

8 / THE Rb-Sr METHOD OF DATING

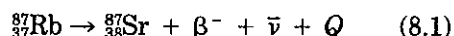
Although the natural radioactivity of rubidium was demonstrated in 1906 by Campbell and Wood, over 30 years elapsed before ^{87}Rb was identified as the naturally occurring radioactive isotope (Hahn et al. 1937; Mattauch, 1937). The feasibility of dating Rb-bearing minerals by the decay of ^{87}Rb to ^{87}Sr was discussed by Hahn and Walling (1938), and the first age determination by this method followed a few years later (Hahn et al., 1943). However, the Rb-Sr method of dating did not come into wide use until the 1950s when mass spectrometers based on Nier's design became available for the isotopic analysis of solids, and the concentrations of rubidium and strontium could be measured by isotope dilution combined with the separation of these elements by ion exchange chromatography. The entire subject of dating by the Rb-Sr method, including its history, theoretical basis, and applicability, have been presented in detail by Faure and Powell (1972).

1 / Geochemistry of Rubidium and Strontium

Rubidium is an alkali metal belonging to Group IA which consists of lithium, sodium, potassium, rubidium, cesium, and francium. Its ionic radius (1.48 Å) is sufficiently similar to that of potassium (1.33 Å) to allow rubidium to substitute for potassium in all K-bearing minerals. Consequently, rubidium is a dispersed element that does not form any minerals of its own, but it occurs in easily detectable amounts

in common K-bearing minerals such as the micas (muscovite, biotite, phlogopite, and lepidolite), K-feldspar (orthoclase and microcline), certain clay minerals, and in evaporite minerals such as sylvite and carnallite.

Rubidium has two naturally occurring isotopes ^{85}Rb and ^{87}Rb whose isotopic abundances are 72.1654 percent and 27.8346 percent, respectively. Its atomic weight is 85.46776 amu (Catanzaro et al., 1969). ^{87}Rb is radioactive and decays to stable ^{87}Sr by emission of a negative beta particle as shown by Equation 8.1:



where β^- is the beta particle, $\bar{\nu}$ is an antineutrino, and Q is the decay energy (see Section 3.1). The decay energy is only 0.275 MeV, which has caused problems in the determination of the specific decay rate of this isotope.

Strontium is a member of the alkaline earths of Group IIA, which consists of beryllium, magnesium, calcium, strontium, barium, and radium. Its ionic radius (1.13 Å) is slightly larger than that of calcium (0.99 Å), which it can replace in many minerals. Thus strontium is also a dispersed element and occurs in K-bearing minerals such as plagioclase, apatite, and calcium carbonate, especially aragonite. The ability of strontium to replace calcium is somewhat restricted by the fact that strontium ions (Sr^{+2}) favor eightfold coordinated sites, whereas calcium ions (Ca^{+2}) can be accommodated in both six- and eightfold coordinated lattice sites because of their smaller size. Moreover, Sr^{+2} ions can be captured in place of K^{+1} ions by K-feldspar, but the replacement of K^{+1} by Sr^{+2} must be coupled by the replace-

Table 8.1 Average concentrations of rubidium, potassium, strontium, and calcium in igneous and sedimentary rocks (Turekian and Wedepohl, 1961)

<i>Rock Type</i>	<i>Rb, ppm</i>	<i>K, ppm</i>	<i>Sr, ppm</i>	<i>Ca ppm</i>
1. Ultrabasic	0.2	40	1	25,000
2. Basaltic	30	8,300	465	76,000
3. High Ca granitic	110	25,200	440	25,000
4. Low Ca granitic	170	42,000	100	5,000
5. Syenite	110	48,000	200	18,000
6. Shale	140	26,600	300	22,000
7. Sandstone	60	10,700	20	10,000
8. Carbonate	3	2,700	610	302,000
9. Deep sea carbonate	10	2,900	2000	312,000
10. Deep sea clay	110	25,000	180	20,000

ment of Si^{+4} by Al^{+3} to preserve electrical neutrality. Strontium is the major cation in strontianite (SrCO_3) and celestite (SrSO_4), both of which occur in certain hydrothermal deposits and in carbonate rocks.

Strontium has four naturally occurring isotopes (^{88}Sr , ^{87}Sr , ^{86}Sr , and ^{84}Sr), all of which are stable. Their isotopic abundances are approximately 82.53 percent, 7.04 percent, 9.87 percent, and 0.56 percent, respectively. The isotopic abundances of strontium isotopes are variable because of the formation of radiogenic ^{87}Sr by the decay of naturally occurring ^{87}Rb . For this reason, the precise isotopic composition of strontium in a rock or mineral that contains rubidium depends on the age and Rb/Sr ratio of that rock or mineral.

The average concentrations of rubidium, potassium, strontium, and calcium in different kinds of igneous and sedimentary rocks are shown in Table 8.1. These data illustrate the general geochemical coherence of rubidium and potassium and of strontium and calcium. The rubidium concentrations of common igneous and sedimentary rocks range from less than 1 part per million (ultramafic rocks and carbonates) to more than 170 ppm in low-calcium granitic rocks. The concentrations of strontium range from a few parts per million (ultramafic rocks) to about 465 ppm in basaltic

rocks and reach very high values in carbonate rocks (up to 2000 ppm or more). Evidently, most common rocks contain appreciable concentrations of rubidium and strontium of the order of tens to several hundred parts per million. The Rb/Sr ratios of common igneous rocks range between wide limits from 0.06 (basaltic rocks) to 1.7, or more, in highly differentiated granitic rocks having low calcium concentrations.

During the fractional crystallization of magma, strontium tends to be concentrated in plagioclase, whereas rubidium remains in the liquid phase. Consequently, the Rb/Sr ratio of the residual magma may increase gradually in the course of progressive crystallization. Suites of differentiated igneous rocks therefore tend to have increasing Rb/Sr ratios with increasing degree of differentiation. The highest Rb/Sr ratios, amounting to 10 or higher, occur in late-stage differentiates including pegmatites.

2 / Dating of Rb-Bearing Minerals in Igneous Rocks

The growth of radiogenic ^{87}Sr in a Rb-rich mineral can be described by an equation derivable from the law of radioactivity (Chapter 4). The

total number of atoms of age is t years is

$$^{87}\text{Sr} =$$

where ^{87}Sr is the number of ^{87}Sr atoms in a unit of present time; ^{87}Rb is the number of ^{87}Rb atoms in a unit of present time; λ is the decay constant in units of reciprocal time; t is the time elapsed in years since the formation of the mineral. We can make each term by itself a constant because ^{87}Sr is not produced and ^{87}Rb is not destroyed during the life of the mineral.

$$\frac{^{87}\text{Sr}}{^{86}\text{Sr}} =$$

This equation is valid only when the number of atoms in the mineral is not changed by the decay of radioactive isotopes. The mineral must be a closed system for rubidium and strontium and not satisfied after it has been added to the system. Its lifetime, the time of solution of the mineral, is not meaning.

The half-life of ^{87}Rb is 4.8×10^{10} years. The decay constant is $1.39 \times 10^{-11} \text{ y}^{-1}$. Careful measurements are required so that the old constants are in use which are not in use. Thus, some of the constants are whereas others are

total number of atoms of ^{87}Sr in a mineral whose age is t years is obtained from Equation 4.15:

$$^{87}\text{Sr} = ^{87}\text{Sr}_i + ^{87}\text{Rb}(e^{\lambda t} - 1) \quad (8.2)$$

where ^{87}Sr is the total number of atoms of this isotope in a unit weight of the mineral at the present time; $^{87}\text{Sr}_i$ is the number of atoms of this isotope that was incorporated into the same unit weight of this mineral at the time of its formation; ^{87}Rb is the number of atoms of this isotope in a unit weight of the mineral at the present time; λ is the decay constant of ^{87}Rb in units of reciprocal years; and t is the time elapsed in years since the time of formation of the minerals, that is, t is the "age" of the mineral. We can modify Equation 8.2 by dividing each term by the number of ^{86}Sr atoms which is constant because this isotope is stable and is not produced by decay of a naturally occurring isotope of another element. Thus we obtain:

$$\frac{^{87}\text{Sr}}{^{86}\text{Sr}} = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_i + \frac{^{87}\text{Rb}}{^{86}\text{Sr}} (e^{\lambda t} - 1) \quad (8.3)$$

This equation is the basis for age determinations by the Rb-Sr method. Equation 8.3 is valid only when the number of ^{87}Sr and ^{87}Rb atoms in the mineral have changed as a result of radioactive decay. In other words, the mineral must be a "closed system" with respect to rubidium and strontium. If this condition is not satisfied and rubidium and strontium have been added to or lost from the mineral during its lifetime, then the value of t calculated by solution of Equation 8.3 may have no real meaning.

The half-life of ^{87}Rb has been measured many times with somewhat contradictory results. As a result, during the 1960s and early 1970s two decay constants were in use in different laboratories: $1.39 \times 10^{-11} \text{ y}^{-1}$ and $1.47 \times 10^{-11} \text{ y}^{-1}$. Careful attention to original sources is required so that dates calculated with these old constants can be corrected to the value now in use which lies between the previous figures. Thus, some old dates increase when corrected whereas others decrease.

Neumann and Huster (1974) obtained a half-life of $(4.88 \pm 0.06 - 0.10) \times 10^{10}$ years by direct counting of the decay of ^{87}Rb . Davis et al. (1977) reported a similar value of $4.89 \pm 0.04 \times 10^{10}$ years from measurements of the amount of radiogenic ^{87}Sr that accumulated in 20 grams of purified Rb perchlorate in 19 years. These and other measurements discussed by Steiger and Jäger (1977) caused the Subcommittee on Geochronology of the International Union of Geological Sciences to accept a value of $1.42 \times 10^{-11} \text{ y}^{-1}$ for the decay constant of ^{87}Rb . This value corresponds to a half-life of 48.8×10^9 years for ^{87}Rb . The Subcommittee also recommended the adoption of the following values of isotope ratios: $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$, $^{84}\text{Sr}/^{86}\text{Sr} = 0.056584$, and $^{85}\text{Rb}/^{87}\text{Rb} = 2.59265$.

To solve Equation 8.3 for t and thus to date a Rb-bearing mineral, the concentrations of rubidium and strontium and its $^{87}\text{Sr}/^{86}\text{Sr}$ ratio must be measured. The concentrations of rubidium and strontium are usually determined either by x-ray fluorescence or by isotope dilution (Chapter 5.4). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is measured on a suitable mass spectrometer using a pure strontium salt obtained from the mineral by dissolving it in acid followed by the separation of strontium using cation exchange chromatography. The ratio of the concentrations of rubidium to strontium is converted into the $^{87}\text{Rb}/^{86}\text{Sr}$ ratio by the following equation:

$$\frac{^{87}\text{Rb}}{^{86}\text{Sr}} = \left(\frac{\text{Rb}}{\text{Sr}} \right) \times \frac{Ab^{87}\text{Rb} \times \text{WSr}}{Ab^{86}\text{Sr} \times \text{WRb}} \quad (8.4)$$

where $^{87}\text{Rb}/^{86}\text{Sr}$ is the ratio of these isotopes in terms of numbers of atoms present in a unit weight of the mineral at the present time, (Rb/Sr) is the ratio of the concentrations of these elements, $Ab^{87}\text{Rb}$ and $Ab^{86}\text{Sr}$ are the isotopic abundances of ^{87}Rb and ^{86}Sr , respectively, and WRb and WSr are the respective atomic weights. Note that the abundance of ^{86}Sr and the atomic weight of strontium depend on the abundance of ^{87}Sr and therefore appropriate values must be calculated for each sample.

The following example will illustrate how this calculation is made. Let us assume that the isotopic composition of a sample of strontium is expressed in terms of the following ratios: $^{87}\text{Sr}/^{86}\text{Sr} = 0.7090$, $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$, $^{84}\text{Sr}/^{88}\text{Sr} = 0.006756$. The abundances of the isotopes can be obtained in the following way:

Isotopic Ratios	Mass	Abundance
$87/88 = 0.08465$	87	0.06991
$86/88 = 0.11940$	86	0.09861
$84/88 = 0.00675$	84	0.00557
$88/88 = 1.00000$	88	0.82590
Sum = 1.21080		Sum = 0.99999

The abundance of ^{86}Sr in this sample of strontium is 0.09861 or 9.861 atom percent. The atomic weight can be calculated from the masses of the isotopes: $^{88}\text{Sr} = 87.9056$ amu, $^{87}\text{Sr} = 86.9088$ amu, $^{86}\text{Sr} = 85.9092$ amu, $^{84}\text{Sr} = 83.9134$ amu (Section 2.2). The atomic weight of this sample of strontium is 87.589 amu. Although the abundance of ^{87}Rb and the atomic weight of rubidium have also changed continuously since nucleosynthesis, all samples of terrestrial, meteoritic, and lunar rubidium have the same isotopic composition and atomic weight at the present time.

To solve Equation 8.3 for t , we must also substitute an appropriate value for $(^{87}\text{Sr}/^{86}\text{Sr})_i$, which is the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the strontium that was incorporated into the mineral at the time of its formation. When the mineral to be dated is strongly enriched in radiogenic ^{87}Sr , the date calculated from Equation 8.3 is insensitive to the value of the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. For example, one may select an initial ratio of 0.704, which is representative of basic volcanic rocks of Recent age, which contain strontium derived primarily from the upper mantle of the Earth.

After the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and the concentrations of rubidium and strontium of a Rb-bearing mineral have been measured and an appropriate value has been chosen for the initial

$^{87}\text{Sr}/^{86}\text{Sr}$ ratio, Equation 8.3 can be solved for t :

$$t = \frac{1}{\lambda} \ln \left[\frac{\frac{^{87}\text{Sr}}{^{86}\text{Sr}} - \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_i}{\frac{^{87}\text{Rb}}{^{86}\text{Sr}}} + 1 \right] \quad (8.5)$$

The numerical value of t is a "date" in the geologic past. This date is the "age" of the mineral only when that mineral has remained a closed system with respect to rubidium and strontium, when the assumed value of the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is appropriate, and when the analytical results are accurate and representative of the material to be dated. The first two conditions define a model for the geologic history of the mineral which is why the date calculated from Equation 8.5 is sometimes called a "model date." It is a valid age determination only to the extent that the assumed model resembles the actual history of the mineral.

Dates calculated from the abundances of radiogenic isotopes are often referred to as "radiometric" dates. This practice is misleading and should be discouraged because it implies that the date was measured with a radiometer, which is an instrument for measuring the intensity of radiant energy. A more appropriate adjective for such dates might be "isotopic," which at least suggests that they are based on the abundances of isotopes produced by radioactive decay.

Igneous rocks of granitic composition may contain both mica minerals and K-feldspar, all of which can be dated by the Rb-Sr method. Ideally, all minerals of an igneous rock should indicate the same date which can then be regarded as the age of the rock. When mineral dates obtained from one rock specimen or from a suite of cogenetic igneous rocks are in agreement, they are said to be "concordant." Unfortunately, "discordance" of mineral dates is more common than "concordance." The reason is that the constituent minerals of a rock may gain or lose radiogenic ^{87}Sr as a result of re-

heating during metamorphism. In such cases, the dates are not reliable. We must therefore be cautious of ourselves if we

3 / Dating

We know that magma and remaining liquids of a magma have the same chemical composition throughout the history of the magma. Moreover, we require for the date to be relatively independent of this age. Under the equation, the slope-intercept

All rock specimens of a suite will plot on a straight line. The line is called the isochron. The age (t) and the slope m of the isochron are the comagmatic

The value of t is determined by the y-intercept of the isochron.

A suite of comagmatic rocks will form an isochron. The age of the suite had the same

dating during regional or contact metamorphism after crystallization from a magma. In such cases, the mineral dates generally are not reliable indicators of the age of the rock. We must therefore turn to the rocks themselves if we want to determine their ages.

Dating of Igneous Rocks

To know that fractional crystallization of a magma and separation of crystals from the remaining liquid result in the formation of suites of comagmatic igneous rocks of differing chemical composition. If the strontium in such a magma was isotopically homogeneous throughout the cooling period, we may assume that all the diverse rocks that formed from the magma had the same initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. Moreover, we may assume that the time required for the crystallization of the magma was relatively short and that all rocks produced by this process have very nearly the same age. Under these conditions, Equation 8.3 is the equation of a family of straight lines in the slope-intercept form:

$$y = b + mx \quad (8.6)$$

All rock specimens belonging to a comagmatic suite will plot as points on a straight line in coordinates of $^{87}\text{Sr}/^{86}\text{Sr}(y)$ and $^{87}\text{Rb}/^{86}\text{Sr}(x)$. This line is called an "isochron" because all points on that line represent systems having the same age (t) and the same initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. The slope m of the isochron is related to the age of the comagmatic rocks by:

$$m = e^{\lambda t} - 1 \quad (8.7)$$

The value of the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is given by the y -intercept:

$$b = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_i \quad (8.8)$$

A suite of comagmatic rocks of age t will define an isochron *only* when each member of that suite had the same initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and

when the rocks have remained closed to rubidium and strontium since crystallization.

To date comagmatic igneous rocks by the whole-rock isochron method, a suite of rocks must be collected that span as wide a range of Rb/Sr ratios as possible so that the slope of the isochron will be well defined. After the necessary analytical results have been obtained, the data are plotted in coordinates of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$. A straight line is then fitted to the resulting points by a suitable statistical procedure and the slope and intercept of the isochron are determined. The age of the suite of rocks is obtained from the slope by solving Equation 8.7. The resulting date indicates the time elapsed since all rocks in the suite had the same initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, which usually refers to the time of their crystallization from a magma. Therefore, whole-rock $\text{Rb}-\text{Sr}$ isochron dates are generally regarded as reliable indicators of the age of the rocks.

The isotopic evolution of strontium in a suite of three hypothetical igneous rocks that formed from a common magma and have different Rb/Sr ratios is illustrated in Figure 8.1. At the time of crystallization, all three rocks plot as

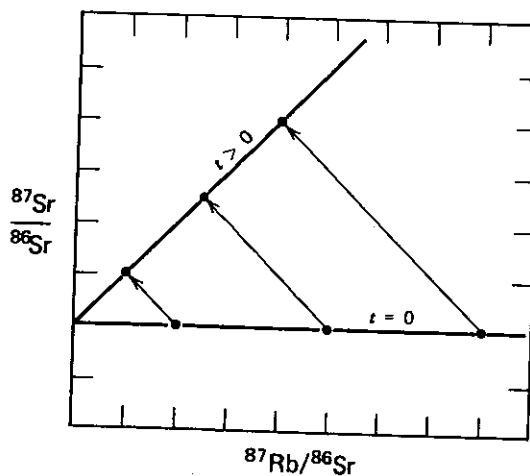


Figure 8.1 Rb-Sr isochron diagram showing the time-dependent isotopic evolution of rock systems after their crystallization from a homogeneous magma.

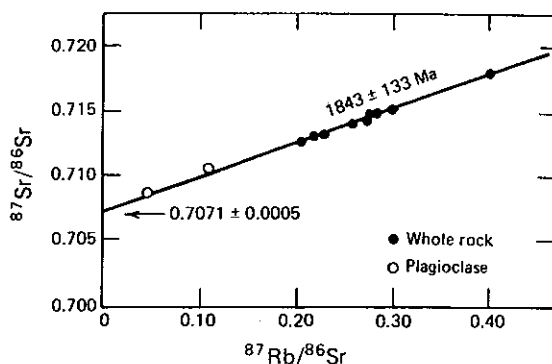


Figure 8.2 Rb-Sr isochron formed by a suite of whole-rock samples and two plagioclase concentrates of gabbro (norite) from Sudbury, Ontario. The so-called Sudbury Nickel Irruption is associated with large ore deposits of nickel, copper, and other metals. The age of these rocks indicated by the slope is $1843 \pm 133 \text{ Ma}$ and the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is 0.7071 ± 0.0005 . (Hurst and Farhat, 1977, recalculated to $\lambda (^{87}\text{Rb}) = 1.42 \times 10^{-11} \text{ y}^{-1}$.)

points on a straight line whose slope is zero because they all have the same $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. After cooling to a temperature at which they become closed systems, their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios begin to increase as a result of decay of ^{87}Rb to ^{87}Sr . Each decay of ^{87}Rb reduces the $^{87}\text{Rb}/^{86}\text{Sr}$ ratio and increases the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio by the same amount. Consequently, these ratios will change along straight lines with a slope of -1 in such a way that the rock samples remain on the isochron as its slope increases as a function of time. The value of the y-intercept, however, remains constant and indicates the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the suite of rocks.

The dating of comagmatic igneous rocks by the whole-rock isochron method is illustrated in Figure 8.2 by an isochron for a suite of norites from Sudbury, Ontario. The assumption was made that the norite samples initially had the same $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and that they formed in an interval of time that is short compared with their common age. The satisfactory fit of

the data points to the isochron indicates that these assumptions are justified, at least to a first approximation. The slope of the isochron indicates a date of $1843 \pm 133 \text{ Ma}$ which was interpreted as the crystallization age of these rocks.

In general, it is apparent that the isochron method of dating suites of cogenetic igneous rocks is superior to calculated model dates based on assumed values of the initial ratio. The isochron yields not only the age of the suite but also indicates their initial ratio. Moreover, the goodness of fit of data points serves as a check of the assumption that all of the specimens have remained closed to rubidium and strontium.

The minerals of igneous rocks that have not been metamorphosed lie on the same isochron as the whole rocks from which they were separated. However, in case the rocks have been heated during regional or contact metamorphism, their minerals commonly depart from the whole-rock isochron and may form separate mineral isochrons to be discussed below.

4 / Dating of Metamorphic Rocks

Rocks may be subjected to physical and chemical processes as a result of which their mineralogical and chemical compositions and even their textures are changed. These processes constitute metamorphism in the broadest sense of the word. Metamorphism almost invariably involves an increase in the ambient temperature, which promotes recrystallization of existing minerals or may cause formation of new minerals at the expense of existing ones. These mineralogical changes imply considerable mobility of the chemical constituents of rocks either by virtue of the presence of an aqueous phase or by diffusion of ions, or both. Metamorphism may also be accompanied by metasomatism and

a result of which the composition of the rock is changed.

It is to be expected that such processes exert a profound influence on the relationships of radioactive isotopes in rock. In fact, the temperature of 100°C has significant effects on the rates of natural decay being reflected in the textural criteria. The parent sensitivity to increases in temperature to the fact that a crystal lattice is sensitive. Moreover, the decay in a mineral and half-lives compare released during calculations or even locally, thus making radiogenic data.

For these reasons, Rb-Sr decay is profoundly affected by temperature and pressure. The observed behavior is treated as the migration of constituent elements. It is undoubtedly likely that the strontium in the rock. Nevertheless, we shall assume that the mobile components of rubidium and strontium are the main essential elements in contact metamorphism.

To help us understand the changes in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio during meta-

ne isochron indicates that both the bulk chemical composition as well as the trace-element composition of the rocks may be changed.

The slope of the isochron of the rocks may be changed. 843 ± 133 Ma was to be expected that metamorphism ex-

crystallization age has a profound effect on the parent-daughter relationships of all of the naturally occurring

apparent that the active isotopes that may be present in a series of cogenetic rocks. In fact, even a modest increase in temperature of 100 to 200°C or so may have drastic effects on the parent-daughter relationships of

only the age of the rocks. Decay schemes without necessarily reflecting the usual mineralogical or petrological criteria for metamorphism. The application that all of the sensitivity of isotopic systems in rocks is closed to rubidium increases in temperature is probably related

to the fact that rates of diffusion of ions through igneous rocks that are in a crystal lattice and across grain boundaries lie on the same sensitive functions of the temperature.

From which they follow, the daughter atoms produced by decay of a mineral are isotopes of different elements and have different ionic charges and are commonly different compared with their parents. The energy released during the decay may produce dislocations or even destroy the crystal lattice locally, thus making it all the more easy for the radiogenic daughters to escape.

For these reasons it is not surprising that radiogenic decay schemes in minerals are probably affected by even modest increases in temperature during metamorphism. The observed behavior of minerals can generally be

described as though it had been caused solely by migration of radiogenic ^{87}Sr among the constituent minerals of a rock. However, this is undoubtedly an oversimplification, and it is

sm in the broad that the concentrations of rubidium and strontium in the minerals are also affected. In the ambient temperature, in the presentation that follows

we shall assume that radiogenic ^{87}Sr is the only cause of the change in the concentrations of rubidium and strontium of the minerals re-

spectively considered essentially constant during regional or contact metamorphism.

Use of an aqueous solution helps us describe the changes that occur in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the minerals of a rock during metamorphism, we now introduce a

useful approximation to Equation 8.3. We expand $e^{\lambda t}$ as a power series:

$$e^{\lambda t} = 1 + \lambda t + \frac{(\lambda t)^2}{2!} + \frac{(\lambda t)^3}{3!} + \dots \quad (8.9)$$

Since the decay constant of ^{87}Rb is very small ($\lambda = 1.42 \times 10^{-11} \text{ y}^{-1}$),

$$1 + \lambda t \gg \frac{(\lambda t)^2}{2!} + \frac{(\lambda t)^3}{3!} + \dots \quad (8.10)$$

even for values of t of the order of 10^9 years. Thus we can rewrite Equation 8.3 to a good approximation as:

$$\frac{^{87}\text{Sr}}{^{86}\text{Sr}} = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_i + \frac{^{87}\text{Rb}}{^{86}\text{Sr}} \lambda t \quad (8.11)$$

This is the equation of a straight line in the familiar slope-intercept form in coordinates of $^{87}\text{Sr}/^{86}\text{Sr}$ and t . It is very useful in describing the time-dependent increase of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Rb-bearing systems because the strontium evolution lines are straight lines whose slopes are $m = (^{87}\text{Rb}/^{86}\text{Sr}) \lambda$. Figure 8.3 is such a strontium development or evolution diagram for four systems having different $^{87}\text{Rb}/^{86}\text{Sr}$ ratios.

Based on experience derived from the study of metamorphosed igneous rocks, it has been found that the following model is an adequate description of the response of the Rb-Sr decay schemes in minerals during thermal metamorphism (Fairbairn et al., 1961). We consider an igneous rock containing two Rb-rich minerals such as biotite and microcline (or orthoclase) and one Rb-poor, but Sr-rich mineral such as apatite. This rock initially formed t_i years ago and at that time the rock and all of its constituent minerals contained strontium of identical isotopic composition represented by $(^{87}\text{Sr}/^{86}\text{Sr})_i$. Some time after crystallization, the rock was subjected to an increase in temperature for a short interval of time Δt . Subsequently, the rock cooled to the ambient temperature t_m years ago and remained undisturbed to the present time. The effects of such

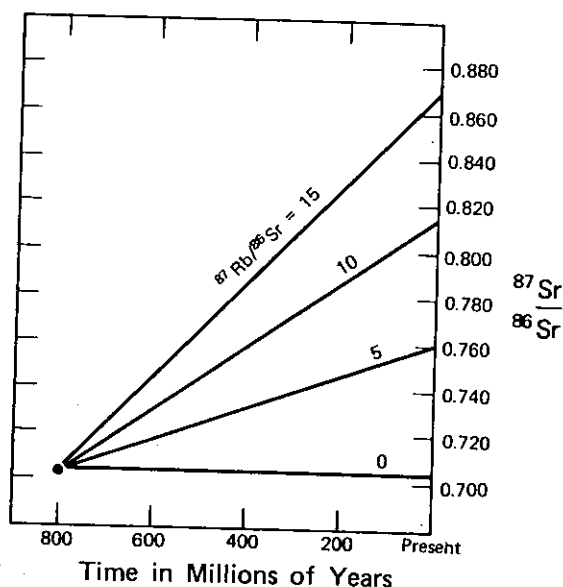


Figure 8.3 Strontium development diagram for a suite of four rock systems having different $^{87}\text{Rb}/^{86}\text{Sr}$ ratios. The four systems came into existence 800 million years ago when each had the same $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.704. Thereafter, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the systems evolved along a set of diverging straight lines whose slopes depend on the $^{87}\text{Rb}/^{86}\text{Sr}$ ratio of each system. Note that the rock system whose $^{87}\text{Rb}/^{86}\text{Sr}$ ratio is zero has a constant $^{87}\text{Sr}/^{86}\text{Sr}$ ratio equal to the initial value of all the systems.

a history on the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the rock and its constituent minerals are shown in Figure 8.4.

Starting t_i years ago when the rock had cooled sufficiently for its minerals to retain radiogenic ^{87}Sr (Dodson, 1973), their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios evolved along straight-line paths at rates controlled by their $^{87}\text{Rb}/^{86}\text{Sr}$ ratios. When the temperature was increased, the Rb-rich phases biotite and K-feldspar lost radiogenic ^{87}Sr , and their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios decreased until they became identical with that of the rock as a whole. (Sometimes K-feldspar actually gains ^{87}Sr .) The radiogenic ^{87}Sr lost by the Rb-rich phases entered the apatite and its $^{87}\text{Sr}/^{86}\text{Sr}$ ratio increased until it, too, was equal to that of the

whole rock. As a result of these changes brought about by the increase in temperature, strontium was isotopically homogenized so that all minerals once again had the same $^{87}\text{Sr}/^{86}\text{Sr}$ ratio equal to $(^{87}\text{Sr}/^{86}\text{Sr})_m$. Note especially that $(^{87}\text{Sr}/^{86}\text{Sr})_m$ is greater than $(^{87}\text{Sr}/^{86}\text{Sr})_i$, and that the whole rock remained a closed system while its minerals exchanged radiogenic ^{87}Sr until the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of all the minerals were equalized. It is entirely possible that the concentrations of rubidium and strontium of the minerals were also affected by this process, although Figure 8.4 was constructed with the assumption that they were not. Changes in the concentrations of rubidium and strontium of the minerals would not affect the interpretation, provided that the rock as a whole remained a closed system. Following isotopic homogenization, the temperature eventually decreased sufficiently for the minerals to become closed systems again at t_m . Their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios then increased to the present at rates consistent with their $^{87}\text{Rb}/^{86}\text{Sr}$ ratios.

There are two meaningful dates in the history outlined above. These are t_i , the time elapsed since crystallization, and t_m , the time elapsed since metamorphism of the igneous rock. The Rb-rich minerals of the rock record only one of these, namely t_m . It can be obtained by solving two simultaneous equations of the form of Equation 8.3 for the biotite and the K-feldspar. Alternatively, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of a Sr-rich mineral such as apatite can be used as the initial ratio to calculate model dates for Rb-rich phases. If isotopic homogenization was complete and is accurately reflected by the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the apatite, the model dates of the biotite and the K-feldspar are concordant. On the other hand, if model dates are calculated for these two minerals by using an inappropriate initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, the resulting dates indicated by t_b and t_f in Figure 8.4 are discordant and meaningless. This illustrates the general unreliability of model dates derived by analysis of separated minerals. Such dates may even exceed the age of the rock, depend-

ing on the summed in the of a metamorphic to determine the mineral phism. In original crystallization the rocks the Figure 8.5 metamorphic constituent minerals and R3 are marked M2 and minerals initial equal to zero

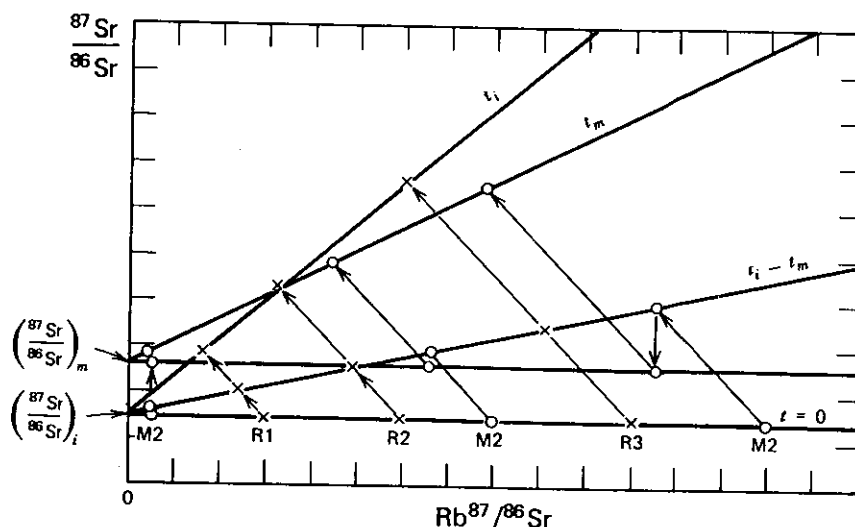


Figure 8.5 Evolution of strontium in three whole rocks (R1, R2, and R3) and in the minerals of R2 (M2). The strontium in the minerals was isotopically homogenized by an episode of thermal metamorphism of short duration. The slope of the whole-rock isochron corresponds to t_i , which is the time elapsed since crystallization of these rocks. The slope of the mineral isochron indicates t_m , which is the time elapsed since the end of the thermal metamorphism.

the meantime evolved on their own isochron, which still includes TR2, but whose slope represents t_m , the time elapsed since the minerals became closed systems after being reequilibrated by thermal metamorphism. The y-intercepts of the whole-rock and the mineral isochrons correspond to $(^{87}\text{Sr}/^{86}\text{Sr})_i$ and $(^{87}\text{Sr}/^{86}\text{Sr})_m$, respectively. Note that we have considered only the minerals of one of the three rocks. The minerals of the other rocks form similar isochrons. Their slopes are identical, but they have different values of $(^{87}\text{Sr}/^{86}\text{Sr})_m$, appropriate to the whole rocks whose constituents they are.

A granite complex at Carn Chuinneag (pronounced Carn Coon-e-ag) in the northern Scottish Highlands provides a good example of an igneous rock that was later regionally metamorphosed (Long, 1964). Figure 8.6a is an isochron formed by four whole rock specimens from this and a related intrusive. The age of

these rocks is 548 ± 10 Ma (recalculated to a $^{87}\text{Rb} = 1.42 \times 10^{-11} \text{ y}^{-1}$) and their initial ratio is 0.710 ± 0.002 . Figure 8.6b shows muscovite, biotite, and feldspar (plagioclase and orthoclase partially converted to microcline) of one of the rock specimens. It can be seen that the parent rock is colinear with its minerals and that they together define another isochron equivalent to a date of 403 ± 5 Ma. Long interpreted this date as being indicative of the late Caledonian metamorphism that caused complete homogenization of the strontium in the minerals of this intrusive. Note that the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the mineral isochron is 0.782, which is very much higher than that of the whole rocks. The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the minerals is determined by the $^{87}\text{Sr}/^{86}\text{Sr}$ of the whole rock at the end of the metamorphic episode, as suggested previously in Figures 8.4 and 8.5.

All of the foregoing discussion is predicated

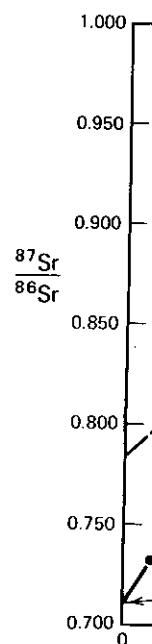


Figure 8.6 (a) northern Scotland, one of the whole-rock intrusive crystallization. The strontium ratios of the whole rock and 8.5. (Data

on the assumption that the whole-rock system was isotopically homogeneous at the time of crystallization and remained closed. If the whole-rock system was not closed, the age of the whole-rock system cannot be determined. The initial crystallization of the whole-rock system was chemically homogeneous, or strontium was homogenized, some time after their formation by the Rb-Sr method. An example of this is presented by Moores (1964).

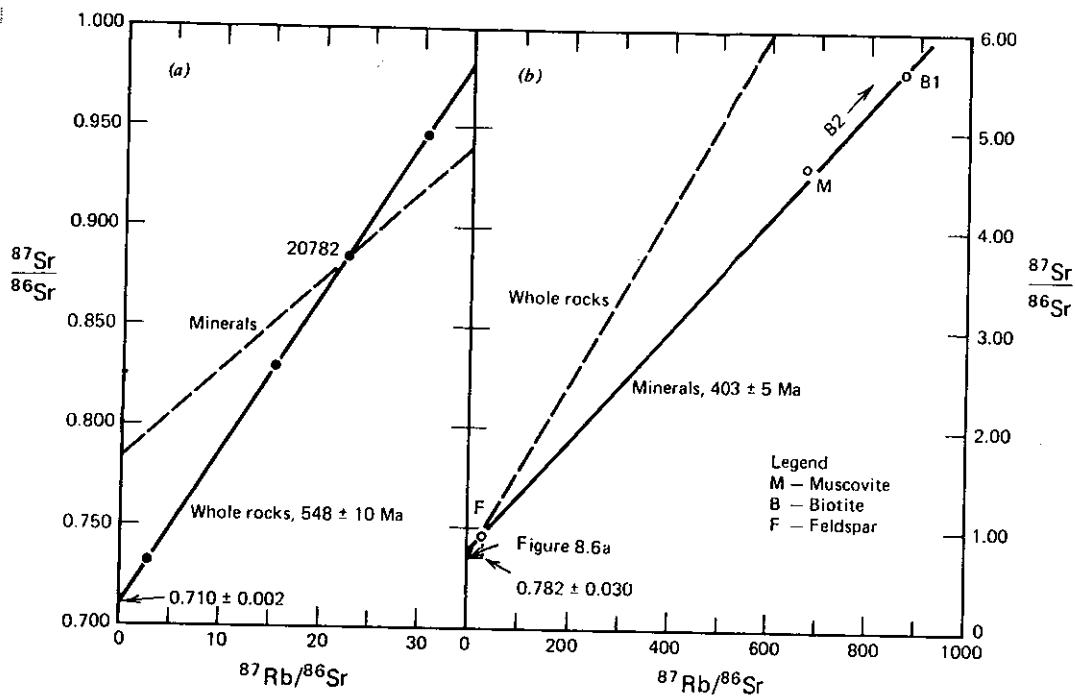


Figure 8.6 (a) Whole rock isochron of granitic rocks from the Carn Chuinneag complex in the northern Scottish Highlands. (b) Mineral isochron formed by feldspar, muscovite, and biotite of one of the whole rock samples. The interpretation of these dates is that the Carn Chuinneag intrusive crystallized 548 Ma ago and was later affected by the Caledonian orogeny 403 Ma ago. The strontium in the minerals was isotopically homogenized as a result of regional metamorphism, while the whole-rock samples remained closed systems. Note the difference in the initial ratios of the two isochrons. The history of these rocks is similar to those depicted in Figures 8.4 and 8.5. (Data from Long, 1964. See also Pidgeon and Johnson, 1974.)

on the assumption that the *minerals* were isotopically homogenized during thermal metamorphism and that *whole-rock* samples of the size of conventional hand specimens remained closed. If homogenization of the minerals was incomplete, the time of metamorphism cannot be determined from them. In this case the whole rocks may still tell the time of initial crystallization. However, if the *rocks* were chemically altered so that rubidium and/or strontium were either added or lost at any time after their formation, they cannot be dated by the Rb-Sr method.

An example of dating granitic gneisses was presented by Moorbath and his colleagues from

Oxford University (Moorbath et al., 1972) for samples of the Amitsoq gneiss from the Godthaab district in southwestern Greenland. The Amitsoq gneiss was formed by deformation, metamorphism, and migmatization of a complex of igneous rocks of granitic composition. Several suites of these rocks from the Godthaab district were dated by the whole-rock Rb-Sr method. Figure 8.7 shows the isochron of Amitsoq gneisses from the Qilangarsuit area. The slope of this isochron yields a date of 3660 ± 99 Ma and an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7009 ± 0.0011 . The Amitsoq gneiss is one of the oldest terrestrial rocks known. The date indicated by the isochron may be the time of

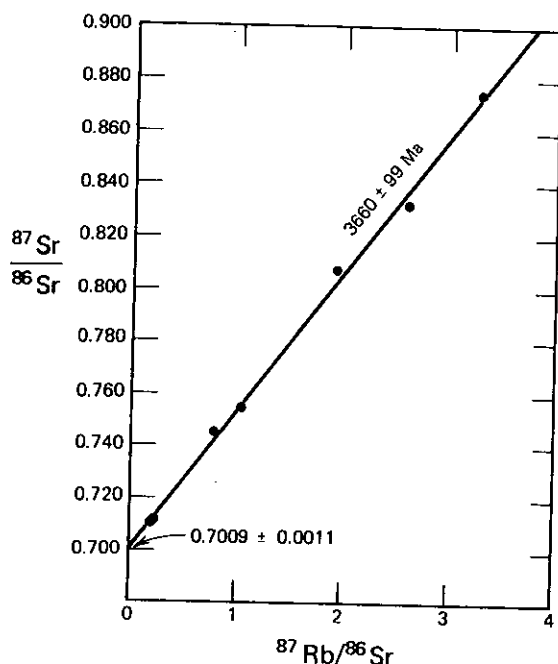


Figure 8.7 Whole-rock isochron for the Amitsoq gneiss from the Quilangarsuit area of the Godthaab district of southwestern Greenland. These are among the oldest terrestrial rocks known. The date probably represents the time elapsed since metamorphism of igneous rocks of granitic composition to form the Amitsoq gneiss. (Data from Moorbath et al., 1972.)

crystallization of the igneous rocks or it may reflect the metamorphic event that produced the Amitsoq gneiss. The latter is preferred in this case.

The antiquity of the Amitsoq gneiss was subsequently confirmed by studies based on a variety of isotopic dating techniques (Baadsgaard, 1973; Moorbath et al., 1975; Moorbath et al., 1977). In addition, Baadsgaard et al. (1976) dated biotite from the Amitsoq gneiss by the K-Ar and Rb-Sr methods. The results indicate that the micas record the end of a major metamorphic event about 1525 Ma ago.

After publication of these results, other examples of very old dates were reported for rocks

in South Africa, Rhodesia, Labrador and Minnesota. These results have significantly expanded our knowledge of Earth history in Early Archean time as indicated by the geologic time scale in Table 6.3.

Metamorphic rocks also form from sequences of *sedimentary rocks* containing minerals that are unstable at elevated temperatures and therefore recrystallize to form new mineral assemblages when the temperature is elevated. The Rb-bearing minerals of such metamorphic rocks (primarily micas and K-feldspars) can be dated either by the isochron method, or by calculating model dates. Such dates generally reflect the time elapsed since the end of the last metamorphic episode to which the rocks were subjected. Whole-rock isochrons may likewise indicate the age of the metamorphic event during which the sediment was recrystallized.

This point is illustrated in Figure 8.8 by an isochron for samples of phyllite and slate from the La Gorce Formation of the Wisconsin Range in the Transantarctic Mountains (Montigny and Faure, 1969). The La Gorce Formation consists of fine-grained detrital sedimentary rocks that were isoclinally folded and metamorphosed to the greenschist facies during the Ross Orogeny in late Cambrian to early Ordovician time. However, several lines of field evidence leave little room for doubt that these rocks were deposited in late Precambrian time. Nevertheless, the isochron defined by whole rock samples of the La Gorce Formation indicates a date of only 450 ± 16 Ma, which apparently reflects the time of metamorphism of these rocks rather than their depositional age. Evidently the strontium in these samples was isotopically reequilibrated on a large scale during metamorphism, thereby resetting the Rb-Sr clocks so that they no longer indicate the time elapsed since deposition. However, dates that are intermediate between the age of the source rocks and the time of metamorphism have also been reported for some metamorphosed sedimentary rocks.

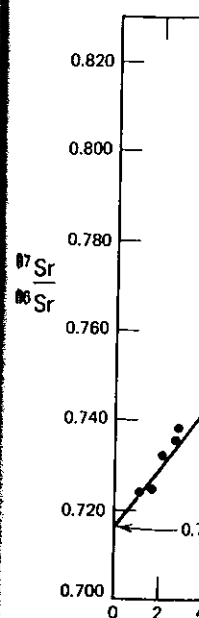


Figure 8.8 Whole-rock isochron for samples of phyllite and slate from the La Gorce Formation of the Wisconsin Range in the Transantarctic Mountains. The date indicated by the isochron represents the time of metamorphism of the rocks, not the time of deposition. (Data from Montigny and Faure, 1969.)

8 / Dating of Sedimentary Rocks

Certain sedimentary rocks that have sufficient measurable radiogenic ^{87}Sr . They may be either authigenic (e.g., clay minerals, K-feldspar, etc.) or

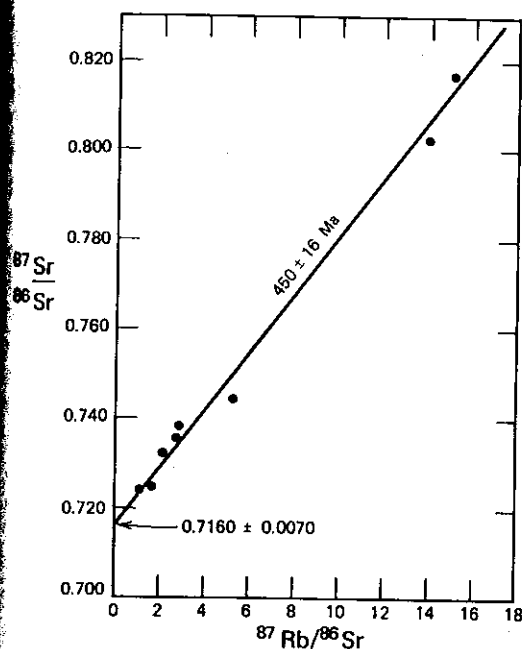


Figure 8.8 Whole-rock isochron of slates and phyllites from the La Gorce Formation of probable late Precambrian age from the Wisconsin Range of the Transantarctic Mountains. The date indicated by the slope of the isochron represents the time of metamorphism and extensive homogenization of the isotopic composition of strontium in these rocks. The scatter of points about the isochron is greater than expected from analytical errors alone and suggests that homogenization was not complete or approached different values in different parts of the formation (Data from Montigny and Faure, 1969.)

5 / Dating of Unmetamorphosed Sedimentary Rocks

Certain sedimentary rocks contain minerals that have sufficiently high Rb/Sr ratios to cause measurable enrichment of their strontium in radiogenic ^{87}Sr . The Rb-bearing minerals may be either authigenic [glauconite, certain other clay minerals, K-feldspar (adularia), sylvite, carnallite, etc.] or allogenic and detrital (mica,

K-feldspar, clay minerals, etc.). Authigenic minerals form within the environment of deposition of sedimentary rocks and therefore may indicate the time elapsed since sedimentation, provided that the minerals in question have remained closed systems.

The use of the term "glauconite" has been discouraged by Odin and Matter (1981) in favor of "glaucony," which refers to a family of minerals that range in composition from glauconitic smectite to glauconitic mica. Nevertheless, K-rich and Fe-bearing clay minerals of the "glaucony facies" may be used to determine the time of deposition of sedimentary rocks by the Rb-Sr method provided that they have not been recrystallized by deep burial, tectonic deformation, or experienced chemical exchange with reactive ground waters. Glauconies containing less than 6 percent K_2O are often not suitable for dating whereas those containing more than 7 percent K_2O are usually reliable for dating by both the K-Ar and the Rb-Sr methods. The state of the art of dating glaucony was reviewed in a series of papers edited by Odin (1982).

Sylvite and carnallite, being evaporite minerals, are likewise easily altered by recrystallization and may undergo more or less continuous recrystallization in equilibrium with connate brines. These minerals therefore do not appear to be reliable geochronometers.

a. Dating of Shale Of special interest is the possibility that fine-grained, unmetamorphosed, detrital sedimentary rocks, such as shales, can be dated by the whole-rock isochron method. Such rocks consist primarily of mineral particles that formed prior to deposition of the sediment and therefore may have extensive prior histories. Nevertheless, it has been demonstrated many times that fine-grained detrital sedimentary rocks form linear arrays on isochron diagrams. The dates determined from such isochrons are difficult to interpret because isotopic homogenization is not