Physics

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UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

THEORETICAL EFFECT OF DIFFUSION ON ISOTOPIC ABUNDANCE RATIOS

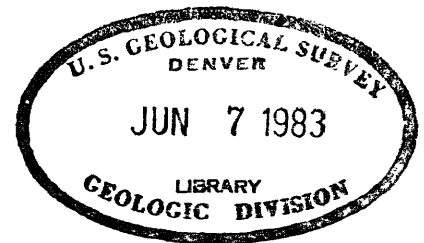IN ROCKS AND ASSOCIATED FLUIDS*

By

F. E. Senftle and J. T. Bracken

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IN ROCKS AND ASSOCIATED FLUIDS

By

F. E. Senftle and J. T. Bracken

ABSTRACT

It is proposed that diffusion be considered as a possible process of isotope fractionation taking place throughout geologic time. Both diffusion in solids and in liquids are considered as possible mechanisms, the latter being more important. Arguments are presented which show that if significant fractionation takes place within a crystal by outward diffusion under solid state conditions, enrichment will be evident only in elements of minor concentration. Similar conclusions are inferred for solid state diffusion across a boundary or for diffusion in liquids. Although the necessary data to confirm these conclusions are scanty, it seems worth while to undertake further work in this direction.

INTRODUCTION

Processes of formation and alteration of rocks that have taken place during geologic time have altered the isotopic abundance ratios of the elements in the earth's crust. The truth of this statement has become increasingly evident during the past decade, as more and more isotopic abundances of a number of elements have been measured in natural specimens, and significant variations have been noted (Ingerson, 1953; Jensen, 1953).

One of the processes of rock alteration is that of diffusion. Although there is some doubt at the present time as to just how important this process is as a geological mechanism of rock alteration, there is a strong belief among geologists and geochemists (Ramberg, 1952) that diffusion may be an important method of material transfer over a period of geologic time. If one postulates diffusion as a geologic process, it would seem that isotopic fractionation due to diffusion might explain some of the observed fractionation in certain circumstances.

When two or more isotopes of a specific element are transferred by a process of diffusion, a change in isotopic abundance ratio would be expected because of the velocity difference of isotopes of a given element. Where the diffusing material is transported over significant distances a substantial variation in abundance ratios can occur. It is the purpose of this paper to outline theoretically the effect of diffusion as a mechanism of isotope separation in natural materials.

DIFFUSION -- A GEOLOGICAL PROCESS

Diffusion is a process by which atoms or ions, motivated by a chemical potential gradient, move from point to point in a solvent phase. The rate of change of concentration with distance is expressed by Fick's Second Law:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right)$$

$$\ldots\ldots\ldots\ldots (1)$$

where C is the concentration of the diffusing solute, x is the distance, t is the time, and D is the diffusion coefficient.

In considering diffusion as a geologic process it is important to distinguish between solid and liquid solvent phases. The term solid

state diffusion generally includes the processes in which the solute diffuses through a solid matrix, along grain boundaries or over surfaces. The present meager experimental data indicate that grain boundary and surface diffusion in ionic crystal aggregates are relatively important compared to lattice diffusion through a crystal, especially at moderately low temperatures ($< 300^\circ$ C). As rocks may consist of an assemblage of crystals having a large over-all area, one might expect that diffusion through the lattice will be much less important than migration along surfaces. For the purposes of this paper, however, solid state diffusion is taken to mean the result of all three processes unless otherwise mentioned, because little is known of these individual processes in geologic materials.

Liquid or solute diffusion refers to diffusion of the solute through a liquid, and here its meaning is confined to the diffusion of ions or atoms in static aqueous or magmatic solutions held intergranularly in saturated rocks.

In both types of diffusion isotopic fractionation can occur but to a different extent and with different limitations. The diffusion coefficients in liquids are larger than the solid state diffusion coefficients by several orders of magnitude. Consequently, solid state diffusion can apply only to short distance phenomena and is operative under geologic circumstances quite different from those supporting diffusion through liquids. Although both processes often occur simultaneously, for the sake of clarity each type is considered separately as an isotope fractionation process.

A third type of diffusion, thermal, or "Soret" diffusion is frequently used in the laboratory for isotope fractionation, particularly in a gas

phase. As a significant geologic process, however, it is probably not very important. Lovering (1950) has shown that up to distances of about 100 meters diffusion under geologic conditions is isothermal, as the heat conductivities are so much larger than ionic or molecular diffusion coefficients. As an isotopic fractionation process, then, thermal diffusion is not considered.

Although there has been a certain amount of disagreement as to the geological importance of diffusion, there are a number of experimental investigations (Urey et al., 1951; Garrels et al., 1949; Jensen, 1951) which indicate that significant material transfer does take place through geologic time. Also from what we know of the laws of diffusion and of past geologic conditions such as temperatures, it is almost certain that some diffusion did take place.

For instance, consider a hydrothermal ore fluid containing zinc moving through a fissure cutting a water-saturated granitic body. At the time of injection the initial solution will undoubtedly fill the open spaces and pores adjacent to the main fissure because of the existing pressure gradient and also capillary action. After gross circulation of the ore solution, zinc ions would start to migrate intergranularly by solute diffusion away from the fissure. Because the temperature is high and because the concentration equilibrium is disturbed, ions also start to migrate by diffusion through the lattice from crystal grains into the intergranular solutions and also from the solutions into the crystal grains. When the temperature drops and solidification has taken place, diffusion continues through the solid mass but at a considerably reduced rate. Diffusion through the intergranular liquids also continues at a significant rate because atoms from the fissure vein are continually

dissolving and moving under concentration gradients into the wall rock.

Assuming the above conditions as a reasonable example, it is appropriate to consider a hypothetical case of diffusing atoms or ions at an interface under semi-infinite conditions. The concentration at any distance x from the interface is given by

$$C_x = C_o \left(1 - \text{erf} \frac{x}{2\sqrt{Dt}} \right)$$

$$\dots\dots\dots\dots (2)$$

where C_o is the concentration of the diffusing atom or ion at the interface, x is the distance from the interface, D is the average diffusion coefficient, and t is the time.[1] If one arbitrarily chooses $\sqrt{Dt}$ as 10 cm, then the change in concentration with distance is shown in curve Ia of figure 1. Any larger value of $\sqrt{Dt}$, such as $\sqrt{Dt} = 50$ cm (curve IIa), will increase the value of x proportionally for a given value of C.

If we further assume that the diffusing atoms comprise light and heavy isotopes of masses M_L and M_H, for example masses 103 and 105, having diffusion coefficients D_L and D_H, respectively, then

$$\frac{D_L}{D_H} = \sqrt{\frac{M_H}{M_L}} = k$$

$$= \sqrt{\frac{105}{103}} = 1.0097$$

$$\dots\dots\dots\dots (3)$$

The isotope enrichment, x cm, from the interface is thus

$$S = \left(\frac{C_L \cdot C_{H_o}}{C_H \cdot C_{L_o}} - 1 \right) \cdot 10^2$$

$$= \left(\left\{ \frac{1 - \text{erf} \frac{x}{2\sqrt{k\,D_H t}}}{1 - \text{erf} \frac{x}{2\sqrt{D_H t}}} \right\} - 1 \right) \cdot 10^2$$

$$\dots\dots\dots\dots (4)$$

[1] Values of the error function (erf) are tabulated in Tables of Probability Functions, 1941.

where the zero subscript refers to the original concentrations. Curve Ib (fig. 1) is the enrichment as a function of x for this hypothetical case, that is $\sqrt{Dt}$ = cm, k = 1.0097. As the value of k differs little from unity for two isotopes of nearly the same mass, and as there is a one-to-one correspondence between x and $\sqrt{Dt}$, then the relationship between the curves Ia and Ib (fig. 1) will be almost the same as that for any other case regardless of the value of $\sqrt{Dt}$ and k.

Both the concentration and isotopic enrichment at any point is a function of the diffusion distance (equations 2 and 4), and these curves show that little isotopic enrichment can be expected until the concentration drops to at least 0.1 of the concentration in the source material. This means that one cannot expect significant isotopic enrichment to take place except at a low concentration diffusion front, and this will only be evident in a small amount of material. In the above-cited case of a hydrothermal zinc solution, significant isotopic enrichment of the lighter isotopes would be expected in the small amount of zinc in the diffusion fronts containing concentrations of the order of 0.1 or less of the concentration found in the fissure. Thus the bulk of diffusion-transported material will not display any significant isotopic enrichment, except possibly where trace quantities of an enriched element in a diffusion front have been removed by some natural process and subsequently concentrated at a particular site. This possibility is discussed below.

SOLID-STATE DIFFUSION

There are two circumstances of solid-state diffusion of particular interest to the geologist: fractionation due to diffusion of an element

from a given specimen or crystal; and diffusional effects across a boundary such as vein-host rock interface.

Isotope fractionation due to diffusion
in a "spherical crystal"

In systems where long periods of geologic time are involved and where somewhat elevated temperatures may prevail, it is conceivable that an istopic separation of several percent might be obtained, especially in small crystals. However, in order to obtain significant changes in the isotopic abundance ratio of a given element, a relatively large fraction of all the isotopes of this element must have diffused out of the original sphere leaving a small remaining fraction enriched in the heavy isotopes. Such a transfer of material must be accompanied by a migration of foreign isotopes to the crystal, i.e., replacement. Replacement represents a typical case where relatively large amounts of a given element can leave a body without destroying the general crystalline texture. With regard to the quantity of material moved, then, isotopic enrichment of the heavier isotope in a given element could be expected in crystals displaying metasomatism, assuming that replacement took place by solid state diffusion and not be recrystallization or some other process.

As an example one may consider the process of replacement of sphalerite by covellite

$$ZnS + CuSO_4 = CuS + ZnSO_4$$
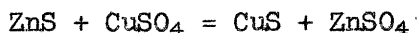
Copper in interstitial water and ground water finds access to the inner parts of the sphalerite. It seems reasonable to assume that both the flow of the copper-bearing solutions and also diffusion of the copper in these solutions will account for the transport of the copper atoms.

Transport within the sphalerite will take place by lattice diffusion. During the process of replacement copper diffuses into the sphalerite crystals and zinc diffuses out in a counter current process. In the case of almost complete replacement the small amount of zinc remaining in the crystals is enriched in the slow-moving or heavy isotope, while at the same time there is an enrichment of the lighter isotope of copper within the crystals.

The average enrichment within the crystals of the lighter and incoming isotopes (copper in this case) would probably not be significant except in the initial stages of diffusion. In the early stages only a minute amount of copper will have entered the sphalerite crystals, and in the later stages so much copper will have diffused into the sphalerite that the average enrichment of the lighter isotopes will be insignificant. Hence, in the following discussion only enrichment of the heavier isotopes in the small amount of residual element left in a replacement crystal is considered.

It is therefore desirable to investigate what the average isotopic fractionation might be within a body, such as a crystal, due to the diffusion of nuclides of different masses out of the crystal. In order to reduce the mathematical manipulations, Bracken and Senftle (1954) have treated the problem for a spherical body. Assuming a spherical crystal and using their qualifying assumptions, the mean percent enrichment, $\bar{S}$, of the heavy isotope within a sphere is

$$\bar{S} = \left(1 - \left\{ \frac{erf \frac{a}{\sqrt{kDt}} + \frac{2}{\sqrt{\pi}}\left(\frac{\sqrt{kDt}}{a}\right)^3 \left(1 - e^{-\frac{a^2}{kDt}}\right) - \frac{\sqrt{kDt}}{a\sqrt{\pi}}\left(3 - e^{-\frac{a^2}{kDt}}\right)}{erf \frac{a}{\sqrt{Dt}} + \frac{2}{\sqrt{\pi}}\left(\frac{\sqrt{Dt}}{a}\right)^3 \left(1 - e^{-\frac{a^2}{Dt}}\right) - \frac{\sqrt{Dt}}{a\sqrt{\pi}}\left(3 - e^{-\frac{a^2}{Dt}}\right)} \right\} \right) \cdot 10^2$$

where a is the radius of the hypothetical crystal, D the diffusion coefficient, t the time, and k is defined by equation 3. This equation can be used to obtain a reasonably good idea of the mean percent enrichment of the heavy isotopes of an element diffusing out of a crystal.

The mean percent enrichment, $\overline{S}$, in a hypothetical spherical crystal is affected by time, the diffusion coefficients, the size of the crystal, and also the percentage difference in the mass of the isotopes. $\overline{S}$ as a function of $\frac{a}{\sqrt{Dt}}$ is plotted in figure 2 for the isotope sets of Li^6 - Li^7 and Pb^{204} - Pb^{208}. Several percent change in isotopic abundance ratio is shown for small values of $\frac{a}{\sqrt{Dt}}$, particularly in the light mass range where the percentage difference in isotopic mass is greatest.

Qualitatively the relation is what one would expect. For small values of $\frac{a}{\sqrt{Dt}}$, that is where D and t are relatively large and the radius of the crystal is small, a larger fraction of the atoms of a particular element will migrate from a crystal than if $\frac{a}{\sqrt{Dt}}$ were large. Consequently the enrichment of the heavy isotope will also be greater from small values of $\frac{a}{\sqrt{Dt}}$. Figure 3 shows how rapidly the quantity, Q, of a given isotope remaining in the crystal decreases with increasing values of the mean percent enrichment of the heavy isotope.

Accepting, for the moment, solid state diffusion as one of the replacement processes in natural crystals, to what extent would such a mechanism fractionate isotopes when considered in terms of practical values of a, D, and t? Figure 4 shows a plot of the mean percent enrichment of the heavy isotope as a function of the radius "a" of a "spherical crystal" containing lithium and lead and for several values of the mean square path, $\sqrt{Dt}$. For values of $\sqrt{Dt}$ below 10^{-3} cm there is no significant isotopic fractionation even in very small crystals, whereas above this value

significant separation can occur particularly in small crystals.

Data on solid state diffusion coefficients in minerals at normal earth temperatures are scanty for most of the elements, but enough is known to indicate that the coefficients are extremely small in most cases. At these temperatures the diffusion coefficients for many elements are less than 10^{-22} cm^2/sec. For the older minerals of the earth, for instance those 1 billion years, t will be about 3×10^{16} seconds which will be approximately an upper limit for any practical value of t. For this near maximum value of t and for the values of D less than 10^{-22} cm^2/sec, the mean enrichment of the heavy isotope within a crystal due to solid state diffusion must be of little importance at normal earth temperatures even for crystals less than 0.10 cm. However, where D is large at these ordinary temperatures, significant fractionation may be possible even for diffusion time somewhat less than a billion years.

Larger values of D exist at high temperatures, increasing according to the general exponential law

$$D = D_0 \, e^{-\frac{A}{RT}}$$

$\cdots\cdots\cdots\cdots$ (6)

where D_0 is the activation constant, A is the activation energy, R is the gas constant, and T is the absolute temperature. For high-temperature minerals (100° - 1000° C) that have cooled slowly over a long period, the average diffusion coefficient could be as large as 10^{-16} cm^2/sec, depending on the temperature, whereas the diffusion coefficient at 20° C will be much smaller. The diffusion time for 1-billion-year old rocks being about 3×10^{16} seconds would thus make $\sqrt{Dt}$ equal to 1.7 cm and, of course, this could vary from this near maximum value all the way down to 10^{-7} cm or

lower depending on t. The larger values of $\sqrt{Dt}$ plotted in figure 4 for

lithium and lead show that under extremely favorable conditions of

diffusion, that is moderate to high temperatures and long periods of

time, several percent change in isotopic abundance ratio could take

place even in mineral specimens as large as 1 or 2 cm in diameter.

Frequently the value of the $\sqrt{Dt}$ will be 10^{-3} cm and smaller; it is

possible that where $\sqrt{Dt}$ is greater than 10^{-3} cm the order of from 0.5

to 1 or 2 percent change in the isotopic abundance could take place.

This would be true especially where the percentage difference in mass is

large, and where a sizable fraction of all the isotopes of a given ele-

ment has diffused from the crystal.

To illustrate the above discussion, consider the diffusion of lead

atoms in a galena lattice. At 27° C the diffusion coefficient for lead

in lead sulfide is about 6.1×10^{-32} cm^2/sec (Anderson and Richards, 1946),

whereas at 460° C it is 4.3×10^{-13} cm^2/sec. Assume, for example, that

the crystals of galena are of the order of a millimeter across and were

formed under high-temperature ($\approx 500^{\circ}$ C) conditions in a calcite matrix.

Shortly after the cessation of crystal growth diffusion of lead into the

calcite lattice becomes the important process. If the high temperature

conditions prevailed for 100,000 years, the $\sqrt{Dt}$ would be 1.3 cm which

would be large enough to indicate substantial isotope enrichment in this

period of time. This example is probably one of the less favorable

instances of isotopic fractionation. A number of other elements have much

larger diffusion coefficients at high temperatures and significant enrich-

ment can take place in a much shorter time (1,000 to 10,000 years).

When a high temperature magmatic body such as a sill or dike is so

situated as to cool slowly over a period of about 100 years to a relatively

low temperature, another possibility for significant isotopic solid state diffusion arises. The crystals formed during the early stages of magmatic differentiation may undergo high-temperature replacement as represented in Bowen's reaction series. For instance, if a calcic plagioclase crystallizes first and continues to react with enclosing liquid magma forming more and more sodic feldspars, the end product might be albite. Assuming that the calcium was replaced by sodium because of a variation in the ion concentration of the fluid magma with subsequent diffusion, substantial isotope separation might take place effectively in the small amount of original calcium remaining in the sodium feldspar crystal lattice. Under these temperature conditions the diffusion coefficients may be as large as 10^{-12} cm^2/sec or higher. In 100 years (t = 10^9 sec) the $\sqrt{Dt}$ would be about 10^{-2} cm. From figure 4 it is seen that about 1 percent change may take place in this relatively short time even if essentially no diffusion took place from that time until the present.

Although significant isotopic separation can take place under these conditions, fractionation will only be evident in some minor element constituent of a crystal, for instance the heavy-isotope-enriched remnant of an element which was once present in large quantities. Thus assuming solid state diffusion as the replacement process in the above example, a partly replaced plagioclase crystal, such as a calci-alkalic plagioclase, would not be expected to show significant enrichment of the heavy calcium isotopes, whereas trace quantities of almost completely replaced calcium in feldspar would probably exhibit some enrichment in the heavy isotopes.

Isotopic fractionation across a boundary

Replacement in the wall rock adjacent to a vein may take place by a diffusion process where a bodily flow of solution is impossible. This is true where initial vein solutions react with the wall rock forming an impermeable interface between the vein and the enclosing rock. Further penetration of the elements of the vein solutions into the wall rock and their replacing of certain constituents of that rock is not an uncommon process and is conceivably due to diffusion through the interface.

Where diffusion and replacement occur under high-temperature conditions a hydrothermal alteration halo will be formed near the vein. The outer edges of this halo are actually low concentration diffusion fronts and as such will carry isotopes enriched in the lighter mass constituent. As the larger separation factors occur in the lower concentration areas at some distance from the contact, it is appropriate to determine what the average isotopic separation might be at the outer edge of the halo rather than the average for the whole halo. The usual equation for infinite diffusion across a boundary is

$$C_x = \frac{C_o}{2} \left(1 - \text{erf}\ \frac{x}{2\sqrt{Dt}} \right)$$

.... (7)

where C_o is the initial concentration and C_x is the concentration at the distance x from the interface. From this Klemm (1943) has developed the equation

$$N = C_o \sqrt{\frac{Dt}{\pi}} \left\{ e^{-\left(\frac{x}{2\sqrt{Dt}}\right)^2} - \frac{x}{2}\sqrt{\frac{\pi}{Dt}} \left(1 - \text{erf}\ \frac{x}{2\sqrt{Dt}} \right) \right\}$$

$$= C_o \sqrt{\frac{Dt}{\pi}}\ \mathcal{J}\left(\frac{x}{2\sqrt{Dt}}\right)$$

.............(8)

where N is the amount of material which has diffused in time t through a 1 cm^2 area situated x cm from the interface. By letting $\sqrt{k} = \sqrt{D_L}/\sqrt{D_H}$ where L and H have the previous meaning then

$$\frac{N_L}{N_H} = \frac{\sqrt{k}\,C_{L_O}}{C_{H_O}} \cdot \frac{\mathscr{G}\left(\frac{x}{2\sqrt{D_L t}}\right)}{\mathscr{G}\left(\frac{x}{2}\sqrt{\frac{k}{D_L t}}\right)}$$

and

$$\overline{S} = \frac{\sqrt{k}\,\mathscr{G}\left(\frac{x}{2\sqrt{D_L t}}\right)}{\mathscr{G}\left(\frac{x}{2}\sqrt{\frac{k}{D_L t}}\right)}$$

.... (9)

where $\overline{S}$ is the mean enrichment of the light isotope in the atoms or ions which have diffused beyond a point x cm from the interface. Klemm (1943) calculates $\overline{S}$ by means of two simple graphs (figs. 5 and 6). Figure 5 is the fractional amount of original material which has diffused beyond x cm as a function of $\frac{x}{2\sqrt{Dt}}$ for various values of the mean square distance. Figure 6 shows a plot of the mean percent enrichment $(\overline{S} - 1) \cdot 10^2$ as a function of $\frac{x}{2\sqrt{Dt}}$ for various percentage mass differences $\frac{\Delta m}{m} \cdot 10^2$.

As an example, let us consider the diffusion of lead in microperthite. At ordinary temperatures the diffusion effect of lead will be small even over geologic periods, but at high temperatures it could be significant in relatively short time. The approximate diffusion coefficient of lead in microperthite at 750° C is given by Rosenquist (1949) as about 7.5 x 10^{-11} cm^2/sec. If a lead-bearing ore is in contact with microperthite at 750° C for a period of a little more than 4 years (about 1.3 x 10^8 sec), the value of $\sqrt{Dt}$ will be approximately 0.1 cm. If we now wish to consider a point x cm from the contact such that the relative amount of lead, $\frac{N}{C_O}$, which has diffused beyond x cm is 0.01, $x/2\sqrt{Dt}$ will be

0.75 (fig. 5). The percentage mass difference for Pb^{204} and Pb^{208} is 1.92 percent, and hence from figure 6 the mean percent enrichment of Pb^{204} in the lead which has diffused beyond x cm will be about 1.5 percent. If the diffusion had taken place for a little more than 40 years instead of 4 years, then the same fraction of the original lead would show about 3 percent enrichment in the light isotope. Isotopes of those elements with larger percentage mass differences will of course show larger enrichment factors. However, such an enrichment of the light isotope will be evident in only a very small fraction of the total lead which has diffused. Thus, the situation for diffusion across a boundary is similar to that considered for a crystal. For very small values of $\sqrt{Dt}$, say·less than 10^{-3} cm, the amount of material exhibiting a large fractionation becomes vanishingly small. It is only where the $\sqrt{Dt}$ becomes greater than 0.1 cm that a significant fractionation takes place at such a distance where it may easily be recovered for isotopic analysis, and then for only a small fraction of the diffusing isotopes. For instance, in the 4-year and 40-year diffusion examples the value of x would be 0.15 cm and 2.90 cm, respectively, for 0.01 of the total number of diffusing lead atoms. In other words, one would expect to find significant isotopic fractionation due to this mechanism, but it would be very sharply localized and in a minor amount of material.

DIFFUSION OF SOLUTES

Up to this point we have considered the effect of solid state diffusion only. However, once an atom diffuses from a solid lattice into an aqueous solution, such as ground-water solutions, it is free to move at much faster rates under similar concentration gradients. Solute

diffusion -- diffusion in an aqueous medium -- is probably a much more important process than solid state diffusion, although both types of diffusion are usually concurrent. It is probable that in nature the wall rocks, although not necessarily wet, retain intergranular surface water films and are permeable to and react with the hydrothermal solutions. Moreover many rocks, such as limestones and dolomites, are porous and contain many cracks and channels. Under these conditions and where there is no fluid flow, solute atoms are free to travel through the intergranular water paths by a diffusion process. The same general laws apply as in the case of solid state diffusion; the really significant difference is that the solute diffusion coefficients are much larger than in the former case. Thus, instead of considering a short distance transfer one can expect a travel distance of the order of several feet. For example, Morris and Lovering (1952) have studied the heavy metal distribution in wall rocks of the Tintic district, Utah, and have shown that the distribution in wall rocks is indeed one which strongly suggests solute diffusion. These results indicate that both nonsteady-state (non-equilibrium) and steady-state (equilibrium) conditions existed, depending on the circumstances.

The results of nonsteady-state conditions will be similar to those shown for solid state diffusion except that the distances of diffusion will be longer for a given diffusion time due to the larger diffusion coefficients. For instance, the solute diffusion coefficients in pure water for 1/2 Zn^{++}, 1/2 Cu^{++}, and 1/2 Pb^{++} at 25° C are 7.3 x 10^{-6}, 7.4 x 10^{-6}, and 9.7 x 10^{-6} cm^2/sec, respectively. An aqueous solution containing zinc ion and flowing in a fissure vein may provide the setting for the fractionation of Zn^{64} and Zn^{68}. Assuming a steady supply of zinc

ion at the vein wall, it can be shown that significant fractionation can take place in the zinc held by the interstitial fluid at such distances where the concentration is only one-tenth of the concentration in the ore vein.

Consider the example of steady state solute diffusion between two parellel veins. Garrels et al. (1949) have shown that such conditions can exist in water-saturated rocks where the diffusion front meets a vein in which pure water is flowing. The zinc removed by the water causes a front of near-zero concentration to exist. Succeeding concentration fronts gradually "catch up" and steady-state conditions rapidly develop. Under steady-state conditions the amount of material, dq, deposited per area, A cm^2, in time, dt, into the flowing water will be

$$dq = \frac{DA(C_O - C_X)\, dt}{x}$$

$$= \frac{DA\, C_O\, dt}{x} \quad (\text{for } C_X = 0)$$

$$\dots\dots\dots\dots\dots\dots (10)$$

where D is the diffusion coefficient and x the distance from the source vein. Assuming C_O to be the same for each isotope, the ratio of light to heavy masses being deposited in the water-carrying vein will simply be

$$\frac{Q_L}{Q_H} = \frac{kD_H}{D_H} = \sqrt{\frac{M_H}{M_L}}$$

$$\dots\dots\dots\dots\dots\dots (11)$$

Thus, under steady-state conditions the isotope separation is simply a constant fraction of the original isotope abundance regardless of the source concentration, time, or length of the diffusion path. It is of interest to point out that under these conditions the percent isotope enrichment would be

$$S = (k - 1) \cdot 10^2$$

Moreover, not only would k be the ratio of any two of the zinc isotopes at any front between the two veins,2/ but it is also the abundance ratio of these isotopes diffusing to the water-carrying vein. Geologically this is of interest because if the light material is continually redeposited at a given point it will give rise to a zinc mineral isotopically lighter than the zinc in the original vein.

DISCUSSION AND EVIDENCE OF ISOTOPIC DIFFUSION

Because there is geological evidence that diffusion plays a part in forming some rocks and minerals, diffusion must be examined as a possible mechanism of natural isotope fractionation. The results presented here indicate that, although substantial isotopic fractionation is possible, it can occur only in very small parts of the original material. It is thus highly improbable that a large body exists in which a major constituent is isotopically enriched by diffusion processes; in other words significant isotopic fractionation will be localized and can be expected to be most apparent in minor elements of a given crystal or mineral. However, it is possible that an enrichment in the lighter isotopes of a major element might take place in replacement bodies formed by elements which have diffused by diffusion of solute in magmatic solutions or in water-saturated rocks. As Garrels et al. (1949) have pointed out, solute diffusion reaches steady-state conditions in a relatively short time, and it has been shown here that under such conditions the enrichment factor will be k, or $\sqrt{M_H/M_L}$. Where steady-state conditions are not attained the separation will be somewhat less than k. Thus a zinc mineral being formed

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2/ In nature C_O will not be the same for any two isotopes, and the ratio at any front will be $\frac{kQ_{H_O}}{Q_{L_O}}$ where Q_{L_O}/Q_{H_O} is the original abundance ratio.

by diffusion-transported zinc ions in solution would be expected to exhibit an enrichment in the light isotope by a factor of k for steady-state condition, or some value less than k for a nonsteady-state condition.

The salient feature of solute diffusion, as opposed to solid-state diffusion as a geologic process, is that more material can be moved faster over longer distances in relatively shorter time. Thus the elemental distribution, and hence isotopic abundance, in some rocks formed from diffusion-transported material will be profoundly influenced by solute diffusion. This assumes, of course, that the fractionation due to other processes which might produce isotopic separation will be comparable to or smaller than diffusion processes.

The experimental evidence for isotopic fractionation due to diffusion is very scanty, but it is worth while to examine some of the existing data. Probably the most direct evidence of isotopic diffusion so far found is the data determined by Silverman (1951) for O^{18} and O^{16}. Across a contact of gabbro and intruding granophyre he made O^{18}/O^{16} measurements of six specimens laterally spread over 20 feet. His results are shown in table 1. The regular change of total oxygen and of the O^{18}/O^{16} ratio strongly suggests a diffusion process. Silverman discusses a number of other possible processes in the light of geological evidence in the formations from which the specimens were taken. He finally concludes that his results indicate some process of permeation, solution, or diffusion in a solid. However, there is some doubt as to whether or not the above situation is one of solid-state diffusion. To explain diffusion transport over 20 feet the diffusion constants would have to be very large, implying a very high temperature, and it seems more probable that solute diffusion

Table 1.--Variation of the O^{18}/O^{16} ratio with concentration
(after Silverman, 1951).

Sample and number	O^{18}/O^{16} ($^o/_{oo}$)	cc O_2/mg sample
Gabbro no. W-187	6.1	0.28
Intermediate rock no. W-137-4	7.7	0.33
Intermediate rock no. W-137-3	8.4	0.35
Contact rock no. W-137-2	8.7	0.36
Granophyre no. W-137-1	9.0	0.39
Granophyre no. W-136-4	9.9	0.36

might be the mechanism.

There are a number of other instances where experimental data point to diffusion as a mechanism of natural isotope enrichment, but as yet no definitive experiments have been performed. It appears probable that diffusion concentration of isotopes is a distinct possibility and should be investigated further.

CONCLUSION

Under favorable conditions at least part of the isotopic fractiona-tion in natural specimens which has taken place during geologic time might be ascribed to a diffusion process. These processes, whether by solid-state or by solute diffusion, will produce significant fractionation up to a few percent in trace elements, but minerals grown over a period of time by small increments of an enriched trace element could display a

bulk enrichment in the whole mineral crystal. To date, fractionation due to chemical differences has been favored as an explanation, but it is the opinion of the authors that both mechanisms are operating, the particular circumstances being the controlling factor as to the importance of each mechanism in a given situation. Actually, experimental data must ultimately decide the issue.

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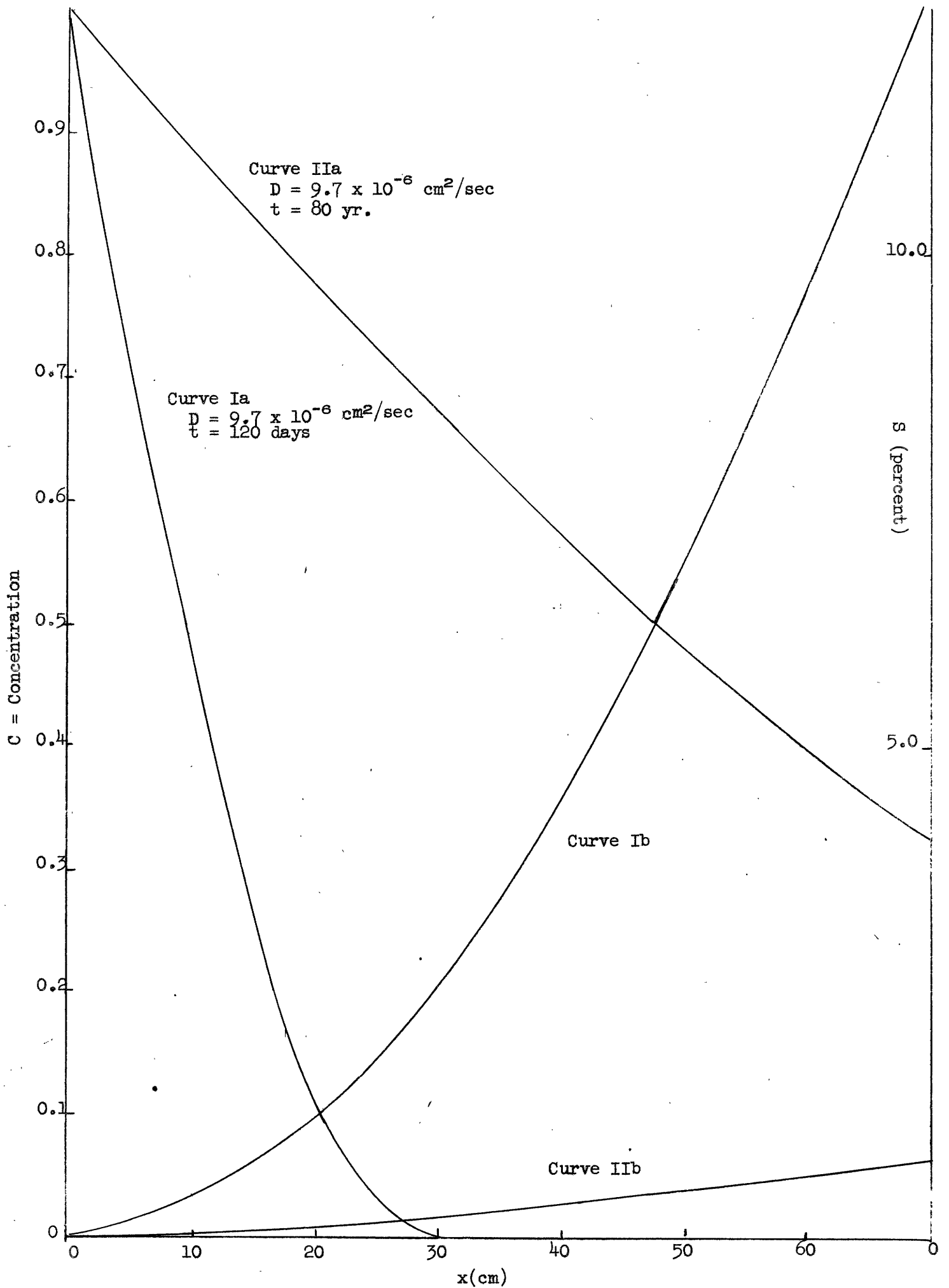
Figure 1.--Curves Ia and IIa: Concentration as a function of distance for a hypothetical element in 120 days and 80 years. Curves Ib and IIb: Percent isotope enrichment as a function of distance under the same conditions and for k = 1.0097.
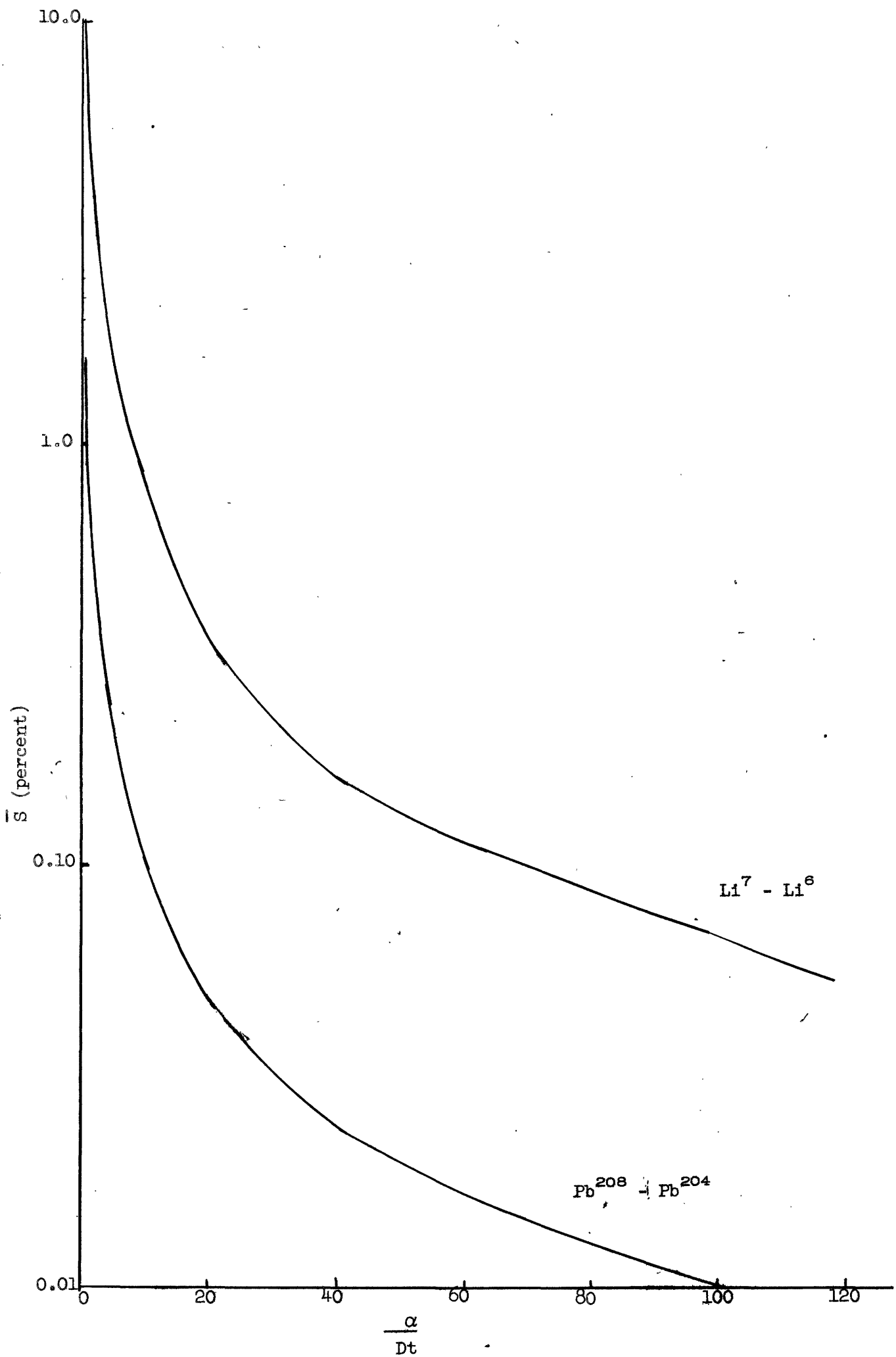
Figure 2.--Mean percent isotope enrichment as a function
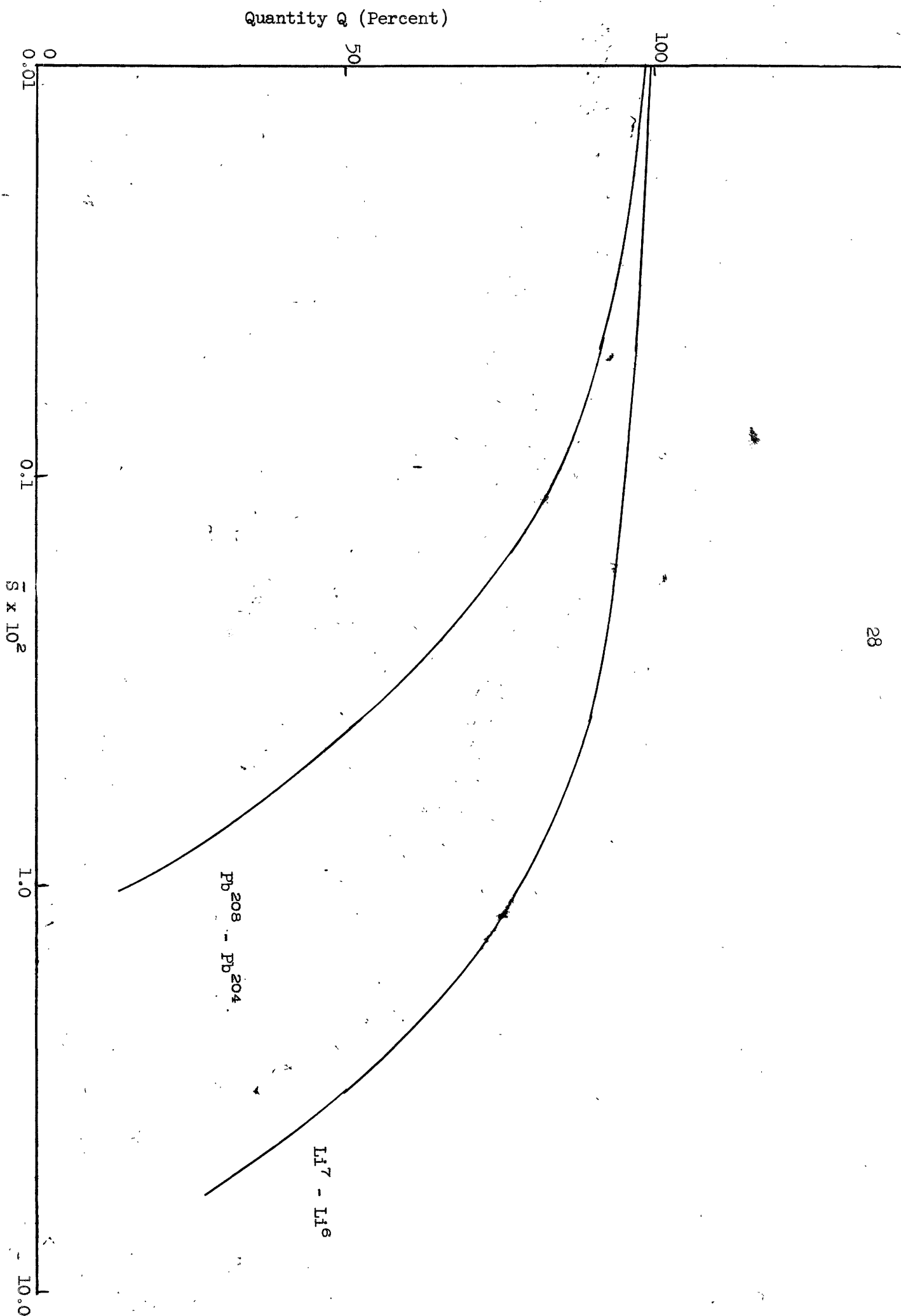of the parameter a/√Dt for lead and lithium.

Figure 3.—Quantity of element removed as a function of the mean percent isotope enrichment for lead and lithium.

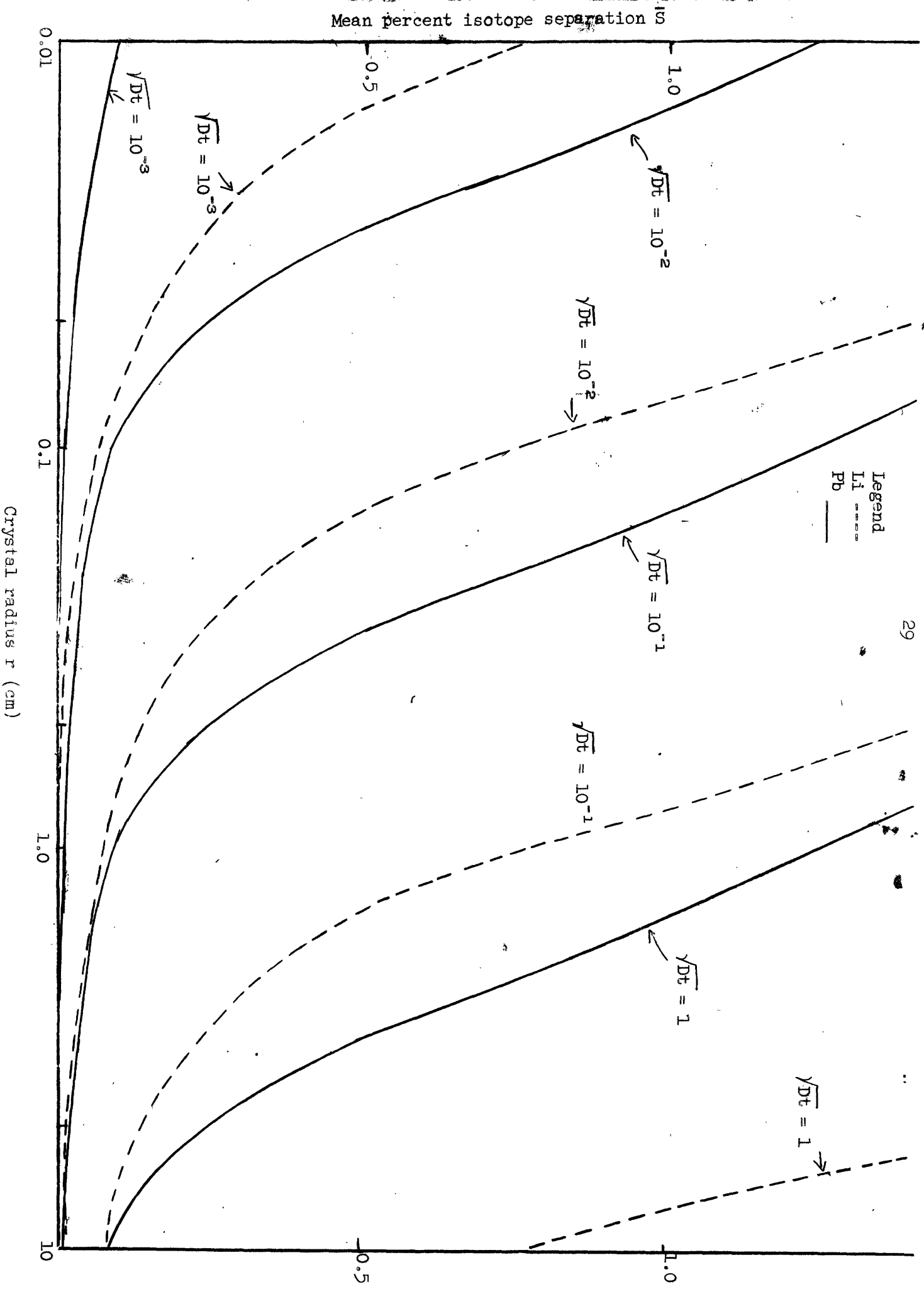Figure 4.--Mean percent isotope enrichment, $\bar{S}$, as a function of crystal radius for lead and lithium for several values of $\sqrt{Dt}$.

Mean percent isotope separation $\bar{S}$

Crystal radius r (cm)

$\sqrt{Dt} = 10^{-3}$

$\sqrt{Dt} = 10^{-3}$

$\sqrt{Dt} = 10^{-2}$

$\sqrt{Dt} = 10^{-2}$

$\sqrt{Dt} = 10^{-1}$

$\sqrt{Dt} = 10^{-1}$

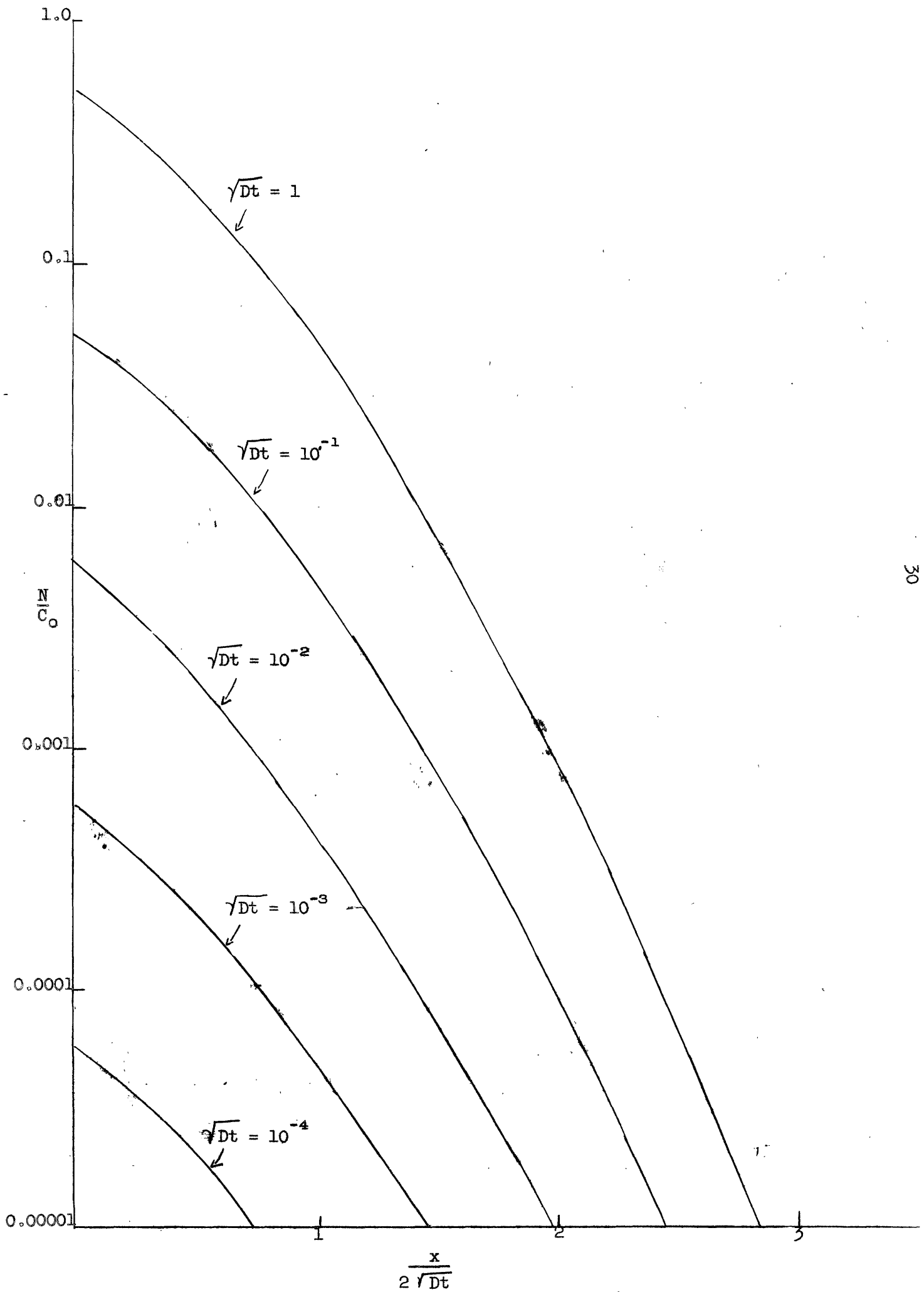$\sqrt{Dt} = 1$

$\sqrt{Dt} = 1$

Legend

Li ====
Pb ——

29

Figure 5.--Fractional amount of original material, $\frac{N}{C_o}$, which has diffused beyond x cm as a function of $x/2\sqrt{Dt}$ for various values of $\sqrt{Dt}$ (after Klemm).
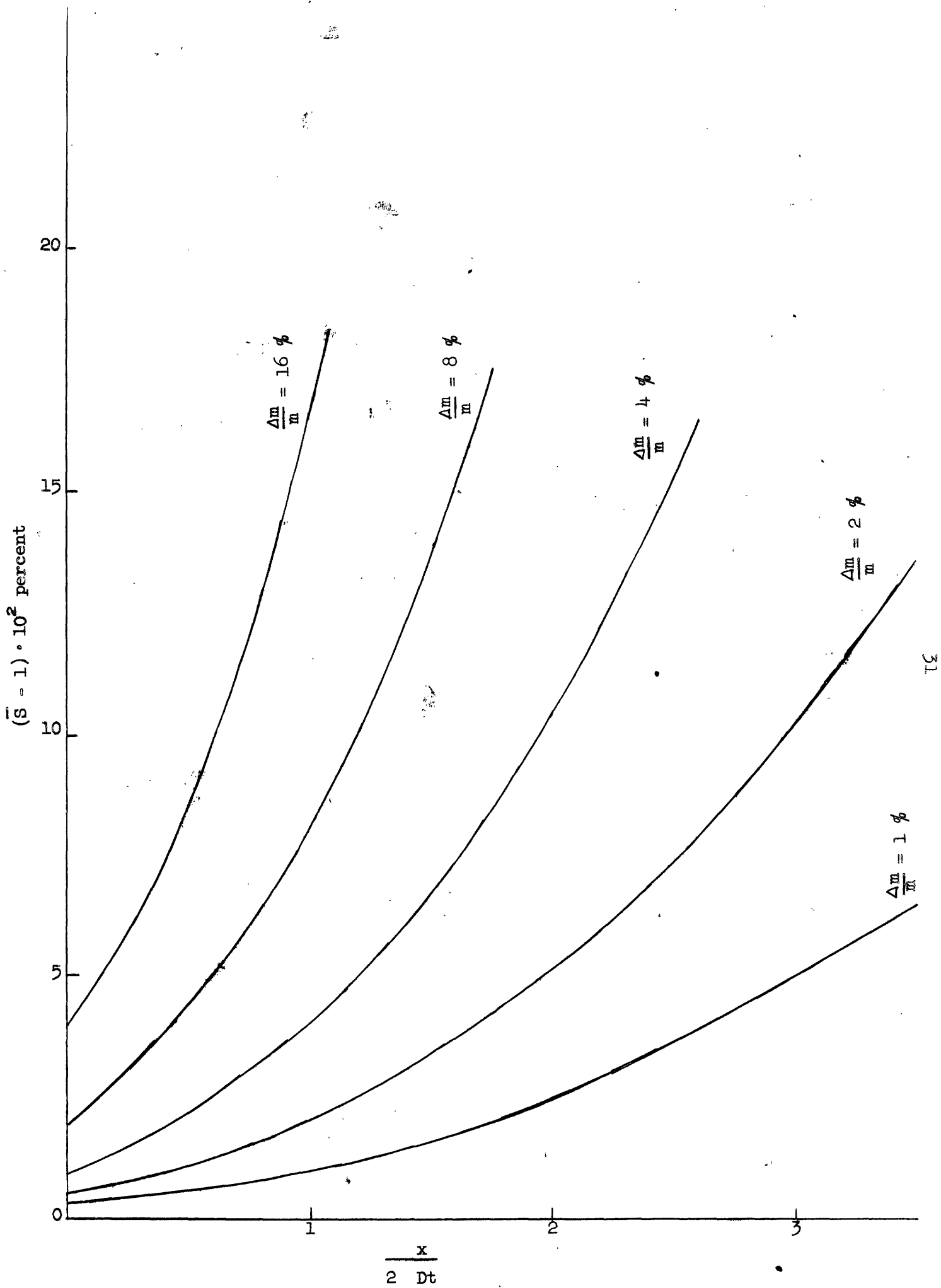
Figure 6.--Mean percent enrichment, $(\bar{S} - 1)\cdot 10^2$, as a function of $x/2\sqrt{Dt}$ for various percentage mass differences, $\frac{\Delta m}{m}\cdot 10^2$ (after Klemm).