ABSTRACT

Title of Thesis:EARTH'S THORIUM AND URANIUM
ABUNDANCE AND DISTRIBUTION

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The abundance and distribution of thorium (Th) and uranium (U) in the Earth can provide important data for constraining its composition, heat budget, and processes of differentiation. This project seeks to constrain the ²³²Th/²³⁸U (K) ratio in different domains of the Earth. We reports more than one hundred thousand ²³²Th/²³⁸U ratios and more than ten thousand time-integrated Pb isotopic ratios (K_{Pb}) for rocks from the continental crust (CC) and modern mantle (MM). The results reveal that these two complementary reservoirs ^{MM} K_{Pb} = 3.87 ^{+0.15}-0.07 and ^{CC} K_{Pb} = 3.94 ^{+0.20}-0.11 tightly bracket the solar system (SS) initial ^{SS} K_{Pb} = 3.890 ± 0.015 (Blichert -Toft et al., 2010), defining a bulk silicate Earth (BSE) composition of ^{BSE} K_{Pb} = 3.90 ^{+0.13}-0.07. The ^{CC} K_{Pb} , ^{MM} K_{Pb} and ^{BSE} K_{Pb} are indistinguishable statistically, which indicates that negligible Th/U fractionation accompanied crust-mantle segregation, accretion and core-mantle segregation.

Open system crustal growth modeling suggests that the changing incompatibility of

Pb during the formation of the continents could on its own account for the kappa conundrum (i.e., $K < K_{Pb}$). The timing of Great Oxidation Event (GOE) coincidently overlapped with the peak of continental crust recycling, but may have no causal relationship or trivially contribution to the kappa conundrum.

EARTH'S THORIUM AND URANIUM ABUNDANCE AND DISTRIBUTION

by

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List of Abbreviations

CC	Continental crust
MORB	Mid-ocean ridge basalt
OIB	Ocean island basalt
BSE	Bulk silicate Earth
Th	Thorium
U	Uranium
Kmeas	²³² Th/ ²³⁸ U
K_{Pb}	Time-integrated Pb kappa ratio
Earth	\oplus

Chapter 1: Introduction

Section 1 Motivation

Thorium (Th) and uranium (U) have various properties, and their abundance and distribution in the Earth can provide important insights into many geological processes. To begin with, Th and U are the major heat producing elements (HPE); they are equally responsible for ~80% of the radiogenic heat produced in the Earth's interior today. Defining their abundances and distributions provides important information about the composition and the heat sources of the Earth. Furthermore, since Th and U are refractory elements (i.e., elements that have a relatively high condensation temperature from a solar nebula) and are found to be in chondritic relative proportions, knowledge of the abundance of one serves as a benchmark for estimating the abundances of other refractory elements in the bulk silicate Earth (BSE) and hence constraining the planet's bulk composition (McDonough and Sun, 1995).

Th and U are the two measureable sources of geoneutrinos. Geoneutrinos are electron antineutrinos produced during β - decay of naturally occurring radioactive elements in the Earth. Those emitted from Th and U decay chain are detectable by the liquid scintillation detectors using the inverse beta decay technique (McDonough et al., 2012). Given an assumption of chondritic proportions of refractory elements, the Earth is assumed to have a chondritic Th/U value. The KamLAND and Borexino experiments have reported their estimates of the Earth's Th/U value with increasing accuracy and precision (Fogli et al., 2010). Independent estimates of the Earth's Th/U ratio from geology and particle physics provides a critical test for geological and geoneutrino measurements and the assumption of chondritic proportions for refractory elements.

Last, Th and U are also radioactive elements. ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb are the decay products of ²³⁸U, ²³⁵U, and ²³²Th, respectively. The calculation of time-integrated Th/U ratio from Pb isotopes provides important information of the time-integrated abundance of Th and U in Earth. By tracking the abundance and distribution of Th and U in the Earth's crust and mantle through Earth's history, we can deduce important information about the Earth's differentiation including core-mantle and crust-mantle separation.

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Section 2 Background and Goals

The mass ratio of 232 Th/ 238 U, referred to as kappa (*K*), is calculated using the molar ratio of 232 Th/ 238 U and their atomic masses, which defines a measured kappa ratio (*K*_{MEAS}) in whole rock samples. In addition, a sample's lead isotope composition, specifically the 208 Pb*/ 206 Pb* value ("*" indicates the radiogenic lead component), is a measure of its time-integrated kappa ratio (*K*_{Pb}), because 208 Pb and 206 Pb are the decay products of 232 Th and 238 U, respectively (Tatsumoto et al. 1973; Galer et al., 1985).

Assuming no recent element mobility, K_{MEAS} and K_{Pb} should be equal. However, studies have observed $K_{MEAS} < K_{Pb}$ in modern mantle (MM) samples, as represented by mid-ocean ridge basalts (MORB) and ocean island basalts (OIB). This disparity, referred to as the kappa conundrum (Elliott et al., 1999), has been used to model the structure of mantle convection (Galer et al., 1985). Studies have evaluated K_{MEAS} and K_{Pb} for MM (Galer et al., 1985; Elliott et al., 1999) and for the continental crust (CC) (Rudnick and Fountain, 1995; Paul et al., 2003; Gao et al., 1998). The estimated K_{MEAS} of the CC ranges from 4 (Rudnick and Fountain, 1995) to 6 (Gao et al., 1998). The study of K_{MEAS} and K_{Pb} in the bulk silicate Earth (BSE) is incomplete.

In this project, the abundance and distribution of Th, U, and K values have been assessed for samples of the CC and MM. Values of K_{MEAS} (K_{Pb}) and Th, U abundance were calculated for 142,805 (23,151) continental crust, 2,558 (936) MORB, and 10,599 (6,576) OIB samples queried from the geochemical database EarthChem (http://www.earthchem.org/; Accessed April 2017).

Comparison of the K_{MEAS} and K_{Pb} for each of the BSE reservoirs quantifies the amount of fractionation of Th from U during metal-silicate and crust-mantle differentiation. A mass balance calculation has been carried out based on the abundance of Th and U in each reservoir and its K_{MEAS} and K_{Pb} values to constrain the bulk silicate Earth's (BSE) $^{BSE}K_{MEAS}$ and $^{BSE}K_{Pb}$. Since the bulk Earth (\oplus) is considered to be only composed of the BSE and the core, the $^{BSE}K_{Pb}$ is the complementary component of $^{Core}K_{Pb}$, and together they should sum up to $^{\oplus}K_{Pb}$. Under the assumption that the Earth is formed by chondritic solar nebula materials, and the relative abundance of refractory elements (for example: Th and U) are similar (different by a factor of 2), the $^{\oplus}K_{Pb}$ should be equal to the solar system (SS) initial $^{SS}K_{Pb} = 3.890 \pm 0.015$ (Blichert-Toft et al., 2010). The comparison between the calculated $^{BSE}K_{Pb}$ and $^{SS}K_{Pb}$ provides the best method for evaluating the degree of K fractionation during core formation. Since scientists are struggling with the proper tools to approach to the Earth's core, Th and U have provide us a rare opportunity to better constrain the HPE abundance of it.

In order to test the possible mechanisms for the kappa conundrum, a Monte Carlo simulation of an open system CC evolutionary model is developed. In this model, BSE is assumed to be comprised of two reservoirs: continental crust and mantle. By tracking the evolution of the Earth's crustal growth and considering different chemical and physical properties of Th, U, and Pb, the constructed model will simulate possible paths of isotopic evolution (²³⁸U, ²³⁵U, ²³²Th, ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb) in the bulk silicate Earth (BSE).

Scientists have proposed a variety of crustal growth model (e.g., Armstrong 1981; McLennan & Taylor, 1982; Dewey & Windley, 1987), which all have CC growth to but not exceed its presentday mass during the entire Earth's history. However, recent findings suggest that up to 60% to 70% of the present-day CC was made by ~3Ga ago, with less than 10% of this old crust remaining present-day. The lack of old crust implies there was intense recycling of CC into mantle during the Earth's history (Magni, 2017). In addition, other studies (e.g., Tang et al., 2016) concluded that the CC may processed at least ~3 crustal mass over the Earth's history. This open system crustal growth model provides us a new perspective by which to infer CC evolution history.

Chapter 2: Methods

Section 1 Calculation of K_{MEAS}

U has three naturally occurring, long-lived (>10⁵ years) isotopes: ²³⁴U, ²³⁵U, and ²³⁸U, where at present ²³⁸U accounts for 99.2743% of the total U isotopic composition with the remainder being primarily ²³⁵U (0.7257%). Th has one, naturally occurring, long-lived (>10¹⁰ years) isotope, ²³²Th.

The K_{MEAS} is calculated using equation (1):

$$K_{MEAS} = \frac{{}^{232}\text{Th}}{{}^{238}\text{U}} = \frac{\text{Th}}{\text{U}*0.992743} = -\frac{1}{0.992743} * \frac{a_{Th}}{a_U} * \frac{\mu_U}{\mu_{Th}}$$
(1)

where, a_U and a_{Th} are the abundance of U and Th, respectively; μ_U and μ_{Th} are the molar mass of U and Th, respectively.

Section 2 Calculation of K_{Pb}

 K_{Pb} is calculated from the measured lead isotope compositions minus its primordial lead contribution. First, following the method of Tatsumoto et al (1973), the lead isotopic composition of a primitive iron meteorite troilite is subtracted from the sample's lead isotopic composition. Troilite is an iron sulfide (FeS) mineral that is uncommon on the Earth, but common to iron meteorites. It is a mineral rich in Pb and depleted in Th and U (below detection limits). In addition, iron meteorites represent some of the earliest solids formed in the solar system (Kleine and Walker, 2017) and thus, the Pb isotopic composition of these troilites are frozen into the mineral at the time of its crystallization and not altered by subsequent radiogenic Pb production. Therefore, these meteoritic troilites record the most primordial Pb isotopic values of the solar system.

A corrected Pb ratio value, referred to as the "radiogenic Pb ratio", is calculated by evaluating the ²⁰⁸Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁴Pb composition of a sample relative to that of troilite, within the Canyon Diablo meteorite (CD) as the standard reference frame.

 K_{Pb} can be calculated using equation (2):

$$K_{Pb} = \frac{\binom{208Pb*}{206Pb*} * (e^{\lambda 238T} - 1)}{e^{\lambda 232T} - 1} \quad (2)$$

where the T is the age of the Earth (assumed to be 4.567 Ga), ${}^{208}Pb*/{}^{206}Pb*$ is the radiogenic Pb ratio, and λ is the decay constant of the isotopes. ${}^{208}Pb*/{}^{206}Pb*$ can be calculated using equation (3):

$$\frac{208Pb*}{206Pb*} = \frac{\left(\frac{208Pb}{204Pb}\right)\text{meas} - \left(\frac{208Pb}{204Pb}\right)CD}{\left(\frac{206Pb}{204Pb}\right)\text{meas} - \left(\frac{206Pb}{204Pb}\right)CD} \quad (3)$$

where the subscripts "meas" and "CD" represent the measured Pb isotope ratios of the sample and Canyon Diablo, respectively. We adopt Canyon Diablo lead values of $(^{208}Pb/^{204}Pb)_{CD} = 29.476$ and $(^{206}Pb/^{204}Pb)_{CD} = 9.307$ (Tatsumoto et al., 1973; Blichert-Toft et al.2010). In a closed system, the development of the radiogenic Pb ratio only depends on time and the Th and U concentration

Section 3 Statistical evaluation of K_{MEAS}, K_{Pb} values, and U and Th concentrations

To evaluate and compare K values and U and Th concentrations for each reservoir, a series of statistical parameters were calculated to characterize each population. Three methods are applied to each reservoir: (1) calculate the mean, geometric mean, and median value; (2) using a best fit line between K and SiO₂, calculate the average K value at 60 wt% SiO₂ as a proxy for the bulk continental crust composition (Rudnick and Gao, 2014); and (3) binning the dataset into different crustal types as defined by CRUST1.0 lithosphere geophysical model (Laske et al., 2013), and calculating a weighted average according to each crustal types' mass fraction. Because of the compositional heterogeneity of the K_{MEAS} and U and Th concentrations within the CC (Figure 1 and 3), the CC dataset is divided into igneous, metamorphic, and sedimentary sub-datasets. Since the K_{Pb} of CC is more homogenous than K_{MEAS} (Figure 2 and 3), only method 1 has been applied to the three sub-datasets. Because of the lithological homogeneity of MORB and OIB, we did not subdivide these data.

Subsection 1 Standard statistical approach

The U and Th concentrations for all suites of rocks follow a non-gaussian distribution. Consequently, we evaluated these data in normal and log-normal space, reporting the mean, geometric mean and median values to estimate a central value for each reservoir.

Subsection 2 Linear regression approach (K_{MEAS} when SiO₂ at 60 wt%)

There is a wide range of K_{MEAS} values for the CC (more than 2 orders of magnitude), whereas the K_{Pb} values for these same rocks are relatively homogeneous. The CC's igneous, metamorphic, and sedimentary datasets were divided into 120, 66, and 38 sub-categories according to the rock names reported for each sample. The mean, geometric mean, median, and SiO₂ values are calculated separately for each sub-category (Supplementary table 1,3, and 5). In order to determine the best fit function (regression line) of SiO₂ (wt%) vs *K*, the 120 datasets were grouped by their average SiO₂ (wt%) values: starting from 45wt%, and 5wt% wide bins (e.g., 45-50wt%, 50-55wt%, etc.). For each bin, the central value of *K* and 1-sigma uncertainty were calculated (Figure 4). The best fit lines were calculated using the least square function and assuming a linear relationship between SiO₂ and K_{MEAS} (Figure 4).

The least square cost function used here takes the following form in equation 4:

$$\Phi(m,d) = \sum_{i=1}^{N} |d_{obs-i} - d_{prd-i}|^{p} \quad (4)$$

where,

m = the matrix that contains the information of the slope and vertical axis intersection of the linear regression line;

 d_{obs-i} = the kth observed data;

 d_{prd-i} = the kth model predicted data;

N = the total number of the data;

P = 2, least square function

The least square function was chosen here for its ability to reduce the differences between predicted K values and the observed K values (Zhou et al., 1951) (Figure 4).

Subsection 3 Weighted average approach

The geophysical model, CRUST1.0 (Laske et al., 2013), subdivides the lithosphere into 7 layers (ice, water, soft sediment, hard sediment, upper crust, middle crust, and lower crust) and 30 different age-dependent, tectono-thermal provinces. Using this reference frame we interrogated

the three sub-datasets of rocks from the CC and divided them into 30 crustal types based on locations (see supplementary material table 7). The central value of K_{MEAS} , U and Th concentration for each crust type are calculated, as well as the weighted mean, geometric mean, and median values according the mass fraction of each crust type.

Because data coverage is not complete, some crust types are not represented by the data collected from Earthchem database, and their masses are ignored for the calculation of mass balance. According to rock types defined by model CRUST 1.0, only 0.10%, of the igneous, 5.26% metamorphic, and 4.71% sedimentary datasets are not represented by sampled data in CC.

Section 4 Mass balance calculation

To determine the BSE composition, this project used the K_{MEAS} , K_{Pb} , and the mass of each reservoir to calculate ${}^{BSE}K_{MEAS}$ and ${}^{BSE}K_{Pb}$. Due to the coincidence with the chondritic value and the observed homogeneity of K_{Pb} in each reservoir, the ${}^{BSE}K_{Pb}$ reveals the Earth's initial K, thus further constraining the uncertainty in the ${}^{Earth}K_{Pb}$ values.

Based on the findings to date, the BSE is assumed to consist of two complementary reservoirs, the modern mantle (MM) and continental crust (CC), and that the MM consists of the depleted mantle (DM) and the enriched mantle (EM), as represented by MORB and OIB samples, respectively (Arevalo et al. 2013). We perform a mass balance calculation using the mass fractions in Huang et al. (2013) for the CC and in Arevalo et al. (2013) for the EM and DM. We use the central values of kappa ratios given above in CC, MORB, and OIB to infer a ^{BSE}K_{MEAS} and ^{BSE}K_{Pb}. By the definition of kappa (equation 1), the ^{BSE}K_{MEAS} and ^{BSE}K_{Pb} are calculated as:

$${}^{BSE}K = ({}^{CC}C_U * {}^{CC}K * {}^{CC}M + {}^{MM}C_U * {}^{MM}K * {}^{MM}M) / ({}^{CC}C_U * {}^{CC}M + {}^{MM}C_U * {}^{MM}M)$$
(5)

$${}^{MM}K = ({}^{MORB}C_U * {}^{MORB}K * {}^{MORB}M + {}^{OIB}C_U * {}^{OIB}K * {}^{OIB}M) / ({}^{MORB}C_U * {}^{MORB}M + {}^{OIB}C_U * {}^{OIB}M)$$
(6)

 ${}^{CC}K = ({}^{IGNE}C_U * {}^{IGNE}K * {}^{IGNE}M + {}^{META}C_U * {}^{META}K * {}^{META}M + {}^{SEDI}C_U * {}^{SEDI}K * {}^{SEDI}M) / ({}^{IGNE}C_U * {}^{IGNE}M + {}^{META}C_U * {}^{META}M + {}^{SEDI}C_U * {}^{SEDI}M)$ (7)

Chapter 3: Data and Results

Section 1 Continental crust

CC is an important component for estimating ^{BSE}*K*, as it contains approximately 30% to 50% of the total heat producing elements within the BSE (Huang et al., 2013; Rudnick and Gao, 2014). However, the massive amounts of the samples and large variety of different rock types make the assessment challenging. The results of previous studies finds that ${}^{CC}K_{MEAS}$ varies from 3.87 (Taylor and McLennan, 1995) to 6.76 (Haack, 1983). The ${}^{CC}K_{MEAS}$ and ${}^{CC}K_{Pb}$ values reported here were calculated for igneous (N = 122,836), metamorphic (N = 8,287), and sedimentary (N = 11,682) rocks using equations (1 - 3) in this project. The geographic distribution of the samples and their ${}^{CC}K_{MEAS}$ and ${}^{CC}K_{Pb}$ are displayed in Figures 1 and 2. Histograms of the distributions are reported in Figure 3. The regression line between SiO₂ (wt%) and *K* (using method 2) is shown in Figure 4. Values for the mean, geometric mean, and median, as well as their weighted equivalents, for ${}^{CC}K_{MEAS}$ and ${}^{CC}K_{Pb}$, and U, Th and Pb isotope concentrations are reported in Tables 1 and 2.

The linear regression approach and weighted CC approach is our best efforts to avoid sample biasing, and the agreement between median ${}^{CC}K_{MEAS}$ and median ${}^{CC}K_{MEAS}$ values at 60 wt% SiO₂ enhances our confident in the unweighted median values (Table 1).

Even though marked differences are found between various values of ${}^{CC}K_{MEAS}$ (Table 1), all of the values of ${}^{CC}K_{Pb}$ ~3.97 (Table 3) are in great agreements and overlaps with previously reported values calculated from Pb isotopic compositions for the continents (Rudnick and Goldstein, 1990). The slightly super-chondritic ${}^{CC}K_{Pb}$ reflects time-integrate difference between Th and U's distribution coefficients during mantle melting. The uniformly low ${}^{CC}K_{MEAS}$ for sedimentary rocks reflects the weathering and the mobility of U under oxidized environment and an oversampling of uranium deposits in the database. Also, the ${}^{CC}K_{Pb}$ value of 4.00 ${}^{+0.11}_{-0.10}$ for sedimentary rocks agrees with the estimate of 4.04 based on the Pb isotopic composition of the upper crust (Millot et al., 2004).

The median and geometric mean of Th and U abundances in CC datasets (Table 2) are in agreement with global average estimates for the bulk CC (Rudnick and Fountain, 1995).

Figure 1. Geographical distribution of ${}^{CC}K_{MEAS}$ for igneous, metamorphic, and sedimentary datasets. Colors indicate ratio from 0 (blue) to 6 (red). The number of samples within each dataset is reported in red at the bottom of each map



Figure 2. Geographical distribution of ${}^{CC}K_{Pb}$ for igneous, metamorphic, and sedimentary datasets. Colors indicate ratio from 0 (blue) to 6 (red), the same as in Figure 1. The number of samples within each dataset is reported in red at the bottom of each map





Figure 3. Histograms of ${}^{CC}K_{MEAS}$ (top row) and ${}^{CC}K_{Pb}$ (bottom row) for igneous, metamorphic, and sedimentary datasets. An arbitrary number of bins was chosen to display the shape of the histogram. Igneous Metamorphic Sedimentary

Figure 4. Linear regression line of SiO₂ vs ${}^{CC}K_{MEAS}$ for Igneous, metamorphic, and sedimentary data sets. The dotted black line extends from 60 wt% SiO₂ (x-axis) to each regression line, then perpendicular to the kappa ratio (y-axis). The red best fit lines refer to the L2 least square regression fit. Data (blue) is averaged for every 5 wt% SiO₂.



	Reservoir	# of data		K _{MEAS}								K_{Pb}	
CC	CC-Igneous	122,836	Mean	Geometric Mean	Median	SiO ₂ at 60 wt%	Weighted mean	Weighted geometric mean	Weighted median	22,318	Mean	Geometric Mean	Median
			4.73	3.42	$3.56^{+1.60}_{-1.29}$	$3.61^{+1.0}_{-0.6}$	4.83	3.70	3.84		3.99	3.97	$3.95\substack{+0.19\\-0.11}$
	CC- Metamorphic	8,287	5.37	3.10	$3.61^{+3.26}_{-2.00}$	$3.57^{+1.8}_{-1.2}$	5.27	3.44	3.67	664	4.12	4.05	$3.99^{+0.40}_{-0.28}$
	CC- Sedimentary	11,682	3.09	1.52	$2.61^{+1.87}_{-2.16}$	$2.60^{+0.9}_{-0.7}$	3.65	2.50	3.09	169	3.99	3.97	$4.00\substack{+0.11\\-0.10}$
			М	ean	Geo	ometric M	metric Mean		Median				
M	MORB	2,558	3	.14			3.05		$3.12^{+0.72}_{-0.71}$		3.84	3.84	$3.84^{+0.09}_{-0.09}$
	OIB	10,599	4	.07		3.66		$3.67^{+0.99}_{-0.62}$		6,576	3.91	3.90	$3.87^{+0.16}_{-0.07}$

Table 1. Summary of K_{MEAS} and K_{Pb} for MORB, OIB, CC-igneous, CC-metamorphic, and CCsedimentary datasets (CC = continental crust). 68% confidence limits are reported alongside the median value for each dataset and method. Weighting by SiO₂ at 60 wt% is also reported for the continental crust (see text for details), the uncertainty is the 1 sigma range calculated from the 10,000 Monte Carlo simulation of the linear regression.

Reservoir	# of data		U	concent	ration (µ	g/g)			Th concentration $(\mu g/g)$				
CC-Igneous	122,836	Mean	Geometric Mean	Median	Weighted mean	Weighted log mean	Weighted median	Mean	Geometric Mean	Median	Weighted mean	Weighted log mean	Weighted median
		7	1.5	$1.7^{+3.9}_{-1.2}$	6.05	1.29	1.36	19	5.2	$5.9^{+15}_{-4.5}$	26.9	4.62	5.01
CC- Metamorphic	8,287	27	1.4	$1.6^{+2.8}_{-1.3}$	16.0	1.09	1.28	25	4.3	$6.0^{+11}_{-5.2}$	16.1	3.66	4.81
CC- Sedimentary	11,682	410	4.5	$3.2^{+9.8}_{-1.9}$	87.6	3.62	2.91	48	6.7	$7.7^{+8.7}_{-4.9}$	27.8	7.93	8.15
MORP	2 550	Mean	Geometric Mean		Me	Median		n Geometric Mean			Median		
MORB	2,336	0.14		0.095		0.093	$0.093\substack{+0.13\\-0.05}$		0.28			0.26	+0.50 -0.15
OIB	10,599	1.6		0.7		0.77	$0.77 {}^{+2.0}_{-0.56}$		2.6			$2.9^{+7.1}_{-2.2}$	

Table 2. Summary of U and Th concentration for MORB, OIB, CC-igneous, CC-metamorphic,
and CC-sedimentary datasets (CC = continental crust). 68% confidence limits are reported
alongside the median value for each dataset and method.

Section 2 Mid-ocean ridge basalt (MORB)

Significant analytical advances over the last few decades allow for a reassessment of the κ value for fresh, unaltered MORB. This dataset include 2,558 samples compiled by Gale et al. (2013) and include the laser ablation datasets on MORB glasses reported in Arevalo and McDonough (2010) and Jenner and O'Neill (2013). The ^{MORB}K_{MEAS} and ^{MORB}K_{Pb} values were calculated using equations (1-3), and the histograms of the data are shown in Figure 5; the geographic distributions and values are shown in Figure 6. The MORB dataset is globally comprehensive, sampling all the major spreading zones. Samples from the southern East Pacific Rise and the southernmost Atlantic show good correlation between ^{MORB}K_{MEAS} and ^{MORB}K_{Pb}, indicating long-term, time-integrated Th and U fractionation in the sources of these basalts. Mean, geometric mean, and median values for the MORB dataset are reported in Tables 1 and 2. Similar to CC samples, the MORB dataset shows a greater variability in the ^{MORB}K_{MEAS} when compared to ^{MORB}K_{Pb} values. Both ^{MORB}K_{MEAS} and ^{MORB}K_{Pb} distributions are approximately gaussian.

The median ${}^{MORB}K_{MEAS}$ of ~3.1 ± 0.7 is comparable to earlier estimates of ~2.5 (Galer and O'Nions, 1985; Elliott et al., 1999; Paul et al., 2003). The ${}^{MORB}K_{Pb}$ of 3.84 ± 0.09 is identical to earlier estimates of ~ 3.8 (Galer and O'Nions, 1985; Elliott et al., 1999; Paul et al., 2003) and overlaps with that of the solar system initial (3.890 ± 0.015). The median ${}^{MORB}K_{Pb}$ value is slightly sub-chondritic, and shows a complementary relationship with the CC values (Table 1). The arithmetic mean of Th and U abundances for MORB are comparable to earlier estimates (Arevalo and McDonough, 2010; Gale et al., 2013).





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Figure 6. Geographical distribution of ^{MORB}K_{MEAS} and ^{MORB}K_{Pb}. Colors indicate ratio from 0 (blue) to 6 (red). The number of samples is reported in red at the bottom of each map ratio from 0 (blue) to 6 (red). The number of samples is reported in red at the bottom of each map



Section 3 Ocean island basalt (OIB)

 K_{MEAS} for 10,599 and K_{Pb} for 6,576 OIB samples are calculated using equation 1-3, with both datasets queried from EarthChem. The OIB data are extracted from the CC (i.e., non-MORB samples) dataset based on samples identified as coming from the ocean basin as defined by CRUST 1.0. Histograms of the data are given in Figure 7, and the geographic distribution of samples and their ^{OIB} K_{MEAS} and ^{OIB} K_{Pb} are displayed in Figure 8. OIB samples come from the Atlantic, Pacific and Indian Oceans. Similar to CC and MORB samples, greater variability is observed in the ^{OIB} K_{MEAS} data. The data distribution for both ^{OIB} K_{MEAS} and ^{OIB} K_{Pb} values are approximately gaussian. The mean, geometric mean, and median values for the OIB dataset are reported in Tables 1 and 2.

The median ${}^{OIB}K_{MEAS}$ of 3.67 ${}^{+0.99}_{-0.63}$ is more variable than that for MORB, whereas the ${}^{OIB}K_{Pb}$ value (3.87 ${}^{+0.16}_{-0.07}$) is comparable to that for MORB and again overlaps with that of the solar system value (Blichert -Toft et al., 2010).





Figure 8. Geographical distribution of ^{OIB}K_{MEAS} and ^{OIB}K_{Pb}. Colors indicate ratio from 0 (blue) to 6 (red). The number of samples is reported in red at the bottom of each map



Section 4 Mass balance results

The K_{MEAS} and K_{Pb} of CC, MORB, BSE, and core are calculated using values from Table 1 according to equation 5-7. The following reservoir masses are adopted for this mass balance calculation:

^{CC}M = 2.06 x10²² ± 2.5 x 10²¹ kg (Huang et al., 2013); ^{MM}M = 4.02 x10²⁴ kg (Huang et al., 2013). The CC is considered to be composite of 45% igneous rock, 45% metamorphic rock, and 10% sedimentary rocks (Wilkinson et al., 2009). Thus, ^{IGNE}M = 9.27 x10²¹ ± 1.1 x 10²¹kg, ^{META}M = 9.27 x10²¹ ± 1.1 x 10²¹kg, and ^{SEDI}M = 2.06 x10²¹ ± 2.5 x 10²⁰kg. Since the melting fraction values of MORB and OIB source region is poorly defined, the ^{*MM*}C_U is calculated according to its mass balance relationship with CC and BSE; the mass fraction between MORB and OIB is adopted from Arevalo et al. (2013). The BSE mass is considered to be the sum of ^{CC}M and ^{MM}M, and its element abundance is adopted for McDonough & Sun (1995). The ^{*CC*}C_U and ^{*MM*}C_U are calculated as:

$$^{CC}C_U = {}^{IGNE}C_U * {}^{IGNE}M + {}^{META}C_U * {}^{META}M + {}^{SEDI}C_U * {}^{SEDI}M / ({}^{IGNE}M + {}^{META}M + {}^{SEDI}M)$$
(8)
$${}^{MM}C_U = {}^{BSE}C_U * {}^{BSE}M - {}^{CC}C_U * {}^{CC}M / {}^{MM}M$$
(9)

The relative mass fraction of MORB and OIB source region are not well constrained, but their similar K_{Pb} values makes the calculated ${}^{MM}K_{Pb}$ mostly independent of MORB and OIB source region's relative sizes. Similar to MM, the calculated ${}^{CC}K_{Pb}$ can also be considered as an independent value of the relative sizes of igneous, metamorphic and sedimentary rock reservoirs.

Since the average ${}^{CC}C_U$ is too large, due to the samples from ~ 200 samples at U mine (USGS 2008), the mean of ${}^{MM}C_U$ is not accessible according to the mass balance relationship (equation 9).

A Monte Carlo mass balance calculation has been performed to estimate the uncertainty of the central value of K_{MEAS} and K_{Pb} using equation 9. K_{MEAS} and K_{Pb} were randomly sampled 5 x 10⁵ times from the available data for each reservoir, avoiding assumptions on distribution shape. In order to avoid the larger U mass than permitted by the assumed bulk Earth model (McDonough & Sun, 1995), re-sampling of the data removed a subset of crustal data with high U abundance, and results in ${}^{CC}K_{MEAS} = 3.64^{+1.49}$ -1.37, ${}^{CC}K_{Pb} = 3.94^{+0.20}$ -0.11, ${}^{MM}K_{MEAS} = 3.54^{+0.96}$ -0.69 and ${}^{MM}K_{Pb} =$

3.87 ^{+0.15}-_{0.07} which are similar to the results reported in Table 1 and 3. The mass weighted estimate for the ${}^{BSE}K_{MEAS} = 3.59 {}^{+1.79} {}_{-1.54}$, ${}^{BSE}K_{Pb} = 3.90 {}^{+0.13} {}_{-0.07}$.

As can be seen from Table 3, the K_{Pb} values for CC, MM, and BSE are uniformly ~3.9, with ${}^{CC}K_{Pb}$ slightly super-chondritic and ${}^{MM}K_{Pb}$ slightly sub-chondritic, but all within the range of ${}^{SS}K_{Pb}$ (3.890 ± 0.015) (Blichert -Toft et al., 2010). K_{MEAS} values for CC and MM are both smaller than their K_{Pb} . In order to investigate the possible fractionation between Th and U during crust - mantle segregation, I further test the relationship between K_{MEAS} and K_{Pb} in CC, MORB, and OIB dataset.

	Mean	Geometric Mean	Median	Weighted mean	Weighted geometric mean	Weighted median	Monte Carlo
$CCC_U \;(\mu g/g)$	56.3	1.76	1.81	18.68	1.43	1.48	-
$^{MM}C_U~(\mu g/g)$	-	0.029	0.029	-	0.027	0.028	-
^{CC} K _{MEAS}	3.67	2.81	3.40	4.45	3.31	3.62	3.64 ^{+1.49} -1.37
^{MM} K _{MEAS}	-	3.45	3.49	-	-	-	3.54 ^{+0.96} _{-0.69}
^{BSE} K _{MEAS}	-	3.30	3.47	-	-	-	3.62 +0.89 -0.72
^{CC} K _{Pb}	4.02	3.99	3.97	-	-	-	3.94 +0.20 -0.11
^{MM} K _{Pb}	-	3.88	3.86	-	-	-	3.87 +0.15 -0.07
^{BSE} K _{Pb}	-	3.91	3.89	-	-	-	3.90 ^{+0.13} _{-0.07}

Table 3. Summarized mass balance calculation results.

Chapter 4: Difference between K_{MEAS} and K_{Pb}

Section 1 Comparison between K_{MEAS} and K_{Pb}

In order to display the relationship between K_{MEAS} and K_{Pb} according to our data, density plots of K_{MEAS} vs K_{Pb} in CC, MORB and OIB are shown in Figure 9. The black line shown in the figure is the 1:1 diagonal line indicating when $K_{MEAS} = K_{Pb}$, and a few of the data are coincident with a 1:1 line of $K_{MEAS} = K_{Pb}$ taken into consideration of the uncertainty. According to the number of data points located on the left and right sides of the diagonal line, there are ~60% of the data in CC have $K_{MEAS} < K_{Pb}$; ~82% of the data in MORB have $K_{MEAS} < K_{Pb}$; and ~56% of OIB samples have $K_{MEAS} < K_{Pb}$ as well. All three reservoirs show varying degrees of recent Th/U fractionation, with the majority being more significantly shifted due to either U enrichment or Th depletion.

Since CC have most widely distributed data and its ${}^{CC}K_{MEAS}$ and ${}^{CC}K_{Pb}$ are statistically indistinguishable, ${}^{CC}K_{MEAS}$ and ${}^{CC}K_{Pb}$ in the continental crust are further compared for 11,858 (68 rock types) igneous, 200 (15 rock types) metamorphic, and 69 (16 rock types) sedimentary rocks by plotting ${}^{CC}K_{MEAS}$ and ${}^{CC}K_{Pb}$ of each rock type in a single plot, the relationship between the two kappa values are easy to observe. The detailed data tables reporting numbers for the rock types are provided in the supplementary material Tables 2, 4 and 6. The median values for ${}^{CC}K_{MEAS}$ and ${}^{CC}K_{Pb}$ vs SiO₂ (wt%) are shown in Figure 10, and the mean and geometric mean values plots are not presented here, but show similar trends. As can be seen in Figure 10, we observe that most igneous and metamorphic data show ${}^{CC}K_{MEAS} \approx {}^{CC}K_{Pb}$. The average ${}^{CC}K_{Pb}$ values are well constrained, between 3.6 and 4.5, except for sovite and quartzite, which are only represented by three data points each; while the ${}^{CC}K_{MEAS}$ values varies between different rock types.

To sum up the relationship between K_{MEAS} and K_{Pb} according to our dataset, the complementary CC and MM both show $K_{MEAS} < K_{Pb}$.

A well-recognized mechanism that can account for the decline of K_{MEAS} relative to K_{Pb} in the MM is the different solubility of U and Th ions in oxidized environments (Elliott et al. 1999). Under known natural conditions, Th has only one state of oxidation, which is the highly insoluble ion Th⁴⁺. On the other hand, at the Earth's surface U has three oxidation states: U⁴⁺, less commonly

 U^{5+} , and U^{6+} . Among those, U^{6+} is a highly soluble ion and accounts for the high concentration in ocean waters relative to Th (3 ng/g U versus sub-ppt concentrations of Th) (Chen et al., 1986). During weathering of the continental crust, some fraction of U is removed, as compared to Th, and eventually dissolved in the oceans. This mobility of U allows it to be recycled back to the mantle during subduction, which potentially decreases $^{MORB}K_{MEAS}$ and increases $^{CC}K_{MEAS}$ (Elliott et al.,1999). Since both 238 U and 232 Th are long-lived isotope systems, the observed differences in K_{MEAS} and K_{Pb} for CC and MM might reflect this change in the solubility of U relative to Th. Moreover, the fact that K_{Pb} value remains close to the chondritic value for both CC and MM indicates that this fractionation is relatively recent (< 3 Ga).

Such a mechanism is supported by the evidence that the oxygen content of the Earth's atmosphere significantly increased between 2.0-2.5 Ga (Holland et al., 1984; Holland et al., 1994; Farquhar et al., 2000), and as a result, some portion of U changed its oxidation state from U^{4+} to U^{6+} . Evidence for this change in the rock record prior to 2 Ga includes, U deposits as UO_2 (uraninite) with no hydrothermal U mineral; after 2 Ga, the situation is reversed (Kimberly et al., 1978). Hence, there appears to have been a major change in the dominant oxidation state of U in the near surface environment at around 2.0-2.5 Ga.

Although this proposed mechanism is elegant, the complementary CC and MM both have smaller K_{MEAS} than K_{Pb} , which is inconsistent with the mechanism discussed above.



Figures 9. Density plot of K_{MEAS} vs K_{Pb} in CC, MORB and OIB. Color bar is scaled from 0 to 1, corresponding to the increasing density of the data points. The black line shown in the figure is the 1:1 diagonal line indicating when $K_{MEAS} = K_{Pb}$. Color scale has arbitrary units. The black circular data points are the median K_{MEAS} and K_{Pb} values of CC, MORB and OIB.



Figure 10. Median ${}^{CC}K_{MEAS}$ and ${}^{CC}K_{Pb}$ vs rock types for CC.

Section 2 A new mechanism for resolving the kappa conundrum

An alternative mechanism is proposed in this project to solve the difference between K_{MEAS} and K_{Pb} in modern mantle.

Hofmann (1988) discovered a Pb concentration anomaly characterized by the average normalized abundances for Pb being deficient in MORB and enriched in CC, which is shown in Figure 11. The order of elements follows the sequence of element incompatibility in oceanic basalts (Hofmann 1988; Sun and McDonough, 1989). This order is determined by the value of the slope of the concentration ratio of two elements versus the concentration of one of the elements in discuss (Hofmann 1988).



Figure 11. Normalized element concentration of average CC and average MORB. The open circle represents the average concentration in CC (Taylor and McLennan, 1995); the closed circle represents the average concentration in MORB (Hofmann, 1988). This figure is a modification of Hofmann 1988's Figure 7.

The negative anomalous are also shown for Sr and Na in the oceanic basalts. In some environments Pb behaves as a chalcophile element and partitions into sulfide minerals. Otherwise, Sr and Pb are typical lithophile elements with 2⁺ valence states. Ca-plagioclase is a potential residue mineral during shallow mantle melting and given their size and ionic radius, Sr and Pb can readily substitute for Ca in this potential restitic phase. Thus, mantle melts with negative anomalies in Pb and Sr can potentially be explained by the buffering effects of Caplagioclase during partial melting. This theory is supported by the present of residual plagioclase in the upper mantle (Klein and Langmuir, 1987; Presnall and Hoover, 1987) and the sulfide saturated MORB (Mathez 1976). To address the Pb anomaly seen in the continental crust, Hofmann (1988) performed a two stage model and proposed that Pb was more incompatible than U and Th during the formation of the CC, and less incompatible than U and Th during the subsequent formation of oceanic crust (OC). The changing distribution coefficient (i.e., D values) for Pb (D_{Pb}) is shown in Figure 12.



Figure 12. Difference in Pb's distribution coefficients in Hofmann's two-stage model. The red arrows show the path of changing value of D_{Pb} . This figure is a modification of Hofmann (1988) Figure 9.

Based on this shift in the partition behavior of Pb during crust formation and its later growth, this project proposes that Pb's changing incompatibility can be shown to provide a satisfactory solution for the kappa conundrum and is offered as an alternative to conventional view of the changing solubility and weathering of U from the CC. The mantle's mass fractional contribution of recycled U, due to U's changing solubility, may be trivial and insufficient to account for the difference between K_{MEAS} and K_{Pb} in the CC, given ${}^{CC}K_{MEAS}$ and ${}^{CC}K_{Pb}$ are sub-equal (Table 1 and Figure 10). On the other hand, since Th is slightly more incompatible than U, the ${}^{CC}K_{MEAS}$ value gradually exceed ${}^{MM}K_{MEAS}$. The increasing ${}^{CC}K_{MEAS}$ caused the corresponding increase of ${}^{CC}K_{Pb}$, and lead to ${}^{CC}K_{Pb} > {}^{MORB}K_{Pb}$. When Pb became less incompatible than Th and U, it became more likely to stay in the mantle than go into CC during melting, and elevated the ${}^{MORB}K_{Pb}$ value by mixing it with the larger ${}^{CC}K_{Pb}$, which can account for the difference between ${}^{MORB}K_{MEAS}$ and ${}^{MORB}K_{Pb}$.

Assume that present day U, Th, and Pb isotope abundances in the CC and MM can be characterized by a specific continental crust growth pattern, rather than an assortment of patterns, an open system CC growth model is therefore developed and constrained from the U, Th, and Pb's isotope concentration in CC and MM. Here we test the possibility of this alternative mechanism proposed above.

Chapter 5: An open system CC growth model

A Monte Carlo simulation to develop an evolutionary model involving open system exchange between different reservoirs in the BSE was carried out to evaluate an alternative process for producing the kappa conundrum. This model assumes two reservoirs in the BSE: CC and MM. The evolution of crustal growth over 1000, equally-spaced time steps are simulated, while taking into consideration the different chemical and physical properties of each element. From the 1000 time steps, the model selects 10 equally distributed, critical time steps (100th; 200th; 300th; etc) that set the trend of the CC growth pattern, while the remaining 990 time steps let the CC mass gradually grow to the adjacent next critical time step's value. The model simulates the possible evolutionary exchange paths for ²³⁸U, ²³⁵U, ²³²Th, ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb in the BSE.

McDonough and Sun (1995) model provides the initial concentrations of each isotopes in the BSE. Since the proportion of MORB source region to OIB source region is not well constrained, the model calculates the MM's isotope concentrations as a complementary reservoir relative to the better known CC composition. We calculated the CC's element abundance (U, Th) and the Pb isotope ratios from Earthchem dataset discussed in section 1.2. The MM isotope abundances are calculated according to its mass balance relationship with CC and BSE. At every time step, the model allows mass to positively or negatively exchanged between the CC and MM randomly. Successful crustal growth patterns are those with ending masses within the uncertainty of the present day CC mass $2.06 \times 10^{22} \pm 2.5 \times 10^{21}$ kg (Huang et al, 2013) and observed element and isotope trends described previously. This model seeks the possible CC growth pattern that can end up with the present-day isotopic abundances using the random-generated growth patterns and the equations below.

Section 1 Equations used in the model

For CC, the mass of each element and the total CC mass starts at zero when T = 0 (the first time-step, 4.57 Ga ago); for the mantle, the mass of each element starts at initial BSE values.

Subsection 1 isotopic parameters

For radioactive isotopes (²³⁸U, ²³⁵U, ²³²Th) and their decay products (²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb), there are two processes that affect their concentration in CC or MM: first, the total mass of the elements that exchanges and the time-dependent mass flux between CC and MM; second, the mass decreased/ increased according to their decay activity.

Equations used in this part of the model (Kumari et al., 2016):

Isotope mass exchange. Using ²³⁸U as the example:

$$\frac{d^{238}U}{dt} = \Sigma F_{(j-i)}^{238} U - \lambda_{238} * {}^{238}_{j} U \quad (10)$$

where, $F_{(j-i)}^{238}U$ is the mass of ²³⁸U exchanged from reservoir j to reservoir i. This equation represents that the mass of ²³⁸U exchanged from reservoir j to reservoir i with time as a function of the mass exchanged with the flux and the decay of the parent elements.

To calculate the mass exchanged from crust to mantle $F_{(CC-MM)}^{238}U$, the physical process envisaged is subduction or CC delamination. $F_{(CC-MM)}^{238}U$ is calculated as following:

$$F_{(\rm CC-MM)}^{238}U = F_{(\rm CC-MM)} * C_{CC}^{238}U$$
(11)

where, $F_{(CC-MM)}$ is the mass exchanged from crust to mantle. $C_{CC}^{238}U$ is the concentration of ^{238}U in crust.

To calculate the mass exchanged from mantle to crust $F_{(MM-CC)}^{238}U$, the process considered here is melting. Thus, $F_{(MM-CC)}^{238}U$ is calculated as following:

$$F_{(MM-CC)}^{238}U = F_{(MM-CC)} * C_{L}^{238}U$$
(12)

where, $C_{L}^{238}U$ represent the concentration of ^{238}U in the melt.

Since Th, U and Pb are incompatible elements, their concentrations in the melt/liquid (C_L) will always be larger than in the solid (C_S). Assume the melting processes during

crust - mantle segregation are all in batch melting, and then the concentrations are calculated as following:

$$C_L = C_0 / (f + (1 - f) * D)$$
 (13)
 $C_S = D * C_L$ (14)

where, C_0 is the initial concentration of element in the BSE, and f is fraction of liquid, and here we calculated f as the mass of the flux exchanged between CC and MM divided by the mass of the MM at each time-step. D is the bulk distribution coefficient of the element in question. For U and Th, the distribution coefficient are assumed to be fluctuating around 0.001; for Pb, whose distribution coefficient has significantly changed during the Earth's history, so it starts off at D_{Pb} around 0.001, and evolve to D_{Pb} around 0.01.

Subsection 2 Stable isotopes

For the stable isotope ²⁰⁴Pb, its concentration in CC or MM is controlled by the bulk mass exchanged between crust and mantle, so equation (10) should be transformed into:

$$\frac{d^{204}Pb}{dt} = \Sigma F_{(j-i)}^{204} Pb \quad (15)$$

Section 2 Parameters used in the model

The parameter values used in the open system CC growth model are summarized in Table 4. T_D is defined as the time when Pb changed its distribution coefficient (T = 0 is the beginning of the Earth's history, T=4.57 Ga is present-day). According to Asafov et al. (2018), the Pb concentration anomaly observed by Hofmann (1988) were documented in the fresh 2.7 Ga old komatiites from the Reliance Formation of the Belingwe Greenstone Belt in Zimbabwe. These lavas are recognized as products of the OIB-MORB mantle post extraction of the continental crust, according to Hofmann (1988). Therefore, the changing of Pb's distribution coefficient should have occurred at least 2.7 Ga prior to present-day. In this model, I test when Pb changes its distribution coefficient after 0.5 Ga, 1.0 Ga, 1.5 Ga, and 2.0 Ga since T=0.

CC growth rate ¹ (km^3/yr)	2.2								
T (Ga)		4.56							
$T_D (Ga)^2$		0.5; 1.0; 1.5; 2.0							
Crust Mass ³ (kg)		2.06E22							
Mantle Mass ⁴ (kg)	4.02E24								
BSE (kg) ⁵	4.04E24								
$\lambda_{235\mathrm{U}}$	9.85E-10								
λ238U	1.55E-10								
λ_{232Th}	4.95E-11								
${ m D_U}^6$	fluctuating around 0.001								
D_{Th}^{6}	fluctuating around 0.001								
	init	tial: fluctuating around 0	.001						
DPb	after 2Ga: fluctuating around 0.01								
	BSE ⁷	CC ⁸	MM ⁹						
²⁰⁶ Pb (kg/kg)	3.61E-08	2.75E-06	2.22E-08						
²⁰⁷ Pb (kg/kg)	3.24E-08	2.33E-06	2.06E-08						
²⁰⁸ Pb (kg/kg)	7.93E-08	5.77E-06	5.02E-08						
²⁰⁴ Pb (kg/kg)	2.14E-09	1.50E-07	1.38E-09						
²³⁸ U (kg/kg)	2.02E-08	1.44E-06	1.29E-08						
²³⁵ U (kg/kg)	1.47E-10	1.05E-8	9.39E-11						
²³² Th (kg/kg)	7.95E-08	4.95E-06	5.45E-08						

Table 4. Open system crustal growth model parameters

1. Hawkesworth et al., 2006.

2. Asafov etal., 2018.

3. Huang et al. (2013);

4. Chambat et al. (2010)

5. BSE mass is calculated as the sum of crust's and mantle's mass.

6. The bulk distribution coefficient of Th, U and Pb are from GREM Distribution Coefficient Database (https://earthref.org/KDD/e:92/).

7. McDonough & Sun,(1995)

8. U and Th concentration are the geometric mean of Earthchem dataset (Table 1); the Pb isotope ratio are the geometric mean of the data from Earthchem. CC is considered to be 45% igneous rock, 45% metamorphic rocks, and 10% sedimentary rocks.

9. MM's isotope concentration are calculated according to its mass balance relationship with CC and BSE.

The changing distribution coefficients of U, Th and Pb with time is shown in Figure 13. The

D values of U and Th fluctuate within the range of [0.0001, 0.002] during entire Earth's history;

the D value of Pb is initially fluctuating within the range of [0.0001, 0.002], and after 0.5Ga, 1Ga, 1.5Ga, and 2Ga, the D value for Pb is fluctuates within the range of [0.0095, 0.015].



Figure 13. Distribution coefficient of Th, U and Pb changing with time. The distribution coefficient of Th and U are always fluctuating around 0.001; Pb's distribution coefficient starts as fluctuating around 0.001, and change to ~0.01 after 0.5 Ga, 1.0 Ga, 1.5 Ga, and 2.0 Ga.

Section 3 Model results

Among the 10,000 models randomly generated for the crustal growth patterns, ~300 CC growth patterns satisfy all the isotope systems (238 U, 235 U, 232 Th, 206 Pb, 207 Pb, and 208 Pb), resulting in the present-day crustal mass, which indicates Pb's changing incompatibility alone could account for the difference between $^{MM}K_{MEAS}$ and $^{MM}K_{Pb}$.

The randomly generated 10,000 CC growth patterns are shown in Figure 14 below. The successful CC growth patterns according to present-day ²³⁸U, ²³⁵U, ²³²Th, ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb isotope concentration in CC and MM are shown in Figure 15.



Figure 14. 10,000 random generated CC growth patterns.



Time (Ga)

Figure 15. Successful CC growth pattern. A) Pb's distribution coefficient changed after 0.5 Ga. There are 209 successful runs out of 10,000 iteration. B) Pb's distribution coefficient changed after 1 Ga. There are 298 successful runs out of 10,000 iteration. C) Pb's distribution coefficient changed after 1.5 Ga. There are 269 successful runs out of 10,000 iteration. D) Pb's distribution coefficient changed after 2 Ga. There are 323 successful runs out of 10,000 iteration.

Chapter 6: Discussion

Section 1 Mass balance

The results of the mass balance calculation find that the ${}^{MM}K_{Pb} = 3.87 {}^{+0.15}$ -0.07 and ${}^{CC}K_{Pb} = 3.94 {}^{+0.20}$ -0.11 sum up to a ${}^{BSE}K_{Pb} = 3.90 {}^{+0.13}$ -0.07 (Table 3), which is statistically indistinguishable from the solar system initial value ${}^{SS}K_{Pb} = 3.890 \pm 0.015$ (Blichert -Toft et al., 2010). This finding suggests: first, the BSE's kappa ratio is unfractionated from the average solar system's value and approximately equal to chondritic meteorites' value, which resolve a long-standing debate on the BSE estimate of its Th/U value (Allègre et al., 1986; Allègre et al., 1988; Rocholl and Jochum, 1993; Javoy and Kaminski, 2014).

Second, the small difference between ${}^{CC}K_{Pb}$ and ${}^{MM}K_{Pb}$ suggests negligible Th/U fractionation accompanied crust - mantle segregation. The < 3% difference between ${}^{CC}K_{Pb}$ and ${}^{MM}K_{Pb}$ reveals either U⁶⁺ recycling back into the mantle has been a relatively recent process or that limited recycling followed atmospheric oxygenation at 2.4 Ga. The results of open system crustal growth model suggest that Pb's changing incompatibility can also account for the small difference between ${}^{CC}K_{Pb}$ and ${}^{MM}K_{Pb}$. These finding are strikingly inconsistent with claims of widespread pollution of the upper mantle with recycled uranium (Andersen et al., 2015) and claims of biologically driven fractionation leaving its imprint on the mantle (Sleep et al., 2013).

Third, the negligible difference between ${}^{BSE}K_{Pb}$ with ${}^{SS}K_{Pb}$ suggests ${}^{Core}K_{Pb}$ should have similar value as well, thus negligible Th/U fractionation accompanied late accretion and core-mantle segregation. Experimental studies reveal that U can weakly partition into metal under high temperature and high pressure conditions, but not Th. Since negligible Th/U fractionation accompanied core formation, negligible Th and U have been sequestered into the Earth's core, and thus U and Th play little to no role in powering the geodynamo (Nimmo, 2015). Likewise, this finding falsifies the hypothesis of a natural nuclear reactor in the Earth's core (Hollenbach and Herndon, 2001).

Section 2 Open system CC growth model

As can be seen from Figure 15, almost all of the successful MC runs follow a comparable uniform pattern: starting from T = 0, the mass of CC gradually grows and peaks at ~ 2 to 3 times that of its present-day's CC mass, and then gradually decrease to today's CC mass after the peak.

By comparing the individual patterns seen in Figure 15, one observes that the model results are not sensitive to different T_D . One noticeable feature of all of the successful CC growth patterns is that the maximum of the CC mass occurs mostly at around 1.5Ga to 3Ga after T=0. This time coincides with ever-increasing evidence for changing composition of CC from mafic to intermediate composition (e.g., Tang et al., 2016; Smit et al., 2017; Johnson et al., 2017). The model performed by Chowdhury et al., 2017 suggests that recycling via delamination would have been widespread during this period of time, and the silicification of the continents would reach a peak at a time roughly coincident with the Great Oxidation Event (GOE) at ~ 2.4 to 2.1 Ga ago (Lyons et al., 2014). Thus, the mechanism of U⁶⁺ recycling into mantle during GOE may be just coincident with Pb changing incompatibility, but have no causal relationship with kappa conundrum.

Additional evidence that supports Pb having changed its bulk distribution coefficient during Earth's history (Hofmann, 1988) comes from Smithies et al. (2009), who tested the distribution coefficients for elements in Paleoarchean CC, which is in agreement with Hofmann's (1988) hypothesis. In Smithies et al., 2009, the study reported calculated bulk distribution coefficients for samples of Th and light Rare Earth elements enriched basalts and basaltic-andesites formed between 3.53 to 3.5 Ga in the Pilbara Craton. By assuming 5% to 20% partial melting and using the partition coefficients from Bedard 2006, the calculated bulk distribution coefficients suggests that Sr and Pb had a similar bulk distribution coefficients similar with Th and U's. Since the Nd isotopic data suggests that the sources of these rocks have an average age of >3.45Ga, with most being >3.5Ga, the bulk distribution of Pb must have changed after 3.5Ga during the Earth's early history. The higher bulk distribution of Pb and Sr corresponding to the buffering of Pb and Sr during crystallization during mantle melting. The calculated distribution coefficients are shown in Figure 16.



Figure 16. Calculated distribution coefficients for Paleoarchean CC. This figure is a modification of Smithies et al., 2009 Figure 4.

Chapter 7: Conclusion

This project finds that complementary reservoirs of ${}^{MM}K_{Pb} = 3.87 {}^{+0.15} {}_{-0.07}$ and ${}^{CC}K_{Pb}$ = 3.94 ${}^{+0.20} {}_{-0.11}$, as defined by data from Earthchem, tightly bracket the solar system initial ${}^{SS}K_{Pb} = 3.890 \pm 0.015$ (Blichert -Toft et al., 2010), and reveals the ${}^{BSE}K_{Pb} =$ 3.90 ${}^{+0.13} {}_{-0.07}$, which resolves a long-standing debate regarding the Earth's Th/U value. The ${}^{CC}K_{Pb}$, ${}^{MM}K_{Pb}$ and ${}^{BSE}K_{Pb}$ are indistinguishable statistically, which indicates that negligible Th/U fractionation accompanied crust-mantle segregation, accretion and core-mantle segregation.

The open system crustal growth model results suggest that recycling of Pb and its changing incompatibility alone could account for the kappa conundrum. The timing of GOE coincidently overlapped with the peak of CC recycling, but may has no causal relationship or has trivial contribution to kappa conundrum.

Appendices

1. Igneous dataset – all available K_{MEAS}

	Average		# of data			
ROCK NAME	SiO_2	# of data	have SiO2	K_{MEAS}	K_{MEAS} (log mean)	<i>K_{MEAS}</i> (median)
SOVITE	6 50	26	25	1/1 Q/	(10g mean) 4 26	(meanin)
	8 70	56	23	11.27	4.00	4.22
	10.92	022	23 690	02 52	4.00	4.32
	10.65	922	009	02.35	4.30	4.00
	21.07	5	3	3.22	5.05	3.03
	31.90	4	4	4.41	4.25	4.07
BERGALITE	34.84	5	3	2.52	2.22	2.20
KATUNGITE	35.10	15	15	4.09	4.02	4.21
KAMAFUGITE	37.99	14	14	5.37	5.34	5.23
MAFURITE	38.80	2	2	4.49	4.48	4.49
GLIMMERITE	39.50	1	1	6.85	6.85	6.85
DUNITE	39.64	171	137	3.13	1.98	2.35
CLINOPYROXENITE	39.64	125	119	3.77	2.96	3.53
NEPHELINITE	40.66	20	18	3.66	3.33	3.53
WEHRLITE	41.23	40	34	1.90	1.40	1.21
UGANDITE	41.27	3	3	4.54	4.53	4.70
HAUYNITE	41.34	3	3	4.44	4.36	4.32
TROCTOLITE	41.55	50	34	3.06	2.68	3.03
THERALITE	41.96	1	1	4.68	4.68	4.68
HARZBURGITE	42.00	130	127	3.61	1.55	2.01
PERIDOTITE	42.21	285	248	3.10	2.08	2.59
LHERZOLITE	42.66	106	99	2.88	1.34	2.52
NEPHELIN-BASALT	43.49	1	1	5.18	5.18	5.18
HORNBLENDITE	43.56	25	25	5.56	3.09	2.38
SANDSTONE	43.80	2	1	3.53	3.53	3.53
PYROXENITE	43.86	193	127	4.47	2.72	2.70
NORITE	44.00	2	1	6.88	3.59	6.88
BASANITE	44.08	1898	1790	4.16	3.76	3.82

FOIDITE	44.23	140	109.00	3.66	3.29	3.24
MADUPITE	44.49	1	1	4.48	4.48	4.48
LAMPROPHYRE	44.68	849	706	5.68	3.60	3.69
EUCRITE	15 51	2	2	5 27	5 76	5 27
	45.51	15	 	5.10	3.20	3.27
DAGANITOD	45.87	15	0	5.19	4.03	4.45
BASANITOID	45.96	/	4	4.16	3.97	3.37
TEPHRITE	45.98	331	324	4.30	3.79	3.77
PICRITE	45.99	107	94	4.07	3.76	3.53
TRACHYDOLERITE	46.15	1	1	4.76	4.76	4.76
ALKALI BASALT	46.61	114	107	3.79	3.61	3.63
LAMPROITE	46.73	39	23	6.54	4.66	4.33
WEBSTERITE	46.79	35	35	2.97	2.57	2.95
LEUCITITE	46.84	7	5	4.12	4.06	3.92
CRINANITE	47.15	7	7	4.26	4.06	4.49
GREENSTONE	47.80	1	1	1.18	1.18	1.18
HAWAIITE	48.33	663	619	3.78	3.63	3.63
PHONOTEPHRITE	48.70	14	10	2.77	2.24	2.88
TRACHYBASALT	48.76	1409	1345	4.08	3.76	3.72
GABBRO	48.80	2486	2272	3.74	3.03	3.32
ABSAROKITE	49.05	48	45	3.72	3.59	3.65
BASALT	49.26	26553	23299	3.73	3.22	3.53
DOLERITE	50.15	1370	1289	4.19	3.78	4.06
KOMATIITE	50.26	6	5	3.56	3.41	4.10
THOLEIITE	50.49	1921	1748	4.27	3.36	3.69
ESSEXITE	50.84	15	14	3.85	3.56	3.27
DIABASE	51.04	2182	1898	4.42	3.90	4.17
ANKARAMITE	51.07	3	3	2.64	2.63	2.77
ORTHOPYROXENITE	51.09	7	7	1.83	1.08	1.76
BONINITE	51.47	207	193	3.25	2.77	3.64
FENITE	51.48	12	11.00	5.86	2.68	4.66
MUGEARITE	51.53	217	197	4.07	3.79	3.74
SPESSARTITE	51.60	36	36	5.19	4.92	4.97

MINETTE	52.01	152	132	4.09	3.76	3.51
TINGUAITE	52.07	6	6	5.57	5.14	4.63
MALIGNITE	52.20	1	1	4.32	4.32	4.32
SPILITE	52.21	23	23	4.00	3.55	3.37
ANORTHOSITE	52.35	9	9	3.42	3.20	2.94
BASALTIC ANDESITE	53.78	346	314	4.19	2.99	3.08
TESCHENITE	53.96	3	3	1.85	1.84	1.81
GRANOPHYRE	54.00	15	11	5.00	4.84	4.92
SHOSHONITE	54.31	467	456	3.98	3.61	3.85
MONZOGABBRO	55.20	2	2	2.94	2.86	2.94
FOYAITE	55.25	9	8.00	4.96	4.36	3.69
PHONOLITE	55.28	1008	847	4.21	3.58	3.47
ORENDITE	55.47	1	1	4.91	4.91	4.91
TRACHYANDESITE	55.70	2118	2071	4.60	4.01	4.01
AGGLOMERATE	56.00	1	1	1.66	1.66	1.66
BENMOREITE	56.83	148	142	3.87	3.49	3.51
ANDESITE	57.36	14749	13149	3.55	3.13	3.27
DIORITE	57.64	2124	1807	3.73	3.11	3.28
NOT GIVEN	57.69	20417	15070	4.26	3.32	3.45
MONZODIORITE	58.72	138	130	3.69	3.38	3.35
MONZOSYENITE	59.17	3	3	4.59	4.51	4.83
SYENITE	59.25	1193	906	4.71	3.56	3.77
VOGESITE	60.50	1	1	2.94	2.94	2.94
TRACHYTE	62.25	2035	1765	4.92	4.18	4.03
LATITE	62.30	854	713	4.06	3.63	3.60
ALBITITE	63.10	12	12	5.83	5.50	5.50
ADAKITE	63.92	678	664	3.62	3.18	3.32
TRACHYDACITE	64.15	10	8	3.73	3.52	3.50
TONALITE	64.17	742	659	3.71	2.59	2.77
MONZONITE	65.42	1334	675	5.77	4.41	4.21
FELSITE	65.95	39	24.00	3.06	2.66	3.09
DACITE	65.95	5677	5080	3.57	3.14	3.22

GRANODIORITE	66.62	3001	2327	4.80	3.82	3.79
RHYODACITE	68.69	815	714	3.33	2.99	3.00
PEGMATITE	69.64	152	83	5.99	2.92	3.02
TUFF	70.07	974	505	4.81	3.29	3.36
KERATOPHYRE	70.45	9	8	2.38	2.16	1.84
APLITE	70.69	240	145	4.53	2.63	2.78
PANTELLERITE	70.81	4	3	3.19	3.19	3.19
ADAMELLITE	70.83	15	6	9.62	5.02	4.12
TRONDHJEMITE	71.09	55	45	3.18	2.29	2.09
GRANITE	71.20	5740	4220	6.22	4.64	4.68
ALASKITE	71.30	73	48	3.79	2.37	3.02
IGNIMBRITE	71.75	9	9	4.93	4.78	4.32
COMENDITE	72.13	174	148	4.64	4.34	4.19
MONZOGRANITE	72.40	134	125	4.54	3.58	3.39
RHYOLITE	72.87	13874	10764	4.08	3.57	3.68
VITROPHERE	73.68	35	14	3.71	3.62	3.67
PYROCLASTIC-FALL	74.55	100	38	3.10	2.99	3.03
TRACHYRHYOLITE	74.56	3	2	4.20	4.17	3.89
PYROCLASTIC- FLOW	74.57	59	5	3.72	3.60	3.64
ENDERBITE	NaN	8	NaN	18.28	17.58	17.51
MELILITITE	NaN	1	NaN	3.53	3.53	3.53
MONCHIQUITE	NaN	1	NaN	0.35	0.35	0.35

2. Igneous dataset – have both K_{MEAS} and K_{Pb}

		# of							
		data		TC	Kmea			K_{pb}	TC
	# of	hav	Avera	K _{MEA}	S (log	V	V.	(100	K_{pb}
	dat	SiO	ge SiO2	s (mea	(log mea	(medi	Λ_{pb}	mea	(medi
ROCK NAME	a	2	(wt%)	n)	n)	an)	n)	n)	an)
				61.6	10.4		,		,
SOVITE	3	3	3.07	4	4	5.55	3.21	2.60	4.33
				100.	100.	100.7			
ALVIKITE	1	1	1.06	73	73	3	4.02	4.02	4.02
E	76	30	5.90	44.7 7	4.20	4.82	4.44	4.00	4.01
KATUNGITE	1	1	36.37	4.61	4.61	4.61	4.24	4.24	4.24
KIMBERLITE	1	1	37.65	3.53	3.53	3.53	3.93	3.93	3.93
LAMPROPHYR									
E	129	123	40.59	4.50	4.11	4.22	4.29	4.16	4.13
LEUCITITE	4	2	43.95	4.22	4.13	4.35	4.13	4.13	4.06
LAMPROITE	29	18	47.40	7.25	4.75	4.33	4.00	4.00	3.99
MINETTE	62	54	52.08	3.87	3.67	3.67	4.02	4.02	4.04
MONZONITE	30	19	72.63	4.17	3.45	3.03	4.03	4.02	4.06
DACITE	377	349	65.69	3.55	3.26	3.15	3.96	3.96	3.92
TRONDHJEMIT									
E	1	1	70.32	2.60	2.60	2.60	3.96	3.96	3.96
GRANITE	152	133	71.59	5.10	3.97	4.70	4.08	4.05	3.97
RHYOLITE	567	484	71.91	4.56	3.80	3.99	4.06	4.05	3.98
IGNIMBRITE	7	7	73.26	5.36	5.27	5.78	3.91	3.91	3.92
COMENDITE	15	11	73.46	6.51	5.91	5.67	4.04	4.03	3.97
ALASKITE	2	0	NaN	3.52	3.25	3.52	3.79	3.79	3.79
APLITE	4	0	NaN	2.99	2.89	2.75	3.78	3.78	3.80
FENITE	1	0	NaN	4.84	4.84	4.84	3.76	3.76	3.76
TUFF	3	0	NaN	2.12	2.09	2.16	3.75	3.75	3.72
				10.4	10.4				
TINGUAITE	1	1	41.79	3	3	10.43	3.94	3.94	3.94
TEPHRITE	67	63	44.89	5.14	4.47	4.30	4.04	4.04	4.05
HAWAIITE	147	134	48.18	3.81	3.63	3.56	3.92	3.92	3.91
MUGEARITE	53	46	52.82	4.38	3.97	3.77	3.98	3.98	3.94
BASALTIC	25	25	53.84	2 4 1	236	2 33	3.83	3 83	3 81
	25	25	55.04	∠.⊤1	2.50	2.55	5.05	5.05	5.01

BONINITE	18	18	52.89	4.17	4.15	4.10	4.17	4.16	4.18
SYENITE	40	30	55.31	4.80	3.96	3.95	4.06	4.05	4.01
TRACHYANDE	42.4	105	55 40	5.26	1.00	4 20	4.00	4.00	4.01
SITE	424	405	55.40	5.36	4.69	4.39	4.09	4.08	4.01
PHONOLITE	103	87	53.42	5.52	3.94	4.40	4.09	4.09	4.04
ANDESITE	1	5	57.12	3.60	3.30	3.33	3.94	3.94	3.92
BENMOREITE	24	23	57.09	3.46	3.26	3.43	3.97	3.97	3.98
DIORITE	139	96	57.19	3.73	3.43	3.56	3.95	3.95	3.91
LATITE	75	63	59.71	4.27	3.97	3.83	4.09	4.08	4.10
TRACHYTE	264	240	63.15	5.41	4.92	4.76	4.10	4.10	4.06
TONALITE	36	20	62.87	5.32	3.77	3.84	3.94	3.94	3.91
ADAKITE	59	54	64.19	4.34	3.51	3.48	3.97	3.97	3.99
GRANODIORIT									
E	107	74	67.78	5.39	4.43	4.44	4.17	4.10	3.99
BERGALITE	2	2	31.56	1.28	1.28	1.28	3.99	3.99	3.99
NEPHELIN- BASALT	1	1	43.49	5.18	5.18	5.18	4.42	4.42	4.42
BASANITE	422	405	43.93	3.97	3.86	3.80	3.92	3.92	3.92
BASANITOID	6	3	46.74	4.20	3.97	3.36	3.79	3.79	3.82
ALKALI									
BASALT	38	37	46.66	3.74	3.60	3.65	3.89	3.89	3.91
GABBRO	90	70	47.23	4.97	4.38	3.93	4.02	4.01	3.99
SHONKINITE	10	2	47.66	4.40	4.32	4.37	4.43	4.43	4.47
ABSAROKITE	23	23	47.99	3.68	3.53	3.62	3.99	3.99	3.95
TRACHYBASA	251	222	40.04	1 2 1	2.01	2 70	4.02	4.02	4.00
	346	295	49.04	4.54	5.91	5.79	4.02	4.02	4.00
BASALT	5	0	48.66	4.11	3.65	3.73	3.98	3.97	3.95
THOLEIITE	335	266	50.78	4.17	3.81	4.01	4.04	4.03	4.01
DOLERITE	123	118	50.72	4.13	3.74	3.98	4.02	4.01	3.99
DIABASE	56	45	50.53	4.29	3.97	3.89	4.08	4.07	4.03
SPESSARTITE	20	20	50.78	5.56	5.30	5.65	4.08	4.08	4.07
SHOSHONITE	81	75	52.97	4.02	3.85	3.87	4.05	4.05	4.06
TROCTOLITE	3	0	NaN	3.01	3.01	3.14	3.75	3.75	3.74
ESSEXITE	1	0	NaN	3.39	3.39	3.39	3.91	3.91	3.91
PERIDOTITE	11	9	33.90	5.44	4.76	4.95	4.09	4.09	4.03
FOIDITE	65	40	40.88	3.46	3.22	3.01	3.98	3.97	3.99

HORNBLENDI									
TE	2	2	46.55	3.65	3.35	3.65	4.26	4.26	4.26
CLINOPYROX									
ENITE	1	1	48.84	3.58	3.58	3.58	3.97	3.97	3.97
WEHRLITE	1	1	36.81	3.61	3.61	3.61	3.49	3.49	3.49
MAFURITE	2	2	38.80	4.49	4.48	4.49	4.27	4.27	4.27
NEPHELINITE	1	0	NaN	5.11	5.11	5.11	3.81	3.81	3.81
UGANDITE	3	3	41.27	4.54	4.53	4.70	4.27	4.27	4.28
PYROXENITE	2	2	44.47	6.14	6.10	6.14	4.14	4.14	4.14
PICRITE	11	7	45.67	3.79	3.55	3.71	3.96	3.96	4.02
	172	146							
Unknown	4	7	53.22	4.43	3.94	3.83	3.97	3.97	3.96
ORENDITE	1	1	55.47	4.91	4.91	4.91	4.08	4.08	4.08
PANTELLERIT									
E	2	1	70.20	3.21	3.21	3.21	3.87	3.87	3.87
SANDSTONE	1	0	NaN	3.68	3.68	3.68	4.05	4.05	4.05

	Average		# of data		K _{MEAS}	
ROCK NAME	SiO ₂ (wt%)	# of data	have SiO ₂	K_{MEAS} (average)	(log mean)	<i>K_{MEAS}</i> (median)
UNKNOWN	57.75	1759	861	4.62	2.69	3.27
GNEISS	67.08	1603	1086	6.81	4.25	4.43
AMPHIBOLITE	50.37	931	859	4.28	2.71	3.18
SCHIST	60.08	792	472	5.74	3.45	3.88
QUARTZITE	78.07	296	119	6.12	3.50	3.94
GRANULITE	51.66	287	242	4.78	2.48	2.68
GREENSTONE	48.93	281	260	2.81	2.55	2.63
METABASALT	49.94	238	226	3.25	2.52	2.57
PHYLLITE	60.15	222	120	4.26	3.57	3.85
METAGRAYWACKE	64.77	156	119	4.27	3.48	3.26
SLATE	65.12	154	105	3.72	3.22	3.26
TOURMALINITE	66.88	145	138	4.31	3.81	3.59
METATUFF	65.25	117	66	4.73	3.92	3.99
METASEDIMENT	67.00	106	83	3.91	2.92	3.51
ORTHOGNEISS	70.34	105	105	4.52	3.26	3.86
GREENSCHIST	49.05	98	89	3.02	2.45	2.81
MARBLE	21.12	91	68	34.01	1.45	1.68
SKARN	43.57	85	17	7.42	1.25	1.43
HORNFELS	56.87	84	46	3.71	2.96	2.75
AUGENGNEISS	70.06	71	59	9.49	6.68	6.38
ARENITE	62.08	70	65	3.33	2.41	3.74
METABASITE	49.21	66	66	3.04	2.55	3.21
ECLOGITE	50.36	55	22	2.79	1.78	1.98
METACONGLOMERATE	61.73	47	8	7.77	4.94	4.20
METATONALITE	63.86	46	43	3.91	2.94	3.23
MIGMATITE	65.75	41	36	6.64	3.97	4.75

3. Metamorphic dataset – all available *K_{MEAS}*

CDANOEELS	67.00	21	21	1 1 1	2.45	1 1 1
UKANUFELS	07.80	51	51	4.44	3.45	4.11
METAARENITE	NaN	31	NaN	4.36	4.26	4.20
METAGRANITE	65.73	25	18	6.45	5.11	4.87
PARAGNEISS	58.84	25	25	6.89	4.92	3.81
METAARGILLITE	63.92	21	9	2.96	2.70	2.62
METAFELSITE	67.98	20	20	3.31	3.12	3.18
SERPENTINITE	45.14	18	18	2.53	1.51	2.01
BUCHITE	68.51	16	16	5.07	4.72	4.41
METADIORITE	55.87	14	12	4.10	3.50	3.19
TONALITE	NaN	13	NaN	0.23	0.22	0.23
GRANITE	NaN	12	NaN	0.26	0.19	0.20
METASANDSTONE	68.44	12	6	3.98	3.69	3.67
CHARNOCKITE	53.80	11	1	11.35	6.30	11.60
CALCSILICATE	59.67	10	7	2.69	1.45	2.32
METACHERT	93.68	9	9	1.08	0.49	0.34
METAPELITE	65.42	9	9	9.45	7.71	7.91
BLUESCHIST	64.68	8	1	5.30	4.02	3.91
METAARKOSE	79.20	8	7	5.45	4.21	4.90
METAGRANODIORITE	60.05	6	2	4.11	3.53	3.78
METAMONZONITE	66.63	6	4	7.93	5.09	4.38
MYLONITE	63.27	6	6	3.87	3.60	3.53
METAGABBRO	47.19	5	5	5.51	2.99	2.01
METAIGNEOUS	47.05	5	2	5.04	4.53	4.78
METARHYODACITE	66.76	5	5	5.67	4.89	6.62
SOAPSTONE	49.24	5	5	1.83	1.66	1.54
METAPYROXENITE	48.25	3	1	1.90	1.77	2.16
META-MONZODIORITE	56.00	2	1	4.85	4.77	4.85
METASPILITE	49.35	2	2	0.99	0.93	0.99
SHALE	55.00	2	2	3.95	3.90	3.95
LEPTITE	76.76	1	1	13.67	13.67	13.67

	1	1	1	1	1	1
MARLSTONE	NaN	1	NaN	1.43	1.43	1.43
METADACITE	66.25	1	1	4.21	4.21	4.21
METAHORNBLENDITE	NaN	1	NaN	3.12	3.12	3.12
METAMAFITE	42.00	1	1	2.99	2.99	2.99
METAPERIDOTITE	47.80	1	1	2.20	2.20	2.20
METAPSAMMITE	82.52	1	1	4.64	4.64	4.64
METARHYOLITE	68.13	1	1	5.25	5.25	5.25
METATRONDHJEMITE	68.80	1	1	5.36	5.36	5.36
MICASCHIST	75.96	1	1	3.16	3.16	3.16
PYROXENITE	NaN	1	NaN	2.29	2.29	2.29

	# of	# of data have	Average SiO ₂	KMEAS	K _{MEAS}	KMEAS	Knh	K_{pb}	K_{pb}
ROCK NAME	data	SiO2	(wt%)	(mean)	mean)	(median)	(mean)	mean)	(median)
METAPELITE	1	1	48.7	3.13	3.13	3.13	3.76	3.76	3.76
ECLOGITE	2	2	48.8	3.34	3.05	3.34	3.35	3.33	3.35
GREENSTONE	1	1	48.8	2.88	2.88	2.88	3.85	3.85	3.85
AMPHIBOLITE	20	16	49.2	3.40	2.97	2.98	3.67	3.60	3.80
GRANULITE	73	49	51.9	5.50	2.46	2.63	4.34	4.29	4.08
PYROXENITE	1	NaN	NaN	2.29	2.29	2.29	3.91	3.91	3.91
SCHIST	17	16	57.9	3.36	2.40	2.91	3.82	3.73	3.58
HORNFELS	3	1	62.9	4.47	3.64	2.70	3.50	3.46	3.29
ORTHOGNEISS	3	3	63.5	4.80	4.04	3.13	3.80	3.80	3.80
GNEISS	36	19	70.2	14.61	8.54	8.49	4.53	4.40	4.08
MICASCHIST	1	1	76	3.16	3.16	3.16	3.82	3.82	3.82
PHYLLITE	1	1	81.5	3.56	3.56	3.56	4.03	4.03	4.03
QUARTZITE	3	NaN	NaN	0.73	0.69	0.75	1.71	1.27	1.24
CHARNOCKITE	2	NaN	NaN	4.83	4.66	4.83	4.02	3.96	4.02
NOT-GIVEN	36	18	67.1	5.07	3.57	4.37	4.12	4.08	4.00

4. Metamorphic dataset -- have both K_{MEAS} and K_{Pb}

						KMEAS
	Averag e SiO ₂	# of	# of data	K_{MEAS} (average	K _{MEAS} (log	(median
ROCK NAME	(wt%)	data	have SiO ₂)	mean))
UNKNOWN	61.55	4275	1012	2.91	1.44	2.71
SANDSTONE	68.11	2751	689	2.99	1.57	2.87
MUDSTONE	63.76	918	97	3.19	2.36	2.71
SILTSTONE	62.88	793	232	3.00	2.05	2.48
PHOSPHORITE	49.92	519	7	0.37	0.17	0.17
CHERT	88.74	421	409	2.75	1.78	2.21
CONGLOMERAT E	63.72	364	50	10.00	2.86	3.14
ARGILLITE	65.13	315	273	3.48	3.06	3.42
LIMESTONE	26.76	304	118	1.76	0.65	0.87
CLAYSTONE	48.24	270	122	3.37	2.77	2.91
ARKOSE	73.43	165	107	4.32	3.67	3.85
SILICICLASTIC	58.72	134	59	2.78	2.23	2.35
BIOGENIC	56.90	103	37	1.77	1.35	1.48
DOLOMITE	26.14	87	64	1.46	0.46	0.38
TURBIDITE	64.82	72	51	3.50	2.75	3.64
GRAYWACKE	60.13	37	37	4.53	3.56	3.15
BRECCIA	58.93	32	9	3.74	2.03	3.04
SAND	82.35	31	6	3.55	2.66	2.31
PELITE	63.30	30	30	3.41	2.98	3.38
CARBONATE	7.47	28	6	15.26	1.86	2.74
LUTITE	NaN	16	NaN	1.93	1.50	1.56
VOLCANICLAST IC	57.84	10	5	2.26	2.18	2.39
BLACK-SHALE	51.65	6	2	1.92	1.01	2.09
PORCELLANITE	24.80	5	5	3.78	3.59	3.96
CLAY	69.66	5	4	3.30	2.81	2.95
DIATOMITE	NaN	5	NaN	2.58	2.27	2.01

5. Sedimentary dataset – all available *K_{MEAS}*

1	1	1	1	1	1	1
PHILLIPSITE	NaN	5	NaN	2.69	2.61	2.56
WACKE	66.65	4	3	5.52	5.32	5.05
MARL	12.19	3	2	3.05	2.76	2.88
OIL SHALE	33.07	3	3	2.29	2.27	2.24
GRAVEL	54.70	2	1	5.54	4.83	5.54
GYPSUM	NaN	2	NaN	3.72	3.70	3.72
QUARTZ ARENITE	15.00	1	1	0.14	0.14	0.14
GRAVEL AND SAND	73.31	1	1	1.80	1.80	1.80
SPICULITE	92.00	1	1	0.03	0.03	0.03
CONCRETION	NaN	1	NaN	1.93	1.93	1.93
MARLSTONE	NaN	1	NaN	5.06	5.06	5.06
SULFATE DEPOSIT	NaN	1	NaN	2.80	2.80	2.80

				=/====,0					
	# of	# of data have	Average SiO ₂	Кмеаs	<i>K_{MEAS}</i> (log	Kmeas	K_{nh}	K _{pb} (log	K_{pb}
ROCK NAME	data	SiO2	(wt%)	(mean)	mean)	(median)	(mean)	mean)	(median)
LIMESTONE	5	NaN	NaN	1.23	0.90	1.27	3.60	3.59	3.63
MARL	1	1	14.99	1.55	1.55	1.55	4.09	4.09	4.09
UNSPECIFIED	2	NaN	NaN	2.90	2.89	2.90	4.07	4.07	4.07
SILICICLASTIC	11	NaN	NaN	2.70	1.68	3.45	3.88	3.87	3.99
GRAVEL	1	1	54.70	2.83	2.83	2.83	4.31	4.31	4.31
BIOGENIC	7	NaN	NaN	1.65	1.47	1.26	4.01	4.01	4.02
MUDSTONE	1	1	55.74	5.65	5.65	5.60	4.07	4.07	4.07
CLAY	3	3	75.80	2.25	2.04	2.76	4.10	4.10	4.05
ARGILLITE	8	8	60.20	3.10	2.77	2.39	4.17	4.08	3.71
SANDSTONE	13	11	NaN	4.63	4.10	4.26	4.39	4.29	4.06
GREYWACKE	1	1	68.40	3.23	3.23	3.23	3.95	3.95	3.95
ARKOSE	4	4	76.93	3.76	3.60	3.70	3.90	3.90	3.87
SAND	2	2	86.85	10.85	8.27	10.85	4.04	4.04	4.04
SILTSTONE	4	NaN	NaN	5.96	5.34	6.83	4.03	4.03	4.03
BRECCIA	5	NaN	NaN	5.19	5.18	5.38	4.02	4.02	4.00
WACKE	1	NaN	NaN	3.88	3.88	3.88	4.17	4.17	4.17

6. Sedimentary dataset – have both K_{MEAS} and K_{Pb}

7. Continental Crust Types

Crust Type	Crust Area (Km ²)	% Total Crust
Platform	6.52E+12	3.42
Slow Thin Platform	3.88E+12	2.04
Archean (Antarctica)	1.61E+12	0.85
Early Archean	1.27E+13	6.67
Late Archean	9.13E+12	4.79
Early/mid Proter.	3.05E+13	15.98
Early/mid Proter. (Antarctica, slow)	4.1E+12	2.15
Late Proter.	2.22E+13	11.64
Slow Late Proter.	2.98E+12	1.56
Island Arc	3.85E+12	2.02
Forearc	1.96E+12	1.03
Continental Arc	1.79E+12	0.94
Slow Continental Arc	2.41E+12	1.27
Extended Crust	7.49E+12	3.93
Fast Extended Crust (Antarctica)	1.78E+12	0.93
Orogen (Antarctica), Thick upper Crust, Thin lower Crust	1.9E+12	1
Orogen, Thick upper Crust, Very Thin Lower Crust	1.26E+13	6.62
Orogen, Thick upper Crust, Fast middle Crust	2.42E+12	1.27
Orogen With Slow Lower Crust (Andes)	1.36E+12	0.71
Slow Orogen (Himalaya)	6.68E+12	3.5
Slow Margin/Shield (Antarctica)	1.57E+12	0.82
Rift	1.98E+12	1.04
Phanerozoic	1.02E+13	5.35
Fast Phanerozoic (E. Australia, S. Africa, N. Siberia)	1.67E+12	0.88
Continental Shelf	1.89E+13	9.94
Continental Slope, Margin, Transition	1.26E+13	6.6
Thinned Cont. Curst, Red Sea	5.35E+11	0.28
Oceanic Plateau With Cont. Crust	4.61E+12	2.42
Caspian Depression	2.88E+11	0.15
Intermed. Cont./OC. Crust, Black Sea	4.05E+11	0.21

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