

B8952
File 178

10032

(101) L. T. Silver

#32

(RH) Patterns of isotopic disturbance in $Pb-U-Th$ systems

~~MS No. 32~~

1 2

DAUGHTER-PARENT ISOTOPE SYSTEMATICS IN U-TH-BEARING IGNEOUS
ACCESSORY MINERAL ASSEMBLAGES AS POTENTIAL INDICES OF
METAMORPHIC HISTORY: A DISCUSSION OF THE CONCEPT

Proofs to:

3 LEON T. SILVER

Division of Geological and Planetary Sciences,
California Institute of Technology,
Pasadena, CA 91125, U.S.A.

abstr. 21

Abstract

It is proposed that the patterns of isotopic disturbance in Pb-U-Th systems for the assemblage of radioactive minerals in any granite or equivalent orthogneiss may have value not only as geochronological tools for determining the time constants of metamorphic events but also may have significant potential as indices of the nature and intensity of metamorphism (including thermal, hydrothermal, deformational, weathering, and other environments of change). One of the special qualities of radiogenic Pb-U-Th geochemistry is the coexistence of three daughter-parent (D/P) systems: $^{206}\text{Pb}/^{238}\text{U}$, $^{207}\text{Pb}/^{235}\text{U}$, and $^{208}\text{Pb}/^{232}\text{Th}$. The uranium pair of D/P systems are coupled chemically so that they lead to rigorously linked isotope ratio variations during disturbance. The thorogenic D/P system, because of the contrasting Th and U chemistry, may behave quite independently, providing special insights into the mobility of Pb, U, and Th.

Accessory mineral assemblages in most rocks contain from three to eight or more radioactive minerals in which U and Th commonly are quite fractionated. Each mineral and its three contained D/P systems appear to have distinctive responses to metamorphism and show differential sensitivity to different metamorphic variables. The responses are conditioned by accumulated radiation damage at the time of metamorphism. Each mineral species has a unique structural response to α -fluence, and commonly shows large inter- and intra-grain variations in accumulated disorder. The rate-competitive roles of structural annealing and metamorphic disturbance are believed to determine the net effect on the D/P systems.

1c alpha

Any individual sample may be treated as an isogradic collection of responses at a given position in a metamorphic gradient. The number of minerals \times 3 D/P systems provides a large matrix of sensitive, precisely measured parameters for characterizing that position in the gradient. Several properly selected samples can characterize the entire gradient. This then offers a general basis for extracting quantitative indices of the nature and intensity of the metamorphism. Ultimately, this may permit calibration of metamorphic effects derived from several important variables neglected in some current thermochronological models. Hypothetical models representing possible assemblage D/P responses derived from different metamorphic disturbances are offered. Some examples from southern California of natural responses to metamorphism are provided: (1) The effects of mylonitization as a modifier of the radioactive mineral assemblages are clearly demonstrated in titanite, apatite, and allanite in a tonalite pluton cut by the Eastern Peninsular Ranges mylonite zone. (2) The correlation of radiation damage with isotopic disturbance in zircons is documented in a Cretaceous granodiorite that was hydrothermally altered during the Miocene.

(2) 131 / 3

INTRODUCTION

Evidence for differential migration of daughter and/or parent isotopes is observed commonly in the natural radioactive/radiogenic systems of minerals employed in geochronology. Open-system behavior appears to defeat basic assumptions for calculation of apparent ages, and generally is assiduously avoided in sampling and minimized in interpretation. For some isotopic systems (e.g., Pb/U pairs in cogenetic zircons; $^{39}\text{Ar}/^{40}\text{Ar}$ plateaus) models have been devised for treating arrays of data for partially opened systems to permit inferences about the closed-system end points that can be taken as primary ages. Currently concordant U-Pb isotope ratios from a zircon, or the well-defined arrays of discordant U-Pb isotope ratios in cogenetic zircon fractions (SILVER and DEUTSCH, 1963) compared to the "Concordia" relationship for ideal closed U-Pb systems (WETHERILL, 1956), are accepted as providing the most precise magmatic ages available. The origins of discordance (e.g., the implications of lower discordia intercepts on "Concordia") usually are not pursued. The Th-Pb isotope ratios in zircons and other minerals are seldom measured, probably because they yield apparent ages that commonly disagree with and lack the independent power of the paired U-Pb ratios.

Developing an understanding of the diverse origins of open-system behavior in geochronological systems has been neglected. The comparative simplicity of substituting thermally activated diffusion models has been favored since the classic works of HANSON and GAST (1967), HART (1964), and HART et al. (1968). The more recent developments of fission track and $^{39}\text{Ar}/^{40}\text{Ar}$ methodologies have contributed elegant insights into cooling or thermal histories related to emplacement, tectonic uplift and/or unroofing (e.g. NAESER, 1979; DODSON, 1979; and many works cited in MCDUGALL and HARRISON, 1988). Thermochronology is an essential component of understanding metamorphism but it does

not provide a comprehensive description in time and in multi-parameter metamorphic space. Fluids, mineral and rock strains, tectonic loading and unloading, changes in bulk rock chemistry, and re-equilibration of minerals also enter into metamorphic processes. For example, many stable isotope investigations have demonstrated the importance of fluids.

In this work, a concept and possible models for extracting more extensive information from opened uranium and thorium daughter-parent (D/P) systems in metamorphosed intermediate to felsic granites are examined. A large number of demonstrably sensitive isotopic parameters in radiogenic systems can be measured with precision, and pragmatically, the three relevant radiogenic isotope systems can all be determined with a single set of chemical and instrumental analytical procedures.

Patterns of imprinted variations are well organized among the families of opened and closed (D/P) isotope systems in an assemblage of several cogenetic uranium and thorium accessory minerals in a meta-igneous rock. How well do the imprints individually or collectively represent responses to the many complex parameters of the metamorphic environments? Are there special correlations with other important metamorphic variables besides temperature, e.g. activity of H_2O ? Do they provide valuable characteristic signatures and quantitative measures of the nature as well as timing of the modifying episode? Can systematic radiogenic D/P isotopic investigations, with independent mineralogical and petrological calibrations, yield significantly more information about the rock history and the metamorphic processes than the primary age and a modeled secondary thermal history?

The U-Th-Pb assemblage approach appears particularly applicable to intermediate to felsic granites which have participated in a single important post-crystallization modification event (e.g. deformation, regional or contact thermal metamorphism, hydrothermal circulation, ancient or modern weathering). Its prospects are most favorable

where a well-defined metamorphic gradient has been established in a uniform granitic mass (or at least, in a single generation of granites) that can be sampled at more than one position. However, preliminary evaluation indicates the approach may be extended into less ideal situations.

The minerals that can be examined might include, in addition, the cogenetic hosts for ^{40}K , ^{87}Rb , ^{147}Sm , etc. Pb-U-Th systematics should and can be compared profitably with other D/P isotopic systems in other cogenetic minerals when data for such systems ^{are} ~~is~~ available (see below). This approach was undertaken in the collective works of HART and his colleagues in their investigation of the contact metamorphic aureole around the Eldora stock in the Colorado Front Range (HART, 1964; DOE and HART, 1963; DAVIS et al., 1968; HART et al., 1968). These authors were primarily concerned with the stabilities of mineral ages and feldspar isotopic endowments in the contact metamorphic thermal gradients of a Paleocene intrusive into a Precambrian schist complex. They found large effects and recognized the potential correlations of modified ages with the metamorphic facies zonation, but they did not attempt to invert their observations to use isotopic systematics as metamorphic indicators.

HANSON et al. (1971) studied the effects of contact metamorphic gradients induced in zircons, titanites, hornblende, and biotites in the Giants Range granite as a result of intrusion of the Duluth gabbro. They found relative ages to be titanite $^{206}\text{Pb}/^{238}\text{U} >$ zircon $^{206}\text{Pb}/^{238}\text{U} >$ hornblende $^{40}\text{K}-^{40}\text{Ar} >$ biotite $^{40}\text{K}-^{40}\text{Ar}$. They inferred any discordance was induced by the thermal ^{e-} affects of contact metamorphism, but could not resolve whether earlier disturbances had influenced the zircons and titanites.

Neither investigation considered the role of fluids. In retrospect, their integration with stable isotope investigations of both accessory and major rock minerals would have been rewarding.

2 31

RATIONALE FOR USING PB-U-TH SYSTEMATICS

In this discussion minerals that contain the Pb-U-Th chemical and isotope systems have been selected because of their peculiar properties and powers and the author's familiarity with a variety of case studies.

$^{238}\text{U} \rightarrow ^{206}\text{Pb}$	$\lambda = 1.5513 \times 10^{-10}/\text{y}$
$^{235}\text{U} \rightarrow ^{207}\text{Pb}$	$\lambda = 9.848 \times 10^{-10}/\text{y}$
$^{232}\text{Th} \rightarrow ^{208}\text{Pb}$	$\lambda = 0.4948 \times 10^{-10}/\text{y}$

λ lambda

Both uranium and thorium commonly are found enriched relative to the bulk rock in a shared group of accessory minerals. Th/U ratios display a great range of fractionation of the actinides among these different primary minerals (Table 1). All of the stable end products of the actinide decay chains are isotopes of lead. Chemical losses or gains of parents or daughters have very different relative effects on the radiogenic lead isotopic evolution in each host. Each mineral species tends to display a different sensitivity and a characteristic style of response (mobilization of lead, uranium and/or thorium) to chemical disturbances. Experimental work (e.g. PIDGEON et al., 1966, 1974) and field observations indicate that fluids can play a major role in opening these systems in zircons. These variable response characteristics make the assemblage approach potentially very powerful.

Table 1

[tn 1]

Exp [te

File 179 30

Mobilization of lead affects all three D/P systems. U and Th mobility influences only two or one D/P system, respectively, permitting considerable discrimination. The paired Pb-U systems have the special property that chemical disturbances affect daughters and parents

in both isotope systems equally. The radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ ratios resulting from the integrated history of the uranium-generated D/P pair can convey unique temporal information.

Typically, an intermediate to felsic granitic rock contains from three to five readily separated radioactive minerals. Less commonly, there may be eight or more such minerals (Fig. 1 and SILVER et al., 1982). In a typical calcalkaline granodiorite or granite with four radioactive minerals (e.g. zircon, titanite, apatite, allanite) a matrix of up to 12 responsive parameters (four minerals \times three D/P isotope ratios) can be utilized to characterize and evaluate the chemical disturbances produced in the metamorphic episode.

To be effective the model assumes that each host mineral phase will

list

- (a) retain its mineralogical identity;
- (b) respond chemically to the modification event with consequences to its contained U, Th, and Pb peculiar to the phase and to the nature of the event;
- (c) contain a sufficiently small initial lead endowment in each mineral relative to the U and Th concentrations (favorable $^{238}\text{U}/^{204}\text{Pb}$ and $^{232}\text{Th}/^{204}\text{Pb}$ ratios); and
- (d) accumulate a radiogenic increment in the total Pb large enough for concentrations to be determined (after correction for initial lead and blank) to better than a few percent precision by isotope chemistry and mass spectrometry.

@ [el6] The initial lead composition is

determined from analysis of cogenetic feldspars, preferably from unaltered granite protolith. It is desirable that the assemblage include minerals with a wide range of sensitivities; observation suggests it commonly does.

The decay constants of the several actinide parents are such that the geologic time constants for examining metamorphic effects appear generally favorable for rocks on the order of 100 Ma or older. With higher yet still reasonable actinide levels, even younger

systems, 10¹-100 Ma, can be utilized. The intervals of post-crystallization cooling to closure of all of the U-Th phases in batholithic rocks emplaced at middle or upper crustal levels generally appear brief relative to a 10⁸ Ma primary age. The duration of the period of open-system behavior during an imposed metamorphic episode can be quite variable depending on the nature and setting of the metamorphic process. For optimal resolution, it should be brief relative to the primary age. When it may not be, the consequent observed dispersion of ages should reveal the extended history. Very young disturbances (e.g. modern weathering, geothermal activity, active faulting, crustal xenoliths in active volcanoes) offer profitable opportunities for testing and calibrating disturbance models.

Inheritance effects from a pre-magmatic history may influence the ratios in some phases, notably zircon. For zircons, discordia projections to "Concordia" can provide proxy ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²³⁵U values for a primary magmatic age when their radioactivity levels are low to moderate. Monazite has been reported to contain inherited lead in some situations. Few other common radioactive mineral species have inheritance documented. In the discussions below, inheritance phenomena will be provisionally accepted as treatable or minimal.

② (31)

ACCESSORY MINERAL SPECIES AND ASSEMBLAGES

In metaluminous quartz-rich calcic to calcalkaline plutonic rocks, an ubiquitous assemblage is zircon, titanite, apatite, allanite ± thorite. In peraluminous rocks zircon, monazite, apatite ± thorite ± xenotime are encountered. Highly differentiated rocks (leucocratic granites, pegmatites, aplites) may be significantly enriched in the actinides and other incompatible elements, and may also contain uraninite, thorianite, cerianite, coffinite, uranothorite, basnaesite-parisite, complex multiple oxides of Nb, Ta, Ti such as fergusonite,

euxenite, brannerite, microlite-pyrochlore, and other exotic phases. Fig. 1 illustrates a complex assemblage. The best age for the rock is $1.411 \pm 0.003 \times 10^9$ y, based on the multiple zircon fractions. D/P ratios have been converted to percentage of the zircon age. The great range of values reflects an extensive Mesozoic disturbance history. Alkaline plutonic rocks may contain, in addition, perovskite, baddeleyite, zirkelite, and various phosphates and carbonates containing significant uranium and thorium.

By far the most prevalent radioactive minerals in common plutonic rocks are, in approximate descending order of abundance: titanite, apatite, allanite, zircon, monazite, thorite, and xenotime. Average values of Pb, U, and Th and the ratios $^{238}\text{U}/^{204}\text{Pb}$ and $^{232}\text{Th}/^{204}\text{Pb}$ for each of these species (xenotime is not present) from a number of plutonic rocks of the eastern Peninsular Ranges batholith are given in Table 1. Various combinations of this group represent the suites of cogenetic minerals which can be considered for general use in this approach. Any given assemblage will contain at least three and probably more phases. The suite zircon-titanite-apatite-allanite \pm thorite \pm an additional unspecified species will be employed in our hypothetical modeling.



INTRASPECIES COMPOSITIONAL VARIATIONS

Comparison of individual grains of any of these mineral species in a given rock sample can show a significant range of uranium and thorium concentrations. These variations may range from factor of two or less in titanite to as great as ten or more in zircons. These grain to grain variations are accompanied by compositional zonation of the actinide elements within individual crystals. Variations among zones may cover a large part of the total grain-to-grain range. In several species, the spectrum of variations in a particular sample can be subdivided into aliquots with quite different actinide endowments.

This is the fundamental basis for generating linear arrays of zircon U-Pb isotope ratios from a single granite population for interpretation of discordant ages (SILVER, 1963a,b; SILVER and DEUTSCH, 1961, 1963). Monazite, titanite, allanite, and thorite are other species where such discrimination is possible and profitable. These qualities extend the potential for detailing the isotopic responses of the radioactive assemblage to metamorphism.

ref?

1963

2

31

RADIATION DAMAGE

Each grain of a radioactive mineral species is exposed over its lifetime to a significant flux of energetic charged nuclear particles (alpha, beta, and spontaneous fission) and gamma radiation from the decay of a fraction of its contained radionuclides. The energy delivered to the crystal lattice, primarily via alpha recoil, introduces various degrees of structural disorder. This disorder is a function of the actinide concentrations, the elapsed time of exposure since crystallization (HOLLAND and GOTTFRIED, 1955; WOODHEAD et al., 1991), and the self-annealing properties of the host structure under various geologic conditions. Thorite, allanite, and zircon show the most conspicuous accumulations of radiation damage. Some may become completely metamict in as little as 10^8 years. An approximate sequence for acquiring damage is thorite > allanite > zircon > titanite > monazite > xenotime > apatite. These accumulations reflect their typical relative actinide contents, and their capacity for self-annealing. The imposition of radiation damage modifies the physical properties and enhances the fundamental chemical susceptibility of each species to metamorphic effects. This, in turn, contributes to the distinctive chemical and isotopic responses recorded in each species.

Ref

31
2
10/11
OBSERVATIONS ON MINERAL SUSCEPTIBILITIES TO DISTURBANCE

A very large body of observations exists on the open or closed nature of uranium- and thorium-enriched minerals used in geochronology.

32
3
Zircon (Zr, Hf, Y, U, Th) SiO_4

The widespread use of populations of cogenetic zircons and their Pb-U isotope pairs (especially on the "Concordia" plot of WETHERILL, 1956) has shown that Precambrian zircons commonly have been opened (TILTON et al., 1957; SILVER and DEUTSCH, 1961, 1963; and by many other workers). SILVER (1963a,b) demonstrated a strong correlation between radioactivity and discordance for families of zircons from several Precambrian granites.

PIDGEON et al. (1966, 1973) reported experimental evidence for the extensive removal of radiogenic lead without disturbance of uranium from a metamict Sri Lanka zircon by high-temperature aqueous saline solutions under hydrothermal conditions equivalent to a depth of about 6 km. BANKS and SILVER (1966) observed that even Cretaceous granitic zircons may be discordant at high radioactivity levels, and that the degree of disturbance correlated with relative radioactivities.

SILVER (1966) suggested that three rate-competitive processes may produce the disturbed, yet orderly, D/P relations commonly observed in zircons. @ [el6]

ref
list
(1) Accumulation of radiation damage in the zircon crystal structure, which is time and actinide-concentration dependent (α -particle fluence), determines the threshold susceptibility and initial rate of response of the zircon to a given modifying geologic process.

(2) Lead removal from the crystal, perhaps initially by local short-term diffusion at elevated temperatures, and ultimately by solution leaching or volatilization, proceeds at rates



determined by the nature of the disturbing geologic process and the residual disorder in the crystal structure.

(3) Crystal structure annealing, which may occur continuously at low rates, can accelerate enormously in more intense (hotter? wetter?) hydrothermal or metamorphic episodes, thereby reducing vulnerability to lead loss. @ [e26]

Process (1) is accumulative. Processes (2) and (3) are dominantly episodic in response to the nature of specific geologic metamorphic episodes in the middle or upper crust. Uranium or thorium gain or loss appears to occur only during growth or reaction of zircon as a phase participating in an evolving metamorphic assemblage. The relative rates of processes (2) and (3) are critical in determining the degree of lead loss, for the typical zircon response is self-quenching of losses by progressive annealing.

The sensitivity of many zircons to disturbance initially surprised workers, especially geochemists less familiar with the details of local geologic history. Since some low-level geologic events are cryptic (i.e. do not leave readily visible macroscopic evidence for their existence on igneous rock outcrops) several other explanations have been suggested, not all of which will be reviewed here (viz. STERN et al., 1966; GOLDICH and MUDREY, 1972; GRAUERT et al., 1974; SOMMERAUER, 1976). Some early workers (NICOLAYSEN, 1957; TILTON, 1960; WASSERBURG, 1963; SHESTAKOV, 1972) proposed models for continuous lead diffusion in zircons as possible disturbance mechanisms to explain the then widening evidence for disturbance in "unmetamorphosed" rocks. Any continuous disturbance mechanism is of concern here because it would tend to obscure the discrete effects of imposed metamorphic episodes. However, no well-documented examples of natural systems which fit uniquely to such diffusion models have been provided. In many case studies, geology-controlled interpretations involving specific disturbance episodes have been more

successful. There still remain some suites and situations for which appropriate independent evidence for discrete geologic disturbances has not been obtained.

In the context of the present proposal, the susceptibility of zircon to disturbance is considered a valuable asset. It is important to note, however, that complete resetting of the isotope systems in zircon has been suggested rarely, and is not documented.

3
32
Titanite (Ca, U, Th, Y) $TiSiO_5$

Since the early analyses of titanite in geochronological studies (TILTON et al., 1955; TILTON and GRUNENFELDER, 1968; MATTINSON, 1972, 1978) it has been observed that cogenetic titanite (sphene) and zircon have dissimilar responses to disturbance. Titanite appears to be more resistant to discordance from low-grade processes but has been found to be totally reset by certain high-grade metamorphic events. It appears to have a relatively high temperature of closure ($\sim 500^\circ C$) and in young undisturbed systems gives ages very close to those of zircons. Radiation damage in titanite is well-established (VANCE and MATSON, 1985), but visually much more subtle than in associated zircons, except in the very radioactive variety, keilhauite. Its isotopic responses to metamorphism have been examined principally by HANSON et al. (1974). (Ref)

3
32
Apatite (Ca, REE, U, Th) $_5$ (PO $_4$) $_3$ (OH, F, Cl)

Lead loss appears to be a principal effect of disturbance in apatite. However, evidence for parent migration and/or exchange has been observed in apatite in radioactive granites (e.g. Fig. 1). Apatite is ubiquitous in granites and rarely displays any evidence of radiation damage. Its uranium and thorium levels and $^{238}U/^{204}Pb$ ratios are much less favorable than found in zircon or titanite (Table 1). Apatite was shown to have distinctly

lower closure temperatures than zircon or titanite during initial cooling (MATTINSON, 1978; SILVER et al., 1982). Its D/P ratios have been observed to be completely reset.

3
32

Allanite (Ca, LREE, Th, U)₂ (Mn, Fe, Al)₂ AlO-OH (Si₂O₇) (SiO₄)

Allanite is relatively abundant in calcic and calcalkaline plutonic rocks. It is characteristically chemically zoned, and may have a corona of epidote. Very little was known about Pb-U-Th systematics of allanite until recently (SILVER, 1989, 1990; SILVER et al., 1991). Radiation damage accumulates rapidly because of its high Th content and crystals usually are extensively metamict even in late Mesozoic plutons. Once metamict, extensive daughter and parent mobility appears characteristic of allanites disturbed by external processes. The threshold for mobility responsive to such disturbances is quite low for Pb and U, and apparently somewhat higher for Th. The author has observed complete or nearly complete resetting of allanite at the garnet-amphibolite grade of regional metamorphism.

3
32

Thorite (Th, U) SiO₄

Thorite (and uranothorite) is an isostructural analogue to zircon and shows limited solid solution with it. When present it is similar in form to zircon and should be carefully discriminated in geochronological work. Its actinide contents are stoichiometric and may be as much as 70% of the bulk composition. This is up to 1000 times the actinide level in associated zircons. Hence, even 60 Ma crystals have been observed to be largely metamict. SILVER (1963a) and SILVER and DEUTSCH (1963) reported extremely disturbed isotopic systems (>90% apparent lead loss) in thorite in Precambrian granites with late Mesozoic tectonic disturbances. BANKS and SILVER (1966) measured a number of uranothorites from

a 115 Ma zircon-age granite and found them to yield apparent U-Pb ages from 86 to 111 Ma. The age variations correlated inversely with the actinide concentrations. If any mineral might be nominated for lead loss by continuous diffusion, it is thorite. However, no demonstration of such loss has yet been made. Clearly, thorite is a very susceptible mineral for chemical and isotopic disturbance. When metamict, it is probably open during normal surface weathering.

3 32

Monazite (Ce, LREE, Th, U) PO₄

Monazite is a common accessory in biotite, muscovite or two-mica granites. Like other phosphates it does not appear to accumulate radiation damage characteristics of silicate minerals with comparable actinide concentrations. ~~A. O.~~ NIER (1939) and ~~A.~~ HOLMES (1954, 1955) utilized monazites to obtain the first isotopic ages in Precambrian nuclei of several continents. They encountered clearly discordant systematics in many of their samples. TILTON and NICOLAYSEN (1957) examined four additional Precambrian monazites. Many showed the property that the $^{206}\text{Pb}/^{238}\text{U}$ apparent age significantly exceeded the $^{207}\text{Pb}/^{206}\text{Pb}$ apparent age (reverse discordance). Others showed the opposite relation (normal discordance). Unfortunately, these workers did not report independent evidence for the effects of metamorphic processes. SILVER et al. (1984) found both types of relations in a single sample and in different samples from the same pluton. These observations illustrate the complex behavior of monazite isotope systems. Workers in central Europe (KÖPPEL and GRUNENFELDER 1971, 1975; GEBAUER and GRUNENFELDER, 1973; KÖPPEL, 1974) measured many concordant monazites in metamorphosed rocks. They suggested monazite can be a powerful tool for dating metamorphic events because of

complete resetting in high-grade regional metamorphism (GEBAUER and GRUNENFELDER, 1979).

3

32

Xenotime (Y HREE, U, Th) PO₄

Xenotime also is isostructural with zircon, but shows little evidence of radiation damage. Least common of the minerals considered available for this assemblage approach, xenotime is quite radioactive. Both U and Th are typically at the 1/2 ^{empirical} 1-1/2% level and overwhelm by radiogenic increment modest initial lead contents. Xenotime isotopic analyses are few in number (SILVER et al., 1982, 1984; L.T. SILVER, unpublished data). They show slight to moderate isotopic disturbance with D/P ratios suggesting apparent lead loss relative to uranium and thorium. Where cogenetic monazites have been analyzed, they show greater isotopic disturbance than xenotime. No instances of complete resetting of xenotime have been encountered. Exp Lte

File 180

50 Analyses of assemblages in 18 tonalites, granodiorites, and monzogranites from the eastern Peninsular Ranges batholith provide some insights into typical initial lead, uranium, and thorium endowments of various mineral species (Table 1). The columns on the right show average ²³⁸U/²⁰⁴Pb and ²³²Th/²⁰⁴Pb values for the different minerals. These values indicate the relative magnitudes of initial lead corrections in calculating the radiogenic D/P ratios for each mineral.

9

31

ASSEMBLAGES IN "UNMETAMORPHOSED" AND METAMORPHOSED GRANITES

There have been comparatively few comprehensive isotopic studies of assemblages of cogenetic radioactive accessory minerals from either undeformed or metamorphosed granitic rocks. TILTON et al. (1955) established the importance of such studies in their

pioneering work on the Essonville granite. That rock was, in fact, a foliated granite gneiss deformed in the later stages of the "Grenville" orogeny. The possible effects of its metamorphic history on the radioactive minerals' systems was not appreciated. BANKS (1963) and BANKS and SILVER (1966) completed a comparable study on two intrusive phases of the apparently undeformed early Cretaceous Rubidoux Mtn. leucogranite in the Peninsular Ranges batholith and found isotopically disturbed systems suggesting a younger episode. MATTINSON (1978) explored zircon-titanite-apatite assemblages in several essentially undeformed Cretaceous granites in the Salinian block of central California, and found differences within the apparent ages of the several species of up to 25%, which he attributed to cooling histories down to ~300°C. LUDWIG and STUCKLESS (1978) examined partial assemblages in some radioactive Precambrian granites in Wyoming and found widespread evidence for isotopic disturbance.

File 180

SILVER et al. (1980, 1982, 1984) examined assemblages from five "unmetamorphosed" radioactive granites from Arizona and California, including their responses to weathering and hydrothermal alteration. They inferred widespread evidence for Mesozoic and Cenozoic disturbances for which independent geological support could be cited. CHEN and MOORE (1982) reported on seven zircon-titanite pairs from the central Sierra Nevada batholith that were close to concordant. DEWITT et al. (1984) reported disturbed U-Th-Pb systematics in zircons and titanites in several samples of a metamorphosed Proterozoic granite complex in the eastern Mojave desert, California. The disturbance reflected more than one metamorphism in the late Mesozoic.

ref

SILVER and JAMES (1988, 1991) have completed assemblage studies on a dozen tonalites to granites or gneissic equivalents from the Cajon Pass deep scientific drill hole in the southwestern Mojave desert. At least half of these rocks are protomylonitic and some

are metamorphosed to upper-amphibolite facies. The evidence points persuasively to a profound late Cretaceous tectonic event which imprinted all of the rock column. The author also has examined nearly 50 complete or partial assemblages from other Cretaceous and Jurassic granites from different petrologic settings and tectonic environments in southwestern North America.

The accumulating evidence points to some generalizations: @ [el6]

list

- (1) Different Pb-U-Th-bearing species have widely different sensitivities to low-grade events.
- (2) Many apparently unmetamorphosed granites have seen unsuspected low-grade events.
- (3) Many late Phanerozoic granites of the Cordilleran batholiths show only slight effects of secondary events on their assemblages.
- (4) More intensely metamorphosed granites show quite different, yet systematic, responses among their mineral assemblages than do weakly modified or cryptically influenced "unmetamorphosed" granites.
- (5) Older granites tend to carry more imprints of low-grade disturbances. Some can be correlated with local or regional tectonic or magmatic events. @ [el6]

In a geological sense the last observation is not surprising. Even the most stable craton has had an ongoing history of vertical tectonics including basin formation, marine transgression, and tectonic uplift, as well as intraplate volcanism and local strain and deformation. Older granite assemblages with greater accumulations of radiation damage in the participating species also have accumulated greater sensitivities. It is this general phenomenon that probably has stimulated continuous diffusion interpretations. In older granites, any new imprints of metamorphism necessarily must be read against any previously acquired background of minor disturbances.

MODELS FOR D/P VARIATIONS IN PROGRADE METAMORPHISM OF RADIOACTIVE MINERAL ASSEMBLAGES

Some assumptions and simplifications must be made in order to present graphic models of conceptual D/P trajectories in metamorphic space for a granite mineral assemblage. Much of the background for these assumptions has already been discussed: @ [el6]

(1) A sample of modified granite represents a point on a metamorphic gradient. Several samples, properly spaced, can define the gradient.

(2) For each kind of prograde metamorphic process, the Pb-U-Th system in each mineral host responds with distinctive patterns reflecting daughter and/or parent mobility. The threshold for initiation of mobility and conditions for complete isotopic resetting are peculiar to that mineral species for the particular metamorphic process. The net effect is a distinctive trajectory in a D/P vs. metamorphic intensity field.

(3) Retrograde phenomena do not significantly modify and blur the prograde record.

(4) External petrology, isotopic and geochemical indicators, and experimental studies, each permit some independent calibration of characteristic D/P trajectories along various kinds of natural metamorphic gradients. @ [el6]

The simplifications applied to the graphic presentation involve additional assumptions: @ [el6]

(5) A single dimension can be used to represent any type of metamorphic gradient even though the metamorphism involves complex variables.

(6) Each granite and each mineral species constituted an initially homogeneous population before being subjected to the metamorphic gradient. The assumption of initial homogeneity will be reexamined below.

List

- (7) The Pb-U-Th systems in the selected mineral species have favorable abundances, and sampling and analysis uncertainties are small relative to the natural D/P variations. In reality, not all systems, especially younger ones, may be treated this way.
- (8) The primary cooling time interval is negligible.

32
3

Model I Thermally Driven Diffusive Loss

In this case the mobility responses of Pb-U-Th bearing minerals are modeled as thermally driven diffusive phenomena governed by an Arrhenius relationship peculiar to each mineral. DODSON (1973, and in subsequent papers) developed a closure temperature model for slow cooling now widely applied for ⁴⁰Ar-⁴⁰K and ³⁹Ar-⁴⁰Ar geochronology (see discussions in MCDUGALL and HARRISON, 1988).

Fig. 2

In Fig. 2 ^[ln 2] a three-dimensional orthogonal rhombohedron is employed to represent the three major parameters: mineral species, metamorphic gradient, and D/P ratios for a particular daughter/parent system. The diagram is designed to illustrate a hypothetical two-stage history: (1) primary crystallization of U-Th mineral assemblages with a negligible cooling interval, whose closed system age is $(D/P)_1$, and (2) a short-duration metamorphic episode that has created a well-defined metamorphic gradient. In the time elapsed since metamorphism new or completely reset systems produced $(D/P)_2$. The diagram is generalized and uncalibrated.

The front face is bounded by the parameters of D/P ratio and intensity of metamorphism along the gradient. In this case, it shows the D/P response in zircon (none). Behind this face are parallel fields for related U-Th minerals in the assemblage. This includes an unspecified species, mineral X, to symbolize the variability possible in such systems. (Alternatively, mineral X might represent a ⁴⁰K, ⁸⁷Rb, ¹⁴⁷Sm, etc., geochronometer.)

Any plane perpendicular to the front face is an isogradic plane. It contains presently observed D/P values in phases of the assemblage collected at a particular point in the metamorphic gradient. The D/P values for each species in three isogradic (isothermal) planes, I_0 , I_{int} , I_{max} , on the metamorphic gradient are represented as heavy dots. At I_0 , the protolith condition, all values are $(D/P)_1$. Within the plane I_{int} , at some intermediate position, the D/P values for three of six species have been reset and show $(D/P)_2$, reflecting individual closure characteristics. In the plane at I_{max} , only zircon has $(D/P)_1$ memory; all others have been reset and have accumulated $(D/P)_2$. It can be seen that the array of D/P values encountered in any isogradic plane is duplicated only over limited intervals along the intensity gradient and could serve as an approximate index of metamorphic grade. Construction of additional diagrams for the other two D/P systems, however, creates a more unique specification of D/P systematics at any point on the metamorphic gradient.

In a temporal sense, the four mineral species in the isogradic plane at I_{max} with D/P values equal to $(D/P)_2$ form a depressed plateau rather analogous to an $^{39}Ar/^{40}Ar$ plateau. Of course, the plane at I_0 displays the primary age $(D/P)_1$ plateau. Thus, the relative D/P values in any intermediate isogradic plane, which can be obtained from any single sample and compared with isogradic patterns from the other pair of D/P systems, can be rich in useful information.

The comparative D/P responses for representatives of each species at all points along the metamorphic gradient produce a locus (heavy patterned line). The locus (or D/P trajectory) reflects the integrated geochemical behavior of the daughter and parent elements in the species along the metamorphic gradient. The illustrated loci are hypothetical. They show sharply defined closure (resetting) temperatures, based upon tendencies observed for each mineral. They are poorly controlled and perhaps quite inappropriate.

Most D/P trajectories in this model show relative daughter loss as ultimately dominant. Daughter loss can be expected. The radiogenic daughters are not structurally ordered in the host phase, are in damaged domains, and may be susceptible to diffusive migration. However, some degree of parent loss or addition is not precluded, even where daughter loss has occurred. Where lower grade metamorphism affects high temperature assemblages, internal re-equilibration might occur. In allanite under certain metamorphic conditions it appears that uranium may be more mobile than lead; hence the D/P ratio $> (D/P)_0$ is shown for part of the allanite trajectory.

For the relatively simple condition of thermally driven diffusive phenomena three different three-dimensional representations like Fig. 2, representing $^{206}\text{Pb}/^{238}\text{U}$, $^{207}\text{Pb}/^{235}\text{U}$, $^{208}\text{Pb}/^{232}\text{Th}$ can be used to analyze daughter versus parent migration. If lead loss alone is involved, the three D/P systems differ but are linked in a simple relation through the different decay constants. If parents are also mobile, more complex D/P trajectory lines for each mineral are generated along the metamorphic gradient. The added complexity adds uniqueness to the array of D/P values developed in the assemblage at a particular level of metamorphic intensity, thereby raising the potential use of D/P arrays as indices of metamorphism.

In summary, it may be possible to apply a Pb-U-Th assemblage approach to a purely thermally driven metamorphic event where such events exist, or if certain species were sensitive only to temperature. However, there is such extensive evidence of multiple variables affecting the Pb-U-Th systems that it seems necessary to consider a more general model. Perhaps it may be possible to assess the role of thermal diffusion when an increased number of case studies with favorable geologic conditions or careful laboratory studies

permit isolation of the contributions of several important variables. Fortunately, argon systems are available for thermochronology.

32
 3
Model II - Complex Disturbance Mechanisms

The complex interplay of several imposed variables defines the character of the metamorphic event and its influence on Pb-U-Th minerals. Temperature, activities of H₂O and other fluids, open chemical systems, and strain are particularly prominent. Indices of these parameters are major targets for investigation.

Fig. 3
 A generalized model for imposed metamorphic modification is provided in Fig. 3. [ln 3]

The parameters of the diagram are the same as in Fig. 2. Again, the isograds, I_o , I_{int} , and I_{max} , are emphasized by heavy dots where the D/P trajectories for each species penetrate the three planes. The D/P trajectories are distinctive curved lines with possible inflection points. Indicated trajectories are hypothetical, largely uncontrolled, except for the biases derived from the author's observations. In this illustration, only at the I_{max} isograd has a well supported plateau developed, with four species displaying (D/P)₂ ratios.

If a family of real D/P trajectories possesses comparably distinctive forms, then the assemblage D/P values contained in any isogradic plane between I_o and I_{max} will differ from the array of values in other planes. Using the trajectories of three D/P systems, the position of a sample in the metamorphic gradient should be uniquely defined, within analytical uncertainties.

Considerations of D/P responses in this model are again influenced by the chemical nature of each mineral species and its radiation damage. However, in this model the form of the trajectories may be equally determined by the nature of the metamorphic process. For example, the effects produced in a mylonite zone should, in principle, be distinguishable

from those produced in a hydrothermal cell, or in a weathering profile. Certainly each process will have its own threshold intensity level for disturbing a particular mineral, and it may or may not achieve complete resetting.

Fig 4

The author currently is pursuing these questions in several types of metamorphic situations. An example from work in progress is given in Fig. 4, [ln 4] which shows mineral assemblage analyses in six different rocks from the San Jacinto Mtns., Riverside Co., California. Ages and D/P ratios vary nearly linearly at this age; only the ages are plotted in this diagram. Five samples are from a nest of three unmetamorphosed plutons described by HILL (1988) and HILL et al. (1988). These samples indicate emplacement of the plutons between 92 and 95 Ma, based on well-defined microdiscordant zircon suites. The sixth sample is a protomylonite from a neighboring tonalite pluton 15 km to the east, from the margin of the great eastern Peninsular Ranges mylonite zone. In addition, titanite, apatite, and allanite have been analyzed in all samples. Previous studies (ARMSTRONG and SUPPE, 1973; MORTON and MILLER, 1987) provide ⁴⁰Ar-⁴⁰K ages in biotite and hornblende from the same plutons in the vicinity of several of the Pb-U-Th samples. The D/P ratios, calculated as ages, are shown for ²⁰⁶Pb/²³⁸U and ²⁰⁸Pb/²³²Th. The ²⁰⁷Pb/²³⁵U ages, within analytical error, track the ²⁰⁶Pb/²³⁸U ages and are omitted. All of the ages of the five unmetamorphosed samples are contained within the stippled envelopes. The range for each mineral should be compared with the indicated analytical uncertainty bars. Exp Cte

File 181

(50) For the five unmetamorphosed samples, the envelope for zircon-titanite-apatite shows progressively slightly younger ages for both D/P systems, suggesting at most, a five million year cooling interval to apatite closure. However, allanite in both systems displays D/P values greater than those for zircon, especially for ²⁰⁶Pb/²³⁸U. This is strong evidence for mobility of U and Th and does not preclude some Pb loss. Because allanite is clearly

disturbed and this disturbance by its magnitude must be post cooling, how much of the D/P differentials between zircon and titanite and apatite also might be post-cooling? Several hornblende and biotite ages are slightly lower ($5\frac{1}{2}$ -10 Ma) than the apatite ages and are part of a gentle local gradient that suggests a modest overprint. Thus the "unmetamorphosed" samples are not quite as pristine as was initially thought. What disturbed them?

In any interpretation the greater sensitivity to the disturbance of allanite, biotite and hornblende compared to zircon-titanite-apatite seems apparent. Was this produced by thermal history alone? Thermal diffusion coefficients for U and Th in partly metamict allanite are not known. Several arguments suggest that the diffusion mechanisms operative in biotite and hornblende must differ from whatever mechanisms are responsible for the disturbance in allanite. More detailed discussion of this problem will be developed in a separate paper. Neglecting allanite, the D/P ratios in the other five minerals would be accepted generally as the product of a simple cooling and uplift history, and suitable for approximately characterizing the I_0 position in models I and II. They will be used in that way, provisionally, for comparison with the sixth sample from the edge of the great mylonite zone to the east.

A geologic reconstruction of the east-dipping eastern Peninsular Ranges mylonite zone (SHARP, 1979) projects some 10 ± 3 km above the other five samples. This zone has been called late Cretaceous or Paleogene, synplutonic or post-emplacement, by various workers, and its age has considerable significance in southern California tectonics. The grade of metamorphism where it is most profoundly mylonitized is amphibolite facies. The sample recorded in Fig. 4 was a tonalite and is now a penetratively foliated tonalite gneiss whose major mineral assemblage, hornblende-biotite-quartz-plagioclase, remains unchanged. Most of the major minerals remain macroscopic and a good yield of all accessory minerals

was obtained. This sample represents an intermediate position in the strain gradient as indicated by its fabric modification. There is no evidence of low grade H₂O-supported alteration. The age of its protolith from nearly concordant zircons is indistinguishable from the other five samples. The D/P ratios (ages) for the other Pb-U-Th systems are lower by 10-35% than the D/P ratios for the emplacement age.

The allanite D/P ratios show the greatest differences and are among the lowest values in the mylonitic accessory mineral suite, indicating that apparent lead loss dominated over parent gain. Thus the character of the D/P responses in the protomylonite allanite is in strong contrast with whatever factors influenced the D/P ratios in allanites in the western samples.

The patterns of ages for the two D/P systems in the protomylonite assemblages cannot yet be related to the post-tectonic cooling and uplift history. Until the gradient sampling is completed, the observed D/P ratios must be used cautiously in any interpretation of the age of mylonitization. If it reflects a thermal anomaly induced by the tectonics which produced the mylonite, one might expect the thermal anomaly and its cooling history to have imprinted the deeper underlying samples as well. Was the intense strain associated with the local fabric development a critical factor in developing the D/P patterns? Answers to the several questions above are not available at this point, but it is the questions are central to the arguments for continued testing and delineation of elements of models I and II.

2

32

Model III - Intraspecies Variations in Actinide Concentrations and Associated D/P Ratios

In presenting models I and II, it was assumed, for purposes of simplification, that each mineral species was a homogeneous population of crystals in a homogeneous granitic

protolith. Even though this is rarely the case, heterogeneity is no real barrier to the consideration of those models provided it is recognized, evaluated, and normalized effectively. If radiation damage is an important factor influencing species responses, then normalization to a common degree of radiation damage can be achieved by comparing actinide concentrations. Some other influential compositional variations may also require normalization. In model III, the intent is to indicate briefly how intraspecies variations can add additional definition to the metamorphic responses recorded in the D/P values of the mineral assemblages.

The correlation between actinide concentrations (dominated by uranium) and degree of discordance in zircon is well established (SILVER, 1963a,b). In model III we propose that this correlation in zircon also may provide a sensitive index of metamorphism, and that other intraspecies variations may be useful. In Fig. 5, ^[ln 5] another block model rather similar to Figs. 2 and 3 is presented. It differs only in that the Mineral Species coordinate has been replaced by Radiation Damage in zircon subsets. Various fractions of a single mineral species, zircon in this case, are separated on the basis of their actinide concentrations and associated radiation damage.

Fig. 5 Present day radiation damage is not the most significant parameter if some annealing has taken place; the accumulated damage at the time of metamorphic disturbance is the relevant value. That value cannot be uniquely determined at present, but one can reasonably assume a proportionality correlated to the present actinide concentration values.

In this model, since the correlation of magnitude of disturbance with magnitude of radiation damage is accepted, the family of zircon subsystems might respond to the metamorphic gradient along the trajectories shown by heavy lines in Fig. 5. The values on the isogradic planes are indicated at I_{int} and I_{max} . The prograde changes are shown by the

model as sufficiently large to be clearly established by isotope dilution mass spectrometry. The disturbance effects in some zircon systems are much larger.

An actual example of this type of response corresponding to an I_{int} isogradic plane has been measured in a Cretaceous granodiorite near Randsburg, California. This intrusive has been intruded, in turn, by a small mid-Tertiary stock which generated a locally intense hydrothermal cell. The granodiorite sample was collected on the outer perimeter of the cell and shows only slight recrystallization affects. However, titanite-apatite-biotite-hornblende D/P ratios all yield Miocene ages. The zircons have been separated into several fractions. Each fraction appears concordant, within analytical error, when plotted on "Concordia."

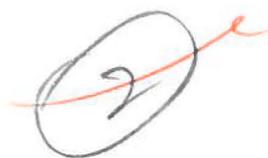
Fig. 6

In Fig. 6, the D/P ratios (as calculated ages) for all three D/P systems are plotted against uranium concentration in four zircon fractions. The Th/U ratio is close to a constant for these fractions and uranium has contributed more than 85% to the total alpha particle fluence. Therefore, uranium is a good indicator of the relative radiation damage at the time metamorphism was imposed. The most radioactive zircons show a 10% discrepancy between the ages for the Pb/U pair and the $^{208}\text{Pb}/^{232}\text{Th}$ ratio. As D/P trends are followed to lower radioactivity fractions, the three D/P systems converge and yield concordant ages well within indicated limits of analytical precision. In effect, for this sample, this graph represents the superimposed I_{int} isogradic plane of Fig. 5 for each of the three D/P systems.

The radioactivity levels of these zircons are quite normal, even slightly low. The pre-metamorphism interval for radiation damage accumulation in the suite was only about 60 Ma. Yet the sensitivity of part of the suite to the particular metamorphic conditions is manifest. What were the conditions that opened zircon D/P systems with more than 300 ppm of uranium but did not significantly affect those with less than 250 ppm? Does the

threshold of susceptibility to disturbance shift downward in uranium concentration along the gradient toward the young intrusive center? How far from the center must samples have been located for all of their zircons to escape disturbance? For their titanite? Apatite, etc.?

Many examples are known of comparably sensitive zircon suites with D/P ratios converging toward concordance with decreasing actinide concentrations. Much less data is available on the D/P behavior of radiation-damaged species such as thorite, allanite, and titanite. Nevertheless, these data do support the possibility of using intraspecies actinide variations and D/P responses in several minerals to obtain more detailed information about the conditions of metamorphism affecting a suite of samples along a metamorphic gradient.



31

SUMMARY



This paper is intended to present the concept that the patterns of isotopic disturbance in Pb-U-Th systems found in radioactive accessory minerals in metamorphosed granites are potentially as rich in information about the nature and intensity of post-magmatic processes as they are about the time constants. The radiogenic daughter-parent ratios can be measured with great precision. They offer a powerful matrix of data which has not been adequately investigated much less utilized. To properly assess their potential, they require careful investigation in selected natural situations where the important characteristics of a metamorphic process can be reasonably unraveled and the influence of key variables on the chemical response of each mineral in an assemblage can be determined. A variety of laboratory experiments involving experimental petrology, mineralogy and geochemistry also can be rewarding (e.g. PIDGEON et al., 1966, 1973). At one end of the metamorphic intensity scale, the behavior of assemblages in the most pristine of granites needs continuing analyses to provide understanding of the base-line isotopic signatures. At the other end of

the intensity scale where new, radioactive metamorphic mineral species enter the assemblages, the petrological stability fields of most of the common igneous accessory minerals are, in large part, unknown. Given the diverse nature of the modifying processes here included in the term metamorphism (e.g. production of granulites, mylonites, ore deposits, soils, etc.) there is a great number and variety of studies to be completed before the validity and the efficiency of the approach can be established. This author will report on a few of them in forthcoming papers.

There is one other significant product that can emerge from these generic studies. The geochemical cycles of uranium, thorium and lead are well established as critical to understanding crustal and planetary evolution. Since the assemblages discussed in this paper represent the principal sites for radiogenic lead, uranium and thorium in the continental crust, their behavior in various modifying environments must be understood. Completion of the types of studies suggested here will vastly improve our comprehension of those cycles.

e[el12]
51

ack

Acknowledgments ^e/_m

The observations leading to the proposals in this paper have been collected with the assistance of many colleagues and students over a period of nearly 40 years. Their discussions and labors are deeply appreciated. Geraldine Silver has been an unflagging partner in this effort for most of that time. During all of that period I have enjoyed the powerful intellectual companionship of Samuel Epstein. I want to thank him for the rich flavors he has contributed to my working environment and for his warm friendship. Parts of the work represented in this paper have been supported at length by the Department of Energy and by a National Science Foundation grant #EAR-851927. Division of Geological and Planetary Sciences, California Institute of Technology, Contribution No. 5045.

Exp Cte

File 182

Key - follow style

all au. names are C/30; sp. btwn initials

3031

REFERENCES

ARMSTRONG R.L. and SUPPE J. (1973) Potassium-argon geochronometry of Mesozoic igneous rocks in Nevada, Utah, and southern California. Bull. Geol. Soc. Amer. **84**, 1375-1392.

BANKS P.O. (1963) Some systematics of uranium and lead distribution in relation to the petrology of the Mt. Rubidoux leucogranites, Riverside Co., California. Ph.D. thesis, 214 p. California Institute of Technology, Pasadena, CA.

BANKS P.O. and SILVER L.T. (1966) Evaluation of the decay constant of uranium 235 from lead isotope ratios. J. Geophys. Res. **71**, 4037-4046.

CHEN J.H. and MOORE J.G. (1982) Uranium-lead isotopic ages from the Sierra Nevada batholith, California. J. Geophys. Res. **87**, 4761-4784.

DAVIS G.L., HART S.R. and TILTON G.R. (1968) Some effects of contact metamorphism on zircon ages. Earth Planet. Sci. Lett. **5**, 27-34.

DEWITT E., ARMSTRONG R.L., SUTTER J.F. and ZARTMAN R.E. (1984) U-Th-Pb, Rb-Sr, and Ar-Ar whole-rock isotopic systematics in a metamorphosed granitic terrane, southeastern California. Bull. Geol. Soc. Amer. **95**, 723-739.

DODSON M.H. (1973) Closure temperatures in cooling geochronological and petrological systems. Contrib. Mineral. Petrol. **40**, 259-274.

DOE B.R. and HART S.R. (1963) The effect of contact metamorphism on lead in potassium feldspars near the Eldora Stock, Colorado. J. Geophys. Res. **68**, 3521-3530.

GEBAUER D. and GRUNENFELDER M. (1973) U-Pb zircon and Rb-Sr systems during progressive metamorphism. Fortsch. Mineral. **50**, 76-78.

GOLDICH S.S. and MUDREY J.R. (1972) Dilatancy model for discordant U-Pb zircon ages. In Contributions to Recent Geochemistry and Analytical Chemistry, (Vinogradov volume), pp. 415-418. Nauka Publ. Office, Moscow.

GRAUERT B., SEITZ M.G. and SOPTRAJANOVE G. (1974) Uranium and lead gain of detrital zircon studied by isotopic analyses and fission track mapping. Earth Planet. Sci. Lett. **21**, 389-399.

HANSON G.N. (1971) Radiogenic argon loss from biotites in whole rock heating experiments. Geochim. Cosmochim. Acta **35**, 101-107.

HANSON G.N. and GAST P. (1967) Kinetic studies in contact metamorphic zones. Geochim. Cosmochim. Acta **31**, 119.

HANSON G.N., CATANZARO E.J. and ANDERSON D.H. (1971) U-Pb ages for sphene in a contact metamorphic zone. Earth Planet. Sci. Lett. **12**, 213-237.

HART S.R. (1964) The petrology and isotopic-mineral age relations of a contact zone in the Front Range, Colorado. J. Geol. 72, 493-525.

HART S.R., DAVIS G.L., STEIGER R.H. and TILTON G.R. (1968) A comparison of the isotopic mineral age variations and petrologic changes induced by contact metamorphism. In Radiometric Dating for Geologists, (eds. E.I. HAMILTON and R.M. FARQUHAR), pp. 73-110. Interscience, New York.

HILL R.I. (1988) San Jacinto Intrusive Complex I. Geology and mineral chemistry, and a model for intermittent recharge of tonalite magma chambers. J. Geophys. Res. 93, B9, 10,325-10,348.

HILL R.I., CHAPPELL B.W. and SILVER L.T. (1988) San Jacinto Intrusive Complex 2. Geochemistry. J. Geophys. Res. 93, (B9) 10,344-10,372.

HOLLAND H.D. and GOTTFRIED D. (1955) The effect of nuclear radiation on the structure of zircon. Acta Crystallogr. 8, 291-300.

HOLMES A. (1954) The oldest dated minerals of the Rhodesian Shield. Nature 173, 612.

HOLMES A. (1955) Dating the Precambrian of peninsular India and Ceylon. Proc. Geol. Assoc. Canada 7, 81-106.

KÖPPEL V. (1974) Isotopic U-Pb ages of monazites and zircons from the crust-mantle transition and adjacent units of the Ivrea and Ceneri zones (southern Alps, Italy). Contrib. Mineral. Petrol. **43**, 55-70.

KÖPPEL V. and GRUNENFELDER M. (1971) A study of inherited and newly formed zircon from paragneisses and granitised sediments of the Strona-Ceneri-zone (southern Alps). Schweiz. Mineral. Petrogr. Mitt. **51**, 385-409.

KÖPPEL V. and GRUNENFELDER M. (1975) Concordant U-Pb ages of monazites from the central Alps and the timing of the high temperature alpine metamorphism, preliminary report. Schweiz. Mineral. Petrogr. Mitt. **55**.

LUDWIG K.R. and STUCKLESS J.S. (1978) Uranium-lead isotope systematics and apparent ages of zircons and other minerals in Precambrian granitic rocks, Granite Mountains, Wyoming. Contrib. Mineral. Petrol. **65**, 2433-2454.

MATTINSON J.M. (1978) Age, origin, and thermal histories of some plutonic rocks from the Salinian block of California. Contrib. Mineral. Petrol. **67**, 233-245.

MCDUGALL I. and HARRISON T.M. (1988) Geochronology and Thermochronology by the ⁴⁰Ar/³⁹Ar Method. Oxford Univ. Press, New York.

MORTON D.M. and MILLER F.K. (1987) K-Ar apparent ages of plutonic rocks from the northern Peninsular Ranges batholith, southern California. *Geol. Soc. Amer. Abstr. Prog.* 19,
no. 6, p. 435.

NAESER C.W. (1979) Fission-track dating and geologic annealing of fission tracks. In *Lectures in Isotope Geology*, (eds. E. JÄEGER and J. HUNZIKER), pp. 154-169. Springer-Verlag, Berlin.

NICOLAYSEN L.O. (1957) Solid diffusion in radioactive minerals and the measurement of absolute age. *Geochim. Cosmochim. Acta* 11, 41.

NIER A.O. (1939) The isotopic composition of radiogenic leads and the measurement of geological time. *Phys. Rev.* 55, 153-163.

PIDGEON R.T., O'NEIL J.R. and SILVER L.T. (1966) Uranium and lead isotopic stability in a metamict zircon under experimental hydrothermal conditions. *Science* 154, 1538-1540.

PIDGEON R.T., O'NEIL J.R. and SILVER L.T. (1973) Observations on the crystallinity and the U-Pb system of a metamict Ceylon zircon under experimental hydrothermal conditions. *Fortschr. Mineral.* 50, 118-119.

SHARP R.V. (1979) Some characteristics of the eastern Peninsular Ranges mylonite zone. In *Proceedings, Conference VII, Analysis of Actual Fault Zones in Bedrock*, U.S. Geol. Survey Open File Rpt., 79-1239, p. 258-267.

3536

SHESTAKOV G.I. (1972) Diffusion of lead in monazite, zircon, sphene and apatite. Trans. Geokhimiya 10, 1197-1202.

SILVER L.T. (1963a) The relation between radioactivity and discordance in zircons. NAS-NRC Nuclear. Geophys. 1075, 34-39.

SILVER L.T. (1963b) The use of cogenetic uranium-lead isotope systems in zircons in geochronology. In Radioactive Dating, pp. 279-287. IAEA, Vienna.

SILVER L.T. (1989) Daughter-parent isotope systematics in U-Th-bearing accessory mineral assemblages as indices of metamorphism: I. the concept. Geol. Soc. Amer. Abstr. Prog. 21, no. (7), A142.

SILVER L.T. (1990) Initial U, Th and Pb concentrations and fractionations in radioactive accessory minerals in some calcic to calcalkaline plutonic rocks. Geol. Soc. Amer. Abstr. Prog. 22, no. 7, A26.

SILVER L.T. and DEUTSCH S. (1961) Uranium-lead method on zircons. New York Acad. Sci. Ann. 91, 279-283.

SILVER L.T., WILLIAMS I.S. and WOODHEAD J.A. (1980) Uranium in Granites from the Southwestern United States: Actinide Parent-Daughter Systems, Sites and Mobilization. 258 pp., DOE-GJBX-45(81), Dept. of Energy, Grand Junction, CO.

SILVER L.T., WOODHEAD J.A. and WILLIAMS I.S. (1982) Primary mineral distribution and secondary mobilization of uranium and thorium in radioactive granites. Uranium Exploration Methods Symposium, pp. 355-366. Paris Proceedings NEA-IAEA.

SILVER L.T., WOODHEAD J.A., WILLIAMS I.S. and CHAPPELL B.W. (1984) Uranium in Granites from the Southwestern United States: Actinide Parent-Daughter Systems, Sites, and Mobilization. 431 pp., DOE-GJBX-7(84), Dept. of Energy, Grand Junction, CO.

SILVER L.T., JAMES E.W., COTKIN S. and CHAPPELL B.W. (1991) Petrology and geochemistry of crystalline basement rocks in the Cajon Pass Scientific Drillhole, San Bernardino Co., CA. (In preparation).

SOMMERAUER J. (1976) Die chemisch-physikalische stabilitat natuerlicher zirkone und ihr U-(Th)-Pb system. Unpubl. Ph.D. thesis ETH Zurich.

STERN T.W., GOLDICH S.S. and NEWELL M.F. (1966) Effects of weathering on the U-Pb ages of zircon from the Morton gneiss, Minnesota. Earth Planet. Sci. Lett. 1, 369-371.

TILTON G.R. (1960) Volume diffusion as a mechanism for discordant lead ages. J. Geophys. Res. 65, 2933-2945.

TILTON G.R. and NICOLAYSEN L.O. (1957) The use of monazites for age determination. Geochim. Cosmochim. Acta 11, 28-40.

to p. 38
key set after next entry

key
insert
from
p. 374

TILTON G.R. and GRUNENFELDER M. (1968) Sphene, uranium-lead ages. Science **159**, 1458-1461.

TILTON G.R., PATTERSON C., BROWN H., INGRAM M., HAYDEN R., HESS D. and LARSEN E. (1955) Isotopic composition and distribution of lead, uranium, and thorium in a precambrian granite. Bull. Geol. Soc. Amer. **66**, 1131-1148.

TILTON G.R., DAVIS G.L., WETHERILL G.W. and ALDRICH L.T. (1957) Isotopic ages of zircon from granites and pegmatites. Trans. Am. Geophys. Union **38**, 360-371.

VANCE E.R. and METSON J.B. (1985) Radiation damage in natural titanites. Phys. Chem. Mineral. **12**, 255-260.

WASSERBURG G.J. (1963) Diffusion processes in lead-uranium systems. J. Geophys. Res. **68**, 4823-4846.

WETHERILL G.S. (1956) Discordant uranium-lead ages, I. Trans. Amer. Geophys. Union **37**, 320-326. \ (102) Exp [te set figs.

Figure Captions

[ls 1] 80 Fig. 1. Graph from SILVER et al. (1982), showing the relative discordance of a large assemblage of radioactive minerals in a sample from a highly evolved, radioactive, middle Proterozoic granite near Bagdad, Arizona. The sample is undeformed and not visibly altered, but it is located 2 km from a major Cretaceous mineralized intrusion. The age of the granite, established by zircon discordia, is 1411 ± 3 Ma. The daughter-parent ratios, $^{206}\text{Pb}/^{238}\text{U}$ and $^{208}\text{Pb}/^{232}\text{Th}$, for each mineral fraction have been calculated as ages. The bars indicate the ages as percentage of the accepted age. Ages deviating from 1411 Ma by more than a few percent reflect post-magmatic chemical and isotopic disturbance, and such disturbance is observed in almost all of the listed minerals. The assemblage of minerals and their diverse styles of open-system behavior indicate the extensive influence of a hydrothermal cell generated by the Cretaceous intrusion. (w) (a) |

[ls 2] 82 Fig. 2. A three-dimensional representation of three parameters: Mineral Species, Metamorphic Gradient and D/P ratios for a model for thermally driven diffusive lead loss in the radioactive minerals. It is used to present hypothetical trajectories for the radiogenic D/P system for each of six minerals showing Arrhenius-relationship disturbance at some abrupt point along a thermal metamorphic gradient. The indicated responses are models assuming $(D/P)_1$ represents an undisturbed primary age system; $(D/P)_2$ represents a D/P system completely reset by metamorphism and since undisturbed. Planes perpendicular to the front face at I_{int} and I_{max} are isograds displaying the accumulated D/P response for each mineral (the piercing points are indicated by heavy dots). An important point is that the form of the array in each isograds plane represents the assemblage for only a

limited interval along the gradient. However, three such trajectory diagrams are provided from the uranogenic and thorogenic systems, contributing to a greater degree of D/P pattern uniqueness. Each point along the gradient is characterized by measurements from a single granite assemblage.

(w/a)

[ls 3] 82

Fig. 3. A three-dimensional representation using the parameters: Mineral Species, Metamorphic Gradient, and D/P ratios for a model in which multiple variables provide a complex metamorphic gradient (pH₂O, strain, temperature, bulk rock chemical changes, etc.). The variables contribute competing influences to the hypothetical trajectory of a given D/P system in each mineral. (D/P)₁ represents the granite primary age, (D/P)₂ represents a completely reset D/P system at time of metamorphism. For such a collection of trajectories, the arrays of piercing points (heavy dots) in the isogradic planes, I_{int}, and I_{max} are unique compared to any other position along the gradient. Each array can be derived from a single sample, and because three such diagrams may be derived from the three D/P systems an even greater degree of specificity of responses to the metamorphic process is possible. It is this capacity for unique characterization which forms the basis for suggesting the family of D/P ratios might provide metamorphic indices.

(w/a)

[ls 4] 82

Fig. 4. Examples of D/P arrays from actual granite samples are shown for ²⁰⁶Pb/²³⁸U and ²⁰⁸Pb/²³²Th. Five closely related granitic samples from the San Jacinto Mtns., southern California yielded D/P ratios (expressed as ages) for the array zircon-titanite-apatite-allanite. In addition, they can be assigned ⁴⁰Ar-⁴⁰K ages in biotite and hornblende, from previous work. The analytical uncertainties are shown by the error figures. The D/P arrays for the two systems in the five samples form rather tight envelopes (stippled) that are in

good agreement (except for allanite), suggesting primary emplacement followed by rapid cooling. They each represent an isogradic plane close to I_0 in Fig. 3. The anomalous allanite ages indicate the sample may have experienced some form of younger overprint involving parent mobilization. A sixth sample is a protomylonitic tonalite gneiss of the same primary age (zircon) from a great mylonite zone 15 km to the east; its assemblage shows markedly lower D/P ratios (ages) for both systems in all minerals except zircon. These displacements suggest that the mylonitic environment can have more pronounced disturbance effects on several of the radioactive minerals compared to zircon.

[ls5]

81

Fig. 5. A three-dimensional representation of the parameters Radiation Damage, D/P ratios, and Metamorphic Gradient, illustrating the influence of the degree of accumulated radiation damage on susceptibility to D/P disturbance in zircons with different actinide concentrations. The diagram is derived from many observations and, while generalized, can be matched from real systems. The arrays of points in the isogradic planes at I_{int} and I_{max} may also serve as indices of the nature and intensity of a metamorphic event. $(D/P)_2$ and $(D/P)_1$ as in Figs. 2 and 3.

[ls6]

81

Fig. 6. A suite of zircons from a Cretaceous granite in the Mojave desert, California, has been analyzed for all Pb-U-Th D/P systems. The sample is from the edge of a hydrothermal cell generated around a Miocene porphyry stock intruded into the granite. All other radioactive minerals, plus biotite and hornblende, have been reset to Miocene ages. The zircon suite shows a systematic correlation of increasing discordance with increasing actinide (uranium) concentration. This is attributed to the effect of differential accumulations of radiation damage present at the time of hydrothermal activity. Arrays in

41 42

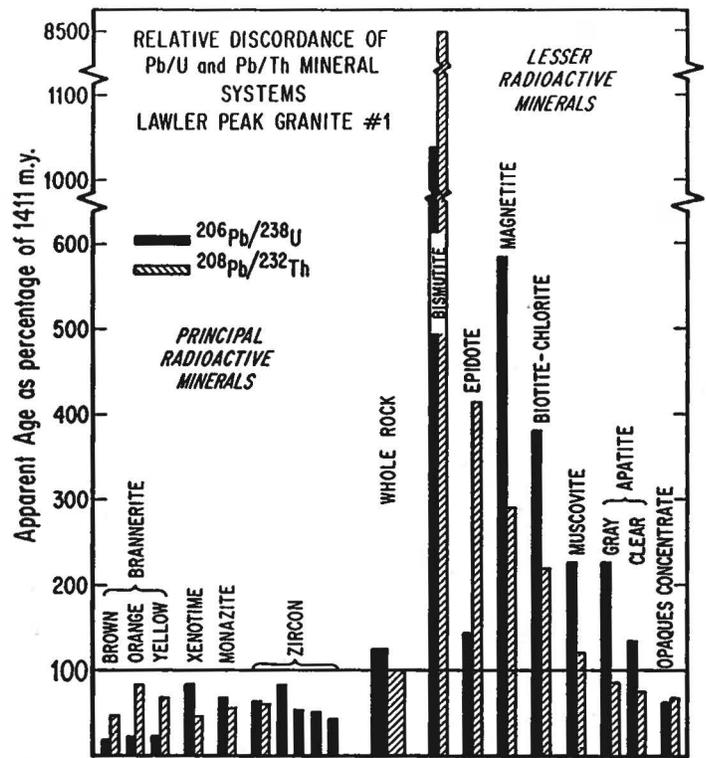
this plot should be compared with the I_{int} isogradic plane in Fig. 5. This graph presents all three D/P systems on the same plane.

103 Cte

[ts 1] Table 1. A summary of Pb, U, Th concentrations and the ratios $^{238}\text{U}/^{204}\text{Pb}$ and $^{232}\text{Th}/^{204}\text{Pb}$ for a representative suite of calcic tonalites to monzogranites from the eastern Peninsular Ranges batholith. The two isotope ratios determine the magnitude of initial lead corrections for calculating radiogenic D/P ratios.

	Data Pts.	Initial Pb ppm	U ppm	Th ppm	$\frac{\text{Th}}{\text{U}}$	$\frac{^{238}\text{U}}{^{204}\text{Pb}}$	$\frac{^{232}\text{Th}}{^{204}\text{Pb}}$
Zircon	(18)	≤ 0.3	665	191	0.29	$> 2 \times 10^5$	$> 5 \times 10^4$
Titanite	(17)	≤ 2.1	175.	285.	1.63	6×10^3	10^4
Apatite	(18)	≤ 3.2	37.	31.	0.84	10^3	$> 7 \times 10^2$
Allanite	(13)	64.X	189.	10000.	53.XX	2×10^2	10^4
Monazite	(1)	11.8	3960	14080	3.55	2.5×10^4	9×10^4

frac bar



F-69 1

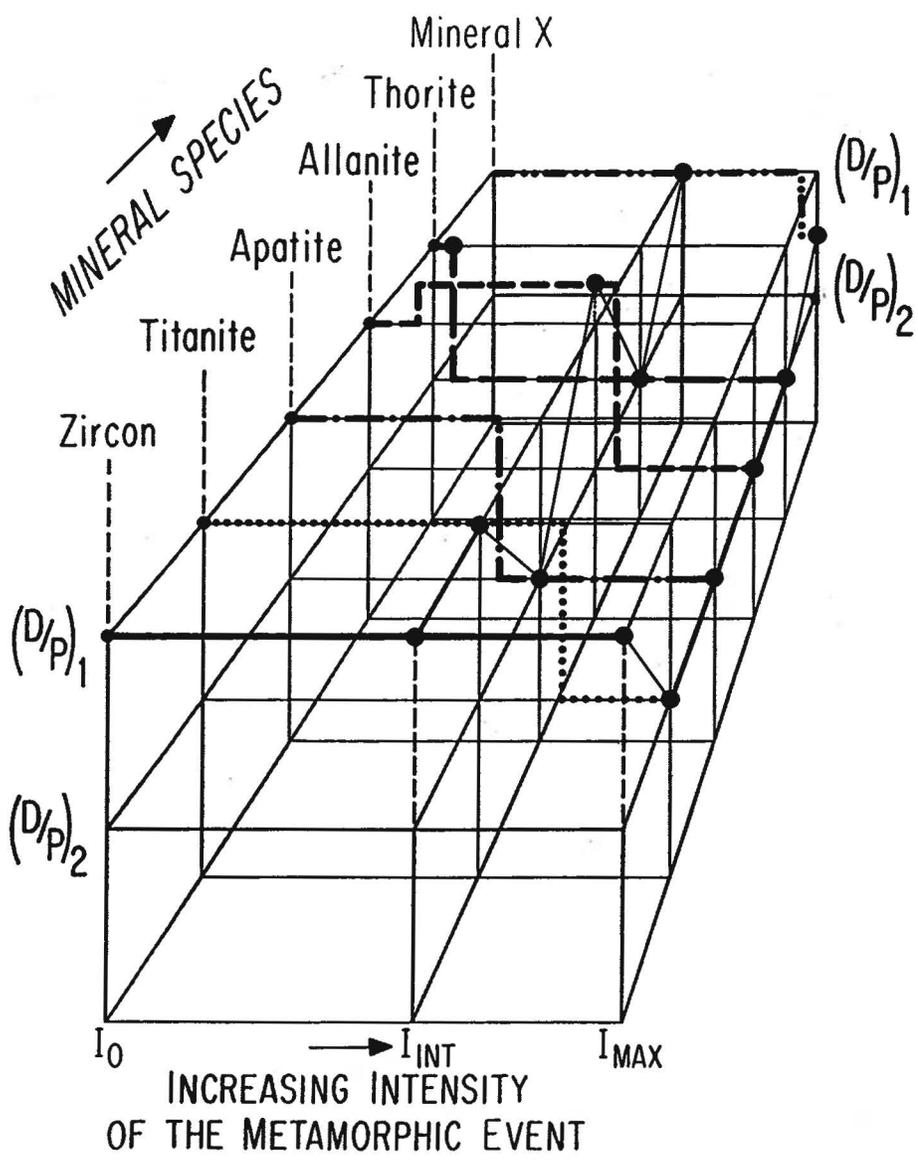
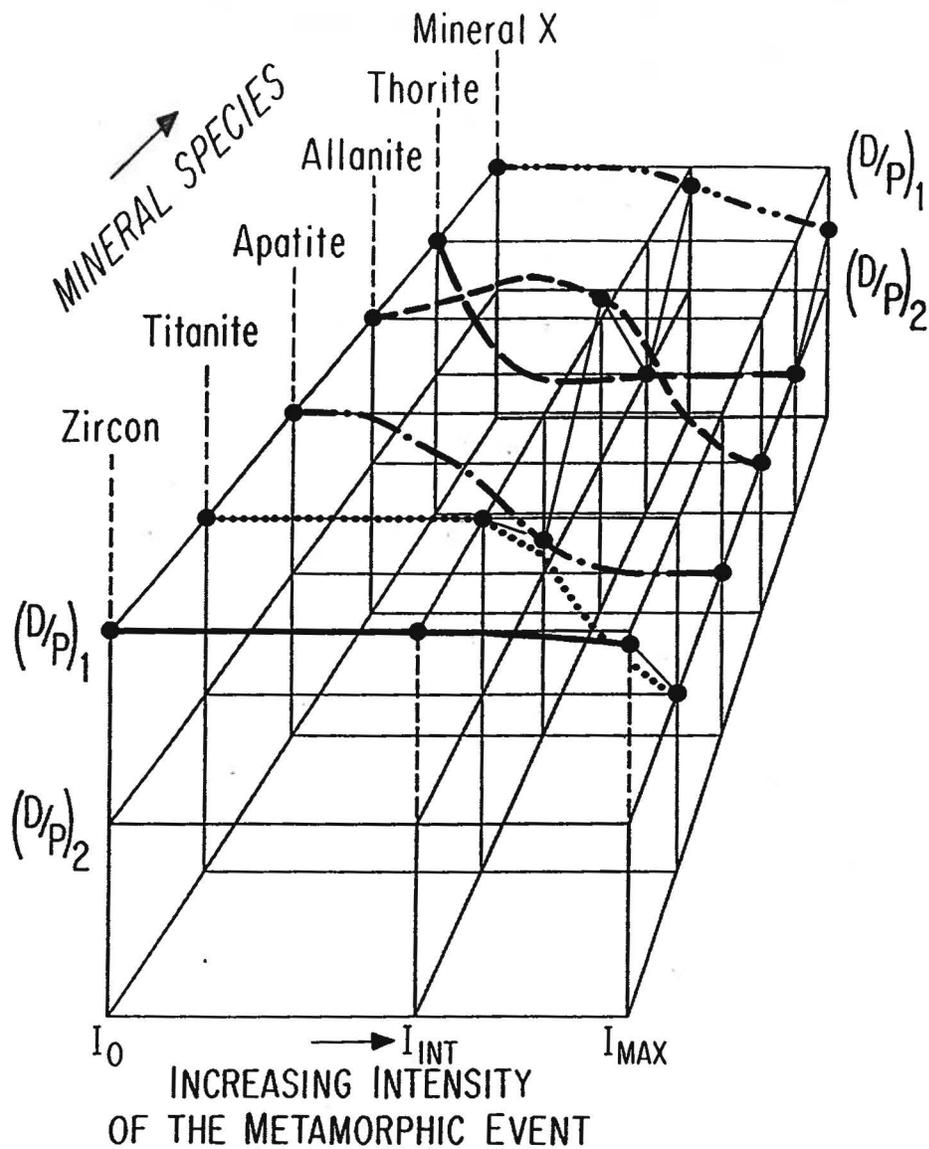


Fig 2



F43.

MINERAL ASSEMBLAGE AGES, SAN JACINTO MTNS., RIVERSIDE CO., CALIF.

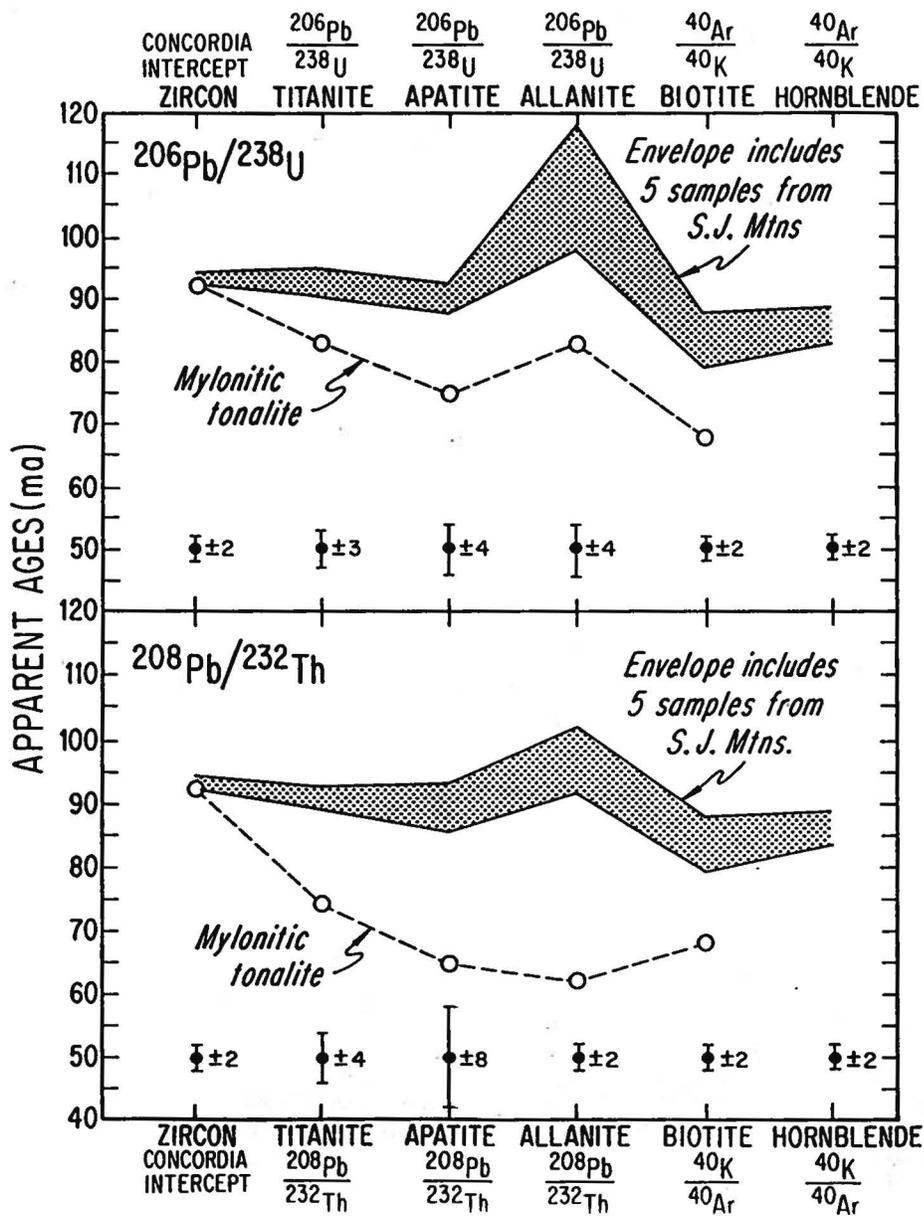


Fig 4.

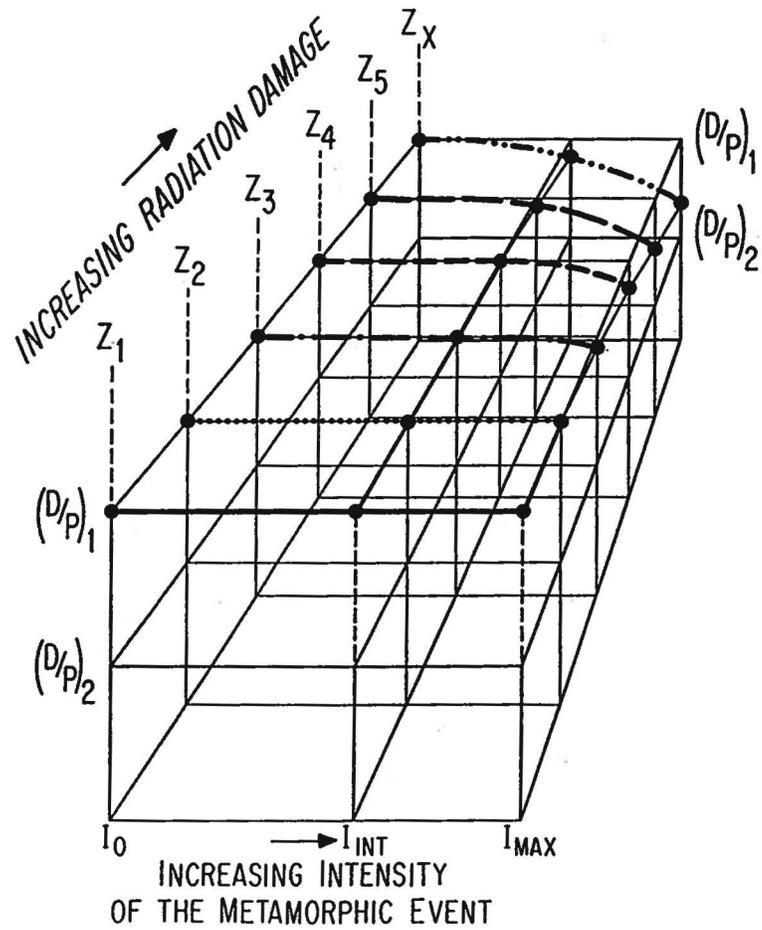


Fig 5.

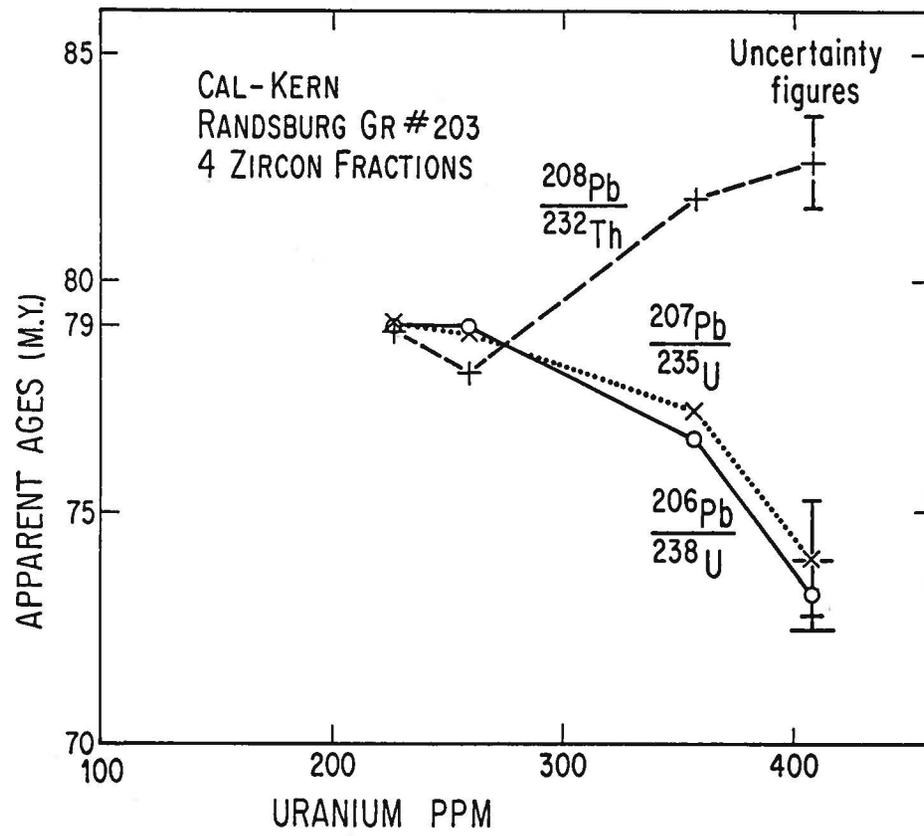


Fig 6.