formed. The basic decay equation is:

$$\frac{dD}{dt} = \lambda P \quad D = daughter; \ P = parent$$

or

$$\frac{-dP}{dt} = \lambda P$$

Integration gives

$$-\ln P = \lambda t + C$$

C is the integration constant which may be expressed in terms of parent atoms at $t = 0$:

$$C = -\ln P_0$$

Substitution of this value gives

$$\ln P - \ln P_0 = -\lambda t$$

Thus

$$P = P_0 e^{-\lambda t} \quad or \quad P_0 = P e^{+\lambda t}$$

Setting the number of daughter atoms produced by time $t = D*$ or $P_o - P$ yields

$$D* = Pe^{\lambda t} - P = P(e^{\lambda t} - 1)$$

Unfortunately, for some radiogenic isotopes at $t = 0$ some daughter atoms may have been present. Therefore, we must account for those daughter atoms in our equation:

$$D = D_0 + D* = D_0 + P(e^{\lambda t} - 1)$$

Rearranging and solving for t

$$t = \frac{1}{\lambda} \ln\left(\frac{D - D_0}{P} + 1\right)$$

To solve this equation for t we measure D and P with the aid of a mass spectrometer, while the decay constant (λ) has been determined by laboratory experimentation. D_O is generally eliminated on the basis of known abundance; ignored by choosing a mineral with low or zero initial concentration of the daughter; or found by plotting D against P since the decay equation has the form $y = ax+b$ and hence is a straight line with intercept $= D$ and slope $= e^{\lambda t} - 1$ (Figure 6.1). The slope is called an *isochron*.
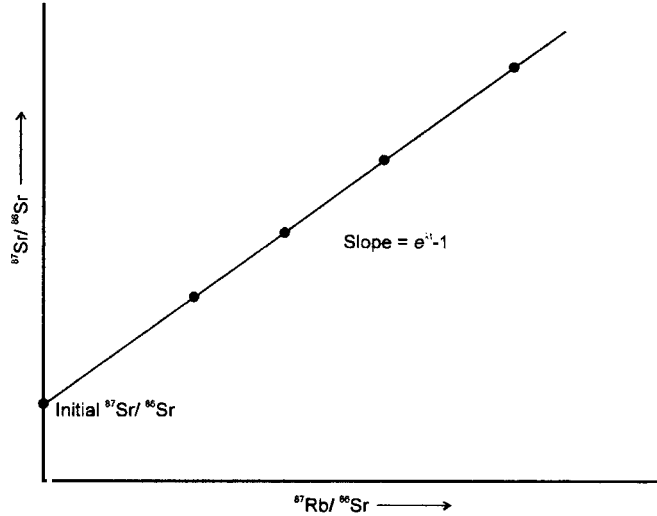

Figure 6.1. Typical isochron diagram for the decay of ^{87}Rb.

More easily visualized than λ, is a related quantity called the *half-life* (Table 6-1). This is the time required for half of any given amount of a radioactive isotope to decay:

$$t_{\frac{1}{2}} = \ln\frac{P}{\frac{1}{2}P_0} \times \frac{1}{\lambda} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$$

Two Key Assumptions:

      1) decay constant has not changed with time - *probably true*
      2) system has been closed - *often questionable*

6.2.1 Rb/Sr

^{87}Rb decays by emission of an electron to ^{87}Sr, thus:

$$^{87}Sr_{tot} = {}^{87}Sr_o + {}^{87}Rb(e^{\lambda t} - 1)$$

Since isotopic ratios are more easily measured the equation is divided through by nonradiogenic ^{86}Sr:

$$\frac{^{87}Sr_{tot}}{^{86}Sr} = \left(\frac{^{87}Sr}{^{86}Sr}\right)_o + \frac{^{87}Rb}{^{86}Sr}(e^{\lambda t} - 1)$$

Solving for t

$$t = \frac{1}{\lambda}\ln\left[\frac{\dfrac{^{87}Sr}{^{86}Sr} - \left(\dfrac{^{87}Sr}{^{86}Sr}\right)_o}{\dfrac{^{87}Rb}{^{86}Sr}} + 1\right]$$

Table 6-1 Radioactive Elements Used for Age Dating

Nuclide	Half-life (yr)	λ (yr^{-1})	Effective Range	Minerals
^{238}U—^{206}Pb	4.50×10^9	1.54×10^{-10}	10^7-10^9	zircon, uraninite
^{235}U—^{207}Pb	0.71×10^9	9.72×10^{-10}	10^7-10^9	zircon, uraninite
^{232}Th—^{208}Pb	1.39×10^{10}	4.99×10^{-11}	10^7-10^9	zircon, monazite
^{87}Rb—^{86}Sr	5.00×10^{10}	1.39×10^{-11}	10^7-10^9	micas, igneous and metamorphic rocks
^{147}Nd—^{143}Sm	1.06×10^{11}	6.54×10^{-12}	10^9	igneous rocks
^{40}K—^{40}Ar	1.3×10^9 (total)	β 4.72×10^{-10} κ 5.85×10^{-1}	10^4-10^9	micas, k-spar, volcanic rocks
^{14}C	5730	1.21×10^{-4}	0-10^5	wood, charcoal

$$\lambda = 1.39 \times 10^{-11} yr^{-1} \qquad \left(\frac{^{87}Sr}{^{86}Sr}\right)_o = 0.704$$

The minerals used most commonly for Rb/Sr age dating include k-feldspar, lepidolite, biotite and muscovite. Unfortunately, scientists soon learned that different minerals from the same rock would often yield different ages. More common today, is the whole-rock analysis. This method plots an isochron diagram (Fig 6.2). Isochrons have proven to be very useful in the study of rocks that give different or *discordant* ages for minerals or rocks in an area. Studies show that whole-rock samples usually less than a cubic meter in size are closed systems during metamorphism while mineral grains in the rock may experience exchange and homogenization of the Sr isotopes during the thermal event.

Such a homogenization causes a resetting of the isochron to a horizontal line as illustrated in Figure 6.2. At this time the radioactive clock would be reset and the strontium would develop a new isochron to give the date of the metamorphic event. However, the isochron for the whole-rock analyses would not be altered and the analyses and plotting of different whole-rock samples would provide a date for the original magmatic event. A diagram illustrating an ideal two-stage isochron for both rocks and minerals indicating both the initial igneous and later metamorphic events is shown in Figure 6.3. In practice, many areas have such complicated histories subsequent events are often difficult to decipher.
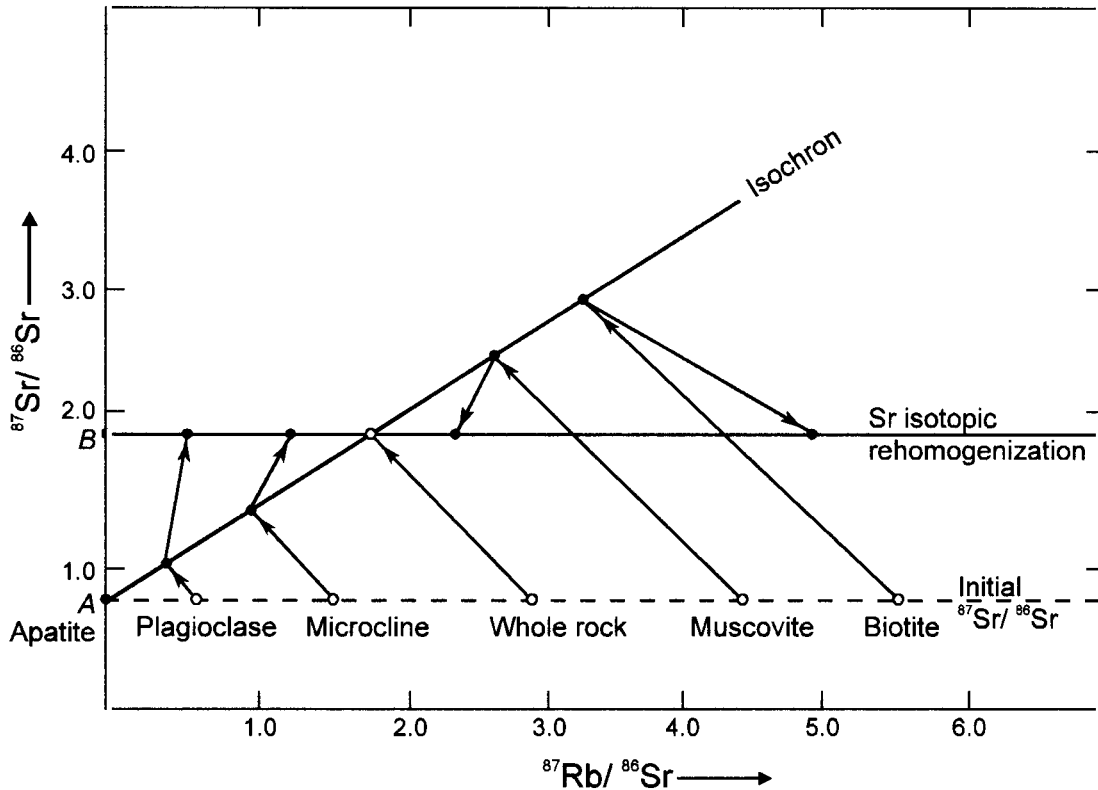
Figure 6.2. Isochron diagram showing the effect of episodic homgenization of Sr. The total rock and component minerals had an initial $^{87}Sr/^{86}Sr$ indicated by *A*. Later metamorphism caused the Sr composition in the minerals to rehomogenize to the whole rock ratio *B*.

$^{87}Sr/^{86}Sr$ ratios have also been used to interpret the genesis of igneous rock suites. During initial differentiation of a molten earth Rb would be enriched in crustal material due to its tendency to substitute for K in crystallizing minerals, while Sr would favor a more uniform distribution in both the mantle and crust because of its substitution for Ca. (Note: K is greatly enriched in the crust relative to the mantle while Ca shows only a slight enrichment in the mantle) Thus, with decay of ^{87}Rb more radiogenic ^{87}Sr would be produced in crustal rocks and the $^{87}Sr/^{86}Sr$ ratio would be greatest in magmas contaminated by crustal material. The initial $^{87}Sr/^{86}Sr$ ratio at the time the Earth formed is thought to be 0.699, as determined from stony meteorites with age dates approximating the postulated age of the earth. Analyses for recently formed mid-ocean ridge basalts gives ratios ranging from 0.704 to 0.707 with most <0.705. Therefore, if a magma was generated from the mantle or lower crust today it should have a ratio less than 0.707. If, however, it is generated in the upper crust or contaminated by significant volumes of crustal material the ratio would be greater than 0.707. Looking at the problem of formation of granites by partial melting of continental crust or differentiation from a basaltic magma we find some ratios are near that for a basalt, thus some granite is probably a differentiate of mantle-derived basalt (*I-type*). Many granites, however, have much higher ratios, as great as 0.730, indicating derivation from preexisting crustal
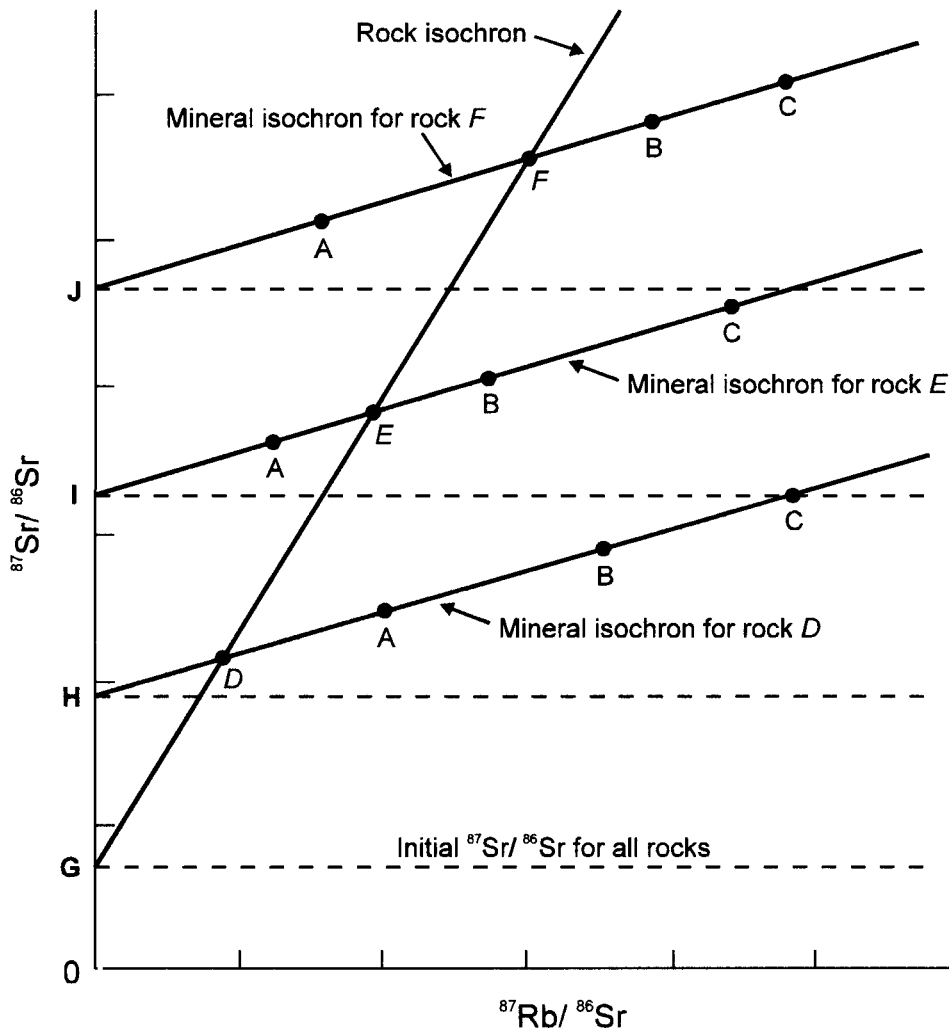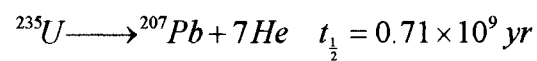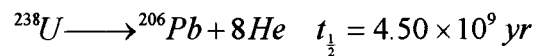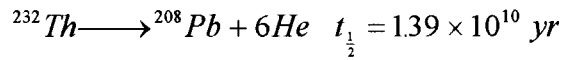
Figure 6.3. Isochron diagram for three related rocks of similar age that have undergone subsequent metamorphism. The rocks (D,E,F) define an isochron representing the age of the rocks. The minerals (A,B,C) define isochrons determined by the time of metamorphism.

material (*A-type*). However, most granites fall in the range 0.707-0.712 indicating some interaction between mantle-derived magmas and crustal rocks (*S-type*).

6.2.2 Uranium-Thorium-Lead

The chief isotope of uranium is ^{238}U (99.3%) with smaller amounts of ^{235}U and ^{234}U. ^{234}U is relatively short lived and is ignored.

$$^{238}U \longrightarrow ^{206}Pb + 8He \quad t_{\frac{1}{2}} = 4.50 \times 10^9 \, yr$$

$$^{235}U \longrightarrow ^{207}Pb + 7He \quad t_{\frac{1}{2}} = 0.71 \times 10^9 \, yr$$

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$$^{232}Th \longrightarrow ^{208}Pb + 6He \quad t_{\frac{1}{2}} = 1.39 \times 10^{10} \ yr$$

The net result, therefore, is that three independent age dates are possible for any rock or mineral containing uranium/thorium. Once again, since ratios are more easily measured the amounts of U, Pb and Th are customarily reported in relation to non-radiogenic ^{204}Pb.

$$\frac{^{206}Pb}{^{204}Pb} = \left(\frac{^{206}Pb}{^{204}Pb} \right)_0 + \frac{^{238}U}{^{204}Pb} \left(e^{\lambda t} - 1 \right)$$

Since lead is a common trace constituent of many igneous rocks, the best age dating method is to choose mineral separates, usually zircons, which exclude lead during crystallization, but do incorporate uranium. If the three independent age dates for ^{238}U, ^{235}U, and ^{232}Th vary by ±2%, the ages are said to be *concordant*. However, often the ages do not agree (*discordant*) meaning that the rock or minerals were not a closed system.

To correct for discordant ages concordia diagrams are used (Fig. 6.4). Concordia diagrams plot the ratio of ^{206}Pb/^{238}U against ^{207}Pb/^{235}U for rocks with concordant ages. These two daughter products (^{206}Pb and ^{207}Pb) accumulate at different rates due to the differing decay constants for the parents, and hence plot as a curve. (Note: *Only rocks which yield concordant ages were used to plot the initial curve in Figure 6.4.*) If no
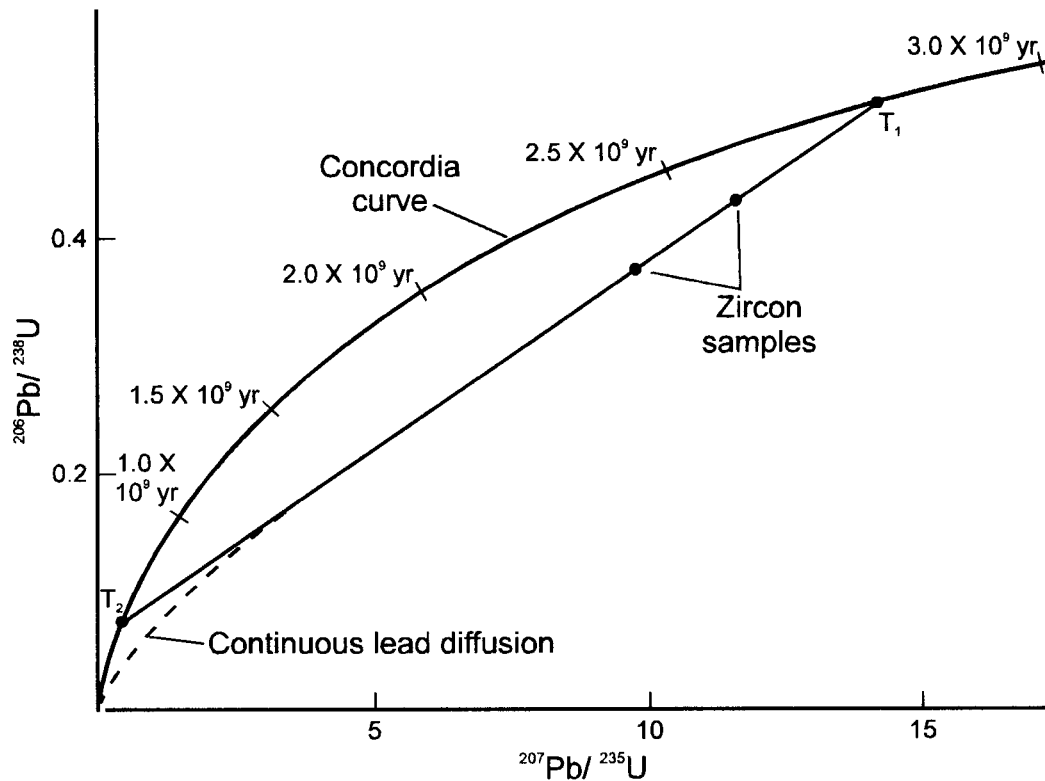

Figure 6.4. Concordia diagram for the U-Pb system. The curve was plotted from rocks/minerals yielding concordant ages. T_1 represents the time of formation of a sample suffering U-Pb loss.

lead has been lost from an unknown sample it should plot as a point on the concordia curve. However, if some lead has been lost subsequent to the crystallization of the rock, perhaps by diffusion during metamorphism, the mineral separates will plot as a series of points lying along a straight line beneath the concordia curve (See Figure 6.4). The points lie on a straight line because any loss of both ^{206}Pb and ^{207}Pb will be uniform (i.e. in a proportional ratio to one another) due to the small difference in mass. The upper intersection of the discordia line with the concordia curve gives the age of the mineral or rock. The lower intersection was originally thought to represent the age of the thermal event which resulted in lead loss, but many now feel Pb loss is the result of a continuous, gradual diffusion subsequent to crystallization and hence the lower intersection has no significance at all.

Another useful concept is the ratio of radiogenic Pb to nonradiogenic ^{204}Pb. It has enabled calculations of the age of the earth using Pb/Pb ratios of meteorites. Troilite (FeS) from iron meteorites is thought to contain the original primordial Pb ratios at the time the earth formed. This hypothesis is based on the belief that troilite would incorporate lead, but no uranium at the time of its crystallization. Stony meteorites, however, contain Pb, as well as U and Th. Plots of 207/204 vs. 206/204 for iron and stony meteorites result in a straight line whose slope is = t or 4.65 billion years, the most commonly accepted age for the Earth.

The use of ordinary or common lead in ores to age date ore deposits has also been attempted. The theory is that since primordial time the ratio of ^{207}Pb to ^{206}Pb has been changing because of the differing half-lives. When Pb is incorporated in a mineral (e.g. galena) the isotopic ratio should fall on a curve indicating the time during which Pb was separated from the source material. This curve is termed a *growth curve*. The growth curve has been prepared from samples which give only concordant ages. Obviously any ratio could be used as a starting point, but again we resort to that of troilite from meteorites (Fig. 6.5). This method of age dating does not work well since some rigid conditions must be met. Prior to separation from the source no Pb or U can be added or subtracted since the time the earth was formed; then in a relatively short time the lead must be cleanly separated to make the ore; and afterward the Pb ore must remain isolated from any contact with U or additional Pb. Obviously such conditions are rarely found in nature. If they are, however, and the age date is thought to be valid we refer to the ores as single stage. Most Pb's are anomalous in that the calculated ages are greater or lesser than the apparent possible ages as predicted by other geological methods. If greater, this is explained by the remobilization of lead deposited at an earlier time. For one group (*J-type*), apparent ages are much less than the accepted geological ages, actually into the future. This suggests changes in the amounts of U and Pb in the source material at one or several times prior to ore deposition and substantial contamination from radiogenic leads (multistage ores). Due to the above problems, Pb/Pb ratios have been used more often to determine possible source materials for the ore fluids rather than to age date ores. The theory is that if lead was originally leached from a single source the lead ratios in the ore deposit ought to be the same as those in the source from which the lead was leached. To work however, the source must be devoid of U (otherwise the ratio would change with
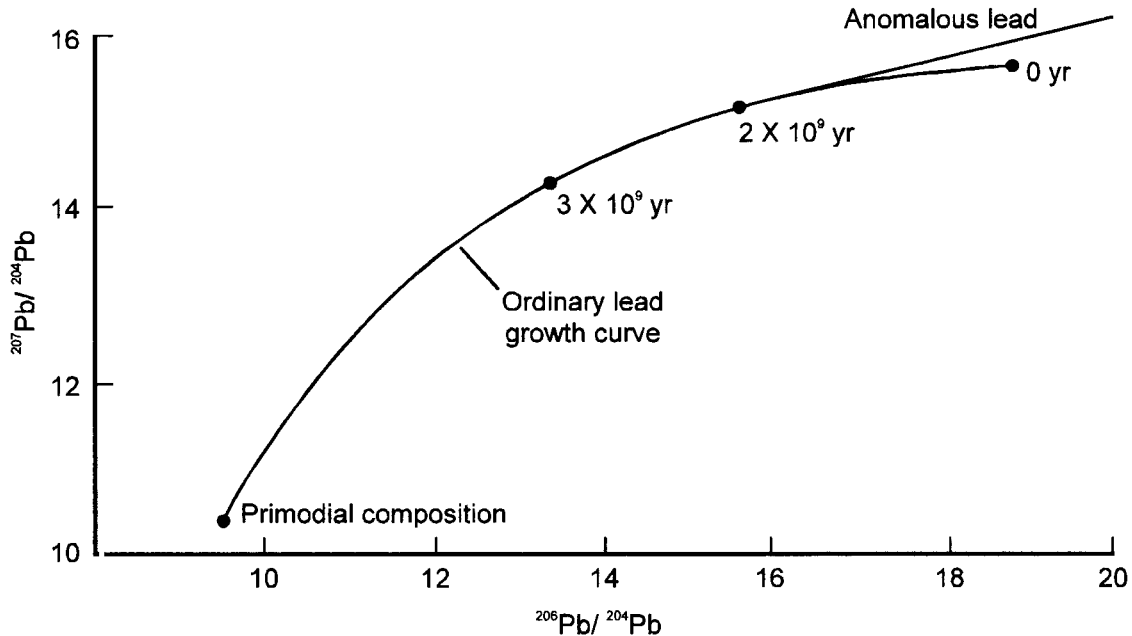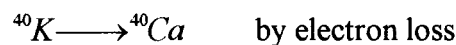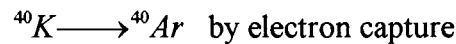
Figure 6.5. Diagram of $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$, indicating the primeval isotopic composition and a growth curve for ordinary lead corresponding to a source region in which $^{238}U/^{204}Pb = 9.08$.

time!) or we must know when the ore deposit formed so we can correct the current ratios of possible source rocks to those that existed at the time the ore deposit was forming.

6.2.3 Potassium-Argon

The decay of ^{40}K occurs by two mechanisms:

$$^{40}K \longrightarrow ^{40}Ar \quad \text{by electron capture}$$

$$^{40}K \longrightarrow ^{40}Ca \quad \text{by electron loss}$$

^{40}K is very rare, only 0.01% of all potassium is ^{40}K. The decay to ^{40}Ca is not usable because ^{40}Ca is the common isotope of calcium. The decay to ^{40}Ar, however, is very useful since potassium is a common element in felsic igneous rocks and any detectable argon, a noble gas, would only be present by decay from ^{40}K. A problem lies in the fact that argon is a gas and can be easily lost by subsequent thermal events. The basic equation written for the sum of the decay constants for ^{40}Ca and ^{40}Ar is:

$$^{40}Ar = {^{40}Ar_0} + \frac{\lambda_a}{\lambda} \times {^{40}K} \left(e^{\lambda t} - 1 \right)$$

$\lambda = $ Total decay constant $\lambda_a = $ decay constant for ^{40}Ar

Since most K-bearing minerals have no original Ar, the value of $^{40}Ar_0$ is generally zero, and the equation simplifies to:

$$^{40}Ar = .110 {^{40}K} \left(e^{\lambda t} - 1 \right)$$

Argon loss is the critical factor. Hornblende gives the best ages followed by biotite and muscovite. Sanidine has also been used successfully, but other k-feldspars give poor results. Unfortunately, argon loss is generally unavoidable in older rocks, and most ages older than 50MY are suspect, as are those from younger volcanic terranes which have been subjected to regional metamorphism. Because of this, few K-Ar dates are published any longer.

6.2.4 Neodymium-Samarium

^{147}Neodymium decays to ^{143}Sm. Both elements are rare earths and as such behave in a chemically similar manner during partitioning. The result is that Nd-Sm age dates are useful in environments where metamorphic overprints are a problem. Studies have shown that any loss of neodymium and samarium during metamorphism will occur in roughly proportional amounts since mass differences are small and chemical behavior is similar. The major problem with Nd-Sm is the small concentrations of these elements in the earth. Their detection requires an extremely sensitive mass spectrometer, of which there are only a small number. In addition, only those geologic materials which accumulate anomalous concentrations of neodymium and samarium are datable. In general, rare earth elements substitute for calcium and as such Nd-Sm dates have found greatest application in oceanic basalts and ultramafic rocks. Both of these rock types are generally severely meta- morphosed and other age dating techniques have been used with only limited success.

6.2.5 Carbon 14

The ^{14}C method used for dating relatively recent geologic events is a decay clock rather than an accumulation clock. Unlike other radioactive isotopes which have survived since the origin of the elements, ^{14}C is being continually produced by the capture of neutrons by ^{14}N in the upper atmosphere. The earth is constantly being bombarded by cosmic rays that produce nuclear particles upon collision with atmospheric molecules. Neutrons are captured by nitrogen according to the equation:

$$^{14}N + n \longrightarrow ^{14}C + H$$

The ^{14}C is radioactive with a half-life of about 5730 years. The carbon formed reacts quickly with oxygen to form radioactive CO_2 which enters the photosynthetic cycle together with stable CO_2. The partially radioactive CO_2 enters and exchanges rapidly with the hydrosphere and biosphere with respect to the ^{14}C half-life. Living plants, animals and their carbonate hard parts had a natural radioactivity of about 16 disintegrations/min-g of carbon until it was changed quite recently by the activities of man/woman. The burning of fossil fuels has added CO_2 to the atmosphere to provide a dilution of about 2% of the normal value. The dilution of ^{14}C by this extra CO_2 has been until recently counterbalanced by the production of ^{14}C by thermonuclear bomb testing. (Please write your congressman and urge a resumption of nuclear testing so we can continue to use ^{14}C age dates without a correction factor!)