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Importance of water for Archaean granitoid petrology: a comparative study of TTG and potassic granitoids from Barberton Mountain Land, South Africa

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Abstract A new model for Archaean granitoid magmatism is presented which reconciles the most important geochemical similarities and differences between tonalite–trondhjemite–granodiorite (TTG) and potassic granitoids. Trace element abundances reveal a strong arc magmatism signature in all studied granitoids from Barberton Mountain Land. Characteristic features include HFSE depletion as well as distinct enrichment peaks of fluid-sensitive trace elements such as Pb in N-MORB normalisation, clearly indicating that all studied granitoids are derived from refertilised mantle above subduction zones. We envisage hydrous basaltic (s.l.) melts as parental liquids, which underwent extensive fractional crystallisation. Distinctive residual cumulates evolved depending on initial water content. High-H_2O melts crystallised garnet/amphibole together with pyroxenes and minor plagioclase, but no olivine. This fractionation path ultimately led to TTG-like melts. Less hydrous basaltic melts also crystallised garnet/amphibole, but the lower compatible element content indicates that olivine was also a liquidus phase. Pronounced negative Eu-anomalies of the granitic melts, correlating with Na, Ca and Al, indicate plagioclase to be of major importance. In the context of our model, the post-Archaean disappearance of TTG and concomitant preponderance of granites (s.l.), therefore, is explained with secular decrease of aqueous fluid transport into subduction zones and/or efficiency of deep fluid release from slabs.

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Introduction

It is widely accepted that, since the Archaean, typical continental crust has formed by peridotite melting in the suprasubduction zone mantle wedge where fluids from dehydrating slabs lower solidus temperatures of mantle peridotite relative to anhydrous conditions (e.g. Stolper and Newman 1994; Wyllie 1995; Ayers 1998; Ulmer 2001). The most straightforward expression of the preponderance of suprasubduction zone melting in continental crust formation is the similarity in trace element composition between average post-Archaean continental crust and magmas that form along recent arcs where the melt source can be inferred from seismic, chemical and isotopic evidence (Woodhead et al. 1998; Macdonald 2000, among others). The process of differentiation of the original basaltic melt into constituents of continental crust is complex. Direct uncontaminated differentiation products of mantle melts are only rarely found. Interaction with pre-existing crust; in particular, assimilation during fractional crystallisation (AFC) almost invariably leads to chemical and isotopic mixing phenomena. Against this complex background, two main petrological differences between post-Archaean and Archaean continental crust can nevertheless be clearly seen. Both point to a fundamental change in the nature of crust formation processes approximately at the end of the Archaean.

The first of these concerns the bimodal distribution of Archaean continental rock types with abundance peaks at basaltic and granitoid compositions, the trondhjemite–basalt suite of Barker and Arth (1976), compared with the unimodal composition of post-Archaean continental crust that is of andesitic composition.

The second difference lies in the high proportion of relatively K-poor, but highly siliceous Archaean rocks that are known as the tonalite–trondhjemite–granodiorite (TTG) suite. Commonly, both differences are ascribed to a threshold in secular mantle cooling. In this context, the petrological and geochemical characteristics of TTG are explained by direct melting of oceanic crust

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in subduction zones, which ceased or became insignificant at the end of the Archaean (e.g. Defant and Drummond 1990; Martin 1999). Here, we suggest an alternative explanation based on a comparison between Archaean TTG and more potassic granitoids [the granodioritic–granitic–monzogranitic (GGM) series of de Wit (1998)] from Barberton Mountain Land. In our model, both suites of rocks are derived from the suprasubductional mantle wedge, where peridotite melting is triggered by slab dehydration. The disappearance of TTG we ascribe to decreasing water content of the mantle-derived melt, which indirectly reflects the efficiency with which water was transported into the suprasubductional mantle wedge. Different amounts of fluids in the mantle wedge-derived melt have led to distinct fractionating assemblages for TTG and GGM, hence identifying aqueous fluids as the driving force behind change in continental petrology.

Review of existing models

Three major competing models for TTG formation are presently discussed in the literature. The purpose of this brief review is to illustrate their strengths and deficiencies rather than providing a full summary of their rationale and logic.

In the most widely applied model, TTG are interpreted as direct melts from subducted oceanic crust at garnet–amphibolite to eclogite facies (Martin 1986; Defant and Drummond 1990; Drummond and Defant 1990). This model mainly addresses the distinct REE patterns of TTG. Residual garnet and amphibole are also compatible with further evidence, such as Sr/Y ratio. Martin (1999) argues that, due to the much higher heat flow in the Archaean Earth, conditions for slab-melting were achieved more easily than today. This rationale apparently explains the much higher abundance of TTG in the Archaean compared with the post-Archaean Earth. The original advocates of this proposal (Martin 1986; Drummond and Defant 1990) have never expanded their test to the full range of trace element data that is now available for many TTG suites and modern adakites. Kamber et al. (2002) have recently compared specific fluid-sensitive trace element ratios of TTG with those of modern adakite. They found that, in agreement with the compilation of Condie (1993) and data presented by Nutman et al. (1999), TTG have a very strong signature inherited from metamorphic dehydration. Thus, the strong overenrichment in fluid-mobile elements such as Pb that is unequivocally attributed to advection of soluble elements with aqueous fluid from dehydrating slab is very pronounced in TTG. This is in marked contrast to modern adakites (i.e. true melts of eclogite slabs), which do not show overenrichment in those elements. In summary, the main problem with the direct slab-melt hypothesis is to explain why TTG are so similar to average modern arc-generated upper crust in almost all aspects other than the extent of HREE depletion.

Smithies' (2000) comparison of Cenozoic adakites and Archaean TTG in terms of the major element chemistry also challenged the view that TTG originated from direct slab-melting. Smithies (2000) found that most, if not all Cenozoic adakite suites include more magnesian and less siliceous chemistries, which are interpreted to have resulted from interaction of the adakitic melt with asthenospheric mantle during ascent through the wedge. Smithies (2000) claimed that TTG did not show such interaction and that their parental melts did not form in the mantle nor ascend through it. As an alternative, Smithies (2000) postulated that at least in terms of major elements, Archaean TTG resembled Phanerozoic Na-rich granitoids, which have been postulated to form by partial melting of a basaltic underplate at the bottom of over-thickened continental crust (Atherton and Petford 1993). In our view, Smithies (2000) provided strong arguments against the adakite–TTG connection. Unfortunately, we are unable to isolate a key factor in Smithies' model, whose temporal evolution could explain the rather fundamental change in granitoid petrology with time.

Kamber et al. (2002), based on their observation that TTG have trace element systematics that can be attributed to fertilisation of peridotite by aqueous fluids from dehydrating slabs, have proposed that TTG must have formed in the suprasubductional mantle wedge. However, Kamber et al. (2002) had to make the ad hoc assumption that the strong depletion in HREE and the LREE overenrichment of TTG could have been a result of fractional crystallisation. Thus, these authors made untested speculations regarding the liquid line of descent of Archaean TTG.

Here we argue that the recently published experimental results of Müntener et al. (2001) provide significant new insight that is relevant not only for TTG, but for other Archaean granitoids as well. We next summarise those findings of Müntener et al. (2001) that we identify to be relevant for Archaean petrogenesis before we formulate an alternative model for TTG formation, which reconciles the three major lines of evidence used by the previously conflicting models: (1) the overabundance of slab-derived fluid-mobile elements; (2) the strong LREE/HREE fractionation; and (3) high concentrations of highly compatible trace elements.

Evidence from crystallisation experiments of wet basaltic melts at high pressure

The role and influence of H_2O content on the crystallisation sequence of basaltic parental melts evolving from suprasubductional peridotite melting has been widely discussed in the recent literature (e.g. Sisson and Grove 1993; Baker et al. 1994; Sobolev and Chaussidon 1996; Müntener et al. 2001; Grove et al. 2002; Wood and Blundy 2002), because aqueous fluids were suspected to have crucial influence on crust formation mechanisms. Müntener et al. (2001) performed experiments under

uppermost mantle conditions and demonstrated the strong influence of water on the evolving crystallisation sequence. At water-undersaturated conditions olivine, clinopyroxene, orthopyroxene and plagioclase crystallise in various proportions. According to Müntener et al.'s experiments (2001), however, a different fractionating assemblage evolves under water-saturated conditions, where the SiO_2-poor phases garnet and hornblende, but not plagioclase, join the websteritic cumulate residue. The late appearance or even absence of plagioclase under water-saturated conditions has long been known from experiments and has been invoked to explain certain aspects of continental differentiation trends (e.g. Grove and Baker 1984; Sisson and Grove 1993). However, from a TTG perspective, the most important finding of Müntener et al. (2001) is the appearance of garnet under water-saturated conditions because of its inherent ability to generate some of the salient geochemical characteristics of TTG (e.g. Drummond and Defant 1990; Martin 1999; Smithies 2000).

An additional important insight from water-undersaturated experiments (Sisson and Grove 1993; Baker et al. 1994) regards prolonged olivine and clinopyroxene crystallisation from basaltic melts as water contents increase in the remaining melt. The compatible element content of TTG (and GGM) requires that, as discussed later, the presence of both mineral phases was minimised during fractional crystallisation (although pyroxene can incidentally help to increase the LREE/HREE ratio). Experimental results indicate that olivine crystallisation occurs over a small temperature interval due to lowering of the liquidus temperature with higher water contents and that olivine-free cumulates can arise from peritectic reaction between olivine and melt to pyroxene (Müntener et al. 2001). However, these experimental findings cannot simply be translated into natural processes because melting of more hydrous mantle yields higher degree melts, which also have higher initial silica contents (Baker et al. 1994). In other words, parental melts from a very hydrous mantle wedge require less fractionation of olivine and pyroxene to produce melt derivatives of andesitic composition. This implies that the experiments by Müntener et al. (2001), who used basaltic andesite as starting material, are particularly relevant to our model.

In most regards, the new experiments by Müntener et al. (2001) agree well with the results of Sisson and Grove (1993) in that with increasing water pressure the temperatures at which anhydrous minerals appear are suppressed in the order: plagioclase > olivine > pyroxene ≥ spinel. The fractionation sequence under water-saturated conditions does not require olivine because garnet, hornblende and/or spinel can also drive silica enrichment in the derivative liquid, which is innately higher in silica content compared with anhydrous parental melts. We propose that this marked difference in fractionation sequence not only has importance for the solution of the andesitic mass balance problem (the main research focus of the paper by Müntener et al. 2001), but that the water content of basaltic (s.l.) suprasubduction zone melts also provides an explanation for most major and trace element characteristics of TTG and GGM.

Geologic setting and sampling

We derived our model for TTG petrology from a case study of rocks from the well-known mid-Archaean region of Barberton Mountain Land (BML), South Africa (Fig. 1). U–Pb zircon ages for BML TTG, which intruded the greenstone units of the Barberton greenstone belt, range from 3.5 to 3.2 Ga (Kamo and Davis 1994). Later deformation affected both greenstones and TTG, but not GGM, for which U–Pb zircon ages indicate a rather long period of emplacement from 3.2 to 2.7 Ga. However, the vast majority intruded at 3.1 Ga (Kamo and Davis 1994). GGM intrusion into the older TTG is observed at high crustal level as relatively thin sheets of large horizontal extent (de Wit 1998). Field relationships further reveal that GGM intrusions were fed by dikes cutting older TTG (Hunter 1974; de Wit 1992). We refer to Lowe (1999) and references therein for a more detailed geological overview of the study area.

Analytical methods

Major and trace elements for GGM and TTG of the BML are presented in Tables 1 and 2, respectively. XRF analyses (major elements) were performed at the University of Fribourg, Switzerland, and followed standard procedures. Trace elements were analysed using a VG Plasma Quad 2+ at the University of Queensland, Australia, following the procedures described in Murphy et al. (2002).

A common origin of Archaean granitoids by extensive fractional crystallisation of mantle-wedge-derived basaltic magma

Fractional crystallisation is often associated with assimilation (AFC), recharge of the magma chamber and eruption, which leads to geochemical mixing phenomena in the melt. Recharge and eruption processes are mainly relevant in long-lasting magma chambers and active volcanoes in an island arc setting (Defant and Nielsen 1990). They do not apply to our model for granitoid genesis. Although assimilation of country rocks during ascent of the magma is very likely to have occurred, liquid lines of descent for major element pairs in the contaminated melts nevertheless strongly resemble those of pure fractional crystallisation series (Defant and Nielsen 1990) and initially represent the composition of the melting region, i.e. mantle (Grove et al. 2002). While the initial trace element budget is mainly controlled by slab-derived fluids (Grove et al. 2002) many incompatible element characteristics are more sensitive to assimi-

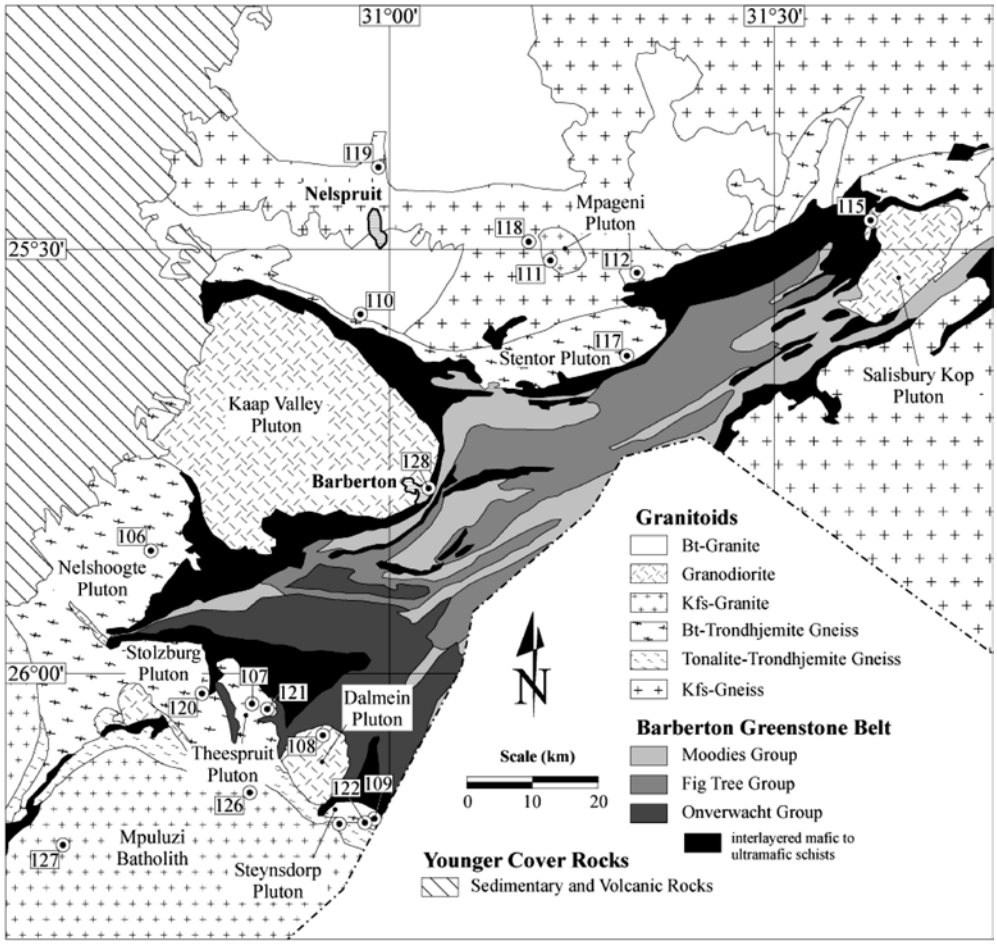

Fig. 1 Simplified geological map of the Barberton Mountain Land (*BML*; South Africa) showing the sample locations (from Schoenberg 2000)

lation than major elements and may serve as tracers for contamination. Certain characteristics, such as heavy REE and HFSE depletion or high concentrations of strongly compatible elements, would not survive large degrees of assimilation.

Geochemical signature of slab-derived fluids in all Archaean granitoids from the Barberton Mountain Land

There is a strong general similarity between GGM and TTG in N-MORB-normalised trace element patterns (Fig. 2). Importantly, both rock types show the typical signature of slab dehydration with overenrichment in fluid-sensitive elements (e.g. Pb) and depletion of Nb and Ta. For example, the Pb/Nd ratios (TTG: 0.548 ± 0.19 and GGM: 0.501 ± 0.44) of both rock groups show strong affinities to typical arc magmas and resemble average post-Archaean continental crust. Both TTG and GGM have sub-chondritic Nb/Ta ratios (TTG: 12.8 ± 2.8 and GGM: 12.9 ± 3.3; note, that GGM sample 99/118 was not included for the Nb/Ta average, because of obvious post-magmatic Ta loss). The sub-chondritic Nb/Ta ratio of continental crust (ca. 12) is another feature that Kamber and Collerson (2000) have attributed to preferential Ta advection from dehydrating slab into the mantle wedge. As recently demonstrated by Kamber et al. (2002), direct slab-melts (i.e. adakites) have considerably higher Nb/Ta ratios, hence there is lack of evidence for preferential retention of Nb over Ta.

The similarity in relative trace element content between TTG and GGM and the strong arc signature of the fluid-mobile elements are difficult to reconcile with the prevailing view that TTG formed by direct melting of oceanic crust. Importantly, the arc geochemical signature of our samples seems to be the rule for Archaean TTG and GGM. For example, Nutman et al. (1999) and Kamber et al. (2002) reported similar patterns for TTG from Greenland and Australia ranging from 3.7 to 2.5 Ga in age. These authors concluded that aqueous fluids played a major role in Archaean granitoid petrogenesis. As the overabundance of fluid-mobile elements reflects the process of metamorphic dehydration, and because dehydration on the scale necessary to produce voluminous magmas is only possible by subduction of vast amounts of hydrated rock into the mantle, it seems unavoidable to conclude that Archaean TTG and GGM were derived from melts that formed in the refertilised mantle wedge. Plenty of evidence can be found in the literature (e.g. de Ronde and de Wit 1994; Lowe 1999, among many others) that some form of plate tectonics

Table 1 Granodioritic–granitic–monzogranitic suite

Pluton Sample ID	Dalmein 99/108	Mpageni 99/111	Salisbury Kop 99/115	Stentor 99/117	Nelspruit 99/118	Nelspruit 99/119	Mpuluzi 99/126	Mpuluzi 99/127
Major elements (wt%)								
SiO_2	69.80	74.30	72.77	77.34	71.95	72.06	72.29	70.00
TiO_2	0.35	0.37	0.32	0.08	0.26	0.34	0.19	0.45
Al_2O_3	15.06	12.34	13.87	12.57	14.39	14.59	14.06	14.51
FeO_T	2.27	1.95	1.89	0.73	1.77	1.75	1.21	2.59
MnO	0.06	0.04	0.04	0.02	0.03	0.02	0.03	0.04
MgO	1.07	0.37	0.66	0.28	0.52	0.59	0.39	0.63
CaO	2.01	1.00	1.86	0.23	1.68	1.68	1.37	1.43
Na_2O	5.34	7.65	5.50	4.94	6.76	4.87	5.86	5.24
K_2O	3.52	5.60	3.59	4.75	3.50	4.18	4.72	4.67
P_2O_5	0.19	0.08	0.13	0.03	0.09	0.10	0.06	0.14
LOI	0.75	0.33	0.63	0.35	0.42	0.55	0.77	0.81
Trace elements (ppm)								
Li	21.2	14.8	21.1	17.0	31.4	40.9	28.4	67.8
Be	2.28	2.36	1.83	0.92	1.22	1.46	3.37	3.21
Sc	3.44	2.52	4.08	2.27	2.17	2.64	3.25	4.84
V	29.1	9.71	24.3	1.98	11.8	19.4	7.82	21.5
Cr	10.1	2.87	7.59	4.37	3.44	10.4	4.19	9.14
Co	5.05	1.43	4.09	0.74	2.56	3.01	1.63	3.57
Ni	6.88	2.25	8.10	3.79	2.88	7.00	3.00	5.72
Cu	7.29	2.41	3.90	8.04	1.23	1.31	0.71	3.72
Zn	64.5	31.8	46.6	11.0	45.1	40.5	43.2	84.0
Ga	17.1	14.0	16.4	13.1	16.4	17.6	18.2	20.4
Rb	100	169	75.5	148	77.2	139	186	201
Sr	593	329	448	21.2	266	291	156	274
Y	17.2	37.8	15.7	25.3	6.50	18.9	18.0	40.2
Zr	182	407	159	86.2	203	282	153	404
Nb	11.7	29.2	10.5	15.4	6.57	10.1	19.3	20.9
Sn	1.92	2.28	1.57	1.59	0.97	2.36	4.44	5.29
Cs	2.20	3.11	1.42	3.13	1.87	1.96	4.01	4.45
Ba	921	1'022	849	280	615	796	376	1,367
La	69.8	271	41.7	26.3	44.1	72.9	22.6	197
Ce	137	496	85.7	56.9	87.8	144	42.3	387
Pr	14.8	47.8	9.66	6.32	9.52	15.1	4.46	41.6
Nd	49.8	136	33.3	20.7	32.1	49.3	14.7	137
Sm	7.80	17.9	5.64	3.91	5.36	7.64	2.85	21.0
Eu	1.79	2.45	1.28	0.34	1.06	1.23	0.48	2.30
Tb	0.67	1.40	0.57	0.64	0.41	0.72	0.46	1.81
Gd	5.32	10.5	4.22	3.68	3.58	5.41	2.65	14.2
Dy	3.30	6.97	2.89	4.08	1.73	3.65	2.89	8.73
Ho	0.61	1.29	0.54	0.91	0.27	0.72	0.62	1.56
Er	1.59	3.49	1.45	2.80	0.61	1.97	1.84	3.92
Tm	0.23	0.53	0.21	0.45	0.08	0.29	0.29	0.54
Yb	1.50	3.37	1.35	3.02	0.49	1.90	1.88	3.23
Lu	0.22	0.46	0.19	0.46	0.08	0.29	0.27	0.44
Hf	4.35	9.16	4.18	3.44	5.32	7.11	4.51	9.13
Ta	0.90	1.94	0.74	1.43	0.12	0.54	2.05	2.20
W	0.10	0.62	0.05	0.19	0.04	0.13	0.19	0.14
Pb	21.7	45.8	15.0	7.13	13.0	15.2	23.0	21.6
Th	13.4	27.8	7.59	5.88	8.46	11.2	11.5	26.2
U	2.28	5.08	1.65	2.23	0.39	1.49	10.1	4.08

(implying operation of the subduction mechanism) operated during Archaean times. Consequently, we argue that subduction (s.l.)-related dehydration was the driving force for continental crust production (including TTG and GGM) in Archaean times as it is today.

Extensive fractional crystallisation as the main petrogenetic process for Archaean granitoids

It has long been known that highly silicic rocks can, at least in laboratory experiments, be derived from a basaltic precursor. However, because the corresponding mafic cumulates that would have formed during such a process are not evident in nature, extreme fractional crystallisation has not seriously been considered as an origin for TTG (and GGM) in the past few decades. We will argue later that the recent experiments of Müntener et al. (2001) provide a solution to this dilemma and will next test whether fractional crystallisation from a basaltic precursor mantle melt could explain the geochemical features of both TTG and GGM.

Basaltic melts that form in the suprasubductional mantle by wet melting of peridotite have relatively

Table 2 Tonalite–trondhjemite–granodioritic suite

Pluton Sample ID	Nelshoogte 99/106	Theespruit 99/107	Steynsdorp 99/109	Nelspruit 99/110	Nelspruit 99/112	Stolzburg 99/120	Theespruit 99/121	Steynsdorp 99/122	Kaap Valley 99/128
Major elements (wt%)									
SiO_2	70.08	69.01	65.24	66.65	68.48	69.78	63.90	65.25	64.51
TiO_2	0.27	0.31	0.48	0.34	0.45	0.28	0.27	0.58	0.51
Al_2O_3	15.40	15.45	16.29	14.59	16.36	15.92	14.13	16.63	16.11
FeO_T	2.02	2.13	3.02	2.11	2.45	1.94	1.79	3.48	3.95
MnO	0.03	0.03	0.05	0.04	0.04	0.05	0.03	0.05	0.06
MgO	0.93	1.29	1.90	0.77	1.14	0.56	1.04	2.08	2.71
CaO	2.72	2.81	3.87	2.51	3.00	2.52	2.38	4.34	4.56
Na_2O	5.88	7.49	6.90	8.50	6.08	6.45	6.32	6.38	6.45
K_2O	1.25	1.63	2.22	1.53	1.49	2.41	1.81	1.48	1.47
P_2O_5	0.09	0.10	0.18	0.12	0.15	0.11	0.08	0.22	0.19
LOI	1.07	0.37	0.42	0.57	0.78	0.33	0.38	0.90	2.20
Trace elements (ppm)									
Li	23.8	39.2	81.8	36.2	65.8	51.8	35.9	103	19.4
Be	0.86	1.42	1.44	3.93	1.65	2.33	1.42	1.21	1.01
Sc	1.54	3.28	5.75	0.81	3.68	2.27	3.25	6.32	8.11
V	22.4	22.1	42.3	20.6	36.0	15.2	21.3	50.4	75.7
Cr	7.88	31.1	57.8	5.17	22.1	3.88	20.8	46.8	74.6
Co	4.84	7.02	10.5	4.25	7.28	3.09	6.18	11.6	15.5
Ni	6.85	39.0	40.2	7.48	12.8	11.1	34.0	35.5	56.3
Cu	9.71	5.67	5.43	4.43	4.12	1.70	0.58	15.1	14.9
Zn	31.8	50.0	57.6	63.5	61.7	83.6	50.1	57.4	54.7
Ga	15.9	18.2	18.3	21.2	18.2	19.6	18.2	18.2	17.3
Rb	41.9	49.0	71.4	75.3	115	68.6	60.5	54.0	39.1
Sr	528	590	558	835	523	638	541	646	572
Y	2.67	5.89	12.7	10.1	7.46	6.00	7.73	10.8	9.00
Zr	158	136	219	279	233	132	133	303	103
Nb	1.99	4.71	6.95	15.8	5.87	13.08	5.85	5.89	3.76
Sn	0.57	1.16	1.58	5.14	1.57	2.22	1.42	1.30	0.71
Cs	0.85	1.98	6.61	5.16	10.4	2.55	2.40	7.04	1.75
Ba	141	316	326	164	133	971	396	340	237
La	22.8	12.7	11.0	86.5	27.0	24.5	15.5	16.6	14.8
Ce	42.8	23.2	22.4	131	48.5	49.0	28.4	32.0	31.7
Pr	4.47	2.66	2.80	11.6	4.94	5.72	3.26	3.92	3.88
Nd	14.7	9.99	11.5	32.4	16.2	20.9	12.3	15.4	15.1
Sm	1.89	2.01	2.65	3.90	2.50	3.46	2.59	3.21	2.99
Eu	0.56	0.64	0.91	0.86	0.70	0.86	0.66	1.05	0.96
Tb	0.11	0.23	0.38	0.36	0.26	0.26	0.29	0.40	0.34
Gd	1.06	1.64	2.55	2.67	1.89	2.27	2.12	2.91	2.48
Dy	0.52	1.17	2.14	1.77	1.40	1.16	1.51	2.12	1.76
Ho	0.09	0.22	0.44	0.34	0.27	0.19	0.28	0.41	0.34
Er	0.26	0.58	1.28	0.97	0.73	0.49	0.74	1.09	0.89
Tm	0.04	0.08	0.21	0.16	0.11	0.07	0.10	0.16	0.13
Yb	0.29	0.52	1.48	1.19	0.72	0.45	0.62	1.00	0.80
Lu	0.05	0.07	0.22	0.20	0.11	0.06	0.09	0.15	0.11
Hf	3.62	3.37	4.66	7.49	4.90	3.52	3.41	6.25	2.55
Ta	0.13	0.39	0.86	1.45	0.45	0.87	0.60	0.38	0.24
W	0.03	0.08	0.02	0.26	0.03	0.01	0.06	0.04	0.06
Pb	3.46	7.18	8.43	14.7	10.5	14.9	8.23	7.04	4.71
Th	2.55	2.91	2.51	15.7	4.25	3.84	3.77	2.39	1.71
U	0.51	0.96	1.47	3.24	3.96	3.83	1.04	1.25	0.47

uniform major element compositions, but the exact chemistry (in particular the SiO_2 content) depends on the amount of available H_2O. On plots of MgO vs SiO_2 and Al_2O_3 vs SiO_2 (Fig. 3) high-H_2O and low-H_2O melts (experimentally derived at similar pressure; data from Müntener et al. 2001) have a similar compositional range despite having considerably different residual assemblages. Thus, if granitoid suites were derived from basaltic (s.l.) melts their compositional co-variation trends are expected to project into the area defined by primary mantle melts. It can be seen, from Fig. 3 that TTG are indeed following this prediction. Importantly, Fig. 3 also reveals that GGM follow an indistinguishable trajectory with the only difference of a slightly higher degree of differentiation. Hence, from a major element point of view, there is no reason to argue that TTG and GGM could not have been derived by fractional crystallisation of parental mantle melts. Contrasting alkali and earth alkali contents (Na, K and Ca) of TTG and GGM are the only significant differences in major element composition. As will be shown later, the Eu anomaly is related to this and can

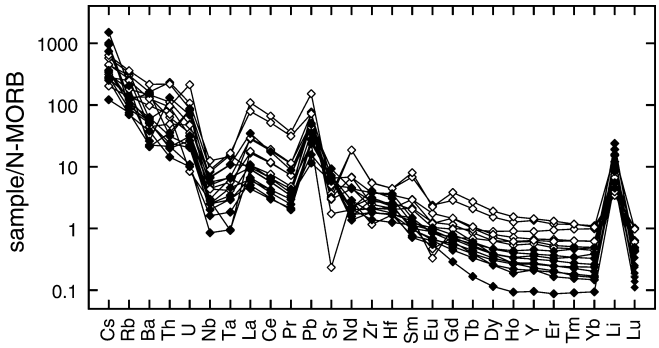

Fig. 2 N-MORB normalised trace element pattern of TTG (*filled diamonds*) and GGM (*open diamonds*) highlighting the enrichment of fluid-mobile elements (Pb, Li) and depletion of Nb, Ta typical for slab-dehydration. The overall similarity between both groups strongly indicates similar processes operating during petrogenesis. For a detailed description about the fluid sensitivity of Li see Kamber et al. (2002). Normalising parameters from Sun and McDonough (1989)

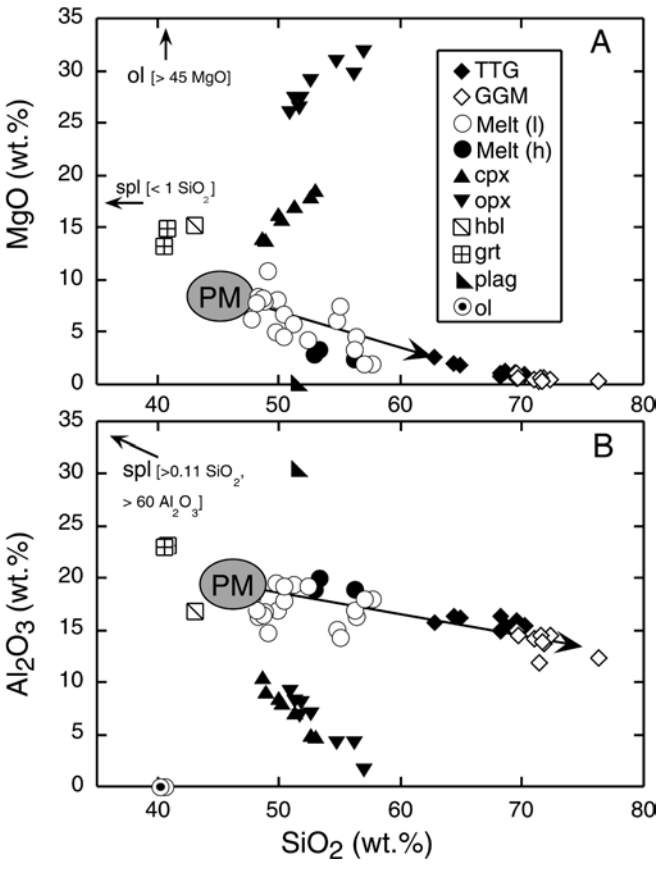

Fig. 3 Harker diagrams of **A** MgO and **B** Al_2O_3 showing liquid lines of descent for TTG and GGM of the BML with experimentally derived liquids from basalt and basaltic andesite (data from Müntener et al. 2001). Locations of possible liquidus phases are also displayed (data from Müntener et al. 2001). Garnet and amphibole fractionation can drive silica enrichment in the derivative liquids. Further discussion in text. *PM* Parental melt; *cpx* clinopyroxene; *opx* orthopyroxene; *hbl* hornblende; *grt* garnet; *plag* plagioclase; *ol* olivine; *spl* spinel; Melt (*l*): low-H_2O melt; Melt (*h*): high-H_2O melt

be entirely explained by differences in crystal fractionation.

An important point illustrated in Fig. 3 is the observation that olivine is not the only phase capable to drive silica enrichment in the derivative liquid. Garnet and amphibole, which are liquidus phases in more hydrous melts, are equally capable of this. Moreover, because hydrous mantle melts are initially more silicic than drier melts, an andesitic derivative melt is obtained with less fractional crystallisation of Si-poor silicates (Baker et al. 1994). A further feature according to the experimental results of Müntener et al. (2001) is that garnet and amphibole are stable as fractionating phases under hydrous conditions whereas plagioclase crystallisation is (at least at the beginning stages of fractional crystallisation) suppressed. Crystallisation of garnet and amphibole in the absence or late appearance of plagioclase could explain the distinctive trace element signatures that characterise TTG in particular.

When applying findings from experimental studies to data obtained in the field, the effect of pressure on the liquid line of descent has to be taken into account also. Müntener et al. (2001) performed their experiments at 1.2 GPa, which corresponds to a crustal depth of roughly 40 km. It is difficult to estimate the thickness of the Kaapvaal craton lithosphere 3.1 Ga ago, but seismic observations (Nguuri et al. 2001; Niu and James 2002) indicate a present crustal thickness of 35 to 40 km. Taking into account that at least 5 km of crust have been eroded since the Archaean, it appears plausible that the Kaapvaal craton was even thicker. Galer and Mezger (1998), based on consideration of continental freeboard, also concluded that Archaean crust was probably thicker by 5–15 km than presently created continents. Hence, if the trace element characteristics of TTG indeed reflect fractional crystallisation of garnet and amphibole, this would imply that the precursor melts ponded at depths corresponding to the crust–mantle boundary. The likelihood of this scenario is difficult to evaluate and comparison with modern arcs would suggest that extensive fractional crystallisation in deep magma chambers is not a typical feature. However, recalling that there is excellent evidence for a fundamental change from bimodal to unimodal distribution of magmatic rocks between 2.5 and 2.0 Ga, it is legitimate to propose a non-uniformitarian process (crystallisation in deep magma chambers) for genesis of at least some Archaean granitoids.

HREE depletion

Contrary to widely held opinion, TTG are not the only Archaean granitoids with very strongly fractionated REE patterns. Whereas TTG on average display steeper patterns (i.e. higher La_N/Yb_N ratios) than GGM (Condie 1993), the patterns of both groups require stronger HREE removal (or retention) than is seen in many post-Archaean granitoids. Indeed, comparison of TTG and

GGM from BML reveals that there exists no discernible difference in REE fractionation. On a plot of La_N/Yb_N vs Eu/Eu* (Fig. 4) it is clearly visible that TTG and GGM of the BML display the same range of LREE/HREE ratios (La_N/Yb_N for TTG and GGM: 5.3–56.4 and 6.2–64.5, respectively).

There are three possible ways to develop such REE patterns: (1) melting of garnet–amphibolite or eclogite in the slab or the lower continental crust; (2) inheritance of a slab-derived fluid REE signature in the precursor mantle melt (Grove et al. 2002); and (3) fractional crystallisation of garnet/amphibole in hydrous mantle melts similar to the experimental findings of Müntener et al. (2001). The first possibility is considered unlikely for reasons outlined recently by Kamber et al. (2002). The other two possibilities are mutually inclusive, as both models require fluid-rich material transfer from the slab to the mantle wedge. Therefore, we suggest that TTG and GGM originated from hydrated mantle melts. Their REE systematics were influenced by preferential transfer of LREE from the slab to the mantle wedge and subsequent HREE retention in garnet and amphibole as the magma evolved towards more silicic compositions in deep-seated chambers. Hence, we explain the HREE depletion in Archaean granitoids with the same minerals as used in the slab model by Drummond and Defant (1990) and Martin (1999), but in the context of a different petrogenetic process. The implication of our proposal is that suprasubduction zone mantle was more effectively hydrated in the Archaean. Stronger hydration of the Archaean mantle wedge appears counterintuitive in the context of higher heat production, but we will later propose that the thermal structure of the mantle is not likely to be the most important factor governing mantle hydration.

Eu anomaly

The extent of the Eu anomaly is the one important aspect of REE systematics in which TTG are significantly different from GGM. The Eu anomaly is generally negative for the GGM (average Eu/Eu*: 0.59), but is not existent or slightly positive for TTG (average Eu/Eu*: 1.01). Negative Eu anomalies are a prominent feature of granites of all ages (Condie 1993), and thus imply that plagioclase fractionation was an essential process of granite formation throughout Earth's history. Importantly, plagioclase fractionation is unrelated to that of garnet/amphibole as there is no correlation between La_N/Yb_N vs Eu/Eu* (Fig. 4). In our model, this implies that both the TTG and GGM series initially experienced garnet/amphibole ± pyroxene fractionation. Fractionation of these minerals in the absence of plagioclase causes a positive Eu anomaly, a feature observed neither in TTG nor GGM of the BML. Hence, it appears that once a certain extent of Si- and Al-enrichment had been reached in the derivative melt, plagioclase joined as a liquidus phase as it is the only phase that can counteract the positive Eu anomalies generated by pyroxene and amphibole crystallisation. Interestingly, Eu/Eu* displays a clear negative correlation with K_2O (Fig. 5a) and a positive correlation with CaO (Fig. 5b). This we take as strong evidence that the Eu anomaly in these rocks is solely caused by crystal fractionation (and is not a source feature), as plagioclase depletes the melt in Ca,

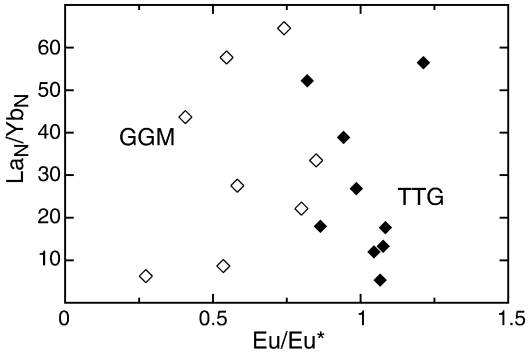

Fig. 4 Similar range of La_N/Yb_N ratios for TTG and GGM. Eu-anomalies vary independently of the La_N/Yb_N ratio with a clear difference between TTG (high) to GGM (low) giving evidence of unrelated garnet/amphibole and plagioclase fractionation

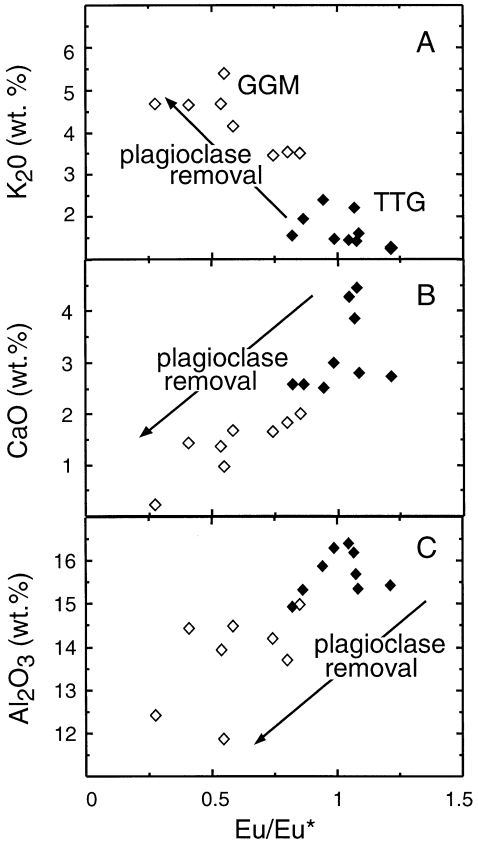

Fig. 5A Negative correlation of K_2O vs Eu/Eu*, and **B** positive correlation of CaO vs Eu/Eu* and **C** Al_2O_3 vs Eu/Eu*, identifying plagioclase crystallisation as the major phase controlling these parameters

Na and Eu and will produce a relative enrichment of K and elevated K/Na and K/Ca ratios in the melt. Supporting evidence for the influence of plagioclase is given by the alumina content, which shows a positive correlation with the Eu anomaly (Fig. 5c). The extent of the Eu anomaly thus simply reflects the degree of plagioclase removal that was higher in GGM than TTG.

Highly compatible trace elements

A prominent difference between TTG and GGM, which remains to be discussed, is the content of highly compatible elements such as Ni, Co and Cr. In case of the BML, TTG show concentrations of up to 56.5, 15.5 and 75.0 μg/g for Ni, Co and Cr, respectively. In contrast, the concentrations for these elements are below 8.5, 5.5 and 10.5 μg/g for GGM. Nickel, Co and Cr are well correlated for the suite of TTG (Fig. 6), indicating their high concentrations were not caused by different degrees of mantle contamination. This observation we regard as evidence against an origin of GGM and TTG as partial melts of garnet–amphibolite or eclogite, which are both depleted in these compatible elements. Partial melts from such rock types would be even more depleted and could only acquire elevated contents of Ni, Co and Cr by peridotite assimilation, a process not supported by the TTG trace element systematics. By contrast, partial melts of hydrated mantle contain Ni, Co and Cr in higher amounts because of high concentrations of these elements in the source region combined with a high degree of melting. Subsequently, the concentrations of these elements in derivative melts are mainly controlled by the degree of olivine (and for Cr also clinopyroxene) crystallisation. The relatively high concentrations of compatible elements in both TTG and GGM (albeit higher in the TTG) suggest a limited role for olivine and clinopyroxene crystallisation. There are two aspects of experimental findings relevant to this issue. Firstly, experimental results of Sisson and Grove (1993) provided evidence for increasing crystallisation of clinopyroxene at the expense of olivine under hydrous conditions. Furthermore, the exact chemical composition of clinopyroxene is strongly dependent on pressure, temperature and H_2O content of the melt. Müntener et al. (2001) showed that at high water contents and pressures the Cr-Tschermak content is low and crystallising clinopyroxenes show variable components of wollastonite and enstatite–ferrosilite at low Cr-Tschermak contents. Hence, albeit clinopyroxene fractionation is likely to have occurred, Cr depletion of the remaining melt was limited due to the low activity of the Cr-Tschermak molecule. Secondly, the generation of olivine-poor or olivine-free cumulates was observed in experiments due to the peritectic reaction of olivine and melt to pyroxene (Müntener et al. 2001). The combined effect is to minimise the roles of olivine and (clino-)pyroxene on an andesite derivative and allows resulting liquids (TTG) to keep highly compatible elements in solution to a greater extent than melts with a cumulates increasingly dominated by olivine and (clino-)pyroxene (GGM).

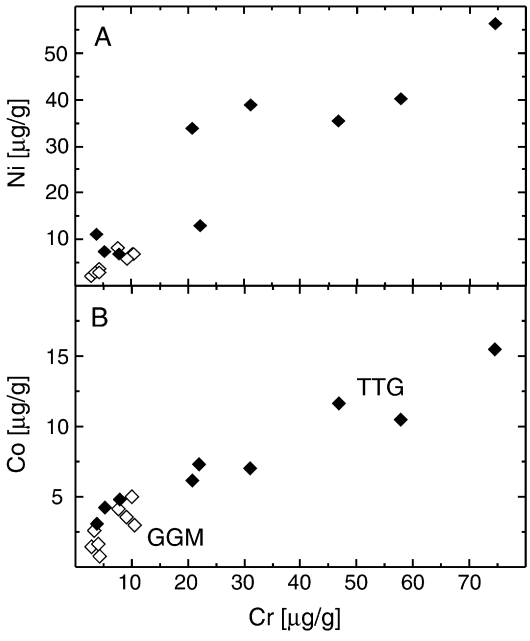

Fig. 6 Concentrations of the highly compatible element pairs **A** Ni–Cr and **B** Co–Cr in TTG and GGM. High compatible element contents are interpreted to reflect a subordinate role of fractional crystallisation of olivine and pyroxene for TTG. For GGM contents of Ni, Co and Cr are lower than in TTG, indicating a higher degree of olivine and clinopyroxene fractionation, which can be explained with initial water contents of the melts. Further discussion in the text

Discussion

High degree of fractional crystallisation

Pure mantle-derived melts of granitoid composition are rare, albeit there is evidence that extensive fractional crystallisation can produce such melts. For example, Kirstein et al. (2000) described rhyolitic magmatism in the Parana province of Uruguay, which they explained as having formed by fractional crystallisation. Jahn et al. (2001) gave evidence for highly evolved granites from the Great Xing'an Mountains in NE China as pure fractional crystallised mantle-derived melts. Macdonald et al. (2000) compiled evidence from quartz phenocrysts in magmas from the Lesser Antilles volcanic arc. These phenocrysts were found in rocks with 59 wt% SiO_2, but they grew in equilibrium with a melt containing >70 wt% SiO_2. Hence, highly siliceous mantle melts do exist, but they require larger amounts of cumulate residues than observed, creating a mass imbalance known as the cumulate problem (e.g. Rudnick 1995; Sylvester 2001). There are two possible solutions to this problem. Firstly, the cumulate problem may only be an apparent paradox if the mean continental crust is less silicic than generally estimated. This explanation would require that

the base of the crust consists of mafic cumulates, which are underrepresented in crustal xenolith suites and remain undetected by seismological studies as suggested by Rudnick (1995). Secondly, cumulates denser than their surrounding mantle might form at the base of the crust or lithosphere. They would be recycled into the mantle and might represent the missing counterpart required by mass balance. Regarding the second explanation, it has been argued in the past that, based on the assumption that olivine, pyroxenes and plagioclase were dominating the early stages of fractional crystallisation, the resulting cumulate would not be denser than surrounding mantle. However, it is now clear from the experiments with hydrated basalt that plagioclase suppression can lead to garnet–pyroxenite cumulates, which can be denser than surrounding mantle. In fact, even the websteritic cumulates with trace amounts of garnet, hornblende or spinel obtained by Müntener et al. (2001) have calculated densities higher than surrounding mantle. Such cumulates would be recycled back into the mantle and would help to solve the mass imbalance during Archaean times if the composition of continental crust is, on average, andesitic (rather than basaltic). However, it has to be stated that such a solution to the cumulate problem could not work for post-Archaean continental crust because of the lack of sufficient HREE depletion and because of low compatible element content. Key to recycling of cumulates is the almost complete absence of plagioclase during the early stages of fractional crystallisation as only trace amounts of this phase make the residue more buoyant than the surrounding mantle (Müntener et al. 2001).

We propose that the BML granitoids bear witness to a change in composition of their residual cumulates. In the beginning stages of fractional crystallisation both granitoid types were fractionating cumulates composed of garnet/amphibole + pyroxene ± olivine, which are less buoyant than the surrounding mantle and, hence, could be recycled back into it. Later in their petrogenesis, both types were affected by fractionation of plagioclase probably in crustal magma chambers. As the TTG crystallised less plagioclase during fractionation than GGM, as evidenced by the degree of their respective Eu anomalies, their associated plagioclase-bearing cumulates are much less voluminous. Plagioclase-bearing cumulates must be stored at the base of or in the lower crust due to their density. Indeed, the existence of such cumulates in the Kimberley region of South Africa has recently been suggested from interpretation of seismic data (Niu and James 2002).

The preponderance of TTG over GGM in almost all Archaean cratons could be a direct reflection of the mass balance problem because TTG require a lesser extent of fractional crystallisation (resulting in less voluminous cumulates) for two reasons. Firstly, they are on average less silicic (Tables 1 and 2) than GGM and secondly, because their parental melts were more hydrous, they started out with a higher content of SiO_2. Regardless, because GGM are far less abundant than TTG in the Archaean rock record, their associated cumulate problem is much less severe for mass balance on the scale of a craton that is dominated by a bimodal suite of TTG and basalt (s.l.).

Mode and efficiency of water release from Archaean subduction zones

We have demonstrated in the previous sections that some important geochemical characteristics of TTG and GGM can be explained by a series of processes that closely resemble modern arc magmatism with the sole difference of a higher initial water content of the basaltic parental mantle melt. Hence, we recognise the extent and efficiency of water transfer into and subsequent hydration of the mantle wedge as the process that changed with time and explains the specific characteristics of Archaean granitoids.

There are two plausible mechanisms to achieve a higher water saturation of primary mantle melts. It could either be argued that the overall mantle was wetter than it is today or it could be postulated that water was more effectively funnelled into the mantle wedge. We consider the first possibility to be unrealistic for three reasons: (1) short-lived radionuclide evidence [particularly iodogenic Xe (Azbel and Tolstikhin 1993)] require very early (i.e. less than 150 Ma from beginning of accretion) mantle degassing and, therefore, even the earliest Archaean mantle seems to have been strongly degassed; (2) the TTG and GGM studied here span emplacement over 400 Ma and, compared with the preceding > 1,000 Ma of Earth history, this time span is short for such a variation in H_2O content of the mantle; and (3) the occurrence of TTG and GGM on different Archaean cratons is diachronous. For instance, GGM in the BML pre-date TTG in parts of the Zimbabwe craton (Taylor et al. 1991).

The alternative explanation requires exploring of the possibility of varying degrees of hydration and dehydration of oceanic crust during the Archaean. Accepting that subduction (s.l.) is the only viable mechanism to transport considerable amounts of water to sufficient mantle depth, it is necessary to further understand the volatile budget of slabs. The initial volatile content of a slab depends on the degree of metasomatic hydration at mid-ocean ridges. The extent of ocean floor alteration is dependent on the spreading rate (Bougalt et al. 1993; Gillis 1995) and, correspondingly, on the thickness of oceanic crust. While hydration of oceanic crust might have been more extensive in the Archaean, it is important to note that, even today, oceanic crust (and exposed mantle portions) are heavily hydrated. Therefore, key to understanding the volatile budget of the suprasubductional mantle is likely to be the history of slab dehydration.

It is beyond the scope of this paper to explore to which extent a different nature and degree of oceanic slab alteration could have influenced the depth of fluid

release, not least because it is unknown how extensive alteration of the mantle portion of the lithosphere was. However, we would like to draw attention to the fact that the conclusion raised by us is compatible with models for komatiite petrology by Parman et al. (1997, 2001) and Grove et al. (1999). Parman et al. (1997, 2001) examined melting and crystallisation conditions for komatiites and concluded that these magmas formed by hydrous mantle melting. Furthermore, they observed a strong geochemical similarity between modern boninites and komatiites in terms of trace elements. As boninites have very high Mg contents and form exclusively in subduction zones by high degrees of hydrous mantle melting (Crawford et al. 1989) Parman et al. (2001) concluded that komatiites were derived in a similar manner. Grove et al. (1999) presented a flux melting model for komatiites and discussed the requirements for the mantle source H_2O budget in that context. They favoured a more intense hydration of subducting slabs and the suprasubductional mantle due to a greater extent of seafloor alteration. In summary, new interpretations of ultramafic and felsic igneous rocks are emerging that both indicate a more hydrous nature of the Archaean suprasubduction zone mantle. Further research will be required to test which combination of physical parameters caused the secular change in continental magmatism.

Compositional change in granitoid magmatism and its causes

Condie (1993) compiled the overall characteristics of Archaean, Proterozoic and Phanerozoic TTG and GGM. Interestingly, both suites share two main gradual changes with time: (1) decreasing LREE/HREE fractionation and (2) an increasing Eu anomaly. As demonstrated before, these two characteristics can be well explained with different fractionating assemblages evolving dependent on fluid-concentration of basaltic melts (s.l.) in the mantle wedge. The former characteristic is mainly a function of decreasing HREE depletion, which is explained by a declining amount of garnet/amphibole fractionation, the latter is controlled by a combined effect of decreasing HREE depletion and increasing influence of plagioclase fractionation. The controlling parameter behind this change, in our opinion, is the amount of water saturation or undersaturation of the parental melt. Macdonald et al. (2000) discussed estimates of water concentrations in tholeiites of the Lesser Antilles volcanic arc, which average at 3 to 5 wt% H_2O in primary mantle melts. The experiments published by Müntener et al. (2001) show that garnet/amphibole start to become important fractional crystallisation products above 5.5 wt% H_2O in the melt. The mechanisms by which Archaean suprasubduction zone melts could have become more hydrated remain poorly explored, but it is clear that at a high degree of hydration of the parental mantle melts plagioclase crystallisation is initially suppressed and, therefore, the REE patterns are largely controlled by garnet and amphibole. This results in liquids with TTG composition. With a decreasing degree of hydration plagioclase starts to gain influence, but garnet and amphibole may still be fractionating phases. This scenario could explain GGM characteristics. Towards the end of the Archaean and beginning of Proterozoic, the extent of hydration of the suprasubductional mantle melts began to fall below the critical limit for garnet and amphibole crystallisation and 'typical' post-Archaean granites (s.l.) were generated. However, the transition was gradual, accounting for some Palaeoproterozoic TTG of typical Archaean geochemistry as well as late-Archaean granites of typical post-Archaean geochemistry. The gradual change in arc magmatism could thus largely reflect the extent to which primary suprasubduction zone melts were hydrated. A consequence of this model is that from Proterozoic times onwards cumulate lower crust should become a more important feature due to increasing influence of plagioclase fractionation.

Conclusions and summary

A model is presented for TTG and GGM formation, which we tested with a suite of granitoids from Barberton Mountain Land. It satisfies the following specific geochemical constraints: (1) overabundance of slab-derived fluid-mobile elements in TTG and GGM; (2) preferential depletion of Nb over Ta in both TTG and GGM; (3) strong LREE/HREE fractionation in TTG and GGM; (4) absence/presence of Eu anomaly; and (5) high concentrations of some compatible trace elements in TTG.

Derivation of these rocks from the suprasubductional refertilised mantle wedge explains the strong signature of slab dehydration. Subsequently, extensive fractional crystallisation from parental basaltic mantle melts reconciles most major and trace element characteristics that TTG and GGM have in common, but also offers a solution to the mass balance problem created by the extent of fractional crystallisation. Slightly different residual assemblages whose evolutions depend on the initial water content of the parental melt can account for the differences seen in TTG and GGM. TTG characteristics can be attained with a parental melt containing high amounts of H_2O and a residual cumulate dominated by garnet/amphibole + clinopyroxene + orthopyroxene and minor plagioclase. This assemblage leads to tonalitic–trondhjemitic melts with high LREE/HREE ratios, no Eu anomalies, and high concentrations of highly compatible elements. GGM characteristics can be produced with a parental melt containing intermediate amounts of H_2O and a residual cumulate of olivine + clinopyroxene + orthopyroxene + plagioclase + garnet/amphibole. This fractionating assemblage produces granitic (s.l.) melts with high LREE/HREE ratios, negative Eu anomalies and lower (compared with TTG)

concentrations of highly compatible elements. In the post-Archaean Earth, the water content of parental basaltic melts probably dropped below a critical limit for the crystallisation of garnet and amphibole leading to siliceous melts of typical post-Archaean potassic granitoids. This model implies that the efficiency of hydrothermal alteration of oceanic crust and hydration/dehydration in subduction zones is of major importance for the change in continental petrology with time because of its inherent ability to explain the disappearance of TTG and increasing preponderance of granitoids with granitic (s.l.) composition.

Although we are presently not in position to single out the most likely reason for the higher water content of Archaean suprasubduction zone melts, our model has identified potential future research avenues that need to be explored in order to improve our understanding of subduction zone melting through time.

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