

U enrichment and Th/U fractionation in Archean boninites: Implications on paleo-ocean oxygenation and U cycling at juvenile subduction zones

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Abstract

Phanerozoic boninites record enrichments of U over Th, giving Th/U 0.5-1.6, relative to intraoceanic island arc tholeiites (IAT) where Th/U averages 2.6. Uranium enrichment is attributed to incorporation of shallow, oxidized fluids, U-rich but Th-poor, from the slab into the melt column of boninites which form in near-trench to forearc settings of suprasubduction zone ophiolites. Well preserved Archean komatiite-tholeiite, plume-derived, oceanic volcanic sequences have primary magmatic Th/U ratios of 4.4-3.6, and Archean convergent margin IAT volcanic sequences, having REE and HFSE compositions similar to Phanerozoic IAT equivalents, preserve primary Th/U of 4-3.6. The best preserved Archean boninites of the 3.0 Ga Olondo and 2.7 Ga Gadwal greenstone belts, hosted in convergent margin ophiolite sequences, also show relative enrichments of U over Th, with low average Th/U ~ 3 relative to coeval IAT, and Phanerozoic counterparts which are devoid of crustal contamination and therefore erupted in an intraoceanic setting, with minimal contemporaneous submarine hydrothermal alteration. Later enrichment of U is unlikely as Th-U-Nb-LREE patterns are coherent in these boninites whereas secondary effects induce dispersion of Th/U ratios. The variation in Th/U ratios from Archean to Phanerozoic boninites of greenstone belts to ophiolitic sequences reflect on genesis of boninitic lavas at different tectono-thermal regimes. Consequently, if the explanation for U enrichment in Phanerozoic boninites also applies to Archean examples, the implication is that U was soluble in oxygenated Archean marine water up to 600 Ma before the proposed great oxygenation event (GOE) at ~ 2.4 Ga. This interpretation is consistent with large Ce anomalies in some hydrothermally altered Archean volcanic sequences aged 3.0-2.7 Ga.

Keywords: boninites; Archean; island arc tholeiites (IAT); U-enrichment; oxic Archean oceans

Introduction and scope

The Precambrian history of the Earth is marked by two major geological events: a pulse of continental crust formation at the end of the Archaean eon with a peak at 2.7 Ga and a weak oxygenation of the atmosphere (the Great Oxidation Event) that followed, at 2.45 Ga ago. This oxygenation has been linked to the emergence of oxygenic cyanobacteria and to changes in the compositions of volcanic gases, but not to the composition of erupting lavas. Geochemical constraints indicate that the oxidation state of basalts and their mantle sources has remained constant since 3.5 Ga ago. However, certain geochemical proxies can provide appropriate constraints on the link between volcanism in diverse tectonic environments and oxygenation-reduction stages in the Ocean. It has been envisaged that mid-oceanic ridge rift systems percolated by hydrothermal fluids have nested marine ecosystems and have contributed towards the oxidation –reduction processes in different levels of the ocean. The descent of the oceanic lithosphere into the mantle marking the initiation of subduction processes at convergent margin settings stands as one of the key factors triggering geochemical cycling and ocean-crust-mantle interaction (Stern et al., 2012; Turner et al., 2014). Subduction initiation is a cornerstone in the edifice of plate tectonics and subduction zones are important components in Earth's geological cycles as it involves recycling of oceanic crust which triggers the magmatic activity, release of fluids and gases and generate valuable mineral deposits. Island arc volcanic rocks provide significant information for understanding crustal and mantle processes. Further, the initiation of subduction triggers the tripartite interactions between the ocean, lithosphere, and mantle play a vital role towards appropriate nutrient supply for life forming processes that garner the Earth to a habitable state (Dohm and Maruyama, 2015; Santosh et al., 2017). The Archean times were marked by smaller plate dimensions and frequent plate convergence. Archean subduction processes have largely contributed towards crustal accretion and continent generation and therefore it can be corroborated the volcanic output during Archean subduction processes influenced the Archean ocean.

Subduction zone magmatism is marked by a diverse compositional spectrum including island arc tholeiites (IAT), calc-alkaline basalts (CAB), basalt-andesite-dacite-rhyolite (BADR) associations, boninites, picrites, siliceous high-Mg basalts (SHMB), adakites, high-Mg andesites and Nb-enriched basalts (Polat and Kerrich, 2006). Boninites are volcanic rocks with >8 wt.% MgO, >52 wt.% SiO₂ and <0.5 wt.% TiO₂. Boninites are a variety of primary and near primary magmas with >a wide range of CaO/Al₂O₃ ratios (< 0.55- >0.75), U-shaped REE patterns. They show low TiO₂, Zr and Nb contents, high Al₂O₃/TiO₂ ratios with negative Nb, Ta, P and Ti anomalies (Crawford et al., 1989; Kerrich et al., 1998; Polat and Kerrich, 2006). These high Mg and high Si

volcanic rocks with extremely depleted incompatible trace element (HREE) signatures and variable enrichment of LILE are generated either during subduction initiation or in hot subduction zones (Crawford et al., 1989; Falloon and Crawford, 1991; Stern and Bloomer, 1992; Ishikawa et al., 2002; Ishizuka et al., 2006). Boninites are the first lavas to erupt at the initial stages of subduction zone processes. The geochemical signatures in Archean boninites preserve significant information about the early stages of subduction. The precise geochemical data obtained over the years has been able to distinguish boninites and boninitic rocks in different older terranes. This increase of data base and various reports of boninites in older greenstone terranes of different cratons of the world are evident that boninites were erupted throughout the Earth's history. The active margins of Pacific Ocean evidenced with boninite eruption during Mesozoic, Cenozoic and majority are from Izu-Bonin-Mariana arc system. Geochemically well characterized Archean boninites include boninites in the 3.12 Ga Whundo volcanic sequence, Pilbara craton, and 2.97-2.95 Mallina sequence, Pilbara Craton, Western Australia; boninite series lavas from the 3.0 Ga Olondo greenstone belt in the Aldan Shield; a 2.8 Ga ophiolite sequence, hosting boninites of the Karelian greenstone belt, Baltic Shield; boninites of the 2.7 Ga Gadwal greenstone terrane, Eastern Dharwar Craton, India; and from the Superior Province, 2.8 Ga boninites in the Opatika Subprovince, and 2.7 Ga examples from the Abitibi terrane, Ontario. Recently Paleo-Mesoarchean boninites have been reported from the 3.4 Ga Older Metamorphic Group (OMG) of the Singhbhum Craton (Manikyamba et al., 2015).

Uranium is systematically enriched over Th in many Phanerozoic boninites relative to most spreading centres and intraoceanic arc volcanic lithologies. Mid-ocean ridge basalts (MORB) and island arc tholeiitic (IAT) basalts are characterized by average Th/U of 2.6, whereas the average for Phanerozoic boninites is 1.6 and in some boninite suites Th/U is as low as 0.5 (Table 1; Kelemen et al., 2003; Vireute et al., 2006; Arevalo and McDonough, 2010). According to Pearce and coworkers, relative enrichment of U is attributed to incorporation of shallow oxygenated fluids, relatively U-rich but Th-poor, from the slab into the melt column of near-trench magmas where boninites are generated (Pearce and Peate, 1995; Pearce and Robinson, 2010 and references therein; Reagan et al., 2010). Recent observations of boninite eruptions in the northeastern Lau basin record the volatile characteristics of the lavas from slab-derived fluids (Resing et al., 2011). Boninites are predominantly generated in near-trench to forearc settings of intraoceanic arcs, and formed at low-pressure (<50 km) in an anomalously hot suprasubduction zone setting (Hickey and Frey, 1982; Crawford et al., 1989; Falloon and Danyushevsky, 2000). In contrast, Th/U ratios of continental arcs, average upper continental crust, and primitive mantle are close to 4 (Table 1; McDonough and Sun, 1995; Kelemen et al., 2003; Rudnick and Gao, 2003).

If U-Th fractionation in Phanerozoic boninites is due to shallow slab-derived, U-rich oxygenated fluids, then it is instructive to examine Th/U ratios in Archean boninites as a test of the oxidation state of Archean oceans, and in turn to evaluate whether the Archean atmosphere-hydrosphere was anoxic until the putative great oxygenation event (GOE) at ~2.4 Ga as argued by several workers (Holland, 2002, 2009; Kump and Barley, 2007). All papers on Archean boninites address elemental compositions and petrogenesis, as well as drawing intercomparisons with Phanerozoic counterparts (Kerrick et al., 1998; Boily and Dion, 2002; Smithies et al., 2004a, b; Puchtel, 2004; Shchipansky et al., 2004; Manikyamba et al., 2005; Khanna et al., 2009). However, none of these studies evaluated Th-U fractionations and the implications for oxygenated Archean oceans. We demonstrate that U is also enriched over Th in many Archean boninites, relative to other coeval volcanic lithologies, and specifically intraoceanic island arc tholeiitic basalts, endorsing soluble U in Archean oceans and early oxygenation of Earth's atmosphere-hydrosphere system as argued from a number of lines of evidence by Ohmoto and coworkers (Ohmoto, 1999, 2004; Ohmoto et al., 2006; Kaufman et al., 2007; Hoashi et al., 2009; Kato et al., 2009), and recently from extreme positive Ce-anomalies in 3.0 Ga hydrothermally altered submarine volcanic sequences (Kerrick and Said, 2011). Further, Th and U being the major heat producing elements in the interior of the earth, their fractionation at various tectonothermal regimes is unclear. Boninitic volcanism originating through mantle melting at subduction zones opens a window to understand Th-U systematics and their fractionation.

2. Boninite compositional characteristics

According to IUGS scheme of classification, boninites are volcanic rocks having >8 wt.% MgO, >52 wt.% SiO₂ and less than 0.5 wt.% TiO₂ (Le Bas, 2000). Archean boninites were first described from the 2.7 Ga Abitibi greenstone belt, Superior Province, Canada (Kerrick et al., 1998), with subsequent reports of numerous other occurrences (Polat and Kerrich, 2006 and references therein). These Archean boninites have generally been termed "boninitic" or "boninite series" given that SiO₂, MgO, and CaO used to classify Phanerozoic boninites (Crawford, 1989) may have been mobile during seafloor hydrothermal alteration and metamorphism. In terms of least mobile elements, the Archean examples share some combination of the following compositional features with Phanerozoic boninites: (1) high Al₂O₃/TiO₂ ratios of 30-60; (2) U-shaped REE patterns with (La/Sm)_N> 1 but (Gd/Yb)_N<1; (3) negative Nb anomalies where Nb/La is less than the primitive mantle value of 1.03; (4) variable normalized enrichments of Zr-Hf/MREE; and (5) high Mg#, Cr, Co, Ni contents relative to IAT (Sun and McDonough, 1989; Kerrich et al., 1998; Smithies et al., 2004 a,b). The combination of low-TiO₂ with high Al₂O₃/TiO₂ ratios of 30-60, (Gd/Yb)_N<1, and

elevated MgO, Cr, and Ni contents is interpreted as a multistage process: (1) an upper mantle source that is refractory due to one or more episodes of basaltic melt extraction generating a residue where $HREE_N > MREE_N > LREE_N$; and (2) later introduction of incompatible elements, having $(La/Sm)_N > 1$, in a hydrous fluid or melt derived from a subducting slab, that fluxes the refractory mantle generating boninite melts with the characteristic U-shaped REE patterns (Sun and Nesbitt, 1978; Hickey and Frey, 1982; Crawford et al., 1989; Smithies et al., 2004a,b; Pearce and Robinson, 2010). The distinctive compositions and petrogenetic requirements of boninites strongly implicate Phanerozoic type subduction processes operating in certain Archean greenstone belt volcanic sequences (Kerrick et al., 1998; Wyman et al., 1999; Puchtel, 2004; Smithies et al., 2004a, b; Shchipansky et al., 2004; Polat and Kerrich, 2006)

These Archean boninites differ from low-Ti tholeiites of Brown and Jenner (1989) which are characterized by $(La/Sm)_N < 1$. Wyman et al., (1999) proposed several compositional criteria that distinguish Archean boninitic flows from altered komatiites, specifically U-shaped REE patterns with $(La/Sm)_N > 1$ but $(Gd/Yb)_N < 1$, whereas Al-undepleted komatiites have flat HREE, Al-depleted komatiites show $(Gd/Yb)_N > 1$, and both feature Al_2O_3/TiO_2 ratios ≤ 20 (Arndt, 2008). Archean boninites also differ from silicious high-Mg basalts (SHMB) which are crustally contaminated komatiites (Sun et al., 1989) in elevated Al_2O_3/TiO_2 ratios and U-shaped REE patterns with $(La/Sm)_N > 1$ but $(Gd/Yb)_N < 1$ (Kerrick et al., 1998; Wyman et al., 1999; Smithies et al., 2004a, b).

3. Methodology and geological setting

We compile high precision elemental data for well characterized Archean boninites. Included are: boninites in the 3.12 Ga Whundo volcanic sequence, Pilbara craton, and 2.97-2.95 Ga Mallina sequence, Pilbara Craton, Western Australia; boninite series lavas from the 3.0 Ga Olondo greenstone belt in the Aldan Shield, E. Siberia; boninites of the 2.7 Ga Gadwal greenstone belt (Guntipalli and Garlapadu), eastern Dharwar Craton; 2.7 Ga Kudrekonda boninites, Shimoga greenstone belt, western Dharwar Craton and the boninites of Older Metamorphic Group (OMG) of Singhbhum Craton, India; 2.8 Ga boninites in the Opatika Subprovince, Superior Province, and 2.7 Ga examples from the Abitibi terrane, Ontario. (Figs. 1, 2).

The Whundo Group is a ~10 km thick sequence dominated by mafic flows; boninites occur in the basal sequence of calc-alkaline basalts and basaltic andesites compositionally akin to Phanerozoic intraoceanic arc volcanics (Smithies et al., 2004a). In the Mallina Basin of the Pilbara Craton, a ~ 300m thick sequence of boninitic flows occurs in a thick siliciclastic sequence (Smithies et al., 2004b). High-Mg boninitic flows and boninitic gabbros are well preserved in the eastern

branch of the 3.0 Ga Olondo greenstone belt, which is dominated by ultramafic and mafic flows with subordinate felsic volcanic units and ultramafic to mafic intrusions. Metamorphic grade varies from epidote-amphibolite to amphibolite facies. Initially reported as komatiites, komatiitic-basalts, tholeiitic basalts, and gabbros these high-Mg flows have been reinterpreted as boninitic (Puchtel, 2004). Amphibolite-facies boninite flows, up to 50 m thick, occur within a larger suprasubduction ophiolite sequence of the North Karelian greenstone belt (Shchipansky et al., 2004).

The 2.7 Ga Gadwal greenstone belt, eastern Dharwar Craton (EDC), is dominated by tholeiitic basalts compositionally akin to primitive intraoceanic arc basalts, with adakites, and subordinate felsic magmatic units. Boninitic flows are well preserved at the Garlapadu and Guntipalli localities where they are associated with tholeiitic basalts (Manikyamba et al., 2005; Khanna et al., 2009). The 2.7 Ga Kudrekonda boninites of Shimoga greenstone belt of western Dharwar Craton are associated with metabasalts (Ganguly et al., 2016) whereas the Paleo-Mesoarchean boninites of OMG, Singhbhum Craton of eastern India are associated with island arc tholeiites erupted at an intraoceanic arc setting (Manikyamba et al., 2015). The Frotet-Evans greenstone belt, Opatika Subprovince, Quebec, has prevalent tholeiitic basalts. Boninitic units are associated with adakites and calc-alkaline andesites to rhyolites characteristic of oceanic arcs (Boily and Dion, 2002). In the Abitibi terrane, boninite flows are present in the Tisdale sequence dominated by tholeiitic basalts and komatiites, where tholeiites resemble basalts from Phanerozoic ocean plateaus (Fan and Kerrich, 1997; Kerr, 2003). Boninites are present at a second locality in the Whitney sequence (Table 1; Kerrich et al., 1998). The conjunction of these lithologies was interpreted as a mantle plume erupting proximal to an oceanic convergent margin (Wyman et al., 1999).

These occurrences of Archean boninites are all hosted in well preserved oceanic suprasubduction zone ophiolites, devoid of crustal contamination, that include pillow basalts endorsing eruption in the submarine environment. They were collected from recently glaciated outcrops (Canada, Finland and Russia) or unweathered outcrop (Australia and India).

4. Results

Boninite series lavas from the Gadwal greenstone belt show coherent multielement normalized diagrams over small ranges of absolute abundances, endorsing limited mobility of the elements (Fig. 2). These flows record all the compositional features of Phanerozoic boninites for alteration insensitive elements (Manikyamba et al., 2005; Khanna et al., 2009). Specifically, there are systematic normalized enrichments of U over Th, where median Th/U ratios are 2.36 and 1.69 respectively for the Guntipalli and Garlapadu samples. Values of Ce/Ce^* [$Ce/Ce^* = Ce_N / (La_N / Pr_N)^{1/2}$;

normalizing factors from Sun and McDonough 1989] span 0.92 to 1.08 (Fig. 2). The ultramafic to mafic lavas from the Olondo greenstone belt are boninite series (Puchtel, 2004). These also feature coherent multielement normalized patterns, with systematic fractionation of U from Th where average Th/U ratios (Table 1; Fig. 2). Values of Ce/Ce* ranges from 0.94 to 1.02 (Fig. 2).

The other four boninitic suites have average Th/U ratios and ranges of Th/U as follows: Whundo (3.98; 3.75-4.17), Mallina (3.37; 2.94-3.85), Opatika (3.61; 2.40-4.44), and Abitibi (3.8; 1.88-6.33). Collectively, ranges of Ce/Ce* in these suites span 0.92-1.15. Boninite series flows, hosted in a suprasubduction ophiolite sequence, of the 2.8 Ga North Karelian greenstone belt have Th/U ratios as low as 2.2, but there is considerable scatter of the data to values of 7.2 with an average of 4.12 (Shchipansky et al., 2004).

5. Discussion

5.1. Hydrothermal activity at Subduction zones and Uranium cycling

Uranium is not mobile during greenschist to amphibolite facies metamorphism (Dostal and Capedri, 1978). Behn et al. (2011) confirm that incompatible element signatures of sediments are stable at 2.7 to 5 GPa and up to 1,050°C. According to Nakamura and Kato (2007), U was immobile during submarine alteration of Archean volcanic sequences due to its insolubility in anoxic marine water. However, in a survey of Archean submarine volcanic and intrusive igneous suites, Kerrich et al. (2013) show that U is immobile in some suites where Ce/Ce*~1, whereas in other suites there are large fractionations of U from Th generally accompanied by Ce-anomalies. Primary U and Th contents of Archean volcanic suites are addressed below.

Mantle processes and magmatism at intraoceanic subduction zones are highly influenced by slab-derived hydrothermal fluids which play an important role in controlling geochemical cycling of elements and evolution of redox conditions in paleo-oceans (Noll Jr. et al., 1996). The aqueous geochemistry of U is unusual as it is more soluble in oxidising, alkaline and carbonate-rich water than under acidic, reducing conditions, where the main species in solution is the uranyl cation UO_2^{2+} in which U exists in its highest (hexavalent) oxidation state (Drever, 1997). Soluble uranyl-carbonate complexes like $\text{UO}_2(\text{CO}_3)_2^{2-}$ predominate in neutral to alkaline oxidising conditions, (Brookins, 1988, Duff et al., 1997). Under reducing conditions, the insoluble U^{4+} oxide, UO_2 and mixed oxides, such as U_3O_8 are formed. Sulphate- and iron-reducing bacteria are known to reduce U^{6+} to U^{4+} (Duff et al., 1997) and this mechanism operated during Archean times in anoxic sedimentary environments. In contrast to the soluble behaviour of U, thorium has low mobility under all environmental conditions, mainly due to the high stability of the insoluble ThO_2 and the strongly resisting nature of its carrier minerals such as monazite and zircon.

Unlike U, Th cannot be oxidised to a stable cation equivalent to the highly mobile uranyl ion UO_2^{2+} . The soluble species $\text{Th}(\text{SO}_4)^{2+}$ may form below pH 3, and under oxidising conditions (Brookins, 1988). Any Th released into solution will be rapidly adsorbed by clay minerals and hydrolysed to the hydrous oxide $\text{Th}(\text{OH})_4$, which will be intimately associated with the clay-mineral fraction, unless it can be mobilised by other inorganic or organic ligands (Hem, 1985). This enrichment is reflected in elevated U/Th ratios in the range 0.4-0.7 in island arc magmas as compared to 0.3 in continental arcs and 0.1-0.2 in pelagic sediments (Bailey and Ragnarsdottir, 1994). Decarbonation of amphibolite facies minerals in the subducting slab are, however, thought to be the most likely candidates for transporting the excess uranium into the subduction zone mantle wedge. Average primitive mantle contains 18 ppb uranium and 64 ppb thorium. Fluid addition of uranium can, therefore, increase U/Th ratios into the range observed in island arcs. Hence, uranium is enriched by the action of H_2O -rich fluids, derived from the dehydration of minerals in the subduction slab (Bailey and Ragnarsdottir, 1994). Staudigel (2003) reviews hydrothermal alteration processes in Recent basalt-gabbro ocean crust. During sea water hydrothermal alteration of basaltic crust, soluble Ca, Na, K, Rb, Cs, B, Sr and U, along with the volatiles H_2O and CO_2 , are transferred from marine water to the crust. Overall, U is enriched in ocean crust, but may be either enriched or depleted in upper crust where seawater hydrothermal fluids are oxidizing. The primary U abundance in fresh MORB is 0.0771 ppm, with a total uptake of 0.037 ppm (Table 1).

A fundamentally different mechanism for lowering the Th/U ratio of the mantle has been suggested by Hoffmann and White (1982), invoking preferential recycling of uranium through dissolution of oxidized (hexavalent) uranium at the continental surface, riverine transport into the oceans, and fixation by ridge-crest hydrothermal circulation and reduction to the tetravalent state. Further, a quantitative “plumbotectonic” model proposed by Zartman and Haines (1988). Staudigel et al. (1995) linked this preferential recycling of uranium into the mantle leading to a change toward oxidizing conditions at the Earth’s surface at a latter stage in the Earth’s history. Holland (1994) presented geological evidence for a rapid atmospheric change toward oxidizing conditions during Early Proterozoic time and this has been confirmed by Farquhar et al. (2000) with new geochemical evidence showing sulfides and sulfates older than 2.4 Ga contain non-mass-dependent sulfur isotope fractionations, which can be explained by high intensity UV radiation in an oxygen-absent atmosphere. Further, the quantitative models developed by Kramers and Tolstikhin (1997) and Elliott et al. (1999) resolved the second lead paradox by starting to recycle uranium into the mantle at 2.5 Ga. Thus, uranium cycle is an excellent example to demonstrate how mantle geochemistry, surface and atmospheric chemistry, and the evolution of life are intimately interconnected. Boninites are generated during initiation of intraoceanic subduction by fluid-induced, shallow-level partial melting of a depleted mantle wedge fluxed by hydrothermal fluids

released through dehydration of downgoing oceanic slab. Therefore, Th/U ratios for Archean boninites are of great importance in understanding geochemical cycling of these elements in paleo oceans. Based on terrestrial lead-isotope systematics, Allegre et al. (1986) concluded that the average Th/U ratio of the Earth's mantle is 4.2, significantly above the CI-chondritic ratio of 3.82 or the chondritic ratio of 3.9 given by Rocholl and Jochum (1993). The data compiled in this study (Table 1) show huge variation of Th/U ratios from Archean to Phanerozoic boninites of greenstone belts to ophiolite sequences. This may be attributed to the changing boninitic magmatism under the influence of slab derived fluids and sediments into the mantle melting in subduction and suprasubduction zones. Trace-element ratios of similar incompatible pairs, such as Th/U, Nb/U, Nb/La, Ba/Th, Sr/Nd, or Pb/Nd are more useful in identifying such source differences, because they are fractionated relatively little during partial melting.

5.2. Th-U-Nb-REE systematics of Archean oceanic volcanic suites

Elliott et al. (1999) suggested that the upper mantle evolves towards markedly lower Th/U ratios after, 2.2 Ga. These authors along with McCulloch and Bennett, (1994) attribute the decreasing Th/U ratios to a change in the oxidation state, hence higher mobility of uranium in the more oxygen-rich environment at the surface of the post-Archean Earth and preferentially recycled into the mantle as a component of altered oceanic crust. On the other hand McLennan and Taylor (1980) suggested that as a result of the reduced mobility of uranium during continental weathering in the Archean, shales of this period have lower mean Th/U ratios than their younger counterparts and this feature was therefore acquired by strongly peraluminous Archean granitic rocks, which were sourced from such protoliths. The higher Th/U ratios of the calc-alkaline and alkaline Archean granites may partly reflect lack of a sedimentary input, in comparison with a contribution from relatively thorium enriched mantle-derived magmas and/or crustal fluids during melting. In these suites, collinear systematics of the most incompatible elements Th-U-Nb-LREE is present as expected from magmatic processes. The tholeiitic basalt-komatiite association present in many Archean greenstone belts are considered to be oceanic plateau suites derived from mantle plumes (Arndt, 2008; Said and Kerrich, 2009, and references therein). For the 2.7 Ga Lunnon basalts of the Kambalda-Norseman greenstone belt, Yilgarn Craton, Sylvester et al. (1997) determined average Th and U as 0.018 ppm and 0.048 respectively, giving Th/U=3.75. Campbell (2002) demonstrated a secular trend of Th/U in plume derived komatiites and basalts from the 3.4 Ga Barberton greenstone belt, 2.7 Ga Abitibi greenstone belt and Cretaceous Gorgona ocean plateau (Th/U= ~4; 3.4 – 3.0 and ~2.5 respectively). This secular trend was attributed to progressive extraction of basaltic ocean crust and continental crust from mantle asthenosphere fractionating Th-U. Similarly, Condie, (2003) reported a secular

trend of Th/U in well preserved mafic-ultramafic sequences from 3.5-3.2 Ga to ~ 2.8-2.7 Ga sequences (Th/U=4.3-3.9 and 4.6-3.6 respectively).

There are several bimodal volcanic suites of the Superior Province with convergent margin IAT elemental signatures where primary magmatic contents of Th and U can be established from collinear behaviour of Th-U-Nb-La. Hollings and Kerrich, (2006) reported average Th/U of 4.7 for low-K series basalts from 2.8 Ga greenstone belts of the Uchi Subprovince, and Polat and Kerrich, (2000) found Th/U averages of 4.0-3.6 in greenstones of the 2.7 Ga Wawa Subprovince. These Neoproterozoic IAT are the best benchmark for comparison with Archean boninites (Table 1).

5.3. Th-U fractionation in Archean boninites

Fractionation of U-Th in Archean boninites may stem from a number of possible causes: (1) primary magmatic processes, (2) secondary submarine hydrothermal alteration, and (3) Recent weathering, or (4) some combination of these processes. The consistently low Th/U ratios of Archean boninites relative to both Archean and Phanerozoic IAT are in consonance with Phanerozoic boninite counterparts (Table 1; Fig. 2). The boninitic suites record a spectrum of U-Th fractionations from low values of Phanerozoic boninites through values typical of IAT, to a few higher ratios in Archean (Table 1; Fig. 2). The most straightforward explanation is that low values represent primary magmatic signatures, as for the Gadwal, Shimoga, Singhbhum, Olondo, and Phanerozoic suites, whereas dispersal to higher Th/U ratios arose from superimposed, variable, secondary U-mobility during contemporaneous submarine hydrothermal alteration. U-mobility during submarine weathering and hydrothermal alteration of Cenozoic ocean crust by low-temperature oxygenated seawater (Staudigal, 2003), is attributed to secondary dispersal of Th-U in Archean counterparts under conditions of low-temperature oxygenated fluids (Figs. 2, 3). This observation is endorsed by variability of Ce/Ce* in the boninitic suites (Fig. 3). The dispersal of Th/U due to Proterozoic alteration events is unlikely for a number of reasons: (1) relict igneous textures and metamorphic mineral assemblages are well preserved; (2) robust radiogenic isotope systems of the boninitic-hosting suites retain Archean ages; (3) trace element patterns, other than Th/U, are coherent and consistent with primary magmatic signatures; and (4) radiogenic isotope systems sensitive to resetting, such as Rb-Sr and Pb-Pb, are undisturbed (Kerrich et al., 1998; Boily and Dion, 2002; Smithies et al., 2004a, b; Smithies et al., 2005; Puchtel, 2004; Shchipansky et al., 2004; Manikyamba et al., 2005; Khanna et al., 2009). Resetting during Proterozoic and/or Phanerozoic tectono-thermal events in the Superior Province is only recorded where lithologies are transected by faults or shear zones (Kerrich and Cassidy, 1994). These boninitic suites were collected from glaciated or unweathered outcrop. Accordingly, disturbance of Archean Th/U ratios by Recent

cryptic weathering is improbable as any weathering under oxidizing conditions would drive Th/U ratios to elevated values by selective dissolution of U.

5.4. *Ce-anomalies*

Least altered Phanerozoic and Recent basalts and fresh basaltic glasses from a range of geodynamic settings are devoid of Ce and Eu anomalies as fractionating phases do not separate these elements from neighbouring REE (Sun and McDonough, 1989). Similarly, least-altered komatiites and basalts from greenschist facies Neoproterozoic belts have zero anomalies at Ce and Eu (Kerrick et al., 1999; Kerrich and Xie, 2002; Arndt, 2008; Manikyamba et al., 2008). Experimental studies have documented that Ce^{4+} is unlikely to exist in magmatic systems given the presence of excess Fe^{2+} (Schreiber et al., 1980). Small primary magmatic negative Ce/Ce* values (0.92) observed in some Recent convergent margin basalts such as at Gough Island, South Atlantic are attributed to inheritance of negative Ce anomalies of subducted sediment on the slab in contrast to contamination by near surface sediments (Plank and Langmuir, 1998; Class and le Roex, 2008). However, none of the Archean boninite suites, contemporaneous IAT, or Phanerozoic boninites, have geochemical signatures of sediment melting on the slab given their intraoceanic setting (Hawkesworth et al., 1997; Plank, 2005; Pearce and Robinson, 2010, and references therein).

During submarine hydrothermal alteration of oceanic crust, the relative mobility of REE decreases from LREE>MREE>HREE. The variable oxidation states of Ce and Eu renders them more mobile than neighbouring REE under specific conditions. Cerium shows both enrichment and depletion during weathering or hydrothermal alteration. Under oxidizing conditions it forms soluble Ce^{4+} relative to Ce^{3+} . Under reducing conditions Eu^{2+} is mobile relative to Eu^{3+} leading to positive or negative Eu-anomalies in hydrothermally altered rocks (Humphries, 1984; Valsami and Cann, 1992; Staudigal, 2003). Accordingly, in the studied rocks, Ce anomalies must have resulted from hydrothermal alteration by oxygenated fluids, as observed in Phanerozoic to Recent submarine hydrothermally altered counterparts (Fig. 3; Humphries, 1984).

5.5. *The ~2.4 Ga great oxygenation event (GOE): arguments and counterarguments*

Two contrasting models have been proposed for the secular evolution of atmospheric oxygen. The first model termed by Ohmoto (1997, 2004) the “Cloud-Walker-Holland-Kasting” (C-W-H-K) model, after the four main researchers, assumes an anoxic Archean atmosphere-hydrosphere where pO_2 changed from $<<1000$ to >0.1 ppm present atmospheric levels (PAL) at ~ 2.4 Ga, which is termed as the putative great oxidation event (GOE; Cloud, 1968; Walker, 1977; Holland, 2002, 2009; Kasting, 2001; Barley et al., 2005). An alternative model, with the Ohmoto (1997) moniker

“Dimroth-Ohmoto” (D-O), envisages emergence of oxygenic photosynthetic microorganisms shortly after formation of the lithosphere at ~ 4 Ga, and pO_2 within 50% of PAL thereafter (Dimroth and Kimberley, 1976; Clemmy and Badham, 1982; Ohmoto, 1997, 1999; Lasaga and Ohmoto, 2002).

The first model was based on five principal observations: (1) detrital uraninite in Archean sedimentary sequences; (2) Fe-depleted Archean paleosols; (3) the absence of redbeds in terrestrial sedimentary rocks of pre-2.4 Ga; (4) the prevalence of banded iron formations (BIF) in the Archean rock record; and (5) the absence of U and Mo enrichments in black shales older than 2.4 Ga (Holland 2009, and references therein; Anbar et al., 2007). None of these observations are tenable to critical evaluation of the rock record. Uraninite is documented in modern terrestrial sediments and Fe-depleted paleosols occurring in Archean through Proterozoic to Phanerozoic eras (Clemmy and Badham, 1982; Ohmoto, 1997, 2004). Archean redbeds were described by Shegelski (1980) and their sparsity may reflect a combination of preservation potential and reduced continental freeboard stemming from intense plume activity in ocean basins (Isley and Abbott, 1999). Mantle plumes and BIF both show common time series; accordingly, BIF are related to mantle plume breakouts in ocean basins throughout the geologic record rather than being restricted to the Archean era (Isley and Abbott, 1999). As well, prominent BIF aged 1.9 Ga present in the Black Hills, S. Dakota and ~ 700 Ma Rapitan BIF are associated with breakup of Rodinia. Algoma-type BIF contemporaneous with volcanic hosted base metal massive sulphide (VMS) deposits are preserved in the Neoproterozoic and Phanerozoic record (Ohmoto, 2004; Frei et al., 2008). Kato et al. (2006) summarise results for Ce and Eu in Archean banded iron formations (BIF): true negative Ce anomalies ($Ce/Ce^* 0.5-0.9$) are present in Paleo- to Mesoarchean Algoman-type BIF and more pronounced anomalies of $Ce/Ce^* 0.1-0.5$ noticed in Neoarchean BIF, signifying that the water columns from which the BIF precipitated were not anoxic. Ce oxidation reactions operated in the Archean oceans as recorded in the Recent ocean water column and hydrogenous precipitates (Bender et al., 1971; Elderfield et al., 1981; Ruhlmann and Owen, 1986; Anschutz et al., 2005; Gurvich, 2006)

Uranium enrichment in black shales has been documented from the ~ 3.8 Ga Isua greenstone belt, W. Greenland as well as the 2.7 Ga Sandur terrane, Dharwar Craton. Systematic U-enrichment over Th in the Sandur black shales associated with prominent negative Ce anomalies are interpreted in terms of U and Ce sequestration from an oxygenated marine water column (Rosing and Frei, 2004; Manikyamba and Kerrich, 2006; Kerrich et al., 2013). Notwithstanding these counterarguments, Anbar et al. (2007) relegate evidence for early oxygenation of Earth to “a whiff of oxygen” or oxygen “oases” in an otherwise reduced terrestrial surface environment.

More recently, mass-independent S-isotope fractionations (MIF-S) in Archean sedimentary rocks have been interpreted as a result of ultraviolet photolysis of volcanic sulphur dioxide in an anoxic atmosphere (Farquhar et al., 2007; 2010 and references therein). Experimental results of Watanabe et al. (2009) signify that anomalous fractionation of S-isotopes may occur during thermochemical sulphate reduction, conferring an alternative mechanism to an anoxic atmosphere. Ohmoto and coworkers present more detailed arguments for an oxygenated Archean atmosphere-hydrosphere prior to the putative GOE, as well as counterarguments against a reducing atmosphere (Ohmoto, 2004; Ohmoto et al., 2006).

5.6. Recent evidence on the GOE question

Systematic large positive Ce-anomalies were reported for hydrothermally altered 2.96 Ga bimodal volcanic rocks distal to the Golden Grove VMS deposit, Murchison Domain, Yilgarn Craton. Rhyolites are anomalously enriched in Mn. These anomalies were attributed to sequestration of Ce⁴⁺ from oxygenated marine water in a low-temperature hydrothermal system peripheral to the VMS deposit (Kerrick and Said, 2011). A survey of a large database of well-preserved Archean volcanic-intrusive sequences, erupted in the submarine environment, record mobility of U relative to Th, with overall U-enrichment, accompanied by positive to negative Ce-anomalies (Kerrick et al., 2013). During weathering and low-temperature hydrothermal alteration of Cenozoic oceanic crust, due to solubility of U and Ce⁴⁺ in oxidized fluids (Humphries, 1984; Staudigal, 2003) an overall uptake of U from marine water with positive to negative anomalies of Ce has been observed.

Additional evidence for oxygenated Archean near-surface fluids comes from fresh Laramide granitoids in Montana. These granites have isotopic data consistent with an Archean supracrustal basement source that record negative Ce anomalies; the magnitude of Ce anomalies correlate with U/Pb and U/Th ratios. Meen (1990) interpreted these results as an Archean basement protolith source to the granitoids that underwent oxidative submarine weathering involving leaching of Ce but enrichment of U. Other recent papers present further robust evidence for an oxygenated hydrosphere prior to the GOE. A deep paleoweathering profile in the 2690 Ma Saganaga tonalite from Minnesota records weakly oxidizing conditions (Driese et al., 2011). Basalts from the Pilbara Craton, Western Australia, were hematized between 2.9 and 2.7 Ga by oxygenated groundwaters between ~500-300 Ma before the supposed GOE (Kato et al., 2009). Occurrence of primary hematite in marine chemical sedimentary rocks of 3.46 Ga Pilbara Craton has been interpreted in terms of oxygenated Mesoarchean seawater (Hoashi et al., 2009).

5.7. Evidence of oxygenated oceans preserved in Archean boninites

Convergent margin volcanic sequences record oxidizing-reducing conditions of the ocean basins. Conservative HFSE and MREE-HREE (Pearce and Peate, 1995) are sensitive monitors of the composition of sub-arc mantle reservoir to arc magmas. Abundance of non-conservative elements serves as important indicators of oxidation state of slab-derived fluids and melts (Pearce and Peate, 1995; Hawkesworth et al., 1997; Pearce, 2008). Elemental systematics of Archean boninite series flows evaluated in this study record evidence of oxygenated Archean oceans at two coeval levels: (1) addition of oxygenated fluids, U-rich but Th-poor, to the melt column of boninites generated the systematically low primary magmatic Th/U ratio of boninites (Th/U 1.9-3.0) relative to coeval IAT (Th/U ~ 4); and (2) post-eruption submarine hydrothermal alteration shifted some flows to greater Th/U by secondary loss of U, accompanied by Ce-anomalies. The most extreme systematic fractionation of U from Th is recorded in 1.9 Ga boninites of the Trans-Hudson orogen, Manitoba (Table 1; Wyman, 1999). In convergent margin tectonic setting, the mantle wedge, the subducted slab and the slab-dehydrated fluids /melts are principal contributors to island arc magmas. The variation in U and Th abundances and Th/U ratios reflect differential solubility of U and Th during slab dehydration and fluid/melt transfer process. U enrichment relative Th in island arc magmas has been ascribed to higher solubility of U than Th in slab dehydrated fluids (Bailey and Ragnarsdottir, 1994).

6. Conclusions

- The relative differences in U and Th in boninites and arc tholeiites may be related to differential solubility of these elements along with the influence of oxidizing and reducing conditions of the ocean water.
- Primary U contents, and Th/U ratios, of Archean ultramafic to mafic volcanic sequences have been established from exceptionally well preserved volcanic suites, devoid of crustal contamination and erupted in an intraoceanic setting, with minimal contemporaneous submarine hydrothermal alteration.
- Boninite series flows of the Gadwal and Olondo greenstone belts preserve coherent downturns from U to Th and are consistent with a primary magmatic origin as secondary hydrothermal alteration generates dispersed major and trace element patterns.

The studied Archean boninites record evidence for paleo-ocean oxygenation through addition of U-rich but Th-poor oxygenated fluids to the melt column of boninites at subduction initiation stage attributing to systematically low primary magmatic Th/U ratio of boninites (Th/U 1.9-3.0) relative to

coeval IAT ($\text{Th/U} \sim 4$) and post-eruption submarine hydrothermal alteration shifted some flows to greater Th/U by secondary loss of U, accompanied by Ce-anomalies. Acknowledgements

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Figure Captions

Figure 1. Map showing the locations of the greenstone belts from where boninites have been considered for present study (Base map courtesy: U.S. Geological Survey)

Figure 2. Multielement normalized diagrams a) Precambrian Boninite series flows from Guntipalli and Garlapadu areas of the 2.7 Ga Gadwal greenstone belt, eastern Dharwar Craton, India (Manikyamba et al., 2005, and Khanna et al., 2009), Kudrekonda, Shimoga greenstone belt (Sohini et al., 2015), OMG boninites of Singhbhum Craton (Manikyamba et al., 2015) and 3.0 Ga Olondo greenstone belt, Aldan Shield, E. Siberia (Puchtel, 2004), 3.1 Ga Whundo volcanic sequence, Pilbara Craton (data source Smithies et al., 2004a), 2.96 Ga Mallina basin, Pilbara Craton (Smithies et al., 2004b), 2.8 Ga Opatika Subprovince, Superior Province (Boily and Dion, 2002), and 2.7 Ga Abitibi greenstone belt (Kerrick et al., 1998). b) Phanerozoic and ophiolitic boninites (references given in Table 1). Normalizing factors from Sun and McDonough (1989).

Figure 3. Histograms of Th/U ratios and Ce/Ce* for boninite series flows: A, B 2.7 Ga Gadwal greenstone belt, eastern Dharwar Craton, India (data sources Manikyamba et al., 2005, and Khanna et al., 2009); C, D, 3.0 Ga Olondo greenstone belt, Aldan Shield, E. Siberia (Puchtel, 2004); E, F, 3.1 Ga Whundo volcanic sequence, Pilbara Craton (Smithies et al., 2005), and 2.96 Ga Mallina basin, Pilbara Craton, western Australia (Smithies et al., 2004b); and from the Superior Province G, H 2.8 Ga Opatika Subprovince (Boily and Dion, 2002) and 2.7 Ga Abitibi greenstone belt (Kerrick et al., 1998).

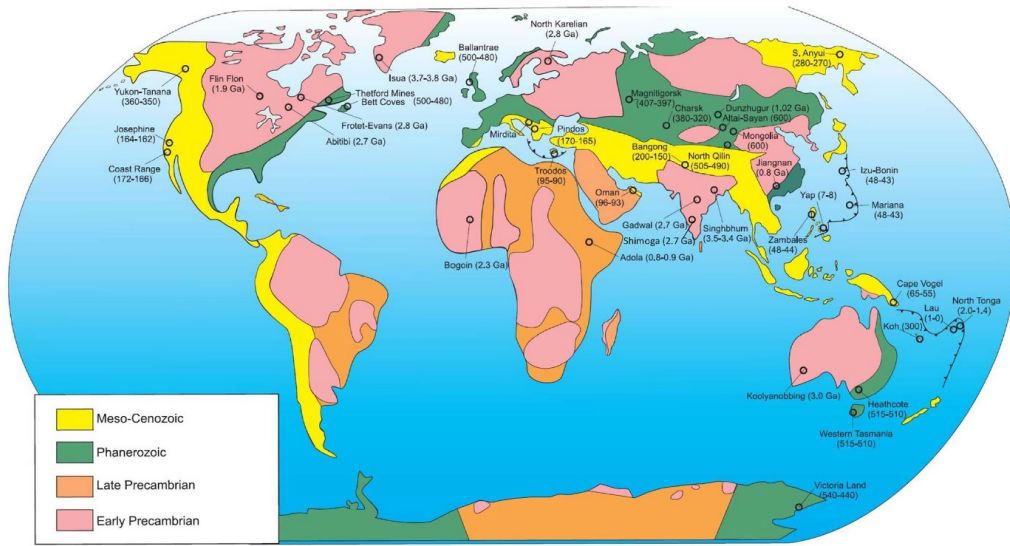


Figure 1.

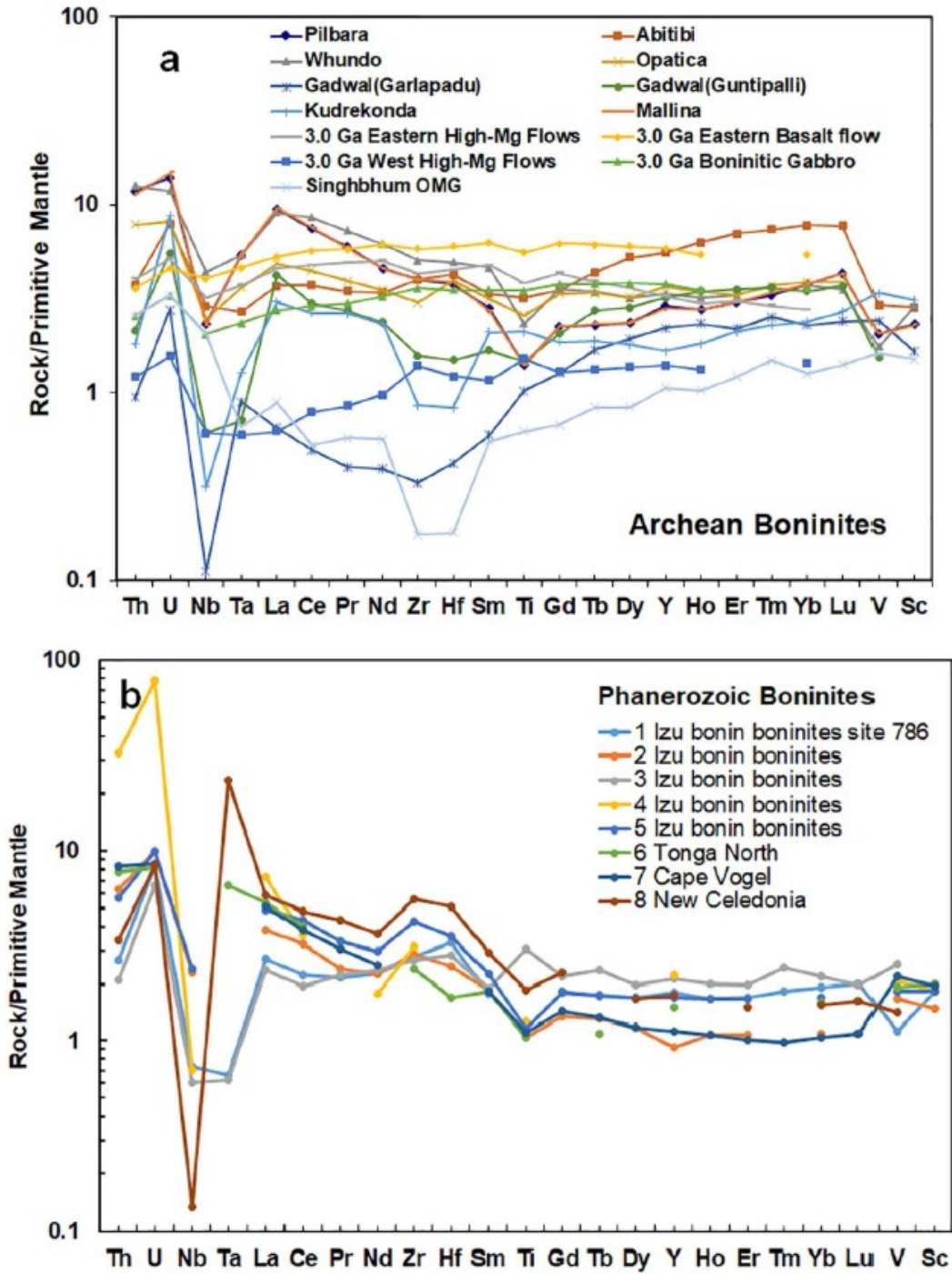


Figure 2

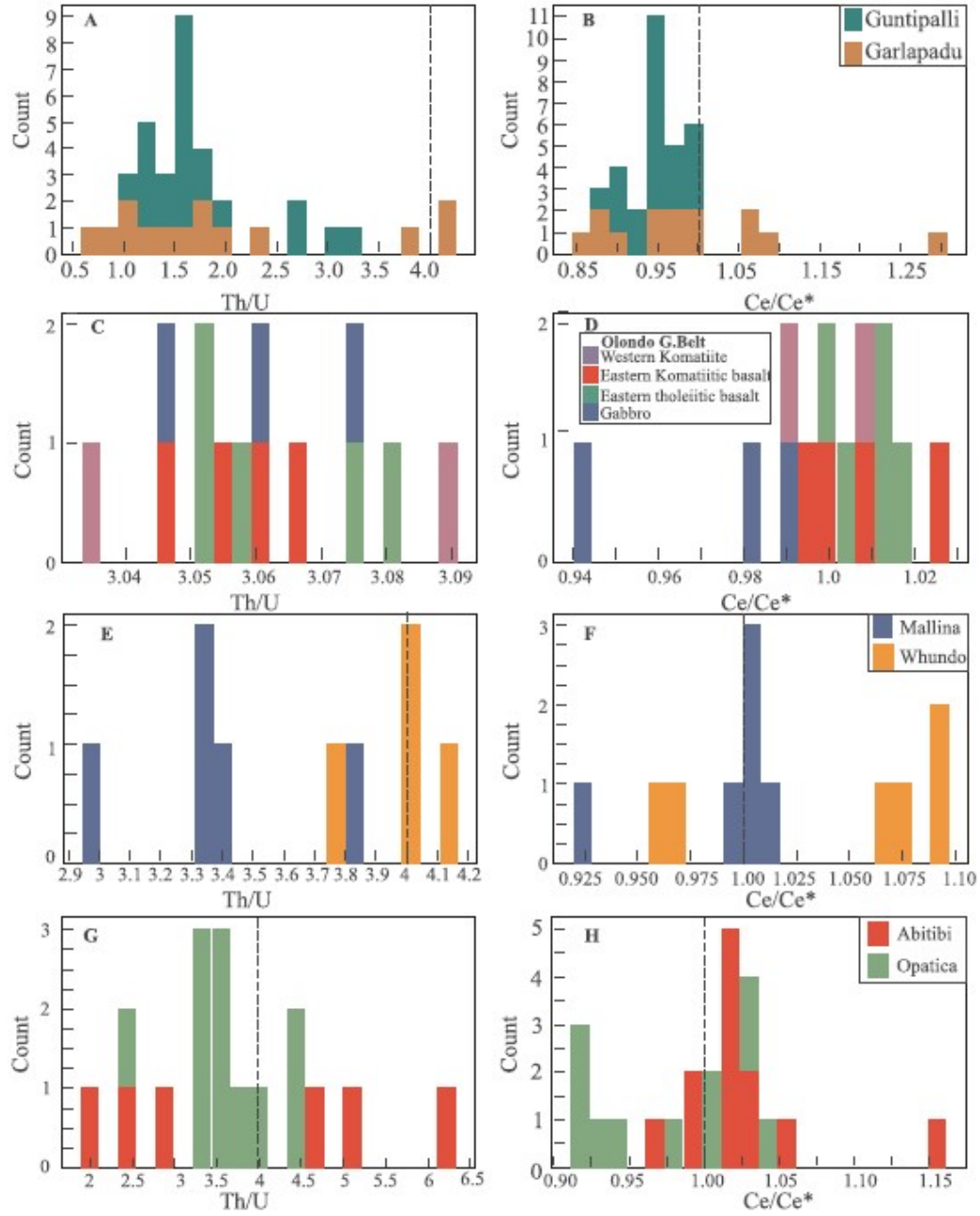


Figure 3

Table 1
Th/U ratios of boninites from various Precambrian and Phanerozoic occurrences

Craton/Greenstone Belt	Location	Th/U Ratio	Reference
Singhbhum/ OMG boninites	Jaganathpur 3.4–3.5 Ga Archean	1.0–4.8	Manikyamba et al. (2015)
Bastar	South Bastar Bengpal Group Archean	1.6–7.0 (Th only, U not available)	Srivastava (2006)
WDC / Shimoga	Kudrekonda; Archean	0.2–4.5	Ganguly et al. (2016)
EDC/ Gadwal	08 Locations; Archean	1.1–3.2	Manikyamba et al. (2005)
Bastar/ Chhattisgarh dykes	Lohara & Raitam; Archean	1–5	Subba Rao et al. (2008)
Mallina Basin, Pilbara Craton, Northwest Australia	Malina; Archean	2.9–3.8	Smithies (2002)
Boninite series / Abitibi Greenstone Belt	2.7 Ga, Archean, Whitney; Kidd, Tisdale	1.8–8.2 3.98	Kerrich et al. (1998) and Fan and Kerrich (1997)
Issua Greenstone belt/West Greenland	3.8–3.7 Archean	0.07–1.1 ppm (Th only)	Polat et al. (2002)
North Karelian intermediate and high calcium boninites	2.8 Ga Archean	2.25–6.5	Shchipansky et al. (2004)
Olondo boninites, Aldan greenstone belt	3.0 Archean	3.05	Puchtel (2004)
Opatica boninites, Frotet-Evans greenstone Belt,	2.5–2.6 Archean	2.4–4.4	Falloon and Crawford (1991) and Boiley and Dion (2002)
Abitibi Int.calboninites	2.7 Ga; Archean	20	Kerrich et al. (1998)
Flin-Flon belt boninites, Trans Hudson orogeny	1.9 Ga Paleoproterozoic	1.16–1.25	Puchtel (2004)
Birch Lake boninites	Paleoproterozoic	1.1–1.2	Cluzel et al. (2016) and Wyman (1999)
Trans Hudson Orogen			
Manitoba boninites	1.9 Ga	1.35	Wyman (1999)
Trans Hudson orogeny	Paleoproterozoic		
Southern	Central Eritrea	2.3–3.0	Teklay (2006) (2012)
Arabian-Nubian shield	Neoproterozoic		
Dunzhugur ophiolitic Boninites	1020 Ma Mesoproterozoic	1.1–3.9	Sklyarov et al. (2016)
Singhbhum/Newer Dykes	Chaibasa & Jashipur, Proterozoic	8.5–13.6	Mir et al. (2015)
New Caledonia,	Koh Ophiolite, Jurassic	NA	Cluzel et al. (2016) and Meffre et al. (1996)
New Caledonia	Nepoui, CE-boninite Jurassic	1.6–2.1	Solovova et al. (2012) and Puchtel (2004)
Cape Vogel boninites	Early Eocene	3.3–4.9	Walker and Cameron (1983) and Konig et al. (2010)
Izu-Bonin ODP site 786	Early Eocene	0.9–2.2, (high cal. boninites) 1.0–2.2, (low cal. boninites) 0.5–2.3, (int. cal. boninites)	Murton et al. (1992)
Betts Cove boninites	Newfoundland, Ordovician	0.55–2.25	Bédard et al. (1998) and Bédard (1999)
Thetford mine	Ordovician	2.1–9.3	Pagé et al. (2009)
Ophiolite boninite lavas			
<i>Miscellaneous</i>			
Primitive Mantle	Pyrolite/Primitive Mantle	3.91	McDonough and Sun (1995)
Ocean plateau komatiites –basalts	3.5–3.2 Ga Archean	4.5–3.7	Campbell (2002) and Condie (2003)
Abitibi komatiites (Al-depleted)	Archean 2.7 Ga	3.0	Kerrich and Xie (2002)
Lunnon basalts, Yilgarn Craton	Archean 2.7 Ga	3.75	Sylvester et al. (1997)
Orlondo boninites	Archean 3.0 Ga	3.0	Puchtel (2004)
Island Arc Tholeiite	Archean 2.8 Ga	4.75	Hollings and Kerrich (2006)
Uchi greenstone terranes			
Island Arc Tholeiite Wawa greenstone terrane, Superior Province	Archean 2.7 Ga	4.0–3.7	Polat and Kerrich (2000)
<i>Phanerozoic</i>			
MORB	Average	1.22	Kelemen et al. (2003)
MORB	Log normal mean	2.58	Arevalo and McDonough (2010)
MORB	0.037 ppm after Hydrothermal alteration	0.071 ppm; (U)	Staudigel (2003)
Ocean plateau, High Mg#	Gorgana, Cretaceous	2.3	Kerr (2003)
Ocean plateau, tholeiite	Gorgana	4.3	Kerr (2003)
Island arc tholeiite (IAT)	Phanerozoic average	2.58	Kelemen et al. (2003)
Boninites	Phanerozoic average	1.61	Kelemen et al. (2003)
Boninites	Early cretaceous Los Ranchos Fm.	2.5	Viruete et al. (2006)
Upper continental crust		3.8	Rudnick and Gao (2003)
TTGs	Neoproterozoic average	5.4	Condie (2005)
Adakite		3.4	Condie (2005)