### Chemical characteristics and genesis of the quartz-feldspathic rocks in the Archean crust of Greenland

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Abstract. A total of 108 samples of meta-tonalites, metagranodiorites, granites and meta-tholeiites representing groups of Early to Late Archean age and different metamorphic history from SW and SE Greenland have been analyzed for Ca, K and 28 trace elements. There is no systematic change of the chemical composition with age observable. The results support petrologic experiments which suggest that tonalites and granodiorites (the most abundant rocks of the Archean crust) are partial melting products of a mafic lower crust. Modelling suggest that this crust consisted of garnet amphibolite derived from a source with a bulk composition resembling a slightly enriched rather than depleted mantle. The  $Ce_N/Yb_N$  ratio is above 10 in the majority of tonalites. Most samples have no Eu anomaly because of a balanced contribution from the minerals of a mafic rock (or a plagioclase-free source). The positive Eu anomaly of some granodiorites and of a minor proportion of tonalites can be explained as being caused by plagioclase accumulation during differentiation or by partial melting of plagioclase-rich fractions. Modelling with Zn excludes an origin of tonalitic melts by differentiation of basaltic to dioritic magmas. The Archean meta-diorites, meta-tonalites and meta-granodiorites from Greenland have generally lost some K and S relative to their suggested magmatic protoliths. Loss of Rb, Tl, Pb and K and relative gain of Ca, Sr, Ba and Sc connected with granulitization of meta-tonalites can be explained in the majority of cases by separation of about 25 percent granitic partial melt. High K/Rb, K/Pb, Zn/Cd and Nb/Th ratios of granulites plus low ratios of granites are almost in balance with intermediate ratios of amphibolite-facies tonalites. Retrogression of granulites into amphibolites was accompanied by introduction of Pb, Tl, Rb, Ba, Sr and K from Na-Cl-rich brines circulating on fractures. A comparison of the abundance of 24 elements (characterized by different compatibility) in the Archean crust of Greenland with the present bulk crust reflects only minor changes (Th, Nb) if at-all in the chemical composition of the continental crust since the Archean.

#### Introduction

This paper is concerned with problems of the chemical fractionation in the early continental crust which was formed from 3.8 to 2.5 Ga before present and is exposed in the coastal areas of Greenland.

The major hypotheses for the formation of the Archean quartz-feldspathic crust (differentiation of mafic magmas; partial melting of eclogites, mafic granulites or amphibolites; partial melting of mantle rocks) have been listed (with references) by Martin (1987). The 108 sampled rocks of this study are mainly meta-tonalites and meta-granodiorites and a few granites, meta-diorites and meta-tholeiites of Early to Late Archean age. All the samples studied have been through amphibolite and/ or granulite facies metamorphism and their present distribution is the result of complex tectonic events. Tonalitic to granodioritic gneisses form ca 70% of the exposed Archean gneiss complex of W Greenland (Kalsbeek 1976). Similar proportions are reported from Archean cratons of other continents (Windley 1976; Barker 1979). Gneissic granites (with more than 20% K-feldspar and supracrustal units dominated by mafic igneous rocks with subordinate semipelitic metasediments form the remaining 30% of the gneiss complex. The generation of the abundant tonalitic to granodioritic intrusives in the Archean crust by partial melting required a thick lower crust with an average mafic composition which could have delaminated during later processes. Calcalkalic magmas ranging from tonalitic to andesitic composition are presently formed at active continental margins (Barker 1979) or at the base of an abnormally thick ocean crust as in Iceland (Oskarsson et al. 1982). A genetic model for the tonalites and granodiorites in Greenland has been derived from experimental partial melting of hydrated mafic rocks (Helz 1973, 1976; Johnston and Wyllie 1988) and material balances. Most of the komatiltic or basaltic rocks of the early crust must have been lost by delamination of the lowest parts of the crust or other processes of tectonism. This assumption is based on a comparison of the Archean crust in Greenland with that in W Australia where the lower crust

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contains not more than 20 to 35 percent mafic materials (Drummond 1988). The high potassium concentrations in the true granites of the Archean in Greenland required crustal preconcentration of this element in tonalitic-trondhjemitic rocks or in sediments before partial melting (Rutter and Wyllie 1987).

We are well aware of the difficulties in the reconstruction of primordial compositions of the listed magmatic rocks in Greenland after their complicated history of prograde and retrograde metamorphism and tectonic displacement.

Progression from amphibolite to granulite facies rocks includes mobilization of fluids or melts (Newton et al. 1980; Condie 1980; Tarney et al. 1979) and retrogression requires advection of fluids. One of the major problems is to explain the mobilization of certain elements during prograde and retrograde metamorphism.

Beside the chemical characterization of the major rock forming processes we will estimate the bulk composition of the Archean crust in Greenland. This is important in connection with the controversal statements by Taylor and McLennan (1985) and by Shaw et al. (1986) about the dissimilarity or similarity between Archean and post-Archean crustal compositions in Australia and Canada.

Our chemical characterization of mafic, calcalkalic and granitic rocks and of processes of partial melting and metamorphism (alteration by brines) is based on concentrations of the major elements K and Ca and the trace elements S, Sc, Cr, Zn, Rb, Sr, Y, Zr, Nb, Cd, Ba, REE, Ta, Tl, Pb and Th.

#### Geology of the areas sampled

The Precambrian basement of Greenland north of the Proterozoic Ketilidian mobile belt (ca. 62°N) is dominated by high grade Archean gneisses. North of ca 66° on the West coast and 64° on the East coast the Archean basement is tectonically reworked and metamorphosed in a series of Proterozoic mobile belts which in some areas include subordinate amounts of juvenile material derived from mantle sources during the Proterozoic (Bridgwater and Myers 1979; Kalsbeek et al. 1984) (c.f. Fig. 1).

General descriptions of parts of the Archean gneiss complex from which material used in these studies are given by McGregor (1973, 1979), Bridgwater et al. (1974, 1976) and Nutman et al. (1989). More detailed studies are quoted in the following text.

# Archean amphibolite and granulite facies gneisses of SW Greenland

1. Early Archean Isua gneisses and Mid-Archean mafic dykes (in amphibolite facies) consist of two major units. First: a series of grey gneisses (tonalites and granodiorites) surround and locally intrude the deformed Isua supra-crustal rocks (mafic and felsic volcanics plus sedimentary materials). Second: the grey gneisses were themselves deformed and intruded during the early Archean by widespread granites and trondhjemites (white gneisses) which form approximately 30 percent of the total rock mass (Nutman et al. 1984; Nutman and Bridgwater 1986). The Isua gneisses and supra-crustals were intruded by several sets of mafic dykes which were metamorphosed up to amphibolite facies in the late Archean. Their bulk chemistry is close to that of Archean basalt lavas (Gill



Fig. 1. Map of Greenland with the belts of Archean rock formations (partly reworked in Proterozoic) exposed at the surface and with the areas of sampling

and Bridgwater 1979). Isotopic results from felsic volcanic rocks within the supracrustal unit show that the sequence was deposited at 3.81 Ga (Baadsgaard et al. 1984; Compston et al. 1986). The tonalites were emplaced between 3.7 and 3.75 Ga and the granites intruded at about 3.59 Ga (Baadsgaard et al. 1986). The mafic dykes are older than 2.8 Ga but younger than 3.4 Ga.

2. Early Archean Amîtsoq grey gneiss from the Faeringehavn terrane, eastern Simiutâ Island, Outer Ameralik Fjord as described by McGregor (1968, 1973) occurs within the Faeringehavn terrane which extends as a  $75 \times 25$  km wide tectonic slice between outer Ameralik and outer Godthåbsfjord (Nutman et al. 1989). The Early Archean orthogneisses within this tectonic slice, some of which contain zircons over 3.8 Ga old (Kinny 1987) were affected by a series of Early Archean events in the period 3.8 to 3.5 Ga, but were not affected by Late Archean granulite facies metamorphism seen in adjacent terranes. Samples of banded gneiss from Simiutâ which are typical of large parts of the Early Archean Amîtsoq gneisses of the Faeringehavn terrane made of two main components, an early tonalitic to granodioritic phase and a slightly younger (circa 3.6 Ga granitic component. The two components cannot be separated in the hand sample and the rocks are treated as a single geochemical unit of amphibolite facics gneiss. A few kilometers to the south the gneiss complex was affected by an Early Archean granulite facies event at circa 3.5 Ga (Griffin et al. 1980) suggesting the present erosion level represents a deep section of the 3.5 Ga crust. The gneisses from Simiutâ were affected by several periods of later metamorphism including an amphibolite facies event at 2.65 Ga but there is no definite evidence of marked element mobility after the migmatisation event at 3.6 Ga.

3. Mid- to Late Archean amphibolite facies grey gneisses have been sampled from several localities in the Godthåbsfjord – Amera-

lik region. These belong to the original Nûk gneiss suite as defined by McGregor (1973) but are now known to represent at least two Archean terranes welded together between 2.65 and 2.8 Ga (see Nutman et al. 1989). The main period of generation of tonalites and granodiorites has been dated by U-Pb methods between 2.9 to 3.1 Ga (Baadsgaard and McGregor 1982; Schiøtte et al. 1989) and were followed by a series of igneous metamorphic events and fluid movement between 2.9 and 2.5 Ga.

4. Late Archean high-grade gneisses have been collected from Kangimut sammisoq and adjacent localities in the Tasiusarssuaq terrane, Central Ameralik Fjord (Friend et al. 1987). This tectonic slice, which occurs as far south as Sermilik, was affected by a granulite facies event at circa 2.82 Ga (Schiøtte et al. 1989). It was thrust over the amphibolite facies Trc Brödre and Faerrringehavn terranes before 2.6 Ga. The granulite facies slice consists of older migmatitic and a younger almost undepleted orthogneiss series. The older rocks yield a U/Pb zircon age of about 2.92 Ga (Kinny 1987; Schiøtte et al. 1989). The younger series of meta-gabbro to meta-tonalite were emplaced just before the high grade metamorphism (2.82 Ga).

The older group of gneisses at Kangimut sammisoq was affected by an appreciable retrogression in the period from 2.82 to 2.65 Ga as the result of upward movement of fluids from crustal slabs of amphibolite facies gneiss below them (Nutman and Friend 1989; Bridgwater et al. 1989). The sample group of younger gneiss was not much disturbed chemically by retrogression according to Rb-Sr isotope data. Both gneiss units were intruded by granite in the period from 2.65 to 2.50 Ga culminating in the Qorqut granite at 2.55 Ga (Baadsgaard 1976).

#### *Mid-Archean granulite facies gneisses from SE Greenland* (partly retrogressed into amphibolite-facies rocks)

(1) (2) Archean granulite facies rocks which have been partly retrogressed during late Archean and Proterozoic tectonic events are found in the northern border zone of the Proterozoic Nagssugtoqidian mobile belt of southern East Greenland at Charcot Fjelde (1) and Storø (2). U-Pb zircon and Rb-Sr whole rock studies show that the granulite facies gneisses were formed between 2.8 and 3.0 Ga (Mengel et al. 1990).

Approximately 90-95% of the granulite facies quartzofeldspathic orthogneisses are tonalitic in composition. Most outcrops contain small, commonly rather diffuse areas of more granitic material interpreted as formed by partial melting of the regional gneisses during high grade metamorphic conditions. The granulite facies gneisses contain sub-vertical shear zones with pegmatites and widespread retrogression to amphibolite facies at ca 2.65 Ga (Pedersen and Bridgwater 1979). The shear zones acted as loci for the widespread injection of tholeiitic basic dykes some of which can be traced for tens of kilometers and are over 50 m in width. Sm-Nd studies suggest that the dykes are at least 2.2 Ga old (Mengel et al. 1990). The regional studies suggest that the post-dykc retrogression represents the thrusting of the Archean high grade terrane in the north of the mobile belt over lower grade rocks to the south. Rb-Sr and U-Pb studies from the center of the Nagssugtoqidian mobile belt yield an approximate age of amphibolite facies metamorphism of about 1.8 to 1.9 Ga (Pedersen and Bridgwater 1979). The combined effect of late Archean and Proterozoic tectonism and fluid movement has been to retrogress the Archean granulite facies mineral assemblages in diffuse zones concentrated along shear planes. In the field the least retrogressed rocks weather brown while more retrogressed rock weather white.

Sampling was carried out during regional mapping by DB and his colleagues while working with the Geological Survey of Greenland. Many of the samples are part of material collected for whole rock isotope studies and weighed over 10 kilograms. All the samples used were over 1 kg before crushing and were collected as representing regionally abundant rock types.

#### Analytical methods

The analysis of Ca, Sc, Sr, Y, Nb, Ba and of the REE was performed by ICP-AES. The lanthanides were preconcentrated by ion exchange on Dowex-50. Additional data on Cr, REE, Cs, Ta and Th provided partly by the Risø National Laboratory (Denmark) partly by Dr. Bohr Ming Jahn (Rennes, France), are from INA and from isotope dilution. K and Rb were measured by atomic emission and Zn by atomic absorption (flame). A graphite tube atomizer was used for the AAS determination of Rb, Cd, Tl, Pb and Bi. Of these elements Cd, Bi and Tl required separation and preconcentration by a volatilization technique (Heinrichs 1979). The volatilization tube of quartz glass was heated in an electrical furnace at 1000–1200° C for a mobilization of the mentioned metals to be transported by a carrier gas to a watercooled condenser. Sulfur data were obtained from a coulometric technique.

Reproducibility of the methods has been evaluated for different ranges of concentration on the basis of duplicate values according to the procedure proposed by Kaiser and Specker (1956). The relative standard deviation of the majority of the trace element data ranges between 3 and 15% with Cd, Bi and Tl going up to 30% at low levels of concentration. The accuracy was tested on numerous international reference rocks. Frequency distributions of values obtained by different methods on the granodiorite GSP-1 and the basalt BCR-1 were presented by Heinrichs et al. (1980). The diagrams confirm the reliability of the methods used for the present investigation.

The elements K, Ca, Zn, Rb, Sr, Zr, Ba and Pb were separately analyzed by J.C. Bailey (Institute of Petrology, University of Copenhagen) using XRF on powder pellets. There is a general good correspondence between the analytical results on the same samples by different techniques. In this case we have used the results from the laboratory at Göttingen for this investigation to be consistent.

# Composition, formation and metamorphic alteration of tonalites, granodiorites and granites

#### Implications from K, Rb, Tl, Pb (and Bi) concentrations on rock alteration by brines and on granite separation

Group averages of meta-tonalites, meta-trondhjemites and meta-granodiorites from the Archean of W Greenland as reported by McGregor (1979) range from 65.7 to 72.7% SiO<sub>2</sub> and from 1.5 to 3.7% K<sub>2</sub>O (1.25% K to 3.1% K) at almost constant Na<sub>2</sub>O concentrations of about 4.8%. CaO concentrations decrease from 4% (2.9% Ca) in meta-tonalites to 2% (1.4% Ca) in metagranodiorites. The K concentrations in meta-tonalites are distinctly lower than in non-metamorphic tonalites and dacites as reported by Chayes (1975), Le Maitre (1976) and Ewart (1979) (c.f. Fig. 2). The Na<sub>2</sub>O concentrations in meta-tonalites are systematically higher relative to non-metamorphic tonalites and dacites which contain on average a little less than 4% Na<sub>2</sub>O (Nockolds 1954; Chayes 1975; Le Maitre 1976). An exchange of K with Na as often being observed from reactions of hot seawater with basalt at temperatures above 200° C could have altered the tonalite parent rock. Natural and experimental evidence for such reactions has been compiled by Wedepohl (1988). Additional evidence for the generally low K concentrations in the felsic meta-intrusives from Greenland relative to their non-metamorphic equivalents can be derived from our investigation. In

Rock type	n	S	K 5020	Ca 75400	Sc	Cr 168	Zn 94 100	Rb 12 14	Sr 128 328	Y 19 28	Zr	Nb 5.6	Cd	Cs
Average mafic rock (dikes, gabbros) Ameralik Fjord (SW Greenland)	5	503			42								0.11	
Average tholeitic basalt (Wedepohl 1975; Heinrichs et al., 1980)			6970	72300	30						137	13	0.09	
a1 Tonalitic gneiss, amphibolite facies, Isua (SW Greenland)	6	77	12000	26000	6	31	50	77	233	16	161	6	0.038	3.9
a4 Tonalitic gneiss granulite facies, Central Ameralik Fjord (SW Greenland)	12	680	6100	36500	9		63	17	250	15	(120)	6.7	0.055	
a3 Tonalitic and dioritic gneiss, amphibolite facies, Nuk (SW Greenland)	14	83	9828	37430	12		69	33	364	14		6.9	0.077	
b1 Tonalitic gneiss, partly amphibolite facies, Charcot Fjelde (SE Greenland)	16	145 ±61	11900 ±2130	$\begin{array}{r} 29300 \\ \pm4300 \end{array}$	5.1 ±3.1	(10)	58 ±27	15 ±5.4	580 ±231	7.2 ±6.4	$\begin{array}{c} 128 \\ \pm  40 \end{array}$	6.6 ±6.0	0.037 ±0.019	
b1 Tonalitic gneiss, granulite facies, Charcot Fjelde (SE Greenland)	22	240 ±162	$\begin{array}{r}10400\\\pm2500\end{array}$	$\begin{array}{r} 34100 \\ \pm6000 \end{array}$	8.6 ±4.9	(14)	62 ±21	10 ± 5.1	451 ±144	10 ±6.2	137 ±53	6.5 ±3.7	$0.041 \pm 0.022$	
Average tonalitic gneiss, North Atlantic Craton (Tarney et al., 1979)	159		16000	24600	(27)	27		51	558	7.5	217	6		
Average tonalitic gneiss, Superior Province Manitoba (Ermanovics et al. 1979)	164		17000	26000	(25)	25		61	512		190			
Average orogenic dacite, worldwide (Ewart 1979)	85– 351		21000	30 0 0 0	11.00	29	82	74	536	(25)	180	14		
b2 Granodiorite, partly amphibolite facies, Storø (SE Greenland)	14	110	25100	15300	3.1	4.7	87	52	751	2.6	131	4.8	0.064	
a2/a3 Granodiorite, Nuk and Simiuta Island (SW Greenland)	6	49	22000	15400	2.3		25	80	374	5		3.8	0.043	
b1 Quartz monzonite, Charcot Fjelde (SE Greenland)	4	310	28800	18 100	10	3.5	61	47	365	14	175	9.0	0.079	
a4 Granite, post-Nuk, Amcralik Fjord (SW Greenland)	3	83	38 500	12100	1.7		22	193	137	5.3		8.3	0.041	
a1 Granite, Isukasia	6	22	41 500	7860	1	3	17	138	140	5.5	128	5	0.029	2.9
Exposed Archean crust Greenland <sup>a</sup>		220	17 500	31 100	11	(33)	63	47	370	10	135	6	0.06	
Bulk Archean crust Greenland <sup>b</sup>	-	246	14900	37300	14	(78)	66	40	358	12	125	6.2	0.064	

Table 1. Average concentrations (in ppm) of selected elements in Archean meta-magmatic rocks of tonalitic to granitic composition from SW Greenland (a) ad SE Greenland (b) in comparison with related rocks quoted in the literature (n: Number of samples used

<sup>a</sup> 40% tonalite, 26% granodiorite, 16% granite, 17% mafic rocks (mainly based on information from Kalsbeek (1976)

<sup>b</sup> 38% tonalite, 25% granodiorite, 15% granite, 22% mafic rocks (based on information from Kalsbeek, 1976 and Drummond, 1988)

Fig. 2 we have plotted K against Ca concentrations in the Archean quartz-feldspathic rocks from SW and SE Greenland. We compare their compositions with those of averages of non-metamorphic post-Archean granites, granodiorites, dacites, quartz monzonites, andesites, diorites and gabbros as reported by Nockolds (1954), Le Maitre (1976), Ewart (1979), Chayes (1975) and Taylor (1977). It is obvious from this comparison that the plots of Archean quartz-feldspathic rocks are generally moved to distinctly lower potassium concentrations rela-

166

Ba	La	Ce	Nd	Sm	Eu	Gd	Tb/Dy	Но	Er	Yb	Lu	Та	Tl	Pb	Bi	Th
57	4.6	16											0.05	4.9	0.037	
246	15	33	19	4.9	1.5	5.5	Tb1.2	1.3	2.8	2.6	0.46	0.5	0.08	3.7	0.03	1.8
205	27	57	22	4.7	1.1	3.5	Tb 0.47	0.59	1.6	1.2	0.18	0.65	0.50	15	0.016	5.3
195	13	32		2.5	0.92		ТЬ0.35			1.1	0.19	(0.38)	0.061	3.1	0.018	
352	19	40	19	4.4	1.1	3.2	Dy 3.0	0.57	1.6	1.3	0.19		0.15	7.5	0.024	
659 ±160	25 ±7.0	43 ±15	18 ±8.4	3.3 ±1.7	0.90 ±0.17	1.6 ±0.9	Dy 1.3 ±0.8	0.26 ±0.17	0.74 ±0.5	$\begin{array}{c} 0.88 \\ \pm 0.89 \end{array}$	0.13 ±0.13	(0.45)	0.066 ±0.016	7.6 ±2.3	$\begin{array}{c} 0.018 \\ \pm 0.006 \end{array}$	(3.2)
553 ±215	23 ±7.8	42 ±16	14	3.1	0.93		Tb 0.41			0.86	0.14	(0.46)	$\begin{array}{c} 0.047 \\ \pm \ 0.022 \end{array}$	4.5 ±2.0	$\begin{array}{c} 0.017 \\ \pm 0.006 \end{array}$	(0.53)
871	29	60												17		7.3
556																
919	40	76								2.4				19		
1600	29	52	15	2.1	0.75		Dy0.48	0.09	0.18	0.11	0.015	0.98	0.18	14	0.019	3.0
562	10	25	9.1	1.7	0.48	1.3	Dy 0.76	0.15	0.35	0.26	0.03		0.34	23	0.017	
2600	24	38	(11)	1.6	0.94		Tb (0.34)			0.47	0.07	(0.57)	0.24	12	0.018	0.26
747	27	52											0.93	43	0.072	
478	25	46	17	2.9	0.59	1.9	Dy 1.1	0.21	0.55	0.36	0.047	0.60	0.75	34	0.022	16
750	20	39	15	2.7	0.78	2.0	0.35/1.4	0.33	0.84	0.70	0.11	0.64	0.22	13	0.023	(3.5)
596	18	37	15	3.0	0.93	2.7	0.50/2.7	0.65	1.5	1.3	0.18	1.1	0.19	11	0.026	(2.8)

for the average; in case of Cr, Zr, Ca, Ta and several REE the number of samples was smaller than n). The analytical data for the individual samples are available on request from K.H.W. or H.H.

tive to those of the non-metamorphic rock equivalents. The discrepancy can be demonstrated with the 70 samples of Archean metatonalites containing 1.0% K compared with 1373 samples of non-metamorphic post-Archean tonalites and dacites from worldwide localities containing on average 1.7 and 1.9% K, respectively

(Chayes 1975; Le Maitre 1976; Ewart 1979). The total of 70 meta-tonalites of our investigation contains 3.3% Ca which can be compared with an average of 97 tonalites and 1276 dacites from world-wide sampling of nonmetamorphic rock species containing 3.9 and 3.1% Ca, respectively.



**Fig. 2.** Plots of Ca against K concentrations in Archean mafic, tonalitic, granodioritic, quartz monzonitic and granitic rocks in granulite and amphibolite facies conditions from Greenland. For

comparison are plotted world-wide averages of magmatic rocks from the literature

Concentrations of Rb, Pb and Tl are reasonably well correlated with the potassium abundance in meta-tonalites, meta-granodiorites and granites because of some resemblance in their crystal chemical behavior (Figs. 3, 4, 5). Systematically high K/Rb, K/Pb and K/Tl ratios are observed in granulite facies relative to amphibolite facies rocks. The K/Rb ratio of amphibolites retrogressed from granulites by fluids is in general smaller than 300 (c.f. Fig. 3). The averages for worldwide sampled granulites and non-metamorphic andesites and dacites as well as for meta-tonalites from Manitoba and Scotland are close to 300 (crosses in Fig. 3). They follow the so-called main differentiation trend in a K/Rb versus Rb plot as reported by Shaw (1968). The same trends in K/Rb, K/Pb and K/Tl were observed for a large variety of rocks by Heinrichs et al. (1980).

Granitic magmas are characterized by low K/Rb ratios because of the larger compatibility of K relative to Rb. Whalen et al. (1987) report average K/Rb ratios as low as 137, 151 and 177 for 205 felsic S-type granites, 578 S-type granites and 421 felsic I-type granites, respectively. Granulitic restites of partial melting have therefore K/Rb ratios exceeding those of their source rocks. Depletion of Rb, Tl and Pb by partial melting was larger than the depletion of K.

Seawater is a product of both reaction with hot basalt at ocean ridges and continental weathering. Its K/Rb ratio is 3270. This ratio is distinctly larger than that of 2100 which is typical for river water (Turekian 1969). The increase from the river water to the seawater ratio reflects the basalt alteration at ocean ridges. This reaction causes a low K/Rb ratio in the altered basalt. We realize that the K/Rb ratio allows to discriminate between residual rocks from two different processes. Restites from granitic partial melts have large ratios and products from reactions with hot brines have low ratios.

The majority of samples from Isua (W Greenland) are especially low in their K/Rb and K/Tl ratios. Six tonalites from this area have an average K/Rb ratio of 156. The extreme (Sample 236961) has a ratio as low as 100. We favour reactions with hot sodium- and chloride-rich brines to explain the low K/Rb, K/Tl and K/Rb



Fig. 3. Plots of Rb against K concentrations of mafic, tonalitic, granodioritic, quartz monzonitic and granitic rocks (*stars*) in granulite (*solid circles*) and amphibolite facies (*open circles*) rocks from Greenland. Crosses designate averages of MORB (Hofmann 1988) continental tholeites (Wedepohl 1975), andesites (Taylor 1977) mafic and felsic granulites (Rudnick and Presper 1990) from world-wide sampling, respectively. Crosses for tonalites (T) and (E) and dacites refer to values from Tarney et al. (1979), Ermanovics et al. (1979) and Ewart (1979), respectively (c.f. Table 1)

ratios as well as the low K concentrations in certain Archean meta-tonalites to meta-granodiorites from Greenland. Retrogression from granulite- into amphibolite-facies rocks in E-Greenland associated with shearing was accompanied by an increase of the chlorine concentration from 200 to about 2500 ppm Cl probably due to reactions with brines. Indication of Rb and Pb gain during retrogression by fluids comes from the displacement of Rb-Sr and Pb-Pb isochrons observed in comparison with ion probe U/Pb dating of zircons (Bridgwater et al. 1989; Schiøtte 1989).

The rare  $Bi^{3+}$  (with some crystal chemical relations to  $Pb^{2+}$ ) is also correlated to the potassium abundance at an average crustal K/Bi ratio of  $2.7 \times 10^5$ . Abnormally large K/Bi ratios are found in the Isua tonalite and the E Greenland granulites. In contrast granites and granodiorites from Greenland and from worldwide sampling have very low K/Bi ratios. Information on the sources of tonalitic magmas from REE and Rb concentrations

Evidence from experimental partial melting of tholeiite and melting of trondhjemite suggests that tonalitic (dacitic) magmas are formed from partial melting of hydrous mafic rocks (Helz 1973, 1976 and Johnston and Wyllie 1988). The latter authors quoted the results from the literature published from 1976 to 1988 and reported about hydrous melting conditions of trondhjemite at 15 kb pressure. Their experiments indicate that trondhjemitic (dacitic) magmas can be produced at intermediate H<sub>2</sub>O contents in the melt (>5% <9%) and intermediate degrees of partial melting of mafic precursors such as garnet amphibolite. Temperatures from about 800 to 900° C are required. Helz (1973, 1976) generated a melt of dacitic composition from a tholeiitic amphibolite at about 800° C.



Fig. 4. Plots of Pb against K concentrations of Archean mafic, tonalitic, granodioritic, quartz monzonitic and granitic rocks in granulite and amphibolite facies conditions from W Greenland (*open circles*) and E Greenland (*solid circles*). Crosses mark averages of MORB (Hofmann 1988), continental tholeites (Wedepohl 1975) and andesites (Taylor 1977) from worldwide sampling, respectively. Additional crosses designate tonalites (T) and (E) and dacites listed in the literatur and in Table 1



Fig. 5. Plots of Tl against K concentrations of Archean mafic, tonalitic, granodioritic, quartz monzonitic and granitic rocks in granulite and amphibolite facies conditions from W Greenland (*open circles*) and E Greenland (*solid circles*). Letters E mark tonalitic gneiss from Isua



Fig. 6a and b Average REE distribution in sets of Archean metamagmatic rocks of tonalitic to granitic composition from Greenland (Sets a1, a3, a4, b1, b2 from Table 1) in comparison with averages of MORB (Hofmann 1988), continental tholeiites (Wedepohl 1975) and andesites (Taylor 1977). The data on these rocks are normalized to chondrites as compiled by Mason (1979).

**c** REE distribution in 11 individual samples of tonalites etc. (partly in amphibolite facies) from Charcot Fjelde (SE Greenland) normalized to chondrites as compiled by Mason (1979). The average of this set is plotted as curve b1 (Amphibolite F.) in **b** and demonstrates the almost complete compensation of positive and negative Eu anomalies

The LREE against HREE fractionation in Archean tonalites, trondhjemites and granodiorites from Greenland is high which could suggest an origin from a garnet bearing mafic source (Fig. 6). If we compute the [La/  $Lu]_N$  or  $[La/Yb]_N$  ratios of a melt in equilibrium with an amphibolite source (continental tholeiite with normalized concentrations of 47 ppm La; 14 ppm Yb; 14 ppm Lu) from the distribution coefficients listed in Table 2 these ratios are close to 5 at about 20% partial melting (F = 0.2) of amphibolite I (containing 50% plagioclase and 50% amphibole). We use for this calculation the simplified equation A on batch melting reported by Shaw (1970) which is listed in Table 2. REE concentrations in rocks are normalized to REE concentrations in chondrites ( $[RE]_N$ ). It must be kept in mind that mineral distribution coefficients of REE vary in the literature (compare Table 2 with Rudnick and Taylor 1986). The  $[La/Lu]_N$  or  $[La/Yb]_N$  ratios of the respective melt will decrease to values a little smaller than 1 if the amphibolite source consists of N-MORB (with normalized concentrations 12.2 ppm La, 20.5 ppm Yb, 17.9 ppm Lu, Hofmann 1988) instead of a continental tholeiite. Average  $[La/Yb]_N$  ratios in the Archean tonalites and granodiorites of our investigation are 12 and 87, respectively. Rudnick and Taylor (1986) report frequency distributions of [La/Lu]<sub>N</sub> ratios in Archean tonalitic granulites from worldwide sampling with the majority of these rocks having ratios between 15 and 50. If we replace our former model amphibolite I by amphibolite II which contains 35% garnet (almandine>pyrope>grossular), 30% plagioclase (oligoclase) and 35% amphibole the  $[La/Yb]_N$  ratio of the melt increases from about 5 to about 13. REE modelling thus suggests that a garnetbearing mafic source is required for partial melting which has formed the tonalitic magmas. Martin (1987) has modelled a comparable source for Archean tonalites from E Finland. Our source must have had [La/Lu]<sub>N</sub> and  $[La/Yb]_N$  ratios above 1 (continental tholeiite) and not below 1 (N-MORB). If the required enriched mantle with a  $[La/Yb]_N > 1$  is formed by a subduction process it needs the introduction of a somehow unusual ocean crust with a composition of more than 10% clay sediment in less than 90% MORB. Chase and Patchett (1988), and Gill and Bridgwater (1979) have demonstrated by Sm-Nd isotopes and by REE pattern of Ameralik mafic dykes, respectively, that a depleted mantle reservoir (which forms N-MORB-type magmas) existed very early in the Earth's history. But their observation must not be generalized for the total upper mantle.

The occurrence of the high pressure mineral garnet in the hydrous mafic rocks of the abundant tonalitic to granodioritic products in the Archean crust requires the assumption of a crust more than 25 km thick. Wells (1979) and Riciputi et al. (1990) have estimated the granulite facies peak conditions in the felsic layer of the Archean crust in SW Greenland at 800° C/10.5 kb and 800° C/8.9  $\pm$  1 kb, respectively. The pressure indicates a minimum thickness of the felsic part of the crust of about 30 km at 2.8 Ga. The unexposed part of the felsic crust below the present erosion level and a mafic layer of unknown thickness must be added to this 30 km.

The REE patterns of averages of groups and of the

Table 2. Distribution coefficients (D) of selected elements between tholeiitic source rock and dacitic partial melt. The table includes mineral/melt partition coefficients (k) for three major minerals and bulk partition coefficients for two amphibolites (I and II) (Amphibolite II: 50% plag, 50% hbl; Amphibolite II: 30% plag, 35% hbl, 35% gar)

	K	Zn	Rb	Sr	Zr	Ba	La	Ce	Sm	Eu	Yb	Lu	Pb
Hornblende (k) Plagioclase (k) Garnet (k)	0.2 0.15 ≤0.009	6.8 0.4 ~1.0	$0.03 \\ 0.05 \le 0.009$	0.2 2.4 0.001	1.5 0.04 0.3	0.07 0.2 ≤0.01	0.2 0.2 <0.05	0.3 0.2 0.1	0.9 0.1 0.3	0.9 1.6 0.4	0.8 0.05 3	0.5 0.05 4	0.15* 0.45 <0.01*
I Amphibolite (D) II Garnet amphibolite (D)	0.18 0.12	3.6 2.8	0.04 0.03	1.3 0.79	0.77 0.64	0.13 0.09	0.2 0.15	0.25 0.20	0.5 0.45	1.3 0.79	0.4 1.3	0.3 1.6	0.3 0.19
References	(a) (f) (g)	(e) (g)	(a) (f) (g)	(a) (f) (g) (i)	(b) (g)	(a) (f)	(g) (h) (i)	(g) (h) (i)	(g) (h) (i)	(g) (h)	(g) (h) (i)	(g) (h)	(d)

(a) Hanson (1978); (b) Fujimaki et al. (1984); (c) Shaw (1972); (d) Leeman (1979); (e) Schock (1977); (f) Gill (1978); (g) Wedepohl (1985); (h) Irving (1978); (i) Dostal et al. (1983)

Equations for batch partial melting according to Shaw (1970)

A)  $c_L/c_o = 1/(D - DF) + F$ 

B)  $c_L/c_o = 1/(D - PF) + F$ 

 $c_L$  = weight concentration of a trace element in a derived melt;  $c_o$  = weight concentration of a trace element in a source rock; D=bulk distribution coefficient of a given trace element formed from mineral distribution coefficients (k) proportional to the modal mineral composition of the rock; P = bulk distribution coefficient of a given trace element formed from mineral distribution coefficients proportional to actual contributions of minerals to the melt; F=weight fraction of melt relative to source rock

total of metatonalites and meta-trondhjemites from W Greenland have no or small negative Eu anomalies (c.f. Fig. 6a+b). The Nuk gneiss of Sample 131582 is the rare case of a distinct positive Eu anomaly of a tonalite from W Greenland. Five out of eleven samples of metatonalites from Charcot Fjelde (SE Greenland) have a positive Eu anomaly, however (Fig. 6c). Only one sample of this group has a negative anomaly. Quartz monzonites and granodiorites from E Greenland have a distinct positive Eu anomaly. Examples without Eu anomaly and with a positive Eu anomaly are almost equally abundant in the compilation by Rudnick and Taylor (1986) on the REE distribution in Archean tonalitetrondhjemite rocks from worldwide sampling. Species with negative anomalies are rare in this record. Mafic source rocks of mantle origin are expected to have no Eu anomaly. Such a REE composition will probably be inherited by partial melts under certain conditions which can be modelled on the basis of distribution coefficients and equation B listed in Table 2. Equation B considers cases in which the contribution of certain minerals to a partial melt exceeds their proportion in the source rock. The proportion of plagioclase to the partial melt must slightly exceed 60% to reduce the size of (D - PF + $F_{E_{u}}$  so that it attains of size of  $(D-PF+F)_{S_{m}}$ . The experiments by Johnston and Wyllie (1988) suggest that larger proportions of plagioclase in the melt are due to higher water concentrations (>6%) in the source. If our source rock contributes its minerals in modal proportions to the partial melt (Eq. A) this melt will have a negative Eu anomaly. Natural observation suggests that many intrusions of mafic melts differentiate and form cumulates. Cumulates with a predominant plagioclase fraction have a positive Eu anomaly and cumulates with a predominant garnet plus amphibole fraction a negative anomaly. If such cumulates are products of local differentiation or sources of partial melts, they can easily cause magma compositions with a positive or negative Eu anomaly or without any anomaly. Kay and Kay (1990) explain the absence of an Eu anomaly from certain tonalites by partial melting of plagioclase free mafic source rocks in very thick crustal sections. The occurrence of small positive or negative Eu anomalies in several of the investigated Archean rocks could be explained by later differentiation at shallower crustal levels. The bulk continental Earth's crust which includes the restites of partial melting should have no Eu anomaly except some fraction with an Eu anomaly is recycled into the mantle. A set of 6 granites from the Early Archean Isua series (W Greenland) (a1 in Fig. 6b) has no Eu anomaly which demonstrates a compensation of positive and negative anomalies from plagioclase and mafic mineral contributions to the specific magmas. Our observation confirms the statement of Taylor and McLennan (1985) about the absence of an Eu anomaly in large parts of the Archean continental crust.

*Yb, Y and Sc* in the Archean quartz feldspathic rocks from Greenland are correlated to the Ca concentration. This reflects the comparable size of the respective ions in the crystal structures of garnet, amphibole and plagioclase in the source rocks of the partial melts.

The degree of partial melting can be estimated by inserting elements with a very low bulk distribution coefficient (close to zero) into equation A of Table 2. Such an element is Rb which has an average concentration of 14 ppm in continental tholeiites (Wedepohl 1975; Heinrichs et al. 1980), 26 ppm in tonalites from Greenland and 74 ppm in unaltered dacites from worldwide sampling (Ewart 1979). From equation A we derive:  $F \approx$  $c_0/c_L$ . For Archean tonalites which have secondarily lost some K and Rb, we get  $F \approx 0.53$  and for dacite melts formed from a continental tholeiite as source we calculate  $F \approx 0.19$ . Results from experimental melting by Johnston and Wyllie (1988) suggest that realistic degrees of partial melting range between 20 and 50% (F=0.2 to 0.5). We have to use the lowest possible value of



Fig. 7. Plots of Sr against Ba concentrations of mafic, tonalitic, granodioritic, quartz monzonitic and granitic rocks (*stars*) in granulite (*solid circles*) and amphibolite facies (*open circles*) conditions from Greenland. Crosses designate averages of andesites (Taylor 1977) from worldwide sampling and granites (*I*- and *S*-type) from Australia (Whalen et al. 1987). Crosses for tonalites (*E*) and (*T*) and dacites are also based on data from the literature (Table 1)

20% partial melting. Otherwise the K concentration in the required source rock is unrealistic high. Continental tholeites which are derived from an enriched mantle or magma chamber, contain on average 0.7% K (Table 2). They can form tonalitic melts with 2% K at 20% partial melting.

### Additional information on the sources of tonalitic magmas from Sr, Ba, Zn, Cd, Zr, Nb, Ta and Th concentrations

The calculations reported in the former sections demonstrate that about 20% partial melting of amphibole bearing mafic granulites with a composition close to an average continental tholeiite can produce tonalitic to granodioritic rocks such as analysed from Greenland. Element accumulations in dacites (tonalites) relative to continental tholeiites increase in the sequence: Zn < Yb < Sm < $Zr < Sr < Ce < La < Pb \sim Ba < Rb$ . This order resembles with a few exceptions the sequence of decreasing bulk distribution coefficients for the garnet amphibolite II (amphibole bearing granulite) source in equilibrium with felsic melts as listed in Table 2. The correlation is weaker in case of amphibolite I (caused by Sr, Yb etc.). This correlation between element accumulation and size of partition coefficients supports our assumptions about a garnet amphibolite source rock of partial melting.

In Fig. 7 we have plotted *Sr against Ba* concentrations in quartz feldspathic rocks from Greenland. Both elements are correlated from mafic to tonalitic (granodioritic) rocks. The correlation of Sr and Ba for granitic rock types occurs at lower Sr concentrations than that for tonalites. We explain the two different trends of element correlations by two different source rocks for partial melting: mafic granulite and tonalite (or a comparable sediment). Mafic granulite has bulk distribution coefficients for Sr and By which are smaller than one (Table 2). These cause higher than source concentrations of Sr and Ba in the partial melts. Tonalites which mainly consist of plagioclase (40-50%), quartz (30%), amphibole (8%), and biotite (8%) have bulk distribution coefficients for Sr and Ba which are almost equal to one or smaller than one ( $D_{Sr}$  1.1;  $D_{Ba}$  0.7) and cause almost equal and larger than source concentrations of these elements in granitic melts. For the calculation of the bulk partition coefficients we have used data on plagioclase and amphibole from Table 2 and have compiled data on biotite from the literature ( $k_{sr}$  0.24;  $k_{Ba}$  8.3).

We can calculate the following ranges of concentrations of Sr and Ba in tonalitic melts at 20% partial melting on the basis of D values for garnet amphibolite listed in Table 2 and Sr and Ba concentrations in mafic dike rocks from Greenland and in continental tholeiites as listed in Table 1: 190 and 490 ppm Sr; 160 and 680 ppm Ba. The average Sr and Ba concentrations in granodiorite samples from Greenland are 460 ppm Sr and 630 ppm Ba (Table 1) which can be explained by partial melting of average continental tholeiites as being derived from an enriched source. The average Sr abundance in tonalitic gneisses from Greenland (400 ppm Sr) is slightly lower than that of recent orogenic dacites of world-wide sampling (536 ppm Sr: Ewart 1979) and of tonalitic gneiss from Canada (512 ppm Sr: Ermanovics et al. 1979) indicating some loss of Sr from the former rocks. Extraordinary large concentrations exceeding 700 ppm Sr can be observed in 8 out of 16 samples of sheared tonalitic granulite from Charcot Fjelde (SE Greenland). Only 2 of these 8 samples have positive Eu anomalies. The general correlation between Sr content and degree of retrogression strongly suggests addition of Sr by fluids.

Ba is distinctly lower in the tonalitic gneisses (446 ppm Ba) and higher in the granodiorites (1290 ppm Ba) from Greenland than in young orogenic dacites (920 ppm Ba) and granodiorites (870 ppm Ba) from worldwide sampling (Ewart 1979; Puchelt 1972). The same fluids which have extracted some S, K, Rb, Pb, TI and Sr from tonalites in Greenland might also have mobilized a certain fraction of the original Ba concentration. Abundances above 700 ppm Ba occur in bleached more than in non-bleached tonalitic granulites from Charcot Fielde (E Greenland) and might be partly introduced by fluids. A general correlation of the Ba concentrations with the degree of retrogression into amphibolite facies rocks is not demonstrable, however. Barium in the majority of granodioritic granulites from Storö and in all quartz monzonitic granulites from Charcot Fielde (SE Greenland) exceeds 1300 ppm. This element could have increased in granulitic metatonalites to metagranodiorites during the separation of a granitic melt. But an increase by this mechanism will not exceed 30% and cannot explain Ba concentrations above 1300 ppm.

Zn is one of the few compatible elements of this investigation characterized by a bulk distribution coefficient between amphibolite and melt of about 3 (Table 2). Separation of about 30% amphibole (or pyroxene) from a basaltic or dioritic melt to produce a tonalitic magma would reduce the original concentration of 70 to 100 ppm Zn in diorites or basalts to about 7 to 10 ppm (estimate based on the equation for Rayleigh fractionation). The average Zn concentration in 70 tonalites of our investigation is 62 ppm Zn. This precludes an origin of tonalite by differentiation of a dioritic/basaltic magma.

The average crustal Zn/Cd ratio of 800 as reported by Heinrichs et al. (1980) can be used as standard to recognize that the Zn/Cd ratio of 1550 in granulitic metatonalites and metatrondhjemites from E Greenland is high. This high ratio is compensated by a low ratio of granites which could have been separated as partial melt from metatonalites during granulite formation. Quartz monzonites and granites from Greenland have a Zn/Cd ratio of 630, granites and granodiorites from worldwide sampling a ratio of 715 (Heinrichs et al. 1980). Averages of meta-tonalites from W Greenland, mafic dikes from Greenland and continental tholeiites from worldwide sampling have Zn/Cd ratios close to 1000. From these data can be assumed that partial melting of mafic source rocks to form tonalitic magmas does not fractionate Zn against Cd. Continental tholeiites as potential source rocks of tonalitic melts contain on average 100 ppm Zn.

We can calculate a Zn concentration of 44 ppm in these tonalitic melts at 30% partial melting (based on the D value of amphibolite II in Table 2). A value of 44 ppm Zn is a little low compared with the 62 ppm Zn in 70 metatonalites from E and W Greenland. The discrepancy might indicate that the proportion of amphibole in the potential source rock is smaller than assumed. The distribution coefficient of hornblende raises the bulk distribution coefficient (c.f. Table 2).

Ratios of the high valence elements Zr/Nb and Nb/Tawith very similar crystal chemical properties are expected not to vary much between abundant cosmic and terrestrial materials. We have some data on Nb abundances and a limited number of Zr and Ta values on the Archean quartzfeldspathic rocks from Greenland. The Nb/ Ta ratio of both cosmic materials (carbonaceous chondrites) and mantle derived MORB is 18 (Jochum et al. 1986; Hofmann 1988). This ratio is 14 for amphibolitefacies and granulite-facies metatonalites from Greenland and represents a minor deviation from the cosmic/mantle value. A slightly larger fractionation between mantle and crust has been observed in case of the Zr/Nb ratio because of the different charge and the slightly larger incompatibility of Nb. The cosmic and primitive mantle ratios of 15.6/15.7 (Jochum et al. 1986; Hofmann 1988) decrease to continental crustal values of 10 and 9 reported by Shaw et al. (1986) and by Taylor and McLennan (1985), respectively, or to a ratio of 13 reported for more than 2000 I-type and S-type granites by Whalen et al. (1987). This low level of Zr/Nb ratios is compensated by higher than cosmic ratios of almost 30 for the depleted mantle and MORB composition (Hofmann 1988). The Archean meta-tonalites from W and E Greenland have an average Zr/Nb ratio of 20 which is intermediate between that of the primitive and the depleted mantle. This ratio could also indicate crustal contamination of the depleted mantle.

Th data on 26 samples are available from the present investigation. They can be supplemented by Th values on 105 gneiss samples from the Fiskenaesset area in W Greenland published by Kalsbeek (1976). The range of variation of Th in tonalites and granodiorites is large.

*Nb/Th ratios* of major rock species reflect the larger incompatibility of Th. The primitive mantle and the depleted mantle (MORB) have average Nb/Th ratios of 7.6 and 18.7, respectively (Hofmann 1988). The continental crust compensates the large ratio of the depleted mantle with a value of about 2 (Shaw et al. 1986). Four granulites from Charcot Fjelde (SE Greenland) have a Nb/Th ratio as high as 15 in contrast to four partly retrogressed rocks from the same locality with a ratio of 6.4. The depletion of Th in the former set can be explained by a separation of granitic melt with a low Nb/Th ratio. Abundant granites have Nb/Th ratios smaller than one (Whalen et al. 1987).

### Sulfur abundance

Worldwide sampled granitoids, gneisses (with mica schists) and mafic rocks contain on average 330 ppm S, 690 ppm S and 900 ppm S, respectively (Wedepohl

1987). The latter concentration is restricted to intrusives and volcanics which have not lost sulfur by degassing during consolidation (Moore and Schilling 1973; Mathez 1976). The mafic dikes in the Godthåbs area and the meta-tonalites to meta-granodiorites from W and E Greenland with averages of 620 and 210 ppm S, respectively, are low in sulfur. They contain only 65 to 50% of their primary sulfur concentration. The dioritic to tonalitic amphibolite facies-gneisses from the Archean Nuk Formation and the granulites from the Tasiusarssuaq terrane (Ameralik Fjord) vary from 9 to 5160 ppm S without any correlation to the K or Ca concentration of these rocks. Bleached granulites from Charcot Fielde (SE Greenland) contain only 60% of the sulfur concentration of the non-bleached rocks from the same area because of partial oxidation of sulfides by circulating fluids. This and the dissolution of sulfides in chloriderich brines are the two processes which cause a decrease of sulfur during metamorphism. The increase of solubilities of common sulfides in relation to chloride concentration was reported by Helgeson (1969).

## Mobilization of elements during amphibolitization or granulitization

It is not easy to characterize the individual prograde and retrograde processes in the complex tectonic history of the Archean units in Greenland. We have selected rock series of common provenance but of different p-T history for comparison.

Granulitic tonalites from Charcot Fielde (SE Greenland) can be compared with bleached samples of the same series which were retrogressed into amphibolite facies rocks. Minor differences between the two sets of 22 and 16 samples are observable in a 10% higher average Ca concentration of the non retrogressed granulites. Average abundances of Zn, Zr, Nb, Cd, Bi and REE are almost the same in both sets. But concentrations of Pb, Tl, Rb, Sr, Ba and K are in this order 50 to 15% higher in the amphibolite facies materials relative to the granulites. A similar effect can be observed in a comparison of the least retrogressed granodiorite Sample 226837 from Storø (SE Greenland) with 14 retrogressed granodiorite samples from the same sampling site. The latter have similar Ca, Zn and Cd concentrations as Sample 226837 but twice as high abundances of Rb and Tl. Glassley and Bridgwater (1985) observed an increase of Si, K, Pb, Cl and SO<sub>4</sub> and a decrease of Ca, Mg and Al during the introduction of H<sub>2</sub>O-rich fluids in a shear zone cutting the granulite facies rocks on Storø. Bridgwater et al. (1989) made a general comparison of granulite facies tonalitic gneisses with their retrogressed equivalents in amphibolite facies in SW and SE Greenland and noted a general increase in total Pb content exceeding a factor of 2. Granulite facies metatonalites and their retrogressed equivalents occur at Kangimut samissoq on the coast of Ameralik in the Tasiusarssuaq terrane (Fig. 1). Both groups of gneisses contain similar Ca, Zn, Sr, Nd and Cd averages but distinctly different Tl, Rb and Pb abundances. The factors of

Tl, Rb and Pb accumulation in the retrogressed amphibolites relative to the unaltered granulites are 3.7, 2.7 and 2, respectively. The K/Rb ratio decreases with retrogression. From this we can deduce that Rb, Tl and Pb are highly and Sr, Ba and K are fairly mobile in the hydrothermal (metasomatic) fluids which cause retrogression from granulite facies to amphibolite facies assemblages. As noted earlier our results indicate high Na, Cl and S concentrations in the fluids.

A second problem is the mobility of elements under prograde conditions. We have no set of samples available in which the same series of quartz feldspathic rocks occurs in a prograde sequence from the amphibolite into the granulite facies. Therefore we only could compare 34 granulitic tonalites with 12 amphibolite-facies tonalites of rather different provenance. The former set contains 12 tonalitic granulites from the Central Ameralik Fjord (SW Greenland) and 22 tonalitic granulites from Charcot Fielde (SE Greenland). The latter set consists of 6 plus 6 amphibolite facies tonalites from Isua and from the Nûk series, respectively. We tried to exclude from this comparison amphibolite-facies rocks which were known to be retrogressed from granulites. The set containing granulites has about 20% higher Ca, Sr, Ba, Sc and Zn concentrations compared with the set of amphibolite-facies rocks. The suggested increase of Ca relative to its primary concentration indicates a loss of major elements in a size which probably could only be attained by melts and not by  $H_2O-CO_2$  fluids. Peak temperatures at 800° C required partial melting of hydroxide bearing quartz feldspathic rocks. Tl, Rb and Pb are 6, 4 and 3 times lower in the granulites relative to the amphibolite facies rocks with the difference in K is only 20%. Most of the gains and losses can be explained by about 25% partial melting and the separation of a granitic melt. The balance has been calculated for the equation: 75% granulitic tonalite plus 25% felsic granite equals 100% amphibolite-facies tonalite. We have used for this balance the data on felsic granites published by Whalen et al. (1987). A part of the granitic melt has formed light constituents of migmatites or veins either preserved in the tonalitic granulite or the higher crust.

# Composition of the exposed and the total Archean crust in Greenland

We have estimated the average abundance of 28 elements in the exposed and in the total Archean crust of Greenland from group averages of tonalites, granodiorites, granites and metamafic rocks as listed in Table 2. These groups are statistically weighted according to their abundance in the Fiskenaesset region as mapped by Kalsbeek (1976) (70% meta-tonalites and granodiorites, 15% granites, 15% mafic rocks). We have additionally calculated the composition of the total Archean crust of Greenland by an increase of the fraction of mafic rocks from 15 to 22% according to the information from Drummond (1988) on the lower crust in W Australia. The abundance of 24 elements in the Archean crust of Greenland (which resembles the Archean Canadian Shield as reported by



Fig. 8. Plots of normalized concentrations of 24 elements in the Archean crust in Greenland (*crosses*) and in the present bulk continental crust as calculated by Taylor and McLennan (1985) (*circles*) and by Wedepohl (1990) (*circles* with *crosses*). All concentrations are normalized by division through the respective concentration

Eade and Fahrig 1971) is compared with the Post-Archean bulk continental crust in Fig. 8. We used two alternative sets of the Post-Archean crust for this comparison: one published by Taylor and McLennan (1985) and one calculated by Wedepohl (1990). The two sets originate from rather different sources. All concentrations were normalized by division through the respective concentration in the primitive mantle as reported by Hofmann (1988). The sequence of elements corresponds to the order of decreasing concentrations in the continental crust as listed by Taylor and McLennan (1985). This is almost conformable with the order of increasing compatibility in mantle minerals. A few elements (Th, Ta, Nb) deviate from a smooth curve of normalized abundances in the Greenland crust partly because of the small number of analytical data on Th and Ta. The two sets for the bulk crust composition converge towards elements with higher compatibility. They both deviate from a smooth curve in case of Sr and HREE. This probably reflects some uncertainties in the alignment of element abundances.

The curves for the Archean and Post-Archean crust do not differ systematically with the exception of a slightly more mafic composition of the Post-Archean crust. This confirms the results by Shaw et al. (1986) in the primitive mantle (as reported by Hofmann, 1988). The composition of the bulk Archean crust of Greenland is tentatively calculated as consisting of 50% tonalite, 15% granodiorite, 14% granite, 22% mafic rocks based on information from Kalsbeek (1976) and Drummond (1988)

based on extensive sampling of the Canadian Shield and is at variance with the suggestion of secular chemical changes by Taylor and McLennan (1985). We come to the conclusion that the typical processes of crust formation started to work rather early in the Archean. This is consistent with the large number of isotope studies which have suggested that sialic crust has been extracted from the mantle from at least 3.8 Ga to the present and that at least half the present continental mass was already formed by 2.5 Ga (Allègre 1982).

### Conclusions

From the absence of trends in the chemical composition it can be concluded that the process of the formation of tonalitic to granodioritic magmas did not change from the Early to the Late Archean. Partial melting of amphibole containing mafic granulite at about 800° C is a likely process to have formed the magmas of the abundant Archean tonalites and granodiorites in SW and SE Greenland. Experimental results suggest and chemical balances support this assumption. The minor occurrence of diorite and the relative high concentration of the compatible element Zn in tonalites precludes their origin from differentiation of mafic to intermediate magmas. Modelling based on K, Rb, Sr, Ba, La and Yb abundances and 20% partial melting demonstrates that a source with the composition of continental tholeiites is required for the formation of tonalitic magmas. These rocks were derived from slightly enriched mantle sections or magma chambers. A larger than 60% contribution of plagioclase to the partial melt (e.g. from plagioclase rich cumulates) has formed granodioritic (and rarely tonalitic) rocks with a positive Eu anomaly. The majority of tonalites has no Eu anomaly because of a balanced contribution of mafic minerals and plagioclase or absence of plagioclase from the source rock.

The Archean meta-tonalites to meta-granodiorites from Greenland have generally lost some K and S and gained Na relative to their non-metamorphic equivalents. A comparable exchange of Na for K is caused by fluids above 200° C at ocean ridges. Dissolution of a certain fraction of the primary sulfides required chloride rich and/or oxidizing fluids. Separation of granitic partial melts during granulitization of tonalites has mobilized Tl, Rb, Pb and K and has accumulated Ca, Sr, Ba and Sc in the restitite. The degree of partial melting was about 25%. Some of the granulitic rocks must have gained their concentrations of Ba (and Sr) by local fluid advection preceding granite separation. Relatively high K/Rb, K/Pb, Zn/Cd and Nb/Th ratios in granulites are compensated by low ratios in granitic melts to be equal to intermediate ratios in amphibolite facies tonalites. Fluids which have retrogressed granulites into amphibolite-facies rocks supplied Rb, Pb, Tl, Ba and Sr to the latter materials. The mobility of Rb, Sr, Pb makes isotope dating in the Rb-Sr and U-Pb system difficult (Bridgwater et al. 1989; Schiøtte 1989).

A comparison of the abundance of 24 elements in the Archean crust in Greenland with the same elements in the present bulk crust as calculated by Taylor and McLennan (1985) and Wedepohl (1990) indicates that the continental crust has not changed much in its chemical composition from the early Archean to present. Averages of elements deviating from a smooth curve which represents the Archean crust (Th, Ta, Nb), are based on a too small number of analytical data.

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