PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Melts and Metasomatic Fluids: Evidence from U-Series Disequilibria and Th Isotopes

J. B. Gill

Phil. Trans. R. Soc. Lond. A 1993 **342**, 79-90
doi: 10.1098/rsta.1993.0006

Melts and metasomatic fluids: evidence from U-series disequilibria and Th isotopes

By J. B. Gill

Earth Sciences Department, University of California, Santa Cruz, California 95064, U.S.A.

Radioactive disequilibria and Th isotopes in volcanic rocks change in response to the extent and rate of partial melting, the attainment of chemical and isotopic equilibrium, and the presence and composition of a vapour phase before and during melting. Enrichments of ^{230}Th with respect to ^{238}U by 10–60 % in MORB and intraplate alkalic magmas are attributed to the greater incompatibility of Th in small degree silicate partial melts. Inverse correlations between $(^{230}\mathrm{Th})/(^{238}\mathrm{U})$ and $(^{230}\mathrm{Th})/(^{232}\mathrm{Th})$ ratios indicate either that partial melting lasts more than 10^5 years, or that smaller degree melts take scores of millenia longer to move from the site of last chemical equilibrium with the source to the eruption site. Disequilibrium enrichments of ^{226}Ra with respect to ^{230}Th and of ^{231}Pa with respect to ^{235}U by 150–300 % occur in oceanic island arc basalts and MORB. The excess ^{226}Ra in arcs is related to magma genesis, but the other disequilibria may reflect alteration or assimilation within the crust. When these large disequilibria accompany magma genesis they indicate transfer times between source and surface of a few decades to a few millenia and suggest an open system or chemical disequilibrium during melting. Th and U isotope and concentration systematics for lamproites suggest that melting was fast enough to preclude chemical equilibrium between source and melt. Non-silicate fluids may fractionate U-series radionuclides differently and to a greater extent than do silicate melts. This property may explain the U–Th–Ra characteristics of carbonate- and water-rich melts, and distinctive Th isotopic compositions in magmas derived from metasomes in the subcontinental lithosphere.

1. Introduction

Natural radioactive disequilibria provide unique information about the chemistry and timescale of magma genesis. Secular radioactive equilibrium is when the numbers of atoms (N) of all nuclides in a decay series are inversely proportional to their decay constants (λ), so that their 'activities' ($\lambda * N$) are equal. Equilibrium is reached after about five times the half-life of the longest-lived intermediate nuclide. Disequilibrium is created when two nuclides in the same decay series are fractionated, so that their activities become unequal. The basic principles are illustrated in figure 1. Although it refers specifically to the ^{238}U–^{230}Th pair, it can be generalized to all parent–daughter pairs in the three decay schemes. Recent reviews of the principles involved, and of the application of disequilibria studies to other aspects of magma genesis such as differentiation, are by Condomines *et al.* (1988), Gill *et al.* (1992), and Gill & Condomines (1992). This paper expands on one section of the latter reference.

Conventions used in this paper are as follows. Parentheses around a nuclide denote activities in dpm g^{-1}, whereas brackets denote concentrations in p.p.m. The

Phil. Trans. R. Soc. Lond. A (1993) **342**, 79–90

Printed in Great Britain

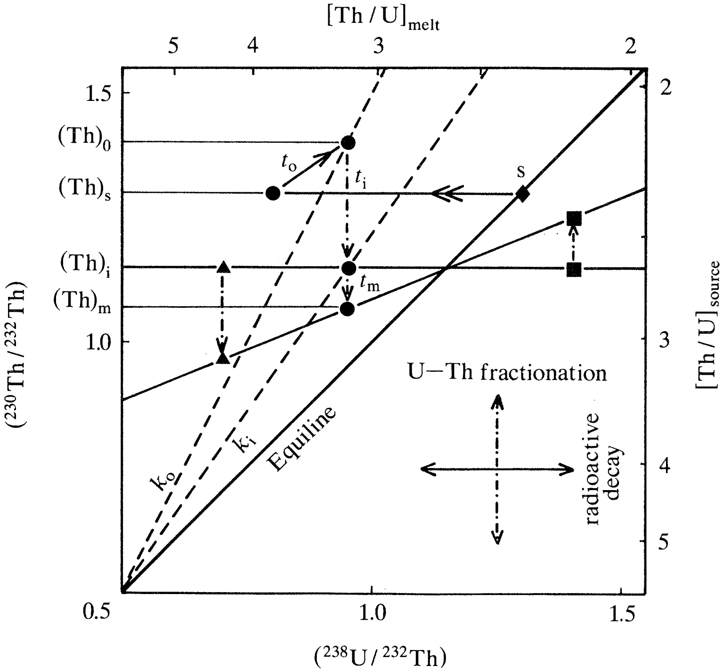

Figure 1. Schematic (^{230}Th)–(^{238}U) isochron diagram. Although it refers specifically to the ^{238}U–^{230}Th pair, it can be generalized to all parent–daughter pairs in the three decay schemes. Disequilibrium is created by fractionating ^{230}Th from ^{238}U during partial melting. Magma is produced by melting source S which is isotopically homogeneous at the scale of melting and initially in radioactive equilibrium (that is, on the Equiline) with $(\mathrm{Th})_s$. If $D_{\mathrm{Th}} < D_{\mathrm{U}}$, then $(^{238}\mathrm{U})/(^{230}\mathrm{Th})$ or $k < 1.0$ in the melt. As the degree of melting increases, the ^{230}Th-enrichment and [Th/U] ratio in the melt decrease. In the example illustrated, the degree of melting is insufficient for the $[\mathrm{Th/U}]_{\mathrm{melt}}$ to decrease to the $[\mathrm{Th/U}]_{\mathrm{source}}$. At the end of melting (after time t_o), the $(^{230}\mathrm{Th})/(^{232}\mathrm{Th})$ ratio in the melt is $(\mathrm{Th})_o$, which exceeds $(\mathrm{Th})_s$ if t_o is long. The $[\mathrm{Th/U}]_{\mathrm{melt}}$ remains constant after the melt ceases to be in chemical equilibrium with its source, but the $(^{230}\mathrm{Th})/(^{232}\mathrm{Th})$ ratio decreases during transfer time t_i to $(\mathrm{Th})_i$ at the time of eruption as the result of unsupported radioactive decay. The ^{230}Th-enrichment decreases from k_o at the end of melting to k_i at the time of eruption. Near the time of eruption the melt precipitates phenocrysts, for some of which $D_{\mathrm{Th}} < D_{\mathrm{Th}}$ (illustrated by the solid triangle) and for others of which $D_{\mathrm{Th}} < D_{\mathrm{U}}$ (illustrated by the solid square). There is isotopic homogeneity, all phases having $(\mathrm{Th})_i$. During the time between eruption and measurement (t_m), all phases evolve toward radioactive equilibrium by pivoting around $(\mathrm{Th})_i$ on the Equiline such that the bulk sample has $(\mathrm{Th})_m$ when measured. In this case, t_m is the conventional age of the lava.

$(^{238}\mathrm{U})/(^{230}\mathrm{Th})$ activity ratio is referred to as k, and the $(^{226}\mathrm{Ra})/(^{230}\mathrm{Th})$ activity ratio as l. The $(^{230}\mathrm{Th})/(^{232}\mathrm{Th})$ activity ratio of a volcanic rock at the time of measurement is referred to as $(\mathrm{Th})_m$; at the time of eruption it is $(\mathrm{Th})_i$, at the end of melting (i.e. at the last chemical equilibration with the source) it is $(\mathrm{Th})_o$, and at the beginning of melting the ratio in the source is $(\mathrm{Th})_s$ (i.e. the initial isotopic composition of the source) (figure 1). The corresponding times between events during the history of a volcanic rock are: t_m, the time between eruption and measurement (the conventional age of the rock); t_i, the time between the end of melting and eruption (the transfer time from the source); and t_o, the mean time between the beginning and end of melting (the duration of partial melting).

The t_o interval is ambiguous for two reasons. First, if dynamic melting occurs throughout a 50 km high column of decompressing mantle, t_o is almost zero where the column first crosses its solidus, but can be a million years at the top of the column; for this paper, t_o is the mean age for any specific aggregate of melts. Second, t_o and t_i are separated by the time at which chemical equilibrium ceases between melt and source. At extremes, these intervals may correspond to the time of permeable flow of primitive melt through the asthenosphere versus ascent and differentiation in sheets or pipes through the lithosphere, respectively. However, a continuum in the porosity and spacing of melt channels is likely. Chemical equilibrium will be reached when channels are closely spaced and solid state diffusion is rapid; chemical disequilibrium is enhanced by the opposite and is likely even during permeable flow in the asthenosphere (Spiegelman & Kenyon 1992).

Some advantages of using short-lived radionuclides to study melting are that disequilibria provide quantitative measurements of trace element fractionation during magma genesis, disequilibria constrain the temporal and perhaps spatial scale of magma formation, Th responds quickly to chemical modifications of the source and is the only isotopic tracer which reflects a current trace element ratio, and Th and Ra are the most incompatible isotopic tracers in silicate melts.

2. Equilibrium melting

(*a*) *Background*

For a quarter century, basalts have been related to different degrees of batch partial melting of mantle peridotite under chemical and isotopic equilibrium (Green & Ringwood 1967; Gast 1968; Minster & Allegre 1978; Hofmann & Hart 1978). The degree of melting was tacitly assumed to equal a melt fraction or porosity (ϕ) that could be calculated by, for example, inverting trace element concentrations of basalts using equations which assume chemical equilibrium between all the melt and all the solid matrix. Effects of melting rate and melt path were ignored. Many trace elements and primitive samples are needed in order to allow inversion of the data because both the *D*s (partition coefficients) and the initial source composition must be known to calculate ϕ. Tholeiitic magmas, such as those erupted at mid-ocean ridges or Kilauea volcano, Hawaii, were found to represent relatively large degrees of melting (10–20%) of fertile peridotite, with more alkalic magmas reflecting smaller percent melts. There were taken to be the ϕs necessary to produce interconnectivity of the melt.

The need to know the source composition and to use undifferentiated samples can be relaxed if there is radioactive equilibrium at the onset of melting and differentiation does not alter activity ratios. Only the *D*s of parent and daughter nuclides are necessary in order to calculate ϕ from the observed disequilibrium.

(*b*) ^{230}Th–^{238}U *disequilibria and* (^{230}Th)/(^{232}Th) *ratios*

Both Th and U are highly incompatible elements and the partition coefficients of Th and U are thought to be similar and very low such that the [Th/U] ratio of melt would differ from that of source peridotite only in highly alkalic magmas. Discovery of 18% excess ^{230}Th ($k = 0.85$) in MORB on average (Condomines *et al.* 1981; Newman *et al.* 1983; Goldstein *et al.* 1990, 1991) was, therefore, surprising. Excess ^{230}Th has now been found in dozens of samples in more than ten laboratories by both mass and alpha spectrometry.

If related to melting, it implies that the mantle was permeable at low porosity and

$D_{Th} < D_U$, so that Th was preferentially enriched at small degrees of melting (McKenzie 1985). Continuous models that involve fractional melting above a small ϕ, and dynamic models involving mixing of small percent melts from variously depleted levels of an ascending source, are required to reconcile the low k values with other geochemical results. If small percent melts or melts from more fertile sources, mix with larger percent melts or melts from more depleted sources, the former will dominate the trace element characteristics of the mixture, including radioactive disequilibria (Williams & Gill 1989; Goldstein *et al.* 1991).

[Th/U] and [Th] decrease with increasing degrees of partial melting until $[\mathrm{Th/U}]_{\mathrm{melt}}$ equals $[\mathrm{Th/U}]_{\mathrm{source}}$. The values of D_U and D_{Th} determine how much total melting is required to achieve this equality; for example, if $D_U = 0.015$ and $D_{Th} = 0.005$, then about 15% melting is required (Williams & Gill 1989). Even if there is chemical and isotopic equilibrium during melting, $(\mathrm{Th})_i$ may differ from $(\mathrm{Th})_s$, and be higher in larger degree melts, for either of two reasons. First, greater degrees of partial melting will be accompanied by higher $(\mathrm{Th})_o$ if t_o is longer than about one half-life of ^{230}Th (Williams & Gill 1989). The amount of increase is a function of partition coefficients and porosity as well as melting rate and time, but the effect is expected to be less than 15% when upwelling rates are greater than 5–10 cm a^{-1}, depending on the maximum depth of melt extraction. If disequilibria are integrated into geochemical models which constrain some of the variables independently for a specific location, then melting rates and geometry can be deduced. On the other hand, $(\mathrm{Th})_i$ will be less than $(\mathrm{Th})_o$, and lower in smaller melt fractions, if melts take millenia to move to the surface from the site of last chemical equilibrium with the source. This effect will be enhanced if smaller melt fractions have longer transfer times than larger melt fractions. Which of the two effects predominates depends on whether chemical equilibrium is maintained until final melt extraction. If it is maintained, $(^{230}\mathrm{Th})/(^{232}\mathrm{Th})$ ratios will rise because the matrix is U-enriched; if chemical equilibrium is not maintained, they fall because the melt is Th-enriched. This is why the change in convention between $(\mathrm{Th})_o$ and $(\mathrm{Th})_i$ occurs at the time of last chemical equilibration with the source.

Whether t_o or t_i is long enough to cause $(\mathrm{Th})_i$ to differ from $(\mathrm{Th})_s$, or whether the total degree of melting is large enough for $[\mathrm{Th/U}]_{\mathrm{melt}}$ to equal $[\mathrm{Th/U}]_{\mathrm{source}}$, depends on melting models and rates, time, and the partition coefficients of Th and U. No study of disequilibria has yet been sufficiently integrated with other trace element and isotopic measures of source homogeneity and percent of melting to address this topic rigorously. However, discovery that k ratios correlate inversely with Th contents and [Th/U] ratios at similar Sr and Th isotope ratios between the Endeavor and southern Juan de Fuca spreading segments in the NE Pacific is an important first step (Goldstein *et al.* 1990, 1991). These results are consistent with chemical and isotopic equilibrium and homogeneity at the scale of melting beneath the two segments, and indicate smaller percent melting beneath the Endeavor. Following the logic above, the 6% higher $(\mathrm{Th})_i$ in the southern Juan de Fuca segment could result from: (i) long t_o (*ca.* 300 Ka to reach 15% melting using the parameters of Williams & Gill (1989)) followed by rapid ascent; or (ii) instantaneous t_o followed by about 22–40 Ka longer t_i for the smaller melt fraction depending on assumptions about $[\mathrm{Th/U}]_{\mathrm{source}}$. Case (i) assumes $(\mathrm{Th})_o = 1.3$ (i.e. $[\mathrm{Th/U}]_{\mathrm{source}} = 2.3$) whereas case (ii) assumes $(\mathrm{Th})_o = 1.5$ or higher. Case (i) is preferable because it better fits the global correlation of Th and Sr isotopes and case (ii) is inconsistent with excess ^{226}Ra if it was acquired during partial melting (see below).

Most oceanic and continental alkali basalts have more ^{230}Th enrichment than ocean island tholeiites (see summaries by Condomines *et al.* 1988; Gill *et al.* 1992), as expected if disequilibrium is primarily a function of the degree of melting. However, no global correlation exists between the amount of excess ^{230}Th and major or trace element measures of percent melting. In part this is because the latter cannot distinguish the effects of smaller percent melting from greater source enrichment. It is also because the extent of radioactive disequilibrium includes the effects of melting rate, partition coefficients, and approach to chemical and isotopic equilibrium (see below) which vary from place to place.

Permeable flow of small degree melts has chromatographic effects, including separation of elements according to small differences in their partition coefficients (Navon & Stolper 1987; McKenzie & O'Nions 1991). This can result in nonlinear mixing effects amongst the isotopic tracers which will be most noticeable for Th because it is the most incompatible tracer except for He. These effects will contribute to variations in disequilibria and to scatter in isotope correlation diagrams involving Th.

(*c*) (^{226}Ra)/(^{230}Th) *and* (^{231}Pa)/(^{235}U) *disequilibria*

Discovery of other, even larger disequilibria followed. Some MORB and island arc volcanic rocks have (^{226}Ra)/(^{230}Th) and (^{231}Pa)/(^{235}U) ratios of 1.5 to 3.0 (Capaldi *et al.* 1983; Rubin & Macdougall 1988; Reinitz & Turekian 1989; Rubin *et al.* 1989; Gill & Williams 1990; Williams & Perrin 1989; Williams *et al.* 1991). Most of the excess ^{226}Ra in arc lavas is attributed to melting processes because it is present in primitive magmas and it decreases in more differentiated lavas of individual volcanoes.

The results for MORB currently are more ambiguous and require further study of well-characterized samples for clarification. Excess ^{226}Ra appears to be a primary magmatic feature, unrelated to surface alteration (Reinitz & Turekian 1989), although the large enrichments of ^{226}Ra in submarine hydrothermal fluids makes alteration a constant concern. Magmatic assimilation of young hydrothermally altered wallrocks or sediments is another possible source of excess ^{226}Ra (Sigmarsson *et al.* 1991). If, however, Ra–Th and Pa–U fractionations occur during partial melting, then some important implications follow.

(^{226}Ra)–(^{230}Th) disequilibria can be used to estimate $t_o + t_i$ if $D_{Ra} = D_{Ba}$, the [Ba/Th] ratio of a source is constant, and the (^{226}Ra)/(^{230}Th) ratios of magmas at the end of partial melting can be estimated from their Ba/Th ratios. Data for some MORB suggest that this sum is about 1 ka (Rubin & Macdougall 1990). Two problems with this approach should be noted, however, in addition to the obvious assumption of no chemical fractionation between Ra and its homologue Ba. First, even at constant D_{Ra} and D_{Th}, (^{226}Ra)/(^{230}Th) ratios vary inversely with melting rate (Williams & Gill 1989). Second, there is inherent ambiguity about the Ba/Th ratio of the source. The 1 ka time estimate above assumed a Ba/Th ratio of 8 for the source of MORB from the East Pacific Rise. This is an order of magnitude lower than usually adopted, and probably indicates considerable source heterogeneity.

The above approach cannot be extended to disequilibrium between ^{231}Pa and ^{235}U because no homologue of Pa is known. None the less, the enrichments of ^{231}Pa and ^{230}Th correlate positively even though the ^{231}Pa enrichments are considerably larger (Williams *et al.* 1991; Goldstein *et al.* 1991). They are of the same magnitude as ^{226}Ra enrichments. If the excess ^{230}Th is related to melting, then the excess ^{231}Pa probably is also, and $D_{Pa} < D_{Th} < D_U$. These results also suggest local consistency in the extent of ^{231}Pa enrichment. That is, if one assumes that (^{231}Pa)/(^{235}U) ratios are constant in the neovolcanic zone and attributes changes in this ratio to time since eruption, then the calculated age (t_m) for off-axis samples is the same as obtained from ^{238}U–^{230}Th disequilibria by assuming constant $(\mathrm{Th})_i$.

3. Disequilibrium melting and accessory minerals

'Disequilibrium melting' has at least three quite different meanings. *Radioactive disequilibrium* is the most likely and accompanies melting whenever parent and daughter elements partition differently into the melt, which is common (see above). *Chemical disequilibrium* occurs whenever melting is too rapid for chemical potentials to be the same in melt and matrix, such that element concentrations in the melt do not reflect the bulk partition coefficients of the residue. The rate-limiting process is volume diffusion in the matrix, which is thought to require 10^4–10^6 years in cm-diameter mantle pyroxenes and garnet for highly charged cations (Bédard 1989). If t_0 is shorter, as implied above, then chemical disequilibrium is likely. The highly incompatible character of Th in melts combined with its slow diffusion in solids results in a high Peclet number (Speigelman & Kenyon 1992) which makes Th the least likely isotopic tracer to achieve chemical equilibrium during permeable flow. *Isotopic disequilibrium* is the least likely and occurs only when the source is isotopically heterogeneous at its solidus and the isotopic composition of the melt depends on the melting mode (O'Nions & Pankhurst 1974). However, Th is more likely to be isotopically heterogeneous in the subsolidus than Sr, because Th responds faster to metasomatism and diffuses more slowly. Consequently, ^{238}U and ^{230}Th may approach radioactive equilibrium within phases faster than Th isotopes are homogenized between phases by diffusion.

Accessory minerals in magma sources can play an important role in all three kinds of disequilibria if they have high concentrations and highly fractionated parent/daughter ratios. Several accessory minerals which may dissolve in or coexist with small degree melts in the mantle have quite high [Th/U] ratios (e.g. phlogopite, amphibole, whitlockite); others have quite low [Th/U] ratios (carbonates, titanates, and perhaps garnet). Any of these would contribute greatly to radioactive disequilibria if they are refractory or if chemical equilibrium is not achieved. Melts in chemical equilibrium with a residual accessory phase acquire trace element characteristics which are the inverse of that phase, in proportion to its weight fraction in the residue (figure 2*a*). This effect is extended during dynamic melting, where melts of more fertile sources routinely blend with melts of more depleted sources. Trace elements can be affected by accessory phases which are residual only in the more fertile source regions whereas major elements are determined by the average extent of melting of the entire melt column (Klein & Langmuir 1987; Williams & Gill 1989; Reagan & Gill 1989). In contrast, an accessory phase consumed during static melting is irrelevant; its elements are simply repartitioned between refractory phases and larger degree melts (figure 2*b*).

Chemical disequilibrium during melting can produce melts with the trace element characteristics of the accessory phase itself when that phase dominates the melting mode. The concentrations of trace elements in the melt remain constant despite variations in the degree of melting as long as the melting mode is constant (Bédard 1989). If the accessory phase is old enough for all phases to be isotopically

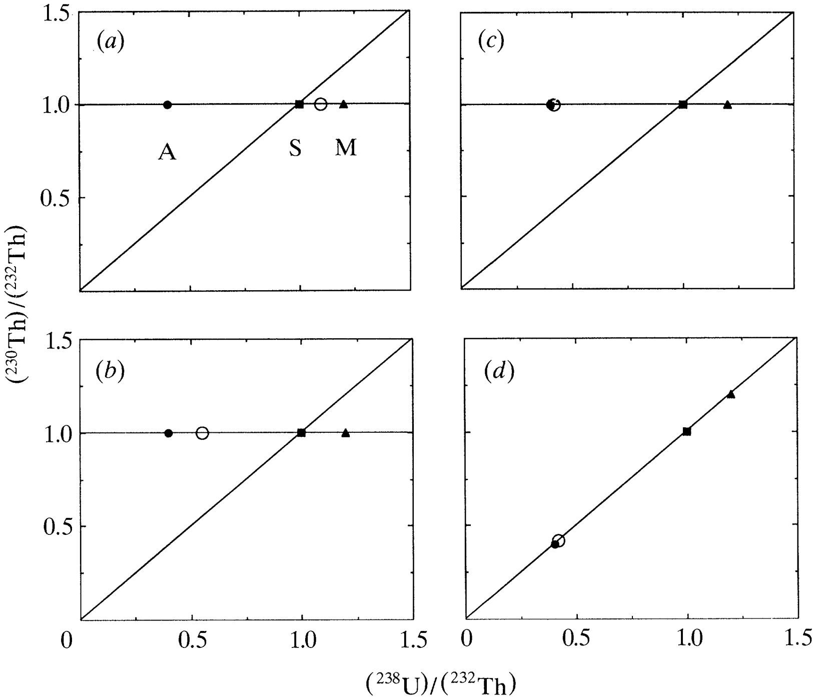

Figure 2. Schematic $^{238}\mathrm{U}$–$^{230}\mathrm{Th}$ isochron diagrams illustrating the effects of various melting models. In each, the solid circle 'A' represents a subsolidus accessory phase with a high Th/U ratio and $D_{\mathrm{Th}} \gg D_{\mathrm{U}}$ (e.g. phlogopite), the solid triangle 'M' represents the matrix (the rest of the source) having bulk $D_{\mathrm{Th}} < D_{\mathrm{U}}$, the solid square 'S' represents the bulk source in radioactive equilibrium at the onset of melting, the open circle represents the liquid formed during partial melting, and both t_0 and t_i are small so that $(\mathrm{Th})_i = (\mathrm{Th})_s$. (*a*) There is chemical and isotopic equilibrium during melting (the simplest case). The accessory phase is refractory and its partition coefficients are sufficiently large to cause the liquid to be slightly $^{238}\mathrm{U}$-enriched. (*b*) As in (*a*) except that the accessory phase is consumed during melting so that the $^{238}\mathrm{U}/^{232}\mathrm{Th}$ ratio is only a function of the percent melting and the bulk partition coefficients of the matrix. (*c*) There is Th isotopic equilibrium but not chemical equilibrium during melting. The $^{238}\mathrm{U}/^{232}\mathrm{Th}$ ratio of the melt approaches that of the accessory phase because it dominates the melting mode. (*d*) As in (*c*) except that there is isotopic as well as chemical disequilibrium during melting. If the accessory phase reaches secular equilibrium before Th isotopes are homogenized by diffusion, then chemical disequilibrium during melting results in radioactive equilibrium such that the isotopic composition of Th is that of the accessory phase instead of the bulk source.

homogeneous despite differences in parent/daughter ratio, then the melt inherits the radioactive disequilibrium of the accessory phase (figure 2*c*).

If there is isotopic as well as chemical disequilibrium during melting, almost anything is possible. Melts will become enriched in the faster diffusing nuclide if diffusion coefficients differ substantially. Ironically, the melt can even wind up in radioactive equilibrium if the time between metasomatism and melting is long with respect to the half-lives involved but too short for all phases to be homogenized isotopically via diffusion (figure 2*d*). Therefore, chemical disequilibrium during melting can lead to radioactive disequilibrium (figure 2*c*), but isotopic disequilibrium during melting can lead to radioactive equilibrium (figure 2*d*)!

All three kinds of disequilibrium may be especially common during the initial melting of a thermal boundary layer in which accessory metasomatic minerals were precipitated during the freezing of earlier fluids and melted during later thermal perturbations. Two examples are the base of the subcontinental lithosphere and the base of the mantle wedge immediately above subducting oceanic crust. These two cases can differ in both the metasomatic fluids involved (hence the kind of radioactive disequilibrium produced in accessory phases when isotopic equilibrium is achieved), and in the time between metasomatism and melting (hence the extent to which isotopic equilibrium is achieved). An example of each is discussed below.

Metasomatism in the subcontinental lithosphere can predate magma genesis by many millions of years and produce minerals with extreme Th/U ratios that entirely melt near the solidus. One example is the role of phlogopite in lamproite genesis. A recent study of Th–U disequilibria in the 56 ka Gaussberg lamproites suggests that these magmas formed too quickly for chemical equilibrium to be achieved. This conclusion rests on the high precision for $(\mathrm{Th})_\mathrm{m}$ and [Th/U] ratios achieved using mass spectrometry (Williams *et al.* 1992). Th and Sr isotopes correlate negatively within the lavas, indicating an isotopically heterogeneous source. However, Th, U, and HFSE concentrations and ratios remain constant in the lavas. The association of greater ^{230}Th excess with higher Sr contents is attributed to smaller degrees of melting. If the isotopic heterogeneity of the lavas reflects variable proportions of old metasomatic phlogopite in the source, then there is a direct correlation between the earlier amount of metasomatism and the later degree of melting. These features could be produced by consumption of all phlogopite during very small degrees of partial melting under chemical equilibrium (figure 2*b*). However, the large amounts of excess ^{230}Th and the high Th concentrations are more easily explained if chemical equilibrium was incomplete. In neither case was there chemical equilibrium with residual phlogopite, so that small degree melts of the subcontinental lithosphere acquired the trace element, isotopic, and radioactive disequilibria characteristics of the accessory phase (phlogopite) which dominated the melting mode.

In contrast, metasomatism of the mantle wedge immediately above subducting lithosphere may precede partial melting beneath the volcanic arc by only a few hundred millenia at most. This is the time necessary for convection of the mantle from the maximum pressure stability of amphibole in the slab (i.e. the depth at which maximum wedge metasomatism occurs) to the maximum pressure stability of amphibole in peridotite (i.e. the depth at or above which melting initiates) (see Tatsumi 1989; Davies & Stevenson 1992; Gill *et al.* 1993). This is sufficient time to achieve radioactive equilibrium between ^{230}Th and ^{238}U, but not homogeneous Th isotope ratios between newly formed amphibole (or other accessory metasomatic minerals) and pre-existing phases. As in the Gaussberg example, lack of chemical equilibrium can produce melts with the [Th/U] and $(^{230}\mathrm{Th})/(^{232}\mathrm{Th})$ ratios of the accessory phase. However, both the accessory phase and the melt will be in radioactive equilibrium in the subduction zone example (figure 2*d*). The difference reflects the time between metasomatism and melting, and may explain the more widespread ^{230}Th–^{238}U equilibrium in arcs compared to other tectonic environments (M. Condomines, personal communication).

4. Fluids and mantle metasomatism

Discovery of extreme Ra and U enrichment in carbonatite called attention to the fractionation of radionuclides by non-silicate fluids (Williams *et al.* 1986; Pyle *et al.* 1991). Carbonate- and halogen-rich C–O–H fluids are present in the mantle, able to flow through it because of their low dihedral angles, and likely to leave both patent and cryptic metasomatism in their wake (Watson *et al*. 1990; Wallace & Green 1988).

The strong dependence of the water-solubility of U on oxidation state at low pressure is well known (Langmuir 1978). Recent experiments have also shown the importance of both Cl and CO_3^{2-} contents in aqueous fluids for the complexing and solubility at high pressure of trace elements including U and Ba (Keppler & Wyllie 1991; Brennan & Watson 1991). Consequently, the igneous geochemistry of Ra, Pa, U, and Th is likely to be sensitive to and informative about the present and past distribution of such fluids.

One obvious application is to the magnitude of the ^{226}Ra–^{230}Th and ^{231}Pa–^{235}U disequilibria observed in some MORB and arc lavas. Eighteen percent excess ^{230}Th in MORB, although surprising, is at least compatible with currently accepted values of 0.5–2% for ϕ during mantle melting if $(D_{\mathrm{U}} - D_{\mathrm{Th}})$ is as large as 0.005 (Williams & Gill 1989). Qualitatively, excess Ra with respect to Th is consistent with peridotite-basalt *D*s if Ra^{2+} behaves like Ba^{2+}. Quantitatively, however, melting models that assume partitioning of elements between silicate solids and liquid cannot account for the extent of radioactive disequilibria observed. For example, if $l = 3.0$, then $\phi = \frac{1}{2}D_{\mathrm{Th}}$ (McKenzie 1987); the required ϕ is absurdly low because D_{Th} is nearly zero.

It was noted earlier that these large disequilibria may prove to be related to alteration or assimilation. However, if they are created during partial melting, the most promising explanations infer the entrainment of Ra and Pa from larger source regions than Th and U (i.e. open systems) (Cortini 1984; Condomines *et al*. 1988; Gill & Williams 1990), their preferential concentration during permeable flow (Navon & Stolper 1987), or chemical disequilibrium during melting. The first requires either the addition of Ra ± Pa-bearing fluids to the source, causing flux-induced melting at the vapour-present solidus, or the extraction of subsolidus vapour adjacent to a partly molten region. In either case, a free vapour phase is necessary. The second postulates that permeable flow of melt through the mantle is analogous to solution flow through a chromatographic column. Chromatography assumes chemical equilibrium and maximizes small differences in *D*. Chemical disequilibrium relies on differences in diffusion coefficients and the effects of accessory phases as discussed above. The lability of short-lived nuclides in radiation damaged sites, and recoil effects from surfaces to melts would also contribute to the effects of chemical disequilibrium.

In general, Ra enrichment is greater in island arc lavas and perhaps mid-ocean ridge basalts than in tholeiitic or alkalic intraplate basalts, where it is usually less than 30% and often zero. This does not seem to reflect longer t_{i} because low Ra enrichments characterize mafic magmas from volcanoes with high levels of historical activity (e.g. Kilauea, Reunion, Nyamuragira, Mt Cameroon). If related to melting processes, the distribution of Ra enrichment implies that the open system or permeable flow conditions characteristic of active plate margins (both divergent and convergent) are absent within plates. This, in turn, suggests either that subsolidus fluid is absent at sites of intraplate melting or that fluid flow regimes differ in the absence of suction at 'corners' such that more of the flow path is characterized by chemical disequilibrium (Spiegelman & McKenzie 1987; Ribe 1987).

The most dramatic example of fluid-caused disequilibria in igneous rocks also may be the least applicable: the extreme Ra and U enrichments in the Na-carbonatites of Oldoinyo Lengaii which has erupted twice in the past 35 years (Williams *et al*. 1986; Pyle *et al*. 1991). Both times it contained excess ^{228}Ra as well as ^{226}Ra in a proportion that correlates with repose time and suggests formation of new carbonatite shortly after each eruption ceases. The most likely genetic mechanism is exsolution from a silicate magma at low pressure. Although this is unlikely to be common during the genesis of common magmas, it is analogous to the vapour exsolution which may be widespread during mantle metasomatism (Wallace & Green 1988).

A second volcano at which carbonate-rich fluid has been important during magma genesis is Nyiragongo, Zaire (Vanlerberghe *et al.* 1987; Williams & Gill 1992; C. Deniel & A. Demant, personal communication). In general, ^{238}U-enriched lavas erupted first, contain groundmass calcite, and have high $(\mathrm{Th})_i$ and the lowest $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios of the Virunga field. Younger (including historical) lavas are ^{230}Th-enriched or in equilibrium and closer to the Sr–Th mantle array. The variations are consistent with a decreasing CO_2 flux through the volcano and with decreasing influence of a carbonate-metasomatized source with time.

Hydrous rather than carbonate fluids are implicated by disequilibria in Gaussberg lamproites (see above). $(\mathrm{Th})_i$ for the Gaussberg lavas also lie above the Sr–Th mantle array, but the divergence at Gaussberg is toward higher rather than lower $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios, in contrast to the results for Nyiragongo. The negative correlation between Th and Sr isotope ratios is attributed to variable amounts of phlogopite in the source. The phlogopite accounts for the increase in [Th/U] ratio during metasomatism such that the modern [Th/U] ratio of the source indicated by Th isotopes (κ_{Th}) exceeds the time-integrated [Th/U] ratio of the source indicated by Pb isotopes (κ_{Pb}) (Williams *et al.* 1992). This pattern is the opposite of that observed in oceanic basalts, indicates that the subcontinental lithosphere includes Th-enriched reservoirs complementary to the depleted mantle, and is consistent with the [Th/U] of the Earth being about 4.2 (Williams & Gill 1992)

I am indebted to R. Williams, M. Condomines, and M. Reagan for discussion, none of whom agrees with all that is said here, and to the Royal Society for making a manuscript prerequisite for accepting their invitation to this meeting.

References

Bédard, J. H. 1989 Disequilibrium mantle melting. *Earth planet. Sci. Lett.* **91**, 359–366.

Brennan, J. M. & Watson, E. B. 1991 Partitioning of trace elements between olivine and aqueous fluids at high *P–T* conditions; implications for the effect of fluid composition on trace element transport. *Earth planet. Sci. Lett.* **107**, 672–688.

Capaldi, G., Cortini, M. & Pece, R. 1983 U and Th decay-series disequilibria in historical lavas from the Eolian islands, Tyrrhenian Sea. *Isotope Geosci.* **1**, 39–55.

Condomines, M., Bouchez, R., Ma, J. L., Tanguy, J. C., Amosse, J. & Piboule, M. 1987 Short-lived radioactive disequilibria and magma dynamics in Etna volcano. *Nature, Lond.* **325**, 607–609.

Condomines, M., Hemond, C. H. & Allègre, C. J. 1988 U–Th–Ra radioactive disequilibria and magmatic processes. *Earth planet. Sci. Lett.* **90**, 243–262.

Condomines, M., Morand, P. & Allègre, C. J. 1981 ^{230}Th–^{238}U radioactive disequilibria in tholeiites from the FAMOUS zone: Th and Sr isotopic geochemistry. *Earth planet Sci. Lett.* **55**, 247–256.

Cortini, M. 1984 Uranium in mantle processes. In *Uranium geochemistry, mineralogy, geology, exploration and resources* (ed. B. DeVivo, F. Ippolito, G. Capaldi & P. R. Simpson), pp. 4–11. London: Institute of Minerals and Metals.

Davies, J. H. & Stevenson, D. J. 1992 Physical model of source region of subduction zone volcanics. *J. geophys. Res.* **97**, 2037–2070.

Gast, P. W. 1968 Trace element fractionation and the origin of tholeiitic and alkaline magma types. *Geochim. cosmochim. Acta* **32**, 1057–1086.

Gill, J. & Condomines, M. 1992 Short-lived radioactivity and magma genesis. *Science, Wash.* **257**, 1368–1376.

Gill, J., Morris, J. & Johnson, R. 1993 Timescale for producing the geochemical signature of island arc magmas: U–Th–Po and B–Be systematics in recent Papua New Guinea lavas. *Geochim. cosmochim. Acta.* (Submitted.)

Gill, J., Pyle, D. & Williams, R. 1992 Igneous rocks. In *Uranium series disequilibrium: applications to environmental problems*, 2nd edn, ch. 7, 207–258 (ed. M. Ivanovich & R. Harmon). Oxford: Clarendon Press.

Gill, J. & Williams, R. 1990 Th isotope and U-series studies of subduction-related volcanic rocks. *Geochim. cosmochim. Acta* **54**, 1427–1442.

Green, D. H. & Ringwood, A. E. 1967 The genesis of basaltic magmas. *Contrib. Miner. Petrol.* **15**, 103–190.

Goldstein, S. J., Murrell, M. T. & Janecky, D. R. 1990 Th and U isotopic systematics of basalts from the Juan de Fuca and Gorda ridges by mass spectrometry. *Earth planet. Sci. Lett.* **96**, 134–146.

Goldstein, S. J., Murrell, M. T., Janecky, D. R., Delaney, J. R. & Clague, D. A. 1991 Geochronology and petrogenesis of MORB from the Juan de Fuca and Gorda ridges by ^{238}U–^{230}Th disequilibrium. *Earth planet. Sci. Lett.* **109**, 255–272.

Hofmann, A. W. & Hart, S. R. 1978 An assessment of local and regional isotopic equilibrium in the mantle. *Earth planet. Sci. Lett.* **38**, 44–62.

Keppler, H. & Wyllie, P. J. 1991 Partitioning of Cu, Sn, Mo, W, U, and Th between melt and aqueous fluid in the systems haplogranite–H_2O–HCl and haplogranite-H_2O–HF. *Contrib. Mineral Petrol.* **109**, 139–150.

Klein, E. M. & Langmuir, C. H. 1987 Global correlations of ocean ridge basalt chemistry with axial depth and crustal thickness. *J. geophys. Res.* **92**, 8089–8115.

Langmuir, D. 1978 U solution-mineral equilibrium at low temperatures with applications to sedimentary ore deposits. *Geochim. cosmochim. Acta* **42**, 547–569.

McKenzie, D. 1985 ^{230}Th–^{238}U disequilibrium and the melting process beneath ridge axes, *Earth planet. Sci. Lett.* **72**, 149–157.

McKenzie, D. 1987 The compaction of igneous and sedimentary rocks. *J. geol. Soc. Lond.* **144**, 299–307.

McKenzie, D. & O'Nions, R. K. 1991 Partial melt distributions from inversion of rare earth element concentrations. *J. Petrology* **32**, 1021–1091.

Minster, J. F. & Allègre, C. J. 1978 Systematic use of trace elements in igneous processes. III. Inverse problem of batch partial melting in volcanic suites. *Contrib. Miner. Petrol.* **69**, 37–52.

Navon, O. & Stolper, E. 1987 Geochemical consequences of melt percolation: the upper mantle as a chromatographic column. *J. Geology* **95**, 285–307.

Newman, S., Finkel, R. C. & Macdougall, J. D. 1983 ^{230}Th–^{238}U disequilibrium systematics in basalts from 21 N on the East Pacific Rise. *Earth planet Sci. Lett.* **65**, 17–23.

O'Nions, R. K. & Pankhurst, R. J. 1974 Petrogenetic significance of isotope and trace element variations in volcanic rocks from the Mid-Atlantic. *J. Petrology* **15**, 603–634.

Pyle, D., Dawson, J. B. & Ivanovich, M. 1991 Short-lived decay series disequilibria in the natrocarbonatite lavas of Ol Doinyo Lengai, Tanzania: constraints on the timing of magma genesis. *Earth planet. Sci. Lett.* **105**, 378–386.

Reagan, M. K. & Gill, J. 1989 Coexisting calcalkaline and high-Nb basalts from Turrialba volcano, Costa Rica: implications for residual titanates in arc magma sources. *J. geophys. Res.* **94**, 4619–4633.

Reinitz, I. & Turekian, K. 1989 ^{230}Th/^{238}U and ^{226}Ra/^{230}Th fractionation in young basaltic glasses from the East Pacific Rise. *Earth planet. Sci. Lett.* **94**, 199–207.

Ribe, N. M. 1987 Theory of melt segregation – a review. *J. Volc. geothermal Res.* **33**, 241–253.

Rubin, K. H. & Macdougall, J. D. 1988 ^{226}Ra excesses in mid-ocean ridge basalts and mantle melting. *Nature, Lond.* **335**, 158–161.

Rubin, K. H. & Macdougall, J. D. 1990 Dating of neovolcanic MORB using (^{226}Ra/^{230}Th) disequilibrium. *Earth planet. Sci. Lett.* **101**, 313–322.

Rubin, K. H., Wheller, G. E., Tanzer, M. O., Macdougall, J. D., Varne, R. & Finkel, R. 1989 ^{238}U decay series systematics of young lavas from Batur volcano, Sunda arc. *J. Volc. geothermal Res.* **38**, 215–226.

Sigmarsson, O., Cohen, A. S. & O'Nions, R. K. 1991 U–Th–Ra systematics in hydrothermal systems at spreading ridges. *Eos, Wash.* **72**, 574.

Spiegelman, M. & Kenyon, P. 1992 The requirements for chemical disequilibrium during magma migration. *Earth planet. Sci. Lett.* **109**, 611–620.

Spiegelman, M. & McKenzie, D. P. 1987 Simple 2D models for melt extraction at mid-ocean ridges and island arcs. *Earth planet. Sci. Lett.* **83**, 137–152.

Tatsumi, Y. 1989 Migration of fluid phases and genesis of basalt magmas in subduction zones. *J. geophys. Res.* **94**, 4697–4707.

Vanlerberghe, L., Hertogen, J. & Macdougall, J. 1987 Geochemical evolution and Th–U isotope systematics of alkaline lavas from Nyiragongo volcano. *Terra Cognita* **7**, 367.

Watson, B., Brennan, J. M. & Baker, D. R. 1990 Distribution of fluids in the continental mantle. In *Continental mantle* (ed. M. A. Menzies), pp. 111–126. Oxford: Clarendon Press.

Wallace, M. E. & Green, D. H. 1988 An experimental determination of primary carbonatite magma composition. *Nature, Lond.* **355**, 343–346.

Williams, R. W., Collerson, K., Gill, J. B. & Deniel, C. 1992 High Th/U ratios in subcontinental lithospheric mantle: mass spectrometric measurement of Th isotopes in Gaussberg lamproites. *Earth planet. Sci. Lett.* **111**, 257–268.

Williams, R. W. & Gill, J. B. 1989 Effects of partial melting on the Uranium decay series, *Geochim. cosmochim. Acta* **53**, 1607–1619.

Williams, R. W. & Gill, J. B. 1992 Th isotopes and U-series disequilibria in some alkali basalts. *Geophys. Res. Lett.* **19**, 139–142.

Williams, R. W., Gill, J. B. & Bruland, K. W. 1986 Ra–Th disequilibria systematics: timescale of carbonatite magma formation at Oldoinyo Lengai volcano, Tanzania. *Geochim. cosmochim. Acta* **50**, 1249–1259.

Williams, R. W., Murrell, M. T. & Goldstein, S. J. 1991 Large ^{231}Pa enrichments in neovolcanic MORB measured by mass spectrometry. *Eos, Wash.* **72**, 295.

Williams, R. W. & Perrin, R. E. 1989 Measurement of ^{231}Pa–^{235}U disequilibrium in young volcanic rocks by mass spectrometry. *Eos, Wash.* **70**, 1398.