

## ECANDREWSITE – ZINCIAN PYROPHANITE FROM LUJAVRITE, PILANSBERG ALKALINE COMPLEX, SOUTH AFRICA

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### ABSTRACT

Ilmenite-group titanates are relatively common accessory minerals in agpaïtic nepheline syenite (lujavrite) in the Pilansberg alkaline complex, South Africa. They crystallized in three generations and form a continuous ecandrewsite – pyrophanite solid-solution extending from  $(\text{Zn}_{0.81}\text{Mn}_{0.12}\text{Fe}_{0.07})\text{TiO}_3$  to  $(\text{Mn}_{0.93}\text{Fe}_{0.7})\text{TiO}_3$ . The earliest generation of ferroan manganoan ecandrewsite of widely varying composition  $(\text{Zn}_{0.81-0.53}\text{Mn}_{0.33-0.12}\text{Fe}_{0.11-0.04})\text{TiO}_3$  is replaced by zincian pyrophanite  $(\text{Mn}_{0.82-0.34}\text{Zn}_{0.50-0.20}\text{Fe}_{0.13-0.06})\text{TiO}_3$ . The latest generation is pyrophanite with only traces of zinc, showing a compositional evolution toward ferroan pyrophanite. The three generations of Zn–Mn titanates recognized on the basis of their paragenesis and composition crystallized during the subsolidus alteration of the lujavrite by evolving deuteric alkaline fluids. The enrichment in Zn, Mn, and Ti in these fluids resulted from the decomposition of earlier-formed magmatic-stage Zn- and Mn-bearing titanate- and zirconosilicates. This is the first reported occurrence of a near-complete ecandrewsite – pyrophanite  $(\text{ZnTiO}_3 - \text{MnTiO}_3)$  solid-solution series.

**Keywords:** ecandrewsite, pyrophanite, solid-solution series, subsolidus alteration, lujavrite, Pilansberg, South Africa.

### SOMMAIRE

Les titanates du groupe de l'ilménite sont des minéraux accessoires relativement répandus dans les venues de syénite néphélinique agpaïtique (lujavrite) du complexe alcalin de Pilansberg, en Afrique du Sud. Ils ont cristallisé en trois générations et définissent une solution solide continue entre ecandrewsite et pyrophanite, allant de  $(\text{Zn}_{0.81}\text{Mn}_{0.12}\text{Fe}_{0.07})\text{TiO}_3$  à  $(\text{Mn}_{0.93}\text{Fe}_{0.7})\text{TiO}_3$ . La génération la plus précoce d'ecandrewsite ferreuse et manganésifère, de composition très variable,  $(\text{Zn}_{0.81-0.53}\text{Mn}_{0.33-0.12}\text{Fe}_{0.11-0.04})\text{TiO}_3$ , se voit remplacée par la pyrophanite zincifère,  $(\text{Mn}_{0.82-0.34}\text{Zn}_{0.50-0.20}\text{Fe}_{0.13-0.06})\text{TiO}_3$ . La génération tardive de cette série est faite de pyrophanite avec seulement des traces de zinc, et montre une évolution compositionnelle vers la pyrophanite ferreuse. Ces trois générations de titanates de Zn–Mn, établies selon des critères paragenétiques et compositionnels, ont cristallisé au cours de l'altération subsolidus de la lujavrite en présence de fluides alcalins deutériques en évolution. L'enrichissement de ces fluides en Zn, Mn, et Ti est le résultat de la déstabilisation de titanosilicates et de zirconosilicates précoces contenant du Zn et du Mn. Nous établissons pour la première fois la présence d'une solution solide quasiment complète entre ecandrewsite et pyrophanite  $(\text{ZnTiO}_3 - \text{MnTiO}_3)$ .

(Traduit par la Rédaction)

**Mots-clés:** ecandrewsite, pyrophanite, solution solide, altération subsolidus, lujavrite, Pilansberg, Afrique du Sud.

### INTRODUCTION

The Pilansberg alkaline complex, located *ca.* 50 km north–northwest of Rustenburg, in the Republic of South Africa, is one of the largest and least-studied differentiated intrusions of agpaïtic sodic syenite. The partially unroofed ring complex (~25 × 24 km), was emplaced at an intraplate extensional structure in the Middle Proterozoic (1250 ± 50 Ma; Retief 1963), along

a contact between granitic and noritic units of the Bushveld complex. Shand (1928) initially described the geology of the complex. Lurie (1986) briefly considered its economic potential, and aspects of the mineralogy of the eudialyte-bearing rocks were studied by Olivo & Williams-Jones (1999). During a comprehensive study (Liferovich & Mitchell, *in prep.*) of the mineralogy of the eudialyte nepheline syenite, *i.e.*, the green syenite of Shand (1928), occurring at Pilansberg, we

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recognized the occurrence of ecandrewsite, zincian pyrophanite and pyrophanite in hypersolvus astrophyllite nepheline syenite or lujavrite (*sensu* Brögger 1890). In this paper, we describe the paragenesis and origin of these rare ilmenite-structured titanates, and provide the first description of a near-complete ecandrewsite – pyrophanite ( $\text{ZnTiO}_3 - \text{MnTiO}_3$ ) solid solution.

#### THE GEOLOGICAL CONTEXT

The Pilansberg complex consists primarily of phonolitic-to-trachytic pyroclastic and lava flow sequences intruded by large arcuate plugs of agpaite feldspathoidal syenite, together with a semicircular dike of tinguaitite. From the periphery to the center, the complex is composed of red nepheline syenite, strongly altered amphibole foyaite, tinguaitite, white foyaite (subsolvus nepheline syenite), lujavrite (or hypersolvus trachytoid green nepheline syenite), and red foyaite. Inwardly dipping dikes of diverse alkaline porphyry, microsyenite and tinguaitite also are present. The emplacement of lujavrite was subsequent to that of the red and white foyaite, and the cone sheets of tinguaitite, but was prior to the late dikes of tinguaitite (Shand 1928, Olivo & Williams-Jones 1999).

The agpaite character of the Pilansberg rocks is indicated by the presence of the sodic minerals: eudialyte, lamprophyllite, astrophyllite–kupletskite, and mosandrite. Intense postmagmatic processes have left their imprint on all the syenites and generated a complex mineralogy by alteration of the primary mineral assemblages. These processes superimposed exotic low-temperature mineralization involving Na, F, P, Mn, Zn, Y, the light rare-earth elements, Zr, Nb, Sr, Pb, U (Lurie 1986) upon pre-existing rocks, and is analogous to the late-stage alteration recognized in the similar Ilímaussaq and Lovozero agpaite sodic complexes (Khomyakov 1995, Markl & Baumgartner 2002).

#### MINERALOGY OF ECANDREWSITE-BEARING LUJAVRITE

The inequigranular samples of melanocratic lujavrite studied were collected from a hillside outcrop in the south-central segment of the Pilansberg complex. This lujavrite has a well-defined trachytic texture, is medium to fine grained, and homogeneous on a hand-sample scale in terms of the distribution of mafic minerals. The rocks consist of euhedral microcline prisms (25–30 vol.%) together with analcite or natrolite pseudomorphs after subhedral nepheline (15–20 vol.%), set in a matrix of flow-aligned aggregates of thin prisms of green aegirine. The pseudomorphs after nepheline contain numerous very small prismatic needle-like crystals of aegirine. Brown-to-bronze astrophyllite occurs as 0.5–2 cm laths comprising 8–10 vol.% of the rock. Sodalite (8–12 vol.%) fills the interstices between the felsic min-

erals. The rock also contains evenly distributed creamy fine-grained pseudomorphs after euhedral crystals of trigonal or ditrigonal habit. These are aligned parallel to the feldspar prisms and comprise 12–15 vol.% of the initial assemblage. The habit of the pseudomorphs matches that of early generations of eudialyte described from the Khibina and Lovozero complexes by Kostyleva-Labuntsova *et al.* (1978). The pseudomorphs consist of titanite, zoned subhedral zircon, optically unidentifiable hydrous Na–Zr silicates(s), analcime, natrolite, late-forming secondary strontian eudialyte, allanite, pyrophanite, siliceous pyrochlore, oxides of Mn, and very small crystals of diverse oxides and silicates (see below). In less-altered lujavrites from Pilansberg, primary eudialyte is partially replaced by a similar mineral assemblage, indicating that the pseudomorphs in the sample studied are formed after primary eudialyte. Accessory minerals present include: calcian niobian loparite-(Ce), manganian astrophyllite, titanite, fluorapatite, sphalerite, and banalsite. Primary albite is not present, and opaque minerals occur as rare single grains or fine-grained aggregates. The texture and mineralogy of the samples examined are similar to those exhibited by lujavrites from the Lovozero, Ilímaussaq and Poços de Caldas agpaite complexes (Gerasimovskiy *et al.* 1966, Ulbrich & Ulbrich 2000, Markl 2001, Pekov 2001).

Postmagmatic processes have resulted in the corrosion and subsolidus replacement of the primary mineral assemblage throughout the whole rock by deuteric alkaline fluids. Secondary voids are not observed in the altered rocks, implying that the alteration was “volume conserving” and similar to the autometamorphic alteration described by Markl & Baumgartner (2002) in lujavrite from Ilímaussaq.

Ecandrewsite, zincian pyrophanite and pyrophanite occur in altered lujavrite. In these rocks, the assemblages of secondary phases forms four paragenetic groups differing in terms of the *alkalinity modulus* of Khomyakov (1990, 1995), which in order of formation and decreasing alkalinity are:

(1) *Moderately agpaite* assemblages containing ecandrewsite (*sensu lato*), together with allanite-(Ce), zircon and Si-bearing pyrochlore.

(2) *Hyperagpaite* assemblages containing zincian pyrophanite formed after ecandrewsite together with ferroan kupletskite, stronalsite, strontian fluorapatite, unidentified REE-bearing- and Na–Zr-bearing silicates.

(3) *Moderately alkaline* assemblages containing Zn-poor, ferroan pyrophanite formed after lamprophyllite or kupletskite together with secondary Sr–Nb-bearing eudialyte, unidentified Pb–Mn and Zn–Mn oxides, and spherulitic zircon.

(4) *Low-alkalinity* assemblages of a modally siliceous stage containing silica, allanite-(La), bastnäsite-(La), sulfatian monazite-(La), manganian biotite, Nb- and Zr-bearing titanite.

Associated with the above are a plethora of very small (typically <5 μm) phases. These include: U–Si-bearing pyrochlore, weloganite-like Sr–Zr silicate, zirconian astrophyllite, K-bearing zirconosilicates, REE-arsenates and phospho-arsenates, gasparite-(Ce), retzian-(Ce), coronadite-like Pb–Mn, Pb–Zn–Mn and Pb–Zn–Th oxides, huttonite, and olekminskite. Many of the minerals occur in association with natrolite or are found as inclusions in acicular aegirine.

A generalized paragenetic sequence for the mineral assemblages found in this metasomatically altered

hypersolvus lujavrite is shown in Figure 1. The mineral compositions and textural relationships suggest that alteration involved at least two stages of subsolidus overprinting by fluids released from cooling nepheline syenitic magma. These fluids in terms of their composition followed the “alkalinity wave” concept introduced by Khomyakov (1991, 1995) and refined by Markl & Baumgartner (2002). A detailed discussion of this process (Liferovich & Mitchell, *in prep.*) is beyond the scope of this paper.

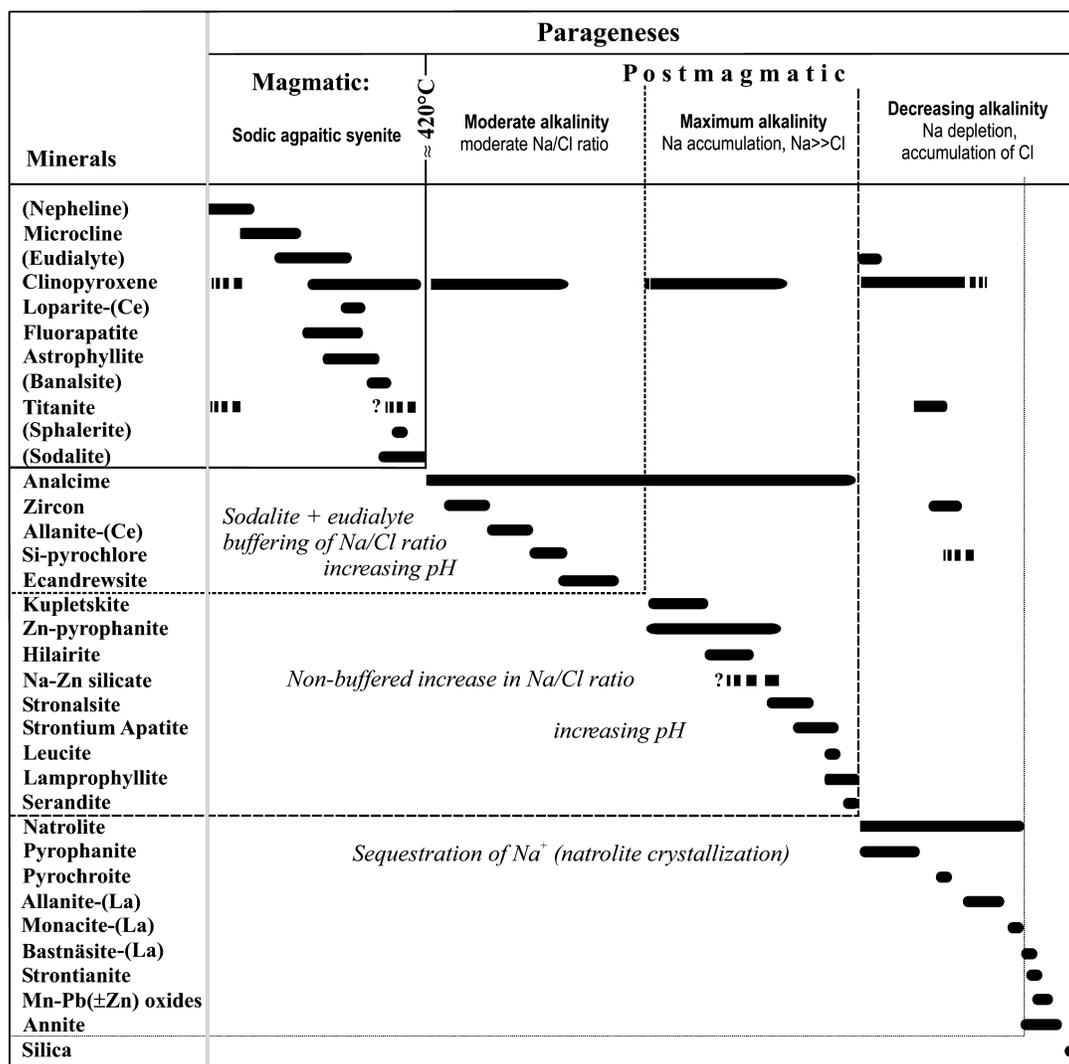


FIG. 1. Generalized sequence of formation of hypersolvus trachytic nepheline syenite (lujavrite) in the Pilansberg complex, South Africa. Minerals given in parentheses were replaced during postmagmatic alteration (as inferred by comparison with less-altered lujavrite). Markl & Baumgartner (2002) gave details of the evolutionary path of pH in the sodic fluids related to lujavrites.

PARAGENESIS OF ECANDREWSITE  
AND ZINCIAN PYROPHANITE

Ecandrewsite and zincian pyrophanite are opaque or orange-brown in thinner fragments. Ecandrewsite primarily forms euhedral plates (0.2–0.4 mm in length) that are strongly corroded and mantled by aggregates of zincian pyrophanite (Fig. 2a). Smaller subhedral grains of ecandrewsite are enclosed by kupletskite or analcime. Rarely, very small grains of well-preserved ecandrewsite fill the interstices of the thin prismatic crystals of aegirine within the analcime. Although the relationships of ecandrewsite to the primary minerals have been obscured by the autometasomatic alteration of the rock, the absence of inclusions of primary minerals in ecandrewsite and its association with analcime replacing nepheline suggest a subsolidus origin.

Zincian pyrophanite postdates ecandrewsite (Figs. 2a, b) and encloses manganian astrophyllite, ferroan kupletskite, hilairite, allanite-(Ce) and Si-bearing

pyrochlore. Zincian pyrophanite can be distinguished from the earlier-forming ecandrewsite only in back-scattered electron images. Zinc-poor to zinc-free pyrophanite was the latest titanate to form (Figs. 2b, c). It has been observed to corrode and replace ferroan kupletskite and lamprophyllite (Fig. 2d).

All three generations of Zn–Mn–Fe titanates became unstable during the later stages of alteration and were corroded and partially replaced by allanite-(La), titanite and manganian biotite (Fig. 2b). A Si-bearing pyrochlore also replaces niobian pyrophanite. At the contact with natrolite, the pyrophanite is commonly replaced by titanite and rarely by a lamprophyllite-like phase, together with plumbopyrochlore.

ANALYTICAL METHODS

Mineral compositions were determined at Lakehead University by energy-dispersion X-ray spectrometry (EDS) using a JEOL JSM-5900 scanning electron mi-

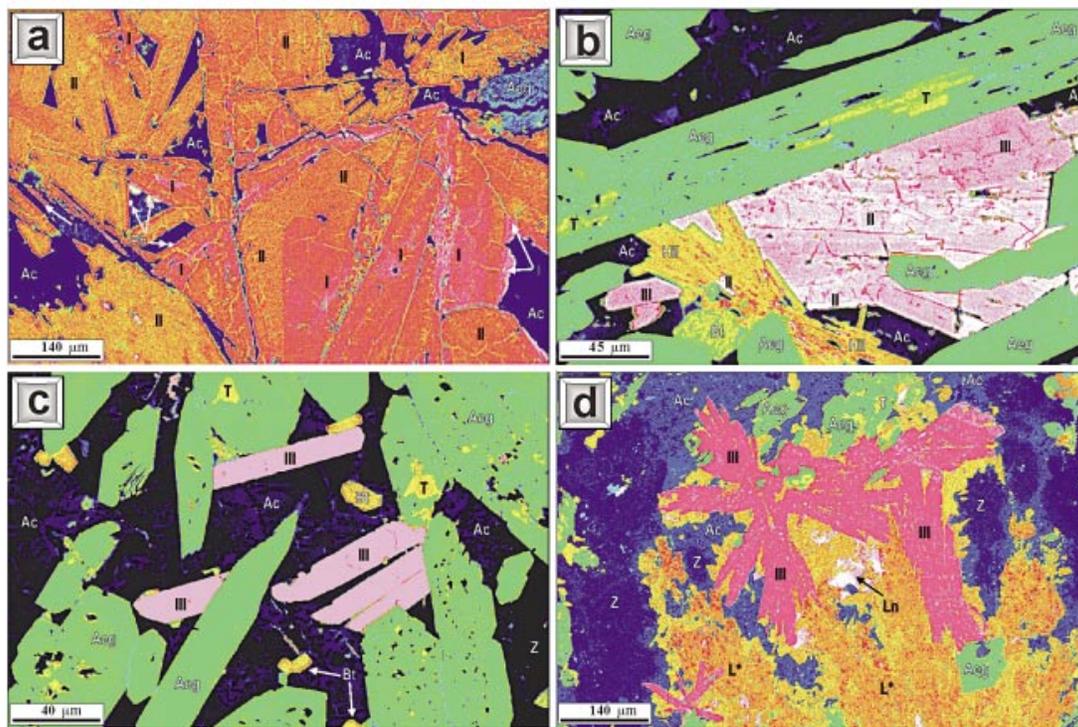


FIG. 2. Back-scattered electron images of some characteristic modes of occurrence of ecandrewsite, zincian pyrophanite and pyrophanite in lujavrite. a) Ecandrewsite cemented by zincian pyrophanite; b) ecandrewsite and zincian pyrophanite in interstices of prismatic aegirine, in association with hilairite; c) latest laths of pyrophanite growing on aegirine crystals (the latter have entrapped irregular grains of titanite); d) aggregates of pyrophanite growing on aegirine, which, in turn, covers a currently decomposed large crystal of primary silicate (lamprophyllite?). Note that the black areas are low-atomic-number phases, mostly zeolites and other silicates. I ecandrewsite, II zincian pyrophanite, III pyrophanite, Ac analcime, Aeg aegirine, Bt biotite, Hil hilairite, L pseudomorphs after lamprophyllite, Ln LREE silicate [lucasite-(Ce)?], and carbonates, Ph siliceous pyrochlore, T titanite, Z latest zeolite (natrolite).

croscope equipped with a Link ISIS 300 analytical system incorporating a Super ATW light-element detector (133 eV FWHM MnK $\alpha$ ). Raw EDS spectra were acquired for 130 s (live time) with an accelerating voltage of 20 kV and a beam current of 0.475 nA on a Ni standard. Spectra were processed with the Link ISIS SEMQUANT software package with full ZAF corrections applied. The following well-characterized mineral and synthetic standards were used: jadeite or loparite (Na), orthoclase (K), corundum (Al), ilmenite (Fe,Ti), periclase (Mg), zircon (Zr), wollastonite (Ca), lueshite (Nb), loparite (REE), barite (Ba), SrTiO<sub>3</sub> (Sr), Zn metal; Mn metal, pyroxene glass DJ35 (Si, Na). For comparative purposes, ecandrewsite was also analyzed by standard wavelength-dispersion methods using a Cameca SX-50 electron microprobe at the University of Manitoba.

Ferric and ferrous iron were calculated from microprobe-obtained values of FeO<sub>T</sub> using the method of Droop (1987). This method can be used to assess only the minimum Fe<sup>3+</sup> content and assumes that Mn is present only as Mn<sup>2+</sup> and that no cation vacancies are present. These assumptions might not be correct, as the minerals of the ecandrewsite – pyrophanite series from Pilansberg exhibit cation deficiencies at the A site of up

to 10%  $\Sigma R^{2+}$ , regardless of analytical method. Similar cation deficiencies are evident in data given for ecandrewsite by Whitney *et al.* (1993).

#### MINERAL COMPOSITIONS

Representative compositions of members of the ecandrewsite – pyrophanite series are given in Table 1. Figure 3 illustrates all data obtained in terms of the Zn–Mn–Fe and Mg–Mn–Fe systems, with comparative data for ilmenite-group titanates from carbonatite, kimberlite and other appaitic syenites. Although the compositional fields of ecandrewsite (field I), zincian pyrophanite (field II), and pyrophanite (field III) do not overlap, these grade nearly continuously from ecandrewsite with ~80 mol.% ZnTiO<sub>3</sub> to Zn-free late pyrophanite.

All of the titanates show considerable variation in terms of the FeTiO<sub>3</sub> component, and only some cores of relatively Zn-poor ecandrewsite and their Zn-rich margins have no detectable Fe. Al is typically below the detection limit (0.2 wt.% Al<sub>2</sub>O<sub>3</sub>) and does not exceed 0.4 wt.% Al<sub>2</sub>O<sub>3</sub>. Nb is present and distributed irregularly within and between crystals. The abundance varies from trace to: 2.5%, 2.9%, and 4.1 wt.% Nb<sub>2</sub>O<sub>5</sub> (average) in ecandrewsite, zincian pyrophanite and

TABLE 1. REPRESENTATIVE COMPOSITIONS OF ECANDREWSITE – PYROPHANITE FROM LUJAVRITE, PILANSBERG ALKALINE COMPLEX, SOUTH AFRICA

Wt.%	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
MgO wt.%	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.11	0.16
Al <sub>2</sub> O <sub>3</sub>	n.d.	0.16	0.30	0.16	n.d.	n.d.	n.d.	0.24	0.11	0.15	0.14	n.d.	n.d.	0.14	0.14
TiO <sub>2</sub>	51.15	50.08	49.44	51.30	51.21	49.63	51.38	52.4	52.20	52.06	53.11	54.04	51.73	52.19	52.04
MnO	5.39	8.61	9.04	16.03	14.88	15.20	20.59	22.69	28.35	30.98	38.46	39.84	40.23	38.37	43.67
FeO <sub>T</sub>	3.03	1.77	2.43	2.22	5.10	5.86	3.07	5.98	2.88	4.07	4.30	3.60	3.72	4.94	3.10
ZnO	39.53	38.80	38.04	29.47	27.52	24.63	22.53	17.41	13.71	10.48	1.95	0.61	0.81	0.40	n.d.
Nb <sub>2</sub> O <sub>5</sub>	0.45	0.19	0.56	0.90	1.12	2.88	0.47	1.79	2.18	1.35	1.78	0.75	2.22	1.70	0.70
Total	99.55	99.61	99.81	100.08	99.83	98.2	98.04	100.51	99.43	99.09	99.74	98.84	98.71	97.85	99.81
Fe <sub>2</sub> O <sub>3</sub> <sup>a</sup>	-	-	0.12	-	-	-	-	-	-	-	-	-	-	-	0.07
FeO <sup>a</sup>	-	-	2.32	-	-	-	-	-	-	-	-	-	-	-	3.07
Structural formulae calculated on the basis of three atoms of oxygen															
Ti <i>apfu</i>	1.015	0.998	0.984	1.001	1.0	0.983	1.013	0.999	1.0	1.0	1.001	1.022	0.988	1.0	0.985
Al	-	0.005	0.009	0.005	-	-	-	0.007	0.003	0.005	0.004	-	-	0.004	0.004
Fe <sup>3+</sup>	-	-	0.002	-	-	-	-	-	-	-	-	-	-	-	0.001
Fe <sup>2+</sup>	0.067	0.039	0.052	0.048	0.111	0.129	0.067	0.127	0.061	0.087	0.090	0.076	0.079	0.105	0.064
Mn	0.120	0.193	0.203	0.352	0.327	0.339	0.457	0.487	0.612	0.670	0.816	0.848	0.866	0.828	0.931
Mg	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.004
Zn	0.770	0.759	0.743	0.564	0.528	0.479	0.436	0.326	0.258	0.198	0.036	0.011	0.015	0.008	-
Nb	0.005	0.002	0.007	0.011	0.013	0.034	0.006	0.021	0.025	0.016	0.020	0.009	0.025	0.02	0.008
Mol.% end-member components															
Ecn	80.21	76.28	74.85	58.04	54.27	49.67	45.27	34.17	27.28	20.48	3.78	1.21	1.56	0.79	-
Pyf	12.55	19.42	20.41	36.22	33.66	35.17	47.46	51.09	64.72	69.46	85.51	90.29	89.0	86.53	93.89
Ilm	6.96	3.94	3.83	4.95	11.39	13.39	6.99	13.29	6.49	9.01	9.44	8.06	8.13	11.0	4.84
Nb <sub>2</sub> O <sub>5</sub>	0.28	0.11	0.34	0.54	0.68	1.78	0.29	1.08	1.33	0.81	1.06	0.45	1.31	1.02	0.40
Al <sub>2</sub> O <sub>3</sub>	-	0.25	0.47	0.25	-	-	-	0.38	0.17	0.23	0.22	-	-	0.22	0.21
Hem	-	-	0.11	-	-	-	-	-	-	-	-	-	-	-	0.06
Gkl	-	-	-	-	-	-	-	-	-	-	-	-	-	0.44	0.61

n.d.: not detected. FeO<sub>T</sub> is total Fe given as FeO. <sup>a</sup> Calculated from stoichiometry. Compositions: 1–5 strongly corroded earliest ecandrewsite cemented by pyrophanite; 6–11 pyrophanite cementing ecandrewsite relics; 12–15 latest euhedral and homogeneous platy crystals of pyrophanite. Symbols: Ecn: ecandrewsite, Pyf: pyrophanite, Ilm: ilmenite, Hem: hematite, Gkl: geikielite.

pyrophanite, respectively. Minor Zr is present (<0.5 wt.% ZrO<sub>2</sub>), and Mg is below the limits of detection (<0.2 wt.% MgO). The incorporation of Nb (and Zr) in the structure does not follow any of the schemes suggested by Chakhmouradian & Mitchell (1999).

Ecandrewsite and zincian pyrophanite are compositionally zoned. The least-altered grains of ecandrewsite in aegirine interstices have a zinc-enriched margin (Figs. 2a, 3), and evolve from a core of (Zn<sub>0.56</sub>Mn<sub>0.35</sub>Fe<sub>0.06</sub>)(Ti<sub>0.99</sub>Nb<sub>0.01</sub>)O<sub>3</sub> to a rim of (Zn<sub>0.66</sub>Mn<sub>0.27</sub>Fe<sub>0.04</sub>)(Ti<sub>0.98</sub>Nb<sub>0.01</sub>Zr<sub>0.01</sub>)O<sub>3</sub>. The most zincian compositions vary from interstitial Fe-free manganoean ecandrewsite to ferroan manganoean ecandrewsite occurring in aggregates cemented and partially replaced by pyrophanite (Figs. 2a, b).

Zincian pyrophanite shows an opposite pattern of zonation, with Zn depletion toward the margins of crystals. Compositional evolution is from manganoean ferroan ecandrewsite to low-Fe pyrophanite with less than 5 mol.% ZnTiO<sub>3</sub> (Fig. 3). Isolated grains of ecandrewsite (Zn<sub>0.72</sub>Mn<sub>0.19</sub>Fe<sub>0.09</sub>)TiO<sub>3</sub> and zincian pyrophanite (Mn<sub>0.82</sub>Zn<sub>0.12</sub>Fe<sub>0.06</sub>)TiO<sub>3</sub> occur within interstices among aegirine crystals. Corrosion, replacement and cementation textures are absent, suggesting that zincian pyrophanite did not form by the replacement of ecandrewsite, and thus represents a distinct generation of Zn–Mn titanate.

#### DISCUSSION

Ecandrewsite has not previously been described from igneous rocks. Ferroan manganoean varieties have been recognized from diverse regionally metamorphosed sedimentary rocks (Birch *et al.* 1988, Whitney *et al.* 1993). The most Zn-rich example reported to date occurs in a pelitic schist found in Death Valley, California, where it forms a solid solution extending from ferroan ecandrewsite with 84 mol.% ZnTiO<sub>3</sub> to near end-member composition ilmenite with 0.9 wt.% MnO and traces of Zn (Whitney *et al.* 1993).

Manganoean zincian ilmenite, with up to 5.4 wt.% ZnO and 9.0% MnO, has been described from miarolitic cavities in a peralkaline rhyolite from Cape Ashizuri, southwestern Japan (Nakashima & Imaoka 1998). Suwa *et al.* (1986) have also described minerals of the zincian pyrophanite – ilmenite series with up to 7.6 wt.% ZnO also in a miarolitic paragenesis from alkaline granite occurring at Kuiqi, Fuzhou, in China. This latter occurrence represents a rather limited natural example of solid solution between ecandrewsite and pyrophanite, extending from 1.3 to 15.4 mol.% ZnTiO<sub>3</sub> (Fig. 3).

Recently, during a comparative study of trachytic subsolvus nepheline syenites from the Poços de Caldas peralkaline complex, in Brazil, we recognized a further occurrence of Zn–Mn titanate (Liferovich & Mitchell, *in prep.*). An early generation of this phase, in association with manganoean sphalerite, fluorite and an unidentified Na–Al–Zn silicate, is zincian to zinc-free

pyrophanite (<7.4 mol.% ZnTiO<sub>3</sub>; Fig. 3). This mineral is overgrown by material transitional between manganoean ecandrewsite and zincian pyrophanite (41–57 mol.% ZnTiO<sub>3</sub>; Fig. 3), and is associated with natrolite, calcite, and strontianite. All titanates at Poços de Caldas have low iron contents (<5 mol.% FeTiO<sub>3</sub>).

Manganoean ilmenite and ferroan pyrophanite are typical minerals of agpaitic and hyperagpaitic pegmatite, related metasomatic rocks and postmagmatic zeolite-rich parageneses in the Lovozero and Khibina complexes (Khomyakov 1995, Pekov 2001, 2002), at Gordon Butte, Montana (Chakhmouradian & Mitchell 2002), and at Mont Saint-Hilaire (Horváth & Gault 1990). Pyrophanite has been described as a common accessory phase in mineralized albite-dominant tuffs in the Pilansberg complex and was considered as a potential source for Nb by Lurie (1986), although data on its composition were not provided.

Agpaitic nepheline syenite complexes and their sodic hyperagpaitic derivatives are typically enriched in zinc compared to the lithosphere (Gerasimovskiy 1969, Markl 2001). According to Pekov (2002), the common mineral of zinc in peralkaline rocks is Fe–Mn-bearing sphalerite. Early postmagmatic Zn mineralization is also present as H<sub>2</sub>O-free minerals such as willemitite, genthelvite, landauite, murataite, nordite and osumillite. Subsolidus, low-temperature autohydration processes result in sequestration of Zn in clay minerals, zeolites and labuntsovite-group minerals. These observations are at variance with the mineralogy and geochemistry of zinc in silica- and alumina-saturated systems (Neumann 1949). In the latter, thermodynamic data indicate that <sup>VI</sup>Zn<sup>2+</sup> is more stable than <sup>IV</sup>Zn<sup>2+</sup> at high temperature, and that Zn is sequestered in gahnite (ZnAl<sub>2</sub>O<sub>4</sub>) rather than as ZnTiO<sub>3</sub> (Whitney *et al.* 1993). From field and textural evidence, Plimer (1990) argued that zincian ilmenite – ecandrewsite solid solutions form by reaction of titanium dioxide(s) or ilmenite with zincian clays or carbonates during prograde metamorphism. This process results in disequilibrium crystallization with significant intergranular variations in the Zn to Fe ratio of the products. Both sphalerite desulfidation and breakdown of zinc-bearing silicates and oxides during retrograde alteration of kyanite schists have also been reported to result in formation of ecandrewsite in metasedimentary rocks (Whitney *et al.* 1993). Zincian ilmenite in association with aegirine and arfvedsonite is also known to precipitate directly from hydrothermal solutions exsolved from peralkaline rocks (Suwa *et al.* 1987, Nakashima & Imaoka 1998).

In the absence of experimental data on the partitioning of Zn into pyrophanite relative to complex silicates, we cannot assess quantitatively the conditions of formation of ecandrewsite and zincian pyrophanite. Moreover, these minerals, at Pilansberg, show very wide intergranular variations in composition, indicating non-equilibrium crystallization. In addition, Whitney *et al.* (1993) showed disagreement between the compositions

of cation-deficient ecandrewsite and zincian ilmenite and thermodynamic calculations of their relative stability. Unfortunately, because of the extensive postmagmatic alteration of the ecandrewsite-bearing lujavrite, there are no equilibrated mineral pairs of silicates and oxides suitable for geothermobarometry of the ecandrewsite and zincian pyrophanite parageneses.

With respect to the genesis of ecandrewsite in agpaitic rocks, none of the hypotheses described above are directly applicable. For example, there is no textural evidence in favor of its formation by replacement of sphalerite at Pilansberg. Although this mineral is present in less-altered lujavrite at Pilansberg, it is absent in the ecandrewsite-bearing rock. Hence, it is possible that the extensive deuteric alteration of the lujavrite has resulted in the complete replacement of primary sphalerite coincident with the breakdown of eudialyte and conversion of nepheline to analcime. However, in opposition to this hypothesis, sphalerite at Poços de Caldas seems to coexist in equilibrium with ecandrewsite. In the absence of other evidence, we conclude that the sources of Mn, Zn and Ti must lie in the decomposition of pre-existing Ti–Mn-bearing silicates (eudialyte, lamprophyllite, kupletskite, *etc.*) followed by concentration of these elements in the residual hydrothermal fluids.

Core-to-rim enrichment of Zn in ecandrewsite grains indicates increasing activity of Zn during the agpaitic stage (Fig. 1). The opposite sense of zoning of zincian pyrophanite, formed during the hyperagpaitic stage, indicates competition for zinc between coeval pyrophanite and Na–Zn silicates (Fig. 1). The sequestration of Zn in pyrochlore, Na zirconosilicates and eudialyte rather than coeval pyrophanite suggests that Mn–Zn diadochy in the ilmenite structure is not feasible at relatively low temperatures, *i.e.*, there is not a complete ecandrewsite–pyrophanite solid solution at low temperatures. This conclusion is supported by our experimental data on the solid-solution series  $Mn_{1-x}Zn_xTiO_3$ , which suggest the maximum solubility of Zn to be about 0.8 *apfu* at low pressure (Mitchell & Liferovich 2004).

As noted above, the evolution of the Pilansberg lujavrite can be divided in several superimposed stages of differing alkalinity (Fig. 1). This evolution essentially follows that occurring in the most evolved rocks of the Lovozero, Khibina and Ilímaussaq peralkaline sodic complexes (Khomyakov 1995, Markl & Baumgartner 2002). In these complexes, the postmagmatic hyperagpaitic fluids have typically segregated as discrete pegmatites and hydrothermal veins and not permeated and altered the host rocks. Pilansberg differs in that the highly evolved assemblages of postmagmatic minerals are superimposed directly on the magmatic agpaitic rocks. The textures and replacement relationships indicate that the development of an *in situ* volatile-rich zeolite-dominant paragenesis is the result of retention of an orthomagmatic volatile-rich fluid exsolved from the cooling agpaitic magma. That the fluid-rich lujavritic magma was emplaced at a shallow level is illustrated

by the abundance of cognate volcanic rocks. The cooling rate and crystallization path of this hypersolvus lujavrite did not permit either fractional crystallization or segregation of volatile-rich fluids, which might under other circumstances have given rise to discrete pegmatites and late hydrothermal veins.

Experiments by Piotrowski & Edgar (1970) showed that the H<sub>2</sub>O-saturated solidus of lujavrite lies at 450°C for a H<sub>2</sub>O pressure of 0.1 GPa. Recently, Markl (2001) showed that the temperature of the nepheline-to-analcime conversion in hydrous albite-free lujavrite is in the range of 420–200°C at  $a(SiO_2) < 0.1$  and  $aH_2O$  ranging from 1.0 to 0.5. As ecandrewsite and zincian pyrophanite appear to have formed contemporaneously with analcime replacing nepheline, we assume that the titanates must have formed at temperatures below 400°C, *i.e.*, they are subsolidus phases.

Markl & Baumgartner (2002) have developed a quantitative model for the evolution of the alkalinity of fluid-rich sodic agpaitic syenites. They infer that the Na:Cl ratio of the fluid buffers the alkalinity, such that the higher the  $aCl^-$ , the lower the pH. The “volume-conserving” replacement of nepheline by analcime in a more-or-less closed system results in successively increasing alkalinity of the fluid, and a dramatic decrease in pH in the final stages due to the sequestration of Na in sodic species with Cl accumulating in the residual solutions. This model explains the formation of zircon, allanite-(Ce), Si-bearing pyrochlore and ecandrewsite during the incipient stages of alteration of the lujavrite, as the pH is buffered until all interstitial sodalite and primary Cl-bearing eudialyte is decomposed. Zinc is incorporated only in ecandrewsite and zincian pyrophanite at this stage. After complete replacement of sodalite and primary eudialyte, alkalinity increases as nepheline is replaced by Cl-free analcime, and at the highest alkalinity Na–Zn silicates are deposited in preference to zincian pyrophanite.

#### CONCLUSIONS

The formation of zinc titanates belonging to the ilmenite structural group in lujavrite at Pilansberg is due to subsolidus reaction of deuteric fluids with the primary magmatic minerals. The titanates form a near-complete solid solution between ecandrewsite and pyrophanite. Changes in the composition of the titanates reflect changes in the alkalinity of the fluids involved. Interestingly, there is only limited solid-solution among ecandrewsite, pyrophanite and ilmenite, even though these minerals are isostructural.

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