Radiogenic Isotopes

W. F. McDonough[1]

[1]*Department of Earth Sciences and Research Center for Neutrino Science, Tohoku University, Sendai 980-8578, Japan*

(Dated: May 23, 2019)

I. SUMMARY

Isotope systems are used to in two general ways in Earth sciences:

Geochronology: date rocks, determine age of Earth, date major fractionation events in Earth (core formation, crust formation). Radiogenic isotopes

Tracers: determine sources of magmas, determine processes affecting magmas (assimilation), paleoclimate (e.g., δ^{18}O in bones and corals), fluid-rock interaction.

— Tracer applications include both radioactive and stable isotope systems.

A. *Types of radioactive decay*

The generic versions of decay schemes* are:

$$\begin{aligned}
\text{Alpha} \quad (\alpha) \qquad & {}^{A}_{Z}X \rightarrow {}^{A-4}_{Z-2}X' + {}^{4}_{2}\alpha + Q, \\
\text{Beta Minus} \quad (\beta^-) \qquad & {}^{A}_{Z}X \rightarrow {}^{A}_{Z+1}X' + e^- + \bar{\nu}_e + Q, \\
\text{Beta Plus} \quad (\beta^+) \qquad & {}^{A}_{Z}X \rightarrow {}^{A}_{Z-1}X' + e^+ + \nu_e + Q, \\
\text{Electron Capture} \quad (\varepsilon) \qquad & {}^{A}_{Z}X + e^- \rightarrow {}^{A}_{Z-1}X' + \nu_e + Q,
\end{aligned} \tag{1}$$

with mass number A, atomic number Z, energy of reaction Q, parent element X, and daughter element X'.

* nuclear fission occurs spontaneously, but typically not as chain reaction. The only known occurrence of a natural nuclear chain reaction is the 1.8 Ga Oklo deposit in Gabon, Africa, (https://en.wikipedia.org/wiki/Natural_nuclear_fission_reactor). At this site there were an number of self-sustaining, nuclear fission reactions that ran for several 10^5 years, averaging ~0.1 MW of thermal power.

Emitted alpha particles are slowed down by collision (losing energy, which is converted to heat) within a crystal lattice. The pathways of these alpha particles leaves tunnels or "tracks" (i.e., which is radiation damage (halo around U-bearing minerals)) and form the basis of fission track dating. Heavy neutron rich, radioactive nuclides will spontaneously fission, releasing lots of energy and particles. Spontaneous fission of ^{238}U (the common heavy isotope to undergo natural fission) produces ~2.07 neutrons per fission, with a fission branching probability of 5.5 x 10^{-7}. The original nucleus fissions (breaks) into two particles of unequal weight, with daughter nuclides have lower Z than parent, usually around masses 95 and 135.

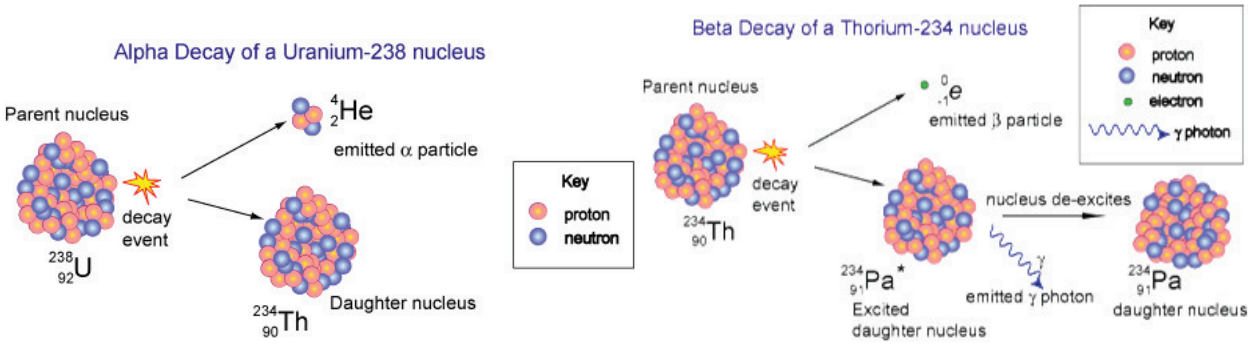

Figure 1: α decay and β decay.

β decay are all "isobaric" state changes (A remains constant and Z goes up or down by 1). The β^- reaction involves the transition of neutron (n) to a proton (p) via the transformation of a down quark to an up quark and the emission of a nuclear e^- and $\bar{\nu}_e$ (or vice versa in the case of β^+ or EC, which involves the emission of a nuclear e^+ and ν_e). These transitions occurs to isotopes plotting on the right hand (β^- in the case of neutron-rich) or left hand (β^+ for neutron-poor) side of stable nuclides in chart of nuclides. Examples of geologically important systems undergoing β^-decay include:

Table of β^-, EC, and α decay isotopic systems *decay data from NNDC*

$^{14}C \rightarrow {}^{14}N + e^- + \bar{\nu}_e$ + Q (0.156 MeV) ($t_{1/2}$ = *5700 a*) (β^-decay) applied to dating young (<10^5 years old) organic materials and oceanographic studies.

$^{87}Rb \rightarrow {}^{87}Sr + e^- + \bar{\nu}_e$ + Q (0.2822 MeV) ($t_{1/2}$ = *48.1 Ga*) (β^-decay) applied to dating a wide range of Earth materials and petrogenetic studies.

$^{40}K + e^- \rightarrow {}^{40}Ar + \nu_e$ + Q (1.504 MeV) ($t_{1/2}$ = *1.248 Ga*) (e^- capture) used to date rocks, particularly useful in unravelling metamorphic time-paths.

$^{176}Lu \rightarrow {}^{176}Hf + e^- + \bar{\nu}_e$ + Q (1.194 MeV) ($t_{1/2}$ = *37.6 Ga*) (β^-decay) used to understand role of garnet in mantle geochemistry, igneous petrogenesis, petrogenetic studies.

$^{187}Re \rightarrow {}^{187}Os + e^- + \bar{\nu}_e$ + Q (0.0025 MeV) ($t_{1/2}$ = *43.3 Ga*) (β^-decay) used to date melt extraction from mantle, date ultramafic rocks, petrogenetic studies.

$^{40}K \rightarrow {}^{40}Ca + e^- + \bar{\nu}_e$ + Q (1.311 MeV) ($t_{1/2}$ = *1.248 Ga*) (β^-decay) – rarely used because ^{40}Ca is the most abundant isotope of Ca (96.97%) and thus it is difficult to measure by mass spectrometry the very small changes that will occur as a result of ^{40}Ca radiogenic in-growth.

$^{138}La \rightarrow {}^{138}Ce + e^- + \bar{\nu}_e$ + Q (1.052 MeV) ($t_{1/2}$ = *102 Ga*) (β^-decay) an uncommonly used system, sometimes used as geochronometer.

$^{147}Sm \rightarrow {}^{143}Nd + \alpha$ + Q (2.311 MeV) ($t_{1/2}$ = *107 Ga*) applied to dating a wide range of Earth materials and petrogenetic studies.

$^{232}Th \rightarrow {}^{228}Ra + \alpha$ + Q (4.082 MeV) ($t_{1/2}$ = *14.0 Ga*) applied to dating a wide range of Earth materials and petrogenetic studies.

$^{235}U \rightarrow {}^{231}Th + \alpha + 1\beta^- \rightarrow {}^{231}Pa$ + Q (4.678 MeV) ($t_{1/2}$ = *0.7038 Ga*) applied to dating magmatic events and coral studies.

$^{238}U \rightarrow {}^{232}Th + \alpha + 2\beta^- \rightarrow {}^{234}U$ + Q (4.270 MeV) ($t_{1/2}$ = *4.270 Ga*) applied to dating magmatic events, coral studies, and petrogenetic studies.

$^{232}Th \rightarrow {}^{208}Pb + 4\beta^- + 6\alpha$ + Q (42.6 MeV) ($t_{1/2}$ = *14.0 Ga*) applied to dating a wide range of Earth materials and petrogenetic studies.

$^{235}U \rightarrow {}^{207}Pb + 4\beta^- + 7\alpha$ + Q (46.4 MeV) ($t_{1/2}$ = *0.7038 Ga*) applied to dating magmatic events and coral studies.

$^{238}U \rightarrow {}^{206}Pb + 6\beta^- + 8\alpha$ + Q (51.7 MeV) ($t_{1/2}$ = *4.270 Ga*) applied to dating magmatic events, coral studies, and petrogenetic studies.

Note that there are small, but recognized differences between decay constants depending on how the constant was determined. ^{87}*Rb is a good example, where physicists report it at 48.1 Ga, whereas geochemists determine it to be 49.2 Ga*

Table I: Long-lived radiogenic isotope systems

Isotope system	Mole frac. (%)	Decay mode	λ (yr^{-1})	Q (MeV)
$^{40}K \rightarrow {}^{40}Ar$	0.01167	ε (10.7%)	5.531×10^{-10}	1.504
$^{40}K \rightarrow {}^{40}Ca$	0.01167	β^- (89.3%)	5.531×10^{-10}	1.311
				(total) 1.332
$^{87}Rb \rightarrow {}^{87}Sr$	27.83	β^-	1.397×10^{-11}	0.2822
$^{138}La \rightarrow {}^{138}Ce$	0.0888	β^-	6.796×10^{-12}	1.052
$^{147}Sm \rightarrow {}^{143}Nd$	14.993	α	6.539×10^{-12}	2.311
$^{176}Lu \rightarrow {}^{176}Hf$	2.598	β^-	1.867×10^{-11}	1.194
$^{187}Re \rightarrow {}^{187}Os$	62.60	β^-	1.666×10^{-11}	0.0025
$^{190}Pt \rightarrow {}^{186}Os$	0.0117	α	1.477×10^{-12}	3.269
$^{232}Th \rightarrow {}^{208}Pb$	100	6α and $4\beta^-$	4.951×10^{-11}	(total) 42.646
$^{235}U \rightarrow {}^{207}Pb$	0.72037	7α and $4\beta^-$	9.8531×10^{-10}	(total) 46.397
$^{238}U \rightarrow {}^{206}Pb$	99.280	8α and $6\beta^-$	1.551×10^{-10}	(total) 51.694

Decay energy Q calculated from mass differences between parent and final daughter isotope mass data from [**?**]; see Table II for details on decay constant λ. $^{238}U/^{235}U = 137.818 \pm 0.045$ [**?**]; $^{234}U/U = (5.5 \pm 0.1) \times 10^{-5}$ [**?**]

Table II: Comparison of half-lives ($t_{1/2}$, in years) and decay constants (λ, in yr^{-1})

	NNDC	**Geology**			
isotope	$t_{1/2}$ ($\pm$)	$t_{1/2}$ ($\pm$)	%$\pm$	Ref	%Δ (NNDC/Geo)
^{40}K	$1.248(3) \times 10^9$	$1.253(3) \times 10^9$	0.2	[**?**]	-0.4
^{87}Rb	$4.81(9) \times 10^{10}$	$4.961(16) \times 10^{10}$	0.3	[**?**]	-3.0
^{138}La	$1.02(1) \times 10^{11}$	$1.02(1) \times 10^{11}$	1.0	[**?**]	0
^{147}Sm	$1.07(1) \times 10^{11}$	$1.06(1) \times 10^{11}$	0.9	[**?**]	0.9
^{176}Lu	$3.76(7) \times 10^{10}$	$3.713(16) \times 10^{10}$	04	[**?**]	1.3
^{187}Re	$4.33(7) \times 10^{10}$	$4.16(4) \times 10^{10}$	1.0	[**?**]	4.1
^{190}Pt	$6.5(3) \times 10^{11}$	$4.69(10) \times 10^{11}$	2.2	[**?**]	39
^{232}Th	$1.40(1) \times 10^{10}$	$1.40(1) \times 10^{10}$	0.7	[**?**]	0
^{235}U	$7.038(5) \times 10^8$	$7.0348(20) \times 10^8$	0.03	[**?**]	0.05
^{238}U	$4.468(3) \times 10^9$	$4.468(3) \times 10^9$	0.07	[**?**]	0

($\pm$) for $t_{1/2}$ values in the parentheses represent uncertainty in the last reported significant figure. %$\pm$ is the relative uncertainty, %Δ is the relative difference between NNDC (National Nuclear Data Center) and Geology. Data source for the NNDC is www.nndc.bnl.gov. References: [**? ? ? ? ? ?**].

B. *Radiometric Dating*

Fundamental points underlie all radiometric dating:

1) For every parent atom that decays, 1 daughter atom forms
2) The rate of decay of the parent is constant.

These rule are expressed mathematically by: $\frac{dN}{dt} = -\lambda N$
where N is the number of parent atoms of a decaying nuclide, t is time, and λ is the decay constant (probability of a decay happening of a unit of time). This expression relates the number of atoms decaying over a time period relative to the initial number of atoms. Integrating this equation between $t = 0$ and t gives: $\int_0^t \frac{dN}{N} = -\lambda \int_0^t dt$ and from this $lnN_t - lnN_0 = ln(\frac{N_t}{N_0}) = -\lambda t$, solving for N_t gives $N_t = N_0 e^{(-\lambda t)}$.

Half life - λ relationship, decay constants and radioactivity
Half life ($t_{1/2}$) = time taken for half of the initial radioactive atoms to decay. By substituting $t_{1/2}$ into the above equations gives $\frac{N_t}{2} = N_0 e^{(-\lambda t_{1/2})}$ and $ln(1) - ln(2) = -\lambda t_{1/2}$, given $ln(1) = 0$), then $\frac{ln(2)}{\lambda} = t_{1/2}$

Decay Constant
Application of radiogenic isotopes depends on precise and accurate decay constants, which can be determined experimentally by measuring the activity of a nuclide over time or empirically by comparisons to multiple decay systems. The activity (defined as λN) is derived by multiplying each side of above decay equation byλ: $\lambda N = \lambda N_0 e^{-\lambda t}$. Thus, for the parent isotope (P) $P = P_0 e^{-\lambda t}$ and $ln\ P = ln\ P_0 - \lambda\ t$, with the latter equation being the slope of a line, where y = lnP, x = t, the slope = $-\lambda$, and the intercept = lnP_0.

C. *Isochrons*

To solve the above expression for t, the age of a rock or mineral, we need to know: - amount of parent isotopes initially present
- amount of parent isotopes currently present.
- amount of daughter isotopes initially present
- amount of daughter isotopes currently present.

What can we measure? *Rb-Sr system*: assuming a rock or minerals has some initial ^{87}Rb and ^{87}Sr at time of crystallization, we can calculate the accumulation of daughter isotopes (D) $D = D_0 + D^*$, where D* = atoms from the radioactive decay of the parent isotope. Substituting $P^* = N(e^{\lambda t} - 1)$, we get $D = D_0 + N(e^{\lambda t} - 1)$. Noting that isotope ratios can be precisely measured on a mass spectrometer and we need to determine 3 critical parameters: P, P_0, and D relative to P_0, which can be accomplished by measuring both isotopes ^{87}Rb and ^{87}Sr relative to ^{86}Sr and thus report ^{87}Rb/^{86}Sr and ^{87}Sr/^{86}Sr values.

$$\left(\frac{^{87}Rb}{^{86}Sr}\right) = \left(\frac{Rb}{Sr}\right) * \left(\frac{Abs-abund.^{87}Rb * Atomic-weight-Sr}{Abs.-abund.^{86}Sr * Atomic-weight-Rb}\right) = \left(\frac{Rb}{Sr}\right) * 2.893$$

$$\left(\frac{^{87}Sr}{^{86}Sr}\right) = \left(\frac{^{87}Sr}{^{86}Sr}\right)_0 + \left(\frac{^{87}Rb}{^{86}Sr}\right)(e^{\lambda t} - 1)$$

This is the basic *isochron equation*. Application of this equation assumes that all rocks or minerals used to form a line on and isochron have the same initial isotopic composition – they are co-genetic. The number of parent and daughter isotopes in the samples changed only through radioactive decay after the formation of the samples (i.e., mineral or rock was closed system with respect to parent and daughter elements). The

first one may be obviously true for some rocks, i.e., different phases of a single pluton might be expected to intrude with the same isotopic composition but parent/daughter may be fractionated between different phases due to presence of different minerals.

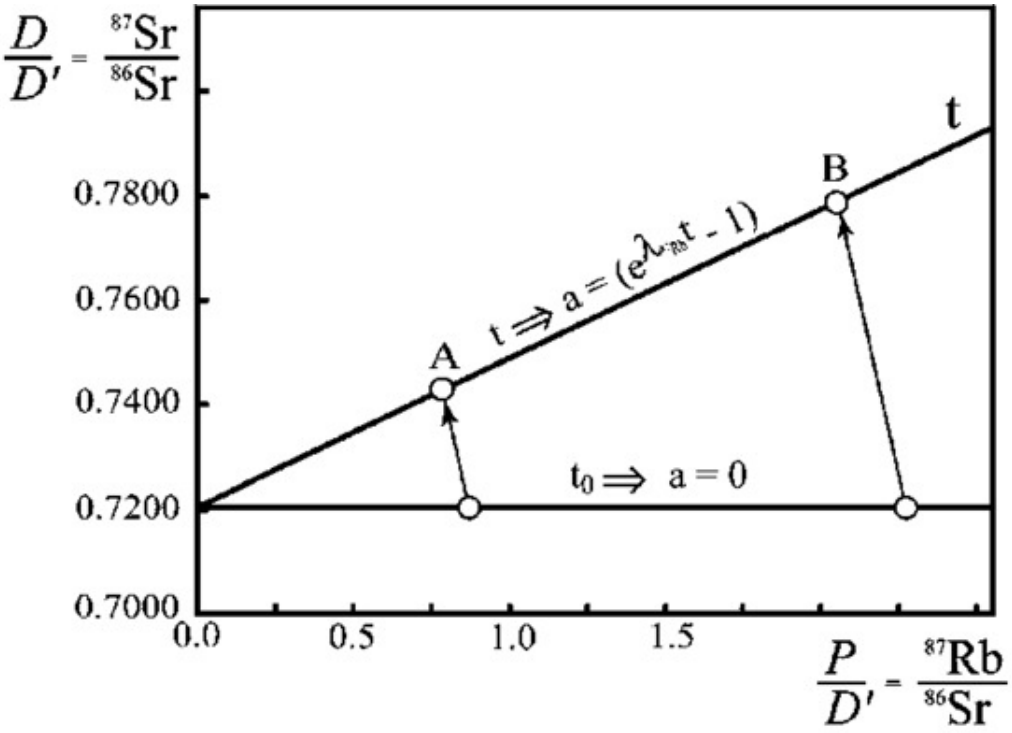

Figure 2: Rb – Sr isochron diagram.

D. *Radiogenic Isotope Tracers*

To use isotopes as tracers of differentiation, we need to know:
1) the isotopic composition and parent/daughter ratio of the Bulk Earth
2) the processes responsible for parent/daughter fractionation and how the parent and daughter fractionate during these processes

The main differentiation events for the Earth: Crust-mantle, Atmosphere-solid Earth, and Core-mantle

Each of these events has an isotope system (or systems) that is fractionated by the processes involved in differentiation. Thus, these isotope systems can be used to determine the timing of differentiation.

Core-mantle: ^{182}Hf-^{182}W (note $t_{1/2}$ for ^{182}Hf is 9 Ma –now extinct look for anomalies in ^{182}W)
Atmosphere-solid: ^{129}I-^{129}Xe (note $t_{1/2}$ for ^{129}I is 17 Ma – now extinct look for anomalies in ^{129}Xe)
Crust-mantle: Rb-Sr, Lu-Hf, Sm-Nd, U-Pb

Furthermore, fractionation of parent/daughter by igneous processes allows using isotope systems as tracers of crustal assimilation, crustal recycling.

For Rb-Sr, what is bulk Earth's $^{87}Sr/^{86}Sr$ isotopic composition? What is its Rb/Sr? How would we determine this value? Are Rb and Sr refractory elements? Volatile elements?
- BABI: Basaltic, Achondrite Best Initial: primitive basaltic meteorite
- Rb: moderately volatile element (50% condensation temperature ∼1080 K)
- Sr: refractory element (50% condensation temperature ∼1300 K)
- In general, expect melts (i.e., the crust, oceanic or continental) to have high Rb/Sr relative to its source region and, consequently, high $^{87}Sr/^{86}Sr$, whereas the mantle will have low Rb/Sr and $^{87}Sr/^{86}Sr$.

For Sm-Nd, both Sm and Nd are REE, with Sm being slightly heavier than Nd. What is the decay process?

What is bulk Earth's isotopic composition? How is it established from chondritic meteorites. Juvinas and chondrites Sm-Nd plot. How can one establish Sm/Nd of Earth? REE are all highly refractory elements. Therefore, can determine the Sm/Nd ratio of the Earth from chondritic meteorites.

$$(^{147}Sm/^{144}Nd)_{BulkEarth} = 0.1960; \qquad (^{147}\text{Sm}/^{144}\text{Nd}) = \text{Sm/Nd} * 0.6042$$

$$(^{143}Nd/^{144}Nd)_{BulkEarth} = 0.512638; \qquad (^{143}\text{Nd}/^{144}\text{Nd})_{DepletedMantle} = 0.513157$$

What processes are responsible for fractionation and how does Sm/Nd change? Do the REE fractionate within the Earth? By what process? Mantle melts are LREE-enriched relative to their source, but extensive crystal fractionation does not change Sm/Nd much.
Is the Earth chrondritic? Note, there are 6 significant figures after decimal. There are variations in Nd, which are generally expressed in parts per 10,000: Notation: Epsilon Nd (ϵ_{Nd})

$$\epsilon_{Nd} = [\frac{(^{143}Nd/^{144}Nd)_{sample}}{(^{143}Nd/^{144}Nd)_{CHUR}} - 1] * 10^4$$

Where CHUR stands for CHondritic Uniform Reservoir. Initial at 4.568 Ga for $^{143}\text{Nd}/^{144}\text{Nd}$ of the average chondrite is 0.506687 and today it is the same as the Bulk Earth value. If a rock's present-day or at the time of crystallization epsilon Nd is negative, what does this tell you about the sample? Sample has lower $^{143}\text{Nd}/^{144}\text{Nd}$ than CHUR, meaning that it evolved for some period of time with LREE enrichment.

CHUR = chondritic evolution DM = depleted mantle evolution

$$(^{143}Nd/^{144}Nd)^{sample}_{today} = (^{143}Nd/^{144}Nd)^{sample}_{0} + (^{147}Sm/^{144}Nd)^{sample}_{today}(e^{\lambda t} - 1)$$

$$(^{143}Nd/^{144}Nd)^{CHUR}_{today} = (^{143}Nd/^{144}Nd)^{CHUR}_{0} + (^{147}Sm/^{144}Nd)^{CHUR}_{today}(e^{\lambda t} - 1)$$

At the time of mantle extraction, what is true about the $^{143}Nd/^{144}Nd$ of the sample compared to CHUR? They are both the same. So we can solve for initial ratio, set the two equations as equal:

$$(^{143}Nd/^{144}Nd)^{CHUR}_{today} - (^{147}Sm/^{144}Nd)^{CHUR}_{today}(e^{\lambda t}-1) - (^{143}Nd/^{144}Nd)^{sample}_{today} = (^{143}Nd/^{144}Nd)^{sample}_{0} + (^{147}Sm/^{144}Nd)^{sample}_{today}(e^{\lambda t}-1)$$

and then solve for T:

$$T_{CHUR} = \frac{1}{\lambda} ln[\frac{(^{143}Nd/^{144}Nd)_{sample} - ^{143}Nd/^{144}Nd)_{CHUR}}{(^{147}Sm/^{144}Nd)_{sample} - ^{147}Sm/^{144}Nd)_{CHUR}}]$$

This is a **Nd model age**; it dates to the time when Sm was fractionated from Nd via melting of a CHUR mantle. Another way to calculate a model age is to assume a DM model. In this case, you will calculate Sm/Nd fractionation from melt a depleted mantle source.

Goldstein vs. DePaolo T_{DM} evolution: *Two widely used models*

1) Creation of DM at some point in past (e.g., 4.56 Ga Goldstein et al., 1984)
2) Progressive depletion of mantle (e.g., DePaolo, 1981).

Inherent features of Nd model ages (use and abuse of crust formation ages):

- implicit assumption that Sm/Nd is fractionated by mantle melting, but not by later processes (e.g., intracrustal differentiation, metamorphism, sedimentation)
- In order for Nd model age to be robust, the sample must have a Sm/Nd ratio significantly different than chondrite (e.g., for crustal rocks, $^{147}Sm/^{144}Nd$ should be <0.13, cf. 0.1960 for CHUR).
- imodel ages cannot be taken too literally:
  multistage fractionation histories lends complexity (Nelson and DePaolo)
  recent changes in Sm/Nd will produce large errors in initial ratios
  mixing between crust and mantle gives rise to mixed age (Arndt and Goldstein)

Applications:

1) Map formation age of continental crust
2) Determine source of plutons (how much pre-existing crust?)
3) Date Earth differentiation

Suggests major crust-forming event at 1.8 Ga, map crustal age domains

References