

HYDROTHERMAL REE-RICH EUDIALYTE FROM THE PILANESBERG COMPLEX, SOUTH AFRICA

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ABSTRACT

The Pilanesberg Complex, in South Africa, one of the world's largest alkaline complexes, contains large resources of Zr and the rare-earth elements (REE). Eudialyte is the main carrier of Zr, and contains appreciable concentrations of REE. It is particularly abundant in the green nepheline syenite (20% by volume). It forms complexly zoned poikilitic domains that enclose aegirine, albite, microcline, nepheline, zircon, pectolite, sodalite, and an unidentified Na–Zr silicate. These domains mantle corroded silicates and replace outer zones of microcline euhedra. The eudialyte is partially replaced by fergusonite-(Y) and britholite. Compositionally, the eudialyte at Pilanesberg is unusual; it contains the highest concentration of Nb (up to 3.8 wt% Nb₂O₅) and the lowest concentrations of Na (<11.4 wt% Na₂O) and Fe (<0.4 wt% FeO) reported in the literature. In addition, it has one of the highest contents of REE (up to 7.6 wt% REE₂O₃, mainly Ce and La and traces of Sm and Nd) and Mn (up to 7.5 wt%) reported in the literature. On the basis of 78 anions, its formula is (Na_{12.30}REE_{1.39}Ca_{0.89}K_{0.20})_{Σ14.78}(Ca_{5.42}Mn_{0.58})_{Σ6}(Mn_{2.96}Fe_{0.04})_{Σ3}(Zr_{2.66}Nb_{0.28}Hf_{0.06})_{Σ3}(Nb_{0.66}Si_{0.28}Ta_{0.06})_{Σ1}Si_{25.64}O₇₄(OH_{1.01}Cl_{0.92}F_{0.07})_{Σ2}•2H₂O. On the basis of textural relationships, the Pilanesberg eudialyte is interpreted to be hydrothermal. It seems to have formed from an orthomagmatic Na–Nb–REE–Cl–F-bearing hydrothermal fluid that exsolved from an agpaïtic syenitic magma. In this system, zirconium was probably remobilized from magmatic zircon as a F-complex (e.g., ZrF₆²⁻), and REE were introduced as Cl- and F-complexes. The incorporation of the REE in eudialyte probably occurred in response to the reduced Cl- and F-activities that accompanied precipitation of sodalite and the unidentified (F-bearing) Na–Zr silicate.

Keywords: eudialyte, nepheline syenite, Pilanesberg, alkaline complex, hydrothermal, rare-earth elements, South Africa.

SOMMAIRE

Le complexe alcalin de Pilanesberg, en Afrique du Sud, un des plus gros au monde, contient des ressources importantes de Zr et de terres rares. L'eudialyte est le porteur principal du Zr, et contient aussi des teneurs importantes de terres rares. Ce minéral est particulièrement abondant dans l'unité de syénite néphélinique verte (20% en volume). Il forme des domaines poécélitiques zonés de façon complexe qui englobent aegyrine, albite, microcline, néphéline, zircon, pectolite, sodalite, et un silicate Na–Zr non identifié. Ces domaines recouvrent des silicates corrodés et remplacent les bordures des cristaux idiomorphes de microcline. L'eudialyte est remplacée en partie par la fergusonite-(Y) et la britholite. Par sa composition, l'eudialyte à Pilanesberg n'est pas courante. Elle possède la concentration la plus élevée en Nb qui soit (jusqu'à 3.8 wt% Nb₂O₅), et des teneurs en Na (<11.4 wt% Na₂O) et Fe (<0.4 wt% FeO) qui sont les plus faibles dans la littérature. De plus, les teneurs en terres rares (TR) (jusqu'à 7.6% TR₂O₃, surtout Ce et La et des traces de Sm et de Nd) et Mn (jusqu'à 7.5 wt% MnO) sont parmi les plus élevées que l'on connaisse. Sur une base de 78 anions, la formule chimique est (Na_{12.30}REE_{1.39}Ca_{0.89}K_{0.20})_{Σ14.78}(Ca_{5.42}Mn_{0.58})_{Σ6}(Mn_{2.96}Fe_{0.04})_{Σ3}(Zr_{2.66}Nb_{0.28}Hf_{0.06})_{Σ3}(Nb_{0.66}Si_{0.28}Ta_{0.06})_{Σ1}Si_{25.64}O₇₄(OH_{1.01}Cl_{0.92}F_{0.07})_{Σ2}•2H₂O. Selon les critères texturaux, nous croyons qu'il s'agit d'une origine hydrothermale. L'eudialyte semble s'être formée à partir de la phase fluide orthomagmatique, porteuse de Na–Nb–REE–Cl–F, issue du magma magmatique agpaïtique. Dans ce système, le zirconium a probablement été remobilisé par dissolution du zircon magmatique sous forme de complexe fluoré (e.g., ZrF₆²⁻), et les terres rares ont été introduites sous forme de complexes chloré ou fluoré. L'incorporation des terres rares dans l'eudialyte résulterait d'une réduction de l'activité de Cl et de F qui accompagna la précipitation de la sodalite et du silicate fluoré à Na–Zr non identifié.

(Traduit par la Rédaction)

Mots-clés: eudialyte, syénite néphélinique, Pilanesberg, complexe alcalin, hydrothermal, terres rares, Afrique du Sud.

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INTRODUCTION

Eudialyte is a rock-forming Na–Ca zirconosilicate that may contain appreciable concentrations of rare-earth elements (*REE*) and Y. The name “eudialyte”, from the Greek words “*eu*” (well) and “*dialytos*” (dissolved), emphasizes an important property of this mineral, namely the ease with which it can be dissolved in dilute acids. This property makes it possible to easily beneficiate eudialyte-bearing ores using conventional heap-leach techniques (Mariano 1989).

Eudialyte commonly occurs in agpaitic syenites and granites. The syenite-hosted occurrences include the Lovozero (Kola Peninsula, Russia), Ilímaussaq (Greenland), and Pilanesberg (South Africa) massifs (Kogarko 1987, Larsen & Sørensen 1987, Lurie 1986), whereas eudialyte in granite has been described at Ascension Island, along the Mid-Atlantic Ridge (Harris *et al.* 1982) and Straumsvola, in the Antarctica (Harris & Rickard 1987). Although many papers have been published on the mode of occurrence and chemistry of eudialyte, the genesis of this mineral has received limited attention. Most investigators, however, favor a magmatic origin (*e.g.*, Portnov 1964, Kogarko *et al.* 1982, Krigman *et al.* 1983, Larsen & Sørensen 1987).

The Pilanesberg complex is an ideal setting in which to investigate the processes controlling the formation of eudialyte and the incorporation of *REE* in its structure. This intrusive complex is unusually rich in this mineral, notably in a green nepheline syenite unit, which contains up to 20% eudialyte by volume. Moreover, this eudialyte contains one of the highest concentrations of *REE* reported in the literature (*cf.* Deer *et al.* 1986, Johnsen & Gault 1997). The purpose of our study is to determine the textural relationships and composition of eudialyte in the green nepheline syenite, and to further our understanding of the processes that led to the crystallization of *REE*-rich eudialyte in this agpaitic syenitic complex.

THE PILANESBERG COMPLEX

The Pilanesberg Complex is one of the world's largest alkaline igneous bodies, covering an area of 570 km²; it was emplaced approximately 1250 ± 50 Ma ago (K–Ar age, Retief 1963), along the eroded contact between the granitic and mafic phases (norite) of the Bushveld Complex (Fig. 1). The rocks of the Pilanesberg complex, which are now partially unroofed, comprise pyroclastic and lava-flow sequences and inwardly dipping ring-dykes (except in the north, where they locally dip outward), concentrically disposed around the core (Lurie 1986). From the core to the outer ring, the arcuate units comprise red and white feldspathoidal syenites, green nepheline syenite, white feldspathoidal syenite [referred to in Lurie (1986) as foyaite], tinguaitite, and red syenite (Fig. 1). The oldest intrusive rock is the red syenite, which was subsequently intruded by the red

feldspathoidal syenite, which forms the core of the structure. Green nepheline syenite postdates the red and white feldspathoidal syenites, as well as a cone sheet of tinguaitite, and is intruded by tinguaitite dykes.

Rocks of the Pilanesberg Complex are enriched in fluorine, strontium, niobium, tantalum, zirconium, hafnium, the rare-earth elements, thorium and uranium (Lurie 1986). Of the major rock-types, the green nepheline syenite, which has also been referred to in the literature as green foyaite and Ledig foyaite, has the highest content of zirconium (up to 19,900 ppm) and rare-earth elements (up to 6,500 ppm) (Table 1). Its high *REE* content has previously been attributed to the presence of britholite, (*REE*,Ca,Y)₅(SiO₄,PO₄)(OH,F), and products of its weathering. However, contrary to previous reports, a large proportion of the *REE* seems to be hosted by eudialyte, which comprises up to 20% of the rock by volume.

THE GREEN NEPHELINE SYENITE

The green nepheline syenite (Fig. 1) is coarse grained and comprises thick layers composed of variable proportions of mafic (mainly aegirine) and felsic minerals. In addition to aegirine, the rock also contains microcline, albite, nepheline, sodalite, pectolite, zircon, eudialyte, britholite, fergusonite-(Y), and traces of an unknown

TABLE 1. COMPOSITION OF THE GREEN NEPHELINE SYENITE, PILANESBERG

	CENTRAL ZONE (this paper)	SOUTHERN-LEDIG ZONE [†]		
		WESTERN PART	CENTRAL PART	EASTERN PART
SiO ₂ (wt%)	51.32*			
Al ₂ O ₃	15.55*			
Fe ₂ O ₃	8.58*			
MnO	1.18*			
MgO	0.03*			
CaO	2.75*			
Na ₂ O	10.76*			
K ₂ O	3.08*			
TiO ₂	0.29*			
P ₂ O ₅	0.03*			
LOI	2.8			
Total	96.36			
La (ppm)	1773	1500	1000	1500
Ce	3216	2400	1600	2400
Pr	268			
Nd	815			
Sm	122			
Eu	16.07			
Gd	90.9			
Tb	15.8			
Dy	93.7			
Ho	18.6			
Er	59.8			
Tm	9.61			
Yb	57.2			
Lu	7.75			
Total REE	6563.43	3900	2600	3900
Zr	19946*–18090	4800	9600	7700
Hf	378	173	155	114
Y	564*–546	230	190	170
Nb	2120	2100	1000	1040
Ta	165	96	63	76
U	21.7	63	23	45
Th	4306	320	110	372
Rb	199	317	300	400
Sr	2113*–1977	410	530	230
Ba	19*–23	0	80	550

* only fusion ICP analysis; the other analyses were conducted using fusion ICP-MS technique.

[†] Lurie (1986)

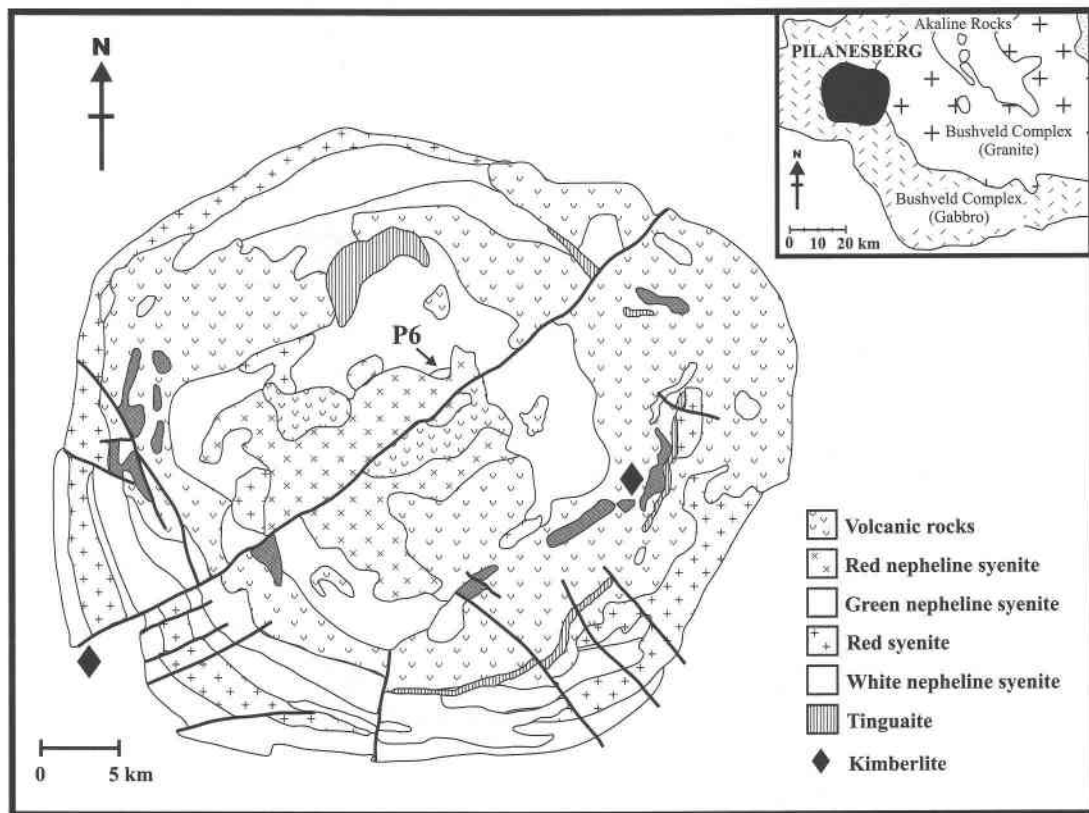


FIG. 1. Geological map of the Pilanesberg Complex; the inset shows its location in relation to the Bushveld complex, western Transvaal, South Africa (after Lurie 1986).

Na-Zr silicate. Aegirine occurs as prismatic crystals interlayered with albite (Fig. 2A), or encloses microcline and nepheline crystals. It is also commonly included in felsic minerals. Nepheline and microcline form tabular poikilitic crystals up to one centimeter in diameter; they contain inclusions of aegirine and albite. In addition, nepheline contains inclusions of microcline, and is commonly replaced by sodalite, clays (Fig. 2B) and eudialyte. Albite also occurs in aggregates with fine-grained microcline. Both feldspars are locally corroded and replaced by sodalite and eudialyte (Figs. 3A, B). Pectolite is found among albite and aegirine crystals, in mafic layers. Zircon forms bipyramidal zoned crystals up to 200 μm in diameter, and is commonly included in eudialyte (Figs. 3C, D). Fergusonite-(Y) occurs as irregular grains (up to 20 μm in diameter) that are interstitial to the silicates or fill cleavages and fractures in and occupy embayments in zircon. The margin of fergusonite-(Y) grains is commonly corroded and coated by britholite, which also replaces eudialyte, zir-

con, aegirine, and feldspar, and fills fractures in the unknown Na-Zr silicate (Figs. 3E, F).

A paragenetic sequence for the minerals in the green nepheline syenite is shown in Figure 4, and a detailed description of textures involving eudialyte is presented in the next section. The mineral assemblage and textural relationships suggest that the green nepheline syenite formed under subsolvus conditions (reflected by the assemblage nepheline-microcline-albite) and underwent extensive subsolidus re-equilibration in the presence of Cl-bearing hydrous fluids (as indicated by the replacement of nepheline, microcline, and albite by sodalite).

TEXTURES INVOLVING EUDIALYTE

Eudialyte typically forms pleochroic (pink), complexly zoned poikilitic domains up to a few centimeters in diameter, which contain aegirine, albite, microcline, nepheline, zircon, pectolite, and the unidentified Na-Zr

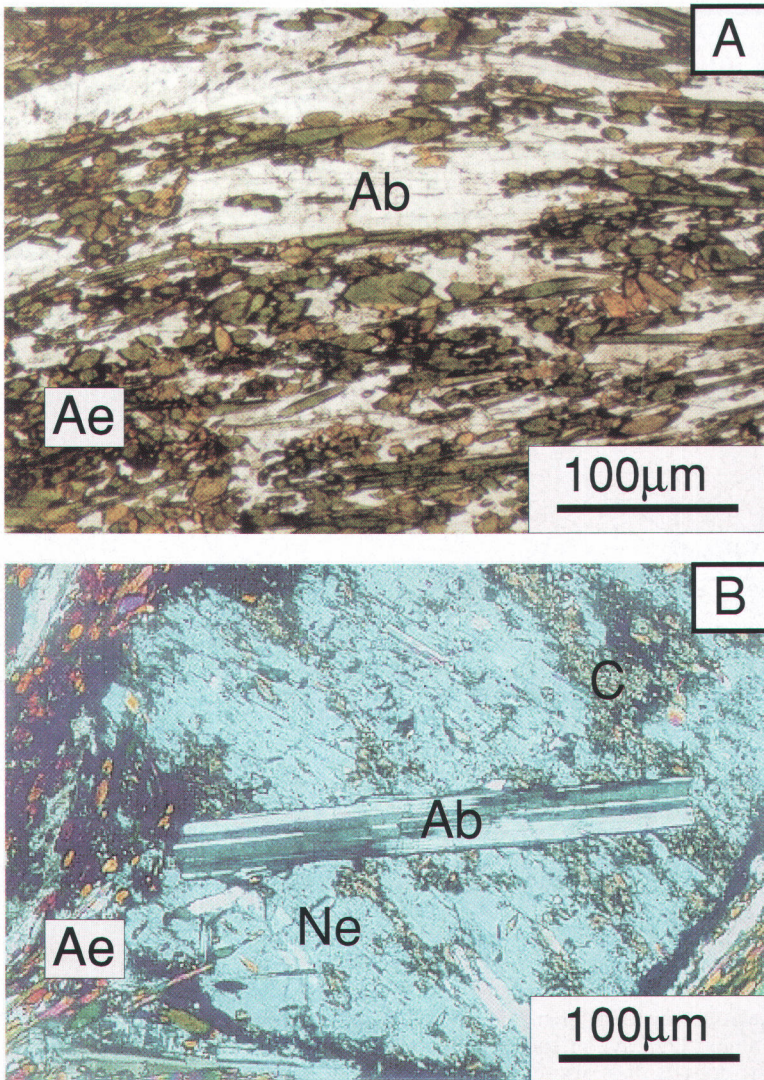


FIG. 2. A. Aegirine (Ae) interlayered with albite crystals (Ab). B. Tabular poikilitic crystals of nepheline altered to sodalite (black) and fine muscovite or clays (C). (Ab: albite; Ae: aegirine). Crossed nicols.

silicate (Figs. 3A to 3F). The eudialyte mantles and occupies embayments in corroded zircon, aegirine, microcline, albite, nepheline, pectolite, and the Na–Zr silicate (Figs. 3C, D). Eudialyte also preferentially replaces outer zones of microcline euhedra, and fills fractures and cleavages in microcline, albite, pectolite, nepheline and the unknown Na–Zr silicate (Fig. 3B). Eudialyte domains are themselves corroded and partially replaced by britholite and fergusonite-(Y) (Figs. 3E, F). The textural relationship between sodalite and eudialyte is am-

biguous. The contacts between these minerals are either sharp or corroded, and commonly, eudialyte fills embayments in sodalite.

The textural relationships described above suggest that eudialyte formed late, replacing most of the magmatic silicates, but it predated britholite and fergusonite-(Y), which replaced it. The occurrence of eudialyte in fractures and cleavages within feldspars suggests that it is post-magmatic, *i.e.*, hydrothermal.

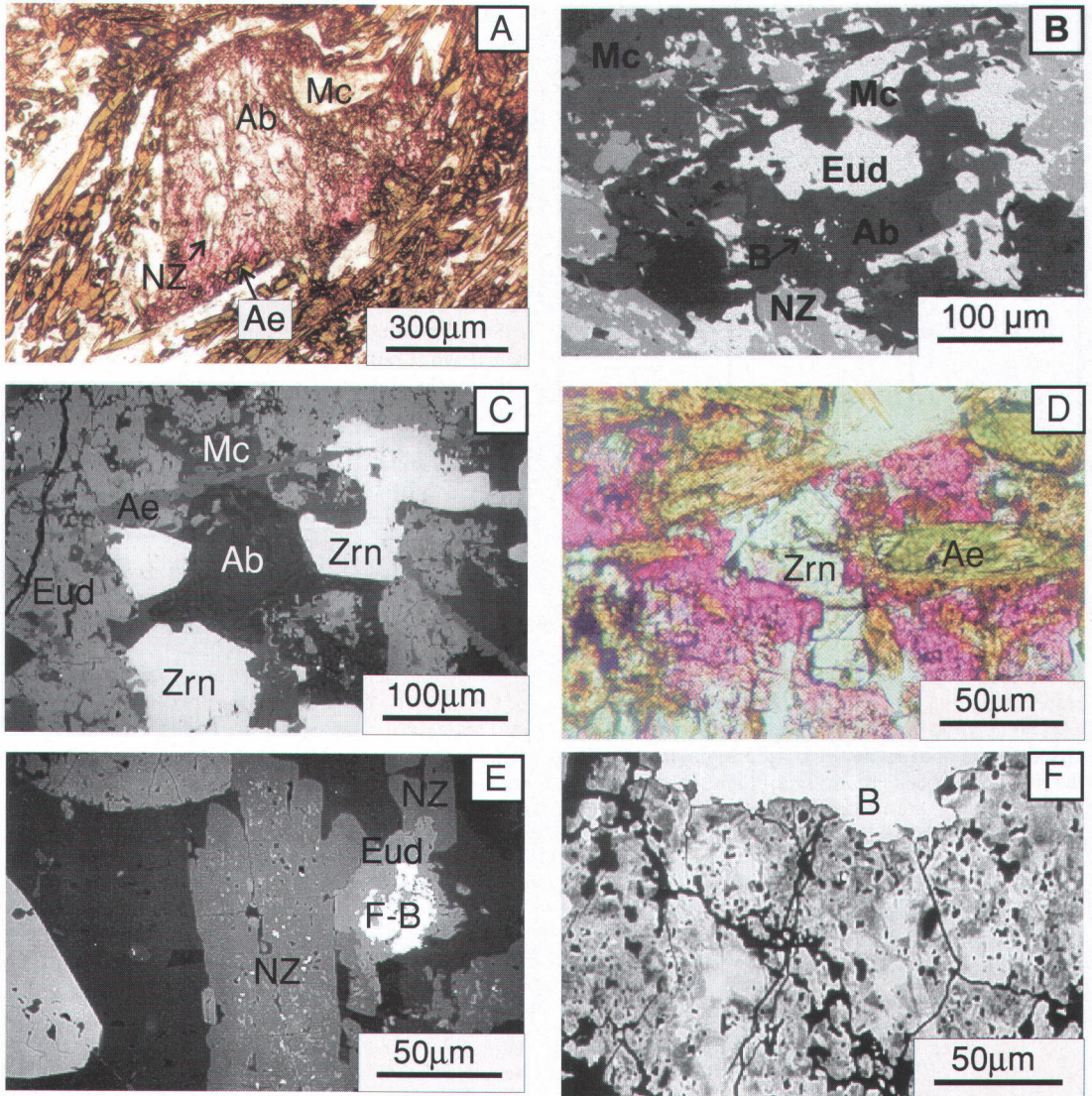


FIG. 3. A. Eudialyte domains (pink) with relict silicate inclusions (Ab: albite, Ae: aegirine, Mc: microcline, NZ: unknown Na-Zr silicate). B. Back-scattered electron image showing eudialyte (Eud) replacing outer zones and cleavages of microcline (Mc), Na-Zr silicate (NZ) and albite (Ab) (B: britholite). C. Back-scattered electron image showing eudialyte domains (Eud) with relict aegirine (Ae), zircon (Zrn), albite (Ab), and microcline (Mc) inclusions. D. Eudialyte (pink) occupying embayments in corroded zircon (Zrn) and altered aegirine (Ae). E. Back-scattered electron image showing eudialyte (Eud) domains occupying embayments in Na-Zr silicate (NZ) which, in turn, is replaced by composite grains of fergusonite-(Y) and britholite (F-B). F. Back-scattered electron image showing complexly zoned eudialyte domains replaced by britholite (B).

CHEMICAL COMPOSITION OF THE GREEN NEPHELINE SYENITE

A representative fused sample of the green nepheline syenite (sample P6; Fig.1) was analyzed for its bulk

chemical composition using inductively coupled plasma – emission spectrometry (ICP-ES) for the major elements and ICP coupled with quadrupole mass spectrometry (ICP-MS) for the minor and trace elements. The results are listed in Table 1. In addition to the high Zr

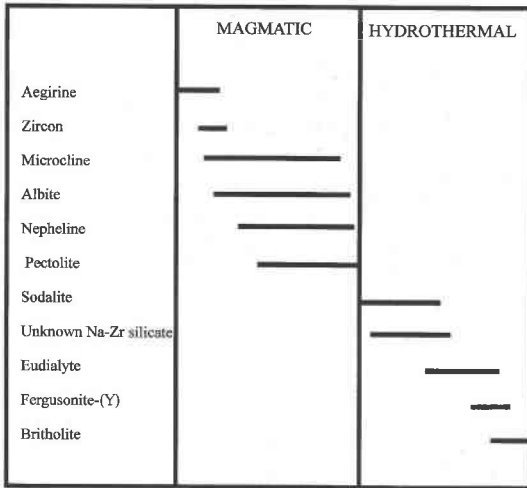


FIG. 4. Paragenetic sequence for the green nepheline syenite from Pílanesberg.

content (2 wt% ZrO_2), this sample also has high concentrations of *REE* and Nb, 6500 ppm and 2120 ppm, respectively.

The agpaite index of the green nepheline syenite, based on the above sample, is 1.35 (similar values for the index have been reported for Pílanesberg nepheline syenites by Kogarko *et al.* 1982). The replacement of nepheline and feldspars by sodalite indicates that the syenite was altered by aqueous fluids enriched in Cl (Wellman 1970) and probably in Na. Consequently, the agpaite index reported may not reflect the original magmatic proportions of Al, K and Na. Nevertheless, the occurrence of magmatic aegirine is consistent with a relatively high agpaite index (Mitchell 1996).

CHEMICAL COMPOSITION OF THE EUDIALYTE

The composition of the eudialyte was determined using a JEOL JXA-8900L automated wavelength-dispersion electron microprobe (EMP) at McGill University. Calibration for the analyses was done using albite (Na), diopside (Si, Ca, and Mg), orthoclase (Al and K), zircon (Zr and Hf), andradite (Fe), spessartine (Mn), $K_2Ta_2O_6$ (Ta), $Na_2Nb_2O_6$ (Nb), TiO_2 (Ti), vanadinite (Cl), CaF_2 (F), and synthetic *REE* phosphate standards (La, Ce, Sm, Nd, and P), and $Y_3Fe_5O_{12}$ (Y). The operating conditions were: accelerating voltage 15 kV and beam current 30 nA. A 10- μm beam was used for analysis, and the concentration of Na was measured first to minimize its loss through volatilization, although Johnsen & Gault (1997) pointed out that Na volatilization and migration do not seem to be a major problem in eudialyte analyzed under similar conditions.

As noted above, the eudialyte is complexly zoned (Fig. 3F). In back-scattered electron images, this zoning is manifested by very irregular light zones (10–30 μm wide) and dark patches commonly narrower than 10 μm . This fact makes the analysis of the dark patches difficult. Sixty analyses were done, most of them in the light zones; the results of representative analyses are presented in Table 2.

The Pílanesberg eudialyte sample, based on analyses of the light zones, is compositionally unusual compared with eudialyte from other localities (*e.g.*, Balashov & Turanskaya 1960, Jones & Larsen 1989, Deer *et al.* 1986, Mandarino & Anderson 1989, Coulson & Chambers 1996, Coulson 1997, Johnsen & Gault 1997). It contains the highest concentration of Nb (up to 3.8 wt% Nb_2O_5) and the lowest concentrations of Na (<11.4 wt% Na_2O) and Fe (<0.4 wt% FeO) reported in the literature. Furthermore, it has one of the highest contents of *REE* (up to 7.6 wt% REE_2O_3 , mainly Ce, La, and traces of Nd and Sm) and Mn (up to 7.5 wt% MnO) reported in the literature. As is common to eudialyte from other localities, it contains Cl (up to 1.2 wt%), and traces of F, Hf, K, Al and Ta, and all the analyses yield low totals (up to 96 wt%), which reflects the presence of H_2O and OH in its structure (Coulson & Chambers 1996). The levels of Y, P and Ti are lower than the detection limit of the EMP. As noted above, the dark zones were difficult to analyze. Consequently results for them are less reliable than for the light zones. However, analyses of the widest dark patches suggest that the dark zones are richer in Ca, Si, Zr, and Fe, and poorer in *REE*, Nb, and Hf than the light zones (Table 2).

THE STOICHIOMETRY OF EUDIALYTE

Eudialyte is a cyclosilicate containing three- and nine-fold rings of silicon–oxygen tetrahedra (Deer *et al.* 1986). It is trigonal and crystallizes in the acentric space-group $R\bar{3}m$ (Giuseppetti *et al.* 1971, Golyshev *et al.* 1971, Johnsen & Gault 1997). Although the formula unit has usually been calculated on the basis of 19 (O,OH,Cl), there is some uncertainty about this convention, and the structural formula of eudialyte has been variously given as: $Na_{12} (Ca, REE)_6 (Fe^{2+}, Fe^{3+}, Mn, Mg)_3 (Zr, Nb)_x Zr_3 [Si_3O_{27-y}(OH)_y]_4 (Si_3O_9)_4 Cl_2$, where $0.1 < x < -0.9$, $1 < y < 3$, $0.7 < z < 1.4$ (Giuseppetti *et al.* 1971), $(Na, Ca, REE)_5 (Fe^{2+}, Mn) (Zr, Ti) [(Si_3O_9)_2] (OH, Cl)$ (Deer *et al.* 1986), and $Na_{15}(Ca)_6 (Fe^{2+}, Mn^{2+}) (Zr)_3 (Si, Nb) (Si_{25}O_{73}) (O, OH, H_2O) (Cl, OH)_2$ (Mandarino 1999). Johnsen & Gault (1997) recently completed an extensive review of the structure and chemical composition of eudialyte. On the basis of this review, and in the absence of specific structural information, they propose the best procedure for determining the stoichiometry of eudialyte is to adopt a basis of 78 anions, using the general formula $ABCDESi_xO_{76} (Cl, OH, F)_2$, where x is 24 to 26, $E = Zr + Hf$ (≈ 3), $D = Nb + Ti$ (≈ 0.5),

$C = \text{Fe} + \text{Mn} (\leq 3)$, $B = \text{Ca} + \text{REE} + \text{remaining of Mn}$ (≈ 6) and $A = \text{Na} + \text{K} + \text{Sr} + \text{Y}$ (15–17).

The difficulty in establishing a satisfactory method for calculating the structural formula of eudialyte is probably due to: (1) the presence of extra ions and H_2O in the large spaces in the structure, (2) extensive substitution in the various sites (Johnsen & Gault 1997), (3) the occurrence of five or more Na sites (Johnsen & Gault 1997), and (4) variations in the number of anions (Johnsen *et al.* 1997).

The empirical formula of the Pilanesberg eudialyte was calculated using the average composition obtained from 23 analyses of the light zones (Table 2); as discussed earlier, the dark zones are commonly finer than the width of the electron-microprobe beam. Using the method proposed by Johnsen & Gault (1997) and Johnsen *et al.* (1998), the stoichiometry of the Pilanesberg eudialyte (sample P6) is: $(\text{Na}_{12.30}\text{REE}_{1.39}\text{Ca}_{0.89}\text{K}_{0.20})_{\Sigma 14.78} (\text{Ca}_{5.42}\text{Mn}_{0.58})_{\Sigma 6} (\text{Mn}_{2.96}\text{Fe}_{0.04})_{\Sigma 3} (\text{Zr}_{2.66}\text{Nb}_{0.28}\text{Hf}_{0.06})_{\Sigma 3} (\text{Nb}_{0.66}\text{Si}_{0.28}\text{Ta}_{0.06})_{\Sigma 1} \text{Si}_{25.64}\text{O}_{74} (\text{OH}_{1.01}\text{Cl}_{0.92}\text{F}_{0.07})_{\Sigma 2} \cdot 2\text{H}_2\text{O}$. This formula is superficially similar to that of kentbrooksit, the Mn–REE–Nb–F end-member of the eudialyte group of minerals (Johnsen *et al.* 1998). However, using the parameters SiCaFeCl and NbREEMnF defined by Johnsen & Gault (1997) and Johnsen *et al.* (1998), the Pilanesberg eudialyte is intermediate in SiCaFeCl between kentbrooksit and eudialyte from the type locality Kangerdluarsuk, Ilímaussaq (Johnsen *et al.* 1998), but enriched in NbREEMnF relative to an intermediate member of the series (Fig. 5). In particular, the Pilanesberg eudialyte contains concentrations of Ca similar to that from Ilímaussaq and twice that of kentbrooksit. For this reason, the eudialyte-group mineral at Pilanesberg is more appropriately referred to as eudialyte.

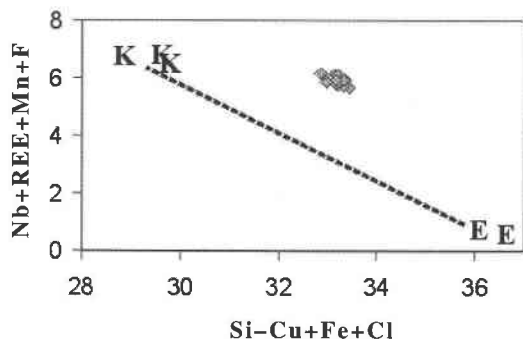


FIG. 5. A plot of $\Sigma\text{SiCaFeCl}$ versus $\Sigma\text{NbREEMnF}$ in atoms per formula unit, *apfu*, comparing the composition of eudialyte from Pilanesberg (diamond) with that of eudialyte (E) from the type locality Kangerdluarsuk, Ilímaussaq, and kentbrooksit (K). Data and tie line from Johnsen & Gault (1997) and Johnsen *et al.* (1998).

ORIGIN OF THE EUDIALYTE

Kogarko *et al.* (1982) have reviewed the textures and compositions of eudialyte-bearing rocks from various alkaline complexes, including Lovozero, Ilímaussaq and Pilanesberg, and concluded that eudialyte is of magmatic origin. They also conducted a limited number of experiments designed to investigate the magmatic crystallization of eudialyte. On the basis of these experimental results, they concluded that eudialyte can crystallize only from agpaite melts. They also showed that the timing of crystallization and hence the morphology of the eudialyte are strongly dependent on the zirconium content of the magma. In agpaite nepheline syenites with over 1 wt% ZrO_2 , eudialyte crystallizes contemporaneously with the main rock-forming minerals, and is idiomorphic. On the other hand, if the melt contains less than 1 wt% ZrO_2 , eudialyte crystallizes later than the main rock-forming minerals, and is poikilitic and xenomorphic.

In the green syenite of the Pilanesberg complex, which is agpaite and contains more than 2 wt% ZrO_2 , eudialyte should be an early crystallizing idiomorphic phase, according to the findings of Kogarko *et al.* (1982). On the contrary, as discussed above, textural relationships suggest that the eudialyte formed late, replacing aegirine, zircon, both feldspars, the Na–Zr silicate, and pectolite. The occurrence of eudialyte in fractures and cleavages within feldspars, nepheline, and the Na–Zr silicate suggests that it is postmagmatic, *i.e.*, hydrothermal. Significantly, the early crystallization of aegirine, followed by feldspar and nepheline in these rocks, suggests crystallization at H_2O pressures higher than 500 bars (Kogarko & Romanchev 1976). Moreover, the replacement of feldspars and nepheline by sodalite indicates that the green nepheline syenite has been metasomatized by Cl- and probably Na-rich aqueous fluids. It is therefore attractive to propose that the eudialyte in the green nepheline syenite crystallized from aqueous fluids exsolved from the magma. In addition to Cl, these orthomagmatic brines also carried F, which is found in minor concentrations in the unknown Na–Zr silicate, in eudialyte (~ 0.1 wt%), and in appreciable concentrations in britholite (~ 1 wt%).

In proposing a hydrothermal origin for eudialyte, the first issue that needs to be addressed is the notion that Zr is generally immobile during hydrothermal alteration. Although it has been widely assumed in the literature that Zr is immobile, and indeed this property has been used to monitor alteration, a number of recent studies have shown that Zr can be quite mobile under certain conditions. For example, Gieré & Williams (1992) reported the presence of zirconolite ($\text{CaZrTi}_2\text{O}_7$) in hydrothermal veins in dolomite adjacent to the Adamello batholith, Italy. Vard & Williams-Jones (1993) documented the occurrence of hydrothermal weloganite [$(\text{Sr}_3\text{Na}_2\text{Zr}(\text{CO}_3)_6 \cdot 3\text{H}_2\text{O})$] in vugs in phonolite sills in the Francon quarry, Montreal, Quebec. Rubin *et al.*

(1993) have described zircon–fluorite replacement bodies in limestone next to bodies of subvolcanic rhyolite in Texas. Unfortunately, the behavior of zirconium in hydrothermal fluids is still poorly understood. To our knowledge, only one study has investigated high-temperature complexation of Zr in aqueous fluids (Aja *et al.* 1995). Although this study was very preliminary, it did demonstrate that Zr forms stable complexes with F^- , SO_4^{2-} and OH^- under hydrothermal conditions, and that appreciable Zr can be mobilized, depending on the activities of these ligands.

In the absence of detailed information on the chemistry of the fluid phase affecting the green nepheline syenite at Pilanesberg, we are unable to evaluate quantitatively the relative importance of different Zr complexes. However, given the likelihood that the hydrothermal fluids responsible for metal transport were orthomagmatic and F-bearing (up to 0.1 wt% in the unknown Na–Zr silicate and in eudialyte), we suggest that Zr could have been mobilized by zirconium–fluoride complexes such as $(ZrF_6)^{2-}$. We also cannot discount the possibility of Zr transport by a hydroxy complex, *e.g.*, $Zr(OH)_4^0$, which is the dominant complex in the absence of significant activities of competing ligands such as F (Aja *et al.* 1995).

On the basis of the textural relationships discussed earlier, we propose that the source of Zr in eudialyte was zircon. In cases where eudialyte replaces zircon, Zr was clearly conserved. Elsewhere, Zr was evidently mobilized, and we propose that this occurred as a result of the dissolution of zircon (zircon crystals are commonly corroded, as described above) by fluorine-bearing orthomagmatic fluids, which transported the Zr as a ZrF_6^{2-} complex and redeposited it as eudialyte.

ENRICHMENT OF EUDIALYTE IN REE

As discussed earlier, the eudialyte in our sample of green nepheline syenite has one of the highest contents of REE reported in the literature. Only eudialyte from Mont Saint-Hilaire and Ascension Island have higher concentrations of REE, up to 9.78 and 8.39 wt% REE_2O_3 , respectively (Johnsen & Gault 1997, Harris *et al.* 1982). By contrast, eudialyte in other major alkaline intrusions, *e.g.*, the Lovozero and Ilímaussaq complexes, typically contains <3 wt% REE_2O_3 (Balashov & Turanskaya 1960, Deer *et al.* 1986). Significantly, eudialyte in these other complexes is interpreted to be of magmatic origin (Kogarko *et al.* 1982).

Why is the eudialyte at Pilanesberg, which is clearly hydrothermal in origin, enriched in REE? In order to understand the behavior of REE in hydrothermal systems, several researchers have investigated the stabilities of aqueous REE complexes (*e.g.*, Wood 1990, Haas *et al.* 1995, Gammons *et al.* 1996). These studies indicate that a variety of ligands, including F^- , Cl^- , OH^- , SO_4^{2-} , CO_3^{2-} , and PO_4^{3-} , are capable of complexing the

REE in hydrothermal fluids. However, at high temperature, high chlorinity, and low pH, conditions that may be inferred for the hydrothermal fluids responsible for eudialyte crystallization (see above), REE are complexed predominantly by chloride and fluoride (Haas *et al.* 1995).

On the basis of textural and chemical features of the green nepheline syenite, and the thermodynamic studies mentioned in this paper, we thus propose that the REE were transported mainly as chloro- and F-complexes in orthomagmatic fluids that metasomatized the green syenite. We furthermore propose that the REE were incorporated in eudialyte as a result of the reduction in Cl- and F-activity that accompanied precipitation of sodalite and the unknown (F-bearing) Na–Zr silicate.

CONCLUSIONS

The eudialyte composition at Pilanesberg is unusual because of its high contents of Nb (up to 3.8 wt%), REE (up to 7.6 wt%, mainly Ce, La, and traces of Nd and Sm), and Mn (up to 7.5 wt%), and its low contents of Na (up to 11.4 wt%) and Fe (up to 0.4 wt%). This chemistry reflects a hydrothermal origin for the mineral, which is supported by textural relationships that demonstrate a secondary or replacement origin. We propose that the eudialyte crystallized from an orthomagmatic Na–Nb–REE–Cl- and F-bearing hydrothermal fluid, which partitioned from an agpaite syenitic magma. We envisage that the Zr was locally remobilized from magmatic zircon as a zirconium–fluoride complex (ZrF_6^{2-}), and that the REE were introduced by the orthomagmatic fluid as Cl- or F-complexes (or both). Incorporation of REE in eudialyte occurred because of a reduction in Cl- and F-activities due to precipitation of sodalite and the unknown Na–Zr silicate.

ACKNOWLEDGEMENTS

We thank R. Harmer for introducing AEJW to the geology of the Pilanesberg Complex and facilitating his visit there, D. Palmer for assisting in the field work, G. Poirier and R. Mineau for valuable advice on conducting EMP and SEM analyses, respectively, and C. Normand for numerous stimulating discussions on the mineralogy of alkaline complexes. The manuscript benefited from reviews by O. Johnsen, R.F. Martin, and an anonymous reviewer. The research was supported by grants from the Natural Sciences and Engineering Research Council of Canada and the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche of Quebec.

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Received October 22, 1998, revised manuscript accepted May 1, 1999.