Zirconium and niobium-bearing ilmenites from the Igaliko dyke swarm, South Greenland

N. J. G. PEARCE

Institute of Earth Studies, University College of Wales, Aberystwyth, Dyfed, SY23 3DB, Wales, U.K.

Abstract

Ilmenites from alkaline basic dykes in the Gardar province, south Greenland have Zr contents up to 3850ppm and Nb contents up to 1030ppm. These elements substitute for Ti in the octahedral site. These are amongst the highest recorded Zr and Nb contents for ilmenites, giving distribution coefficients ($Kd^{\text{ilmenite/matrix}}$) for Zr up to 11.6 and Nb up to 70.3. Fractionation of ilmenite may thus have a dramatic effect on residual Zr and Nb contents. These effects are discussed in relation to the use of trace element tectonomagmatic discrimination diagrams.

KEYWORDS: zirconium, niobium, ilmenite, Gardar province, Greenland, Igaliko dyke swarm.

Introduction

ZIRCONIUM and niobium are generally assumed to be incompatible elements. They typically show low mineral/matrix distribution coefficients and tend to concentrate in the residual liquid during magmatic fractionation. Because of this behaviour, these elements, in conjunction with other incompatible elements (such as Ti, Y, P), have often been used in petrogenetic models to place constraints on terrestrial magma source regions, degrees of partial melting and tectonic environment (e.g. Pearce and Cann, 1973; Pearce and Norry, 1979; Meschede, 1986). This study shows that both Zr and Nb are concentrated into primary ilmenites from basic dykes of the Igaliko dyke swarm, south Greenland. Ilmenite crystallization may thus influence the behaviour of Zr and Nb during magmatic fractionation.

Geologic setting

The Igaliko Dyke Swarm, an extensive mid-Proterozoic alkaline dyke swarm of Gardar age (1300–1120 Ma), crops out near Narssarssuaq, south Greenland (approx. 61° 12′N, 45° 27′W). The dykes are related to either (i) Si-undersaturated central complexes of the Igaliko Nepheline Syenite Complex (see Emeleus and Harry, 1970) or (ii) Si-oversaturated magmatism of the Tugtutoq–Narssaq–Nunataq dyke swarm (see Upton and Fitton, 1985; Upton and Emeleus, 1987). Both swarms contain small amounts of basic material, being dominated by intermediate to evolved compositions (benmoreite, trachyte and phonolite or rhyolite).

Analytical techniques

During routine EDS microprobe studies of the mineralogy of a representative suite of dykes it was noted that minor amounts of Zr (close to the lower limits of detection) were being recorded from ilmenites in two basic dykes: 325992,* an alkali basalt and 43867, a mafic syeno-gabbro. Initially zircon inclusions were suspected of interfering with the analysis, but these were later ruled out by optical studies. Nb was not detected in any of the ilmenites by EDS analysis. Due to the weak nature of the Zr-$L\alpha$ peak and the low reported Zr contents, the presence of Zr in these samples was confirmed by scanning across the Zr peak using the Durham University WDS microprobe. In view of these early results, and the association of Zr and Nb in opaque phases (e.g. Blank *et al.*, 1984), a systematic study of the opaque minerals in these two samples was undertaken using the Manchester University Cameca EDS/WDS microprobe. Analyses were made using a 14.5 nA specimen current (measured on cobalt metal) at an accelerating voltage of 15kV. Si, Ti, Al, Fe, Mn and Mg were determined using a Link Systems 860–500 EDS system. Zr and Nb were determined simultaneously by WDS from their $L\alpha$ emission lines, diffracted by a PET crystal and

* Sample numbers refer to the collections of the Geological Survey of Greenland (GGU).

standardized against pure metals. All data were corrected for atomic number, adsorption and fluorescence using ZAF–14/FLS software. Lower limits of detection (2σ) were about 250 ppm for Zr and 220 ppm for Nb.

Results

Table 1 gives selected analyses of ilmenites from these samples along with some whole rock data, Table 2 presents the Zr and Nb contents of all analysed ilmenites. From these data it is clear that both Zr and Nb show a strong preference for the ilmenite crystal structure with distribution coefficients ($Kd^{\text{ilmenite/matrix}}, kd^{i/m}$) reaching a maximum of 11.6 for Zr and 70.3 for Nb. Zr^{4+} will substitute simply for Ti^{4+} in the octahedral site; substitution of Nb^{5+}, also for Ti^{4+} in the octahedral site, may involve a coupled exchange to maintain charge balance ($Zr^{4+} = 0.072$ nm, $Nb^{5+} = 0.064$ nm, $Ti^{4+} = 0.0605$ nm; Shannon, 1976). In both samples ilmenite is an abundant phase (6–10% modally) and easily accounts for all Zr and Nb in the rock. Ilmenite is however a relatively rare mineral in dykes of the Igaliko swarm, having been confirmed by microprobe analysis in only 9 of about 110 analysed samples. EDS analysis did not detect Zr or Nb in any of these other ilmenites. Nonetheless, samples 43867 and 325992 are representative of much of the basic material in the Igaliko swarm (Pearce, 1988; Upton and Emeleus, 1987; Upton and Fitton, 1985; Emeleus and Harry, 1970).

Table 1. Selected analyses of ilmenite.

GGU No.*	43867/02	43867/04	325992/06	325992/10
SiO_2	0.40	0.40	0.36	0.39
TiO_2	53.02	53.25	49.30	49.69
Al_2O_3	-	0.27	0.16	-
FeO	44.53	44.48	47.72	46.10
MnO	0.90	0.86	2.47	2.35
MgO	1.35	1.56	0.16	0.17
Nb_2O_5	0.072	0.089	0.151	0.033
ZrO_2	0.151	0.034	0.168	0.518
Total	100.423	100.943	100.489	99.548
Zr/Nb	2.22	0.41	1.18	16.61

Whole rock characteristics

Zr ppm	187	332
Nb ppm	65	15
Zr/Nb	2.88	22.13
TiO_2 wt%	9.56	2.78
FeO wt%	20.80	16.10
Y ppm	42	46
Normative Il. wt%	14.97	5.45

* – Sample numbers refer to the collections of the Geological Survey of Greenland, GGU.

Table 2. Zr and Nb contents of all analysed ilmenites.

GGU No.	Zr ppm	Nb ppm	Zr/Nb	Kd_{Zr}	Kd_{Nb}
43867/01	489	-	-	2.61	-
43867/02	1117	503	2.22	5.97	7.74
43867/03	570	-	-	3.05	-
43967/04	252	622	0.41	1.35	9.57
43867/05	1192	-	-	6.37	-
325992/01[C]	1147	259	4.43	3.45	17.27
325992/02[R]	888	412	2.15	2.67	27.47
325992/03	-	-	-	-	-
325992/04	2828	-	-	8.52	-
325992/05	1022	489	2.09	3.08	32.60
325992/06	1244	1055	1.18	3.75	70.33
325992/07	577	-	-	1.74	-
325992/08[C]	1281	-	-	3.86	-
325992/09[R]	-	-	-	-	-
325992/10	3835	231	16.61	11.55	15.40

Consecutive samples marked [C] and [R] are core and rim analyses from the same grain.

Discussion

The maximum distribution coefficients calculated here for Zr and Nb into ilmenite exceed the values of 0.28 (for Zr) and 0.8 (for Nb) cited by Pearce and Norry (1979) by factors of up to 41× and 87× respectively. Clearly Zr and Nb cannot be regarded as incompatible in the ilmenite crystal structure in basic rocks of these compositions.

Zr and Nb are only rarely reported from terrestrial ilmenites, but have both been documented from lunar examples. Zr contents in ilmenite from an Apollo 14 sample reach 4000 ppm in a rock containing 962 ppm (El Gorsey *et al.*, 1971; Taylor and McCallister, 1972). This gives $Kd^{i/m} = 4.16$ which is considerably lower than the $Kd^{i/m}$ for the Igaliko samples. Apollo 15 ilmenites contain higher Zr (up to 4200 ppm; Taylor and McCallister, 1972), although these authors do not cite the whole–rock Zr content, their main concern being Zr distribution between coexisting ilmenite and ulvöspinel. These ilmenites' Zr contents are slightly in excess of the maximum value recorded from the Igaliko examples.

Nb has received less attention in lunar ilmenites. Blank *et al.* (1984) recorded up to 2020 ppm Nb from an Apollo 14 sample, almost twice the maximum value recorded from the Igaliko examples. They also studied the partitioning of Zr and Nb between coexisting opaque phases in a selection of Apollo 17 and Apollo 14 ilmenites using a proton microprobe. They detected variable Zr/Nb ratios from individual grains, ranging from 0.12 to 17.0, concluding that Nb shows a greater preference for ilmenites than Zr. These ratios appear to depend (i) on the presence or absence of coexisting Zr- or Nb-bearing phases such as ulvöspinel, armalcolite, zircon, rutile and chromite; and (ii) on the crystallization order of the relevant phases in these low f_{O_2} rocks. They do not however cite whole-rock Zr or Nb contents. In the Igaliko ilmenites Nb is generally subordinate to Zr with Zr/Nb ratios varying from 0.41 to 11.55.

A wide variation in Zr and Nb contents of ilmenites from the Igaliko dykes is seen in the same sample (see Table 2). This probably reflects the strong partitioning of both Zr and Nb into ilmenites at an early stage of crystallization, leaving the residual liquid depleted in these elements. This may lead to the observed variation between individual grains. The extent of zoning of Zr and Nb is poorly constrained. In one grain, Zr decreases from the core to the rim while Nb increases (325992/1 and 325992/2); in the other Nb was below detection limits and again Zr decreased from core to rim (325992/8 and 325992/9).

Although zircons were not observed enclosed within the Igaliko dyke ilmenites, the presence of these or other Zr- and Nb-bearing phases in the groundmass may also account for some of the observed variation (cf. lunar examples). Particularly, the presence of such other minerals may also be responsible for the fact that Zr contents of ilmenites from the other analysed samples are below EDS detection limits, many of which possess higher bulk-rock Zr. This may in turn be a reflection of other compositional features, possibly a_{SiO_2} or f_{O_2}.

Having shown Zr and Nb to be compatible in ilmenites from these rocks, substantial ilmenite fractionation could produce large variations in residual Zr and Nb contents. This in turn would cause variation in trace element ratios such as La/Nb, Zr/Nb, Nb/Y, etc., ratios which have commonly been used to place tectonomagmatic constraints on the origins of basic rocks (e.g. Pearce and Cann, 1973; Floyd and Winchester, 1975; Pearce and Norry, 1979; Meschede, 1986). Conversely, ilmenite accumulation could produce changes in these ratios when compared to fractionation of an opposite and possibly enhanced magnitude. As Hf and Ta generally behave in similar ways to Zr and Nb, these elements may also be affected by ilmenite fractionation (cf. discrimination diagram of Wood *et al.*, 1979).

The effects of ilmenite extraction on Zr and Nb contents of residual basalts can be easily calculated for selected tectonomagmatic discrimination diagrams using the distribution coefficients given here. To cite just two examples, using Meschede's (1986) 2Nb–Zr/4–Y plot, ilmenite fractionation could produce N-type MORB from a transitional alkaline-tholeiitic within plate basalt and using Pearce and Cann's (1973) Zr–Ti/100–3Y diagram, ilmenite fractionation could transform calc-alkaline basalts, island arc tholeiites or MORB's into within plate basalts. The effect ilmenite fractionation has upon the various diagrams does not consistently produce the same result and may confuse the picture even further. In the case of the Igaliko dykes, formed during mid-Proterozoic rifting, basic rock analyses cluster in the within plate fields in most diagrams, implying that fractionation of ilmenites such as these was not an important process in their evolution.

In conclusion, if ilmenite fractionation was involved in the evolution of a suite of basic rocks from which trace element contents are to be used to erect tectonic and petrogenetic models, the possible effects on whole-rock Zr and Nb should be considered. At the least this should include analysis of ilmenite for Zr and Nb. In this way any variations in whole-rock ratios involving Zr and Nb can be ascribed either to variations in source geochemistry and tectonic setting or to superimposed effects of fractionation.

Acknowledgements

This work was carried out whilst in receipt of a NERC research studentship at the Department of Geological Sciences, University of Durham, for which I am grateful. EDS microprobe analyses were conducted at Manchester University and thanks are due to Tim Hopkins and Dave Plant for their assistance. WDS microprobe analyses were conducted at Durham University by Dr A. Peckett. The manuscript has benefited from the comments of A. Peckett and C. H. Emeleus. This paper is published with the permission of the Director of the Geological Survey of Greenland. Institute of Earth Studies publication number 116.

References

Blank G., El Goresy, A., Janicke, J., Nobiling, R., and Traxel, K. (1984) Partitioning of Zr and Nb between coexisting opaque phases in lunar rocks—determined by quantitative proton microprobe analysis. *Earth. Planet. Sci. Lett.* **68**, 19–63.

El Goresy. A., Ramdhor, P., and Taylor, L. A. (1971) The geochemistry of the opaque minerals in Apollo 14 crystalline rocks. Ibid. **13**, 121–9.

Emeleus, C. H. and Harry, W. T. (1970) The Igaliko Nepheline Syenite Complex. *Bull. Grønl. Geol. Unders.* **85** (also *Medel. Grønl.* **186**, No. 3) 116 pp.

Floyd, P. A. and Winchester, J. A. (1975) Magma type and tectonic setting discrimination using immobile elements. *Earth. Planet. Sci. Lett.* **27** 211–18

Meschede, M. (1986) A method of discriminating between different types of mid-ocean ridge basalts and continental tholeiites using the Nb–Zr–Y diagram. *Chem. Geol.* **56**, 206–18.

Pearce, J. A. and Cann, J. R. (1973) Tectonic setting of basic volcanic rocks determined using trace element analyses. *Earth. Planet. Sci. Lett.* **19**, 290–300.

—— and Norry, M. J. (1979) Petrogenetic implications of Ti, Zr, Y, and Nb variations in volcanic rocks. *Contrib. Mineral. Petrol.* **69**, 33–47.

Pearce, N. J. G. (1988) *The Petrology and Geochemistry of the Igaliko Dyke Swarm, South Greenland.* Unpubl. PhD Thesis, University of Durham.

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

Taylor, L. A. and McCallister, R. H. (1972) An experimental investigation of the significance of zirconium partitioning in lunar ilmenite and ulvöspinel. *Earth. Planet. Sci. Lett.* **17**, 105–9.

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.) Geol. Soc. Spec. Publ. No. 30.

—— Fitton, J. G. (1985) Gardar dykes north of the Igaliko Syenite complex, Southern Greenland. *Rapp. Grønl. Geol. Unders.* **127**.

Wood, D. A., Joron, J. L., and Treuil, M. (1979) A re-appraisal of the use of trace elements to classify and discriminate between magma series erupted in different tectonic settings. *Earth. Planet. Sci. Lett.* **45**, 326–36.

[*Manuscript received 9 August 1989; revised 12 May 1990*]