DATING OF YOUNG MORB

Report of a J01-USSAC Sponsored workshop

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SUMMARY

In order to obtain a detailed, quantitative understanding of the origin of ocean crust and lithosphere at mid-ocean ridges, it is necessary to be able to date young mid-ocean ridge basalt (MORB) accurately and with precision. The JOI-USSAC sponsored workshop "Dating of young MORB" examined ways of achieving this capability. The participants, mostly geochronologists and geochemists, discussed available and possible new dating techniques which offer promise for dating young MORB.

The capability of indirect dating of young MORB by dating the oldest sediment or hydrothermal material overlying igneous basement already exists. A variety of oceanic sediments 10^2-10^6 yrs in age are suitable for precise dating by ^{14}C using accelerator mass spectrometry (AMS), ^{10}Be, thermoluminescence (TL), oxygen isotope chronology and a variety of other techniques. In addition, many kinds of hydrothermal products can be dated with U-Th disequilibria techniques. Under most circumstances, it should be possible to obtain concordant ages by several techniques. It is thus possible at the present time to approach several simple but important questions such as whether spreading on the time scale of 10^2-10^5 years is steady, episodic or periodic. The workshop participants strongly endorsed continued work on indirect dating techniques. Some techniques require further testing, inter calibration and development but

offer wide and almost immediate application.

Indirect techniques, however all have the inherent disadvantage that they do not provide direct igneous crystallization ages. Obviously, there are many natural processes capable of adding complications to the interpretation of indirect dates. Thus, the participants unanimously agreed that direct dating techniques should be developed. The difficulty of dating young MORB is a long-standing problem. During the workshop, we re-evaluated the potential of existing techniques, most of which have had only limited success. Existing methods, such as glass hydration (palagonitization) rates offer some future promise, but a great deal of further work is required. In contrast, a number of techniques offer promise on a much shorter time scale (1-3 yrs). The techniques which seem most promising with only limited additional development and testing include: K-Ar and $^{40}Ar/^{39}Ar$ dating using laser fusion of small (10-100 mg) samples of plagioclase, U-series disequilibrium dating with a mass spectrometric (MS) technique for determining $^{230}Th/^{232}Th$ in MORB glasses, and possible TL dating of MORB plagioclase separates. Several other new techniques which may be applicable to dating young MORB were also discussed. Some of these still require much additional testing or require using MORB samples of unusual chemistry. Even so, because of the urgent and critical need for accurate ages of young MORB, further work of these techniques is also warranted. The recommendation of this workshop is that most effort and resources should be devoted to

the development and testing of the Ar-laser-fusion, $^{230}Th/^{232}Th$ MS and TL techniques.

INTRODUCTION

The accurate dating of young igneous and sedimentary materials is a problem of long standing and remains a challenge to geochronology. Solutions to many fundamental questions in earth sciences, ocean sciences and related fields depend upon accurate and precise ages of crystallization and deposition of rocks. Obviously, quantitative estimates of the rates of natural processes cannot be made unless one can measure time. There exist many examples of greatly accelerated progress in particular disciplines due to the availability of new geochronologic techniques. At the same time, the lack of appropriate geochronolgic data can seriously impede progress on important scientific questions.

In submarine geology and geophysics, the recent availability of high-precision mapping and sampling techniques has made it possible to study the ocean floor in unprecedented detail. This has naturally led to the development of ideas and hypotheses to explain these new data. For example the availability of new, high-resolution data on the morphology of active submarine plate boundaries has led to great recent progress in understanding the dynamics of mid-ocean ridges and the origin of oceanic crust. However, testing these ideas requires accurate dating of the

ocean crust in the time range $1-10^6$ years. Of particular interest is the need to date young (10^3-10^6 yrs) MORB directly, a capability that is presently lacking.

Because of the urgent need for reliable ages of young ocean crust, the JOI-USSAC committee, a part of the U.S. effort within the Ocean Drilling Program (ODP), sponsored a workshop on dating of young MORB. The purpose of this report is to briefly summarize the discussion and opinions of the participants expressed during the 2-day workshop. The participants discussed the relative advantages and disadvantages of a wide variety of dating techniques as they might be applied to dating sea-floor materials. The entire spectrum of existing techniques, possible improvements to existing techniques and new, untested techniques were evaluated. Discussion focused on the applicability of existing methods and evaluating the prospects of success and the steps needed to develop and test new ones.

INDIRECT METHODS OF DATING MORB

Clearly, dating of any event that is younger than the age of the igneous part of the crust provides important constraints on the crustal formation age. In particular, dating of events that are temporally and spatially closely associated with crustal formation, such as ridge-crust hydrothermal activity, offers promise for indirect dating of the igneous basement. Dating the oldest sediment overlying basement using fossils and direct

dating of secondary minerals in basalt (Staudigal and Hart, 1985; Hart and Staudigel, 1986) have been used successfully to estimate the age of old (>10Ma) oceanic crust within several Ma or less.

These indirect techniques have several disadvantages, however, especially for high resolution (10-10^{4}yrs) dating of ocean crust less than 5-10 Ma in age. Sediment dating with fossils typically lacks resolution better than ˜3x10^{5}yrs. Furthermore, it requires reasonably high sedimentation rates and good preservation. Bioturbation, sediment reworking and other factors may complicate the interpretations of paleontological ages. In many cases, there is a hiatus of unknown duration between the crystallization age of a flow and the start of deposition of its overlying sedimentary cover. The duration of this hiatus may vary locally in response to a variety of factors such as sediment sources, topography, local oceanographic conditions and others. In most areas, however, this hiatus is probably shorter (less than 10^4 yrs) than the age resolution provided by fossils. If it could be demonstrated that the absolute duration of these lacunae is acceptably short and the problem of their variability could be surmounted (perhaps by multiple cores in a small area), then for many purposes, high precision dating of sediment could be very useful. Later, we discuss several existing techniques for doing this.

Dating of sea floor hydrothermal deposits and secondary alteration products in basalt also offers some promise for indirect dating of MORB. For example, sulfide minerals and other

constituents of submarine high temperature vents can be dated by using disequilibria among the naturally occurring isotopes in the ^{238}U and ^{232}Th decay chains. As a dating tool for MORB, such methods can yield only a lower age limit, as emplacement of hydrothermal deposits will post-date the eruption of lava upon the seafloor. Buried sulfides, such as might be recovered by drilling on young crust could also be dated.

Lalou and Brichet (1982) used several isotopes to constrain the ages of fossil and active chimneys on the EPR at 21 degrees N. These authors showed that for fossil deposits, ages can be determined by measuring the $^{230}Th/^{238}U$ activity ratio of the sample. In this method, the extent of ingrowth of ^{230}Th (half-life=75,200 yr) into its parent 238^U is measured. It must be assumed that no ^{230}Th is initially present (which is probably true if no ^{232}Th is detected). Lalou and Brichet determined that the age of fossil deposits found 700 m off axis was 4000 years. They estimated the basement age to be ~20,000 yr from the mean half-spreading rate of 3 cm yr-1. However, if such deposits cannot develop far from the active axis, the spreading rate would have to be much higher.

The concentration of uranium in sulfide deposits is not generally high (typically 1-2 ppm) but measurements of this element can easily be made on 1-5 g of material using alpha spectrometry. The limit of possible ages determined by this method is controlled by the ^{230}Th content: For samples of age <~4000 years not enough ^{230}Th will have grown in to be detected.

The upper age limit is ~300,000 years which represents several half lives of ^{230}Th. It is doubtful however that hydrothermal deposits will survive for that length of time on the seafloor.

For samples collected in the central part of the rift valley, Lalou and Brichet measured different short-lived decay products of the uranium and thorium series. They suggested that if initial values (at time of deposition) of these isotopes can be determined, then ages of the deposits can be calculated. Two isotopic pairs are useful in this regard: ^{210}Pb/Pb and ^{228}Ra/^{226}Ra.

Pb-210 (half life=22.3 y) normalized to stable lead can be used to date deposits as old as ~100 years. Lalou et al. (1985) and Kadko et al. (1985/ 1986) determined initial 210Pb/Pb ratios on deposits from the EPR at 13 degrees N and the Endeavour Ridge, respectively. They found similar initial ratios of ~0.60 dpm/ug. Kadko et al. (1985/1986) further showed that these ratios were close to that of the basalts of the area, and Kadko and Moore (1988) later found that these ratios in fact, matched precisely the ^{210}Pb/Pb ratios of the hot vent fluid. It appears therefore, that the initial ratios of these deposits are well understood, so that the ^{210}Pb/Pb method is a viable dating tool for ridge crest hydrothermal deposits. Typically, there is >100 dpm/g of ^{210}Pb in these deposits which can be detected by non-destructive gamma spectroscopy or by alpha counting its short lived daughter, Po-210.

^{228}Ra (half=5.77 yrs), normalized to ^{226}Ra (which is relatively stable in young deposits) can be used to date deposits as old as ~25 years. To date such deposits, a radium rich phase, such as barite, is required. Recently, hydrothermal barites from the axial Seamount on the Juan de Fuca Ridge were found to contain ^{228}Ra and ^{226}Ra activities greater than 1000 dpm/g (Grasty et al. submitted). These activities are easily measured by non-destructive gamma spectroscopy or by alpha counting their short-lived daughters, ^{228}Th and ^{222}Rn. Kadko and Moore (1988) determined that the ^{228}Ra/^{226}Ra ratio of hot vent fluid from the Endeavour Ridge is close to that of basalts from the area. This suggests that the initial ratio of barites forming from these solutions should likewise have the same ratio, by analogy to the ^{210}Pb/Pb system. Therefore, the ^{228}Ra/^{226}Ra ratio technique should be useful in dating young hydrothermal deposits.

In summary, there exist today techniques which utilize naturally occurring radioisotopes that allow young hydrothermal deposits (<100 years), and fossil deposits (>4000 years) to be dated. Analytical methods are already well developed and the systematics of these isotopes in these deposits are fairly well understood.

Dating of young MORB indirectly with ages of sulfide deposits offers promise. Obviously, though its application is limited by the occurrence of sulfide deposits, which cover much less than 1% of active mid-ocean ridges. Dating of secondary minerals in altered MORB is also a useful indirect dating

method, especially if the secondary minerals are from high temperature alteration processes near the ridge. If so, then their formation age is close to the cooling age of the basalt (Hart and Standigel, 1986). However, continued low temperature alteration of the ocean crust is thought to occur for long periods (10^7-10^8 years) after formation, (Mottl, 1983; Honnorez, 1980). For young altered ocean crust, reliable quartz ages (by TL or ESR dating), calcite ages (by ESR and ^{238}U-^{230}Th disequilibria) and possibly ages of clay minerals (by TL) could be very useful provided their site (or age) of deposition could be well-constrained by independent evidence.

Though the rate of deposition varies locally, deposition of amorphous Fe-Mn oxyhydroxides on MORB probably begins immediately after eruption on the sea-floor (Ballard and Van Andel, 1979; Hekinian and Hoffert, 1975). It may be possible to date such crusts on MORB by the ^{230}Th-^{234}U disequilibrium method. Studies of Mn-nodules have shown that these oxy-hydroxides precipitate from seawater with excess ^{230}TH with respect to ^{234}U. Previous work concentrated on determining nodule growth rates by peeling off layers and measuring the amount of unsupported ^{230}Th with depth in the nodule. By measuring these nuclides in the entire thickness of crust precipitated on a given area, it may be possible to date the total time of accumulation. Integrating the flux of the nuclides to the crust over time eliminates the task of accurately identifying the peeled off layers, which may be impossible, and extends the timespan of utility of the

disequilibrium method. The assumptions of this techniques are:

(1) constant and known radionuclide concentration in seawater;

(2) constant partition coefficients for U and Th between crust and seawater;

(3) constant rate of crust precipitation;

(4) and closed system behavior after precipitation.

It is unlikely that all of these assumptions will remain valid over the total timespan of crust precipitation. However, data exist which seem to indicate that in some cases, at least, this dating technique will work. For example, Newman et al. (1983) published analyses of Th and U isotopes for Mn-crust from a basalt within the Brunhes-Matuyama reversal area of the EPR at 21 degrees N, which they estimated to be at least 670 ka. Using average values for the Th and U concentration and isotopic composition of seawater and calculating partition coefficients from the concentrations of these elements measured in the Mn-crust, this dating technique gives an age of 700 (-50/+75) ka.

Precise dating of sediments overlying young basalt basement offers a good possibility for indirect dating of MORB. One advantage is that several techniques are available, thus affording the chance of obtaining concordant ages. Another advantage is that many of these techniques are presently available and could be tested on suitable sediment. One disadvantage, in addition to the ones mentioned earlier, is that suitable material either from coring or drilling of young (<5Ma) ocean crest to basement is difficult to obtain. It would be

desirable to have at least 5 or 6 cores from a single locality to determine the range of "basement ages" obtained. Precise dating of sediment is possible with several techniques. [14]C dating using accelerator mass spectrometry can be done for 10 mg samples of $CaCO_3$ with a precision of 1% or less. [14]C ages of sediments could be obtained for samples up to $4-5 \times 10^4$ years old. [10]Be ages of sediments could be obtained for ages possibly as old as 15×10^6 years. Sample sizes are much less than 1 gram but the precision of the technique is presently hampered not only by low [10]Be abundances (and instrument sensitivity) but also by uncertainties in the cosmogenic production of [10]Be in the past (Southon et al, 1987; Raisbeck et al, 1985).

The thermoluminescence (TL) dating methods have the unusual distinction of permitting the absolute dating of two kinds of events or processes: 1) the last cooling, useful for igneous plagioclase, and 2) the last exposure to sunlight (e.g. Aitken, 1985; Berger, 1986), useful for sediment dating. Of particular importance is the applicable age range -- from a few hundred up to perhaps several hundred thousand years. These characteristics of TL dating provide a unique capability for the direct and indirect dating of MORB.

Dating of a sediment's last exposure to sunlight is possible using the partial bleach thermoluminence (TL) techniques (Aitken, 1985; Huntley, 1985; Berger et al, 1984; Berger et al, 1986; Wintle and Huntley, 1982). This technique is the only one of the three common TL methods for sediment dating that permits reliable

correction for the presence of the relict TL signal in waterlain sediments (ambient light does not reduce the TL signal to zero at deposition for any sediment, but the relict TL is especially variable for subaqueous material). Ages concordant with ^{14}C have been obtained to the upper age limit of ^{14}C and this technique may be useful for sediments as old as 1Ma. Additional techniques for precise dating of sediments <~1Ma old include U-series disequilibrium (Ku, 1965; Huntley et al, 1986), trend dating (Pierce, 1986) and, of course, the ^{18}O record (Imbrie et al, 1984). While additional work and testing is needed for several of the above techniques, the possibility of obtaining precise (~10^4 years), concordant, indirect, crust-formation ages from sediment should be carefully evaluated.

In addition to the indirect methods discussed above, there are other indirect techniques that could be applied to ferromongnese crusts, marine sediment and various hydrothermal mineral phases (Faure, 1986). While at the workshop, we focused mainly on those techniques with the widest applicability and greatest reliability in the age range 10^3-10^6 years, these other techniques may prove useful. For example, techniques for dating lava surfaces in the age range of several months to 10-20 years, of great interest for volcanologic studies, may arise from on-going studies of biological colonization of new lava surfaces (C. Van Dover and L. Mullineaux, personal comm.). Since at the moment there exist no proven reliable direct method of dating

MORB in the age range 1-10^6 years, all promising techniques, even indirect ones, should be evaluated.

DIRECT DATING OF MORB

Previous attempts to directly date young MORB include fission tracks (Fleischer et al, 1986; Fisher, 1969; Macdougall, 1976), palagonite thickness (Hekinian and Hoffert 1975; Moore et al, 1985), K-Ar and $^{40}Ar/^{39}Ar$ (e.g. Honda et al, 1986), U-series disequilibrium (Newman et al, 1983), and He-isotope disequilibrium (Graham et al, 1987). Most isotopic techniques are extremely difficult because of the low contents of radioactive parents and the small decay constants. Additional problems have included inherited daughter products (e.g. excess ^{40}Ar) and failure of the closed system assumption by addition and loss of parent and/or daughter isotope. Even in cases where reliable ages have apparently been obtained (e.g. Newman et al, 1983; Honda et al, 1986; Graham, et al, 1987; R. Duncan, unpublished data), it is difficult to assess their quality because of the lack of concordant ages by another technique. At the moment, new radiometric ages can be compared only with ages derived from the assumptions of constant spreading rate (from magnetic anomalies) from the axis of a mid-ocean ridge.

In recent years, however, several new techniques have been developed which offer great future promise for direct dating of young MORB. Further, it is possible that using several of these

techniques, concordant ages could be obtained. These techniques were mainly developed for young (<1Ma) continental volcanic rocks with high contents of K, Rb, U and Th relative to MORB. Mostly, they remain untested on young MORB, but calculations indicate they should be able to provide reliable ages in the range 10^3-10^6 years. The workshop participants all felt that testing these techniques on samples of MORB is a vital step. Appropriate samples for such a test from submersible studies of MORB, Hawaii, Iceland and other young tholeiitic volcanoes are readily available. Additional materials from the same localities as MORB samples (sediment cores, Fe-Mn crusts, sulfide deposits) needed for development of indirect techniques are also available in many cases or could be specifically collected for future dating studies. Below, we discuss possible approaches to direct dating of young MORB based on fission tracks, glass hydration rates, TL, K-Ar and U-Th series disequilibrium studies. Of these, the last three appear to be the most promising.

Fission track dating: The fission track method makes use of the fact that uranium-238 (which is present at about the 50ppb level in MORB glasses) undergoes spontaneous fission with a half-life of about 10^{17} years. In the fission process two massive and heavily charged particles are shot away from each other with ~200 Mev, depositing this energy along a channel approximately 10 to 20 microns in length. This leaves behind a "tunnel" composed of atoms with disordered electron structure; it is thus chemically reactive and, upon etching with a suitable reagent, will dissolve

preferentially to the surface of the sample, leaving a microscopically visible track.

The density of these spontaneous fission tracks is proportional to both the age and the uranium content of the rock. Tracks induced by a subsequent neutron irradiation are proportional only to the uranium content and the neutron flux (which is separately monitored); therefore the age of the sample can be calculated from the ratio of induced tracks to spontaneous tracks. The method has the advantage that only small amounts of sample are needed, however typically MORB glass uranium levels of 50ppb lead to lower age limits of greater than several million years. This is because spontaneous fission track densities of only a few tracks per square centimeter will be formed in a one million year old glass. It is difficult to scan one square centimeter, so statistical considerations due to low track counts will lead to an excessive error in ages less than a few million years.

This is complicated by two further problems:

Basaltic glasses are notoriously amenable to track fading over geological times. Such fading (due to thermal annealing of the disordered radiation-damaged tunnel) is generally estimated by measuring the size of the spontaneous tracks as compared to those induced by neutron irradiation (which have not faded). But the comparison must be done on a large number of tracks, and so is impossible when only a few spontaneous tracks are found.

Another problem is even more serious. When spontaneous densities of only a few per square centimeter are found, each track may be confused with bubbles and other non-track artifacts. With a high density of tracks this is not a problem, but with only a few tracks to count, experience shows that total confidence in what is and is not a track wanes quickly (with something like the inverse square of the track density).

Certain accessory minearls show uranium enrichments and better track stability, but it is difficult to find the pertinent accessory minerals in sufficient size in MORB (the tracks are ~10 microns in length, so crystals of at least 50-100 micron dimensions are needed). Minerals that retain tracks for geological time spans and are enriched in uranium are zircon, apatite, and sphene; these are not prevalent in MORB.

The fission track technique is going to be of very limited usefulness. Occasionally samples with high uranium concentrations and stable annealing characteristics such as sphene, zircon, or apatite may be found, but these are certainly not ubiquitous in MORB. Glass dating will be valid only for samples with unusual chemistry (high U concentrations) and/or high ages (greater than ten million years). Glass dating will not be possible for young MORB of normal chemistry.

Glass hydration: Glass hydration and its potential for dating of young MORB are discussed in detail in Appendix 1. In nature, the thickness of palagonite layers is determined by the interaction of several independent processes including:

absorption/desorption, ion exchange, hydration, hydrolysis, solution, precipitation and mechanical processes. Most of these processes are temperature dependent. The rate of growth of palagonite layers on natural sea floor basalts may eventually be useful as a dating technique, however much work is needed before it could be routinely employed. Emperical studies, (Hekinian and Hoffert, 1975; Moore et al, 1985) especially in case where independent age calibration is available, should be combined with laboratory and theoretical studies of the simple processes that act together to form palagonite rims on MORB glass. Appendix one discusses this combined approach in detail.

Thermoluminescence (TL) Dating: Thermoluminescence (TL) is the emission of light by certain crystals (including common rock-forming minerals such as quartz and plagioclase) when they are heated. The heating can be represented by a plot of light intensity versus temperature or "glow-curve", shown as curve (a) in Figure 1. When the mineral is reheated, only the background "black-body" curve remains (also shown in Figure 1). The difference between the two curves is the TL energy stored in the mineral during its exposure to radiation over the time since it was last heated. This radiation comes from cosmic rays and minute quantities of the radioactive atoms U, Th and ^{40}K which are present to varying degrees in the host rock. Since these radioactive atoms have half-lives greater than 10^9 years, their concentrations are effectively constant for millions of years. The constant radioactive dose rate to which the TL mineral is
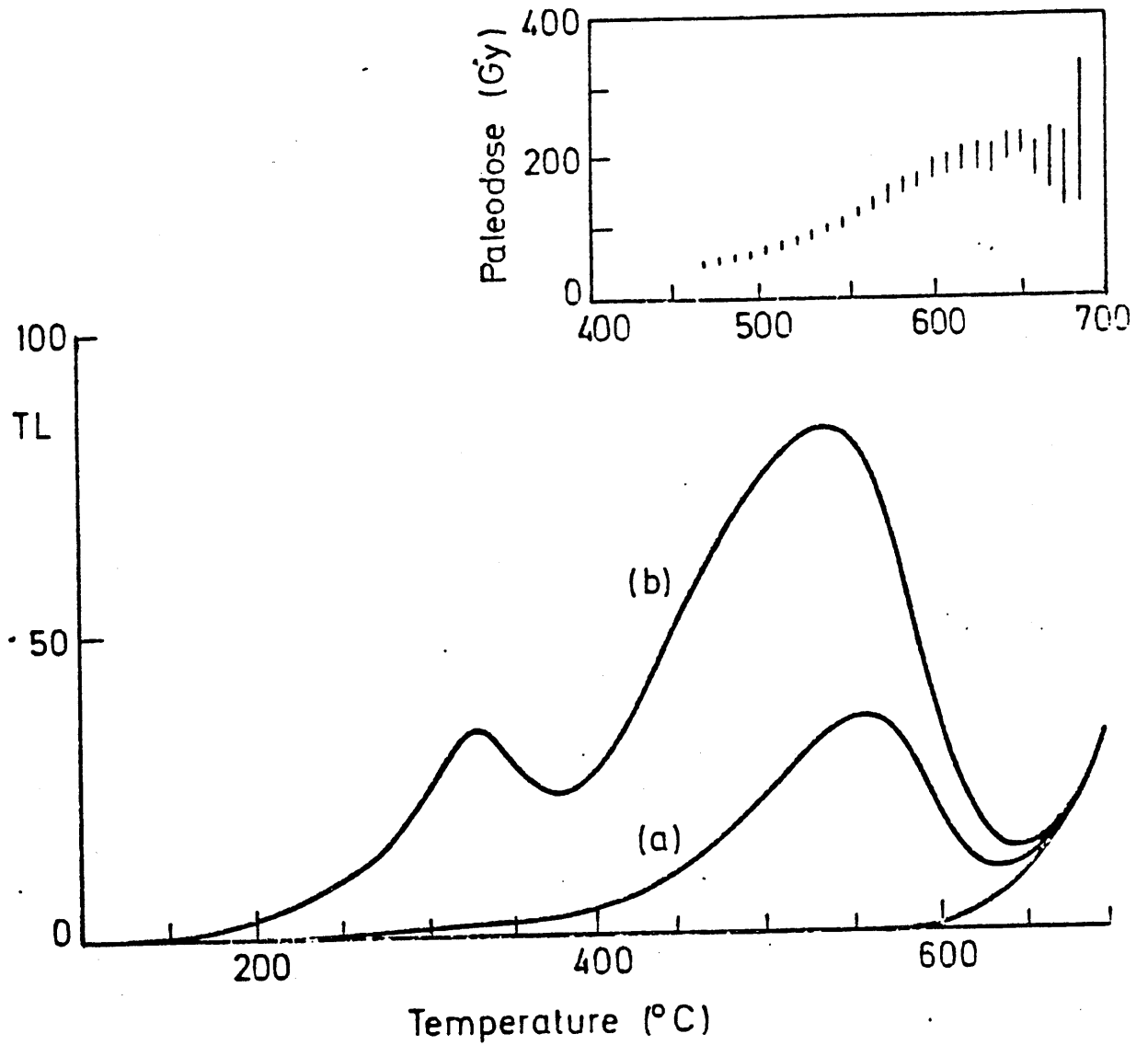
Figure 1: NTL (a) and ATL (b) curves for a sample of Labradorite along
with the paleodose from the ratio of NTL to ATL (in inset)
which gives an indication of a plateau. After Guérin and
Valladas (1980) and Aitken (1985).

subjected can then be calculated from the U, Th and ^{40}K concentrations. By measuring the sensitivity of a mineral to acquiring TL (by exposing it to calibrated radioactive sources), it is then possible to calculate its equivalent paleodose of radiation, as well as the effective dose rate and hence its age using the equation

$$age\ =\ equivalent\ paleodose/effective\ dose\ rate$$

TL dating was first applied to dating of rocks and pottery by Daniels et al (1953). Although these initial attempts at dating were not very successful, TL dating has now matured into a reliable and widely used technique, especially for authenticity verification on ceramics and pottery (Fleming and Stoneham, 1973; Fleming, 1979). It has also been used for dating excursions of the geomagnetic field (Gillot et al, 1979). One reason for its popularity in the verification of potentially valuable artifacts is that it yields data over a wide range of temperatures, each temperature being in principle capable of yielding a TL date. This has led to the so-called "plateau test", where the ratio of natural TL (NTL) to artificially-induced TL (ATL) is plotted as a function of temperature (Figure 1). A stable plateau, such as that appearing in Figure 1, gives a good indication as to whether the NTL and ATL were acquired in a similar fashion.

In spite of its success in dating pottery and ceramics, TL dating has not until recently been very successful in dating

volcanic rocks, usually yielding ages that were too low. Wintle (1973) showed that most volcanic plagioclases did not show a stable plateau in the usual temperature range of study (350-450 degrees C), a phenomenon referred to as "anomalous fading". However, Guerin and Valladas (1980) have shown that by using higher temperatures (530-730 degrees C) in conjunction with a glass UV-pass optical filter and preglow heat treatment, the glow peaks of volcanic plagioclases were unaffected by anomalous fading. Furthermore, they obtained dates from samples ranging in age from 8,980±1,150 to 215,800±20,500 years that agreed very well with conventional ^{14}C, baked clay TL and K-Ar ages. Various researchers (Mejdahl and Winther-Nielsen 1982; Wintle et al, 1984; Wintle and Westgate, 1986) have also used a brief preglow heating to ensure that an NTL/ATL plateau is observed. Huxtable et al. (1972), Templer (1985), and Berger (1987) used a preheat step to remove a fading component in minerals rather than storing samples for long periods of time.

MORB-associated heating events that are potentially datable by TL methods are, in probable order of increasing difficulty: 1) the baking of sediment in contact with extruded lava (e.g. sheet flows), 2) the formation of feldspar crystals within lava (e.g. pillows), and 3) the formation of glass around quenched lava (e.g. on pillows). Sediment baked in contact with subaerial lava flows has been successfully dated by Huxtable et al. (1978), while Berger and Huntley (unpublished data) have studied a sample of baked sediment from the FAMOUS area of the Mid-Atlantic Ridge.

Guerin and Valladas (1980) dated the feldspars within several subaerial flows and, although their techniques have not yet been successfully applied to MORB, there is substantial promise in this direct approach. Gillot and Cornette (1986) presented concordant K-Ar ages with the Cassignol K-Ar technique (Gillot et al, 1982), TL and ^{14}C ages for subaerial high K-lavas (Figure 2). K-Ar and TL ages were concordant for rocks up to 200,000 years at high precision. The siliceous glass in airfall tephra has been successfully dated by Berger (1985, 1986, 1987), but preliminary tests made by G. Berger after the workshop (see Appendix 2) indicate that MORB glass has TL properties that are unfavorable for dating. In contrast, the TL characteristics of plagioclase are in many cases favorable, as discussed earlier.

Electron spin resonance (ESR) dating is similar to TL dating but differs in some important respects. Appendix 3 outlines the principles of ESR dating which presently are most applicable to indirect dating of MORB. This technique is relatively new and may show promise in certain applications of MORB dating.

U-Th-He disequilibrium dating: Figure 3 (from Faure, 1986) shows the decay of ^{238}U, ^{235}U and ^{232}Th to ^{206}Pb, ^{207}Pb and ^{208}Pb respectively. Table 1 (Faure, 1986) gives the half lives of several intermediate decay products of uranium that have proved useful as geochronometers. At equilibrium, the activities of all the intermediate daughter products are equal. However because the intermediate daughter products comprise many elements, whose geochemical behavior differs, the intermediate daughter products
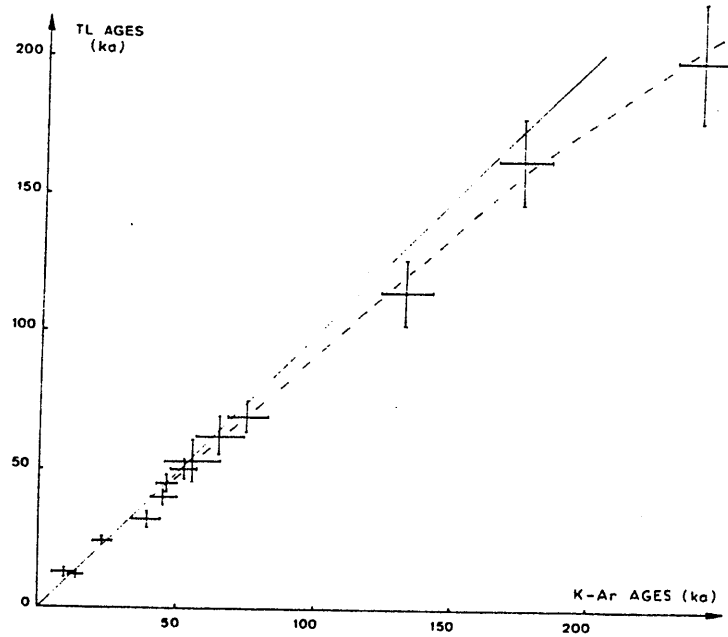
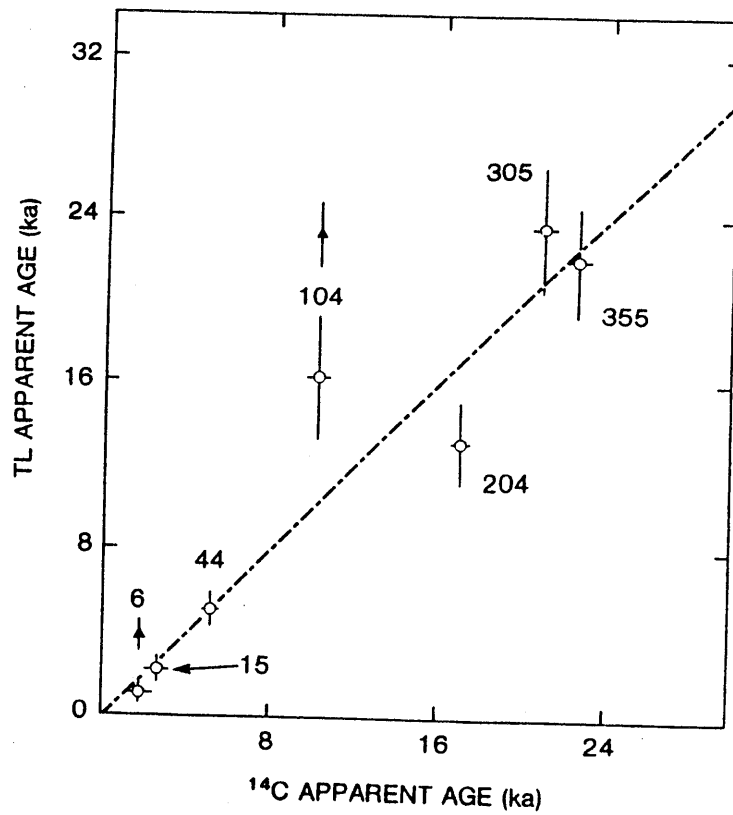Figure 2 - Concordant TL and K-Ar ages (a) from Gillot and Cornett (1986), (b) concordant TL and ^{14}C ages from Berger et al (1986).
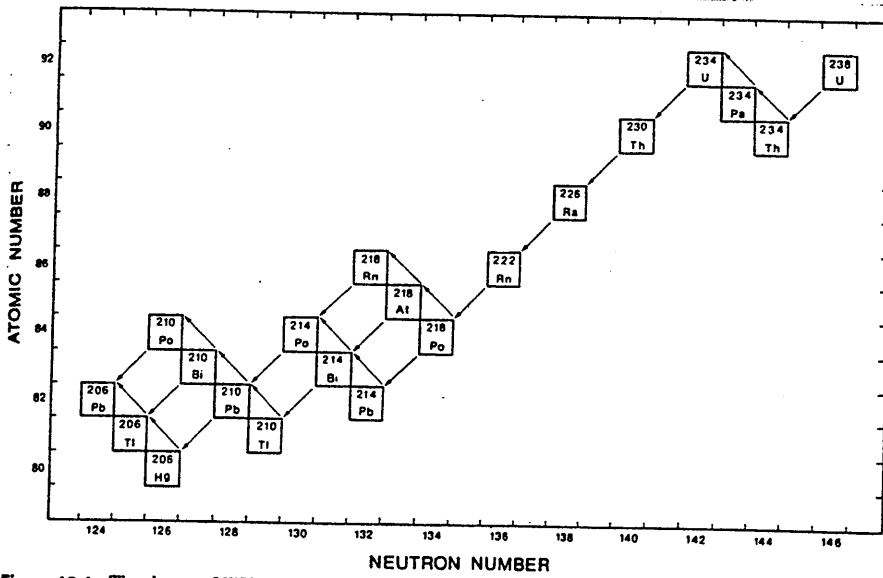
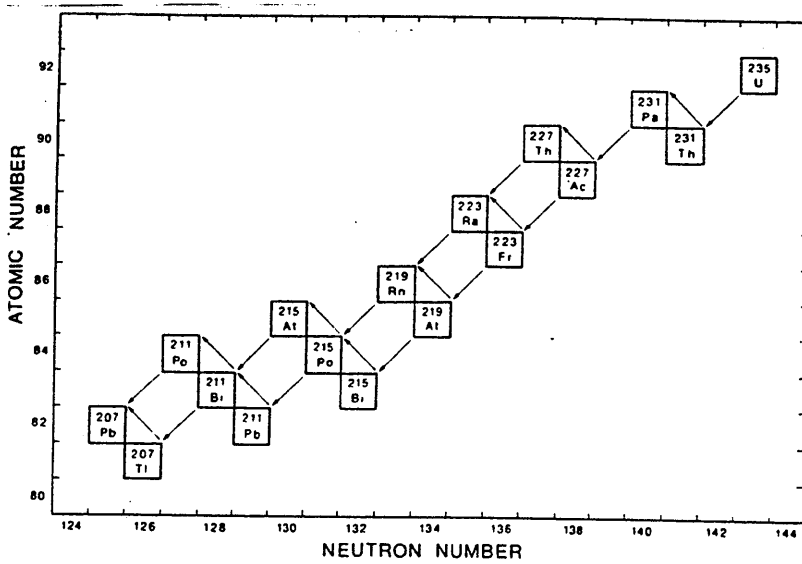**Figure 18.1** The decay of ^{238}U to stable ^{206}Pb.

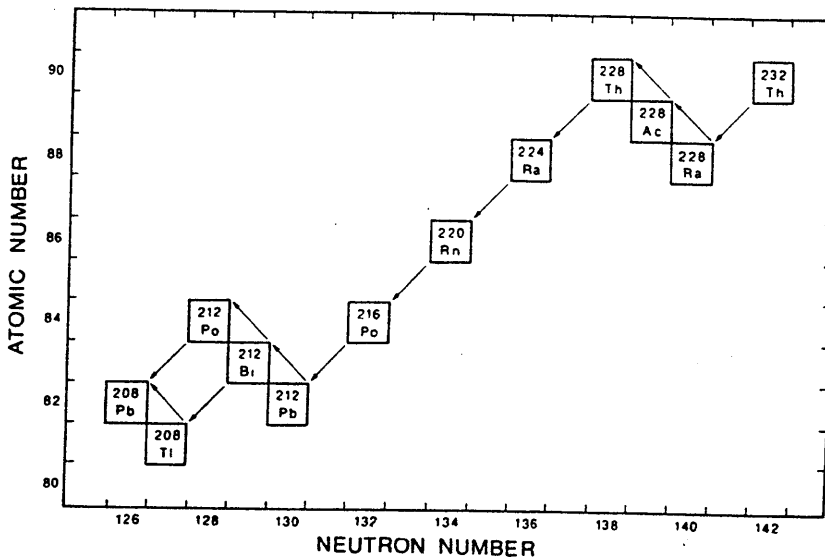**Figure 18.2** The decay of ^{235}U to stable ^{207}Pb.

Figure 18.3 The decay of ^{232}Th

Figure 3 - Taken from Faure (1986).

Table 21.1 Naturally-occurring radioactive
isotopes of radium (Lederer et al., 1967)

Parent	Ra isotope	Half-life
^{238}U	^{226}Ra	1602 y
^{235}U	^{223}Ra	11.435 d
^{232}Th	^{228}Ra	6.7 y
^{232}Th	^{224}Ra	3.64 d

Table 21.2 Half-lives and decay constants of the
daughters of uranium used in geochronometry

Nuclide	Half-life, Years	Decay Constant, y^{-1}
$^{234}_{92}$U	2.48×10^5	2.794×10^{-6}
$^{230}_{90}$Th	7.52×10^4	9.217×10^{-6}
$^{226}_{88}$Ra	1.622×10^3	4.272×10^{-4}
$^{210}_{82}$Pb	22.26	3.11×10^{-2}
$^{231}_{91}$Pa	3.248×10^4	2.134×10^{-5}

Table 1 - useful half-lives, taken from Faure (1986).

can be seperated from each other and their parent by processes such as weathering, melting and crystallization. Dating such fractionation events is possible either by measuring the decay of a separated daughter product or by determining the time needed to reestablish isotopic equilibrium after it has been disturbed by a fractionation event. In both cases the initial parent-daughter ratio must be known.

^{230}Th, also called ionium, has been used for dating magmatic events preserved in young volcanic rocks (Condomines et al, 1982). The immediate parent of ionium is ^{234}U. In theory, disequilibrium between ^{238}U and ^{230}Th produced during magma formation and/or crystallization could be used to date young (<350 ky) oceanic basalt in two ways: 1) using whole rock data, compare measured $^{230}Th/^{232}Th$ values to an inferred initial value and interpret differences as due to the decay or ingrowth of ^{230}Th with time (Newman et al, 1983;) or 2) use mineral separates to construct an isochron (e.g. Allegre and Condomines, 1976). Newman et al (1983) directly dated two off-axis MORB samples at 21 degrees N by assuming that the initial value of $^{230}Th/^{232}Th$ was the same as those from the nearby EPR axis. They obtained ages of 25,000 years and 75,000 years for the two samples, which compare favorably with ages calculated from spreading rates (37,000±30,000 and 83,000±30,000). These results indicate that even without mass spectrometric techniques, reasonable results can be obtained with alpha counting techniques. Alpha counting, however, is difficult and time consuming due mainly to the large

sample-size (5-10g basalt). The small degree of Th-U fractionation initially present in MORB is difficult to resolve with low precision data (2-5%, 1 sigma for alpha counting) and it is difficult to collect enough glass free from sea-water alteration for whole rock measurements or to separate large quantities of individual mineral phases for isochrons.

Great reductions in sample-size and improved precision over alpha spectrometry are possible using mass spectrometry. This has been demonstrated recently be Edwards et al. (1987) using ^{234}U-^{230}Th systematics to date corals. Unfortunately, the techniques of Edwards et al. cannot be immediately applied to the dating of basalt since the isotopic ratios are much less favorable than for corals ($^{230}Th/^{232}Th > 10$-3 in corals vs. 10^5 to 10^6 in MORB). To make high precision Th and U measurements in volcanic rocks requires a mass spectrometer with high resolution and abundance sensitivity, and a technique for producing high Th (and U) ionization efficiency (e.g. ionization efficiencies > 0.1% for nanogram Th samples will be required for $\pm 1\%$ precision). Such mass spectrometers exist (e.g. Los Alamos, Battelle Northwest) but high efficiency ionization techniques may be harder to come-by. However, there are a number of groups currently working on applications of mass spectrometry to the U-decay series and it is reasonable to expect the technical difficulties to be worked out in the near-future. As sample-size drops into the 10-100 mg basalt range and precision improves to

the 1% level, it will become possible to properly evaluate $^{238}U/^{230}Th$ disequilibrium techniques for dating MORB.

Future plans at Los Alamos (M. Murrell) are to continue to look for more efficient ways of ionizing Th. But there are measurements they can make now with their current capabilities. They plan to make U and Th isotopic measurements in samples of young, unaltered basalt (Juan de Fuca Ridge glass) in order to better define the magnitude of Th-U fractionation in unaltered, oceanic basalt and to show what precision to expect from the current ionization techniques.

Mass spectrometric determinations of $^{230}Th/^{232}Th$ and $^{238}U/^{232}Th$ for dating by either the whole rock or isochron technique offer great promise for dating MORB in the range $3x10^5$ years of less. Other intermediate daughters in ^{238}U and ^{232}Th decay chain also may be useful. Appendix 4 discusses the use of ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{228}Th and ^{210}Po for dating volcanic rocks such as MORB in the range 0.05-8000 years.

Direct dating of sea floor basalts (though not depleted MORB) has also been done using $^3He/^4He$ disequilibrium (Graham et al, 1987). Graham et al dated about 12 samples of alkali basalt and enriched MORB or transitional basalt recovered by submerisible studies and dredging of seamount 6 located on 3Ma old crust near the EPR. They obtained ages ranging from 3000 years to about one million years in qualitative agreement with field observations and one $^{40}Ar/^{39}Ar$ date from seamount 6 (Honda et al, 1987). Disequilibrium between the $^3He/^4He$ found in

vesicles (measured by crushing extraction) versus the $^3He/^4He$ in glass (from fusion) is needed in order to apply this technique. Unfortunately, this disequilibrium has not been detected in many samples of depleted MORB, thus the technique may be useful only in certain cases.

K-Ar and 40Ar/39Ar techniques: Historically the isotopic method of choice for directly determining crystallization ages of volcanic rocks is that of K-Ar geochronology (Dalrymple and Lanphere, 1969). This is because K is a common (if minor) element in all volcanic rocks, analytical methods are well described and many laboratories are intercalibrated worldwide, and in optimum circumstances measurements can be made to analytical uncertainties of 1% or less.

With regard to dating volcanic rocks in the age range 10^3 to 10^6 years, however, several difficulties arise, particularly for rocks from the ocean floor spreading centers. First, the radioactive isotope ^{40}K has a very long half-life (1.25×10^9 yr) which means that for the age range of interest only 0.06 to 0.0006% of the ^{40}K in the rock at the time of crystallization has decayed to ^{40}Ar. This, coupled with the second concern, that ocean floor basalts generally have very small amounts of K compared with ocean island and continental basalts, means that there are only exceedingly small amounts of radiogenic ^{40}Ar (10^{-13} moles) to measure. Rare gas mass spectrometers are now available which can measure these small quantities of gas but the remaining problem is to correct for the large amount of non-

radiogenic ^{40}Ar present as atmospheric contamination within the rock and within the argon extraction system.

Of additional concern for dating submarine rocks is the presence of a non-atmospheric component of argon derived with the melt from the mantle which may be partially trapped as the rock cools at high hydrostatic pressures. Dalrymple and Moore (1968) have shown that this component is present only in the glassy rims of pillows erupted at depths greater than about 1500 m. The more slowly crystallized centers of pillows apparently completely equilibrate their initial argon composition with atmosphere (seawater) at the time of cooling.

Recently, the K-Ar method has been used to determine reliable crystallization ages for high-K subaerially-erupted volcanic rocks down to 10^3 years (Gillot et al, 1979; Cassignol and Gillot, 1982; Levi et al, 1987). Improvements include higher sensitivity mass spectrometers and very precise monitoring of the major correction for atmospheric argon. In these cases several tenths of one percent radiogenic argon can be detected in the total ^{40}Ar. Samples used in these studies have generally higher K-contents than those found in MORB's and, coming from subaerial flows, do not produce the additional uncertainties of inherited mantle argon and K mobility. For direct dating of MORB's by K-Ar, however, it should be possible to determine reliable ages in the 10^5 to 10^6 year range with these improvements.

Another signficant contribution for extending the K-Ar dating range down to 10^3 years has been the intercalibration of

K-Ar, ^{14}C and thermoluminescence (TL) dating methods (Gillot et al, 1982). Hence, TL is now a much more attractive possibility for direct dating of MORB's because it has been compared favorably with K-Ar methods, at least for higher K basaltic samples.

The ^{40}Ar-^{39}Ar dating method is a variation of the K-Ar method in which the sample is first irradiated in a stream of epithermal neutrons (via nuclear reactor) which causes a proportion of ^{39}K to become ^{39}Ar by neutron capture. The "yield" or efficiency of this reaction is monitored by irradiating a standard material of known age with the unknown samples. Both the parent and daughter elements in the natural decay scheme can now be measured directly by mass spectrometry. This produces a number of advantages for dating MORB's. Incremental heating experiments can be performed to determine the argon compositions of K-rich (usually low-temperature release) and K-poor (usually high-temperature release) sites within the sample. This has been used to distinguish primary from alteration K-bearing sites. Isochron plots can be constructed from these various gas compositions to determine the initial composition of argon in the rock to check the assumption that no inherited mantle argon was trapped when the rock crystallized.

Methods now exist for the ^{40}Ar-^{39}Ar dating of very small ($\geq$ 1 microgram) samples with high precision using a high-power continuous laser, mini-extraction line (<200 cc), and an ultra-clean, ultra-sensitive rare gas mass spectrometer. This new

method results in very low atmospheric ^{40}Ar contamination because only single crystals of the sample are heated. The possible application of this technique is discussed in Appendix 5.

It would be relatively straighforward to construct a larger version of the laser heating system capable of fusing and analyzing samples of 10-100 milligrams. Such sample sizes might permit the dating of plagioclase crystals (and perhaps other phases) from MORB's (0.1% K) as young as 10^5 years. The success of such a system depends on whether or not the present systems (e.g. the U.S. Geological Survey, Menlo Park; Berkeley; Univ. Toronto; Princeton University) could be scaled up for larger sample sizes without also increasing the atmospheric blank. Based on the experience at the U.S. Geological Survey laboratory (Appendix 5) scaling up of the laser system should not result in higher atmospheric argon system blanks and the increase in sample size should provide adequate amounts of radiogenic ^{40}Ar for analysis.

Other techniques: In addition to the direct techniques discussed above, several others were discussed at the workshop. For example, the possibility of using temporal variation in magnetic declination and inclination, as done for Hawaiian lava flows <1500 yrs in age by Holcomb et al, (1986), was discussed. The problem in applying this technique to MORB is that the magnetic secular variation probably varies from place to place, so a reference curve must be calibrated for each new location using independent dates. After this has been done, the magnetic

properties of undated samples can be used to infer their age provided it is within the period that has been well calibrated.

J. Morris evaluated the possibility of using ^{7}Li (Alpha, p) ^{10}Be and ^{26}Al production for direct dating of MORB. Given the natural elemental and isotopic abundances of Li, Na, Al and Be, this possible technique was not considered feasible. With greatly improved precision of isotopic measurements, these techniques may be applicable, but this is unlikely in the next few years.

K. Turekian discussed a U-series disequilibrium method which under favorable conditions could be used to constrain the age of MORB. This technique, which employs ^{226}Ra and the K/U ratio could be used to tell whether rocks have ages of greater than or less than 8000 years. (See also appendix 4).

R. Hart discussed a variant of U-Th-He dating which, like ^{40}Ar/^{39}Ar employs a nuclear reactor to produce short-lived radioactive products. With this technique, one would produce ^{85}Kr or ^{133}Xe from U by fission reactions in the reactor and then construct an isochon plot of ^{4}He/^{3}He vs. ^{85}Kr/^{3}He or ^{133}Xe/^{3}He. This technique would employ incremental heating to produce different gas fractions and could be used to date rocks from 3000-10^5 years. Calculation indicate that this technique may be quite useful for MORB, but further work is needed for testing and calibration.

The possible use of alpha-tracks in minerals and glass was considered by G. Brass, but was discarded because it does not

appear to be feasible. Racemization of amino acids in fossils was considered as a possible indirect method, however uncertainties in the thermal history pose a potentially serious problem.

Ballard et al. (1982) used estimates of percent sediment covering basalt outcrops to estimate the relative ages of basalt pillows near the axis of the Galapagos spreading center. If calibrated with reliable absolute ages, such techniques would be useful, in that they are easy to use and relatively unexpensive.

WORKSHOP RECOMMENDATIONS

The workshop participants were unanimous on several issues:

-Developing dating techniques for young MORB is vital for future progress on many important scientific questions such as the origin of oceanic crust, dynamic processes at mid-ocean ridges and off-axis volcanism

-Direct dating techniques are preferable to indirect techniques

-Direct techniques for providing reliable ages of MORB in the age range 10^3-10^6 years are feasible and a very high priority should be given to trying and testing promising techniques.

Naturally, there was some disagreement on the best strategy and to some extent, on which techniques offer the most promise. Most of the participants agreed that K-Ar and ^{40}Ar/^{39}Ar, U-Th disequilibrium (especially ^{238}U-^{230}Th with mass spectrometry) and

TL were very promising. Some participants thought that resources should be channeled toward only one or another technique so that progress could be made more quickly. Other participants argued that given the uncertainties and work still needed to evaluate the success of a particular technique, a better strategy would be to work on all promising techniques simultaneously. A majority of the participants advocated accelerated efforts with the three promising techniques listed above, with continued efforts to evaluate other direct and indirect techniques. Some indirect techniques, for example U-series dating of Mn-crusts, seem very promising. Precise techniques for dating sediment in the age range of interest are presently available and could be very valuable not only for providing reliable ages of volcanic basement but also calibrations and testing of direct methods.

In order to make timely progress on the problem of dating young MORB, the participants agreed that:

-Appropriate sample sets should be made available or collected in order to evaluate measurements by various techniques

-Interlaboratory calibration is very important. Standard materials have been prepared in several laboratories (e.g. P. Gillot, CEA-CNRS, France) and should be analyzed by others.

-Concordant ages by different independent techniques are needed to assess the accuracy and precision of any technique.

-The funding agencies, both in the U.S. and abroad, should be encouraged to fund proposals to date young MORB. Such proposals will be in the high-risk category, but obviously if no

funding is available, much of the needed work will not be accomplished.

A majority of the participants thought that another meeting in a few years, to review progress on the question of dating young MORB, would be useful.

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APPENDIX 1

DATING OF MORB BY PALAGONITE LAYER THICKNESS MEASUREMENT

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CONTENTS:

I PRINCIPLES OF DATING TECHNIQUE

A. BACKGROUND

Palagonites are solid products of reaction of basalt glass surfaces with aqueous solutions. Palagonite layers of a range of thickness have been measured in MORB and other basaltic glasses, and there is ample evidence from field and experimental systems that the thickness of palagonite layers depends on the duration of exposure of basalt glass surfaces to aqueous solutions. For these measured thicknesses to be useful for absolute dating, the exact functional relation of the layer thickness growth to time has to be determined. In addition, the dependence of layer growth rates to glass composition and environmental variables other than time also needs to be fully understood. It should be emphasized at the onset that, at best, the "age" that can be derived from palagonite layer measurement can only represent the length of time the glass surface was able to react with aqueous solution; this "age," hereafter referred to as the exposure age, may or may not correspond to the eruption age of the volcanic glass.

The physical characteristics of palagonites have been summarized in an extensive review by HONNOREZ [1980]. Honnorez [1980] noted that the term palagonite has been historically applied to "a mixture, in variable proportions, of altered, hydrated, and oxidized glass . . . with authigenic minerals such as clays, zeolites, and chlorite." The variability of chemical and mineralogical composition of palagonites reflects differences in the conditions and extent of water-rock reaction. Despite the availability of detailed characterizations of

palagonites produced in various natural and experimental systems, some questions concerning their mechanism(s) of formation remain unresolved.

There are two independent but complementary approaches that could be used to define the kinetics of palagonite formation. One is to study naturally formed palagonite layers on basaltic glasses, as has been done by a number of previous investigators (below). This requires independent knowledge of the duration of exposure of the basalt glass surface to aqueous solution. A key problem with this empirical approach is the present inability to accurately determine the exposure ages of young basaltic glasses erupted in submarine environments. For example, Moore [1966] and Hekinian and Hoffert [1975] used exposure ages determined from the thicknesses of manganese coatings on basaltic glasses. Uncertainties associated with the calibration of Mn-accumulation rates therefore become incorporated to the palagonitization rate determination. Unfortunately, the absolute rate of manganese accumulation, e.g., as affected by location relative to submarine hydrothermal systems, and its variability in time are not fully understood at present [e.g., BRYAN and MOORE, 1977]. Better constraints on eruption ages from historic and pre-historic "records" (e.g., visual observation, 14C, paleomagnetic) may be available for subaerially erupted lavas that have been subsequently altered in subaerial or submarine environments. It is not clear, however, that hydration processes and rates in submarine MORB settings are comparable to weathering of lavas in subaerial environments [e.g., MORGENSTEIN and RILEY, 1975; ABRAJANO et al., 1985] or in shallow submarine environments [MOORE et al., 1985]. Indeed it is possible that different MORB environments may yield different intrinsic hydration rates.

The second approach to defining the long-term kinetics of palagonite layer formation in MORBs is a combination of experimentation and mechanistic modeling. Through this approach, intrinsic rates of individual processes leading to palagonite formation can be better measured with respect to carefully defined environmental conditions. The pitfall of this approach lies in our inability to (1) simulate and accelerate natural interactions in the laboratory and (2) reliably extrapolate from experimental to geological time sacles. Geochemists have been quite successful in experimentally duplicating certain natural conditions in the laboratory but simulating long-term interactions has been more difficult. Palagonitization is an overall process which, itself, is a complex combination of several more fundamental processes. These fundamental processes include adsorption/desorption, ion-exchange, diffusion, hydration, hydrolysis, solution, precipitation, and mechanical consolidation or erosion. Acceleration of part but not all of these fundamental processes in an experimental system can lead to results that are different from the overall natural process being simulated. The success of the experimental approach is therefore dependent on our understanding the manner by which individual processes occurring during palagonitization are coupled and how this coupling determines long-term palagonitization rates in the environments of interest.

B. FIELD STUDIES OF PALAGONITIZATION: SOME EXAMPLES

One of the earliest studies of palagonitization rates in natural systems was that of Moore (1966). Using dredged samples of basalts from Hawaii,

he estimated a range of parabolic rate constants, C (C = S(2)/t; S is thickness and t is time), for palagonite layer growth of 480 to 2000 um2/ky (1.5 to 10 deg-C). The corresponding linear rate constants (C = S/t) fall in the range 0.7 to 12 um/ky (excluding Kilauea samples) [cf. MOORE et al., 1985]. The exposure ages of the samples were determined from the thicknesses of Mn coatings assuming a constant Mn accumulation rate of 3 um/ky.

Palagonite growth rates on dredged MORB samples from the Mid-Atlantic Ridge have been studied by Hekinian and Hoffert [1975] and Bryan and Moore [1977]. Figure 1 summarizes the results of these studies and that of Moore (1966). A linear rate of palagonite layer growth may be inferred from Figure 1 if it is assumed that a similar linear growth rate applies to the Mn accumulation rate. Using Hekinian and Hoffert's data alone, the palagonitization rate may be estimated to range from 2.6 to 4.3 um/ky (0 to 5 deg-C), assuming a constant Mn accumulation rate of 3 um/ky. A considerable scatter of data points is evident in Figure 1. As Bryan and Moore [1977] pointed out, Mn accumulation rates are variable (up to 20 um/ky) near the ridge axis and palagonitization rates could be up to three times faster than Mn accumulation rates [cf. HEKINIAN and HOFFERT, 1975]. If an average Mn accumulation rate of 3 um/ky is applied to Bryan and Moore's FAMOUS data, a slightly higher palagonitization rate of 5 um/ky may be estimated.

Basaltic glasses erupted historically have also been used to determine palagonitization rates at different temperatures. Moore et al. [1985] summarized data collected from Hawaii and other locations (see their Table 3). At 23 to 25 deg-C, the rates range from 15 (Etna) to 100 um/ky (Mauna Loa). Rates of 4.7 to 9.4 um/ky were estimated for the 1877 Mauna Loa lavas hydrated at 4 to 6 deg-C whereas samples from Fuji hydrated in a freshwater lake at 5 to 15 deg-C showed a range of 6.4 to 8.2 um/ky. Jakobsson and Moore (1986) performed a similar study of palagonite layers formed on basaltic glasses from Surtsey, and they estimated rates of 11 to 28 um/ky for a submarine-erupted sample altered at temperatures from 7 to 10 deg-C. Other palagonitization rates estimated by Moore et al. and Jakobsson and Moore for various integrated temperatures are summarized in Figure 2. Finally, Morgenstein and Rosendahl [1976; also see MORGENSTEIN and RILEY, 1975] measured palagonite layer thicknesses on a variety of Hawaiian basaltic glasses of known eruption ages, and concluded that a linear rate of 11.77 um/ky at 25 deg-C best describes palagonite layer growth with time. This rate, however, is a subaerial hydration rate which is expected to be lower than subaqueous hydration rates estimated by others [e.g., MOORE et al., 1985] at the same temperature [ABRAJANO et al., 1985].

C. EXPERIMENTAL PALAGONITIZATION

In addition to field-based studies noted above, considerable effort has also gone into experimental simulation of the palagonitization process. Only those studies that specifically addressed the growth rates of palagonite layers are included in the following brief summary. In general, palagonitization rates are difficult to determine in the temperature range 0 to 25 deg-C because of extremely slow reaction rates

relative to experimental time scales. Many experimental palagonitization studies therefore have been performed at higher temperatures. This approach necessitates that the relation between palagonitization rate and temperature be established in order to make valid inferences about low-temperature palagonitization rates. Fortunately, some higher temperature natural palagonitization rates also have been measured (Figure 2) so that the temperature dependence of palagonitization rates in natural and experimental systems can be compared.

Furnes [1975] was among the first to experimentally determine palagonitization rates of basaltic glasses at various temperatures in seawater solution (Figure 3). The three glass compositions (alkali basalt, olivine tholeiite, and basaltic andesite remelted in an oxidizing atmosphere) examined by Furnes showed rather peculiar palagonitization behavior wherein the rate apparently decreased continuously in the first ten months then increased subsequently. No strong differences in palagonitization rates were noted for the three glass compositions. Crovisier et al. [1983] also measured the growth of alteration layers in a tholeiitic basalt glass at 50 deg-C and showed palagonitization rates that systematically decreased with time up to 20 months (Figure 4). The initial palagonitization rate for Crovisier's experiments is about 14,000 um/ky whereas the final rate is about 600 um/ky.

Crovisier et al. [1986] measured palagonitization rates for tholeiitic basalt glass at 3 and 60 deg-C and the results are summarized in Figure 3. The rates noted in Figure 3 are linear rates for single samples which, judging from Figure 4, are probably overestimated. Malow et al. [1984] and Moore et al. [1985] measured alteration layer thickness of 30 um and 3 to 6 um for Hawaiian basalt glass samples reacted with seawater at 200 deg-C for 30 days and 100 deg-C for one year, respectively. Recently, Berger et al. [1987] measured alteration layer thickness of about 5, 0.25, and <0.1 um (last two estimated from their Figure 5) for MORB glasses reacted with artificial acidic seawater (pH < 5) at, respectively, 320 deg-C for 17 hours, 300 deg-C for 30 minutes, and 150 deg-C for 60 minutes. Murakami et al. [1987] also measured palagonite layer thickness formed on a synthetic basalt reacted with NaCl, NaCl/MgCl, and deionized water solutions at 70 deg-C for 301 days and found, respectively, 0.2 to 1 um, 1 um, and 2 to 3 um layers. The corresponding rate constants, assuming linear growth kinetics for all single sample measurements, are plotted in Figure 3.

Synthetic basaltic glasses have also been reacted in steam environments at various temperatures. Figure 3 shows some palagonitization rates measured at Argonne National Laboratory based on published and unpublished work. A declining palagonitization rate with time similar to those observed during reaction with aqueous solutions [FURNES, 1975; CROVISIER et al., 1983] have also been observed during vapor hydration (Figure 5, [BYERS et al., 1984]). However, alteration layer growth rates during hydration of multicomponent silicate glasses including basalts have been shown to be higher in aqueous solution than in water vapor at similar temperatures [ABRAJANO et al., 1985].

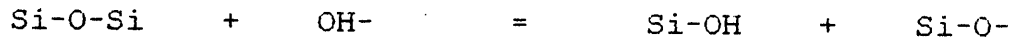## D. FUNDAMENTAL PROCESSES DURING PALAGONITIZATION:

The reaction of basalt glass surfaces with seawater results in chemical and structural modification of the glass surface. As noted above, the end-result of the overall interaction is the formation of hydrated glass and amorphous and crystalline products (i.e., palagonite) at the glass-solution interface region. However, since these final products need not have all resulted from a single fundamental reaction, the kinetic description of the overall palagonitization process must also reflect the multitude of fundamental processes that have occurred. This section identifies some of these fundamental reactions and examine how they potentially affect overall palagonitization rates.

A useful starting point for a mechanistic analysis of palagonitization is a brief description of the initial molecular structure of the unreacted glass. The classical random-network theory of Zachariasen as well as the "crystallite" and "discrete-ion" theories have been proposed as alternative models for the structure of silicate glasses [e.g., MACKENZIE, 1960]. In these and other theories recently advanced, [e.g., GOODMAN, 1982], it is generally accepted that the fundamental structural unit is the SiO_4 tetrahedron. In silica glass, this unit is linked to four other similar tetrahedra by sharing the apical oxygen atoms, the latter hence called bridging oxygen (BO). Addition of network modifying alkalis or alkaline earths leads to the formation of non-bridging oxygens (NBO) wherein, respectively, one or two NBO are formed per alkali or alkaline earth atom introduced. Addition of Al_2O_3 or Fe_2O_3 can lead to the formation of tetrahedra with net negative charges which are subsequently charge-compensated by network modifiers. A non-bridging oxygen site is therefore destroyed per atom of Al or Fe^{3+} added. Alkali and alkaline earth components in charge-compensating positions are less exchangeable than those in network-modifying sites. It is therefore to be expected that glass structure and reactivity depend on its composition; the exact nature of this dependence and its implication to the palagonitization rates of glasses with relatively minor compositional variations (e.g., MORBs) are not yet fully understood. On the average, MORBs have less than one (~0.9) NBO per tetrahedron.

Upon contact with seawater, adsorption of seawater components onto the basalt glass surface takes place. This is followed by the site exchange of mobile components from the glass surface (e.g., alkalis in surficial NBO sites) and the adsorbed component, and the desorption of the mobile glass component from the surface. In simple alkali silicate glasses, the exchange of alkalis with adsorbed proton or hydronium is followed by bulk interdiffusion of proton or hydronium with alkalis from deeper portions of the glass [e.g., DORFMUS, 1973]. The interdiffusion layer becomes chemically distinct from the bulk glass because of this exchange between hydrogen species and mobile glass components. However, because the composition varies gradually from the bulk glass-interdiffusion zone boundary to the interdiffusion zone-solution boundary, the interdiffusion zone may not be physically distinguishable from the bulk glass. There is strong evidence from experimental systems that this type of bulk exchange process also occurs during reaction of water with multicomponent glasses such as basalt [BYERS et al., 1984; ABRAJANO et al., 1985; ABRAJANO and BATES, 1987; BERGER et al., 1987]. This process

alone should lead to formation of an interdiffusion layer that grows parabolically with time. The growth of this layer is governed by the interdiffusion coefficient, D, whose value approaches that of the self diffusion coefficient of the slowest diffusing species as the difference between the self diffusion coefficients between interdiffusing species becomes large [DOREMUS, 1973].

Hydrolysis of bridging bonds is another process known to occur during glass/water interaction. This is usually characterized as a nucleophilic attack:

$$Si-O-Si \quad + \quad OH- \quad = \quad Si-OH \quad + \quad Si-O-$$

because the direct reaction of molecular water with BO is a highly activated process. The ultimate product of this process during the interaction of basalt glass surfaces with seawater is the detachment of monomeric or polymeric silicate units from the surface (i.e., etching). Where both interdiffusion and etching occur during reaction of a glass surface with aqueous solution, the etching front has been shown to lag behind the interdiffusion front. An interdiffusion layer that advances into the glass but which, itself, is continuously destroyed by etching is thus produced. Etching is known to follow zeroth order kinetics at the initial stages of dissolution (i.e., low solution concentration of dissolved glass components) [ABRAJANO and BATES, 1987; CROVISIER et al., 1987] so that coupling of parabolic interdiffusion and linear etching processes will determine the rate of growth of the interdiffusion layer. Mathematical descriptions of layer growth kinetics under these conditions have been formulated [e.g., BOKSAY et al., 1969; SULLIVAN, 1979; ABRAJANO and BATES, 1987] with the essential result that layer growth is parabolic at t << D/U2 (D is the interdiffusion coefficient and U is the constant etching velocity) and that a steady-state (i.e., constant layer thickness) is approached at t > D/U2. The latter simply means that the layer stops growing regardless of the length of exposure to aqueous solution.

The detachment of network formers and other unexchanged components (etching) is an eventual result of hydrolysis of the interconnected silica tetrahedra in the interdiffusion zone. However, partial hydrolysis of the anionic glass framework represents the initial step in this detachment process. The solution side of the interdiffusion layer is therefore expected to undergo structural transformation leading to the formation of a "gel" layer between the interdiffusion layer and aqueous solution. Studies of the physical integrity of this "gel" layer formed on multicomponent silicate glasses reacted with water for long periods of time tend to suggest that transport through this layer cannot be the rate controlling step in the influx of hydrogen species into the glass at long reaction times [CROVISIER et al., 1987; ABRAJANO and BATES, 1987; cf. BERGER et al., 1987]. The "gel" layer appears to maintain an open porosity which enable transport of silicic acid and larger dissolved species through it. Because of its inherent instability, the "gel" layer can eventually repolymerize to a more highly cross-linked amorphous product [e.g., BUNKER et al., 1983] or transform into a crystalline mineral product (e.g., smectite clay) [BERGER et al., 1987].

The solution release pattern of network formers (e.g., Si) during

experimental basalt dissolution and physical observations on reacted glass surfaces [BYERS et al., 1984; ABRAJANO et al., 1985; CROVISIER et al., 1985, 1987; BERGER et al., 1987], appears to suggest that linear etching the "gel" cannot occur indefinitely. Repolymerization and crystallization of this layer and precipitation of relatively insoluble components in it tend to alter or even stop etching at the "gel"-solution interface. Dissolution of the network may still occur within the "gel" if a porosity that will allow diffusion of silicic acid or larger silica polymers is present. Despite the apparent complexity of processes occurring, the compounded rate of growth of the altered layer (i.e., interdiffusion layer + gel layer) is still determined by the coupling of the advance of the interdiffusion front into the fresh glass and the retreat of the surface by etching. If the "gel" is transformed to a "stable" phase (e.g., saponite), the "gel"/solution interface (i.e., etching front) will stop retreating and the altered layer will grow at a rate controlled solely by the interdiffusion process (see below). The transformation of the "gel" layer to a more stable phase is not expected to affect the layer growth kinetics so long as this transformed layer does not retard transport across it. Note that the altered layer, as defined in this case, excludes mineral or amorphous products that grew beyond the "gel"-solution interface or were precipitated onto this interface from components already dissolved in solution [e.g., CROVISIER, 1987].

It was noted above that opening up of the "gel" layer by network hydrolysis and subsequent structural transformation of this layer may allow rapid transport of mobile glass species through the layer [e.g., BUNKER, 1983]. When this occurs, an interdiffusion zone, whose thickness is now determined by the rates of interdiffusion and network hydration, will continue to control the rate of penetration of the entire altered layer into the bulk glass. Where a steady-state is reached between interdiffusion and network hydrolysis, the rate of advance of the interdiffusion front into the fresh glass is expected to become linear with time; this constant rate is equal to the rate of advance of the "gel" layer into the interdiffusion zone and the interdiffusion zone at steady state will have a constant thickness. Transport of mobile glass species and hydrogen species across this "barrier" of constant thickness (i.e., interdiffusion zone) will become the rate-controlling step in the long-term palagonitization process.

Field and experimental observations on palagonite layers summarized earlier could be reconciled with the above description of the fundamental processes that occur during the reaction of basaltic glass surfaces and aqueous solutions. Zeroth and first order kinetics that are commonly inferred from measurements of palagonite layer thicknesses may be attributed to the dominance of particular interactions relative to others. For example, linear palagonitization kinetics could result from a combination of (1) stabilization of the palagonite layer surface from etching by transformation to a porous clay layer [e.g., BERGER et al., 1987] and (2) control of fresh glass hydration by interdiffusion across a transition zone of constant thickness. First order (e.g., parabolic) kinetics that are often observed in experimental systems could result from non-steady state growth of the interdiffusion layer.

Note that whereas mineral products can be formed within the palagonite layer, the entire layer is viewed in the above discussion as "residual"

products of non-stoichiometric dissolution of basalt. On the contrary, others have suggested that basalts dissolve stoichiometrically and that palagonites are composed entirely of precipitates that form from dissolved components in solution [CROVISIER et al., 1986, 1987]. In this case, palagonite layer growth is determined by the rate of precipitation from solution. Although this mechanism results in the same overall incongruent reaction (basalt glass + water = palagonite + dissolved products), the rate of formation of palagonite and the rate law governing this formation can be very different from those described above. The integrated mass of precipitates that form as a function of reaction progress (i.e., the palagonitization rate according to the "precipitation model") may not be simply related to the mass of material dissolved as implied by Crovisier et al. [1987; p. 2987]. Open seawater has the ability to retain some basalt components in solution [cf. CROVISIER et al., 1987; p. 2988], and as basaltic glass dissolves, the number of alteration phases that reach saturation increases with time. Hence if stoichiometric glass dissolution rate is zeroth order as suggested by Crovisier et al. [1986, 1987] and if the precipitate layer is not a significant transport barrier, the palagonite "precipitation" rate should, in general, increase with time until the final alteration phase assemblage has been stabilized. Whereas this effect is expected to be more noticeable in less open syatems (e.g., static leaching experiments), the palagonitization rate actually decreased, rather than increased, during Crovisier et al.'s (1983) experiments (Figure 4).

It is also notable, from comparison of Figures 2 and 3, that experimentally measured palagonitization rates tend to be higher than rates inferred from field measurements at similar temperatures. One explanation offered by Crovisier et al. [1987] is that the solution chemistry in experimental and natural systems (pH and dissolved components) is different such that natural palagonitization rates are expected to be slow. This explanation is unlikely because closed-system experimental systems are probably more affected by saturation or feed-back effects compared to open-system natural ocean environments. The experiments conducted near pH 8 are close to the minima in solubility and reaction rates of basaltic glasses [MAZER, 1987] so that pH differences between experimental and natural systems are also not likely to provide the answer. Whereas this is clearly a problem that needs to be addressed further, the time dependence of palagonitization rates shown in Figure 4 seems already to provide a clue. The palagonitization rate for Crovisier's experiments in Figure 4 is decreasing to a near steady-state value. As noted above, the final rate in this curve, which is statistically almost indistinguishable from zero, is still about 600 um/ky. It is therefore obvious that the 0 to 5 deg-C natural palagonitization rate of 4 um/ky (see above) is an experimentally slow, and probably indeterminable, rate. Experimental measurement of this rate would require being able to measure a 0.04 um increase in palagonite layer thickness after ten years of reaction ! It appears therefore that the long-term rates measured in natural systems may correspond to the slow to virtually steady-state rates in experiments, and it is the process controlling the rate at this close to steady-state stage that must be examined experimentally or predicted theoretically. Extreme care is required in the use of experimental results in understanding natural palagonitization.
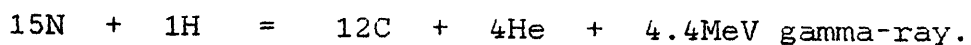
II. RECOMMENDATIONS

The above discussions have highlighted some unresolved issues related to the application of palagonite layer measurements to dating MORBs and other basaltic glasses. Two related problematic issues are apparent. First, the rate law and absolute rates for a given condition (e.g., appropriate for MORB glass) are not fully known. Existing estimates based on field studies such those noted above remain to be calibrated using an absolute dating technique. This makes absolute age determination using palagonite layers inaccurate at present. Relative exposure ages could be useful but only in a qualitative sense because the rate law remains to be established. Second, the discrepancies between experimental and field observations remain to be satisfactorily explained. Experiments can potentially provide an alternate source of independent calibration, but it is clear that this is far from being realized at present. The long-term rate law of palagonitization remains to be meaningfully addressed in experimental systems.

Several approaches can be used either to make dating by palagonite layer measurement more realistic or to demonstrate that it cannot be generally applied. The types of field studies performed by Moore [1966], Hekinian and Hoffert [1975] and Bryan and Moore [1977] should be augmented by an absolute dating technique (i.e., not Mn coating thickness measurement). Hekinian and Hoffert's [1975] attempt to relate the palagonite growth to fission track dates is a step in the right direction but it remains to be shown that fission track ages are also credible for MORBs. Until an independent absolute dating technique is developed for MORBs, experimental systems are the only avenues for determining the palagonitization rate law. However, non-MOR basaltic glasses hydrated in submarine environments and whose eruption ages are tightly contrained, either by historical records or applicable dating technique (e.g., 14C), may offer some very important field constraints on palagonitization rate law. These tightly constrained systems could also be useful for determining statistical variability of palagonite layer thicknesses in samples with identical exposure ages. Nevertheless, the problem of applicability of such results to MOR systems will have to be addressed.

Systematic experiments designed to address the question of rate law applicable to natural palagonitization process have not been performed. This requires long-term experiments conducted at a wide range of conditions (e.g., temperature, flow rates, water composition) coupled with detailed characterization of the palagonite layers formed at different stages of reaction. These experiments should use actual MORB glasses and synthetic MORB of controlled variable compositions (including simplified compositions for mechanistic studies). Crucial to determining long-term palagonitization rate and rate law from experiments are (1) understanding the mechanistic origin of natural palagonites and (2) ensuring that the process being experimentally investigated is truly analogous to natural palagonitization. This requires parallel and detailed characterization of natural and experimentally-produced palagonites [cf. CROVISIER et al., 1987].

Even after the above issues have been resolved, a number of application problems will have to be addressed. For example, it may be that a simplified rate law that is useful for dating applies only to the first few thousand years of glass exposure to seawater. If so, the dating technique will have to be applied only to glasses whose exposure ages belong to this age range. Furthermore, the emphasis in all the discussions made above is on glass surfaces exposed to open seawater. A study of how, if at all, slight to extensive sedimentation (including Mn accumulation) will affect the palagonitization process has to be conducted. Otherwise, only samples continously exposed to open seawater throughout their submarine history should be used. One also has to be certain that the palagonite layers were not disturbed (e.g., by mechanical erosion) from the time of initial exposure to seawater. Strict criteria will thus have to be developed to determine the types of samples suitable for dating.

The standard tool for measuring palagonite layer thicknesses has been the optical microscope. This method allows layers a few microns to hundreds of microns thick to be measured accurately. Indeed some layers may be thick enough for visual measurements to be made. Herein lies one of the most significant merits of this dating technique, that of simplicity and availability of analytical tools. In some cases, the scanning electron microscope (SEM) has been employed to show the details of the palagonite layer structure or to determine the origin of multiple palagonite layers. Even the SEM, however, has become standard equipment in geological departments. Nevertheless, experimental or even some natural systems may produce palagonite layers that are only sub-micrometer thick. The problem with these exceedingly thin layers is that while some may still be theoretically observable under the SEM, existing sample preparation techniques (mounting and polishing) are often unable to preserve the delicate thin layers. Depth profiling techniques that are more suited for this purpose exist but are available only in a few laboratories. Two examples of depth profiling techniques that have been used for measuring thin alteration layers on glasses include secondary ion mass spectrometry (SIMS) and resonant nuclear reaction spectrometry (RNRS). The former is based on mass spectrometric measurement of charged or neutral species sputtered off the surface of interest and has multielement capability. The latter is based on measurement of nuclear particle intensities resulting from reaction of bombarded ions and specific isotopes intrinsically present in the sample. Examples of the application of RNRS profiling techniques to determine altered layer thicknesses on glasses can be found in Berger et al. [1987] and Abrajano and Bates [1987]. In both cases, hydrogen distribution was measured using the reaction:

$$15N + 1H = 12C + 4He + 4.4MeV \text{ gamma-ray.}$$

Other techniques (not necessarily for depth profiling, e.g., transmission electron microscopy) for measuring very thin layers are available but, like the two examples noted above, they are best used in detailed characterization of palagonite layers rather than in routine thickness measurement. Such detailed characterization will be necessary in experimental studies of reaction mechanisms. If there is interest in MORBs with exposure ages of less than a few hundred years, these high resolution techniques may, nevertheless, be very useful dating tools.

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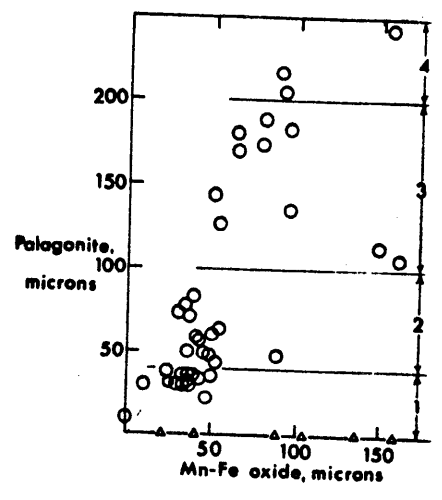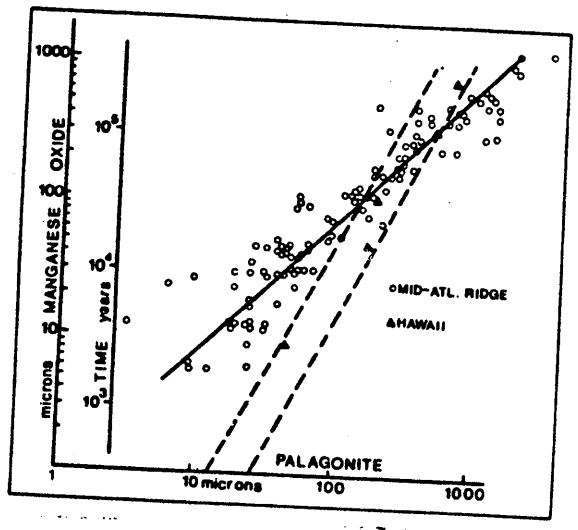
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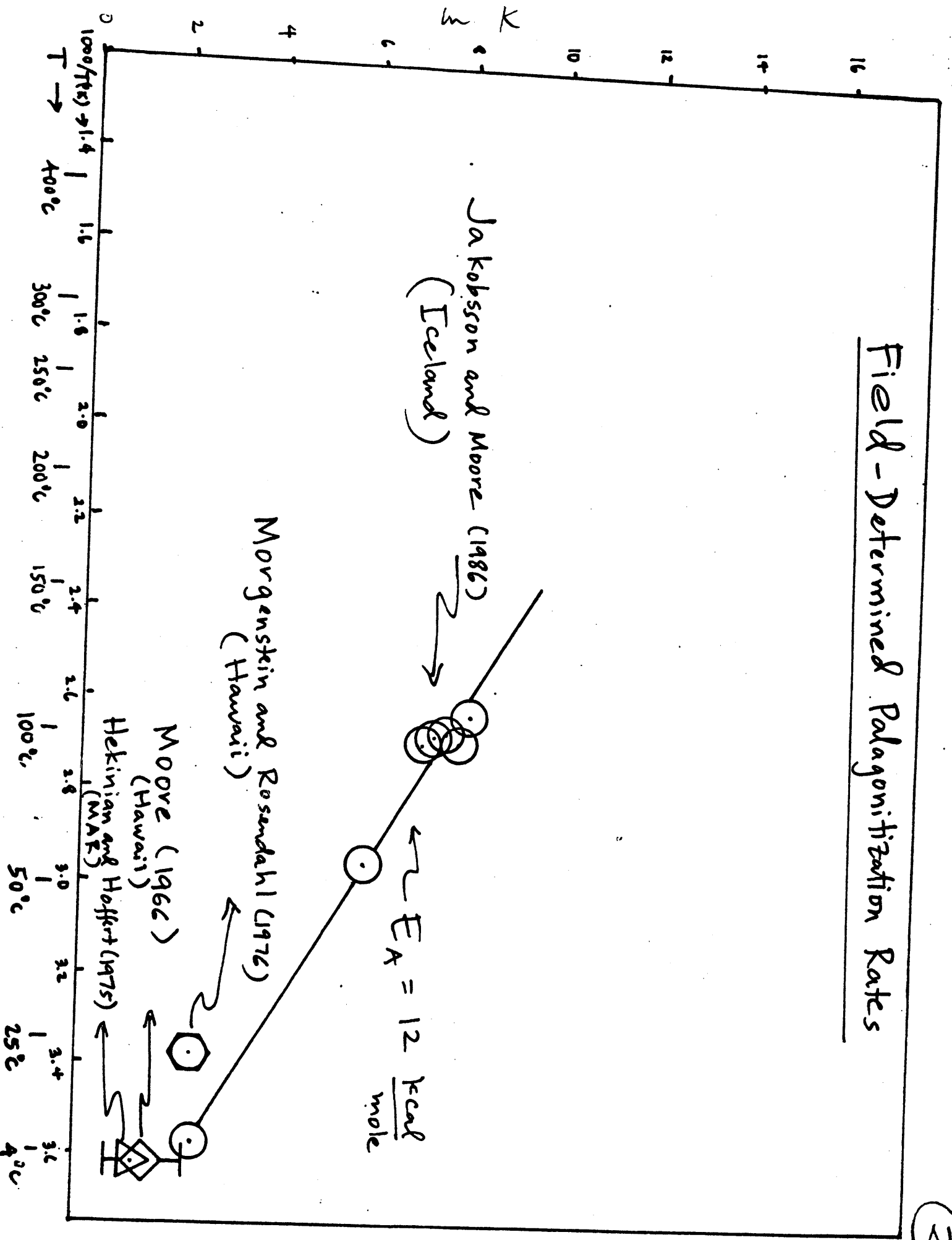
Figure Captions:

Figure 1.   Palagonite layer thickness plotted against Mn coating
            thickness. From studies of Moore [1966] and Hekinian
            and Hoffert [1975] (A: Figure from Crovisier et al.
            [1987]) and Bryan and Moore [1977] (B).

Figure 2.   Arrhenius plot showing variation of palagonitization
            rate constants with temperature in natural basaltic
            systems.

Figure 3.   Arrhenius plot showing variation of palagonitization
            rate constants with temperature in experimental
            basaltic systems.

Figure 4.   Variation of palagonite layer thickness formed on
            synthetic tholeiitic basalt with time after leaching at
            50 deg-C and 43 deg-C (From Crovisier et al., 1983).

Figure 5.   Variation of palagonite layer thickness formed on
            synthetic alkalic basalt with time after vapor hydration
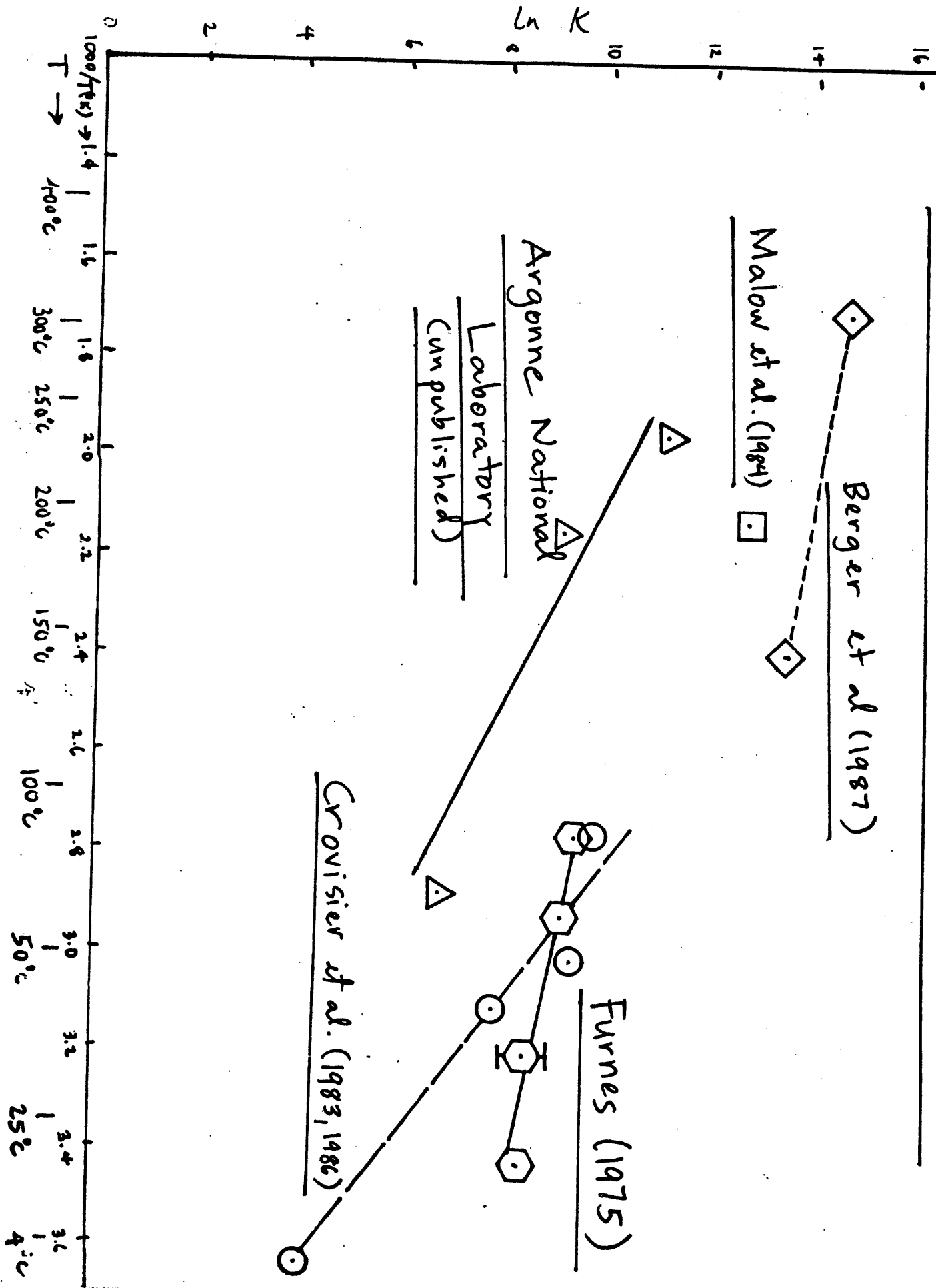   at 240 deg-C (From Byers et al., 1985)
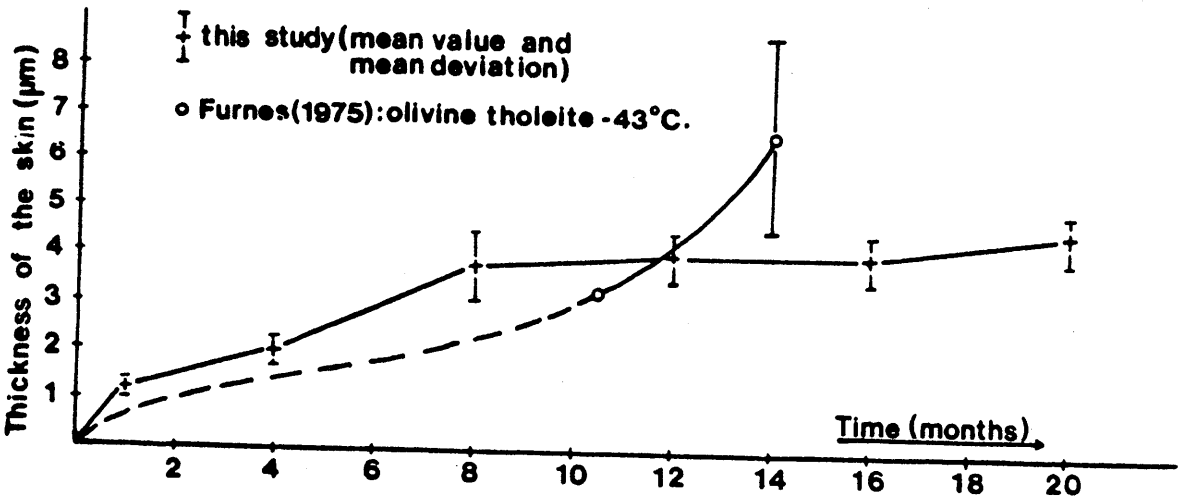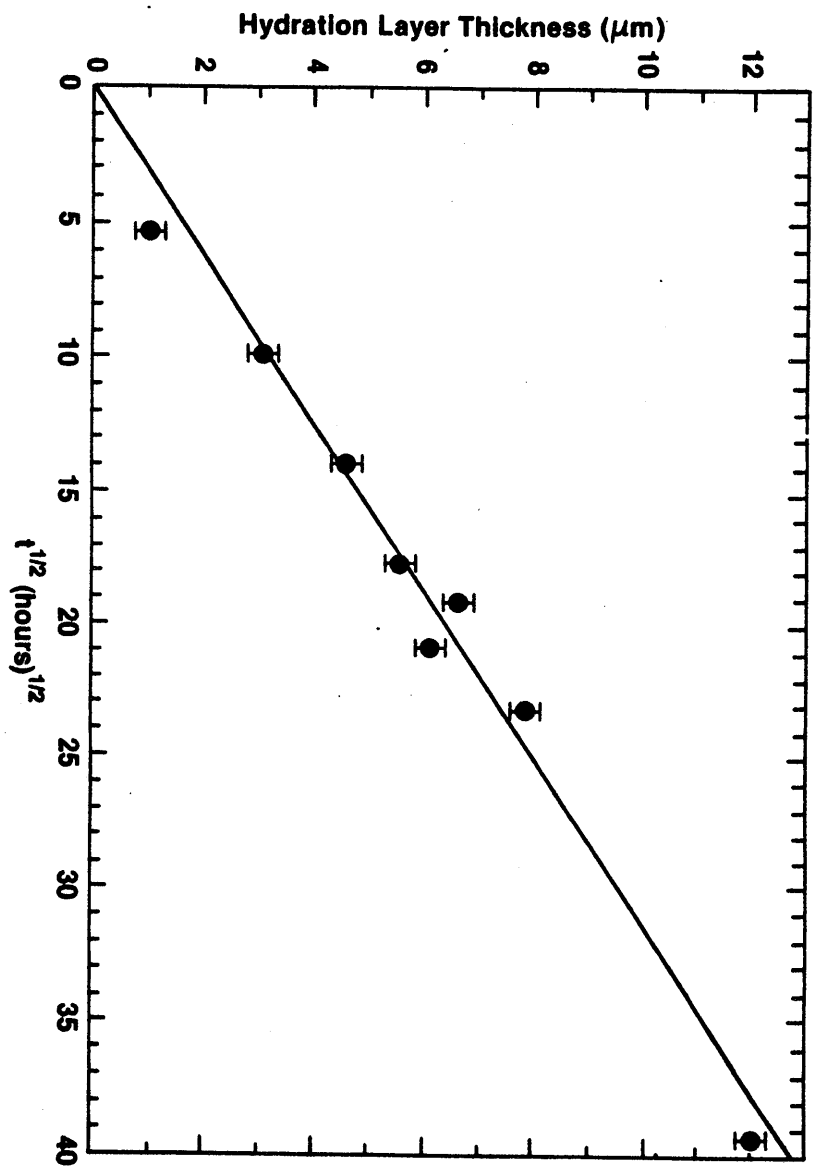
Field-Determined Palagonitization Rates

K

Jakobsson and Moore (1986)
(Iceland)

Morgenstein and Rosendahl (1976)
(Hawaii)

Moore (1966)
(Hawaii)
Hekinian and Hoffert (1975)
(MAR)

$E_A = 12 \frac{kcal}{mole}$

T

100/(T°K) →1.4

400°C 300°C 250°C 200°C 150°C 100°C 50°C 25°C 4°C

②

Experimentally-Determined Palagonitization Rates

Thickness of the skin (µm) vs. Time (months)

Legend:
- this study (mean value and mean deviation)
- o Furnes (1975): olivine tholeite -43°C.

Department of Geology
21 Jan. 1988

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Dear Rodey,

I've just completed several tests on the 62-149 μm grain-size fractions of two samples of crushed MORB glass: your D19-3 and one (K18) David Christie gave me. There was no natural TL signal in either sample, but this is not surprising given that both have been extensively exposed to daylight. While the ionizing radiation sensitivity of K18 is too slight to be useful, D19 is about 30 times more sensitive, and therefore potentially more useful. However, positive as this observation may be, other characteristics dampen my interest.

In particular, K18 showed no evidence of the presence of high temperature traps (those filled in the lab irradiation would empty at room temp in a few days or weeks) that are necessary for TL dating. While D19 did have more of the "stable" traps, a very large portion of its TL signal represents thermally unstable traps (i.e. the TL is observed at low glow-curve temp.) Furthermore, a controlled heating test (a la BERGER (1987)   ) suggests that a lot of the induced TL exhibits anomalous fading. In addition to these negative features, D19 showed large subsample inhomogeneity in the TL. Specifically, one of the discs gave a glow curve that was totally unlike that of a glass, suggesting that a more complicated sample prep would be required (but without the assurance of success). Finally, an optical bleaching test on D19 produced significant reduction in the TL after exposure to light somewhat more orange than sodium light.

Well, it doesn't look promising at this time,

Although several MORE

lab tests could be done.

My feeling now is that TL is more likely to be useful for providing indirect dates of MORB, than direct dates. This presupposes that TL will not work on the feldspars in the rock.

Cheers,

Glenn Berger

APPENDIX 3

ESR DATING: POSSIBILITY FOR DATING YOUNG MID OCEAN RIDGE BASALTS

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<u>Electron Spin Resonance Dating</u>

<u>Introduction to ESR</u>

It was suggested by Zeller et al. (1967) that electron spin resonance (ESR) spectroscopy could be used as a method to date geological and archaeological samples. Materials on which ESR dating has been performed thus far are: speleothems, corals, mollusc shells, teeth, as well as samples from geological processes such as volcanic eruptions, and fault movements.

<u>Physical Principles</u>

Paramagnetic centers in a mineral arise from trapping unpaired electrons (e^-) or holes (e^+) at charge defects incorporated into the crystal lattice upon formation. A defect is any position in the crystal structure representing a violation of the symmetry described by the symmetry space group of the crystal. In particular, charge defects are sites at which the effective charge is less than that required by the symmetric structure.

Radioactive impurities (U, Th, K, Rb, ^{14}C) incorporated into the sample itself and the surrounding matrix emit high energy particles ($\alpha-$, $\beta-$, and $\gamma-$ radiation) when they decay. Energy can be transferred from these high energy particles to electrons which are elevated from the valence to the conduction band. After a short time of diffusion the electrons recombine with holes near the valence band. The same electrons may however, be trapped at a defect site and form a paramagnetic center (Figure 1).
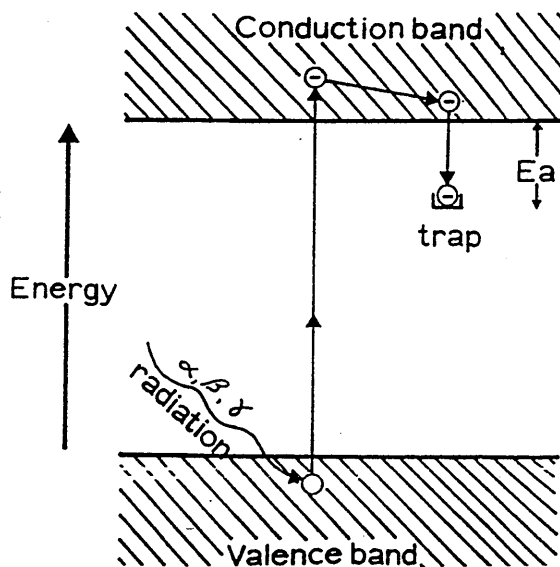

Figure 1. Illustration of the trapping scheme of electrons in minerals

The number of trapped electrons which is proportional to the ESR signal, is a function of the radiation dose rate and the time (=age) the sample was exposed to this radiation field.

An age can be deduced from the following equation:

$$AD = \int_0^t DR(t)\ dt$$

where AD is the radioactive dose the sample has accumulated over time and DR is the rate at which the dose has collected in the sample.

The accumulated dose (AD) is determined by the "additive dose method" where the ESR intensity of the natural sample is measured along with the ESR intensities of aliquots which were all γ-irradiated at different levels. Back extrapolation to zero ESR intensity gives the AD of the sample which is measured in Grays (Gy) (Figure 2).
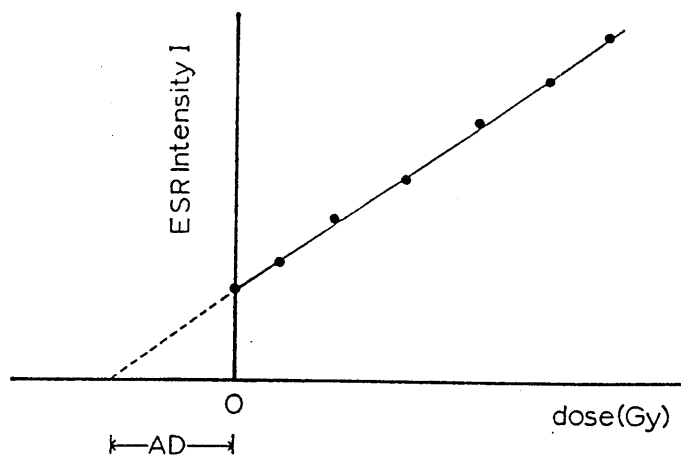

Figure 2. Determination of AD by the additive dose method; back extrapolation to zero-ESR intensity gives the AD value.

Determination of DR

To determine the dose rate, precise information about the amount of radiation that the sample has received from internal and external radioactive impurities is needed. External γ-and cosmic radiation dose rates can be determined by inserting a portable dosimeter unit directly into or near the sample site for a period of time.

The determination of U and Th (through neutron activation) and K (XRF) in the matrix surrounding the sample, and within the sample itself gives the α- and β- external and internal dose rates respectively. The measured concentration of radioactive elements can be converted into dose rates by the use of published tables (e.g. Nambi and Aitken, 1986). If external γ-and cosmic dose rates are not measured in situ then the γ- dose rate can be calculated from chemical analysis; the cosmic dose rate is dependent on altitude, latitude and attenuation by overlying sediment and water and can be estimated by graphs published by Prescott and Stephan (1982).

In general the calculation of DR is performed by an equation in the form shown below:

$$
\begin{aligned}
DR = [& C_U (k \cdot W_\alpha \cdot G_{U-\alpha} D_\alpha + W_\beta \cdot G_{U-\beta} \cdot D_\beta + W_\gamma \cdot D\gamma) \\
+ & C_{Th} (k \cdot W_\alpha \cdot G_{Th-\alpha} \cdot D_\alpha + W_\beta \cdot G_{Th-\beta} \cdot D_\beta + W_\gamma \cdot D_\gamma) \\
+ & C_K (W_\beta \cdot G_{K-\beta} \cdot D_\beta + W_\gamma \cdot D_\gamma) + G_{cos} D_{cos}]_{external} \\
+ & [C_U (k \cdot G_{U-\alpha} D_\alpha + G_{U-\beta} \cdot D_\beta + D_\gamma) \\
+ & C_{Th} (k \cdot G_{Th-\alpha} \cdot D_\alpha + G_{Th-\beta} \cdot D_\beta + D_\gamma) \\
+ & C_K (G_{K-\beta} \cdot D_\beta + D_\gamma)]_{internal}
\end{aligned}
$$

(note that the activity ratios for the U and Th decay chains should be determined in order for an accurate dose rate to be determined).

Where $G_{\alpha, \beta, \gamma, cos}$ = attenuation factors for α, β, γ, and cosmic rays

$W_{\alpha, \beta, \gamma}$ = water correction factors for α, β, and γ rays (incorporated into the equation if the % of water in the matrix is known)

D = dose rate per unit concentration

D_{cos} = cosmic dose rate

k = α efficiency

$C_{U, Th, K}$ = concentration of radioactive elements present

- if the external γ- and cosmic dose rates are measured by a portable dosimeter the above formula is simplified to:

$$
\begin{aligned}
DR = [& C_U (k \cdot W_\alpha \cdot G_{U-\alpha} D_\alpha + W_\beta \cdot G_{U-\beta} \cdot D_\beta) \\
+ & C_{Th} (k \cdot W_\alpha \cdot G_{Th-\alpha} \cdot D_\alpha + W_\beta \cdot G_{Th-\beta} \cdot D_\beta) \\
+ & C_K (W_\beta \cdot G_{K-\beta} \cdot D_\beta) + MD_\gamma + MD_{cos}]_{external} \\
+ & [C_U (k \cdot G_{U-\alpha} D_\alpha + G_{U-\beta} \cdot D_\beta + D_\gamma) \\
+ & C_{Th} (k \cdot G_{Th-\alpha} \cdot D_\alpha + G_{Th-\beta} \cdot D_\beta + D_\gamma) \\
+ & C_K (G_{K-\beta} \cdot D_\beta + D_\gamma)]_{internal}
\end{aligned}
$$

where $MD_{\gamma, cos}$ = measured dose rate of γ, and cosmic rays

Application of ESR for dating recent MORBs

The use of the ESR dating method is restricted to minerals with a low iron content due to the strong paramagnetic nature of Fe which tends to overwhelm all other ESR signals. Plagioclase is the only mineral with a low Fe concentration of significant quantity for ESR dating obtainable from MORBs. However, problems arise when attempting to use plagioclase for ESR dating in that the two most common trapping centers (Al and Ti) may be stress sensitive. Crushing techniques used to separate the feldspar from the other basalt components may alter the ESR signal intensity thereby giving a false age.

Accurate ESR dating of MORBs also may be hampered by sea-floor weathering, particularly if the primary calcic plagioclase has been replaced by sodic plagioclase which will alter the ESR signal intensity.

ESR is, therefore, not an adequate dating tool for primary MORBs but may become useful as a secondary dating method on materials related to MORBs, such as weathered sediments between lava flows. In principle, the ESR signals can be reset by the thermal baking of MORB flows capping the sediments. Depending on the sediment thickness, there should be an aureole produced where all of the trapping centers in the detrital feldspar should have been zeroed (temperatures required to reset ESR traps are not reached outside the aureole and thus the centers are not zeroed at the time of the lava emplacement). ESR ages obtained from minerals within this aureole should all give the same ages to establish a plateau which would be an indication of center resetting due to the lava flow (Figure 3). Weathering of detrital plagioclase in the sediment may not be as pronounced as for the fresh lava and ESR signal intensity would not be altered significantly. It therefore, may be possible to date MORB flows through resetting of ESR signals in these materials.
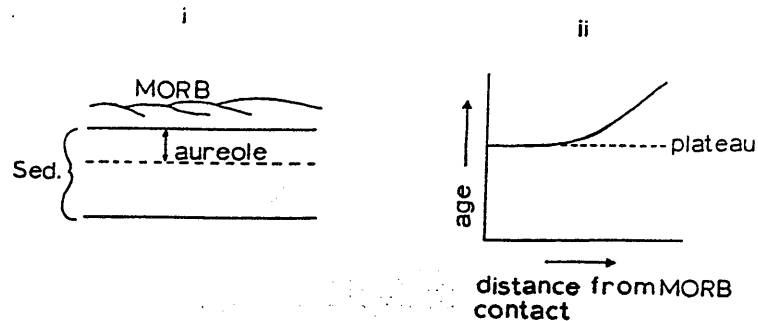

Figure 3. i) Illustration of a "zeroed" aureole in the detrital sediment created by the MORB flow above.
ii) Equal age plateau along which are samples that have been totally reset by the thermal baking of the MORB flow.

Another problem that arises for ESR dating of MORBs is the extremely low concentrations of the radionuclides (uranium, thorium and potassium) needed to build up the electron charge in the material. Without a significant buildup of ESR signal intensity an ESR spectrum may not be detectable and accurate age determinations of young MORBs may not be possible.

It appears that there are a number of problems related to ESR dating of young MORB samples yet it may be worth while to attempt to look at the ESR signals in the plagioclase (and possibly quartz if there is any present) in detrital sediments associated with MORB flows and cross check the dates obtained with other dating methods.

To do this one would require at least 10 g of detrital material in loose aggregate form for each of these types of deposits obtained during sampling, preserved in water tight plastic bags or containers. It would also be helpful if a measured γ-dose could be taken by a portable dosimeter at each of the samples locations.

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APPENDIX 4

Dating magmas directly using short-lived ^{238}U and ^{232}Th decay-series nuclides

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The decay of ^{238}U and ^{232}Th to stable Pb daughters is stepwise, involving intermediate nuclides with half-lives ranging from 2.45×10^5 y to < 1 μs. Decay series are in equilibrium when all of their nuclides have the same activity. Chemical fractionation changes nuclide activity ratios and creates disequilibrium that can be used to date the fractionation processes over a time scale of less than about 5 times the half-life of the fractionated nuclides. The nuclides discussed here (^{226}Ra, $T_{1/2}$ = 1600 y; ^{210}Pb, $T_{1/2}$ = 22.3 y; ^{228}Ra, $T_{1/2}$ = 5.76 y; ^{228}Th, $T_{1/2}$ = 1.91 y; and ^{210}Po, $T_{1/2}$ = 138 d) can be used for dating over the range of about 8,000-0.05 y.

Most basalts and many andesites and dacites erupt with (^{226}Ra) (parentheses indicate activities) significantly exceeding (^{230}Th) ($T_{1/2}$ = 75,200 years). Unaltered samples showing ^{226}Ra enrichment are unambiguously less than 8000 y old. More precise dating requires determination of the initial (^{226}Ra)/(^{230}Th) ratio. An isochron plot of (^{226}Ra)/Ba versus (^{230}Th)/Ba for a comagmatic suite of samples or separated phases from a single sample (Fig. 1) can conceivably accomplish this. Note, however, that this method is only valid in circumstances where Ra and Ba partition identically between the phases involved in magma genesis or differentiation. At present, it is unclear whether this frequently holds true. The only results that have been published so far show that Ba and Ra do indeed behave nearly identically in carbonatites from Ol Doinyo Lengai volcano in Tanzania (Williams, et al., 1986).

Minerals that take in Th, but exclude Ra can be accurately dated because the initial $(^{226}Ra)/(^{230}Th)$ can be assumed to be about zero. Zircon is apparently such a mineral (D_{Th} = 17-230, Fukuoka, 1974; D_{Ba} probably < 1 , Irving and Frey, 1984), but its limited occurrence and the potential for an inherited age restricts its usefulness.

Disequilibrium between ^{210}Pb and ^{226}Ra can be used to date magmatic differentiation and generation events that are less than about 110 years old. The simple presence of ^{210}Pb-^{226}Ra disequilibrium in a lava indicates that it erupted (and possibly was generated or differentiated) less than about 110 years before the date of measurement. However, ^{210}Pb-^{226}Ra disequilibrium is apparently not as common as ^{226}Ra-^{230}Th disequilibrium in zero-age volcanic rocks (c.f. Bennett et al., 1982; Condomines et al., 1987), and this method may not be useful in many areas.

Magmatic minerals that fractionate Pb and Ra (e.g. sulfides: $D_{Ba}/D_{Pb} \simeq$ 0, biotite: D_{Ba}/D_{Pb} = 3-300, and sanidine: $D_{Ba}/D_{Pb} \simeq$ 10; Nash and Crecraft, 1985) can be used for dating crystal growth in a < 110 year time frame. Such minerals can be used for precise dating by using an isochron plot of $(^{210}Pb)/Pb$ versus $(^{226}Ra)/Pb$ to determine the initial $(^{210}Pb)/(^{226}Ra)$ ratio (see Fig. 2). Unfortunately, these minerals are rare in basaltic rocks, and partition coefficient ratios between Ra (or Ba) and Pb are generally poorly known for common minerals in basaltic rocks such as plagioclase, augite, and magnetite. Thus, it is presently unclear whether phenocrysts can be used to date basaltic rocks using ^{210}Pb-^{226}Ra techniques. Recently-erupted plagioclase phenocrysts from Arenal volcano in Costa Rica apparently have $^{210}Pb/^{226}Ra$ > 1, suggesting that plagioclase potentially can be used for ^{210}Pb-^{226}Ra dating (M.K. Reagan unpub. data, 1987).

2

Volcanic rocks from Kilauea, Arenal, and Mount St. Helens (Gill et al., 1985; Bennett et al., 1982) have $(^{210}Po)/(^{210}Pb) \approx 0$ at the time of eruption, indicating that basalts, andesites, and dacites degas Po during eruption. It is likely, therefore, that submarine eruptives of unknown age can be shown to be less or more than a year old simply by determining whether they have $(^{210}Po)/(^{210}Pb) < 1$ or $= 1$.

Disequilibria between ^{232}Th, ^{228}Th, and ^{228}Ra can be used for dating rocks on a less than 30 year time scale. Like the previously described methods, these disequilibria can be used for giving a maximum age (using a single mineral or whole-rock analysis) or an absolute age (if the initial (^{232}Th), (^{228}Th), and (^{228}Ra) are known). ^{228}Th-^{228}Ra disequilibrium indicates less than 10 years lapsed before the dates of eruption and measurement; ^{228}Ra-^{232}Th disequilibrium indicates less than 30 years. Absolute ages can be determined using an isochron plot of $(^{228}Th)/(^{232}Th)$ versus $(^{228}Ra)/(^{232}Th)$ (not reproduced here). This plot differs from those discussed previously in that equilibrium is represented by the point were $(^{228}Th)/(^{232}Th)$ and $(^{228}Ra)/(^{232}Th) = 1$.

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Figure Captions

Figure 1. ^{226}Ra-^{230}Th isochron diagram using Ba to normalization data. Arrows show changes in isotopic composition with time for comagmatic samples or mineral separates from a single sample.

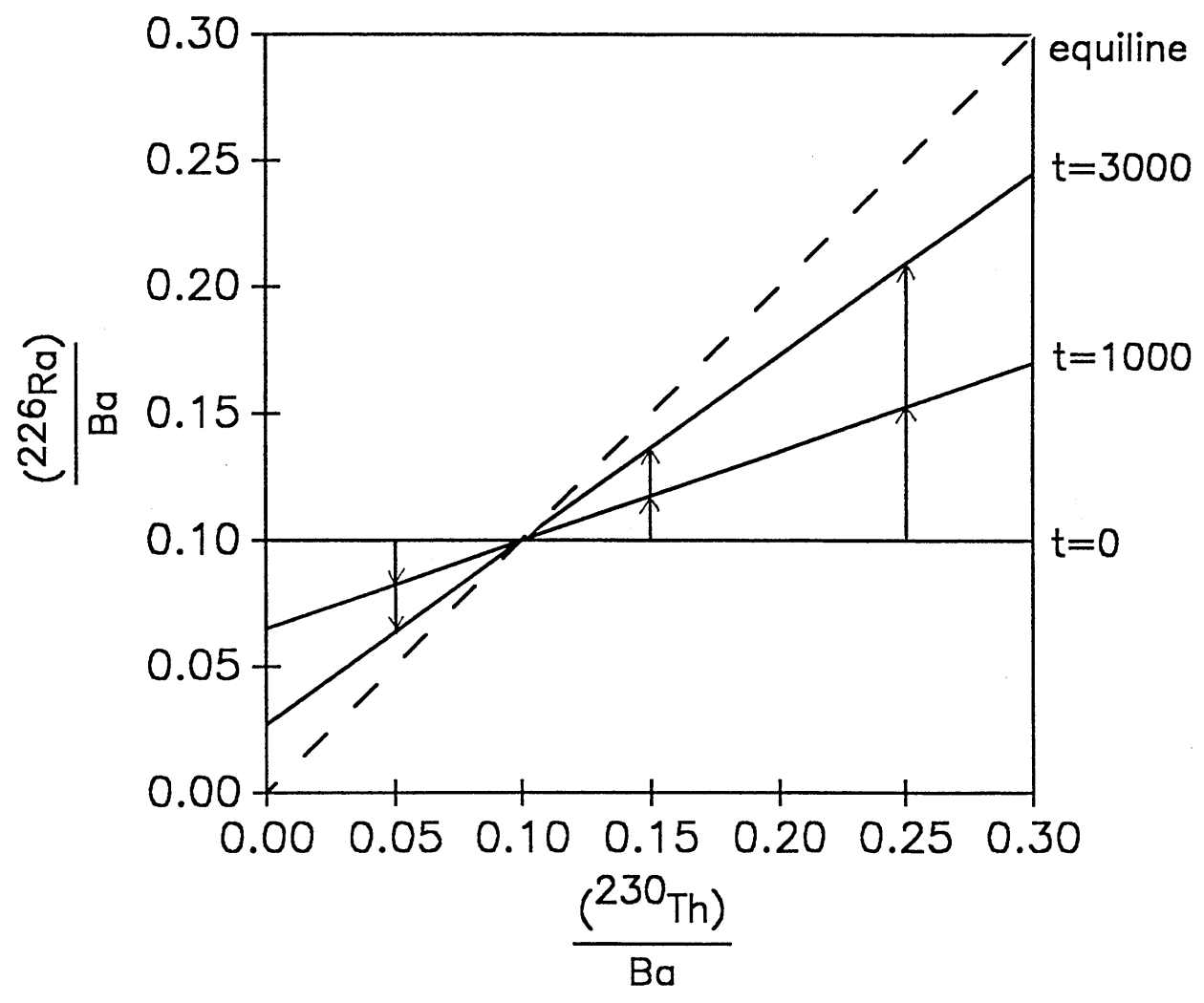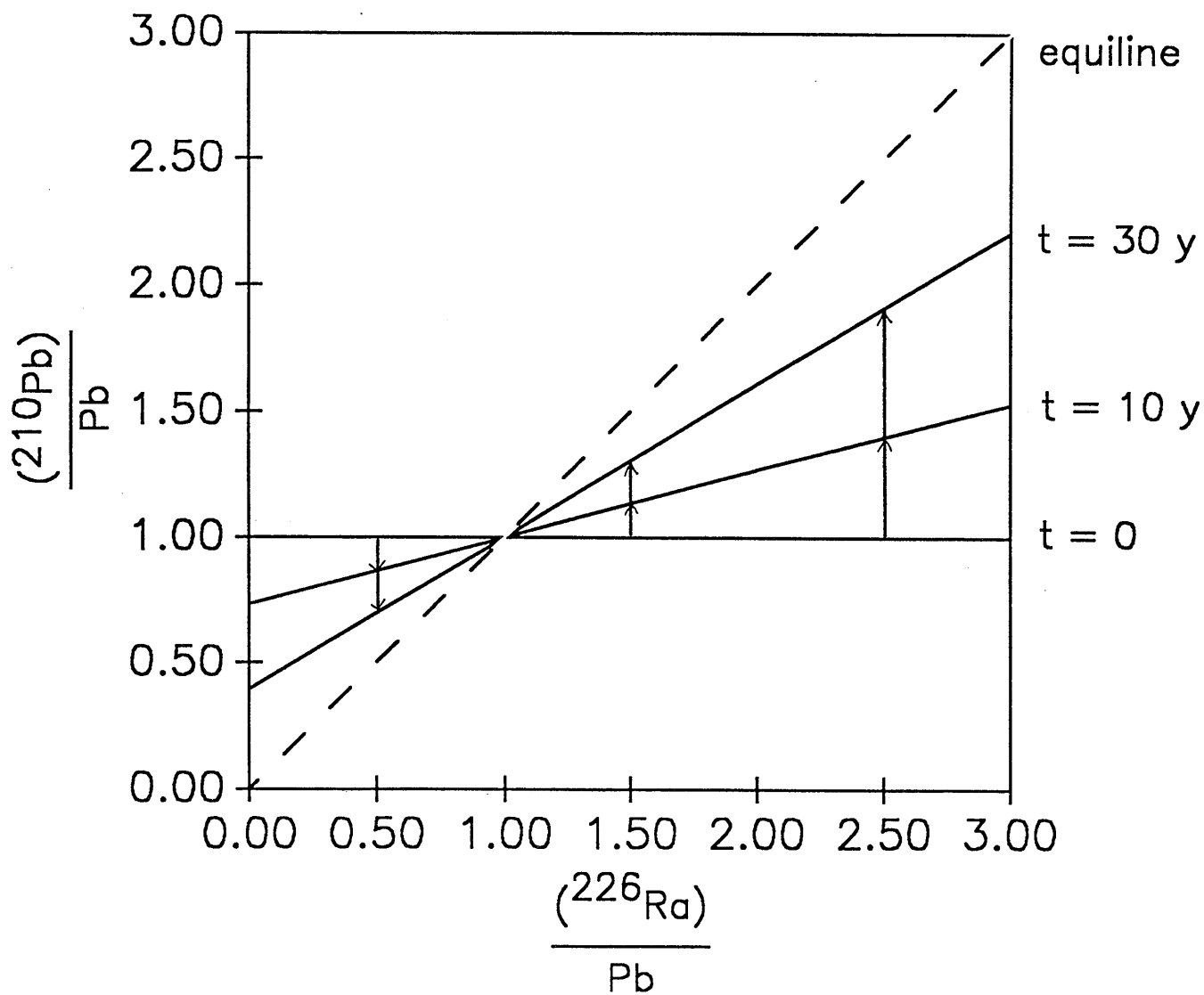Figure 2. ^{210}Pb-^{226}Ra isochron diagram.

Figure 1.

Figure 2.

APPENDIX 5

Possibility of Dating Young Tholeiitic Basalts

by the $^{40}Ar/^{39}Ar$ Method

by Brent Dalrymple

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Methods now exists for the $^{40}Ar/^{39}Ar$ dating of very small (to 1 microgram) samples with high precision using a high-power continuous laser, mini-extraction line (less than 200 cc), and ultra-clean, ultra-sensitive rare gas mass spectrometer. This relatively new method results in very low atmospheric Ar contamination and rapid (30 min.) analyses. At present, such instruments are operating at the University of Toronto, Princeton University, the Berkeley Geochronology Center, and the U.S. Geological Survey in Menlo Park.

These instruments are unsuitable for tholeiites of less than 1 Ma in age because the very low K_2O contents would not yield sufficient radiogenic ^{40}Ar using the sample sizes for which the instruments were designed (1-1000 micrograms).

It would be relatively straightforward, however, to construct a "mega" version of the laser system capable of analyzing samples of 10-100 milligrams. Such sample sizes might permit the dating of plagioclase crystals (and perhaps other phases) from tholeiitic basalts as young as 0.1 Ma. The success of such a system depends on whether or not the present systems

can be "scaled up" for larger sample sizes without also increasing the atmospheric blank, and on achieving significant reductions in the non-radiogenic Ar component by preheating the sample with the laser. Scaling up of the laser system should not result in higher atmospheric system blanks and the increase in sample size should provide adequate amounts of radiogenic ^{40}Ar for analysis. Preliminary experiments with the U.S.G.S. laser system indicates that pre-heating of feldspar samples is effective in reducing the non-radiogenic (atmospheric) component. The new system would consist of a larger (20-30 watt) Ar-ion laser, a newly designed "mega-mini" extraction system, and the same type of mass spectrometer (MAP216 or equal) now in use on the smaller systems.

Feasibility

Fifty milligrams of feldspar with 0.1% K_2O produces 7.20 $x10^{-15}$ mol $^{40}Ar_{rad}$ in 1 Ma. In the U.S.G.S. laser system at Menlo Park, this produces a signal of 0.45 V, which is 45x background and can be measured with a precision of 0.2% or better. Laser analyses of 0.2 mg samples of feldspar separated from basalt recovered from Cretaceous seamounts yield $^{40}Ar_{atm}$ contents of between $8x10^{-16}$ and $8x10^{-17}$ mol. How this will scale up to larger samples is unknown, but the limiting conditions using the higher value are:

Best case = all $^{40}Ar_{atm}$ from system. Then the analysis
   of 50 mg. of 1 Ma plagioclase would have a
   $^{40}Ar_{rad}$ yield of 90%

Worst case = $^{40}Ar_{atm}$ oc to sample wt. Then the analysis would have a $^{40}Ar_{rad}$ yield of 5% (or 0.5% for a 0.1 Ma sample)

Either of these are acceptable, but experience with the Menlo Park System suggests that the realistic case will be between the best and worst cases, and probably closer to the best. Laser preheating typically reduces the $^{40}Ar_{atm}$ by 10x, which results in a worst case $^{40}Ar_{rad}$ yield of 52% for a 1 ma sample or 5.2% for a 0.1 Ma sample.

In order to minimize interference from $^{36}Ar_{ca}$, the irradiation time in the U.S.G.S. TRIGA reactor would be 0.5 MWh (30 min) for a 1 Ma plagioclase sample. This produces 3.5 x10^{-14} mol ^{39}Ar/gm and a $^{40}Ar_{rad}/^{40}Ar_K$ ratio of 4.1. The $^{39}Ar_K$ would produce a signal of 0.11V, which is 1000X background. For a 0.1 Ma sample, the figures would be 10x lower but still within the acceptable range.

For laser preheating, the 50mg sample should be spread over an area of about 70mm^2 to form a layer no more than 2 grains thick. Preheating power density requirements should be in the range of 5W/mm^3 for a total of 360W. This is impractical, but the beam from a 20-30W laser could be defocused to an area of 4-6mm^2 and moved over the grain field to preheat the grains in 1-2 minutes. Fusion could be accomplished by the same technique only with a more highly focused laser beam.

Conclusions

1. Radiogenic ^{40}Ar from a 50 mg plagioclase sample less than 1 Ma will be sufficient for accurate

measurement.

2. Atmospheric ^{40}Ar contamination can probably be held to acceptable levels.

3. Irradiation times can be adjusted to provide sufficient ^{39}Ar and minimize interference from $^{36}Ar_{ca}$ without unacceptably compromising analytical precision.

4. There is a good possibility that very young, low K_2O basalts can be dated directly by $^{40}Ar/^{39}Ar$ techniques, provided fresh material can be obtained.

Why a New System?

Existing systems are optimized for analysis of very small (single grain) samples and their adaption to dating of large samples might compromise their use for other purposes. The Toronto (18W, Ar-ion) and Princeton (17.5W, Nd-YAG) lasers are marginally large enough, but the other two systems utilize Ar-ion lasers that are too small (7-8W). Development, testing, and application to young basalts for JOI and DOSEC purposes would tie up a system for many years.

Cost and Construction

A new system could be built in one year and might require one year of testing on young basalts to refine sample preparation and extraction methods. The laser, optics, mass-spectrometer, and much of the extraction system would consist of currently available and easily assembled equipment. Construction of the

4

remainder of the extraction line would pose no particular technical problems. System cost would be about $250-300k for equipment (depending on exchange rates with the British pound). Additional costs would be encountered for technical assistance during construction and testing, and possibly reactor charges; these costs would depend heavily on the institution that undertakes construction and testing.

Note that this is a "no lose" proposal. If successful this system would be invaluable to both the DOSEC Hawaii drilling and to JOI for dating sea-floor basalts. If it does not work on young basalts, it could be converted to a state-of-the-art single crystal dating facility at a very small (<$10K) additional cost.

APPENDIX 6

Dating Methods

13

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ABSTRACT

Geologic assessment of active tectonism depends on two key measures: the age and the amount of deformation of a given stratigraphic unit. The amount of deformation can normally be measured with greater accuracy than the age. Adequate age control is thus a limiting factor in studies of active tectonism.

About 26 dating techniques can be applied to dating deposits and deformation of late Cenozoic age (past few million years). These techniques can be grouped as numerical, relative dating, and correlation. Numerical techniques are best, but datable materials are often lacking, and in these cases age estimation must be made using relative-dating or correlation techniques. Relative-dating techniques are nearly always applicable but are not precise and require calibration. Correlation techniques are locally useful and depend on recognition of an event whose age is known, such as a volcanic eruption or a paleomagnetic reversal.

Geologic studies of active tectonism are greatly aided by definition and time calibration of local stratigraphic sequences. Because all dating techniques may be subject to considerable error, reliability should be assessed by stratigraphic consistency between results of different dating methods or of the same method. Numerical ages may have large, nonanalytical errors. For example, radiocarbon dating is one of the most useful techniques in the 0-50-ka range (ka = thousand years old), but contamination can result in dates as young as 15 ka for deposits that should be isotopically dead ($>$40-70 ka).

Improvements in our ability to date active tectonism and define its rates will come from continued refinement of established techniques, such as carbon-14 dating, and development of experimental techniques, of which thermoluminescence seems to offer special promise. Experimental isotopic-dating techniques such as ^{10}Be, ^{36}Cl, and ^{26}Al also offer potential for dating faulting and other deformation. However, refinement of relative-dating techniques, such as soil development, rock weathering, and progressive landform modification are likely, because of their general applicability, to provide much of the needed age control.

For a given fault or other feature of active tectonism, deformation rates need to be determined over different time spans to recognize any variations in deformation rate and how attempts at prediction of future deformation may relate to these variations. If grouping of faulting events has occurred, hazard assessment based on deformation rates depends on the combination of the pattern of deformation and the time window of observation.

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INTRODUCTION

Dating is a critical tool in the assessment of active tectonism. The two primary measures of active tectonism are the age and the amount of deformation of a stratigraphic unit, which together define rates of deformation. Although slip or other deformation rates may vary through time, such rates are still one of the most useful measures of active tectonism (Slemmons, 1977).

Dating of active tectonism is commonly accomplished by dating surficial or volcanic deposits. In addition to dating conventional stratigraphic units, materials such as calcite infillings may be deposited in a fault plane and dating of these infillings used to determine the history of faulting. With either conventional stratigraphic units or materials infilling a fault zone, if the material is unbroken its age provides a minimum age for the last faulting; and if it is broken, it provides a maximum age for the last faulting. Although individual fault offsets obviously occur in jumps, the overall slip rate can be determined from the amount of offset, especially for multiple events, divided by the geologic time interval involved.

In the past few decades, our ability to date geologically young deformation and associated deposits has improved greatly. In this time, dozens of dating techniques (Tables 13.1 and 13.2) have been either developed or greatly refined. As few as 10 yr ago, estimates of the age of Quaternary deposits were commonly in error by severalfold, and it was not uncommon for age estimates to have been off by a factor of 10. Although we have recently learned much about the ages of young deposits and deformation, we still have a long way to go, for one of the greatest constraints in our understanding active tectonism is accurate and reliable dating in order to define rates of past deformation and times of past earthquakes (Allen, Chapter 9, this volume).

An appreciation of the amount of dating control needed is illustrated in Figure 13.1, which shows one model of fault activity through time. Predictions based on such a model require multiple dates to determine (1) the slope of the line shown as "accumulation rate," (2) the interval between fault movements, and (3) the time since the last movement. To define a fault history involving multiple events, at least one age is needed to define each event. This kind of model depends on the assumption of a constant accumulation or slip rate; dating control spanning different time intervals is needed to know if the assumption of a constant slip rate is warranted.

More than one age determination is required to establish reliable age control. Numerical ages are preferred, but relative-dating and correlation methods are important because they can provide age control in the absence
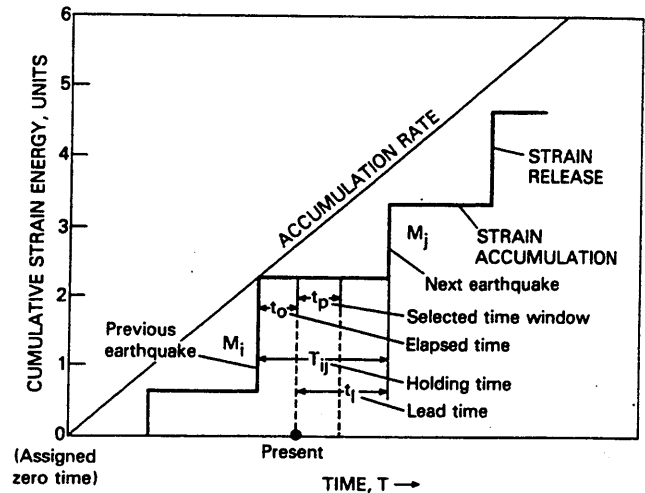

FIGURE 13.1 Diagram of the earthquake-generation process of Cluff et al. (1980) showing importance of time (horizontal scale) in earthquake history and prediction. In order to predict the time of a future earthquake based on this model, note how much dating control is needed to define holding time, accumulation rate (similar to slip rate), and elapsed time, even for this example in which accumulation rate is assumed to be constant.

of numerical techniques, or they can be used to evaluate the numerical ages, which can be subject to large nonanalytical errors. Surficial geologic studies and local time-calibrated stratigraphies are vital in the study of active tectonism, both to provide dating control and to evaluate the reliability of specific age estimates for tectonic events.

OVERVIEW OF DATING METHODS

About 26 different dating methods can be used in dating active tectonism. Table 13.1 categorizes these methods as primarily numerical, relative dating, or correlation (Table 13.1). The numerical methods are based on processes that do not require further calibration. Relative-dating methods are applied to a local sequence of deposits that differ in age but are similar in other characteristics, such as a sequence of glacial moraines or a flight of alluvial terrace deposits. Relative-dating methods provide information on the magnitude of age differences between stratigraphic units. If calibrated, relative-dating methods can be used to estimate numerical ages. This normally requires calibration by numerical methods and an understanding of the process being measured and its relevant history (e.g., temperature, precipitation). The correlation methods do not directly yield a numerical age, but if a feature can be correlated with an event whose age is known, such as a volcanic ash

TABLE 13.1 Classification of Methods Applicable to Dating Active Tectonism[a]

Numerical Methods			Relative Dating Methods		Correlation Methods
1. Annual	2. Radiometric	3. Other Radiologic	4. Simple Process	5. Complex Processes	6. Correlation
1. *Historical records*	4. *Carbon-14*	8. *Uranium trend*	11. *Amino-acid racemization*	15. *Soil development*	21. *Stratigraphy*
2. Dendrocronology	5. *Uranium series*	9. *Thermoluminescence and electron-spin resonance*	12. *Obsidian hydration*	16. *Rock and mineral weathering*	22. *Tephrochronology*
3. Varves	6. *Potassium-argon*		13. Tephra hydration	17. *Progressive landform modification*	23. *Paleomagnetism*
	7. *Fission track*		14. Lichenometry		24. *Fossils and artifacts*
		10. *Cosmogenic isotopes other than carbon-14 (^{10}Be, ^{36}Cl, ^{26}Al, and others)*		18. Deposition rate	25. Stable isotopes
				19. Geomorphic position and incision rate	26. Tektites and microtektites
				20. Deformation rate	

[a]All methods listed are briefly described in Table 13.2. Methods given in italics are discussed in the text.

eruption or a paleomagnetic reversal, precise age control can be obtained.

A dating technique, whether it be primarily a numerical, relative-dating, or correlation method, may be converted to the other two categories of methods (Table 13.1). For example, the relative-dating methods of amino-acid racemization or soil development can also serve either as local correlation techniques or, if calibrated by numerical dating, as numerical techniques.

Table 13.2 briefly summarizes 26 different dating methods noting their general applicability to studies of active tectonism, the age range of each method and the *optimum* accuracy within parts of this age range, and the basis of the method and the key problems in its use. The six columns (Table 13.1) are discussed in the next six sections. Beyond those given in Table 13.2 , the criteria for selecting individual methods for discussion include at least two of the following: (1) the method is particularly applicable to dating active tectonics, (2) the method provides a good illustration of the six general categories (columns of Table 13.1), and (3) the method has complexities or problems that merit discussion.

After this manuscript was completed, two books on Quaternary dating methods became available (Mahaney, 1984; Rutter, 1985). The reader interested in more extensive description and references to the literature may wish to consult these books.

ANNUAL METHODS

Annual methods (Table 13.1, column 1), generally accurate to the nearest year, provide the most precise dating of active tectonism. But excepting varve chronology, annual methods span too short a time interval to assess active tectonism, particularly in the western hem-

isphere. Only limited use has been made of dendrochronology and varve chronology.

In the western hemisphere, historical records of faulting are restricted to about 200 yr (Bonilla, 1967). Based on the long historical records of seismicity from China (3000 yr) and Japan and the Middle East (2000 yr), Allen (1975, p. 1041) concluded that historical seismicity there shows "surprisingly large long-term temporal and spatial variations. The very short historical record in North America should, therefore, be used with extreme caution in estimating possible future seismic activity. The geologic history of late Quaternary faulting is the most promising source of statistics on frequency and location of large shocks."

RADIOMETRIC METHODS

Because radiometric methods (Table 13.1, column 2) yield accurate numerical ages, samples for such dating are searched for in geologic studies of active tectonism. In many cases datable materials cannot be found. Additionally, radiometric methods may be subject to major errors and should be evaluated in their geologic context by other methods that, although not as precise, will normally be a valid indicator of the general age.

Carbon-14 Dating

Carbon-14 dating is generally the most precise and applicable numerical method for dating prehistoric faulting. Indeed, the chronology of the late Quaternary and particularly the Holocene (past 10 ka) is based on this method (for review, see Grootes, 1983). The analytical uncertainty is generally less than a few percent.

Two applications of carbon-14 dating to active tec-

TABLE 13.2   Summary of Quaternary Dating Methods and Their Applicability to Dating Active Tectonism
(from Colman and Pierce, 1979)

Method	Applicability	Age Range and Optimum Resolution					Basis of Method and Remarks
		10^2	10^3	10^4	10^5	10^6	
1. Historical records	X to XXX	========					Requires preservation of pertinent records; applicability depends on quality and detail of records. Limited to several hundred years in western hemisphere.
2. Dendrochronology	XX	=======					Requires either direct counting of annual rings back from present or construction of a chronology based on variation in annual ring growth. Restricted to areas where trees of the required age and (or) environmental sensitivity are preserved.
3. Varve chronology	X	=======+++					Requires either direct counting of varves back from present or construction of a chronology based on overlapping successions of continuous varved lake sediments. Subject to errors in matching separate sequences and to misidentification of annual layers.
4. Carbon-14	X to XXX	o• —+++======?					Depends on availability of carbon. Based on decay of ^{14}C, produced by cosmic radiation, to ^{14}N. Subject to errors due to contamination, particularly in older deposits and in carbonate material (such as mollusk shells, marl, soil carbonate). See text.
5. Uranium series	XX		•• —————++++—				Used to date coral, mollusks, bone, cave carbonate, and carbonate coats on stones. Potentially useful in dating travertine and soil carbonate. A variety of isotopes of the U-decay series are used including ^{230}Th/^{234}U (most common and method described to left), ^{234}U/^{238}U (with a range back to 600,000 yr), ^{231}Pa/^{235}U (10,000-120,000 yr), U-He (0-2 m.y.), and ^{226}Ra/^{230}Th (<10,000 yr). Errors due to the lack of a closed chemical system are a common problem, especially in mollusks and bone.
6. Potassium-argon	X			•••——+++++			Directly applicable only to igneous rocks and glauconite. Requires K-bearing phases such as feldspar, mica, and glass. Based on decay of ^{40}K to ^{40}Ar. Subject to errors due to excess argon, loss of argon, and contamination.
7. Fission track	X			•••———+++			Directly applicable only to igneous rocks (including volcanic ash); requires uranium-bearing material (zircon, sphene, apatite, glass). Based on the continuous accumulation of tracks (strained zones) caused by recoiling U fission products. Subject to errors due to track misidentification and to track annealing.
8. Uranium trend	XXXX		ooo•• ————••				Based on open-system flux of uranium through sediment and soil; ^{238}U, ^{234}U, ^{230}Th, and ^{232}Th must be measured on about five different samples from a given aged deposit and a isochron constructed to determine age.
9. Thermoluminescence (TL) and electron-spin resonance (ESR)	XXXX		ooo•••••• ——————••				Based on displacement of electrons from parent atoms by alpha, beta, and gamma radiation. Applicable to feldspar and quartz in sediments and carbonate in soils. TL based on amount of light released as sample is heated compared with that released after known radiation dose. TL precision better than indicated for ceramics in 400-10,000-year range.
10. Cosmogenic isotopes other than carbon-14	X	—?–?–?–?–?–?–?–?–?					Dating methods analogous to ^{14}C-dating are based on the cosmogenic isotopes (half-life in hyears in parentheses) ^{32}Si (300), ^{41}Ca (1.3 × 10^5), ^{36}Cl (3.08 × 10^5), ^{26}Al (7.3 × 10^5), ^{10}Be (1.5 × 10^6), ^{129}I (1.6 × 10^7), and ^{53}Mn (3.7 × 10^6). Dating requires knowledge of the generation rates, flux rates, and retention efficiency of the deposit dated. These radio-isotopes occur in very low abundances and are measured by accelerator mass spectrometry.

TABLE 13.2 Continued

Method	Applicability	Age Range and Optimum Resolution					Basis of Method and Remarks
		10^2	10^3	10^4	10^5	10^6	
11. Amino acid racemization	XX	●●●●●●●●●●●●●—————————●●●					Requires shell or skeletal material. Based on release of amino acids from protein and subsequent inversion of their stereoisomers. Shells tend to be more reliable than bone, wood, or organic-rich sediment. Is strongly dependent on other variables, especially temperature and leaching history. Commonly used as a relative dating or correlation technique, but yields numerical ages when calibrated by other techniques.
12. Obsidian hydration	X	——————————————————●●●					Based on thickness of the hydrated layer along obsidian crack or surface formed during given event. Age proportional to the thickness squared. Calibration depends on experimental determination of hydration rate or numerical dating. Subject to errors due to temperature history and variation in chemical composition.
13. Tephra hydration	X	oooooooo●●●●●●●●					Requires volcanic ash. Based on the progressive filling of bubble cavities in glass shards with water. Subject to the same limits as obsidian hydration, plus others, including the geometry of ash shards and bubble cavities.
14. Lichenometry	X to XXX	————●●●●					Requires exposed, stable rock substrates suitable for lichen growth. Most common in alpine and arctic regions, where lichen thallus diameter is proportional to age. Subject to error due to climatic differences, lichen kill, and misidentification. The limit of the useful range varies considerably with climate and rock type.
15. Soil development	XXXX	ooooo●●●●●● ————————●●●					Encompasses a number of soil properties that develop with time, all of which are dependent on other variables in addition to time (parent material, climate, vegetation, topography). Is most effective when these other variables are held constant or can be evaluated. Precision varies with the soil property measured; for example, accumulation of soil carbonate locally yields age estimates within ±20 percent.
16. Rock and mineral weathering	XX	ooooo●●●●●● ————————●●●					Includes a number of rock and mineral-weathering features that develop with time, such as thickness of weathering rinds, solution of limestone, etching of pyroxene, grussification of granite, and buildup of desert varnish. Has the same basic limitations as soil development. Precision varies with the weathering feature measured.
17. Progressive landform modification	XXX	ooooooooo●●●●●●●●●ooo					In addition to time, depends on factors such as climate and lithology. Depends on reconstruction of original landform and understanding of processes resulting in change of landform, including creep and erosion.
18. Rate of deposition	XX	——?——?——?——?—?——					Requires relatively constant rate of sedimentation over time intervals considered. Numerical ages based on sediment thickness between horizons dated by other methods. Quite variable in alluvial deposition.
19. Geomorphic position and incision rate	XXX	ooooooooo●●●●●●● —?—?—					Geomorphic incision rates depend on stream size, sediment load, bedrock resistance to erosion, and uplift rates or other base-level changes. If one terrace level is dated, other terrace levels may be dated assuming constant rate of incision.
20. Rate of deformation	XXX	●●?●●?●●?●●?●●?●●?●●?●●?●●?					Dating assumes deformation rate constant over interval of concern and requires numerical dating for calibration. At spreading centers and plate boundaries, nearly constant rates may be valid for intervals of millions of years.

TABLE 13.2   Continued

Method	Applicability	Age Range and Optimum Resolution					Basis of Method and Remarks
		10^2	10^3	10^4	10^5	10^6	
21. Stratigraphy	XXXX						Based on physical properties and sequence of units, which includes superposition and inset relations. Depends on the establishment of time equivalence of units; deposition of Quaternary units normally occurs in response to cyclic climatic changes.
22. Tephrochronology	X						Requires volcanic ash (tephra) and unique chemical or petrographic identification and (or) dating of the ash. Very useful in correlation because an ash eruption represents a virtually instantaneous geologic event.
23. Paleomagnetism	XX						Depends on correlation of remnant magnetic vector, which includes polarity, or a sequence of vectors with a known chronology of magnetic variation. Subject to errors due to chemical magnetic overprinting and physical disturbance.
24. Fossils and artifacts	XX						Depends on the availability of fossils, including pollen, and artifacts. Resolution depends on the rate of evolution or change of organisms or cultures and on calibration by other techniques. Subject to errors due to misidentification and interpretation.
25. Stable isotopes	X						Depends on correlation of the sequence of isotopic changes with an age-controlled master chronology. Oxygen isotopic record is useful in deep-sea and ice-cap cores and perhaps in cave deposits.
26. Tektites and microtektites	X						Depends on recognition and dating of glassy material (tektites) formed during impact of extraterrestrial masses. Tektites are scattered over large areas, such as the Australo-Asian tektite field, formed about 700 ka.

RESOLUTION DEPENDS ON RECOGNITION OF FEATURE AND ACCURACY OF DATING THAT FEATURE

APPLICABILITY

XXXX, nearly always applicable   XX, often applicable
XXX, very often applicable   X, seldom applicable

OPTIMUM RESOLUTION

======, <2 percent   ••••••, 25-75 percent
++++++, 2-8 percent   oooooo, 75-200 percent
------, 8-25 percent

tonism illustrate powerful applications of this method. Along the San Andreas Fault 55 km northeast of Los Angeles at Pallet Creek, about 50 carbon-14 ages date 11 episodes of faulting in the 1700 yr prior to the 1857 historical rupture and define an average recurrence interval of about 145 yr (Figure 13.2; Sieh, 1984). For the south Boso Peninsula of Japan, carbon-14 dating defines four stepwise uplifts of land relative to sea level in the last 7000 yr (Figure 13.3). Shimazaki and Nakata (1980) concluded that the offset history supports a time-predictable recurrence model; that is, the larger the amount of the coseismic slip, the longer the interval before the next earthquake (Figure 13.3).

Carbon-14 ages may be in error by much more than the analytical uncertainty. Because of the extensive use of carbon-14 dating in studies of active tectonism, consideration should be given to the following three types of carbon-14 dating problems.

Fluctuations in Atmospheric Carbon-14   Based on carbon-14 dating of tree rings whose absolute age is known, carbon-14 ages deviate from actual ages by amounts that are significant for some tectonic studies. For example, in the interval from 5000 to 8000 yr ago, carbon-14 ages are about 500-900 yr too young (Klein *et al.*, 1982). In the late Holocene, fluctuations in atmospheric carbon-14 introduce significant uncertainty in dating tectonic events (Figure 13.4). For example, a carbon-14 age of 150 + 20 ya (years before AD 1950) only defines an age in the interval from 0 to 295 *calendar* years before AD 1950 (Klein *et al.*, 1982, Table 2).

Contamination with Old Carbon   Independent of the age of the sample, the effect of contamination with old carbon is constant (Figure 13.5, upper left half). Regardless of whether a sample is 1 or 30 ka, incorporation of 10 percent "dead" carbon will make ages 800 yr too

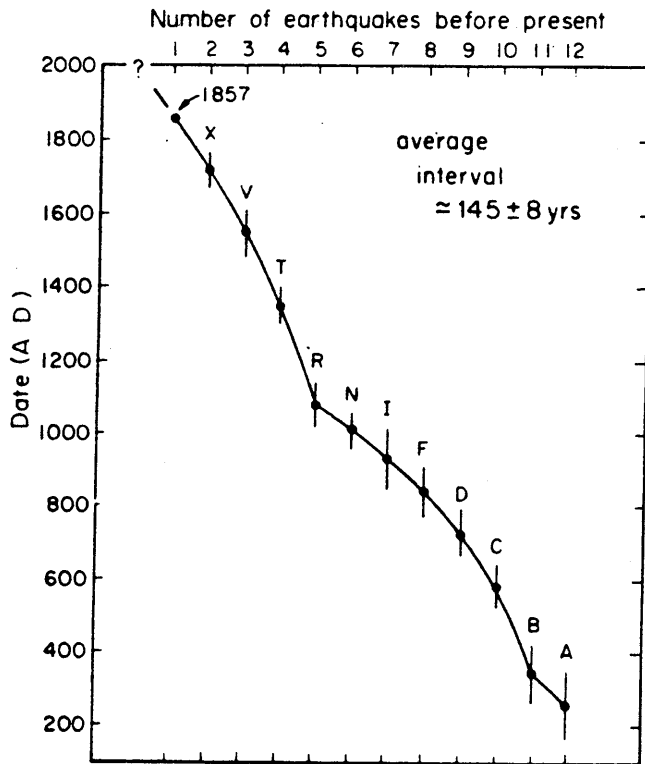## Number of earthquakes before present

FIGURE 13.2 Ages of faulting events (letters) on San Andreas Fault at Pallet Creek (from Sieh, 1984). Ages are based on about 50 carbon-14 dates and detailed trench mapping.

old. Old carbon may contaminate a sample in two ways. First, detrital carbon, such as that from coal of pre-Quaternary age which contains no carbon-14 or that from humic soil material which may have an age of several thousand years, may be incorporated in a sample. Second, plants and animals living underwater can incorporate lower activity carbon from CO_2 in the water either because the water is old or because it has bicarbonate from old rocks. For marine mollusks from the North Atlantic, the age of CO_2 in ocean water increases ages by 400 to 750 yr (Mangerud and Gulleksen, 1975).

Contamination with Young Carbon Contamination with recent carbon can alter ages greatly. Samples whose ages are beyond the range of carbon dating (>75 ka) that are contaminated with only half a percent of recent carbon will yield an age of about 40 ka (Figure 13.5, lower right half). Even the most exacting of analyses can be in error: a carbon-14 enrichment age of 71 ka (representing only 0.014 percent of the original carbon-14 activity) was thought to date the Salmon Springs glaciation of northwest Washington State (Stuiver *et al.*,

1978) until associated ash deposits were fission-track dated at 700 and 800 ka (Easterbrook *et al.*, 1981).

Contamination with younger carbon may be responsible for many of the finite carbon-14 ages in the 20- to 70-ka range. Contamination of carbon samples with recent carbon produces effects that are not generally appreciated (Figure 13.5). Examination of this nonlinear effect also should provide a caution about assuming that "consistency" in age results necessarily is an argument for the validity of carbon-14 ages. For example, the consistency of many dates falling in the 25- to 40-ka range may only reflect contamination of samples older than about 50 ka with the equivalent of 0.5-2 percent of recent carbon (Figure 13.5). Several hundred carbon dates in the 25- to 40-ka range have been obtained from coastal deposits in the eastern United States. Many researchers (referenced in Bloom, 1983) have concluded that these samples date a mid-Wisconsin high stand of sea level, in part based on the apparent "consistency" of a large number of dates in this age range. After thorough analysis of this problem, Bloom (1983, pp. 215-218) concluded that these ages are invalid. Amino-acid racemization studies on mollusks asssociated with samples yielding caron-14 dates in the 25- to 40-ka range also indicate that the carbon-14 dates are erroneously young (Belknap, 1984).

Samples may be contaminated by in situ additions of younger carbon. Soil carbonate, mollusks, or corals are particularly susceptible to addition of young carbon, especially when subject to repeated wetting or drying. Contamination by microorganisms incorporating young carbon may occur either before or after a sample has been collected. Marine cores stored for 5 yr were found to be contaminated by enough terrestrial bacteria to account for 5-10 percent contamination with modern carbon (Geyh *et al.*, 1974). In-place contamination of samples is not well studied, but it may be possible if microbial activity consumes CO_2 from air or HCO_3^- from water with a higher carbon-14 activity than the age of the sample. For example, methanogens participate in terminal stages of the degradation of organic matter, living on and presumably incorporating carbon dioxide and hydrogen produced by anaerobic bacteria into their tissue (see Maugh, 1977).

Extra care should be taken in order to minimize contamination with recent organic material during sampling and sample preparation. In addition, samples should be examined for visible contamination, particularly by roots. Removing modern roots will not, of course, remove contamination caused by older, largely decayed roots. Common sample pretreatment before carbon-14 dating removes base-soluble fulvic acids and acid-soluble humic acids, leaving a residue called
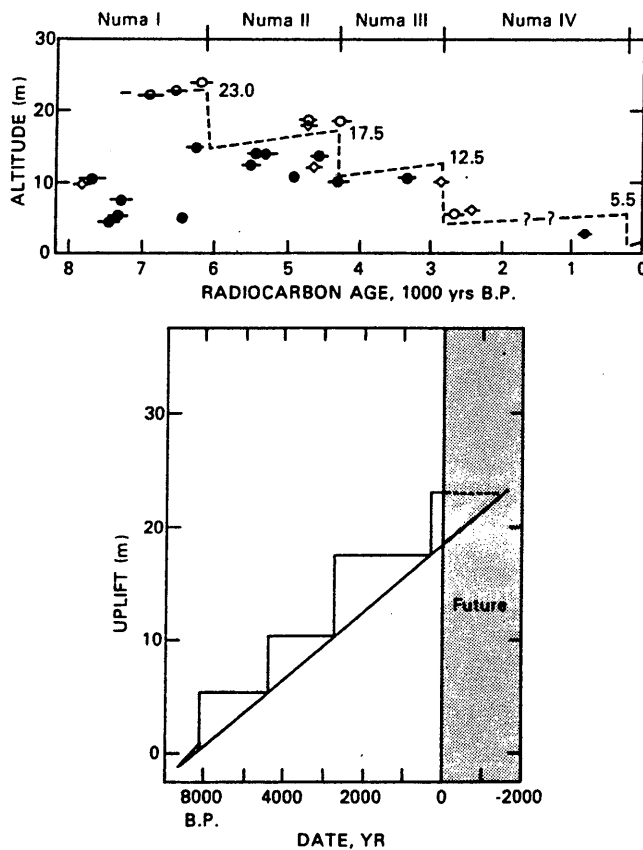
FIGURE 13.3   Four stepwise uplifts of the coast of the southern Boso Peninsula, Japan, determined by about 25 carbon-14 dates (from Shimazaki and Nakata, 1980). The open, half-closed, and closed circles indicate samples from above, near, and below the former sea level, respectively. Lower part of figure shows cumulative uplift versus time; line through corners of stairstep plot shows that uplift, inferred to be caused by coseismic faulting, conforms to a time-predictable model.

FIGURE 13.4   Carbon-14 age as a function of dendrochronological age for the past 1000 yr (from Stuiver, 1982). Note deviations from concordance line that have a 100-200-yr period.
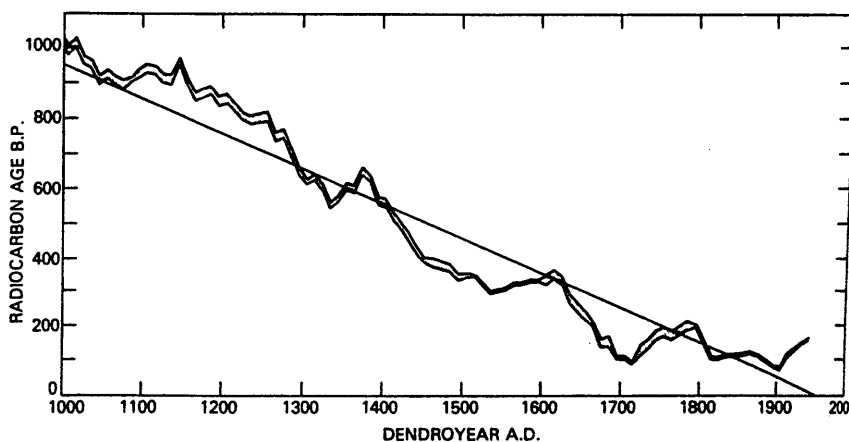
humin or humate. Such pretreatment is commonly employed, but it does not remove all forms of contamination by younger carbon. For example, dating studies by Goh *et al.* (1977) have obtained ages as young as 17,750 ± 2050 ya on humin from deposits whose "best" carbon-14 ages are *more than* 40,600 ya.

Uranium-Series Dating

The $^{230}Th/^{234}U$ disequilibrium method is the most commonly used dating technique of the many based on the radioactive decay series of uranium (Table 13.2; Ivanovich and Harmon, 1982). Because uranium is
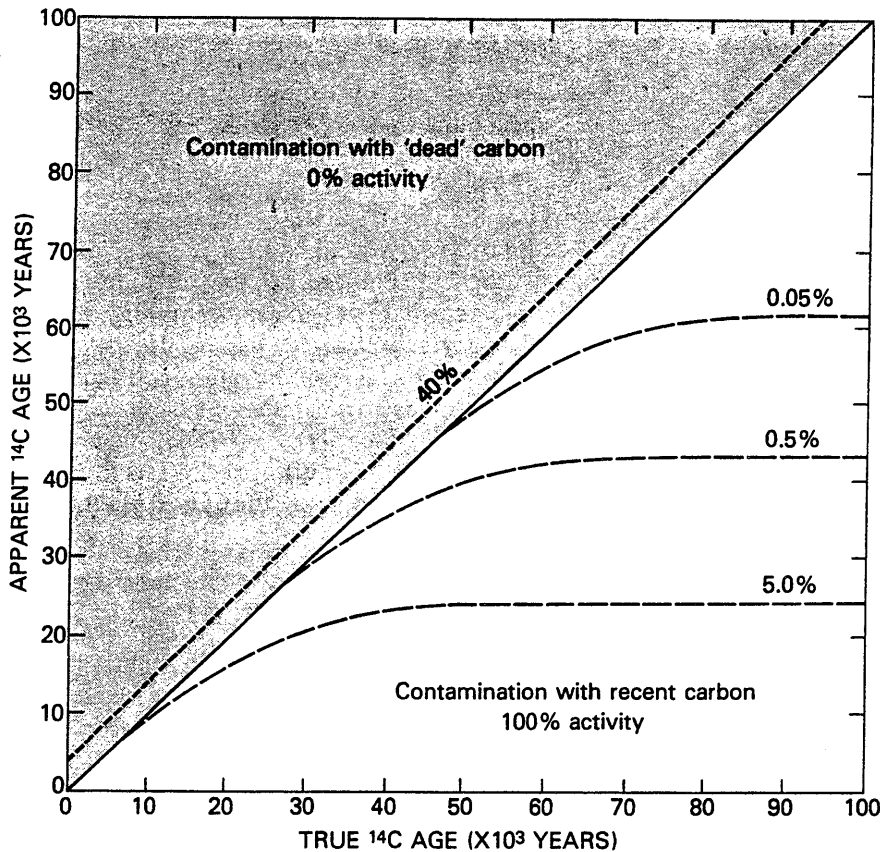
FIGURE 13.5 Unequal effects of contamination with recent and dead carbon on carbon-14 ages (from Grootes, 1983). For contamination with dead carbon (shaded area), effect is a simple ratio. But for samples with true ages older than a few tens of thousands of years, the apparent age can be dictated by only small amounts of contamination with recent carbon.

much more soluble than thorium, materials precipitated from solution such as corals, mollusks, calcic soils, carbonate deposits in caves and fault zones, and fossil bones are greatly enriched in uranium with respect to thorium. This provides a system in which radioactive growth of ^{230}Th is a function of time until it reaches a steady-state relation with its parent ^{234}U. The most reliable application of the method is to pure cave carbonate and to samples of corals in which the original aragonite is unaltered. For the time interval of 50 ka to about 300 ka, age control for deformation of coastal areas is largely based on uranium-series dating of corals.

For corals and cave deposits, uranium is incorporated in the sample at the time of deposition and, under appropriate conditions, the sample acts as a closed system with respect to uranium. Dating problems generally result from migration of uranium after initial deposition or contamination with thorium in detrital material at the time of deposition. Living mollusk shells or bones contain only about a tenth of the uranium that becomes incorporated after burial. If ages are calculated on the basis of a closed system, the uranium in the sample should ideally have been introduced in a time interval that is short relative to the age of the sample, and none of this secondary uranium should have been leached away. If uranium is incorporated at later times in the history of the sample, the apparent Th/U age is too young. Conversely, if uranium is leached during the later history of a sample, the apparent Th/U age is too old. Kaufman et al. (1971) concluded that for samples of known age, ^{230}Th/^{234}U dating of mollusks gave ages within their analytical uncertainty no more than half the time.

For active tectonism in semiarid and drier areas, ^{230}Th/^{234}U dating of carbonate may date fault movements. Soils may contain carbonate coats on the undersides of stones that can date faulted alluvial surfaces. Along the Arco fault scarp in central Idaho, a surface vertically offset about 19 m by faulting has 1-cm-thick carbonate coats that can be subdivided into outer, middle, and inner parts (Pierce, 1985). Analyses of both the soluble (carbonate) and insoluble (detrital residue) fractions from these layers yield ages as shown in Figure 13.6
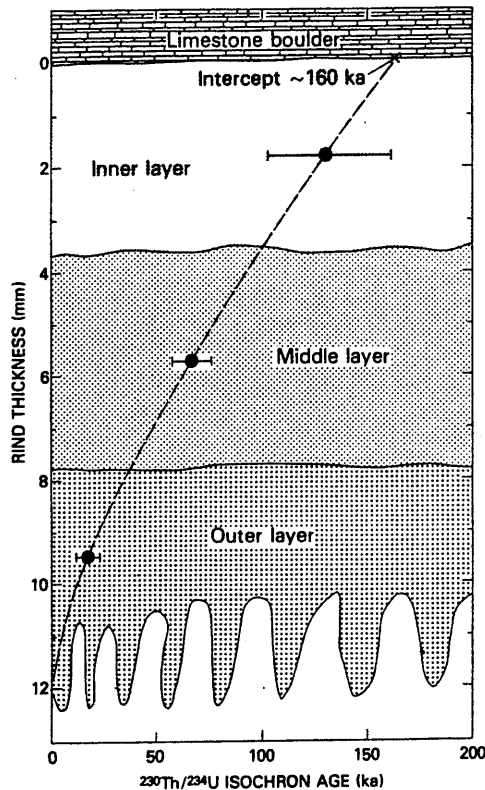
FIGURE 13.6 Three stratigraphically consistent ^{230}Th/^{234}U ages from a stratified carbonate coat. This plot of age versus thickness defines an age of about 160 ka for an alluvial fan surface offset about 19 m along the same range-front fault, but 50 km south of the part offset during the 1983 Borah Peak earthquake, central Idaho. ^{230}Th/^{234}U isochron ages from Szabo and Rosholt (1982, Figure 10.5) are plotted at midpoint of sampled layer. The carbonate coats form on the underside of stones in the soil on an alluvial fan.

(Szabo and Rosholt, 1982). These ages are stratigraphically consistent and indicate a time span of 160 ka for 19 m of offset and a long-term slip rate of about 1 m/ka.

Potassium-Argon Dating

The potassium-argon (K-Ar) method is limited in its applicability to dating active tectonics by its primary use with igneous rocks and general lack of resolving power for rocks younger than a few tens of thousands of years. Nevertheless, most of the correlation methods (Table 13.1, column 6) and calibration of many of the relative-dating methods (Table 13.1, columns 4 and 5) depend on K-Ar dating for their age control. More important to the study of active tectonism, both the paleomagnetic time scale, which was critical in establishing the theory of plate tectonics, and the relative rates of plate motions are largely based on K-Ar dating.

Fission-Track Dating

Fission-track dating is generally limited to rhyolitic volcanic rocks older than about 100 ka and is commonly better than the K-Ar method for dating volcanic ash.

Fission-track dating can also be used in areas of high relief and rapid uplift to estimate long-term rates of uplift. Because fission tracks in apatite anneal if warmer than about 120°C, fission-track dating of apatite determines the time a rock has been below this temperature and consequently at relatively shallow depths. If the geothermal gradient is known, the rate of uplift and erosion of a mountainous area can thereby be determined. Using this method, Naeser et al. (1983) estimated that the late Cenozoic rate of uplift of the Wasatch Mountains has averaged 0.4 m/ka over the past 10 Ma (million years).

OTHER RADIOLOGIC METHODS

Other radiologic methods (Table 13.1, column 3) involve radioactive processes but may also depend on other nonradioactive processes that must be either estimated or accounted for by calibration using other numerical methods.

Thermoluminescence (TL) and Electron-Spin-Resonance (ESR) Dating

Thermoluminescence (TL) dating (Wintle and Huntley, 1982) may be widely applicable to dating active tectonics, but the method has been used rarely in the United States. Owing to the effects of radiation, many minerals emit light when progressively heated, and the changing intensity of light emission yields a glow curve. A starting point for buildup of TL can be the time of crystallization of carbonate in a soil, the growth of a shell, the firing of a ceramic, the eruption of a lava flow, or the time of burial after exposure to sunlight. The glow curve becomes stronger the greater and longer the radiation exposure. The flux of radiation is related to the modern content of uranium, thorium, and potassium. The response of the dosimeter grains is calibrated by artificial irradiation (alpha, beta, and gamma) and measurement of the induced glow curves. Several hours of exposure to sunlight "zeros" the TL in grains of quartz and feldspar, which are nearly ubiquitous in surficial deposits. Thus, many surficial deposits offset by faulting are potentially datable by TL.

Because water adsorbs some of the gamma radiation, the amount of water present over the history of the sample needs to be measured or estimated and its effect on the in situ sample calculated. Also, radiogenic isotopes

are assumed not to have been added to or leached from the sample. Wintle and Huntley (1982) listed criteria for evaluating TL dates of sediment and discussed problems that merit further research.

TL dating of loesses has yielded reasonable results. Late Pleistocene loess in Germany yielded TL ages that are stratigraphically consistent and concordant with carbon-14 ages of an associated ash (Wintle and Brunnacker, 1982; Figure 13.7).

Electron spin resonance (ESR) dating is similar to TL dating in that a mineral acts as a dosimeter for local radiation, but differs in the feature measured and the method of measurement. ESR dating of corals from marine terraces of Japan yielded results in good agreement with carbon-14 (2-4 ka) and $^{230}Th/^{234}U$ (40->200 ka) dating (Ikeya and Ohmura, 1983).

Uranium-Trend Dating

Uranium-trend dating is an isochron-type method for dating Quaternary sediments and soils (Rosholt, 1980; Szabo and Rosholt, 1982). Rather than requiring a closed system as do most uranium-series methods, this method depends on a flux of uranium (mostly ^{238}U) through sediments and the consequent embedding of recoil products ^{234}U and ^{230}Th in the sediments. The method can be used on almost all sedimentary materials and has produced generally reasonable ages (Rosholt, 1980). The calibration of the method initially depended on ages determined by other methods, but ages can now be calculated using the established calibration. The method is expensive, requiring determination of ^{238}U, ^{234}U, ^{230}Th, and ^{232}Th for five or more samples from a given deposit. Although widely applicable, the method has so far experienced limited use because of its newness, complexity, and cost.

Cosmogenic Isotopes Other Than Carbon-14

Similar to carbon-14, several other radiogenic isotopes are generated by cosmic-ray bombardment and may be useful in tectonic studies. Dating rationales exist for ^{32}Si, ^{41}Ca, ^{36}Cl, ^{26}Al, ^{10}Be, ^{129}I, and ^{53}Mn, which are analyzed by accelerator mass spectrometry (half-lives given in Table 13.2).

Beryllium-10 is produced by cosmic-ray bombardment and is carried to the Earth's surface by rain and dust. Pavich *et al.* (1984) showed that ^{10}Be is adsorbed onto clays in soils and systematically increases in abundance with soil age for at least the first 100 ka of soil development. More research is needed to evaluate this method for dating surface and buried soils.

RELATIVE-DATING METHODS, SIMPLE PROCESS

These methods (Table 13.1, column 4) do not depend on radiogenic processes but are based on relatively simple chemical or biological processes whose rates are related to controlling variables such as temperature and chemical composition or species effects.
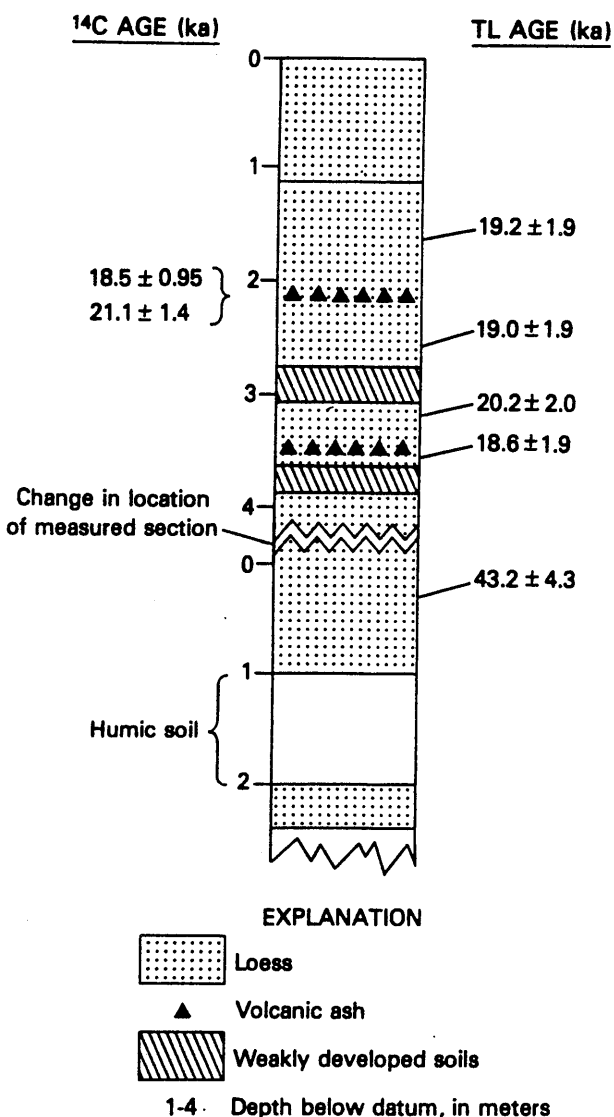

FIGURE 13.7 Thermoluminescence (TL) dating of loess deposits in West Germany showing that the TL ages are both stratigraphically consistent and concordant with existing carbon-14 ages on the volcanic ash that was dated elsewhere (redrawn from Wintle and Brunnacker, 1982).

Obsidian-Hydration Dating

Obsidian hydration has been used to date the last two glaciations in the Rocky Mountain region (Pierce *et al.*, 1976). If temperature and chemical composition are constant, hydration thickness increases proportional to the square root of time. Figure 13.8 shows the increase in hydration with time as determined by the hydration thicknesses of two K-Ar-dated rhyolite flows and carbon-14-dated recessional deposits. The deposits of the next to last, or Bull Lake, glaciation date at about 140 ka (Pierce *et al.*, 1976). This age for the Bull Lake glaciation is about 5 times older than the age considered correct 20 yr ago. The importance of the dating at West Yellowstone to studies of active tectonism is that these ages can be inferred for many deposits throughout the western United States if they can be correlated with

those at West Yellowstone on the basis of criteria such as soil development, morphologic changes, and weathering rinds (see Figure 13.9).

Amino Acid Racemization

Amino acid racemization (and epimerization) has provided important age information for deciphering late Quaternary deformation along the West Coast of the United States (Lajoie, Chapter 6, this volume). Because racemization rates for a given species depend on temperature and a kinetic model (Wehmiller, 1982), the method works best if calibrated by numerical methods. On the California coast, uranium-series dating of corals has provided a few calibration points, but even with this calibration the amino acid ratios on mollusk samples did not allow distinction between three global sea-level culminations known from elsewhere to date at about 80, 95, and 125 ka. The problem of distinguishing these three high-sea stands has been resolved by combined studies using amino acid and uranium-series dating, temperature gradients along the coast, and paleontological identification of cool (oxygen isotope substages 5a or b) and warm (substage 5e) faunas (Lajoie, Chapter 6, this volume).

RELATIVE-DATING METHODS, COMPLEX PROCESSES

This group of dating methods includes some of the most widely applicable methods (Table 13.1, column 5). Numerical ages can be empirically estimated by these methods. Rigorous evaluation of these complex methods would require modeling of each process and quantification of their relative effects. Nevertheless empirical quantification has been done, and some age estimates based on these methods (Table 13.1, column 4) may be more reliable than, if not so precise as, some carbon-14 ages.

Rock and Mineral Weathering

Rock and mineral weathering (Table 13.1, column 5) includes such relative-dating techniques as mineral grain etching, seismic velocities in weathered stones, pitting on stone surfaces, and weathering rinds.

Weathering rinds on basaltic and andesitic stones from the B horizons of soils have yielded age information on middle and late Quaternary deposits at seven different areas in the western United States (Figure 13.9; Colman and Pierce, 1981). Multiple measurements of rind thicknesses from a given stratigraphic unit are consistent; and, for a succession of deposits, rind
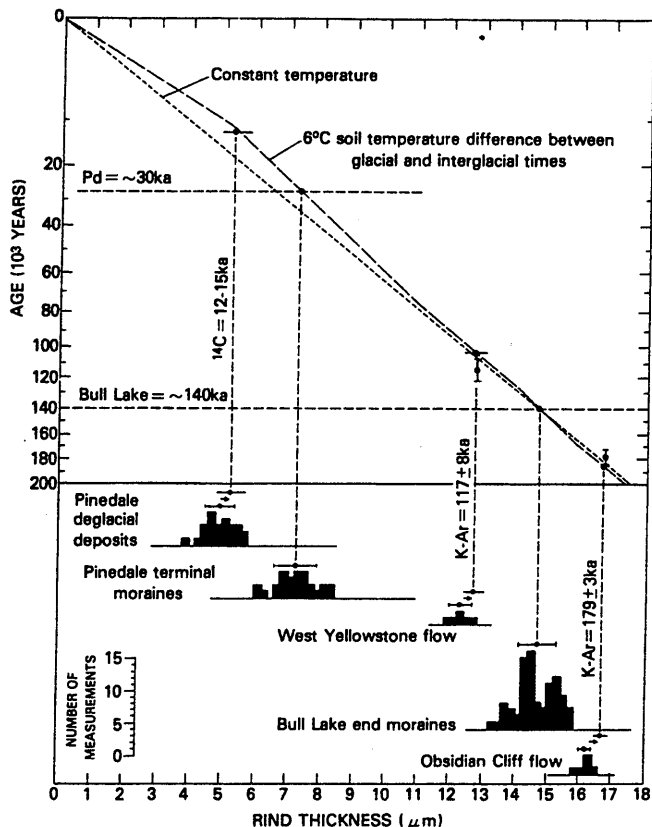

FIGURE 13.8 Obsidian-hydration dating of the Pinedale and Bull Lake Glaciations near West Yellowstone, Montana (from Pierce *et al.*, 1976). Dashed line shows increase in hydration thickness with age based on hydration thickness measured on deposits dated by K-Ar or ¹⁴C methods. Above histograms, short lines with dots are means and standard deviations of hydration-thickness measurements, some of which are offset (small arrows) to account for small temperature differences between localities.
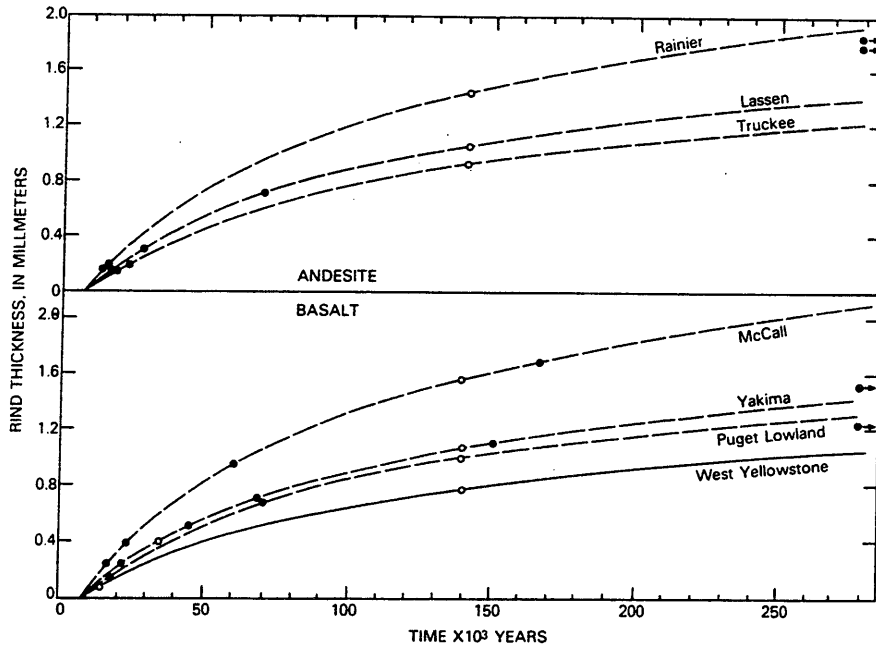
FIGURE 13.9 Use of weathering rinds to date and correlate glacial deposits in seven areas in the western United States. As shown by decreasing curvature of lines, rind thickness is assumed to increase logarithmically with time (from Colman and Pierce, 1984). Open circles are for deposits independently dated at West Yellowstone and for deposits correlated on basis of soils and other criteria with 140,000-yr-old deposits at West Yellowstone. Solid circles are for other glacial deposits plotted on the appropriate curve according to their rind thickness.

thickness increases with stratigraphic age. Local calibration by numerical dating indicates that rind thicknesses increase logarithmically with time. Based on a logarithmic increase in rind thickness and on the assumption that deposits with a certain relative moraine form and degree of soil development correlate with deposits of the Bull Lake glaciation at West Yellowstone (oxygen-isotope stage 6), ages can be estimated for all the deposits in seven glacial successions in the western United States. Deposits representing isotope stages 2 and 6 apparently are present in all areas sampled, but moraines representing stages 3 and 4 were apparently obliterated in many areas by glaciation during stage 2 (Figure 13.9).

Recent developments in the study of desert varnish suggest that systematic changes in varnish properties, such as decreasing ratios of leachable cations to manganese, occur with time (Dorn, 1983). With local calibration, age estimates on faults in desert environments may be obtained by this method.

Soil Development

On land, soil development is nearly always pertinent to estimating the age of deformation. Soil development is a function of climate, parent material, organisms, topography, and time. If all the factors other than time can be held constant, the effect of time on soil development can be isolated and used to calibrate soil development with time at other sites.

Recently, Harden (1982) devised the soil "Profile Development Index" based on quantification of standard field descriptions of soils, including such features as color, clay content, texture, and soil-horizon thickness. Each of 10 or so soil properties is objectively quantified for each soil horizon on a scale that goes from zero to the maximum observed development. For the Merced, California, area, an individual soil property such as rubification (reddening and brightening of soil colors) shows a progressive increase with time from 100 yr to more than 1 m.y. (rubification, Figure 13.10A). The Profile Development Index (Figure 13.10B) combines several soil properties such as texture, pH, dry consistence, and soil structure and shows the cumulative effect of the development of many soil properties with time. Dating by this soil Profile Development Index is improved by using only soil properties that show the highest correlation with age (see Index of four best properties, Harden and Taylor, 1983).

Although calibration of soil Profile Development Index with age is best restricted to local areas where climate and parent material are the same, soils from four different areas of the United States appear to show similar Profile Development Index values with increasing age (Figure 13.10C). The soil Profile Development Index should prove useful in estimating ages of deformation, for it is based on readily describable field properties, provides an objective numerical basis for comparison between soils, and eliminates the need for subjective estimates of a soil's "development."
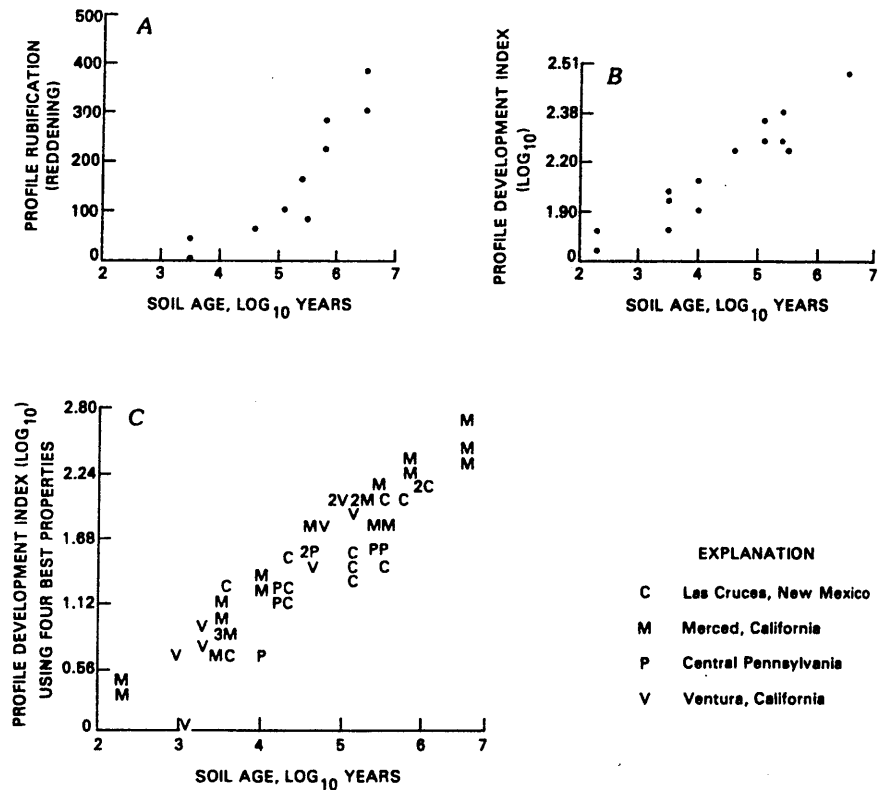
FIGURE 13.10 Increase in soil development with time (from Harden, 1982; Harden and Taylor, 1983). A, one soil property (rubification) in Merced, California, area. B, Soil Profile Index based on multiple properties in Merced area. C, Soil Profile Index for climatically different areas. Numbers indicate the number of points that plot in one place.

Some individual soil properties can be measured to estimate age. Such properties include increases in clay (Levine and Ciolkosz, 1983; Reheis, 1984; Pierce, 1979), secondary carbonate (Machette, 1978), secondary gypsum (Reheis, 1984), and secondary iron oxides (McFadden, 1982) as well as major-element chemistry (Harden and Taylor, 1983, Reheis, 1984). These measurements of changes are for an individual process and are like the simple-process, relative-dating methods (Table 13.1, column 4) but are discussed here because they are a component of soil development.

On the downwind and downthrown side of a fault offsetting a flat, former basin floor of the Rio Grande rift, New Mexico, fault movements were rapidly followed by deposition of eolian sand. During stable periods, five different calcic soils developed on these eolian sands and were subsequently buried (Figure 13.11). The time taken to form each soil is based on the total pedogenic $CaCO_3$ (g/cm²-soil column) divided by the accumulation rate of pedogenic $CaCO_3$ determined from the 500-ka surface soil on the upthrown side of the fault. The deposit thickness indicates fault offset, whereas the amount of pedogenic $CaCO_3$ indicates the interval between fault episodes (Figure 13.11). The deformation history inferred from this information (Figure 13.12) shows an apparently decelerating rate of faulting.

Progressive Landform Modification

Recognition of active tectonism commonly depends on detection of landforms created or modified by deformation, which is the subject area of tectonic geomorphology. To the trained eye, tectonic landforms tell much about the degree of tectonic activity, and new quantitative methods are making tectonic geomorphology a more exact science (Keller, Chapter 8, this volume). The effects may be subtle, such as alterations of river courses and gradients (Schumm, Chapter 5, this volume) or dramatic, such as bold, mountain-front escarpments (Keller, Chapter 8, this volume).

Geomorphic modification of fault scarps is particularly important to studies of active tectonism (Wallace, 1977; Nash, Chapter 12, this volume; Keller, Chapter 8, this volume). As with soils, the environmental variables such as lithology, climate, and vegetation need to be held constant or accounted for otherwise.
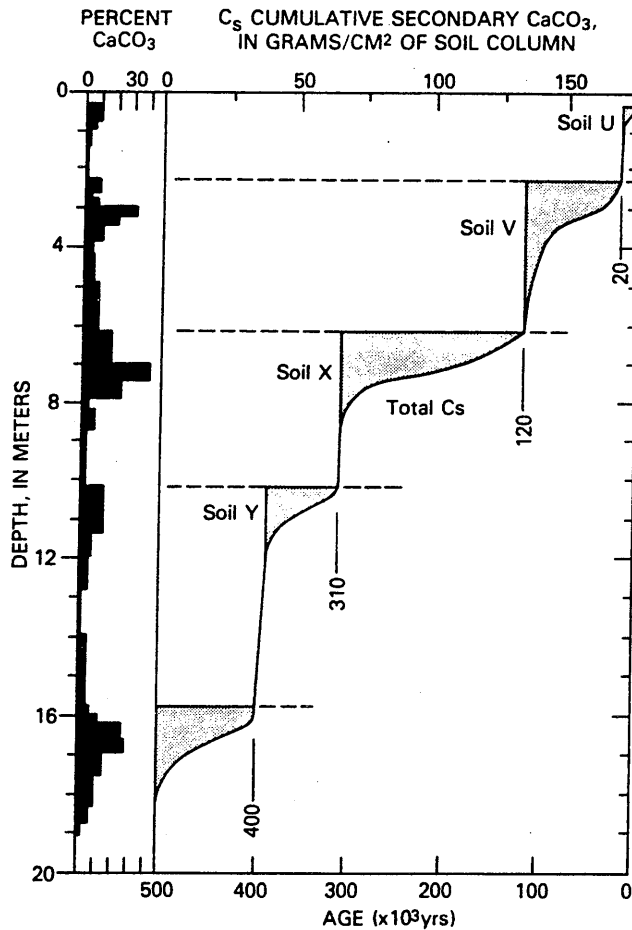
FIGURE 13.11 Dating of fault-related buried soils based on the accumulation of carbonate in calcic soils near Albuquerque, New Mexico (from Machette, 1978).

CORRELATION METHODS

If a feature can be correlated with an event of known age, reliable and precise age control can be obtained. Methods such as those listed in Table 13.1 (column 6) may provide accurate numerical dates or exact correlation between deformed areas.

Stratigraphy

Stratigraphy, including lithologic characteristics and the sequence of units, is basic to understanding the history of active tectonism. In surficial geology, the sequence of units may not be based on superposition but on geomorphic relations such as a sequence of successively lower and younger stream terraces. The origin of

deposits also may be important in understanding the stratigraphy of surficial deposits. If the age of a unit can be determined in one place, that age can be applied to correlative units or be used to provide age constraints for sequentially younger or older units. Many surficial geologic units are causally related to the cycles of climatic change that characterize the Quaternary, such as successions of glacial till, sequences of loess separated by buried soils, and sequences of marine or alluvial terraces.

Numerical dating control is normally obtainable only at scattered localities, and extension of this dating control to sites of deformation depends on stratigraphic correlation over distances of tens to even hundreds of kilometers. The age of stratigraphic units in Quaternary geologic successions is the subject of much current research. Such research addresses many unresolved dating problems, results in new and commonly significantly revised ages, and leads to development of new strategies for obtaining ages. Studies centered on stratigraphy offer the best method to check a given dating technique through comparison with other age information from related stratigraphic units. Thus, although laboratory and numerical analyses are important in obtaining ages, stratigraphic work based on field studies is fundamental
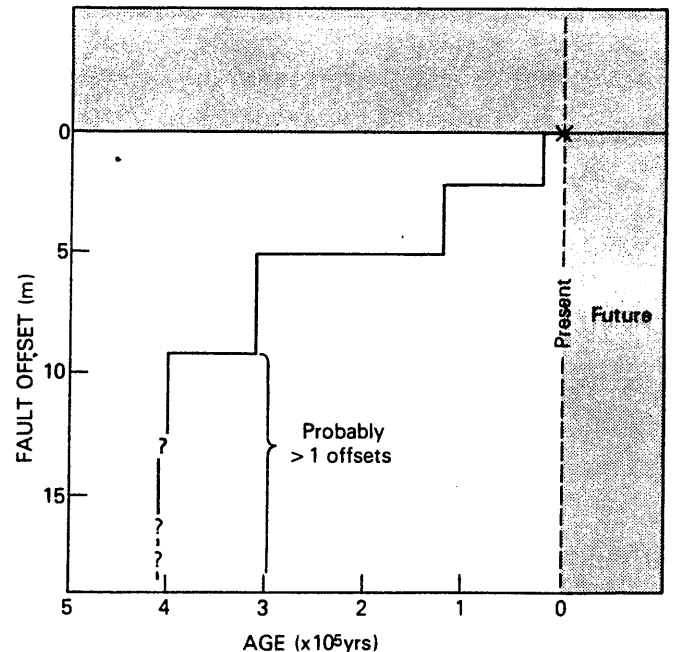

FIGURE 13.12 Fault offset versus time as determined by accumulation of soil carbonate in buried soils near Albuquerque, New Mexico (drawn from data in Machette, 1978).

in judging the reliability of these ages, and relating ages to deformation of stratigraphic units.

Tephrochronology

A volcanic ash can provide a time-parallel marker whose age is as accurate as the best dating either at any of its occurrences or of the correlative volcanic rocks in its source area. Recognition of a given ash bed should be based on multiple criteria, especially the petrography and chemistry of the glass and phenocrysts, as well as stratigraphy, paleomagnetism, paleontology, and radiometric dating (Westgate and Gorton, 1981). Tephrochronology has proved of great value in dating active tectonics. For example, in southern California deposits containing the 0.7-Ma Bishop ash are laterally offset about 6.6 km on the San Jacinto Fault (Sharp, 1981), and deposits containing 0.6-, 0.7-, and 1.2-Ma volcanic ashes are uplifted and tilted along the Ventura Fault (Yeats, Chapter 4, this volume). Tephrochronology is also important in calibrating other relative-dating and correlation methods, such as soil development, uranium-trend dating, amino-acid racemization, thermoluminescence dating, and dating of faunal boundaries. These calibrated methods can then, in turn, be used to date active tectonism.

Improvements in tephrochronology have led to major revisions in Quaternary stratigraphy and age assignments. In the 1960s, the Pearlette ash (known present distribution from California to Iowa) was considered to be of a single age, and the stratigraphy and paleontology of older Quaternary deposits all the way from the mid-continent to the Rocky Mountains were founded on the assumption that the Pearlette ash represented one eruption of late Kansan age. Careful petrographic and chemical study of the Pearlette ash has shown that it actually includes ashes from three different and distinct eruptions from the Yellowstone area that differ in age by a factor of 3 (Huckleberry Ridge ash, 2 Ma; Mesa Falls ash, 1.2 Ma; and Lava Creek ash, 0.6 Ma; Izett, 1981).

Paleomagnetism

The orientation of the Earth's magnetic field is recorded by the orientation of magnetic minerals at the time of deposition of many fine-grained sedimentary deposits. Dating control can be obtained if the paleomagnetic record determined from a sequence of late Cenozoic sediments or volcanic rocks can be correlated with the established paleomagnetic polarity time scale (Mankinen and Dalrymple, 1979; see Barendregt, 1981, for a review). For example, the change from the Matuyama Reversed-Polarity Chron to the present Brunhes

Normal-Polarity Chron occurred about 730 ka. This change provides a global datum for the assessment of long-term tectonic rates and calibration of relative-dating methods.

The established polarity time scale also dates the age of the ocean floor outward from the ocean-ridge spreading centers. The rates of movement of crustal plates away from these spreading centers is based on the age and width of the normal and reversed polarity stripes of the ocean floors.

Within the Brunhes Normal-Polarity Chron, potential age control may be provided excursions or reversed-polarity subchrons that lasted a few thousand years; about five such events have been suggested. In addition, secular variation in the geomagnetic field with periodicities of thousands to tens of thousands of years may provide a basis for local correlation and dating. The record of secular variation is best studied in lacustrine and other environments of continuous fine-grained sediment deposition. Such sediment dated by paleomagnetic criteria may also record sediment deformation associated with nearby earthquakes.

Fossils and Artifacts

Fossils have been of limited value in dating young deposits because the amount of Quaternary evolutionary change has been small. Some organisms, such as the rapidly evolving microtine rodents, do show several changes each million years and can therefore be of great value in estimating long-term deformation rates. An example of dating active tectonics comes from east of San Francisco Bay where the Verona Fault offsets Livermore Gravel and is mapped within 60 m of the General Electric Test Reactor at Vallecitos (Herd, 1977). The age of this faulted gravel was poorly known until it was dated using small mammal faunas as about 500 ka (C. A. Repenning, U.S. Geological Survey, personnal communication, 1984).

The cyclic climatic changes of the Quaternary Period resulted in cyclic changes in plant and animal populations. Such plant or animal changes also provide a basis for dating active tectonism. For example, pollen assemblages representing climate considerably colder than at present may be used to infer a pre-Holocene age (>10 ka).

WHY DATING SPANNING DIFFERENT TIME INTERVALS IS NEEDED

Geologic prediction of future deformation requires enough dating control to understand if and how deformation has changed through time. For most active tec-

tonism, we know little about whether strain rates are uniform through time. Even with the simplifying assumption that strain and long-term slip rates are uniform, a fault scarp with evidence of recent movement can yield dramatically different predictions: (1) if the slip rate is fast, future movements are likely soon, or (2) if the slip rate is slow, future movements are unlikely soon.

Spreading rates at oceanic ridges and movement rates of crustal plates appear to be rather constant over the planning intervals of concern to man and his activities. Consequently, constant strain rates may be appropriate for some major tectonic features. For many individual faults, however, this assumption is probably not valid. Even for some faults in the boundary zone between crustal plates, slip rates have changed greatly. On the San Jacinto Fault southeast of Los Angeles, the slip rate for the past 730 ka has averaged about 9 mm/yr, whereas the rate between 0.4 and 6 ka averaged about one-fifth that (Table 13.3; Sharp, 1981). These large differences in rate may have resulted from differential movements between the Pacific and American plates being localized at times on the San Jacinto Fault and at other times on the nearby San Andreas Fault (Sharp, 1981).

On a fault in the Rio Grande rift near Albuquerque, New Mexico, the rates of deformation have decelerated over the last 400 ka. Recurrence intervals on this fault are quite long, averaging more than 100 ka (Figure 13.12).

For the total Basin and Range province encompassing the 700-km distance between the crests of the Wasatch Mountains of Utah and the Sierra Nevada of California, the overall rate of extension may be relatively constant. But Holocene and historical activity in the Basin and Range is spatially clustered in zones. Holocene tectonic events (M_s about 7 or larger) define an eastern and western zone; these zones are separated by a zone about 300-km wide encompassing the Nevada-Utah border in which no late Quaternary scarps are recognized (Wallace, 1981).

Grouping of events in time may also occur. Some segments of the Wasatch Fault zone have had three or more

Holocene (last 10 ka) offsets and exhibit slip rates during the Holocene of 1.3 + 0.1 m/ka, yet other sections of the Wasatch Fault zone have not been active in the Holocene (Schwartz *et al.*, 1983). In addition, based on fission-track annealing ages, the uplift rate of the Wasatch Mountains for the past 10 Ma has been about one-third the Holocene rate, or about 0.4 m/ka (Naeser *et al.*, 1983). Work in progress on deposits as old as 250 ka sheds light on the meaning of these rates (Machette, 1984). As dated by calcic-soil development, the slip rate has been on the order of 1 m/ka during the last 5 ka; this rate appears to have been more than 5 times greater than that over the past 250 ka, suggesting variable slip rates and temporal grouping of fault offsets (Machette, 1984).
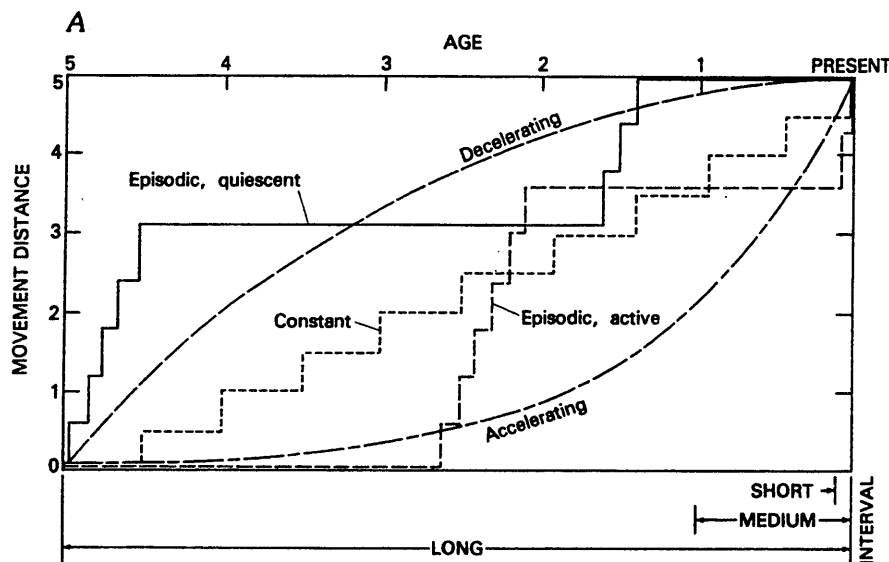
Rates of fault slip or other deformation are dependent on both the deformation pattern through time *and the time window of observation*. To illustrate this point, Figure 13.13 shows the effect of short, medium, and long time windows on the slip rates for five patterns of deformation: accelerating, constant, decelerating, episodic-quiescent, and episodic-active. For convenience, the deformation patterns are shown as systematic, and the deformation rates are arbitrarily set at 1 for the longest interval. Depending on the time window, deformation rates for each pattern may differ by more than an order of magnitude. Also, although the long-term rate is arbitrarily set at 1, the short interval has rates that differ by more than 2 orders of magnitude (Figure 13.13B).

Deformation rates determined for differing time intervals will contribute to an understanding of deformation patterns through time in different tectonic settings. Few fault histories such as those shown by Figures 13.2, 13.3, and 13.12 have been determined. Deformation histories like that shown by lines for episodic-active and episodic-quiescent (Figure 13.13) have not been well documented, but, as discussed previously, some evidence suggests that these patterns of deformation have occurred.

Only by understanding the history of a fault can we better understand what can be expected in the future. Consequently, the deformation history needs to be defined by multiple dates. The simplifying assumption that tectonic events such as rates of faulting or rates of uplift are constant may be useful as a first approximation, but this assumption may be quite misleading in some tectonic environments. Few fault histories are well enough dated to know in what cases the assumption of constant slip rate is valid and in what cases it is not. By detailed documentation, we can construct predictive models appropriate to a given tectonic setting. If movements on a given fault are grouped in time, or if faults in an area alternate in activity, concepts such as constant

TABLE 13.3 Variable Slip Rates Through Time, San Jacinto Fault, Southern California (from Sharp, 1981)

Time Interval	Slip Rate (mm/yr)	Change in Slip Rate Through Time
0–400	3.9 ± 1.1	Twofold increase
400–6000	1.7 ± 0.3	Fivefold decrease
0–730,000	9^{+3}_{-1}	

FIGURE 13.13 A, five patterns of fault off-set versus time. B, contrasting slip rates for these five patterns over short, medium, and long intervals of time. Slip rates are in arbitrary distance/time units, and long-term deformation for all patterns has been arbitrarily set at 1.

slip rate or constant recurrence intervals would be, of course, quite misleading.

Thus, sufficient dating related to deformation histories is required to understand the character of faulting in different tectonic settings and thereby to anticipate more intelligently the future deformation over time intervals of concern to man. Dating of a single fault history without concern for related faults may be examining too small a component, for relatively constant tectonic activity may be unevenly distributed among a group of faults.

The definition of rates and knowledge of the constancy or variation of these rates through time permit quantitative ranking of tectonic activity, both for the purposes of scientific understanding and hazard assessment.

DATING METHODS IN FUTURE RESEARCH ON ACTIVE TECTONISM

All the dating methods discussed (Tables 13.1 and 13.2) have importance to studies of active tectonism. In the last decade, much improvement, refinement, and evaluation of the reliability of these methods have been associated with studies of active tectonism.

Because experimental methods such as ^{36}Cl and ^{26}Al are numerical and based on radioactive decay, some may consider such methods the most promising for future advances. But such methods also involve assumptions concerning nonradiometric processes—one assumes that the isotope measured both accumulated at a known rate and no subsequent leaching has occurred. These nonradiometric factors are difficult to evaluate rigorously and have similarities with, for example, the extremely complex process of soil development. For example, ^{10}Be accumulation in soils is influenced by the clays in the soil, which generally increase in quality and may change mineralogically as the soil develops. The recent quantification of soil development using the Profile Development Index, as well as analyses of changes in individual soil components such as soil carbonate or clay, can provide useful but not precise dating control; soil development is nearly always applicable to the dating of active tectonism.

Because of their nearly universal applicability, thermoluminescence and uranium-trend dating of sediments are promising methods for dating deformation, especially in the 10^4- to 10^6-yr range. Compared to this potential, research by laboratories on these methods and application to active tectonics have been limited.

Carbon-14 dating is the most important method in the range of about 30,000 yr to the present. Research using current methods of organic chemistry may help to resolve problems with the method and the mechanisms of contamination. Even before sample collection, microbes may have lived in organic material and incorporated younger carbon from the surrounding water or air. Important carbon-14 samples might be quantitatively examined for such microbes and other potential contaminants to estimate the importance of their effect, as was done by Geyh *et al.* (1974).

Carbon-14 dating using accelerator mass spectrometry permits the dating of milligram-sized samples (Grootes, 1983). If only small samples are present, this offers obvious advantages, but contamination within, for example, an individual grain of charcoal, may still be present. Special organic concentrates in combination with accelerator dating may offer real improvements. For example, a whale bone sample from northern Alaska has been carbon-14 dated, but considerable question remains about the reliability of the ages (D. L. Carter, USGS, personnal communication, 1984). Because one amino acid is common in bone but not in the likely contaminating materials, dating of this amino-acid sample may provide a reliable carbon-14 age. The amino acid concentrate will be small, requiring dating by accelerator mass spectrometry.

In the quest for better dating of active tectonism, the importance of local, time-calibrated stratigraphies should not be underestimated. Datable materials are commonly not found where a given stratigraphic unit is offset but may be found elsewhere in that stratigraphic unit. Because the stratigraphy of many Quaternary deposits reflects the cycles of climatic changes, the ages of faulted or uplifted datums can be inferred if relations between stratigraphic units and climatic cycles are known. Study of active tectonism and Quaternary stratigraphy should proceed together also because evidence of tectonism and climatic change is commonly similar. For example, gravel deposition may result from uplift, from climatic change, or from both uplift and climatic change.

In conclusion, knowledge of active tectonism of a given area progresses as both the amount and age of deformation are determined. Such knowledge commonly develops by documenting first the age and amount of the most recent movement; second, the history of the last several movements; third, deformation over contrasting time intervals, including long intervals; and last, the relation between the dated deformations on associated faults.

Dating control is commonly the limiting factor in understanding active tectonism. Normally, several dating methods need to be used because of (1) the limited range of a given technique, (2) the presence of appropriate materials, and (3) the need to check the reliability of any given dating technique by using another method. For studies of a fault segment, for example, dating control for Holocene activity can be determined by carbon-14, and studies of surface and buried soils can be made to provide dating control in the 10^4- to 10^5-yr range as well as to provide a check on the reasonableness of the carbon-14 dates. Tables 13.1 and 13.2 list 26 methods. Development or refinement of the methods, particularly those listed in columns 3 to 6 of Table 13.1, has advanced greatly in the past decade, in part because of the impetus to date active tectonics. With continued effort, comparable advances are possible in the future.

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APPENDIX 1

DATING OF MORB BY PALAGONITE LAYER THICKNESS MEASUREMENT

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CONTENTS:

I PRINCIPLES OF DATING TECHNIQUE

A. BACKGROUND

Palagonites are solid products of reaction of basalt glass surfaces with aqueous solutions. Palagonite layers of a range of thickness have been measured in MORB and other basaltic glasses, and there is ample evidence from field and experimental systems that the thickness of palagonite layers depends on the duration of exposure of basalt glass surfaces to aqueous solutions. For these measured thicknesses to be useful for absolute dating, the exact functional relation of the layer thickness growth to time has to be determined. In addition, the dependence of layer growth rates to glass composition and environmental variables other than time also needs to be fully understood. It should be emphasized at the onset that, at best, the "age" that can be derived from palagonite layer measurement can only represent the length of time the glass surface was able to react with aqueous solution; this "age," hereafter referred to as the exposure age, may or may not correspond to the eruption age of the volcanic glass.

The physical characteristics of palagonites have been summarized in an extensive review by HONNOREZ [1980]. Honnorez [1980] noted that the term palagonite has been historically applied to "a mixture, in variable proportions, of altered, hydrated, and oxidized glass . . . with authigenic minerals such as clays, zeolites, and chlorite." The variability of chemical and mineralogical composition of palagonites reflects differences in the conditions and extent of water-rock reaction. Despite the availability of detailed characterizations of

palagonites produced in various natural and experimental systems, some questions concerning their mechanism(s) of formation remain unresolved.

There are two independent but complementary approaches that could be used to define the kinetics of palagonite formation. One is to study naturally formed palagonite layers on basaltic glasses, as has been done by a number of previous investigators (below). This requires independent knowledge of the duration of exposure of the basalt glass surface to aqueous solution. A key problem with this empirical approach is the present inability to accurately determine the exposure ages of young basaltic glasses erupted in submarine environments. For example, Moore [1966] and Hekinian and Hoffert [1975] used exposure ages determined from the thicknesses of manganese coatings on basaltic glasses. Uncertainties associated with the calibration of Mn-accumulation rates therefore become incorporated to the palagonitization rate determination. Unfortunately, the absolute rate of manganese accumulation, e.g., as affected by location relative to submarine hydrothermal systems, and its variability in time are not fully understood at present [e.g., BRYAN and MOORE, 1977]. Better constraints on eruption ages from historic and pre-historic "records" (e.g., visual observation, 14C, paleomagnetic) may be available for subaerially erupted lavas that have been subsequently altered in subaerial or submarine environments. It is not clear, however, that hydration processes and rates in submarine MORB settings are comparable to weathering of lavas in subaerial environments [e.g., MORGENSTEIN and RILEY, 1975; ABRAJANO et al., 1985] or in shallow submarine environments [MOORE et al., 1985]. Indeed it is possible that different MORB environments may yield different intrinsic hydration rates.

The second approach to defining the long-term kinetics of palagonite layer formation in MORBs is a combination of experimentation and mechanistic modeling. Through this approach, intrinsic rates of individual processes leading to palagonite formation can be better measured with respect to carefully defined environmental conditions. The pitfall of this approach lies in our inability to (1) simulate and accelerate natural interactions in the laboratory and (2) reliably extrapolate from experimental to geological time sacles. Geochemists have been quite successful in experimentally duplicating certain natural conditions in the laboratory but simulating long-term interactions has been more difficult. Palagonitization is an overall process which, itself, is a complex combination of several more fundamental processes. These fundamental processes include adsorption/desorption, ion-exchange, diffusion, hydration, hydrolysis, solution, precipitation, and mechanical consolidation or erosion. Acceleration of part but not all of these fundamental processes in an experimental system can lead to results that are different from the overall natural process being simulated. The success of the experimental approach is therefore dependent on our understanding the manner by which individual processes occurring during palagonitization are coupled and how this coupling determines long-term palagonitization rates in the environments of interest.

B. FIELD STUDIES OF PALAGONITIZATION: SOME EXAMPLES

One of the earliest studies of palagonitization rates in natural systems was that of Moore (1966). Using dredged samples of basalts from Hawaii,

he estimated a range of parabolic rate constants, C (C = S(2)/t; S is thickness and t is time), for palagonite layer growth of 480 to 2000 um2/ky (1.5 to 10 deg-C). The corresponding linear rate constants (C = S/t) fall in the range 0.7 to 12 um/ky (excluding Kilauea samples) [cf. MOORE et al., 1985]. The exposure ages of the samples were determined from the thicknesses of Mn coatings assuming a constant Mn accumulation rate of 3 um/ky.

Palagonite growth rates on dredged MORB samples from the Mid-Atlantic Ridge have been studied by Hekinian and Hoffert [1975] and Bryan and Moore [1977]. Figure 1 summarizes the results of these studies and that of Moore (1966). A linear rate of palagonite layer growth may be inferred from Figure 1 if it is assumed that a similar linear growth rate applies to the Mn accumulation rate. Using Hekinian and Hoffert's data alone, the palagonitization rate may be estimated to range from 2.6 to 4.3 um/ky (0 to 5 deg-C), assuming a constant Mn accumulation rate of 3 um/ky. A considerable scatter of data points is evident in Figure 1. As Bryan and Moore [1977] pointed out, Mn accumulation rates are variable (up to 20 um/ky) near the ridge axis and palagonitization rates could be up to three times faster than Mn accumulation rates [cf. HEKINIAN and HOFFERT, 1975]. If an average Mn accumulation rate of 3 um/ky is applied to Bryan and Moore's FAMOUS data, a slightly higher palagonitization rate of 5 um/ky may be estimated.

Basaltic glasses erupted historically have also been used to determine palagonitization rates at different temperatures. Moore et al. [1985] summarized data collected from Hawaii and other locations (see their Table 3). At 23 to 25 deg-C, the rates range from 15 (Etna) to 100 um/ky (Mauna Loa). Rates of 4.7 to 9.4 um/ky were estimated for the 1877 Mauna Loa lavas hydrated at 4 to 6 deg-C whereas samples from Fuji hydrated in a freshwater lake at 5 to 15 deg-C showed a range of 6.4 to 8.2 um/ky. Jakobsson and Moore (1986) performed a similar study of palagonite layers formed on basaltic glasses from Surtsey, and they estimated rates of 11 to 28 um/ky for a submarine-erupted sample altered at temperatures from 7 to 10 deg-C. Other palagonitization rates estimated by Moore et al. and Jakobsson and Moore for various integrated temperatures are summarized in Figure 2. Finally, Morgenstein and Rosendahl [1976; also see MORGENSTEIN and RILEY, 1975] measured palagonite layer thicknesses on a variety of Hawaiian basaltic glasses of known eruption ages, and concluded that a linear rate of 11.77 um/ky at 25 deg-C best describes palagonite layer growth with time. This rate, however, is a subaerial hydration rate which is expected to be lower than subaqueous hydration rates estimated by others [e.g., MOORE et al., 1985] at the same temperature [ABRAJANO et al., 1985].

C. EXPERIMENTAL PALAGONITIZATION

In addition to field-based studies noted above, considerable effort has also gone into experimental simulation of the palagonitization process. Only those studies that specifically addressed the growth rates of palagonite layers are included in the following brief summary. In general, palagonitization rates are difficult to determine in the temperature range 0 to 25 deg-C because of extremely slow reaction rates

relative to experimental time scales. Many experimental palagonitization studies therefore have been performed at higher temperatures. This approach necessitates that the relation between palagonitization rate and temperature be established in order to make valid inferences about low-temperature palagonitization rates. Fortunately, some higher temperature natural palagonitization rates also have been measured (Figure 2) so that the temperature dependence of palagonitization rates in natural and experimental systems can be compared.

Furnes [1975] was among the first to experimentally determine palagonitization rates of basaltic glasses at various temperatures in seawater solution (Figure 3). The three glass compositions (alkali basalt, olivine tholeiite, and basaltic andesite remelted in an oxidizing atmosphere) examined by Furnes showed rather peculiar palagonitization behavior wherein the rate apparently decreased continuously in the first ten months then increased subsequently. No strong differences in palagonitization rates were noted for the three glass compositions. Crovisier et al. [1983] also measured the growth of alteration layers in a tholeiitic basalt glass at 50 deg-C and showed palagonitization rates that systematically decreased with time up to 20 months (Figure 4). The initial palagonitization rate for Crovisier's experiments is about 14,000 um/ky whereas the final rate is about 600 um/ky.

Crovisier et al. [1986] measured palagonitization rates for tholeiitic basalt glass at 3 and 60 deg-C and the results are summarized in Figure 3. The rates noted in Figure 3 are linear rates for single samples which, judging from Figure 4, are probably overestimated. Malow et al. [1984] and Moore et al. [1985] measured alteration layer thickness of 30 um and 3 to 6 um for Hawaiian basalt glass samples reacted with seawater at 200 deg-C for 30 days and 100 deg-C for one year, respectively. Recently, Berger et al. [1987] measured alteration layer thickness of about 5, 0.25, and <0.1 um (last two estimated from their Figure 5) for MORB glasses reacted with artificial acidic seawater (pH < 5) at, respectively, 320 deg-C for 17 hours, 300 deg-C for 30 minutes, and 150 deg-C for 60 minutes. Murakami et al. [1987] also measured palagonite layer thickness formed on a synthetic basalt reacted with NaCl, NaCl/MgCl, and deionized water solutions at 70 deg-C for 301 days and found, respectively, 0.2 to 1 um, 1 um, and 2 to 3 um layers. The corresponding rate constants, assuming linear growth kinetics for all single sample measurements, are plotted in Figure 3.

Synthetic basaltic glasses have also been reacted in steam environments at various temperatures. Figure 3 shows some palagonitization rates measured at Argonne National Laboratory based on published and unpublished work. A declining palagonitization rate with time similar to those observed during reaction with aqueous solutions [FURNES, 1975; CROVISIER et al., 1983] have also been observed during vapor hydration (Figure 5, [BYERS et al., 1984]). However, alteration layer growth rates during hydration of multicomponent silicate glasses including basalts have been shown to be higher in aqueous solution than in water vapor at similar temperatures [ABRAJANO et al., 1985].

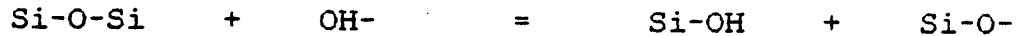## D. FUNDAMENTAL PROCESSES DURING PALAGONITIZATION:

The reaction of basalt glass surfaces with seawater results in chemical and structural modification of the glass surface. As noted above, the end-result of the overall interaction is the formation of hydrated glass and amorphous and crystalline products (i.e., palagonite) at the glass-solution interface region. However, since these final products need not have all resulted from a single fundamental reaction, the kinetic description of the overall palagonitization process must also reflect the multitude of fundamental processes that have occurred. This section identifies some of these fundamental reactions and examine how they potentially affect overall palagonitization rates.

A useful starting point for a mechanistic analysis of palagonitization is a brief description of the initial molecular structure of the unreacted glass. The classical random-network theory of Zachariasen as well as the "crystallite" and "discrete-ion" theories have been proposed as alternative models for the structure of silicate glasses [e.g., MACKENZIE, 1960]. In these and other theories recently advanced, [e.g., GOODMAN, 1982], it is generally accepted that the fundamental structural unit is the SiO_4 tetrahedron. In silica glass, this unit is linked to four other similar tetrahedra by sharing the apical oxygen atoms, the latter hence called bridging oxygen (BO). Addition of network modifying alkalis or alkaline earths leads to the formation of non-bridging oxygens (NBO) wherein, respectively, one or two NBO are formed per alkali or alkaline earth atom introduced. Addition of Al_2O_3 or Fe_2O_3 can lead to the formation of tetrahedra with net negative charges which are subsequently charge-compensated by network modifiers. A non-bridging oxygen site is therefore destroyed per atom of Al or Fe^{3+} added. Alkali and alkaline earth components in charge-compensating positions are less exchangeable than those in network-modifying sites. It is therefore to be expected that glass structure and reactivity depend on its composition; the exact nature of this dependence and its implication to the palagonitization rates of glasses with relatively minor compositional variations (e.g., MORBs) are not yet fully understood. On the average, MORBs have less than one (~0.9) NBO per tetrahedron.

Upon contact with seawater, adsorption of seawater components onto the basalt glass surface takes place. This is followed by the site exchange of mobile components from the glass surface (e.g., alkalis in surficial NBO sites) and the adsorbed component, and the desorption of the mobile glass component from the surface. In simple alkali silicate glasses, the exchange of alkalis with adsorbed proton or hydronium is followed by bulk interdiffusion of proton or hydronium with alkalis from deeper portions of the glass [e.g., DORFMUS, 1973]. The interdiffusion layer becomes chemically distinct from the bulk glass because of this exchange between hydrogen species and mobile glass components. However, because the composition varies gradually from the bulk glass-interdiffusion zone boundary to the interdiffusion zone-solution boundary, the interdiffusion zone may not be physically distinguishable from the bulk glass. There is strong evidence from experimental systems that this type of bulk exchange process also occurs during reaction of water with multicomponent glasses such as basalt [BYERS et al., 1984; ABRAJANO et al., 1985; ABRAJANO and BATES, 1987; BERGER et al., 1987]. This process

alone should lead to formation of an interdiffusion layer that grows parabolically with time. The growth of this layer is governed by the interdiffusion coefficient, D, whose value approaches that of the self diffusion coefficient of the slowest diffusing species as the difference between the self diffusion coefficients between interdiffusing species becomes large [DOREMUS, 1973].

Hydrolysis of bridging bonds is another process known to occur during glass/water interaction. This is usually characterized as a nucleophilic attack:

$$Si-O-Si \quad + \quad OH- \quad = \quad Si-OH \quad + \quad Si-O-$$

because the direct reaction of molecular water with BO is a highly activated process. The ultimate product of this process during the interaction of basalt glass surfaces with seawater is the detachment of monomeric or polymeric silicate units from the surface (i.e., etching). Where both interdiffusion and etching occur during reaction of a glass surface with aqueous solution, the etching front has been shown to lag behind the interdiffusion front. An interdiffusion layer that advances into the glass but which, itself, is continuously destroyed by etching is thus produced. Etching is known to follow zeroth order kinetics at the initial stages of dissolution (i.e., low solution concentration of dissolved glass components) [ABRAJANO and BATES, 1987; CROVISIER et al., 1987] so that coupling of parabolic interdiffusion and linear etching processes will determine the rate of growth of the interdiffusion layer. Mathematical descriptions of layer growth kinetics under these conditions have been formulated [e.g., BOKSAY et al., 1969; SULLIVAN, 1979; ABRAJANO and BATES, 1987] with the essential result that layer growth is parabolic at $t << D/U2$ (D is the interdiffusion coefficient and U is the constant etching velocity) and that a steady-state (i.e., constant layer thickness) is approached at $t > D/U2$. The latter simply means that the layer stops growing regardless of the length of exposure to aqueous solution.

The detachment of network formers and other unexchanged components (etching) is an eventual result of hydrolysis of the interconnected silica tetrahedra in the interdiffusion zone. However, partial hydrolysis of the anionic glass framework represents the initial step in this detachment process. The solution side of the interdiffusion layer is therefore expected to undergo structural transformation leading to the formation of a "gel" layer between the interdiffusion layer and aqueous solution. Studies of the physical integrity of this "gel" layer formed on multicomponent silicate glasses reacted with water for long periods of time tend to suggest that transport through this layer cannot be the rate controlling step in the influx of hydrogen species into the glass at long reaction times [CROVISIER et al., 1987; ABRAJANO and BATES, 1987; cf. BERGER et al., 1987]. The "gel" layer appears to maintain an open porosity which enable transport of silicic acid and larger dissolved species through it. Because of its inherent instability, the "gel" layer can eventually repolymerize to a more highly cross-linked amorphous product [e.g., BUNKER et al., 1983] or transform into a crystalline mineral product (e.g., smectite clay) [BERGER et al., 1987].

The solution release pattern of network formers (e.g., Si) during

experimental basalt dissolution and physical observations on reacted glass surfaces [BYERS et al., 1984; ABRAJANO et al., 1985; CROVISIER et al., 1985, 1987; BERGER et al., 1987], appears to suggest that linear etching the "gel" cannot occur indefinitely. Repolymerization and crystallization of this layer and precipitation of relatively insoluble components in it tend to alter or even stop etching at the "gel"-solution interface. Dissolution of the network may still occur within the "gel" if a porosity that will allow diffusion of silicic acid or larger silica polymers is present. Despite the apparent complexity of processes occurring, the compounded rate of growth of the altered layer (i.e., interdiffusion layer + gel layer) is still determined by the coupling of the advance of the interdiffusion front into the fresh glass and the retreat of the surface by etching. If the "gel" is transformed to a "stable" phase (e.g., saponite), the "gel"/solution interface (i.e., etching front) will stop retreating and the altered layer will grow at a rate controlled solely by the interdiffusion process (see below). The transformation of the "gel" layer to a more stable phase is not expected to affect the layer growth kinetics so long as this transformed layer does not retard transport across it. Note that the altered layer, as defined in this case, excludes mineral or amorphous products that grew beyond the "gel"-solution interface or were precipitated onto this interface from components already dissolved in solution [e.g., CROVISIER, 1987].

It was noted above that opening up of the "gel" layer by network hydrolysis and subsequent structural transformation of this layer may allow rapid transport of mobile glass species through the layer [e.g., BUNKER, 1983]. When this occurs, an interdiffusion zone, whose thickness is now determined by the rates of interdiffusion and network hydration, will continue to control the rate of penetration of the entire altered layer into the bulk glass. Where a steady-state is reached between interdiffusion and network hydrolysis, the rate of advance of the interdiffusion front into the fresh glass is expected to become linear with time; this constant rate is equal to the rate of advance of the "gel" layer into the interdiffusion zone and the interdiffusion zone at steady state will have a constant thickness. Transport of mobile glass species and hydrogen species across this "barrier" of constant thickness (i.e., interdiffusion zone) will become the rate-controlling step in the long-term palagonitization process.

Field and experimental observations on palagonite layers summarized earlier could be reconciled with the above description of the fundamental processes that occur during the reaction of basaltic glass surfaces and aqueous solutions. Zeroth and first order kinetics that are commonly inferred from measurements of palagonite layer thicknesses may be attributed to the dominance of particular interactions relative to others. For example, linear palagonitization kinetics could result from a combination of (1) stabilization of the palagonite layer surface from etching by transformation to a porous clay layer [e.g., BERGER et al., 1987] and (2) control of fresh glass hydration by interdiffusion across a transition zone of constant thickness. First order (e.g., parabolic) kinetics that are often observed in experimental systems could result from non-steady state growth of the interdiffusion layer.

Note that whereas mineral products can be formed within the palagonite layer, the entire layer is viewed in the above discussion as "residual"

products of non-stoichiometric dissolution of basalt. On the contrary, others have suggested that basalts dissolve stoichiometrically and that palagonites are composed entirely of precipitates that form from dissolved components in solution [CROVISIER et al., 1986, 1987]. In this case, palagonite layer growth is determined by the rate of precipitation from solution. Although this mechanism results in the same overall incongruent reaction (basalt glass + water = palagonite + dissolved products), the rate of formation of palagonite and the rate law governing this formation can be very different from those described above. The integrated mass of precipitates that form as a function of reaction progress (i.e., the palagonitization rate according to the "precipitation model") may not be simply related to the mass of material dissolved as implied by Crovisier et al. [1987; p. 2987]. Open seawater has the ability to retain some basalt components in solution [cf. CROVISIER et al., 1987; p. 2988], and as basaltic glass dissolves, the number of alteration phases that reach saturation increases with time. Hence if stoichiometric glass dissolution rate is zeroth order as suggested by Crovisier et al. [1986, 1987] and if the precipitate layer is not a significant transport barrier, the palagonite "precipitation" rate should, in general, increase with time until the final alteration phase assemblage has been stabilized. Whereas this effect is expected to be more noticeable in less open systems (e.g., static leaching experiments), the palagonitization rate actually decreased, rather than increased, during Crovisier et al.'s (1983) experiments (Figure 4).

It is also notable, from comparison of Figures 2 and 3, that experimentally measured palagonitization rates tend to be higher than rates inferred from field measurements at similar temperatures. One explanation offered by Crovisier et al. [1987] is that the solution chemistry in experimental and natural systems (pH and dissolved components) is different such that natural palagonitization rates are expected to be slow. This explanation is unlikely because closed-system experimental systems are probably more affected by saturation or feed-back effects compared to open-system natural ocean environments. The experiments conducted near pH 8 are close to the minima in solubility and reaction rates of basaltic glasses [MAZER, 1987] so that pH differences between experimental and natural systems are also not likely to provide the answer. Whereas this is clearly a problem that needs to be addressed further, the time dependence of palagonitization rates shown in Figure 4 seems already to provide a clue. The palagonitization rate for Crovisier's experiments in Figure 4 is decreasing to a near steady-state value. As noted above, the final rate in this curve, which is statistically almost indistinguishable from zero, is still about 600 um/ky. It is therefore obvious that the 0 to 5 deg-C natural palagonitization rate of 4 um/ky (see above) is an experimentally slow, and probably indeterminable, rate. Experimental measurement of this rate would require being able to measure a 0.04 um increase in palagonite layer thickness after ten years of reaction ! It appears therefore that the long-term rates measured in natural systems may correspond to the slow to virtually steady-state rates in experiments, and it is the process controlling the rate at this close to steady-state stage that must be examined experimentally or predicted theoretically. Extreme care is required in the use of experimental results in understanding natural palagonitization.
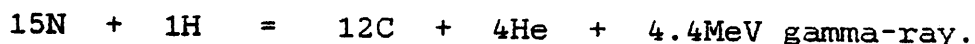
II. RECOMMENDATIONS

The above discussions have highlighted some unresolved issues related to the application of palagonite layer measurements to dating MORBs and other basaltic glasses. Two related problematic issues are apparent. First, the rate law and absolute rates for a given condition (e.g., appropriate for MORB glass) are not fully known. Existing estimates based on field studies such those noted above remain to be calibrated using an absolute dating technique. This makes absolute age determination using palagonite layers inaccurate at present. Relative exposure ages could be useful but only in a qualitative sense because the rate law remains to be established. Second, the discrepancies between experimental and field observations remain to be satisfactorily explained. Experiments can potentially provide an alternate source of independent calibration, but it is clear that this is far from being realized at present. The long-term rate law of palagonitization remains to be meaningfully addressed in experimental systems.

Several approaches can be used either to make dating by palagonite layer measurement more realistic or to demonstrate that it cannot be generally applied. The types of field studies performed by Moore [1966], Hekinian and Hoffert [1975] and Bryan and Moore [1977] should be augmented by an absolute dating technique (i.e., not Mn coating thickness measurement). Hekinian and Hoffert's [1975] attempt to relate the palagonite growth to fission track dates is a step in the right direction but it remains to be shown that fission track ages are also credible for MORBs. Until an independent absolute dating technique is developed for MORBs, experimental systems are the only avenues for determining the palagonitization rate law. However, non-MOR basaltic glasses hydrated in submarine environments and whose eruption ages are tightly contrained, either by historical records or applicable dating technique (e.g., 14C), may offer some very important field constraints on palagonitization rate law. These tightly constrained systems could also be useful for determining statistical variability of palagonite layer thicknesses in samples with identical exposure ages. Nevertheless, the problem of applicability of such results to MOR systems will have to be addressed.

Systematic experiments designed to address the question of rate law applicable to natural palagonitization process have not been performed. This requires long-term experiments conducted at a wide range of conditions (e.g., temperature, flow rates, water composition) coupled with detailed characterization of the palagonite layers formed at different stages of reaction. These experiments should use actual MORB glasses and synthetic MORB of controlled variable compositions (including simplified compositions for mechanistic studies). Crucial to determining long-term palagonitization rate and rate law from experiments are (1) understanding the mechanistic origin of natural palagonites and (2) ensuring that the process being experimentally investigated is truly analogous to natural palagonitization. This requires parallel and detailed characterization of natural and experimentally-produced palagonites [cf. CROVISIER et al., 1987].

Even after the above issues have been resolved, a number of application problems will have to be addressed. For example, it may be that a simplified rate law that is useful for dating applies only to the first few thousand years of glass exposure to seawater. If so, the dating technique will have to be applied only to glasses whose exposure ages belong to this age range. Furthermore, the emphasis in all the discussions made above is on glass surfaces exposed to open seawater. A study of how, if at all, slight to extensive sedimentation (including Mn accumulation) will affect the palagonitization process has to be conducted. Otherwise, only samples continously exposed to open seawater throughout their submarine history should be used. One also has to be certain that the palagonite layers were not disturbed (e.g., by mechanical erosion) from the time of initial exposure to seawater. Strict criteria will thus have to be developed to determine the types of samples suitable for dating.

The standard tool for measuring palagonite layer thicknesses has been the optical microscope. This method allows layers a few microns to hundreds of microns thick to be measured accurately. Indeed some layers may be thick enough for visual measurements to be made. Herein lies one of the most significant merits of this dating technique, that of simplicity and availability of analytical tools. In some cases, the scanning electron microscope (SEM) has been employed to show the details of the palagonite layer structure or to determine the origin of multiple palagonite layers. Even the SEM, however, has become standard equipment in geological departments. Nevertheless, experimental or even some natural systems may produce palagonite layers that are only sub-micrometer thick. The problem with these exceedingly thin layers is that while some may still be theoretically observable under the SEM, existing sample preparation techniques (mounting and polishing) are often unable to preserve the delicate thin layers. Depth profiling techniques that are more suited for this purpose exist but are available only in a few laboratories. Two examples of depth profiling techniques that have been used for measuring thin alteration layers on glasses include secondary ion mass spectrometry (SIMS) and resonant nuclear reaction spectrometry (RNRS). The former is based on mass spectrometric measurement of charged or neutral species sputtered off the surface of interest and has multielement capability. The latter is based on measurement of nuclear particle intensities resulting from reaction of bombarded ions and specific isotopes intrinsically present in the sample. Examples of the application of RNRS profiling techniques to determine altered layer thicknesses on glasses can be found in Berger et al. [1987] and Abrajano and Bates [1987]. In both cases, hydrogen distribution was measured using the reaction:

$$15N \ + \ 1H \ = \ 12C \ + \ 4He \ + \ 4.4MeV \ \text{gamma-ray}.$$

Other techniques (not necessarily for depth profiling, e.g., transmission electron microscopy) for measuring very thin layers are available but, like the two examples noted above, they are best used in detailed characterization of palagonite layers rather than in routine thickness measurement. Such detailed characterization will be necessary in experimental studies of reaction mechanisms. If there is interest in MORBs with exposure ages of less than a few hundred years, these high resolution techniques may, nevertheless, be very useful dating tools.
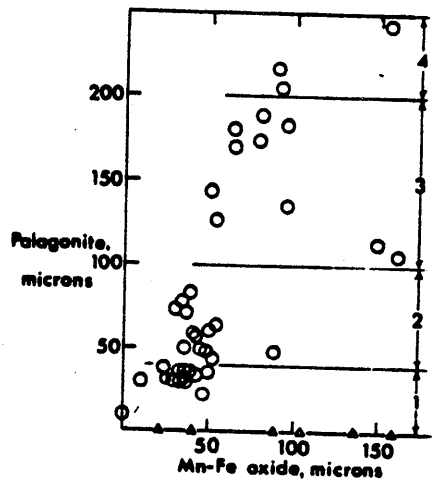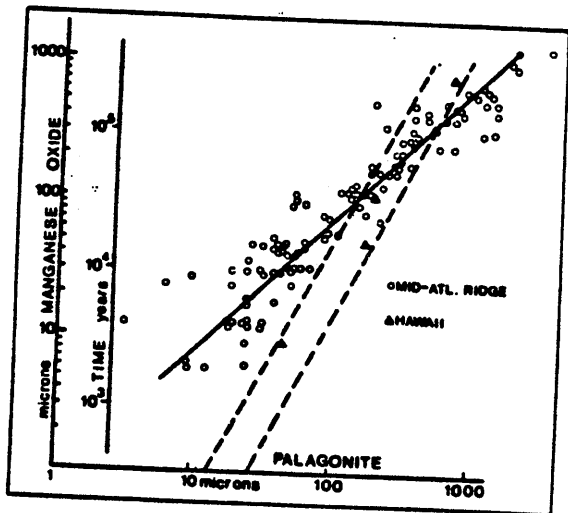
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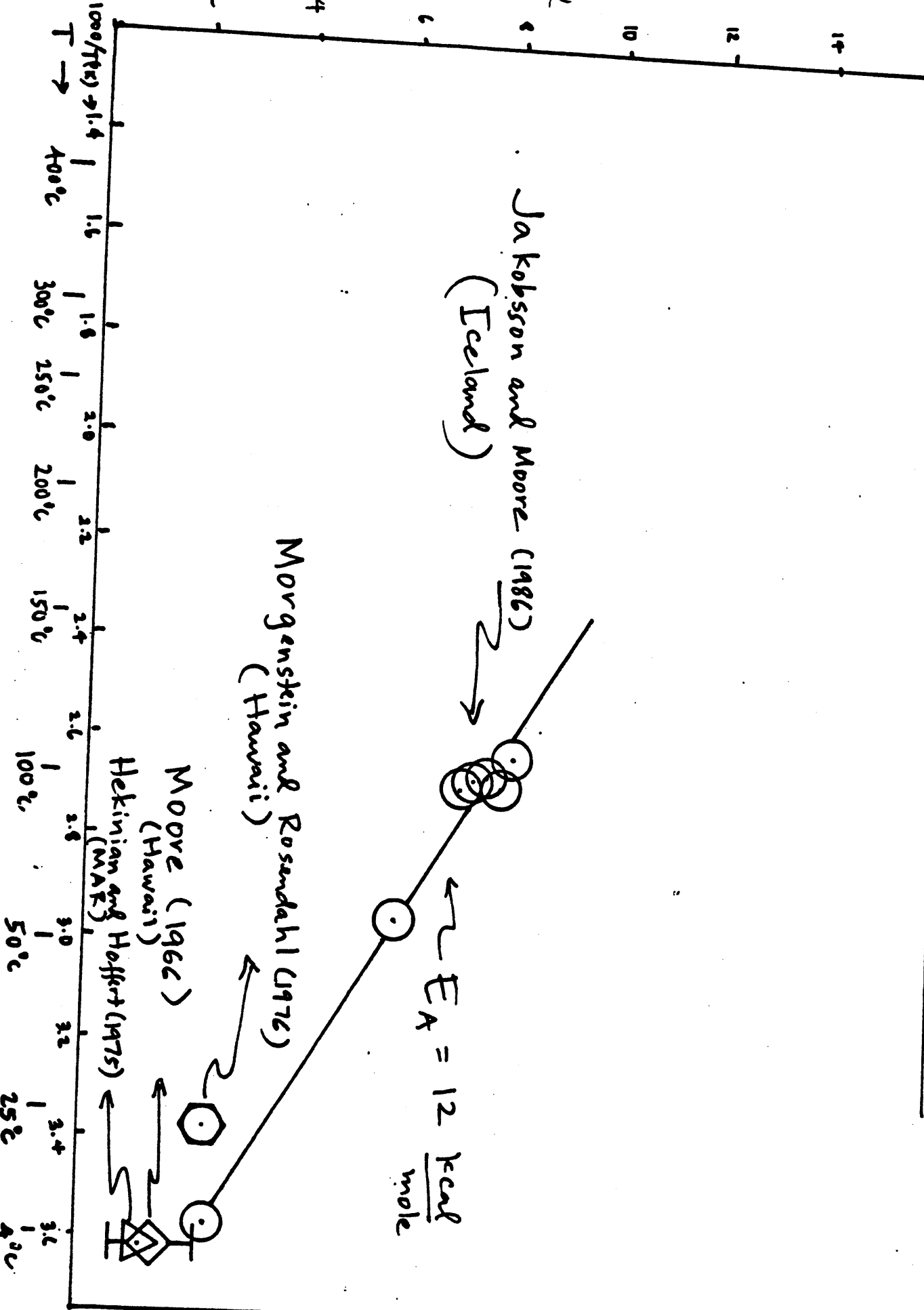
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Modeling of Diffusional Processes Within the Hydrated Layer of Vitrified
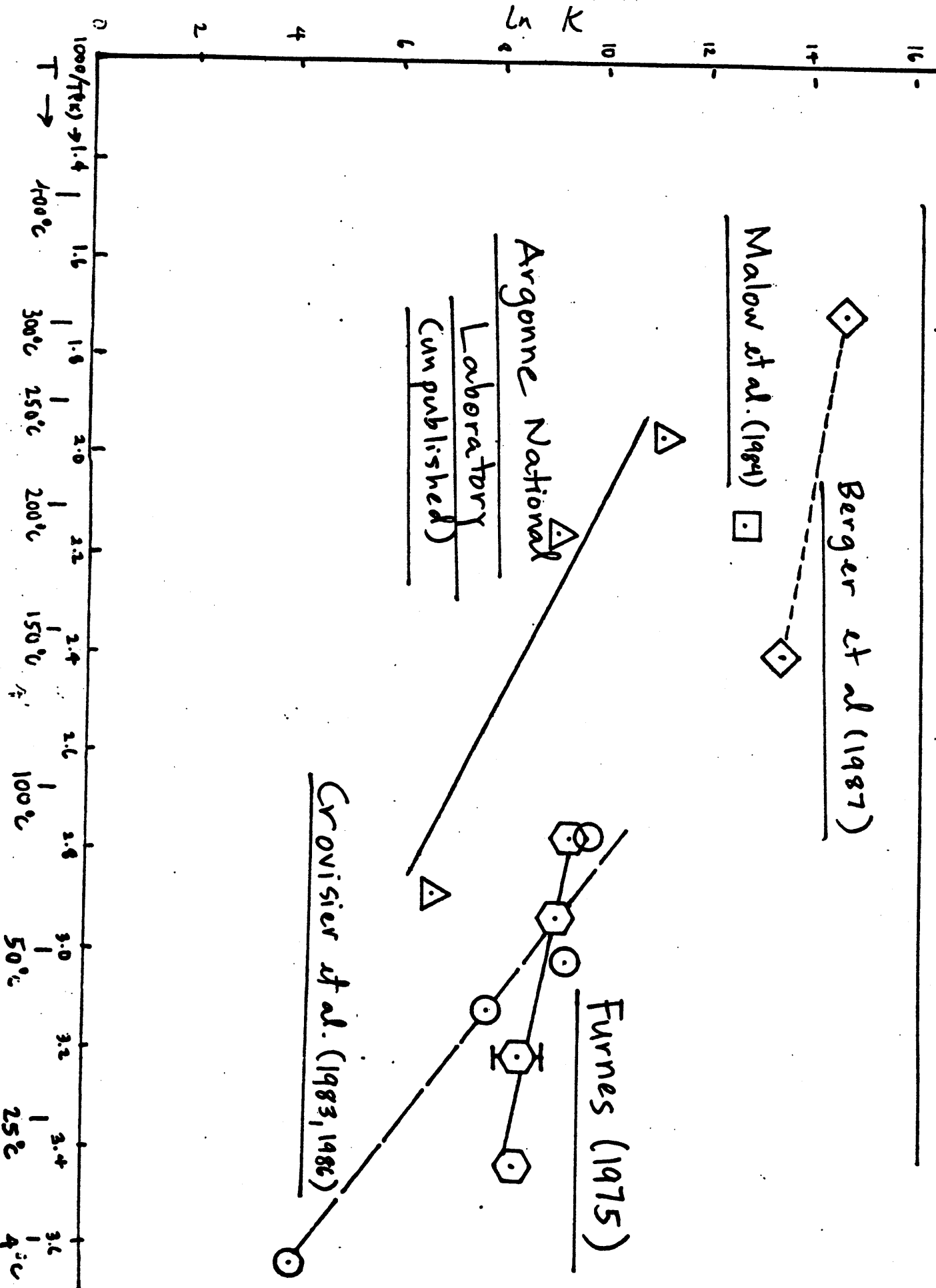Nuclear Waste Forms, Ph.D.   Thesis, University of Illinois, 163 p.

Figure Captions:

Figure 1. Palagonite layer thickness plotted against Mn coating thickness. From studies of Moore [1966] and Hekinian and Hoffert [1975] (A: Figure from Crovisier et al. [1987]) and Bryan and Moore [1977] (B).

Figure 2. Arrhenius plot showing variation of palagonitization rate constants with temperature in natural basaltic systems.

Figure 3. Arrhenius plot showing variation of palagonitization rate constants with temperature in experimental basaltic systems.

Figure 4. Variation of palagonite layer thickness formed on synthetic tholeiitic basalt with time after leaching at 50 deg-C and 43 deg-C (From Crovisier et al., 1983).

Figure 5. Variation of palagonite layer thickness formed on synthetic alkalic basalt with time after vapor hydration at 240 deg-C (From Byers et al., 1985)
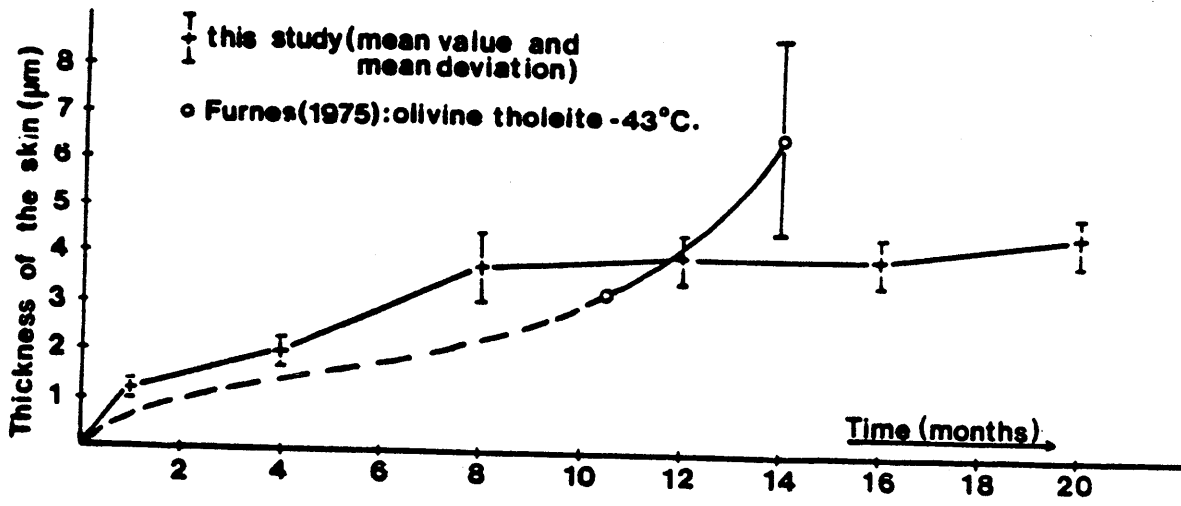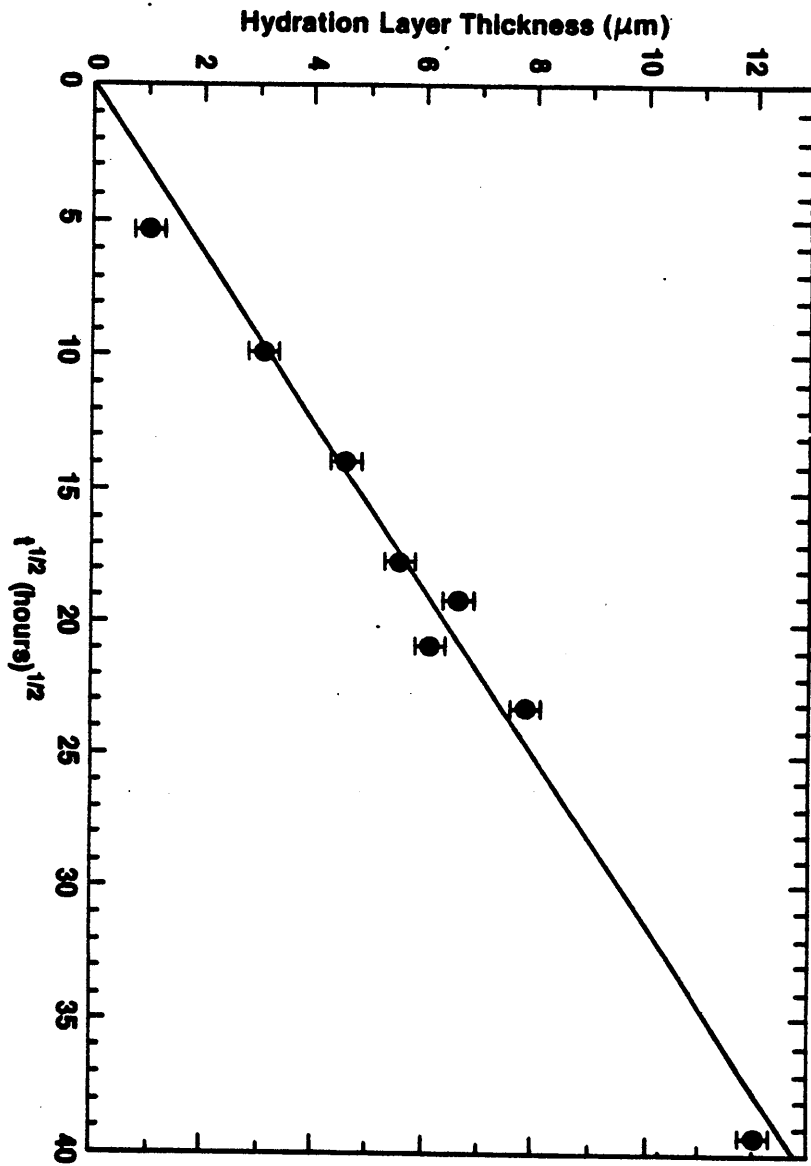
Field-Determined Palagonitization Rates

Jakobson and Moore (1986)
(Iceland)

Morgenstein and Rosendahl (1976)
(Hawaii)

Moore (1966)
(Hawaii)

Hekinian and Hoffert (1975)
(MAR)

$E_A = 12 \dfrac{kcal}{mole}$

100/T(k) →1.4

400°C   300°C 250°C   200°C   150°C   100°C   50°C   25°C 4°C

2

4

6

8

10

12

14

16

R
K

T →

②

Experimentally-Determined Palagonitization Rates

this study(mean value and mean deviation)

o Furnes(1975):olivine tholeite -43°C.

Department of Geology
21 Jan. 1988

Dr. Rodey Batiza
Dept. of Geol. Sciences
Northwestern University
Evanston, IL 60208

Dear Rodey,

I've just completed several tests on the 62-149 μm grain-size fractions of two samples of crushed MORB glass: your D19-3 and one (K18) David Christie gave me. There was no natural TL signal in either sample, but this is not surprising given that both have been extensively exposed to daylight. While the ionizing radiation sensitivity of K18 is too slight to be useful, D19 is about 30 times more sensitive, and therefore potentially more useful. However, positive as this observation may be, other characteristics dampen my interest.

In particular, K18 showed no evidence of the presence of high temperature traps (those filled in the lab irradiation would empty at room temp in a few days or weeks) that are necessary for TL dating. While D19 did have more of the "stable" traps, a very large portion of its TL signal represents thermally unstable traps (i.e. the TL is observed at low glow-curve temp.) Furthermore, a controlled heating test (a la *BERGER (1987)*) suggests that a lot of the induced TL exhibits anomalous fading. In addition to these negative features, D19 showed large subsample inhomogeneity in the TL. Specifically, one of the discs gave a glow curve that was totally unlike that of a glass, suggesting that a more complicated sample prep would be required (but without the assurance of success). Finally, an optical bleaching test on D19 produced significant reduction in the TL after exposure to light somewhat more orange than sodium light.

Well, it doesn't look promising at this time, *Although several MORE* lab tests could be done.

My feeling now is that TL is more likely to be useful for providing indirect dates of MORB, than direct dates. This presupposes that TL will not work on the feldspars in the rock.

Cheers,

Glenn Berger

APPENDIX 3

<u>ESR DATING: POSSIBILITY FOR DATING YOUNG MID OCEAN RIDGE BASALTS</u>

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Electron Spin Resonance Dating

Introduction to ESR

It was suggested by Zeller et al. (1967) that electron spin resonance (ESR) spectroscopy could be used as a method to date geological and archaeological samples. Materials on which ESR dating has been performed thus far are: speleothems, corals, mollusc shells, teeth, as well as samples from geological processes such as volcanic eruptions, and fault movements.

Physical Principles

Paramagnetic centers in a mineral arise from trapping unpaired electrons (e^-) or holes (e^+) at charge defects incorporated into the crystal lattice upon formation. A defect is any position in the crystal structure representing a violation of the symmetry described by the symmetry space group of the crystal. In particular, charge defects are sites at which the effective charge is less than that required by the symmetric structure.

Radioactive impurities (U, Th, K, Rb, ^{14}C) incorporated into the sample itself and the surrounding matrix emit high energy particles ($\alpha-$, $\beta-$, and $\gamma-$ radiation) when they decay. Energy can be transferred from these high energy particles to electrons which are elevated from the valence to the conduction band. After a short time of diffusion the electrons recombine with holes near the valence band. The same electrons may however, be trapped at a defect site and form a paramagnetic center (Figure 1).
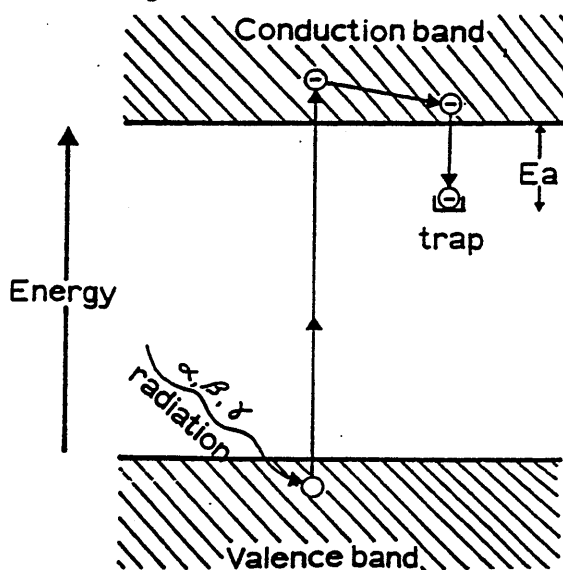

Figure 1. Illustration of the trapping scheme of electrons in minerals

The number of trapped electrons which is proportional to the ESR signal, is a function of the radiation dose rate and the time (=age) the sample was exposed to this radiation field.

An age can be deduced from the following equation:

$$AD = \int_0^t DR(t)\, dt$$

where AD is the radioactive dose the sample has accumulated over time and DR is the rate at which the dose has collected in the sample.

The accumulated dose (AD) is determined by the "additive dose method" where the ESR intensity of the natural sample is measured along with the ESR intensities of aliquots which were all γ-irradiated at different levels. Back extrapolation to zero ESR intensity gives the AD of the sample which is measured in Grays (Gy) (Figure 2).
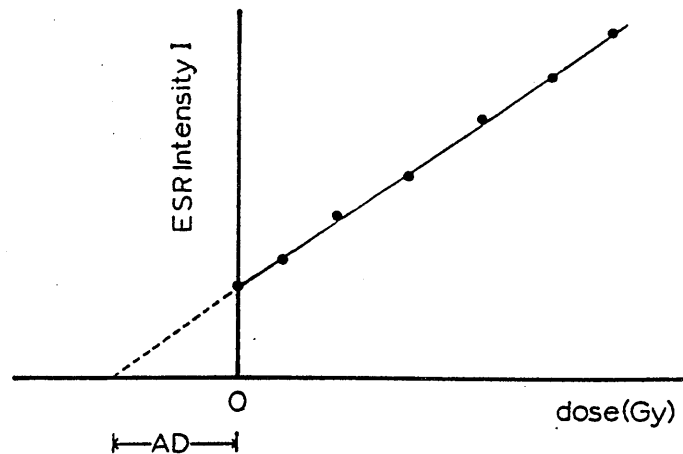

Figure 2. Determination of AD by the additive dose method; back extrapolation to zero-ESR intensity gives the AD value.

Determination of DR

To determine the dose rate, precise information about the amount of radiation that the sample has received from internal and external radioactive impurities is needed. External γ-and cosmic radiation dose rates can be determined by inserting a portable dosimeter unit directly into or near the sample site for a period of time.

The determination of U and Th (through neutron activation) and K (XRF) in the matrix surrounding the sample, and within the sample itself gives the α- and β- external and internal dose rates respectively. The measured concentration of radioactive elements can be converted into dose rates by the use of published tables (e.g. Nambi and Aitken, 1986). If external γ-and cosmic dose rates are not measured in situ then the γ- dose rate can be calculated from chemical analysis; the cosmic dose rate is dependent on altitude, latitude and attenuation by overlying sediment and water and can be estimated by graphs published by Prescott and Stephan (1982).

In general the calculation of DR is performed by an equation in the form shown below:

$$
\begin{aligned}
DR = {} & [C_U \, (k \cdot W_\alpha \cdot G_{U-\alpha} D_\alpha + W_\beta \cdot G_{U-\beta} \cdot D_\beta + W_\gamma \cdot D\gamma) \\
& + C_{Th} \, (k \cdot W_\alpha \cdot G_{Th-\alpha} \cdot D_\alpha + W_\beta \cdot G_{Th-\beta} \cdot D_\beta + W_\gamma \cdot D_\gamma) \\
& + C_K \, (W_\beta \cdot G_{K-\beta} \cdot D_\beta + W_\gamma \cdot D_\gamma) + G_{cos} D_{cos}]_{external} \\
& + [C_U \, (k \cdot G_{U-\alpha} D_\alpha + G_{U-\beta} \cdot D_\beta + D_\gamma) \\
& + C_{Th} \, (k \cdot G_{Th-\alpha} \cdot D_\alpha + G_{Th-\beta} \cdot D_\beta + D_\gamma) \\
& + C_K \, (G_{K-\beta} \cdot D_\beta + D_\gamma)]_{internal}
\end{aligned}
$$

(note that the activity ratios for the U and Th decay chains should be determined in order for an accurate dose rate to be determined).

Where $G_{\alpha,\beta,\gamma,cos}$ = attenuation factors for α, β, γ, and cosmic rays

$W_{\alpha,\beta,\gamma}$ = water correction factors for α, β, and γ rays (incorporated into the equation if the % of water in the matrix is known)

D = dose rate per unit concentration

D_{cos} = cosmic dose rate

k = α efficiency

$C_{U,Th,K}$ = concentration of radioactive elements present

- if the external γ- and cosmic dose rates are measured by a portable dosimeter the above formula is simplified to:

$$
\begin{aligned}
DR = {} & [C_U \, (k \cdot W_\alpha \cdot G_{U-\alpha} D_\alpha + W_\beta \cdot G_{U-\beta} \cdot D_\beta) \\
& + C_{Th} \, (k \cdot W_\alpha \cdot G_{Th-\alpha} \cdot D_\alpha + W_\beta \cdot G_{Th-\beta} \cdot D_\beta) \\
& + C_K \, (W_\beta \cdot G_{K-\beta} \cdot D_\beta) + MD_\gamma + MD_{cos}]_{external} \\
& + [C_U \, (k \cdot G_{U-\alpha} D_\alpha + G_{U-\beta} \cdot D_\beta + D_\gamma) \\
& + C_{Th} \, (k \cdot G_{Th-\alpha} \cdot D_\alpha + G_{Th-\beta} \cdot D_\beta + D_\gamma) \\
& + C_K \, (G_{K-\beta} \cdot D_\beta + D_\gamma)]_{internal}
\end{aligned}
$$

where $MD_{\gamma,cos}$ = measured dose rate of γ, and cosmic rays

Application of ESR for dating recent MORBs

The use of the ESR dating method is restricted to minerals with a low iron content due to the strong paramagnetic nature of Fe which tends to overwhelm all other ESR signals. Plagioclase is the only mineral with a low Fe concentration of significant quantity for ESR dating obtainable from MORBs. However, problems arise when attempting to use plagioclase for ESR dating in that the two most common trapping centers (Al and Ti) may be stress sensitive. Crushing techniques used to separate the feldspar from the other basalt components may alter the ESR signal intensity thereby giving a false age.

Accurate ESR dating of MORBs also may be hampered by sea-floor weathering, particularly if the primary calcic plagioclase has been replaced by sodic plagioclase which will alter the ESR signal intensity.

ESR is, therefore, not an adequate dating tool for primary MORBs but may become useful as a secondary dating method on materials related to MORBs, such as weathered sediments between lava flows. In principle, the ESR signals can be reset by the thermal baking of MORB flows capping the sediments. Depending on the sediment thickness, there should be an aureole produced where all of the trapping centers in the detrital feldspar should have been zeroed (temperatures required to reset ESR traps are not reached outside the aureole and thus the centers are not zeroed at the time of the lava emplacement). ESR ages obtained from minerals within this aureole should all give the same ages to establish a plateau which would be an indication of center resetting due to the lava flow (Figure 3). Weathering of detrital plagioclase in the sediment may not be as pronounced as for the fresh lava and ESR signal intensity would not be altered significantly. It therefore, may be possible to date MORB flows through resetting of ESR signals in these materials.
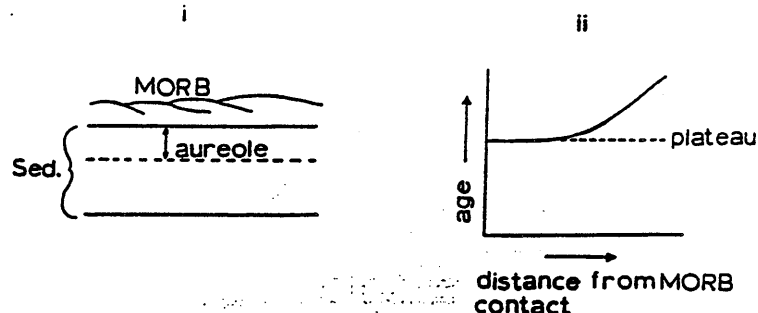

Figure 3. i) Illustration of a "zeroed" aureole in the detrital sediment created by the MORB flow above.
ii) Equal age plateau along which are samples that have been totally reset by the thermal baking of the MORB flow.

Another problem that arises for ESR dating of MORBs is the extremely low concentrations of the radionuclides (uranium, thorium and potassium) needed to build up the electron charge in the material. Without a significant buildup of ESR signal intensity an ESR spectrum may not be detectable and accurate age determinations of young MORBs may not be possible.

It appears that there are a number of problems related to ESR dating of young MORB samples yet it may be worth while to attempt to look at the ESR signals in the plagioclase (and possibly quartz if there is any present) in detrital sediments associated with MORB flows and cross check the dates obtained with other dating methods.

To do this one would require at least 10 g of detrital material in loose aggregate form for each of these types of deposits obtained during sampling, preserved in water tight plastic bags or containers. It would also be helpful if a measured γ-dose could be taken by a portable dosimeter at each of the samples locations.

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