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Discussion of K/U fractionation during low degree melting

A first important step in the discussion of K/U ratios on Earth is to ascertain if the variations observed might have been caused by melting processes alone. It is possible that the mantle contains K-bearing minerals and melting with such a phase in the residue would be expected to display lower K/U than the source of melting. It could therefore be speculated that the difference observed between MORB and OIB (Arevalo et al., 2009) might simply be related to a systematic difference in degree of melting of these reservoirs. For normal MORB, it has clearly been demonstrated that K and U do not fractionate during melting (Arevalo et al., 2009) and that the average MORB source must have K/U ~17,000-21,000. Almost all OIB exhibit K/U ~9,000-13,000 (Arevalo et al., 2009; Paul et al., 2003), which in principle would be consistent with OIB on average being made up of low degree melts where at least one K-rich phase remained in the residue. However, there is no difference in K/U when comparing the overall K/U of different OIBs to sample subsets that are likely to represent high degrees of melting (Table S1). In addition, K and U have recently been shown to not fractionate from the source of the St. Helena hotspot (Arevalo and McDonough, 2010; Willbold and Stracke, 2006). It is therefore most probable that K/U in OIB largely represents that of the enriched mantle source from which it is extracted.

Model description

A summary of all the parameters used is shown in Table DR2. Specific values used to obtain the results shown in Fig. 1 are also outlined in Table DR2. The model solution with constant weathering fluxes though time (Fig. 3) utilises the same parameters as Fig. 1 except for the weathering fluxes, which are shown in Fig. DR1b. The excel spreadsheet of the model is available as supplemental material and readers are encouraged to explore the range of solutions possible as the number of free variables are too many to outline all the responses to changes in specific parameters.

There are a number of constraints on what constitutes a successful model run. Firstly, the K/U of the continental crust, OIB and MORB mantles reservoirs must be consistent with present day values of $13,000 \pm 3,000, 11,900 \pm 2,200$ and $19,000 \pm 2,600$ (Arevalo et al., 2009), respectively. It must also be consistent with the Th/U ratios of these reservoirs which are characterised by CC = 5 ± 1 (McLennan and Taylor, 1980; Paul et al., 2003; Rudnick and Gao, 2003), OIB = 3.3-4 (Paul et al., 2003) and MORB = 2.3-2.7 (Elliott et al., 1999; Paul et al., 2003). In addition, the observed temporal increase of Th/U in the continental crust from 4 at ca. 2.5 Ga to 5.5 at present (McLennan and Taylor, 1980) should be reproduced as well.

All equations used are either linear changes over time (e.g. ocean crust production, degree of melting, weathering fluxes) or simple mass balance equations. As an example oceanic crust consists of a flux supplied by sedimentation and alteration in addition to an igneous component governed by mantle melting:

$$M_{\rm EI} = C_{\rm mantle} * M_{\rm OC}/F_{\rm melt} , \qquad (1)$$

where M_{EI} is the mass flux of the element supplied from mantle melting, C_{mantle} is the concentration of the element in the mantle, M_{OC} is the oceanic crust production rate and F_{melt} is the degree of melting. It is assumed that the partition coefficient for K, U and Th are all effectively 0, which is reasonable at degrees of melting >10%. In order to calculate the concentration of an element in the total oceanic crust one needs to add the weathering flux which is defined as a function of time in Fig. DR1. Thus:

$$C_{OC} = (M_{EI} + M_W)/M_{OC}, \qquad (2)$$

where C_{OC} is the concentration of the element in the oceanic crust and M_W is the weathering flux. Note that all parameters in (2) are fluxes and so C_{OC} becomes a concentration. All equations in the model work in this simple way of adding and subtracting mass from the three different silicate reservoirs. Below is outlined the processes responsible for transporting the elements between each reservoir.

The model is constructed in million-year time intervals. Each time interval consists of three steps: first extraction of oceanic crust by melting of the mantle, then alteration of and sedimentation onto the oceanic crust, and lastly subduction back into the mantle (with simultaneous continental crust extraction). Subduction is assumed to start at between 3800 and 4300 Ma, with the best results obtained when beginning subduction before 4000 Ma.

Oceanic crust production is assumed to have decreased linearly from 5-7 $\times 10^{17}$ g/yr at the start of subduction to the current value of 6×10^{16} g/yr (Mottl, 2003). The same is the case for the degree of melting which decreases linearly from 20% to 10%. In total this results in ~30-35% of the mass of the mantle being recycled over Earth history.

At the start of the model the mass of the mantle is taken as 4×10^{24} kg and it is assumed that at this stage 0-30% of the incompatible trace element budget of the mantle has already been extracted to the continental crust (Harrison, 2009). Removal of material into the continental crust is assumed to have a negligible effect on the mass of the mantle, which is acceptable as the total mass of the continental crust is <1% of the mantle. The concentrations of K, U and Th in the bulk silicate Earth (BSE) are taken to be 280, 0.021 and 0.084 ppm, respectively (Arevalo et al., 2009; McDonough and Sun, 1995), though model runs with K contents of the BSE of 250-310 ppm are also successful.

The oceanic crust is treated as one homogenous reservoir and includes both sediments and igneous lithologies. The weathering flux of K, U and Th to the igneous oceanic crust can be divided into physical (sedimentation) and chemical (alteration and authigenic precipitation) components. The Th flux is purely sedimentary and the model works well for physical weathering fluxes at the start of the model both lower and higher than the present-day Th-flux of $\sim 9 \times 10^9$ g/yr (Plank and Langmuir, 1998). In principle, a range between 4-40 x 10^9 g/yr can produce acceptable model solutions. Potassium and uranium are both delivered to the ocean crust via physical and chemical processes. Figure 3 illustrates that using an invariant K flux through time results in K/U and Th/U ratios that are inconsistent with all silicate reservoirs and therefore the K flux must have been significantly higher in the Archean than today. However, as models with highly variable Th fluxes are successful it is only the chemical weathering in the Archean that necessarily *must* have been higher than today (though it could have been both). The temporal total weathering fluxes (both physical and chemical) for Figs. 1 and 3 are shown in Fig. DR1, where it can be seen that the U weathering flux is tied to Th before 2200 Ma because U

only has a physical weathering component and tied to K after 2200 Ma when chemical weathering of U commences. In general, K fluxes at the start of the model of ~2-5 x 10^{14} g/yr yield satisfactory solutions.

The high chemical weathering rate required for the Archean can be reconciled when inferring that the long-term average supply of dissolved material from the continents is controlled by the supply of freshly exposed igneous crust, which must have been higher in the Archean (Hawkesworth and Kemp, 2006). In addition, it has been suggested that temperatures (Knauth and Lowe, 2003; Robert and Chaussidon, 2006) and atmospheric concentrations of CO_2 (Hessler et al., 2004; Rye et al., 1995; Sleep and Zahnle, 2001) were higher than present-day, which would also have generated high chemical weathering rates. However, conceptually it is here assumed that the supply of igneous crust to the surface of the continents (not necessarily the same as continental crust growth) scales with Earth's heat flux, which we know has decreased consistently since the Hadean (Harrison, 2009). Since, it is known that weathering of igneous material accounts for a disproportionately large fraction of modern weathering (Dessert et al., 2003) it is thus assumed that magmatic activity has been the main control of the supply rate of dissolved material to the oceans.

Present-day element fluxes to the oceanic crust (sediments and alteration) are taken as $K = 4.8 \times 10^{13} \text{ g/yr}$, $U = 4.8 \times 10^9 \text{ g/yr}$ and $Th = 9 \times 10^9 \text{ g/yr}$. These numbers are consistent with current estimates based on average sediments and ocean crust alteration (Kelley et al., 2003; Plank and Langmuir, 1998; Staudigel, 2003).

Subduction is modelled to occur in two different styles. Before 2.5 Ga, melting was the main process controlling the elemental transfer out of the subducting lithosphere due to the steep geothermal gradient (Martin, 1986). Slab melting would result in very little net elemental fractionation between K, U and Th and the best results are obtained when 30-70% of these elements (always with no elemental fractionation) are removed to produce continental crust. No independent estimate exists for this parameter and hence we simply use the range of values which generates successful model runs.

High mantle temperatures and consequently more vigorous convection in the Archean is assumed to have caused the residual slab to be mixed directly back into the upper mantle. After 2.5 Ga, fluid discharge became the dominant force that determined how much K, U and Th was transferred out of the subducting slab (Martin, 1986). This was a result of lower ambient mantle temperatures combined with the subduction of older and thereby colder and denser oceanic lithosphere. This is incorporated into the model by assuming that after 2.5 Ga residual slabs sink to the bottom of the mantle to form a separate lower mantle reservoir, which is what today is sampled by OIB.

From arc lavas and experimental studies we know that the fluid mobility of potassium, uranium and thorium are in the order K>U>Th (Bezos et al., 2009; Klimm et al., 2008). It has previously been suggested that 30-40% of slab U is released during crust dehydration (Bach et al., 2003). Using this U flux, correct model solutions are computed for fluid assisted K and Th fluxes of 45-65% and 0-15%, respectively. The fluid-induced fractionation of K, U and Th during subduction exerts a particularly strong control on the model solutions. For example, using a 30% U fluid flux limits the Th fluid flux to <10%.

Considering that the sub-arc mantle is often observed to have been metasomatised by fluids (Maury et al., 1992; Parkinson and Arculus, 1999) it appears to be a realistic inference that a portion of slab-derived fluids are mixed back into the upper mantle via

the corner flow in the mantle wedge. This particular process is very poorly constrained and there are no direct measurements of how fluids and trace elements from the slab are divided between arc volcanoes and the upper mantle. It should be noted that this process is essential in order to reproduce the Th/U ratios observed in MORB and OIB, whereas the distribution of K and U in the mantle is largely set by the Archean weathering regime. Elliott et al (1999) incorporated this process into their model in a somewhat ad hoc way by assuming direct transfer of excess U added to altered oceanic crust into the upper mantle without qualifying exactly how it took place.

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Fig. DR1: Fluxes of Th, U and K supplied to the oceanic crust from weathering used in Figs.1 (a) and 3 (b). Note that the U weathering flux is tied to Th before 2.2 Ga such

that Th/U = 4, because these elements would have been mobilised through physical weathering and were therefore not fractionated from the composition of continental crust. After 2.2 Ga, when chemical weathering of U commences, the U flux is tied to K in the proportions we observe for present day (K/U = 10,000)

TABLE DR1: K/U IN OCEAN ISLAND BASALTS (OIB)							
OIB	K/U All samples*	s.d.	n	K/U High- degree melts [†]	s.d.	n	
Kerguelen	19087	9898	80	18589	6537	23	
Hawaii	13628	4559	658	12433	3980	159	
East Australia	12665	10511	156	9380	6459	28	
Galapagos	11783	4123	121	15133	7733	17	
Samoa	11552	3927	99	13111	4469	41	
Reunion	11195	3026	250	11962	4515	72	
Iceland	10909	2615	143	10473	1194	12	
Azores	10282	2331	96	10500	816	20	
Comores	10079	2919	70	8956	3435	21	
Cape Verde	9652	5788	77	8583	4361	24	
Canaries	8865	3079	197	8910	3231	79	
Societies	8755	2396	33	9024	2633	19	
Austral-Cook	6297	2200	34	5991	2416	17	

Note: Only samples containing more than 0.2% K₂O considered here due to the large uncertainty on potassium measurements at low concentrations. Data compiled from the Georoc database.

*Only samples containing 4%–16% MgO included.

[†]High-degree melts defined as samples containing 10%–16% MgO and less than 4% Na₂O.

Table DR2: Parameters used in mantle evolution model

Fixed Parameters	Value	Values for variable parameters used in Figure 1	Value
Oceanic crust production today	6 x 10 ¹⁶ g/yr	Oceanic crust production at T=0	6 x 10 ¹⁷ g/yr
K flux to oceanic crust today	4.8 x 10 ¹³ g/yr	K flux to oceanic crust at T=0	3 x 10 ¹⁴ g/yr
U flux to oceanic crust today	4.8 x 10 ⁹ g/yr	U flux to oceanic crust at T=0	2.25 x 10 ⁹ g/vr
Th flux to oceanic crust today BSE U concentration BSE Th concentration	9 x 10 ⁹ g/yr 0.021 ppm 0.084 ppm	Th flux to oceanic crust at T=0 BSE K concentration Start of subduction	9 x 10 ⁹ g/yr 280 ppm 4200 Ma
Age of switch from slab melting to fluid discharge	2500 Ma	Fraction of K, U and Th extracted to form CC prior to T=0	20%
Age of switch from anoxic to oxic oceans	2200 Ma	Fraction of K, U and Th extracted from slab during Archean Subduction	40%
Total Mantle mass	4 x 10 ²⁷ g	Fraction of K extracted from slab during modern subduction	60%
Mantle melting degree at T=0	20%	Fraction of U extracted from slab during modern subduction	40%
Mantle melting degree today	10%	Fraction of Th extracted from slab during modern subduction	8%
		Fraction of K, U and Th delivered from slab to crust during modern subduction	50%