

Balz S. Kamber · Anthony Ewart · Kenneth D. Collerson
Michael C. Bruce · Graeme D. McDonald

Fluid-mobile trace element constraints on the role of slab melting and implications for Archaean crustal growth models

Received: 12 July 2001 / Accepted: 9 May 2002 / Published online: 8 August 2002
© Springer-Verlag 2002

Abstract We use published and new trace element data to identify element ratios which discriminate between arc magmas from the supra-subduction zone mantle wedge and those formed by direct melting of subducted crust (i.e. adakites). The clearest distinction is obtained with those element ratios which are strongly fractionated during refertilisation of the depleted mantle wedge, ultimately reflecting slab dehydration. Hence, adakites have significantly lower Pb/Nd and B/Be but higher Nb/Ta than typical arc magmas and continental crust as a whole. Although Li and Be are also overenriched in continental crust, behaviour of Li/Yb and Be/Nd is more complex and these ratios do not provide unique signatures of slab melting. Archaean tonalite–trondhjemite–granodiorites (TTGs) strongly resemble ordinary mantle wedge-derived arc magmas in terms of fluid-mobile trace element content, implying that they did not form by slab melting but that they originated from mantle which was hydrated and enriched in elements lost from slabs during prograde dehydration. We suggest that Archaean TTGs formed by extensive fractional crystallisation from a mafic precursor. It is widely claimed that the time between the creation and subduction of oceanic lithosphere was significantly shorter in the Archaean (i.e. 20 Ma) than it is today. This difference was seen as an attractive explanation for the presumed preponderance of adakitic magmas during the first half of Earth's history. However, when we consider the effects of a higher potential mantle temperature on the thickness of oceanic crust, it follows that the mean age of oceanic lithosphere has remained virtually con-

stant. Formation of adakites has therefore always depended on local plate geometry and not on potential mantle temperature.

Introduction

The majority of magmas which form along present convergent plate boundaries derive from the supra-subduction zone asthenospheric mantle wedge. Melting of mantle wedge peridotite is triggered by aqueous fluids which originate from prograde dehydration of subducted slab. Composition of typical arc melts can therefore be quantified by slab dehydration, hydration of the overlying mantle wedge, melting of mantle wedge peridotite, and fractional crystallisation/crustal assimilation (e.g. Ayers 1998). Direct melting of the oceanic lithosphere, on the other hand, is very rare. It is possible where the subducted lithosphere is exceptionally young and therefore relatively hot (Defant and Drummond 1990). Gutscher et al. (2000) proposed a model of flat subduction which explains direct slab melting of apparently older and colder oceanic lithosphere. An alternative model for melting of old oceanic lithosphere was presented by Yogodzinski et al. (2001) who found that the edge of a torn slab can be exposed to mantle flow, resulting in slab ablation, heating, and eventually melting. Magmas thought to represent melts from subducted slabs are collectively known as adakitic melts (Defant and Drummond 1990; following Marsh 1976, and Kay 1978). They are typically andesitic to dacitic in composition and characterised by strongly fractionated rare-earth-element (REE) patterns. Their depletion in the heavy REEs (HREEs) relative to the light REEs (LREEs) is commonly interpreted to reflect residual garnet (and amphibole) in the melt source. Kay (1978) proposed that the incompatible trace element contents of adakites required a metabasaltic rather than a peridotitic source. Adakites are thus believed to form by wet melting of subducted basaltic eclogite.

B.S. Kamber (✉) · K.D. Collerson
ACQUIRE Centre, Department of Earth Sciences,
University of Queensland, Brisbane,
Queensland 4072, Australia
E-mail: kamber@earth.uq.edu.au

A. Ewart · M.C. Bruce · G.D. McDonald
Department of Earth Sciences, University of Queensland,
Brisbane, Queensland 4072, Australia

Editorial responsibility: T.L. Grove

Based on the similarity in REE patterns between Archaean tonalite–trondhjemite–granodiorites (TTGs) and modern adakites, Martin (1986) proposed that both could represent direct melting products of subducted (eclogite facies) oceanic lithosphere. Martin (1986) and many subsequent proponents of Archaean slab melting speculated that the Earth's higher heat output in the Archaean and, in particular, the higher potential mantle temperature would have led to higher oceanic crust production rate and hence subduction of, on average, younger and hotter slabs which would have facilitated direct slab melting, thereby providing the tectonic rationale for the alleged preponderance of direct slab melting in the Archaean.

Since postulation of the adakite–TTG connection, our understanding of arc magmatism has improved considerably. Yet modern experimental, observational, and geophysical evidence has rarely been used to scrutinise the claim for the adakite–TTG connection. In this paper, we review some of the salient geochemical features created by material transfer between slab and mantle wedge and verify whether, in true adakites, fingerprints of slab dehydration are indeed suppressed. We find, based on fluid-sensitive geochemical criteria, that typical Archaean TTGs are not adakites and that their strong LREE/HREE fractionation was not caused by residual garnet in oceanic eclogite. We demonstrate also that, on average, Archaean oceanic lithosphere was not significantly younger than at present because of the effects of higher Archaean potential mantle temperature on the thickness of melt column (e.g. Galer 1991).

Fingerprints of slab dehydration

Stronger HREE depletion of adakites compared to mantle wedge-derived arc magmas is but one diagnostic feature of direct slab melting (note that because the Y/Ho ratio is constant in terrestrial samples, Y-based ratios are simply another way of expressing HREE depletion). Recent experimental constraints (e.g. Brenan et al. 1995a; Keppler 1996; Tatsumi and Kogiso 1997; Brenan et al. 1998a; Stalder et al. 1998), continually improving understanding of arc magma chemistry (e.g. Ryan and Langmuir 1988; Woodhead et al. 1998; Ewart et al. 1998; Tomascak et al. 2000), and accurate determination of trace element contents of high-pressure metamorphic rocks and particularly eclogites (Henry et al. 1996; Becker et al. 2000) have revealed a number of geochemical features which can be directly linked to dehydration of subducted slabs, rather than to the hypothesised residual source mineralogy. These geochemical fingerprints are based on the observation that dehydration-driven element transport from the slab to the overlying mantle wedge is capable of fractionating element pairs which have very similar solid/melt distribution coefficients. If adakites and Archaean TTGs were direct slab melting products, they would be expected to be less enriched than typical arc magmas in elements

which are preferentially transported into the mantle wedge. On this premise, we review some geochemical features of modern island arc basalts which we identify as potential discriminators between adakites and ordinary arc melts.

Element transport from dehydrating slabs to the overlying mantle wedge is ultimately expressed in the chemical inventory of the continental crust as a whole. The degree to which elements are enriched in continental crust follows, in general, the order of incompatibility found in mid-ocean-ridge basalts (MORBs). This is visualised by the negative slope in a plot of MORB-normalised concentration of incompatible elements in average continental crust arranged in order of decreasing enrichment of average MORB (Fig. 1). There are, however, some important exceptions to this rule (Hofmann 1988; Brenan et al. 1998a): Pb, B, and Li are overproportionally concentrated in continental crust, and contents of the pentavalent elements Nb, Ta, and Ti are lower than expected. There is general agreement that overenrichment of island arc magmas and the continental crust as a whole in Pb and B is the result of preferential transfer of these elements to the mantle wedge by fluids originating from subducted slabs (e.g. Ryan and Langmuir 1993; Miller et al. 1994; Brenan et al. 1995a). The reason behind this phenomenon is that the slab mineralogy/fluid partition coefficients of Pb and B are more than one order of magnitude smaller than those of the similarly compatible (in MORB melting) Nd and Be (Brenan et al. 1995a, 1998a, 1998b). However, due to the continuous nature of dehydration in a subducted slab (Schmidt and Poli 1998), and due to the progressive change in slab mineralogy, the extent of overenrichment of the fluid in mobile element depends on a large number of factors. The most straightforward

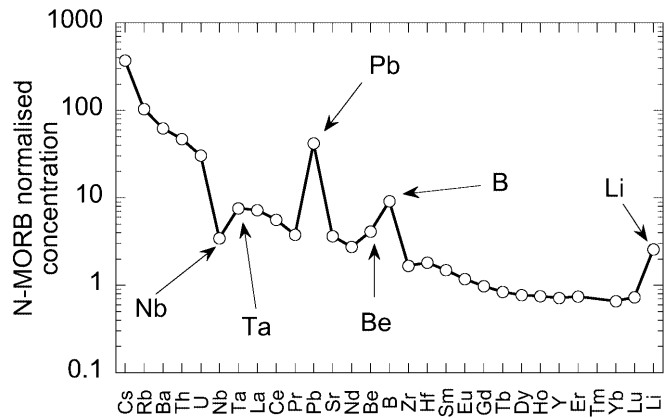


Fig. 1. N-MORB-normalised (Sun and McDonough 1989) trace element pattern of average continental crust (estimate by Rudnick and Fountain 1995, except for Nb, Ta, B, and Be which were taken from McLennan 2001). Elements are arranged in decreasing MORB-melting compatibility (after Sun and McDonough 1989). MORB Be concentration was calculated using a constant Be/Nd ratio of 0.05 (Ryan and Langmuir 1988), and B concentration was estimated using a constant B/Be ratio of 3 (Ryan and Langmuir 1993)

expression of this phenomenon is the observation that trace element chemistry of magmas changes systematically across some arcs at least (Ryan et al. 1995; Woodhead et al. 1998). These variations most probably relate to the slab depth which, in turn, determines the volume and chemistry of fluid expelled to the overlying mantle wedge. Nevertheless, for the highly mobile elements Pb and B, overenrichment can be expected in expelled fluids from a range of depths. It is thus reasonable to expect that typical adakites should have lower Pb/Nd and B/Be ratios than melts which are derived from hydrated mantle wedge. Furthermore, by the time the crustal portion of the slab has metamorphosed to garnet amphibolite or eclogite, prograde dehydration will have removed substantial fractions of the original Pb and B, such that the Pb/Nd and B/Be ratios of the metamorphosed slab can be expected to be lower than in the hydrated oceanic crustal protolith (Brenan et al. 1995a, 1998a; Kamber and Collerson 2000; Becker et al. 2000).

Current estimates of the Li content of continental crust suggest that, like Pb and B, Li is also preferentially transported from slabs to the overlying mantle wedge. Indeed, Li/Yb (or Li/Y for sample sets without accurate HREE data) are generally high in those arc magmas where a high, slab-derived fluid flux is implied by other geochemical tracers. In the few cases where Li-isotope data are available, it appears that the excess Li is derived from altered oceanic crust (Chan et al. 1999; Tomascak et al. 2000). However, compared to Pb and B, the behaviour of Li in the mantle wedge is more complicated. Firstly, because Li is quite compatible in olivine (Brenan et al. 1995b), melts from Li-enriched mantle wedge peridotite may not necessarily inherit a high Li/Yb ratio from their source. Secondly, release of Li with fluid during metamorphic dehydration may be more strongly controlled by mineralogy than release of Pb and B. For example, Li/Zr ratios of metamorphic veins (interpreted as having precipitated from synmetamorphic fluids) in high-P, low-T metamorphic rocks from the Western Alps (Henry et al. 1996) are highly variable. In many samples, the ratio in the vein is identical to that in the wall rock whereas, in other cases, the veins are very strongly enriched in Li. Thirdly, because Li is compared to the HREE Yb which is severely depleted in adakites, it is not clear that Li/Yb ratios in adakites should be lower than in typical arc melts.

A further element which seems to be mildly overenriched in continental crust is Be (Fig. 1). Compared to B, which has a very similar distribution coefficient in MORB melting (Ryan and Langmuir 1993), the enrichment is not nearly as strong. Transfer of Be from hydrated oceanic crust or from sediment into the mantle wedge and ultimately into island arc magmas is directly expressed in the overabundance of the cosmogenic nuclide ^{10}Be in some island arc volcanics (Brown et al. 1982). Preferential Be loss during metamorphic dehydration is also evident in the data of Henry et al. (1996), because the Be/Zr ratio of most synmetamorphic veins is

higher than that in the corresponding wall rocks. However, at higher metamorphic grade when clinopyroxene is part of the mineral assemblage, it can be expected from experimental data (Brenan et al. 1995a) that Be remains immobile and is retained in the slab. The Be/Nd ratio of island arc magmas may thus hold potential to constrain possible metamorphic dehydration reactions in the subducting slab.

The *collective* depletion of Nb, Ta and Ti is not a conclusive fingerprint for slab dehydration but Jochum et al. (1989) and Green (1995) have demonstrated that the geochemical twins Nb and Ta are depleted in the continents to surprisingly different degrees. Fig. 1 shows that Ta is noticeably less depleted than its geochemical twin Nb. Given the near-chondritic Nb/Ta ratio of MORB, this translates to a substantially subchondritic continental Nb/Ta ratio of ca. 10. Empirical observations and experimental constraints indicate that complexing in aqueous fluids is a likely process which fractionates elements of identical charge and near-identical effective ionic radius (Bau 1996; Kamber and Collerson 2000), implying that the low continental Nb/Ta ratio reflects preferential transport of Ta over Nb during slab dehydration. The Nb/Ta ratio is thus an equivalent tool to the Pb/Nd ratio (Miller et al. 1994; Brenan et al. 1995a) but has the advantage that it is less affected by crystal fractionation (Klein et al. 1997; Münker 1998). Again, if adakites and Archaean TTGs were direct slab melts, they are predicted to have near-chondritic (or higher than chondritic) Nb/Ta ratios, regardless of collective depletion in Nb, Ta, and Ti.

In brief, there is now very strong experimental and empirical evidence (both from island arc volcanics and metamorphic rocks) that the characteristic, relative enrichment and depletion of average continental crust in some elements is due to the transfer and retention of elements from subducting slabs into the mantle wedge. This leaves little doubt that the bulk of continental crust has been extracted from the supra-subduction zone mantle wedge. If TTGs, which represent a prominent group of Archaean magmatic rocks, formed by a different process (i.e. direct fusion of subducted oceanic crust), we can reasonably expect them to have, at least on average, relative trace element contents which are not characteristic of hydrous element transfer. Before we test this hypothesis with new trace element data for early and late Archaean TTGs, we inspect whether modern direct slab melts (i.e. adakites) confirm these geochemical predictions.

Geochemistry of modern adakites

It is widely recognised that the chemistry of rocks which classify as adakites is invariably more complex than could be expected from a direct melt derived from garnet–amphibolite or eclogite facies MORB (e.g. Stern and Kilian 1996). Several factors are believed to complicate adakite chemistry, the most important of which is that

adakites always occur as volumetrically minor parts together with island arc volcanics of more typical chemistry. The coexistence of melts from the slab itself and from the supra-subduction zone mantle wedge is expected because prograde dehydration from relatively hot slabs triggers melting of the mantle wedge peridotite. This bears the potential of creating hybrid melts in which the typical adakite geochemical fingerprint is obscured. A further factor which complicates adakite chemistry is the possibility of peridotite assimilation upon migration through the mantle wedge. This process is inferred on the basis of elevated compatible trace element content in some adakites, which would be expected to be depleted in elements like Cr and Ni. It is generally argued that peridotite assimilation should not greatly disturb the original incompatible element ratios. However, the incompatible element inventory could be seriously affected if the melts were not derived from pure MORB but had a contribution from the thin veneer of sediment which is sometimes subducted on top of slabs. Because this sediment material inherits the chemical signature of continental crust (Fig. 1), relatively small melt contribution from metasediments can effectively mimic typical island arc, volcanic incompatible element geochemistry even though the melt is derived from the slab. Finally, adakite geochemistry can further be modified by fractional crystallisation (Romick et al. 1992) and assimilation of crustal material.

There exists thus a category of rocks which have some adakitic affinity but whose chemical integrity has been seriously compromised by one or more of these processes. Although crustal contamination or sediment contribution to the source can be monitored with radiogenic isotopes (Stern and Kilian 1996), the general lack of isotope data for many postulated adakite occurrences compromises the interpretation of literature data. Despite all these complications, we show below that adakitic rocks still yield, on average, significantly higher Nb/Ta and lower Pb/Nd, B/Be, and Be/Nd than mantle wedge-derived arc magmas and continental crust as a whole.

Review of literature data

The majority of geochemical studies on adakites have focused on REE distribution because it was the strong HREE depletion which led to their discovery and definition (Kay 1978). Very few complete trace element data sets for Phanerozoic adakites are available. Therefore, we discuss adakite geochemistry in order of specific trace element ratios rather than occurrence.

Adakite Nb/Ta systematics

Drummond et al. (1996) published a comprehensive overview of world-wide Cenozoic adakites. Their composite average Cenozoic adakite is quoted to reflect a

database comprising 140 samples (their Table 1) but it seems improbable that complete data sets were available for all samples, and average Nb and Ta values are expected to be defined on a much smaller number of samples. Nevertheless, the average adakite Nb/Ta calculated from the Drummond et al. (1996) compilation is 15.7, which is only slightly lower than modern MORB (16.66; Kamber and Collerson 2000) and clearly higher than average continental crust (10).

Smith and Leeman (1987) reported Nb, Ta, and Be (but not Li, Pb, and B) concentration data for adakitic dacites and rhyolites from Mt. St. Helens. The median Nb/Ta ratio of those lavas is 17.3 ± 2.4 ($n=10$), which is much higher than that of continental crust. It is also considerably higher than median Nb/Ta ratios of arc lavas which are derived from previously depleted supra-subduction zone mantle wedge which was metasomatised by slab-derived fluids. For example, the average Nb/Ta ratio of Tongan lavas is 12.9 ± 2.7 ($n=21$; Tonga Island only, data from Ewart et al. 1998), and that of New Britain Island Arc lavas from sectors E and F is 14.0 ± 0.9 ($n=16$; data from Woodhead et al. 1998).

Stern and Kilian (1996) presented a combined trace element and radiogenic isotope data set for adakites from the south Andean Austral Volcanic Zone (Chile). After evaluation of radiogenic isotope signatures, they concluded that only adakitic andesites from Cook Island volcano are pure melts from an eclogitic assemblage with MORB composition. These samples (Ck-3-198, Ck-1-468, Ck-3-197; Table 1 of Stern and Kilian 1996) have the high average Nb/Ta ratio of 17.6 ± 1.8 predicted for direct slab melts. Adakitic rocks from the other volcanic centres which, based on radiogenic isotopes (*not* Nb/Ta considerations) were postulated to contain a sediment component, have invariably lower ratios (average of 11.3 ± 2.83). No Pb, Li, B, and Be concentration data were reported for these rocks.

High-Mg andesites from the Ryukyu Arc, Japan, which share many similarities with adakites (Shinjo 1999), also have a high median Nb/Ta ratio of 16.82 ± 2.02 . Bruce and Niu (2000a, 2000b) recently published complete geochemical data for early Permian adakitic intrusives from the Marlborough Block and Percy Isles, Eastern Australia. These rocks (samples MB 20, 73, and 74b) have a high average Nb/Ta ratio of 20.09 ± 3.04 .

The only adakites for which available data suggest relatively low Nb/Ta ratios (14.83 ± 1.36) are from the Philippines (Prouteau et al. 2000). It is unclear whether this is due to the use of mixed ICP-MS (Nb) and INAA (Ta) analytical techniques, fractionation by Ti phases (Prouteau et al. 2000), or a non-slab melt origin of these adakites (Yumul et al. 2000). High Pb/Nd ratios (Yumul et al. 2000) from Central Luzon back-arc adakites appear to favour the latter explanation.

In summary, the Nb/Ta ratio of adakites and high-Mg andesites of adakitic affinity is similar to that of MORB (Fig. 2a) and clearly higher than that of average continental crust or typical island arc volcanics.

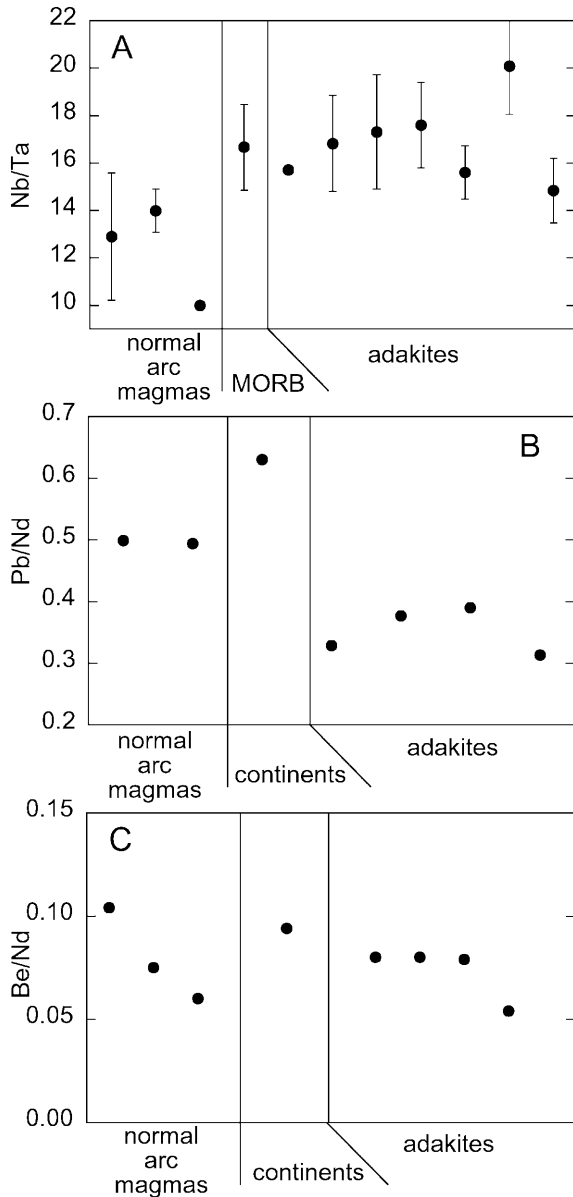


Fig. 2a-c. Fluid-sensitive element ratios in normal arc magmas compared to adakites and lavas of adakitic affinity. Literature sources are given in text. **a** Nb/Ta ratio: normal arc magmas (from left to right) are Tonga, New Britain Arc, and average continental crust; average N-MORB from Sun and McDonough (1989); adakites are (from left to right) average compiled by Drummond et al. (1996), Ryukyu Arc, Mt. St. Helens, Cook Island, Aleutian Arc, East Queensland, and Philippines. **b** Pb/Nd ratio: normal arc magmas are from Tonga and New Britain Arc; adakites (from left to right) are from Ryukyu Arc, Aleutian Arc, East Queensland, and Baja California. **c** Be/Nd ratio: normal arc magmas are from New Britain Arc, Tonga, and Panama; adakites are from Mt. St. Helens, East Queensland, Panama, and Aleutian Arc

Adakite B/Be systematics

To our knowledge, adakites from Panama are the only occurrence for which combined B and Be data exist (Tomascak et al. 2000). The average B/Be of four adakites is 6.76 ± 1.01 , lower than the average of six

older, calc-alkaline lavas which yield a B/Be ratio of 11.3 ± 6.1 . In other arcs with strong dehydration signature, such as the Vanuatu Arc, even higher B/Be of 18.2 ± 12.6 has been recorded (Peate et al. 1997). Higher still is the average B/Be ratio (36.5 ± 30.2) for Central American Volcanic arc lavas published by Chan et al. (1999). Hence, from the limited evidence available to date, it appears that the geochemical prediction is confirmed in that adakites are not nearly as enriched in B as typical island arc magmas.

Adakite Pb/Nd systematics

Surprisingly few data sets exist in the literature which contain Nd and Pb concentration measurements for adakites. The median Pb/Nd ratio of 0.329 ± 0.105 of high-Mg andesites from the Ryukyu Arc (Japan) is lower than estimates of typical continental crust which range from 0.5 (McLennan 2001) to 0.63 (Rudnick and Fountain 1995). The early Permian adakites from eastern Australia also have variable but low Pb/Nd (0.390 ± 0.405 ; data from Bruce and Niu 2000a, 2000b). Late Miocene adakites and Nb-enriched basalts from Baja California ($n=5$) have similarly low Pb/Nd ratios of 0.313 ± 0.323 (Aguillón-Robles et al. 2001). When compared to lavas from Tonga (0.499 ± 0.280 ; Tonga Island only, data from Ewart et al. 1998) and from the New Britain Island Arc (0.494 ± 0.161 ; data from sectors E and F from Woodhead et al. 1998), it appears that adakites have, on average, consistently lower Pb/Nd ratio (Fig. 2b), again confirming geochemical predictions.

Adakite Li/Yb systematics

Both in lavas from Tonga (data from Ewart et al. 1998) and from the New Britain Arc (Woodhead et al. 1998), the Li/Yb ratio is positively correlated with the Pb/Nd, Nb/Ta, and Be/Nd ratios. The correlation ($r=0.782$) between Li/Yb and Pb/Nd in the Tongan data set, which implies that those samples with the strongest overenrichment in Li also have strongest overenrichment in Pb (and Ta and Be), which supports the interpretation of element abundance in the continental crust (Fig. 1). However, Li/Yb ratios of adakites are higher than those in typical continental crust. Two samples from Panama have a Li/Yb ratio of 36.4 ± 15.67 (Defant et al. 1991a, 1991b; Tomascak et al. 2000), and three adakitic samples of eastern Australia yield a ratio of 16.48 ± 19.7 . This observation has two plausible explanations. Firstly, the Li/Yb ratio is strongly biased by the adakites' Yb depletion (due to garnet in their source). Secondly, because the peridotite source of normal arc basalts contains olivine, Li can be retained in the slab whereas Li is lost from the garnet-clinopyroxene source of adakites. Thus, despite the clear overenrichment of continental crust in Li, the Li/Yb ratio is not a

suitable discriminator between adakites and mantle wedge-derived island arc volcanics.

Be/Nd systematics

From the relative abundance in continental crust, we can expect that adakites will have a slightly lower Be/Nd ratio than continental crust (Fig. 1). A comprehensive data set ($n=26$) exists for Mt. St. Helens adakitic lavas (Smith and Leeman 1987) in which the average Be/Nd ratio is 0.080 ± 0.024 (note that Nd abundance was estimated from Sm concentration with the average Cenozoic adakite Sm/Nd ratio of 0.1564; Drummond et al. 1996). This is identical to the average Be/Nd ratio (0.08 ± 0.03) of three early Permian adakites from eastern Australia (Bruce and Niu 2000a, 2000b), and that of adakites (0.079 ± 0.058) from Panama (Defant et al. 1991a, 1991b; Tomascak et al. 2000). These values are indeed lower than average continental crust which, according to McLennan's (2001) compilation, has a Be/Nd ratio of 0.094. Equally, the New Britain Arc lavas from sectors E–F have a higher Be/Nd ratio (0.104 ± 0.014 , $n=16$; data from Woodhead et al. 1998). However, lavas from the Island of Tonga (Ewart et al. 1998) have lower Be/Nd (0.075 ± 0.025) than continental crust, as have Panamense lavas (0.060 ± 0.015) with slab-derived Li (Defant et al. 1991a, 1991b; Tomascak et al. 2000). This comparison therefore shows (Fig. 2c) that similar amounts of Be and Nd are lost during slab dehydration and, although Be/Nd ratios of adakites appear to be low, they do not constitute conclusive evidence for or against direct slab melting.

In summary, a review of the geochemical literature confirms that Nb/Ta, Pb/Nd, and B/Be, representing element pairs with similar MORB melting partition coefficients but different fluid/solid partition coefficients, clearly discriminate between possible direct slab melts and typical arc melts from hydrated mantle wedge peridotite (Fig. 2a, b). The Be/Nd ratio has similar behaviour but, due to the relative immobility of Be (despite incontrovertible cosmogenic Be evidence), its resolution is insufficient (Fig. 2c). Li/Yb systematics of arc magmas are compromised by the role of garnet (Yb retention) and olivine (Li retention) which can lead to chromatographic effects (Tomascak et al. 2000).

New geochemical data for Aleutian lavas

In order to substantiate the findings from the literature survey and to test whether an adakitic component can be detected in hybrid melts, we report new trace element data for lavas from the Aleutian Arc (Table 1). The samples are from Adak Island (nine samples), Bogoslof Island (three samples) and Great Sitkin Island (one sample). None of them classifies as adakite, as they are not enough evolved (Table 1), their LREE/HREE fractionation is not sufficiently strong (Fig. 3), and their

average Sr/Y ratio (42) is not as high as that of proper adakites (61; Drummond et al. 1996). Nevertheless, the average Sr/Y ratio is still much higher than in average continental crust (13; McLennan 2001). There is a discernible positive correlation between Sr/Y and La/Yb ratios in the Aleutian data set which follows the trend of global arc magmas (Fig. 4). Although the Aleutian samples measured in this study are not as depleted in HREE and not as enriched in La and Sr as most adakites, they nevertheless are clearly resolved from more typical arc magmas like those from Tonga (Fig. 4). This could suggest that the Tonga-Lau basin represents an end-member oceanic arc system which is poor in alkalis and alkaline earths, and very depleted in high-field-strength elements after pronounced and ongoing mantle wedge depletion. Interestingly, some of the samples from the extreme northern end of the arc system, where the slab is being torn (and is shallowing), seem to be developing 'adakitic' affinity.

In comparing the Aleutian data (and many Cenozoic island arc volcanics of adakitic affinity), we also have to consider that their HREE depletion is not as pronounced as that of Archaean TTGs (Fig. 3). The average Archaean TTG SiO₂ content is 70.2 wt%, which is much higher than that of Cenozoic adakites (63.9; Drummond et al. 1996). Our samples from Adak and nearby islands have an even lower SiO₂ content (51.45 wt%, Table 1). It is obvious from major-element chemistry alone that rocks with adakitic affinity from the Aleutian Arc, including the type-locality 'adakites', are not pure slab melts. Instead, it has been argued that they represent hybrid magmas derived from melting of eclogitic subducted MORB, a subducted sediment component and a supra-subduction zone component, with less evolved REE patterns (e.g. von Drach et al. 1986). Myers and Marsh (1987) presented Pb-isotope data (Fig. 5) for lavas from Adak and Atka islands which clearly demonstrate a mixing relationship. Although the mixing end members could not be uniquely constrained, Myers and Marsh (1987) speculated that the original melt of Adak Island lavas could have derived from direct slab melting. Here we use their isotope data to complement interpretation of our new, comprehensive trace element data (Table 1). The aim is to explore, within the framework of our preceding discussion of adakite trace element systematics, whether a direct slab component can be isolated.

The Aleutian lavas show a wide spread in Pb/Nd ratio (Fig. 6a), ranging from 0.16 to 0.55 (sample AD-72 has an even higher ratio of 0.78 which we regard as anomalous). The samples at the higher end of the spectrum are comparable to typical island arc basalts, with Pb/Nd between 0.5 and 0.65 (Fig. 2b) whereas many of the Adak and Bogoslof samples have much lower ratios, similar to adakites (Fig. 2b). There is a scattered anti-correlation between the Pb/Nd and La/Yb ratio, indicating that the samples most strongly enriched in Pb also have the lowest La/Yb ratios, whereas those with steeper REE patterns clearly have Pb/Nd ratios

Table 1. Chemical compositions of Aleutian Arc lavas (all trace elements by ICP-MS)

Tectonic unit Aleutian Arc													
Locality	Adak									Bogoslof			Great Sitkin
Sample ID	AD-14	AD-17	AD-36	AD-39	AD-44	AD-49	AD-51	AD-61	AD-72	BOG-3	BOG-5	BOG-6	GS-4
Reference ^a	1	1	1	1	1	1	1	1	1	2	2	3	1
Major element (wt%)													
SiO ₂	49.93	48.39	50.87	51.39	55.27	56.34	51.98	52.14	57.63	48.09	47.23	47.95	52.39
TiO ₂	0.90	0.92	0.75	0.84	0.70	0.72	0.64	0.67	0.54	1.29	1.33	1.30	0.89
Al ₂ O ₃	19.46	17.90	16.12	18.78	18.12	17.17	18.63	19.44	16.13	18.00	17.50	17.97	18.88
Fe ₂ O ₃	3.24	4.48	4.76	4.96	3.90	4.83	4.28	4.79	3.28	5.45	5.11	5.51	3.12
FeO	6.30	6.30	4.54	4.83	4.11	2.76	3.87	4.25	3.64	4.73	5.59	4.73	6.35
MnO	0.18	0.17	0.16	0.18	0.16	0.14	0.12	0.19	0.15	0.16	0.17	0.16	0.19
MgO	5.07	6.13	6.83	4.38	3.73	4.80	3.86	3.73	5.52	5.30	5.74	5.29	4.39
CaO	10.43	11.83	10.84	10.16	8.53	8.97	8.40	9.79	8.88	11.72	12.17	11.18	9.52
Na ₂ O	3.31	2.98	4.16	3.09	3.68	1.32	2.93	2.92	2.93	2.91	2.91	3.02	3.26
K ₂ O	1.05	1.00	1.34	1.31	1.48	1.89	0.87	0.59	1.22	1.80	1.65	1.83	1.08
P ₂ O ₅	0.23	0.30	0.19	0.23	0.20	0.24	0.14	0.19	0.15	0.34	0.38	0.37	0.25
Trace element (ppm)													
Li	6.98	5.06	9.79	9.06	10.4	12.9	4.50	5.88	13.9	6.08	5.42	5.70	9.49
Be	0.62	0.62	0.68	0.64	0.74	0.89	0.43	0.62	0.66	0.92	0.85	1.03	0.62
Sc	23.0	44.5	36.7	26.2	18.0	25.5	10.8	13.4	27.2	37.7	47.4	31.0	22.9
V	244	340	277	320	193	236	136	134	159	328	361	315	224
Cr	23.3	37.0	125	10.1	7.58	55.1	2.69	3.85	234	24.3	40.9	20.3	5.20
Co	28.5	39.5	34.5	32.9	21.4	21.9	14.5	19.1	23.1	31.9	35.5	31.1	26.1
Ni	13.1	19.7	36.9	10.7	8.88	17.6	4.20	4.84	39.6	19.1	22.0	18.3	9.89
Cu	44.7	70.4	78.8	104	59.9	49.2	31.5	30.3	32.3	89.1	78.5	59.7	107
Zn	72.3	85.3	63.2	79.6	59.4	55.8	45.0	65.3	49.2	72.3	74.1	73.7	72.8
Ga	18.3	18.1	17.5	19.0	17.5	17.5	12.9	18.1	15.7	19.3	18.7	19.7	18.8
Rb	21.7	22.7	19.6	20.7	30.2	29.4	9.67	10.7	27.1	44.2	40.0	44.2	18.0
Sr	451	390	652	564	467	740	353	580	474	754	717	790	488
Y	15.1	16.5	12.0	13.8	14.1	10.3	7.77	9.87	10.2	18.0	18.1	18.7	18.2
Zr	60.8	57.6	58.3	60.6	77.9	57.2	43.1	56.7	53.3	95.1	88.6	104	77.2
Nb	1.70	1.66	1.48	1.59	1.84	2.02	0.79	1.16	1.51	3.07	2.61	3.45	1.84
Sn	0.78	0.97	0.80	0.86	0.68	0.74	0.36	0.49	0.48	1.57	2.04	1.63	0.98
Cs	0.76	0.54	0.81	0.36	0.78	1.08	0.29	0.28	1.62	0.67	1.32	0.51	0.93
Ba	424	455	364	396	537	504	235	286	504	839	726	860	511
La	7.79	7.48	8.46	7.83	9.64	9.91	5.98	6.28	7.64	13.7	12.5	15.5	7.94
Ce	18.0	17.7	19.4	18.6	21.1	21.6	12.8	14.7	16.1	34.4	32.1	37.9	19.3
Pr	2.66	2.69	2.82	2.75	2.92	3.00	1.81	2.15	2.15	5.20	4.97	5.65	2.85
Nd	11.6	12.1	12.2	12.3	12.1	12.7	7.50	9.47	8.76	23.1	22.2	24.5	12.6
Sm	2.83	3.12	2.81	2.99	2.76	2.80	1.68	2.26	2.00	5.15	5.00	5.30	3.25
Eu	0.97	1.03	0.88	0.96	0.89	0.87	0.56	0.85	0.68	1.49	1.51	1.55	1.07
Gd	2.85	3.26	2.54	2.86	2.64	2.32	1.59	2.13	1.89	4.46	4.38	4.54	3.39
Tb	0.44	0.51	0.38	0.43	0.41	0.33	0.24	0.31	0.30	0.63	0.64	0.65	0.54
Dy	2.81	3.22	2.31	2.68	2.58	1.98	1.46	1.91	1.90	3.71	3.75	3.77	3.42
Ho	0.60	0.68	0.49	0.56	0.55	0.41	0.31	0.39	0.40	0.74	0.74	0.76	0.73
Er	1.72	1.89	1.38	1.59	1.59	1.17	0.88	1.11	1.16	1.99	1.99	2.11	2.13
Tm	0.26	0.28	0.21	0.23	0.25	0.18	0.13	0.16	0.18	0.29	0.29	0.31	0.32
Yb	1.68	1.75	1.31	1.52	1.63	1.15	0.87	1.08	1.22	1.83	1.81	1.92	2.08
Lu	0.26	0.27	0.20	0.23	0.26	0.18	0.14	0.17	0.19	0.27	0.27	0.29	0.32
Hf	1.76	1.81	1.75	1.80	2.19	1.88	1.21	1.64	1.65	2.98	2.83	3.11	2.24
Ta	0.10	0.10	0.10	0.10	0.13	0.13	0.06	0.08	0.11	0.20	0.16	0.20	0.12
Pb	4.56	4.63	4.59	6.58	5.17	4.36	2.73	2.57	6.82	3.62	4.07	4.14	7.01
Th	1.98	2.08	2.14	1.94	3.14	2.82	1.46	1.09	2.74	3.12	2.63	3.51	2.16
U	0.89	0.93	0.94	0.89	1.46	1.11	0.65	0.56	1.27	1.39	1.21	1.59	0.92

^aMajor-element data from 1, Marsh (1976); 2, Marsh and Leitz (1978); 3, von Drach et al. (1986)

much lower than typical island arc magmas or continental crust as a whole. Importantly, in our view, the Pb/Nd ratios of the Adak Island lavas are strongly controlled by the abundance of Pb (Fig. 6b) and not by the abundance of Nd. Although no published Nd concentration data exist for the samples for which Myers and Marsh (1987) obtained Pb-isotope data, the good correlation between Pb content and Pb/Nd ratio

(Fig. 6b) allows interpretation of a plot of Pb-isotope ratio vs. Pb content (Fig. 6c) in terms of source contribution. There is good correlation between Pb content and Pb-isotope composition, with the Pb-depleted samples plotting at unradiogenic isotope ratios whereas Pb-rich samples plot at the radiogenic end of the mixing line. Hence, combined chemical and isotopic information for Adak Island lavas reveals that those samples

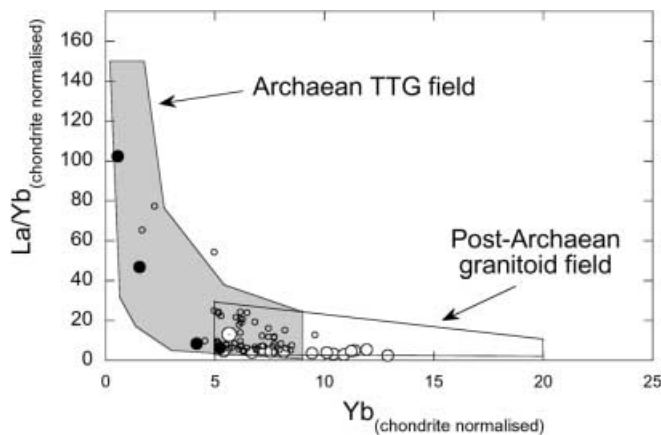


Fig. 3. Plot of La/Yb versus Yb content after Martin (1986). Archaean TTGs define a field characterised by high La/Yb ratios at comparatively low Yb contents (*shaded*, after Martin 1986), thought to reflect HREE depletion. Post-Archaeal granitoids define a field with comparatively lower La/Yb ratios and higher Yb contents (*nonshaded*, after Martin 1986). Chondrite values are from McDonough and Sun (1995). Average of Cenozoic adakites (*dotted open circle*) after Drummond et al. (1996) plots into the overlapping area of both fields. The majority of other subrecent adakites (*small open circles*) from the Andean Austral Volcanic Zone, Chile (Stern and Kilian 1996), Solander Island, New Zealand (Reay and Parkinson 1997), and Mount St. Helens, USA (Smith and Leeman 1987) also plot into the area of overlap between Archaean and post-Archaeal granitoids. Five data points for Permian SE Queensland adakites (*closed circles*) plot into the Archaean TTG field (note that the most HREE-depleted sample plots off-scale). Island arc volcanics from the Aleutian Islands (*large open circles*) are only weakly depleted in Yb. Four samples (from Adak Island) plot into the area of overlap between Archaean and post-Archaeal granitoids. The remaining samples (five from Adak Island, three from Bogosofof Island, and one from Great Sitkin Island) plot into the post-Archaeal granitoid field

with the highest La/Yb ratios and the lowest Pb/Nd ratios (i.e. those with the strongest adakitic affinity) have Pb-isotope characteristics of MORB or the MORB-source mantle. This we interpret as evidence that these melts, albeit hybridised with ordinary wedge-derived melts or contaminated by peridotite (Yogodzinski et al. 1995), were originally of adakitic parentage. For the purpose of this paper, we therefore suggest that the samples with the lowest Pb/Nd and Be/Nd and highest Nb/Ta should be used to estimate the Aleutian adakite component. We regard the median ratios (Nb/Ta = 15.6 ± 1.1 ; Pb/Nd = 0.377 ± 0.174 ; Be/Nd = 0.054 ± 0.011) as minima (Nb/Ta) and maxima (Pb/Nd and Be/Nd) respectively.

The more evolved Pb-isotope end member could represent an enriched mantle domain in the supra-subduction zone wedge, a sediment component in the slab, or a lithospheric contaminant. An interesting aspect of the Aleutian data set is shown by the three Bogosofof samples which represent the back arc. These samples have high Nb/Ta and low Pb/Nd, Li/Yb and Be/Nd ratios, indicating that they derive from a part of the mantle which has not experienced as much enrichment driven by dehydration of the slab, but there is never-

theless an affinity with the Adak Island lavas in La/Yb and Sr/Y. It appears that back-arc volcanics show closer affinities with their associated arc volcanoes than to each other (Fig. 4). This could suggest that Bogosofof (and Adak) lavas were derived from a less depleted mantle wedge than the Niua fo'ou back arcs and their associated Tonga-Lau arc volcanics.

In summary, careful inspection of complex island arc lavas for which an adakitic component is indicated by traditional geochemical fingerprints (i.e. Sr/Y) requires concentration data for elements which are fluid sensitive (Pb, Ta, B, Li) and elements with comparable solid/melt distribution coefficients (Nd, Nb, Be, Yb). Characterisation of the adakitic component is possible in Phanerozoic lavas, even in hybrid examples such as the Adak Island, and should therefore also be feasible in Archaean TTGs, provided that fresh samples are used which have not experienced metamorphic loss of fluid-sensitive elements.

Geochemistry of Archaean TTGs

Comparison of trace element ratios in adakites vs. Archaean TTGs must take into account that TTGs are, on average, more evolved than adakites and, due to their coarse-grained nature, also chemically more heterogeneous on the scale of typical hand specimens. Variations in ratios of trace elements of similar compatibility can therefore amount to > 50% in highly evolved plutonic samples, even for a suite of samples from a single pluton. For example, the Pb/Nd ratio of the arc-related 375-Ma Shelburne Pluton (southern Nova Scotia; data from Currie et al. 1998) varies by 67% (1 standard deviation) yet the median ratio of 0.94 is typical of arc magmas. An additional source of chemical variability comes from the possibility of multiple melt sources and assimilation (both in the mantle and in the crust). Our characterisation of TTG geochemistry therefore relies on comparison of average values.

New geochemical data for early and late Archaean TTGs

We report new trace element data for three sets of Archaean TTGs (Tables 2, 3). Firstly, for a suite of five 3.80-Ga tonalitic Itsaq gneisses which were collected 6 to 20 km south of the Isua greenstone belt (SW Greenland). The geology of this area has been described by Nutman et al. (1999) who concluded that the exposed gneisses represent the best-preserved early Archaean crust known on Earth. Intrusion ages cluster tightly between 3.79 and 3.81 Ga (Nutman et al. 1999). Secondly, for a suite of ten type-locality Amîtsoq gneisses from the Godthabsfjord area and the Isua dome in West Greenland. These samples belong to a relatively late suite of intrusions and are widely believed to be 3.65 Ga old (e.g. Whitehouse et al. 1999). They yield 3.65-Ga Pb/

Fig. 4. Covariation between La/Yb and Sr/Y ratio in arc magmas. In the Tonga-Lau basin there is a gradational increase in both ratios from typical MORB values to oceanic arc values, with precursor Lau Basin arc lavas from ODP site 839 plotting midway between MORB-like basalts and proper Tongan arc lavas. The most evolved lavas in these ratios are those from the northern end of Tonga where the slab is being torn and is shallowing. Typical adakites have much higher La/Yb and Sr/Y ratios. Aleutian arc lavas of 'adakitic' affinity are resolvable more evolved in these ratios than typical oceanic arc lavas. Tongan data are from Ewart et al. (1998), and typical adakites include those quoted in Fig. 3, plus data for adakitic rocks from Ecuador (Bourdon et al. 2002) and Borneo (Proust et al. 2001)

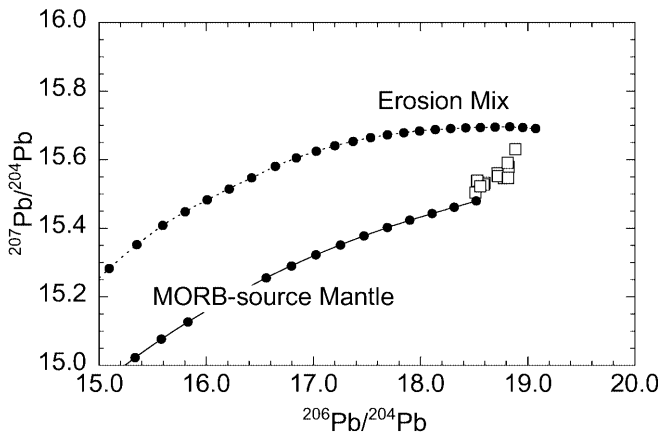
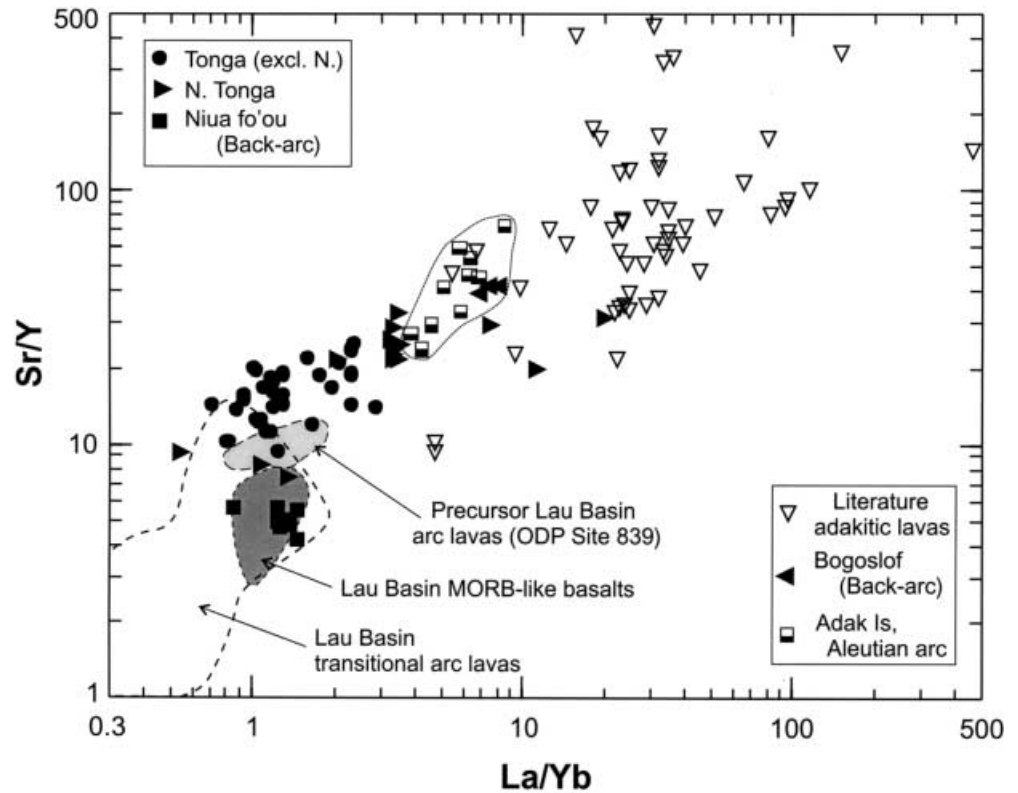


Fig. 5. Common Pb isotope diagram. Adakites from Adak Island (squares; data from Myers and Marsh 1987) define a binary mixing line. According to the Pb-isotope evolution model of Kramers and Tolstikhin (1997), the more primitive end member represents modern MORB-source mantle (circles connected by solid line; spacing represents 100-Ma time steps). The more radiogenic end member is represented by modern 'erosion mix' (circles connected by broken line; spacing represents 100-Ma time steps). Both end members could be hosted by the subducted slab if the unradiogenic Pb was derived from the oceanic crust and the radiogenic Pb was derived from subducted sediment. Alternatively, the radiogenic end member could represent enriched mantle or assimilated crust

Pb, Sm–Nd, and Rb–Sr regression ages and intercepts indicative of juvenile origin. They are not part of the sample suite for which some authors claim ages older than 3.65 Ga. Thirdly, for a set of five late Archaean tonalitic to granodioritic Black Angel gneisses from the

Mount Isa Block in NE Australia. The Black Angel gneisses have interpreted U/Pb ion-probe zircon intrusion ages of 2.46 to 2.51 Ga and show juvenile Nd-isotope characteristics (McDonald et al. 1997).

When the median trace element concentrations of these TTGs are normalised to MORB it is evident that, unlike adakites, they have very pronounced overenrichment of Pb, Be and Li, and a distinctively subchondritic Nb/Ta ratio (Fig. 7). The Nb/Ta medians of the Itsaq gneisses (8.81), the type-Amîtsoq gneisses (13.64), and the Black Angel gneisses (12.67) are in good agreement with bulk continental crust (10). Similarly, the Itsaq Gneiss median Pb/Nd is 1.77, that of the type-Amîtsoq gneisses 0.75, and that of the Black Angel gneisses 0.445, which compare well with average continental crust (0.63; Rudnick and Fountain 1995). The median Pb/Nd ratio of 0.75 for the type-Amîtsoq gneisses is higher than that of bulk continental crust but the uniquely unradiogenic Pb of these gneisses negates the involvement of older crustal material in their genesis (Kamber and Moorbath 1998). Rather, the high Pb/Nd ratio reflects a similar (slab-) dehydration process which is responsible for the continuing Pb enrichment of the continents (Miller et al. 1994). Similar trace element patterns were obtained for 3.80-Ga Itsaq TTGs by Nutman et al. (1999) who concluded that a substantial role of fluids is implied by the chemistry of these tonalites. The juvenile mantle origin of the Black Angel gneisses is evident from their radiogenic initial Nd isotopes (initial ϵ_{Nd} between +3.9 and +5.8) which are similar to that of coeval depleted mantle (e.g. Nägler and

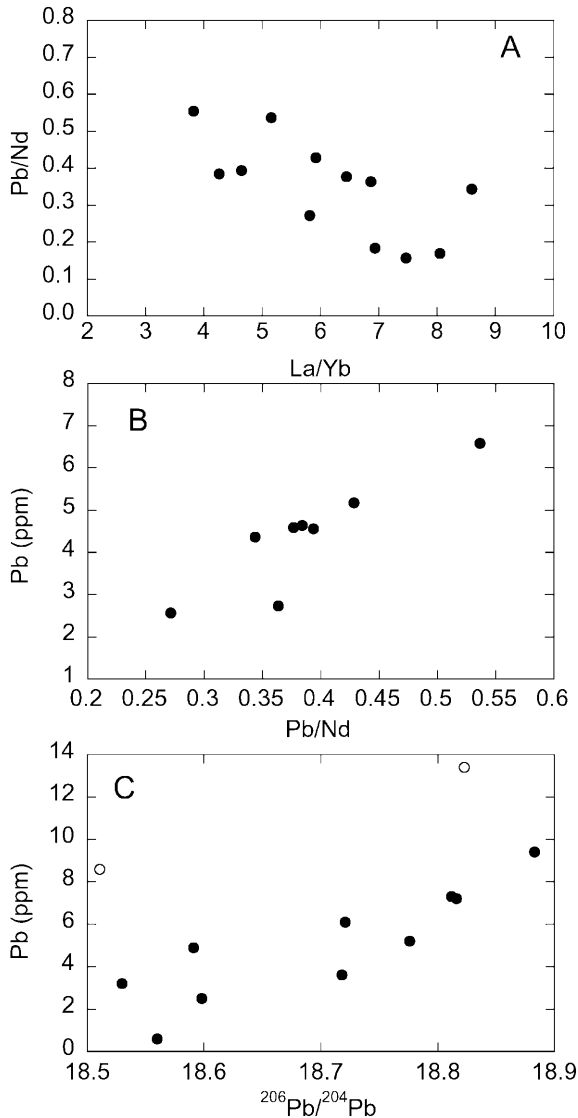


Fig. 6a–c. Selected trace element and Pb-isotope systematics of Aleutian lavas. **a** Although scattered, there is a discernible anticorrelation between La/Yb and Pb/Nd in the data set, with the exception of a single sample (AD-72; Table 1). **b** Strong positive linear correlation ($r^2=0.7984$) exists between the Pb content (in ppm) and the Pb/Nd ratio of the samples from Adak Island (again omitting AD-72). No correlation ($r^2=0.1839$) is found between the Nd content and the Pb/Nd ratio (not shown). **c** The Pb-isotope composition of Adak Island lavas is positively correlated with the Pb content, indicating that the Pb-poor samples have a MORB-like Pb-isotope composition and that the Pb-rich samples contain crustal Pb. The two samples (of twelve) which have the highest Pb contents (*open circles*) do not follow the trend. Data are from Myers and Marsh (1987)

Kramers 1998). The overenrichment in Pb and the subchondritic Nb/Ta ratio of the Black Angel gneisses are thus not caused by assimilation of pre-existing crust but are genuine features of continental crust formation.

The median Be/Nd ratios of all three sets of TTGs (Black Angel gneisses = 0.073; type-Amîtsoq gneisses = 0.07; 3.80-Ga Itsaq gneisses = 0.19) are within the range of typical continental crust. Median Li/Yb ratios

are higher than in typical continental crust (Black Angel gneisses = 32; type-Amîtsoq gneisses = 34; 3.80-Ga Itsaq gneisses = 118). Although this indicates that metamorphic, fluid-related light-element loss is evidently not an issue with these samples, the Li/Yb ratio is not a strong discriminator for Archaean petrogenesis. For example, if the median Li concentration is divided by the Yb concentration of average continental crust, we obtain Li/Yb ratios between 11 and 15 (instead of 32–118). This shows that the Li/Yb ratio is largely controlled by HREE depletion and not by addition of fluid-mobile elements. Nevertheless, Pb/Nd and Nb/Ta ratios clearly show that none of these TTGs can be considered to be adakites.

The geochemistry of Itsaq, Amîtsoq, and Black Angel gneiss samples is by no means exceptional. Condie (1993) demonstrated that the La/Yb ratios of TTGs decreased from 30 in the Archaean to 17.33 in the Proterozoic and 14.7 in the Phanerozoic, but Nb/Ta and Pb/Nd ratios have remained virtually constant (10.7, 11.25, 12.3, and 0.86, 0.75, 0.82 respectively), in good agreement with the median Nb/Ta ratio (9.82) of 174 Archaean, high-Al trondhjemite–tonalite–dacites compiled by Drummond et al. (1996). Subchondritic Nb/Ta and overproportional Pb concentration are therefore typical for Archaean TTGs. We conclude that, at least since ca. 3.8 Ga, element transport by aqueous fluids in the mantle has been an integral part of continent formation.

Smithies (2000) recently argued, based on differences in major- and compatible-element contents, that TTGs could not be analogues of adakites but that they may have formed through melting of hydrous basaltic material at the base of the crust. Kramers (1988) and Ridley and Kramers (1990) also stressed that whatever mode of TTG formation is envisaged, partial hydration of mantle melts and fractionation of amphibole appear unavoidable. Nutman et al. (1999) noted that the high relative abundances of Rb, Cs, Sr, Ba, and Pb made an origin from direct eclogite melting impossible, and pointed to a substantial role of fluids in early crust formation. Our results agree with the findings of these authors and we conclude that the strong LREE–HREE fractionation of Archaean TTGs must have an other origin than residual garnet in the eclogite source of a subducted oceanic crust.

Alternative explanation for strong HREE depletion of TTGs

There are two important observations regarding the HREE depletion of Archaean TTGs which, in our view, have not been sufficiently considered. These concern the average composition of upper continental crust as approximated by sedimentary rocks, and the fact that TTGs are, on average, also overly enriched in LREEs. Condie (1993) convincingly demonstrated that there is a mismatch between estimates of upper Archaean crust calculated from relative rock abundance and sedimentary rock composition. The relative contribution of

Table 2. Chemical compositions of TTGs from the Itsaq Gneiss Terrain, Godthabsfjord, Greenland (all trace elements by ICP-MS)

Tectonic unit	Itsaq Gneiss Terrain, Greenland									
Locality	Godthabsfjord, type-locality Amitsoq Gneiss									
Sample ID	155702	155708	155710	155724	155736	155739	155768	155774	155807	155810
Major element (wt%) ^a										
SiO ₂	66.49	72.93	51.85	80.12	66.67	69.25	75.93	66.90	70.47	65.17
TiO ₂	0.79	0.17	1.80	0.05	0.99	0.37	0.27	0.31	0.22	0.47
Al ₂ O ₃	14.38	14.61	14.85	11.08	13.39	13.43	11.73	15.44	16.08	17.47
Fe ₂ O ₃	5.50	1.62	14.49	0.51	6.68	6.13	2.60	4.39	2.00	3.77
FeO	—	—	—	—	—	—	—	—	—	—
MnO	0.07	0.02	0.16	0.01	0.11	0.05	0.04	0.05	0.03	0.05
MgO	0.88	0.34	3.25	0.05	0.98	0.33	0.60	0.94	0.98	1.99
CaO	3.27	1.71	7.69	1.42	3.74	2.09	2.63	3.22	3.54	4.75
Na ₂ O	3.67	4.04	4.18	2.90	3.11	3.09	4.10	5.37	5.59	5.13
K ₂ O	3.67	4.09	0.94	3.58	3.20	4.44	1.20	1.49	1.34	1.26
P ₂ O ₅	0.14	0.01	0.23	0.00	0.30	0.04	0.12	0.07	0.03	0.05
Trace element (ppm)										
Li	26.5	19.2	20.1	10.4	60.4	69.1	24.1	42.5	41.0	40.2
Be	1.50	0.81	1.29	0.91	1.26	0.72	1.88	2.56	1.23	1.26
Sc	19.3	2.75	29.6	0.15	11.6	7.15	0.76	2.93	2.77	9.16
V	57.3	17.9	327	3.10	48.5	14.5	12.6	28.8	19.9	54.1
Cr	14.9	11.9	3.46	0.47	8.27	11.2	1.63	8.90	25.7	44.9
Co	12.7	4.11	48.0	1.15	10.1	5.02	4.05	10.2	5.23	15.0
Ni	7.84	4.36	19.2	0.71	4.23	3.18	3.14	10.3	10.7	41.5
Cu	16.8	2.47	47.2	1.17	16.8	4.15	2.03	3.73	20.7	8.86
Zn	98.0	35.7	141	10.3	88.4	49.7	37.7	74.9	29.8	53.4
Ga	22.2	19.6	24.1	12.0	21.8	19.4	13.6	20.9	17.8	20.8
Rb	87.6	86.3	6.6	93.5	88.0	130	57.0	94.1	50.3	56.1
Sr	193	194	255	80.1	237	108	189	275	520	426
Y	57.0	6.15	26.6	1.71	28.0	28.7	4.79	3.28	4.30	10.5
Zr	572	258	26.0	8.78	259	432	158	145	83.5	128.6
Nb	10.5	1.06	3.78	0.77	7.78	4.62	2.33	2.46	1.37	2.39
Sn	0.86	0.43	1.66	0.29	1.01	0.50	0.64	0.66	0.62	1.28
Cs	0.72	0.69	0.09	0.43	6.68	4.24	1.05	3.86	1.75	1.65
Ba	532	655	173	203	771	317	93.9	173	209	400
La	36.6	15.2	26.0	7.06	29.5	54.3	33.2	8.00	22.9	15.6
Ce	99.3	23.0	58.2	8.17	71.2	106	62.1	15.0	41.2	37.0
Pr	15.3	2.32	7.79	0.64	10.1	12.8	6.94	1.75	4.61	5.04
Nd	68.9	7.83	31.8	1.66	43.4	46.5	22.5	6.25	15.5	20.4
Sm	16.7	1.30	6.66	0.24	8.89	8.22	2.98	1.09	2.37	4.04
Eu	3.16	0.87	1.87	1.32	2.87	1.27	0.74	0.39	0.81	1.11
Gd	15.9	1.14	6.22	0.22	7.79	6.94	1.71	0.90	1.61	3.19
Tb	2.25	0.17	0.91	0.04	1.06	1.00	0.19	0.12	0.19	0.42
Dy	12.7	1.05	5.40	0.29	5.98	5.98	0.96	0.65	0.94	2.28
Ho	2.45	0.23	1.08	0.07	1.15	1.24	0.18	0.13	0.16	0.42
Er	6.14	0.69	2.93	0.21	3.06	3.42	0.47	0.35	0.41	1.09
Tm	0.79	0.11	0.42	0.03	0.41	0.47	0.07	0.05	0.05	0.15
Yb	4.56	0.73	2.56	0.24	2.54	2.85	0.46	0.34	0.33	0.90
Lu	0.65	0.12	0.39	0.04	0.39	0.42	0.07	0.06	0.05	0.13
Hf	15.1	7.44	1.19	0.39	6.65	11.48	4.06	3.75	2.18	3.19
Ta	0.74	0.11	0.28	0.10	0.57	0.22	0.29	0.08	0.10	0.10
Pb	13.8	20.4	9.11	17.4	12.8	17.4	19.5	13.2	18.1	13.0
Th	0.42	0.46	0.16	0.98	0.52	2.96	6.97	0.98	2.82	0.13
U	0.38	0.32	0.02	0.16	0.25	0.26	0.54	0.23	0.17	0.25

^aMajor-element data by ICP-OES

TTGs to average Archaean cratonic areas at their *present* erosion level is ca. 50%, and that of granites is ca. 20% (Condie 1993). Both TTGs and granites are strongly depleted in HREEs and have average Sm/Nd ratios of 0.155 and 0.137 respectively (Condie 1993). Estimates of the Sm/Nd ratio of Archaean to early Proterozoic shales and pelites, on the other hand, are considerably higher and range between 0.175 (Condie 1993), 0.188 (Jahn and Condie 1995), and 0.201

(McLennan and Hemming 1992). This suggests that relative lithological contributions to the present erosion level are not at all representative of original upper Archaean crust. Condie (1993) concluded that typical upper Archaean crust prior to erosion to its present level was composed of up to 60% mafic lithologies. This finding is of direct relevance to models for the origin of TTGs as it indicates that, on average, the REE composition of upper continental crust has not changed with

Table 3. Chemical compositions of TTGs from the Itsaq Gneiss Terrain, unnamed block south of the Isua Belt, Greenland, and the Black Angel Gneiss, Australia (all trace elements by ICP-MS)

Tectonic unit Locality	3.8-Ga Itsaq Gneiss Terrain, Greenland					2.5-Ga Black Angel Gneiss, Australia				
	Unnamed block south of Isua Belt					Mt. Isa Block, North Queensland				
Sample ID	SM/GR/ 98/1	SM/GR/ 98/2	SM/GR/ 98/3	SM/GR/ 98/4	SM/GR/ 98/34	GM94–100	GM95–31	GM95–34	GM95–36A	GM95–38
Major element (wt%) ^a										
SiO ₂	–	–	–	–	–	61.93	63.16	66.88	65.76	64.23
TiO ₂	–	–	–	–	–	1.05	0.90	0.74	0.79	0.93
Al ₂ O ₃	–	–	–	–	–	15.46	16.03	15.97	16.17	16.25
Fe ₂ O ₃	–	–	–	–	–	7.51	6.20	4.43	4.85	5.65
FeO	–	–	–	–	–	5.32	4.28	2.62	3.14	3.91
MnO	–	–	–	–	–	0.09	0.07	0.05	0.06	0.06
MgO	–	–	–	–	–	3.71	2.21	1.32	1.48	1.68
CaO	–	–	–	–	–	5.09	4.64	4.18	4.24	4.57
Na ₂ O	–	–	–	–	–	1.95	2.32	2.71	2.79	2.55
K ₂ O	–	–	–	–	–	2.82	2.49	2.00	2.01	2.11
P ₂ O ₅	–	–	–	–	–	0.36	0.17	0.13	0.15	0.17
Trace element (ppm)										
Li	33.0	23.8	30.8	31.0	28.0	23.9	26.5	16.4	18.9	25.8
Be	1.73	1.23	2.33	1.17	1.45	2.18	2.09	2.48	3.07	1.79
Sc	11.9	6.20	2.64	1.87	1.95	19.6	11.8	7.68	7.64	7.70
V	102	45.8	10.1	7.56	19.8	113	82.8	35.9	40.8	47.2
Cr	44.7	23.0	6.65	2.80	286	47.5	43.3	16.5	15.1	19.1
Co	31.6	28.5	26.6	28.4	29.9	71.5	14.9	9.94	10.3	11.7
Ni	51.2	23.2	11.1	8.82	94.8	40.6	10.1	3.06	3.59	4.19
Cu	47.1	9.49	2.84	3.13	3.37	54.6	18.3	5.15	12.8	6.82
Zn	77.9	54.0	24.8	26.1	44.5	115	80.5	33.5	52.5	73.4
Ga	22.4	19.7	19.5	18.6	16.5	22.1	22.3	21.1	22.4	22.6
Rb	47.9	34.7	29.1	20.6	44.9	148	124	98.3	108	102
Sr	452	371	219	258	297	514	431	382	386	467
Y	10.9	7.60	2.49	2.22	1.83	15.1	12.5	5.86	10.1	7.21
Zr	79.3	151	66.5	81.1	89.9	99.0	224	177	233	257
Nb	4.80	3.65	5.74	1.10	3.02	12.4	11.0	10.6	9.70	9.96
Sn	0.37	0.57	0.73	0.53	0.62	–	–	–	–	–
Cs	1.89	0.94	3.54	1.45	2.05	5.54	5.43	3.09	4.21	4.74
Ba	207	238	78.4	112	276	927	600	364	443	505
La	16.9	28.4	3.43	7.96	5.62	55.9	46.7	30.4	40.9	45.8
Ce	38.1	50.3	5.50	13.4	9.22	106	85.7	60.0	77.0	84.1
Pr	5.61	6.67	0.72	1.79	1.14	12.5	9.20	7.12	9.24	10.0
Nd	23.1	23.7	2.65	6.22	4.01	42.5	29.0	23.4	29.9	31.8
Sm	4.72	3.78	0.68	1.04	0.70	8.49	4.27	3.61	4.83	4.63
Eu	1.13	0.94	0.34	0.38	0.46	1.79	1.13	1.07	1.10	1.28
Gd	3.59	2.58	0.68	0.70	0.57	5.69	3.57	2.31	3.25	2.97
Tb	0.45	0.32	0.10	0.08	0.07	0.57	0.51	0.28	0.41	0.34
Dy	2.38	1.64	0.53	0.45	0.37	2.97	2.48	1.32	2.11	1.64
Ho	0.43	0.30	0.09	0.08	0.07	0.52	0.55	0.23	0.39	0.28
Er	1.07	0.76	0.21	0.24	0.17	1.59	1.21	0.55	0.97	0.69
Tm	0.15	0.11	0.03	0.04	0.02	0.18	0.14	0.07	0.12	0.08
Yb	0.88	0.64	0.15	0.27	0.15	1.22	0.91	0.43	0.76	0.53
Lu	0.13	0.09	0.02	0.04	0.02	0.17	0.15	0.06	0.11	0.07
Hf	2.34	3.94	1.98	2.42	2.57	2.62	4.76	4.08	5.16	5.10
Ta	0.47	0.35	0.90	0.43	0.34	1.61	0.84	0.82	0.90	0.71
Pb	13.6	9.15	18.7	11.0	14.4	11.4	14.0	13.7	14.4	12.9
Th	3.20	2.82	0.52	1.71	0.37	18.02	8.97	5.80	8.41	7.74
U	0.74	0.17	0.17	0.25	0.23	2.21	1.16	1.34	1.38	0.93

^aMajor-element data by XRF

time. This contradicts the view that TTGs are direct slab melts because clearly, substantial addition of strongly HREE-depleted material to ordinary continental crust would have lowered the average Sm/Nd ratio.

Furthermore, the notion that Archaean TTGs have high La/Yb because of HREE depletion is not entirely correct as it also reflects the fact that many TTGs are

overly enriched in LREEs. For example, Condie's (1993) average La concentration of both TTGs and granites dropped from 30 and 50 ppm in the Archaean to 25 and 40 ppm respectively in the Phanerozoic. At the same time, average Yb concentrations increased in these rock types from 1.0 and 2.0 to 1.7 and 3.2 respectively. The change in La content thus contributes 19% (TTGs) and

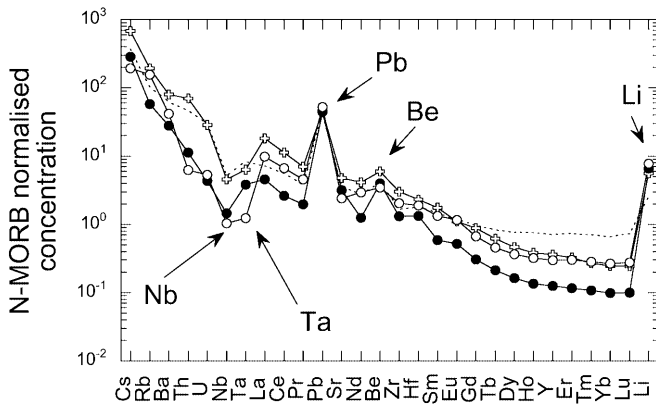


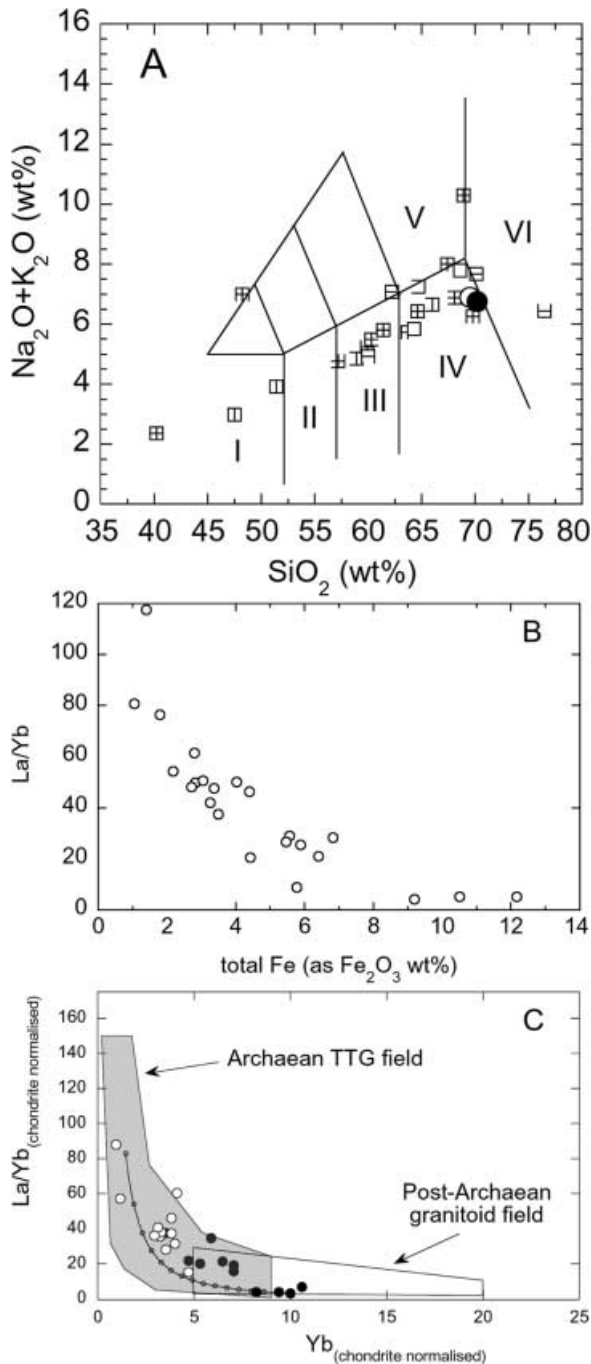
Fig. 7. N-MORB-normalised (Sun and McDonough 1989) trace element pattern of Archaean TTGs (medians) compared to average continental crust estimate (*stippled line*, no symbols) of Rudnick and Fountain (1995). All three types of TTGs (Black Angel gneisses as *open crosses*, 3.81-Ga Itsaq gneisses as *closed circles*, and 3.65 type-Amîtsoq gneisses as *open circles*) show strong enrichment in Pb, Li, and Be and subchondritic Nb/Ta ratio. They also display strong LREE/HREE fractionation typical of Archaean TTGs. Elements are arranged in decreasing MORB-melting compatibility, and normalisation parameters are identical to those used in Fig. 1

25% (granites) to the resulting decrease in La/Yb ratio. This observation is illustrated by the REE patterns of the type-Amîtsoq gneisses and the Black Angel gneisses (Fig. 7), in that they are more enriched in LREEs than average continental crust. In order for the average La/Yb ratio of cratonic shales to have remained constant (Condie 1993), a higher proportion of low La/Yb magmas must have been present in the Archaean upper crust. In other words, at least in terms of REEs, the bulk of material which formed continental crust has not significantly changed through time. This is also true for the major elements and the majority of incompatible elements. Only the abundances of compatible elements have decreased with time in average upper continental crust, due to the decline in mafic magmas reaching the surface. It is therefore plausible that it was the intensity and mode of intracrustal differentiation which changed over time, rather than the composition of the parental melt itself (and consequently the processes which form that melt).

Theoretically, the strong HREE depletion of Archaean TTGs (e.g. Fig. 7) could indicate significant fractional crystallisation of a mineral with $D_{Yb}^{mineral/melt} \gg D_{La}^{mineral/melt}$ during magma differentiation. Between 80 and 90% of fractional crystallisation is required to produce residual TTGs from a basaltic parent melt. Drummond et al. (1996, p. 206) regarded such degrees of fractional crystallisation as unlikely because of “the lack of high proportions of mafic to intermediate igneous rocks”. However, shale and pelite geochemistry shows that the lack of mafic and intermediate rocks is only apparent, and that the ancient exposed crust was in fact dominated by such rocks. It is difficult to quantitatively demonstrate the origin of tonalitic rocks by fractional crystallisation because the mafic members of

the fractionation series are rarely exposed (e.g. Brophy 1989). In cases where discrete intrusive complexes contain mafic to silicic constituents, fractional crystallisation models are often successful in providing a magmatic lineage (e.g. Tate et al. 1999) comparable to those derived from experimental constraints (e.g. Grove and Baker 1984). Archaean TTGs are even more problematic than Phanerozoic TTGs because post-magmatic tectonism has complicated field relationships between potential co-magmatic phases, and because the igneous mineralogy or mineral chemistry is rarely preserved.

Nevertheless, some Archaean greenstone belts contain volcanic successions of mafic to very silicic composition. One example for which high-quality trace element data is available is the Kalgoorlie Terrane (a greenstone belt in the Yilgarn craton of Australia) which contains the 2.68-Ga, dominantly felsic volcanic Black Flag Group (Morris and Wit 1997). Morris and Wit (1997, p. 95) postulated that “in terms of both volume relationships and chemistry, it is unlikely that Black Flag Group basalts were parental to andesites, or were derived by melting of the same source ...” and they stated that the basalts were “... not considered further in this paper”. However, the first argument appears questionable in view of Condie’s (1993) observation regarding shale and pelite geochemistry. Morris and Wit’s (1997) rejection of consanguinity of the Black Flag Group volcanics thus depends on their interpretation of geochemistry. They refer to their Fig. 2d which is a plot of SiO_2 versus Cr concentration (Morris and Wit 1997; p. 93) showing that some of their *andesites* have anomalously high Cr contents. They implicitly conclude that if basalts were parental, they are expected to have even higher Cr contents, which they do not. However, other compatible elements in these rocks do not seem to share this feature. For example, there is a strong negative correlation between TiO_2 and SiO_2 (Fig. 2a of Morris and Wit 1997) for the entire volcanic sequence (including the basalts), and Ni contents show a good positive correlation with MgO ($r^2 = 0.737$; not shown by Morris and Wit 1997). Furthermore, if the Black Flag volcanics are plotted in Le Maître et al.’s (1989) classification diagram (Fig. 8a), they yield a well-defined subalkaline trend indicative of differentiation. The most evolved samples require removal of between 70–80% solids. Interestingly, the samples also yield a very well-defined negative correlation in a plot of total Fe versus La/Yb (Fig. 8b), which could indicate fractional crystallisation of mineral with $D_{HREE}^{mineral/melt} \gg D_{LREE}^{mineral/melt}$, notably amphibole (e.g. Arth and Barker 1976; Klein et al. 1997). Morris and Wit (1997) proposed that the basalts show no clear relationship to the more felsic volcanics in terms of REEs. However, their Fig. 3b (Morris and Wit 1997, p. 94) clearly shows that the basalts have lower LREE but higher HREE contents than andesites, which is what would be expected if they were related by fractional crystallisation of amphibole. The REE systematics of the Black Flag volcanics demonstrate that the degree of HREE, and even MREE depletion critically



depends on how strongly differentiated the samples are (Fig. 8b). In the La/Yb versus Yb concentration diagram (Fig. 8c) of Martin (1986), the basalts plot into the field of post-Archaean granitoids, dacites and rhyolites plot into the field of Archaean TTGs whereas the andesites plot mainly into the field of overlap. When compared to a calculated fractional crystallisation trajectory (75% amphibole and 25% garnet), it appears that the earlier stages of fractional crystallisation required more garnet removal, and that the later stages could have been dominated by amphibole. We therefore conclude that in spite of the general scepticism towards



Fig. 8. **a** Volcanic rock classification diagram after Le Maitre et al. (1989). Black Flag Group volcanics (squares; data from Morris and Witt 1997) form a succession from (micro-)basalt (field I), basaltic andesite (field II), andesite (field III), dacite (field IV) to trachydacite (field V) and rhyolite (field VI). The tight trend defined by all but one samples represents a typical subalkaline differentiation series. Plotted for comparison are the estimates for average TTG by Condie (1993; open circle) and by Drummond et al. (1996; closed circle). **b** Plot of total Fe (as Fe_2O_3 wt%) versus La/Yb ratio of 2.7-Ga Black Flag Group volcanics (same data as in a). Strong correlation indicates that HREE depletion could be caused by fractional crystallisation of hornblende and/or clinopyroxene. **c** Plot of La/Yb versus Yb content (scale, fields and normalisation as in Fig. 3). Plotted are the same samples as in a: shaded field Archaean TTGs, closed circles basalts, open circles dacites, and dotted open circles rhyolites. Shown for comparison is a fractional crystallisation trajectory (solid curve) calculated for removal of mixture of amphibole (75%) and garnet (25%), starting from the most evolved basalt sample data point. Open circles along this trajectory are spaced at intervals of 5% remaining liquid from 100 to 25%. Distribution coefficients are from Zack et al. (1997)

differentiation models, the fact remains that rocks of tonalitic composition can be generated from a mafic parental magma. Trace element geochemistry of TTGs has changed over geological time but we believe that differences have been overplayed in the past.

It is not our aim to discuss in detail how mechanisms which drive fractional crystallisation could have changed over time, if only for the fact that surprisingly little is known about the effects of these processes on Phanerozoic magmas. Primary differentiation of modern arc magmas starts within the mantle wedge, probably at depths where rising melt-matrix domes encounter the steep geothermal gradient which is maintained under the lithosphere by wedge convection (e.g. Tatsumi and Eggins 1995). It would thus appear that the thermal structure in the mantle wedge and across the base of the lithosphere could have an effect on how strongly primary arc magmas fractionated. Differentiation (and assimilation) also occurs at the base of and within the crust, especially in continental arcs. It appears that structure and thickness of the crust influence the degree of magma fractionation (Ewart 1979). Furthermore, the chemistry and oxidation stage of the primary magma also affect the sequence of phases which crystallise (e.g. Grove and Baker 1984). Müntener et al. (2001) have presented evidence that the initial water content of the basaltic melt within the mantle wedge has a surprisingly strong influence on the sequence of fractional crystallisation. At water-saturated conditions, garnet and amphibole, instead of olivine and plagioclase, crystallise together with clino- and orthopyroxene. Both amphibole and garnet strongly fractionate REEs in the direction required by TTG. Importantly, Müntener et al. (2001) showed that the garnet-bearing cumulate is denser than the surrounding mantle and could thus have been recycled, alleviating the mass balance problem of obtaining continental crust of, on average, andesitic composition from basaltic parental melt. Finally, for melts which were not fully water-saturated, the relative importance of cooling vs. ascent to drive crystallisation of magma

has to be considered. Blundy and Cashman (2001) recently showed that highly silicic melts can be produced only at shallow depth. It is likely that all the factors involved in these processes have changed over time, possibly in response to cooling of the Earth. Thus, it is premature to reject a TTG origin by differentiation from a basaltic precursor.

Discussion

Trace element chemistry of Archaean TTGs requires differential transport of fluid-mobile elements to the mantle melt source. The only feasible mechanism by which significant volumes of water can be transported sufficiently deep into the mantle is by emplacement of relatively dense, cold and hydrated oceanic lithosphere. Hydrated oceanic lithosphere must have existed since the establishment of a liquid hydrosphere (dating back to at least 3.65 Ga; Whitehouse et al. 1999) but this in itself does not imply operation of subduction in the present form since 3.65 Ga. However, it seems difficult to transport water into the deeper mantle in the absence of some form of subduction. Because heat loss across the surface boundary layer of a planet without subduction is restricted to conduction through a (thick) stable oceanic lithosphere, an unstable boundary layer would form *below* the lithosphere in the uppermost asthenosphere (Campbell and Griffiths 1993). Instability from this boundary layer would lead to sinking of cold plumes of depleted mantle material but not hydrated crust. We therefore agree with Campbell and Griffiths (1993) that the birth of subduction is marked by creation and preservation of the first continental lithosphere at ca. 3.8 Ga.

The hypothesis that Archaean TTGs represent direct slab melts implicitly assumes operation of subduction. The prevalence for slab melting in the Archaean was logically linked to the cooling history of the Earth (e.g. Martin 1986). In short, a hotter Archaean Earth dissipated more heat via oceanic crust production, which in turn implies higher spreading and subduction rates. Thus, it was hypothesised that on average Archaean oceanic lithosphere was younger and hotter when subducted, such that direct slab melting was more feasible. Although this logic appears intuitively correct, it ignores a number of physical constraints on the relationship between terrestrial cooling and oceanic plate production (Galer 1991).

Firstly, it is undisputed that radiogenic heat production has declined with time, but the potential upper mantle temperature is equally dependent on the cumulative heat loss which the Archaean Earth has experienced. Hence, although assumed implicitly in the slab-melting model, the assumption of a hotter upper Archaean mantle has not been explicitly quantified. For example, some petrologists argue that the Archaean mantle was substantially hotter than it is today, based on petrological arguments relating to anhydrous mantle melting to yield komatiite. Since virtually all terrestrial

heat is lost by production and cooling of oceanic plates (Stacey 1980), the hypothesis of a very hot Archaean mantle would actually imply a *reduced* oceanic plate production rate and hence no preponderance of hot and young subducted plates. If, on the other hand, it is accepted that the cooling rate of the mantle is some function of its convection pattern (e.g. Stacey 1980), the particular temperature of the upper mantle at any given time is still ill constrained.

The second aspect that the slab melting model does not consider is that the ridge driving force, which ultimately determines the plate generation rate, is largely a function of the thermal structure of the oceanic plates. Thus, the cooler the average subducted plate, the higher the ridge driving force and hence the plate production rate, and vice versa. Parsons (1982) concluded from this interrelationship that fluctuations in the areal rate of generation and destruction of oceanic plates would be limited narrowly about a basic state.

Thirdly, if the potential upper mantle temperature was indeed higher in the Archaean, its effect on the thickness of oceanic lithosphere produced along spreading ridges has to be considered also (McKenzie and Bickle 1988; Galer 1991). In the following we explore the extent to which thicker Archaean oceanic crust could compensate the increase in spreading rate (and hence decrease in mean age of oceanic lithosphere) required by considerations of heat dissipation.

As noted above, the least constrained parameters are the secular change in potential upper mantle temperature and the oceanic crust production rate through time. For the purpose of testing the direct slab melting hypothesis, it is necessary and reasonable to propose that oceanic crust production rate in the Archaean was higher than at present. Kramers and Tolstikhin (1997) adopted an oceanic crust production rate (\emptyset) which is sufficient to account for post-accretion degassing:

$$\emptyset = 33e^{-0.37t} \cdot 10^{16} \text{ga}^{-1} \quad (1)$$

where age (t) is time in Ma. This function is displayed in Fig. 9a and yields a realistic present-day oceanic crust production rate of $6.1 \times 10^{16} \text{g a}^{-1}$ (Reymer and Schubert 1984). The following calculations clearly depend on the exact shape of this function but we reiterate that the purpose of this calculation is to test the hypothesis of TTG origin by direct slab melting, in which a higher oceanic crust production rate is implicit. In the next step, we estimate potential shallow mantle temperature (T_{PSM}). Galer and Mezger (1998) have given a comprehensive review of estimated cooling rates for the Earth. Using a present-day T_{PSM} of 1,350 °C and a mean time-averaged cooling rate of 45 °C Ga⁻¹, we obtain a T_{PSM} of 1,555 °C at time zero. We describe the temporal evolution of T_{PSM} with a slightly exponential decay function (Fig. 9b):

$$T_{\text{PSM}} = 1,555 \text{ °C} \cdot e^{-0.031t} \quad (2)$$

which gives a present-day T_{PSM} of 1,350 °C. We do not regard this function to be valid for the Hadean era

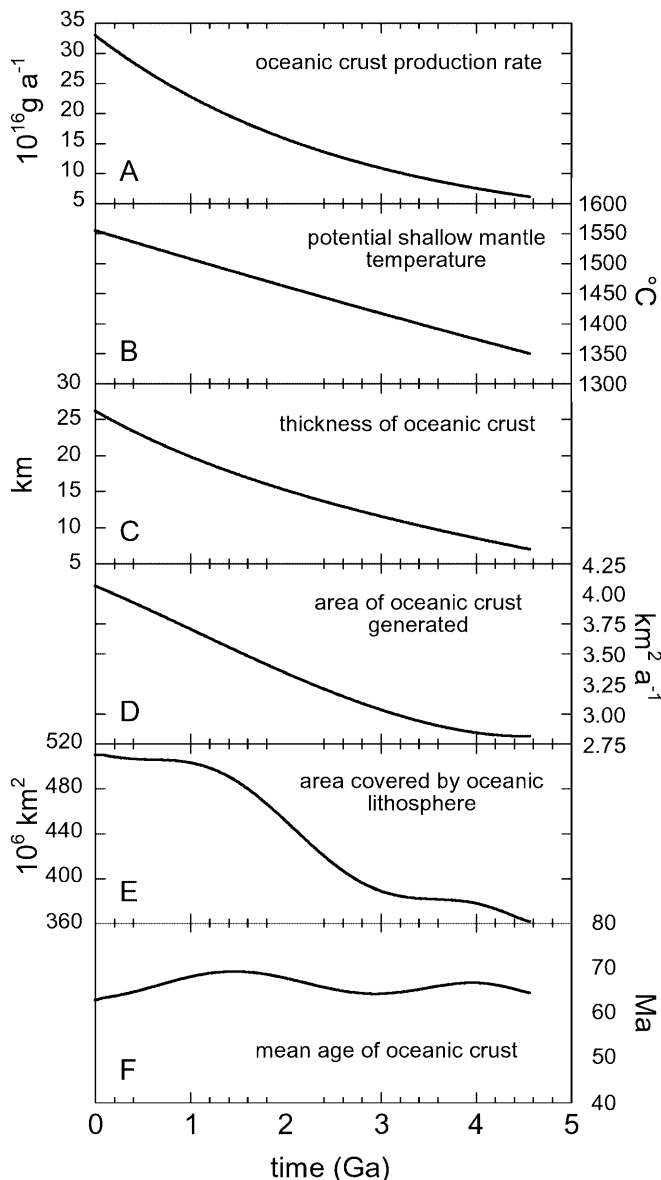


Fig. 9a-f. Time series of calculated **a** oceanic crust production rate, **b** potential shallow mantle temperature, **c** thickness of oceanic crust, **d** area of annually generated oceanic crust, **e** area covered by oceanic lithosphere, and **f** mean age of oceanic crust (for details of calculation see text)

during which subduction may not have operated. Oceanic crustal thickness (h) can be calculated as a function of temperature (T_{PSM}) using isentropic melting models. In combination with Eq. (2), we obtain oceanic crustal thickness as a function of time (t). In this calculation we adopted the results of isentropic batch melting models by Iwamori et al. (1995), using an entropy change (ΔS) of $350 \text{ J kg}^{-1} \text{ K}^{-1}$. It is important to note that relative change of thickness predicted by any isentropic melting model (Fig. 9c) is much greater than the relative change in T_{PSM} because of the exponential increase of melt fraction with T_{PSM} . There are still many uncertainties as to how efficiently melt is extracted from the mantle

column (and what thickness the resulting crust attains) but a general decrease of oceanic crustal thickness with time seems unavoidable.

The rate of ocean floor production (i.e. spreading rate) can then be obtained by division of the crust production rate (Φ) by the crust thickness (h) for any given mean density of oceanic crust. For a density of 2.85 g cm^{-3} we obtain a present rate of ocean floor production of ca. $3.0 \text{ km}^2 \text{ a}^{-1}$ which, by definition, is very similar to the estimate of Reymer and Schubert (1984), itself an input parameter for Eq. (1). The somewhat surprising finding for the past is that spreading rate has only varied between ca. 3.0 and $4.5 \text{ km}^2 \text{ a}^{-1}$ through geological time. These calculations show that oceanic crustal thickness has to be considered when attempting to estimate past spreading rates. Thus, we disagree with Martin (1986) and subsequent proponents that spreading rates were two to three times higher during the Archaean.

The real issue, however, is to estimate the mean age of oceanic lithosphere prior to subduction. In view of the unconstrained length of active margins and ridges in the past, we assume an equilibrium between oceanic crust production and destruction (Parsons 1982). We therefore estimate the mean age of oceanic lithosphere by calculating the time it would take to cover half the area occupied by oceanic basins ($T_{1/2\text{OB}}$), with new oceanic lithosphere created at the spreading rate shown in Fig. 9d. For the present situation this estimate predicts a mean age of oceanic crust of 59 Ma, which is in good agreement with independent estimates. In order to perform this calculation for the past, we first have to estimate the temporal change in area covered by ocean basins. We used the continental mass versus time curve of Collerson and Kamber (1999) and a present-day area occupied by continents and continental margins of $1.48 \times 10^8 \text{ km}^2$. Our estimate (Fig. 9e) assumes constant continental thickness. If Archaean continents were thicker (as argued by Galer and Mezger 1998), we would slightly underestimate the area of ocean basins. Regardless, because Archaean ocean basins covered a larger area, the somewhat higher spreading rates are almost compensated and the mean age of oceanic crust has only varied slightly with time (Fig. 9f). This finding appears to confirm Parsons' (1982) prediction that the plate driving force has not varied strongly with time. Therefore, if the Archaean mantle was indeed hotter, it would not imply that at the time of subduction, oceanic lithosphere was significantly hotter than it is today. Rather, it appears that the most likely mechanism to accommodate higher Archaean heat loss was by creation of a thicker oceanic plate.

These basic considerations are too simplistic and the parameters derived in Fig. 9 should not be used as an approximation to reality, yet the calculations demonstrate that the superficially logical link between proposed Archaean slab melting and hotter Archaean oceanic lithosphere is, in fact, flawed. We emphasize that the true issue which governed the thermal structure of subducted Archaean oceanic plates is the

question whether thick plates (such as those used in this calculation) could at all be subducted. Continental crust volume versus time curves certainly document great variability in net crustal growth rates throughout the Archaean (e.g. Kramers and Tolstikhin 1997; Collerson and Kamber 1999) which may indicate that efficient subduction in the modern sense only became feasible beyond a certain maximum thickness of oceanic plates.

Conclusion

A review of Phanerozoic adakite trace element geochemistry confirms that these melts contain a component which is derived by direct melting of subducted slabs but pure slab melts do not appear to exist. Nevertheless, rocks with adakite affinity can be distinguished from mantle wedge-derived arc magmas by element ratios which are most strongly fractionated by refertilisation of the depleted mantle wedge (i.e. reflecting element fractionation during slab dehydration). Using these fingerprints, we conclude that Archaean TTGs are melting products from the supra-subduction zone mantle wedge. TTGs thus inherit typical continental element ratios from the refertilised mantle wedge, much in the same way as modern arc magmas.

A key feature of generation of continental crust is dehydration-related element transport in the mantle. Preferential element transport by fluids requires dehydration due to pressure-induced phase changes, which in turn requires environments of low geothermal gradients in the mantle. It is difficult to imagine tectonic environments other than subduction zones in which relatively cold material is deeply entrained into the mantle such that dehydration occurs before direct melting. The hypothesis that Archaean TTGs are adakites is not supported by in-depth study of their trace element geochemistry nor can it be expected from the Earth's cooling history.

Evidence for a secular decrease in HREE depletion in arc-related, highly silicic magmas remains strong but cannot be interpreted to indicate a prevalence of direct slab melting in the Archaean. REE geochemistry of pelites and shales demonstrates that the degree of HREE depletion of the bulk of the material extracted along arcs has remained constant through time (Condie 1993). It thus appears that the stronger HREE depletion of ancient arc magmas simply reflects more efficient crustal differentiation.

Acknowledgements Journal reviewers J. Ryan and K. Condie significantly improved this manuscript. S.J.G. Galer is thanked for discussing oceanic plate production rates. Any remaining shortcomings of this paper are entirely the authors' responsibility. Stephen Moorbath kindly provided the Greenland tonalite samples. This research was funded by the Swiss National Science Foundation grant 8220-050352 to BSK, and by an ARC Large Grant (#A00104754) to KDC. Our trace element and isotope facility is supported by UQ.

References

- Aguillón-Robles A, Calmus T, Benoit M, Bellon H, Maury RC, Cotten J, Bourgois J, Michaud F (2001) Late Miocene adakites and Nb-enriched basalts from Vizcaion Peninsula, Mexico: Indicators of East Pacific Rise subduction below southern Baja California? *Geology* 29:531–534
- Arth JG, Barker F (1976) Rare-earth partitioning between hornblende and dacitic liquid and implications for genesis of trondhjemitic-tonalitic magmas. *Geology* 4:534–546
- Ayers J (1998) μ modeling of aqueous fluid – peridotite interaction in the mantle wedge of subduction zones. *Contrib Mineral Petrol* 132:390–404
- Bau M (1996) Controls on the fractionation of isovalent trace elements in magmatic and aqueous systems – evidence from Y/Ho, Zr/Hf, and lanthanide tetrad effect. *Contrib Mineral Petrol* 123:323–333
- Becker H, Jochum KP, Carlson RW (2000) Trace element fractionation during dehydration of eclogites from high-pressure terranes and the implications for element fluxes in subduction zones. *Chem Geol* 163:65–99
- Blundy J, Cashman K (2001) Ascent-driven crystallisation of dacite magmas at Mount St Helens, 1980–1986. *Contrib Mineral Petrol* 140:631–650
- Bourdon E, Eissen JP, Monzier M, Robin C, Martin H, Cotten J, Hall ML (2002) Adakite-like lavas from Antisana volcano (Ecuador): evidence for slab melt metasomatism beneath the Andean northern volcanic zone. *J Petrol* 43:199–217
- Brenan JM, Shaw HF, Ryerson FJ (1995a) Experimental evidence for the origin of lead enrichment in convergent-margin magmas. *Nature* 378:54–56
- Brenan JM, Shaw HF, Ryerson FJ, Phinney DL (1995b) Mineral-aqueous fluid partitioning of trace elements at 900 °C and 2.0 GPa: constraints on the trace element chemistry of mantle and deep crustal fluids. *Geochim Cosmochim Acta* 59:3331–3350
- Brenan JM, Ryerson FJ, Shaw HF (1998a) The role of aqueous fluids in the slab-to-mantle transfer of boron, beryllium, and lithium during subduction: experiments and models. *Geochim Cosmochim Acta* 62:3337–3347
- Brenan JM, Neroda E, Lundstrom CC, Shaw HF, Ryerson FJ, Phinney DL (1998b) Behaviour of boron, beryllium, and lithium during melting and crystallisation: constraints from mineral-melt partitioning experiments. *Geochim Cosmochim Acta* 62:2129–2141
- Brophy JG (1989) Can high-alumina arc basalt be derived from low-alumina arc basalt? Evidence from Kanaga Island, Aleutian Arc, Alaska. *Geology* 17:333–336
- Brown L, Klein J, Middleton R, Selwyn Sacks I, Tera F (1982) ^{10}Be in island-arc volcanoes and implications for subduction. *Nature* 299:718–720
- Bruce MC, Niu Y (2000a) Early Permian supra-subduction assemblage of the South Island terrane, Percy Isles, New England Fold Belt, Queensland. *Aust J Earth Sci* 47:1077–1085
- Bruce MC, Niu Y (2000b) Evidence for Palaeozoic magmatism recorded in the Late Neoproterozoic Marlborough ophiolite, New England Fold Belt, central Queensland. *Aust J Earth Sci* 47:1065–1076
- Campbell IH, Griffiths RW (1993) The evolution of the mantle's chemical-structure. *Lithos* 30:389–399
- Chan LH, Leeman WP, You CF (1999) Lithium isotopic composition of Central American volcanic arc lavas: Implications for modification of the sub-arc mantle by slab-derived fluids. *Chem Geol* 160:255–280
- Collerson KD, Kamber BS (1999) Evolution of the continents and the atmosphere inferred from Th-U-Nb systematics of the depleted mantle. *Science* 283:1519–1522
- Condie KC (1993) Chemical composition and evolution of the upper continental crust: Contrasting results from surface samples and shales. *Chem Geol* 104:1–37

- Currie KL, Whalen JB, Davis WJ, Longstaffe FJ, Cousens BL (1998) Geochemical evolution of peraluminous plutons in southern Nova Scotia, Canada – a pegmatite-poor suite. *Lithos* 44:117–140
- Defant MJ, Drummond MS (1990) Derivation of some modern arc magmas by melting of young subducted lithosphere. *Nature* 347:662–665
- Defant MJ, Clark LF, Steward RH, Drummond MS, de Boer JZ, Maury RC, Bellon H, Jackson TE, Restrepo JF (1991a) Andesite and dacite genesis via contrasting processes: the geology and geochemistry of El Valle Volcano, Panama. *Contrib Mineral Petrol* 106:309–324
- Defant MJ, Richerson PM, de Boer JZ, Steward RH, Maury R, Bellon H, Drummond MS, Feigenson MD, Jackson TE (1991b) Dacite genesis via both slab melting and differentiation: Petrogenesis of La Yeguada Volcanic Complex, Panama. *J Petrol* 32:1101–1142
- Drummond MS, Defant MJ, Kepezhinskas PK (1996) Petrogenesis of slab-derived trondhjemite-tonalite-dacite/adakite magmas. *Trans R Soc Edinburgh Earth Sci* 87:205–215
- Ewart A (1979) A review of the mineralogy and chemistry of Tertiary-recent dacitic, latitic, rhyolitic, and related salic volcanic rocks. In: Barker F (ed) *Trondhjemites, dacites, and related igneous rocks*. Elsevier, New York, pp 13–122
- Ewart A, Collerson KD, Regelous M, Wendt JI, Niu Y (1998) Geochemical evolution within the Tonga-Kermadec-Lau arc-back-arc systems: the role of varying mantle wedge composition in space and time. *J Petrol* 39:331–368
- Galer SJG (1991) Interrelationships between continental freeboard, tectonics, and mantle temperature. *Earth Planet Sci Lett* 105:214–228
- Galer SJG, Mezger K (1998) Metamorphism, denudation and sea level in the Archaean and cooling of the Earth. *Precambrian Res* 92:389–412
- Green TH (1995) Significance of Nb/Ta as an indicator of geochemical processes in the crust-mantle system. *Chem Geol* 120:347–359
- Grove TL, Baker MB (1984) Phase equilibrium controls on the tholeiitic versus calc-alkaline differentiation trends. *J Geophys Res* 89:3253–3274
- Gutscher MA, Maury R, Eissen JP, Bourdon E (2000) Can slab melting be caused by flat subduction? *Geology* 28:535–538
- Henry C, Burkhard M, Goffé B (1996) Evolution of synmetamorphic veins and their wallrocks through a Western Alps transect: no evidence for large-scale fluid flow. Stable isotope, major- and trace element systematics. *Chem Geol* 127:81–109
- Hofmann AW (1988) Chemical differentiation of the Earth: the relationship between mantle, continental crust, and oceanic crust. *Earth Planet Sci Lett* 90:297–314
- Iwamori H, McKenzie D, Takahashi E (1995) Melt generation by isentropic upwelling. *Earth Planet Sci Lett* 134:253–266
- Jahn B-M, Condie KC (1995) Evolution of the Kaapvaal Craton as viewed from geochemical and Sm-Nd isotopic analyses of intracratonic pelites. *Geochim Cosmochim Acta* 59:2239–2258
- Jochum KP, McDonough WF, Palme H, Spettel B (1989) Compositional constraints on the continental lithospheric mantle from trace elements in spinel peridotite xenoliths. *Nature* 340:548–550
- Kamber BS, Collerson KD (2000) Role of ‘hidden’ deeply subducted slabs in mantle depletion. *Chem Geol* 166:241–254
- Kamber BS, Moorbath S (1998) Initial Pb of the Amitsoq gneiss revisited: implication for the timing of early Archaean crustal evolution in West Greenland. *Chem Geol* 150:19–41
- Kay RW (1978) Aleutian magnesian andesites: melts from subducted Pacific Ocean crust. *J Volcanol Geotherm Res* 4:117–132
- Keppler H (1996) Constraints from partitioning experiments on the composition of subduction-zone fluids. *Nature* 380:237–240
- Klein M, Stosh H-G, Seck HA (1997) Partitioning of high field-strength and rare-earth elements between amphibole and quartz-dioritic to tonalitic melts: an experimental study. *Chem Geol* 138:257–271
- Kramers JD (1988) An open-system fractional crystallization model for very early continental crust formation. *Precambrian Res* 38:281–295
- Kramers JD, Tolstikhin IN (1997) Two terrestrial lead isotope paradoxes, forward transport modelling, core formation and the history of the continental crust. *Chem Geol* 139:75–110
- Le Maître RW et al. (1989) A classification of igneous rocks and glossary of terms. Blackwell, Oxford
- Marsh BD (1976) Some Aleutian andesites: their nature and source. *J Geol* 84:27–45
- Marsh BD, Leitz RE (1978) Geology of Amak Island, Aleutian Islands, Alaska. *J Geol* 87:715–723
- Martin H (1986) Effect of steeper Archaean geothermal gradient on geochemistry of subduction zone magmas. *Geology* 14:753–756
- McDonald GD, Collerson KD, Kinny PD (1997) Late Archaean and early Proterozoic crustal evolution of the Mount Isa Block, northwestern Queensland, Australia. *Geology* 25:1095–1099
- McDonough WF, Sun SS (1995) The composition of the Earth. *Chem Geol* 120:223–253
- McKenzie D, Bickle MJ (1988) The volume and composition of melt generated by extension of the lithosphere. *J Petrol* 29:625–679
- McLennan SM (2001) Relationships between the trace element composition of sedimentary rocks and upper continental crust. G-cubed 2:2000GC000109
- McLennan SM, Hemming S (1992) Sm/Nd elemental and isotopic systematics in sedimentary rocks. *Geochim Cosmochim Acta* 56:887–898
- Miller DM, Goldstein SL, Langmuir CH (1994) Cerium/lead and lead isotope ratios in arc magmas and the enrichment of lead in the continents. *Nature* 368:514–520
- Morris PA, Witt WK (1997) Geochemistry and tectonic setting of two contrasting Archaean felsic volcanic associations in the Eastern Goldfields, Western Australia. *Precambrian Res* 83:83–107
- Münker C (1998) Nb/Ta fractionation in a Cambrian arc/back arc system, New Zealand: source constraints and application of refined ICPMS techniques. *Chem Geol* 144:23–45
- Müntener O, Kelemen PB, Grove TL (2001) The role of H₂O during crystallisation of primitive arc magmas under uppermost mantle conditions and genesis of igneous pyroxenites: an experimental study. *Contrib Mineral Petrol* 141:643–658
- Myers JD, Marsh BD (1987) Aleutian lead isotopic data: additional evidence for the evolution of lithospheric plumbing systems. *Geochim Cosmochim Acta* 51:1833–1842
- Nägler TF, Kramers JD (1998) Nd isotopic evolution of the upper mantle during the Precambrian: Models, data and the uncertainty of both. *Precambrian Res* 91:233–252
- Nutman AP, Bennett VC, Friend CRL, Norman MD (1999) Meta-igneous (non-gneissic) tonalites and quartz-diorites from an extensive ca. 3800 Ma terrain south of the Isua supracrustal belt, southern West Greenland: constraints on early crust formation. *Contrib Mineral Petrol* 137:364–388
- Parsons B (1982) Causes and consequences of the relation between area and age of the ocean floor. *J Geophys Res* 87:289–302
- Peate DW, Pearce JA, Hawkesworth CJ, Colley H, Edwards CMH, Hirose K (1997) Geochemical variations in Vanuatu arc lavas: the role of subducted material and a variable mantle wedge composition. *J Petrol* 38:1331–1358
- Prouteau G, Maury RC, Sajona FG, Cotten J, Cotten JL (2000) Behavior of niobium, tantalum and other high field strength elements in adakites and related lavas from The Philippines. *Island Arc* 9:487–498
- Prouteau G, Maury RC, Pubellier M, Cotten J, Bellon H (2001) Le magmatisme post-collisionnel du Nord-Ouest de Bornéo, produit de la fusion d’un fragment de croûte océanique ancré dans le manteau supérieur. *Bull Soc Géol Fr* 172:319–332
- Reay A, Parkinson D (1997) Adakites from Solander Island, New Zealand. *N Z J Geol Geophys* 40:121–126
- Reymer A, Schubert G (1984) Phanerozoic addition rates to the continental crust and crustal growth. *Tectonics* 3:63–77

- Ridley JR, Kramers JD (1990) The evolution and tectonic consequences of a tonalitic magma layer within Archean continents. *Can J Earth Sci* 27:219–228
- Romick JD, Kay SM, Kay RW (1992) The influence of amphibole fractionation on the evolution of calc-alkaline andesite and dacite tephra from the central Aleutians, Alaska. *Contrib Mineral Petrol* 112:101–118
- Rudnick RL, Fountain DM (1995) Nature and composition of the continental crust: a lower crustal perspective. *Rev Geophys* 33:267–309
- Ryan JG, Langmuir CH (1988) Beryllium systematics in young volcanic rocks: implications for ^{10}Be . *Geochim Cosmochim Acta* 52:237–244
- Ryan JG, Langmuir CH (1993) The systematics of boron abundances in young volcanic rocks. *Geochim Cosmochim Acta* 51:1727–1741
- Ryan JG, Morris J, Tera F, Leeman DH, Tsvetkov A (1995) Cross-arc geochemical variations in the Kurile arc as a function of slab depth. *Science* 270:625–627
- Schmidt MW, Poli S (1998) Experimentally based water budgets for dehydrating slabs and consequences for arc magma generation. *Earth Planet Sci Lett* 163:361–379
- Shinjo R (1999) Geochemistry of high Mg andesites and the tectonic evolution of the Okinawa Trough Ryukyu arc system. *Chem Geol* 157:69–88
- Smith DR, Leeman WP (1987) Petrogenesis of Mount St. Helens dacitic magmas. *J Geophys Res* 92:10,313–10,334
- Smithies RH (2000) The Archean tonalite-trondhjemite-granodiorite (TTG) series is not an analogue of Cenozoic adakite. *Earth Planet Sci Lett* 182:115–125
- Stacey FD (1980) The cooling Earth: a reappraisal. *Phys Earth Planet Inter* 22:89–96
- Stalder R, Foley SF, Brey GP, Horn I (1998) Mineral-aqueous fluid partitioning of trace elements at 900–1200 °C and 3.0–5.7 GPa: new experimental data for garnet, clinopyroxene, and rutile, and implications for mantle metasomatism. *Geochim Cosmochim Acta* 62:1781–1801
- Stern CR, Kilian R (1996) Role of the subducted slab, mantle wedge and continental crust in the generation of adakites from the Andean Austral Volcanic Zone. *Contrib Mineral Petrol* 123:263–281
- Sun S-S, McDonough WF (1989) Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. In: Saunders AD, Norry MJ (eds) *Magmatism in ocean basins*. Geol Soc Lond Spec Publ, pp 313–345
- Tate MC, Norman MD, Johnson SE, Fanning CM, Anderson JL (1999) Generation of tonalite and trondhjemite by subvolcanic fractionation and partial melting in the Zarza intrusive complex, Western Peninsular Ranges Batholith, Northwestern Mexico. *J Petrol* 40:983–1010
- Tatsumi Y, Eggins S (1995) Subduction zone magmatism. Blackwell, Cambridge, USA
- Tatsumi Y, Kogiso T (1997) Trace element transport during dehydration processes in the subducted oceanic crust. 2. Origin of chemical and physical characteristics in arc magmatism. *Earth Planet Sci Lett* 148:207–221
- Tomascak PB, Ryan JG, Defant MJ (2000) Lithium isotope evidence for light element decoupling in the Panama subarc mantle. *Geology* 28:507–510
- von Drach V, Marsh BD, Wasserburg GJ (1986) Nd and Sr isotopes in the Aleutians: multicomponent parenthood of island-arc magmas. *Contrib Mineral Petrol* 92:13–34
- Whitehouse M, Kamber BS, Moorbath S (1999) Age significance of ion-microprobe U-Th-Pb zircon data from early Archean rocks of West Greenland – a reassessment based on new combined ion-microprobe and imaging studies. *Chem Geol* 160:204–221
- Woodhead JD, Eggins SM, Johnson RW (1998) Magma genesis in the New Britain Island arc: further insights into melting and mass transfer processes. *J Petrol* 39:1641–1668
- Yogodzinski GM, Kay RW, Volynets ON, Kolosov AV, Kay SM (1995) Magnesian andesite in the western Aleutian Komandorsky region: implications for slab melting and processes in the mantle wedge. *GSA Bull* 107:505–519
- Yogodzinski GM, Lees JM, Churikova TG, Dorendorf F, Woerner G, Volynets ON (2001) Geochemical evidence for the melting of subducting oceanic lithosphere at plate edges. *Nature* 409:500–504
- Yumul GP, Dimalanta CB, Bellon H, Faustino DV, De Jesus JV, Tamayo RA, Jumawan FT (2000) Adakitic lavas in the Central Luzon back-arc region, Philippines: lower crust partial melting products? *Island Arc* 9:499–512
- Zack T, Foley SF, Jenner GA (1997) A consistent partition coefficient set for clinopyroxene, amphibole and garnet from laser ablation microprobe analysis of garnet pyroxenites from Kakanui, New Zealand. *N Jahrb Miner Abh* 172:23–41