# Zirconium-bearing amphiboles from the Igaliko Dyke Swarm, South Greenland

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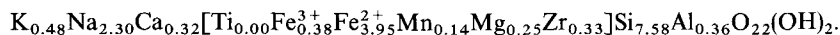
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Abstract

Sodic-calcic and alkali amphiboles from benmoreitic members of the Igaliko Dyke Swarm contain up to 4.13 wt. % ZrO_2. It is proposed that Zr enters the amphiboles by a coupled substitution of

$$Zr_C^{4+} + Al_T^{3+} \rightleftharpoons Fe_C^{3+} + Si_T^{4+}$$
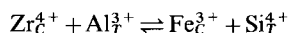
(where C = octahedral site and T = tetrahedral site) to produce the richest Zr-bearing amphiboles so far identified, with compositions ranging up to

$$K_{0.48}Na_{2.30}Ca_{0.32}[Ti_{0.00}Fe_{0.38}^{3+}Fe_{3.95}^{2+}Mn_{0.14}Mg_{0.25}Zr_{0.33}]Si_{7.58}Al_{0.36}O_{22}(OH)_2.$$

These amphiboles crystallize at a late stage from magmas which were Zr-rich, highly peralkaline and hydrous, with an f_{O_2} close to the synthetic QMF buffer. The incorporation of Zr in to the amphibole is a consequence of the failure of other Zr-bearing phases (such as zircon, baddeleyite, eudialyte) to crystallize.

KEYWORDS: Zr-bearing amphiboles, amphiboles, Igaliko Dyke Swarm, Greenland.

Introduction

MINOR amounts of Zr have been reported in alkali rich amphiboles in only a few cases. Nash and Wilkinson (1970) report 0.8 wt. % ZrO_2 in an arfvedsonite from the Shonkin Sag laccolith; Larsen (1976) reports 0.78 wt. % from an arfvedsonite from the Ilímaussaq complex; and Jones (1980) detected 0.75 wt. % from an arfvedsonite in the Motzfeldt centre, South Greenland. Dana (1892, p. 400) presents an analysis of a riebeckite with 0.75 wt. % ZrO_2. As far as the author is aware contents of ZrO_2 in alkali-rich amphiboles in excess of 0.8 wt. % have not previously been reported.

Zirconium, however, has been found to be an important constituent of late crystallizing alkali amphiboles from benmoreitic members of the Igaliko Dyke Swarm, South Greenland, reaching contents of 4.13 wt. % ZrO_2.

Geological setting

The Igaliko Dyke Swarm is a mid-Proterozoic dyke swarm largely related to Late-Gardar activity

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in South Greenland (Emeleus and Harry, 1970). Two major swarms of dykes can be recognized in the area tending to either Si-oversaturated or Si-undersaturated residual compositions and these can be distinguished by their Zr/Nb ratios (Pearce, 1988). The oversaturated dykes in the area are members of the larger Tugtutôq–Ilímaussaq–Nunataq dyke swarm and the undersaturated members are related to nepheline syenite central complex activity in the Igaliko region (Upton and Emeleus, 1987).

Analytical methods and data recalculation

All mineral analyses were made using a modified Cambridge Instruments Company Geoscan electron microprobe fitted with a Link Systems 860–500 energy-dispersive spectrometer. A 3nA specimen current (measured on cobalt metal) was used at an accelerating voltage of 15 kV with a spectrometer 'live-time' of 100 seconds. Zr analyses were made from the Zr-Lα line and standardized against Zr metal. Lower limits of detection for ZrO_2 were about 0.29 wt. % (2σ).

Total Fe is reported as FeO in Table 1, but Fe^{3+}/Fe^{2+} ratios were calculated following the suggestion of Leake (1978), adjusting the ratio to

sum all cations excluding Ca, Na, K and Ba to 13 on a 23 oxygen basis (i.e. $T+C$ cations $= 13$). Leake (1978) does not mention Zr when assigning cations to their structural sites. In these analyses Zr has been assigned to the octahedral C site, although Zr is known to occupy larger co-ordination sites e.g. [4+4] in zircon.

Table 1
Analyses of Zr-bearing amphiboles from benmoreites of the Igaliko Dyke Swarm.

GGU no.	325986.45	325986.46	326211.72	58241.31	326207.15	59779.95	58206.54
SiO_2	46.24	45.60	47.11	44.92	44.07	47.77	44.27
TiO_2	0.0	0.63	0.87	0.33	0.56	0.0	1.93
Al_2O_3	1.88	2.50	1.87	2.12	3.87	1.59	3.18
FeO*	31.61	31.41	31.54	34.48	33.25	32.70	34.23
MnO	1.03	0.71	1.37	0.83	1.05	0.74	1.02
MgO	1.02	1.28	1.22	0.26	0.90	0.93	0.48
CaO	1.84	1.66	1.37	4.76	4.27	3.82	4.44
Na_2O	7.25	7.66	8.14	5.76	5.97	6.78	5.96
K_2O	2.32	1.95	1.94	1.75	1.75	2.01	1.70
ZrO_2	4.13	3.39	2.38	1.41	2.02	1.47	0.60
Total	97.32	96.79	97.71	96.62	97.71	97.81	97.81
Atoms per 23 oxygens, T+C=13							
T⎰ Si	7.58	7.46	7.54	7.46	7.15	7.79	7.21
⎱ Al	0.36	0.48	0.38	0.42	0.74	0.31	0.61
⎡ Ti	0.0	0.08	0.06	0.04	0.07	0.0	0.24
Fe³⁺	0.38	0.48	0.69	0.43	0.76	0.0	0.64
Fe²⁺	3.95	3.82	3.60	4.36	3.75	4.46	4.00
C⎨ Mn	0.14	0.10	0.18	0.12	0.14	0.10	0.14
Mg	0.25	0.31	0.38	0.06	0.22	0.23	0.12
⎣ Zr	0.33	0.27	0.16	0.11	0.16	0.12	0.05
A⎡ Ca	0.32	0.29	0.31	0.85	0.74	0.67	0.77
+⎨ Na	2.30	2.43	2.35	1.86	1.88	2.14	1.87
B⎣ K	0.48	0.41	0.42	0.37	0.36	0.42	0.35
Type†	Arf	Arf	Arf	Kat	Kat	F-r	Kat
Whole rock characteristics							
P.I.	0.87		0.89	1.04		0.92	0.93
D.I.	73.30		79.90	78.78	Not	78.47	78.14
Norm‡	0.68Qz		2.42Hy	7.14Qz	analysed	2.24Ne	2.94Qz
Zr ppm	1884		744	3697		821	1539
Zr/Nb	6.22		3.80	6.10		4.41	6.16

* - Total iron reported as FeO. † - Type according to Leake (1978) classification ie. Arf Arfvedsonite, Kat katophorite, F-r Ferro-richterite. P.I. - Peralkalinity Index. D.I. - Thornton-Tuttle Differentiation Index. ‡ - Normative characteristics in terms of quartz (Qz), hypersthene (Hy) or nepheline (Ne).

Results

Table 1 lists a selection of analyses of Zr-bearing amphiboles. In the fine-grained benmoreitic dykes amphibole always forms as interstitial grains to feldspar and may form as an overgrowth on pyroxenes of compositions ranging from ferrosalite to aegirine-augite. The amphiboles are often zoned from katophorite (pleochroic in dark browns and greens) next to the pyroxene to margins of dark blue-green arfvedsonite. In those grains which were large enough to analyse, the margins were all more alkali-rich and Zr-rich.

The major chemical variation in the composition of the Igaliko dyke amphiboles can be conveniently described in terms of

$$Ca^B + Al^T \rightleftharpoons Na^B + Si^T.$$
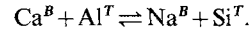
The parameter (Na^B-Al^T) ranges from -1.5 to $+2.0$ and in Fig. 1 high positive values of (Na^B-Al^T) are associated with higher Zr contents of the amphiboles. It is only in benmoreitic rocks that Zr achieves contents above 0.05 atoms per 23 oxygens (i.e. above c. 0.6 wt. % ZrO_2). The phonolitic rocks, which are typically higher in bulk rock Zr show low to moderate Zr contents in their alkali-rich amphiboles. Classification of these Zr-rich amphiboles on the suggestions of Leake (1978) shows them mostly to be arfvedsonites or katophorites. Some more-basic amphiboles also contain detectable Zr (e.g. 59779.95, a ferrorichterite).

The end-member arfvedsonite has the formula $NaNa_2Fe_4^{2+}Fe^{3+}Si_8O_{22}(OH)_2$. Examination of the analyses in Table 1 shows that all the Zr-bearing amphiboles have small amounts of Al which must occupy the tetrahedral site and a possible coupled substitution is

$$Zr_C^{4+} + Al_T^{3+} \rightleftharpoons Fe_C^{3+} + Si_T^{4+}$$
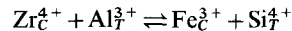
The limit of this substitution into arfvedsonite, governed by the total replacement of Fe^{3+} is $Na_3Fe_4^{2+}ZrSi_7AlO_{22}(OH)_2$. The shortfall in $Si_T^{4+} + Al_T^{3+}$ observed in some analyses in Table 1 might indicate the presence of Fe_T^{3+} and the coupled substitution of

$$Fe_C^{3+} + Si_T^{4+} \rightleftharpoons Zr_C^{4+} + Fe_T^{3+}$$

or simply

$$Si_T^{4+} \rightleftharpoons Zr_T^{4+}.$$
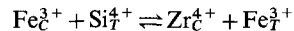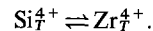
However, on the basis of ionic radii given by Shannon (1976), substitution of Zr into T seems unlikely. The Zr-richest sample from the Igaliko Dyke Swarm has Zr at 0.33 atoms (Table 1).

Conditions of formation

The restriction of Zr-rich amphiboles to the benmoreitic members of the Igaliko dykes suggests that their formation is dependent upon fairly restricted physico-chemical conditions.

The Zr content of these amphiboles is not directly related to bulk rock Zr, nor would it appear to be related to bulk rock Si-saturation, with Q, Hy or Ne normative rocks containing Zr-bearing amphibole. In samples containing Zr-rich amphiboles other Zr-rich minerals such as zircon, baddeleyite or eudialyte (often common in alkaline rocks) are absent.
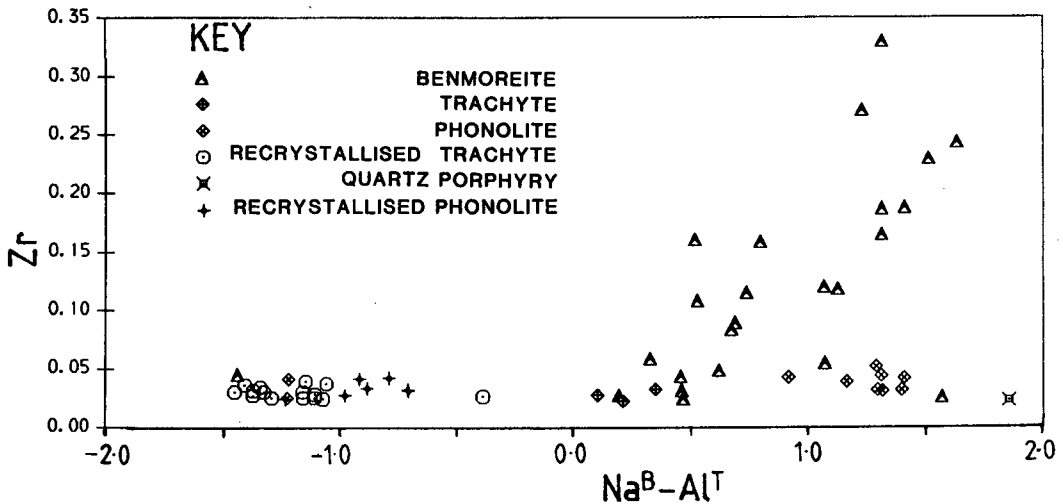
FIG. 1. Zr vs Na^B-Al^T as atoms per 23 oxygens. Symbols indicate different rock types. Note the only highly Zr-rich amphiboles are from benmoreitic dykes.

Fayalitic olivine is a minor component of these samples. It is often rimmed by opaque oxide and implies that the f_{O_2} of these samples is at or close to the synthetic QMF buffer. Pyroxene compositional variation in these rocks, which only shows an increase of alkalis at low $Mg/(Mg+Fe)$ ratios, also indicates a low f_{O_2} (low Fe^{3+} contents, cf. Larsen, 1976).

The bulk-rock chemistry (see Table 1) shows that these benmoreites are mostly sub-alkaline (peralkalinity as moles $(Na_2O+K_2O)/Al_2O_3 < 1$). Crystallization of alkali feldspar from these rocks caused an increase in alkalis relative to Al (the 'orthoclase effect', Bailey and Schairer, 1966) and thus, the residual interstitial liquids became peralkaline. Pyroxene, initially salite or ferro-salite, became zoned to more alkali rich compositions. As the water content of the interstitial residue increased as crystallization proceeded, alkali pyroxene became unstable (Yagi, 1953) and reacted to form alkali amphiboles.

Zr solubility in evolved compositions has been shown to be critically dependent upon peralkalinity, although relatively independent of temperature, SiO_2 concentration or melt Na_2O/K_2O (Watson, 1979). Watson suggests that Zr may be present in these peralkaline liquids in species such as $Na_4Zr(SiO_4)_2$. He also notes that Ca, a minor component of the benmoreitic dykes, causes a slight reduction in the solubility of Zr in peralkaline liquids and results in the precipitation of Zr-rich phases at lower Zr contents.

In the Igaliko benmoreites, Zr would not have been incorporated in the early crystallizing alkali feldspar and salitic pyroxene, but would have built up in the residual liquid, which would also have had an increasing peralkalinity, and thus an increasing level of Zr saturation. Zr would have eventually partitioned into either pyroxene (see for example Jones and Peckett, 1980, and high Zr pyroxenes are recorded from the Igaliko dykes; Pearce, 1988), or into late crystallising alkali amphiboles, when the water content made the pyroxene unstable. This would, however, have been dependent upon the absence of any other Zr-rich phases, which would have acted as a sink for Zr.

It is, however, notable that no highly Zr-rich alkali amphiboles occur in the phonolitic members of the Igaliko Dyke Swarm (see Fig. 1). This may reflect a higher initial peralkalinity than in the benmoreites resulting in increased solubility of Zr in interstitial liquids. Higher f_{O_2} in the phonolites than in the benmoreites, producing higher Fe^{3+}/Fe^{2+} ratios, may also have promoted higher peralkalinity and thus increased Zr solubility. Lower CaO in the phonolites than in the benmoreites would increase the level of Zr saturation. In these dykes Zr may have entered submicroscopic minerals at grain boundaries which are the last phases to crystallize (cf. Macdonald and Parker, 1970). These are not detected, although bulk rock Zr is generally higher than in the benmoreites.

Larsen (1976) noted from Ilímaussaq that ZrO_2 in pyroxene was approximately half that of the ZrO_2 content in coexisting amphiboles with similar Na/Ca ratios. No such simple relationship was

noted in the Igaliko dykes, with an erratic distribution of Zr between these two phases being observed.

In conclusion, it appears that the special and limited conditions exhibited by the late-stage interstitial liquids of the benmoreites of f_{O_2} close to the QMF buffer, high peralkalinity (much greater than 1), high bulk Zr and high water contents are responsible for the formation of the Zr-rich alkali amphiboles.

References

Bailey, D. K. and Schairer, J. F. (1966) The system $Na_2O-Al_2O_3-Fe_2O_3-SiO_2$ at 1 atmosphere and the petrogenesis of alkali rocks. *J. Petrol.* **7**, 114–70.

Dana, E. S. (1892) *A System of Mineralogy*, 6th ed. John Wiley and Sons, New York.

Emeleus, C. H. and Harry, W. T. (1970) The Igaliko Nepheline Syenite Complex. *Bull. Grønlands Geologiske Undersøgelese* **85**; also *Meddels. Grønland* **186**, No. 3. 116 pp.

Jones, A. P. (1980) *The petrology and structure of the Motzfeldt Centre, Igaliko, South Greenland.* Unpublished PhD Thesis, University of Durham.

——and Peckett, A. (1980) Zirconium-bearing aegirines from Motzfeldt, South Greenland. *Contrib. Mineral. Petrol.* **75**, 251–5.

Larsen, L. M. (1976) Clinopyroxenes and coexisting mafic minerals from the alkaline Ilímaussaq intrusion, South Greenland. *J. Petrol.* **17**, 258–90.

Leake, B. E. (1978) Nomenclature of amphiboles. *Mineral. Mag.* **42**, 533–63.

Macdonald, R. and Parker, A. (1970) Zirconium in alkaline dykes from the Tugtutôq region, South Greenland. *Bull. Geol. Soc. Denmark*, **20**, 59–63.

Nash, W. P. and Wilkinson, J. F. G. (1970) Shonkin Sag laccolith, Montana. I. Mafic minerals and estimates of temperature, pressure, oxygen fugacity and silica activity. *Contrib. Mineral. Petrol.* **25**, 241–69.

Pearce, N. J. G. (1988) *The petrology and geochemistry of the Igaliko Dyke Swarm, South Greenland.* Unpublished PhD thesis, University of Durham.

Shannon, R. D. (1976) Effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* Section A, **32**, 751–67.

Upton, B. G. J. and Emeleus, C. H. (1987) Mid-Proterozoic alkaline magmatism in Southern Greenland: The Gardar Province. In *Alkaline Igneous Rocks* (Fitton, J. G. and Upton, B, G. J., eds) Spec. Publ. Geol. Soc. London, No. 30.

Watson, E. B. (1979) Zircon saturation in felsic liquids; experimental results and applications to trace element geochemistry. *Contrib. Mineral. Petrol.* **70**, 407–19.

Yagi, K. (1953) Petrochemical studies on the alkalic rocks of Morotu district, Sakhalin. *Geol. Soc. Am. Bull.* **64**, 769–810.