



HAL
open science

Structurally-controlled hydrothermal alteration in the syntectonic Neoproterozoic Upper Ruvubu Alkaline Plutonic Complex (Burundi): Implications for REE and HFSE mobilities

Sophie Decrée, Philippe Boulvais, Corentin Cobert, Jean-Marc Baele, Gilbert Midende, Véronique Gardien, Luc Tack, Gérard Nimpagaritse, Daniel Demaiffe

► To cite this version:

Sophie Decrée, Philippe Boulvais, Corentin Cobert, Jean-Marc Baele, Gilbert Midende, et al.. Structurally-controlled hydrothermal alteration in the syntectonic Neoproterozoic Upper Ruvubu Alkaline Plutonic Complex (Burundi): Implications for REE and HFSE mobilities. *Precambrian Research*, 2015, 269, pp.281-295. 10.1016/j.precamres.2015.08.016 . insu-01186043

HAL Id: insu-01186043

<https://insu.hal.science/insu-01186043>

Submitted on 24 Aug 2015

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 Structurally-controlled hydrothermal alteration in the syntectonic
2 Neoproterozoic Upper Ruvubu Alkaline Plutonic Complex (Burundi):
3 implications for REE and HFSE mobilities
4

5 Sophie Decrée^{1,2,*}, Philippe Boulvais³, Corentin Cobert⁴, Jean-Marc Baele⁴, Gilbert Midende⁵,
6 Véronique Gardien⁶, Luc Tack², Gérard Nimpagaritse², Daniel Demaiffe⁷

7
8 ¹ Royal Belgian Institute of Natural Sciences, Brussels (Belgium)

9 * Corresponding author: sophie.decree@naturalsciences.be

10 ² Royal Museum for Central Africa, Tervuren (Belgium). E-mail: luc.tack@africamuseum.be;
11 gerard.nimpagaritse@africamuseum.be

12 ³ Géosciences Rennes – UMR 6118 - Université de Rennes 1 (France). E-mail : [philippe.boulvais@univ-](mailto:philippe.boulvais@univ-rennes1.fr)
13 [rennes1.fr](mailto:philippe.boulvais@univ-rennes1.fr)

14 ⁴ University of Mons (Belgium). E-mail: jean-marc.baele@umons.ac.be; corentin.cobert@umons.ac.be

15 ⁵ Université du Burundi. E-mail: midendegilbert@yahoo.com

16 ⁶ LGL :TPE UMR5276, Université Lyon 1 (France). E-mail: vgardien@univ-lyon1.fr

17 ⁷ Géochimie (CP 160/02), Université Libre de Bruxelles (Belgium). E-mail : ddemaif@ulb.ac.be

18
19 **Abstract**

20 The Neoproterozoic Upper Ruvubu Alkaline Plutonic Complex (URAPC), Burundi, is
21 located along the western branch of the East African Rift. It comprises oversaturated and
22 undersaturated syenites and a shallow level carbonatite body (the Matongo carbonatite) that
23 does not outcrop but has been sampled by drill-cores. The elliptic map contour of the URAPC

1 points to a syntectonic emplacement. Large shear zones that were active during magmatic
2 emplacement have accommodated a regional NE-SW shortening. Mineralization features of
3 late-magmatic to hydrothermal origin are associated with the carbonatite, which, by itself,
4 contains a dense network of calcitic veins. HFSE mineralization occurring as zircon and
5 ilmenite megacrysts can be found in an area of intense and extensive K-fenitization, which
6 lead to the transformation of the surrounding syenite into a dominant K-feldspar + biotite
7 mineral assemblage (Inamvumvu area). Carbonatitic dykes (overprinted by a hydrothermal
8 alteration) are present a few kilometers north of the Matongo carbonatite, within highly
9 deformed zones in the syenite. These dykes occur along with Na-fenites (resulting from the
10 transformation of the feldspathoidal syenite into an albite-dominant paragenesis) and are
11 enriched in REE-minerals (monazite and ancylite-(Ce)). Many magmatic (pegmatoid) dykes
12 and hydrothermal (quartz+hematite) veins also occur in shear zones in the URAPC. Most of
13 them can be interpreted as tension gashes. The chondrite-normalized REE patterns of some
14 carbonatite whole rock samples are highly disturbed, in relation to post-magmatic
15 hydrothermal alteration. The HFSE and REE distribution in the minerals from the
16 hydrothermal veins/dykes (calcitic veins within the carbonatite, carbonatite dykes overprinted
17 by a hydrothermal alteration in deformed zones, and zircon and ilmenite megacrysts) attests
18 for a complex behaviour of REE during alteration. Oxygen and carbon isotope compositions
19 of the Matongo carbonatite and the carbonatitic dykes have a magmatic signature, with $7.2 <$
20 $\delta^{18}\text{O}$ (vs. SMOW) $< 8.5\text{‰}$ and $-4.7 < \delta^{13}\text{C}$ (vs. PDB) $< -5.4\text{‰}$ in agreement with the Sr
21 isotopic composition. The oxygen isotope composition of zircon and ilmenite megacrysts
22 ($\delta^{18}\text{O}_{\text{Zr}} = 4$ to 4.7‰ , $\delta^{18}\text{O}_{\text{Ilm}} = -4.3$ to -1.5‰ respectively) also point to a magmato-
23 hydrothermal origin of the forming fluids. Some samples of the Matongo carbonatite and the
24 carbonatitic dykes, with high $\delta^{18}\text{O}$ values ($\delta^{18}\text{O} = 8.6$ to 21.8‰), show evidence of a
25 medium- to low-temperature hydrothermal alteration event by an aqueous fluid. Calcitic

1 veins in the carbonatite record another alteration event, outlined by the co-variation of $\delta^{18}\text{O}$
2 and $\delta^{13}\text{C}$ values ($\delta^{18}\text{O} = 16.3$ to 24.7% and $\delta^{13}\text{C} = -4.7$ to 0.2%), implying the involvement
3 of a mixed $\text{H}_2\text{O}-\text{CO}_2$ fluid. As a whole, the circulation of fluids in the URAPC was initiated
4 during magmatic emplacement and the geometry of this circulation was controlled by the
5 syn-emplacement crustal scale shear zones. Element mobility, one expression of which being
6 the mineralization features described here, follow the same scheme.

7

8 **Keywords:** Alkaline complex, carbonatite, syn-tectonic magmatism, stable isotopes,
9 Neoproterozoic, mineralization

10

11 **1. Introduction**

12 Alkaline massifs are composite magmatic intrusions. They are commonly enriched in
13 a number of strategic elements, among which Rare Earth Elements (REE) and High Field
14 Strength Elements (HFSE) (Chakmouradian, 2006; Pell, 1996; Mitchell, 2014; Wall and
15 Mariano, 1996). Magmatic processes may lead to economic concentrations of these metals
16 (Chakhmouradian, 2006; Chakhmouradian and Zaitsev, 2012; Wyllie et al., 1996). In
17 addition, fluid-rock interaction at the time of emplacement can also account for high metal
18 concentrations in veins or metasomatic rocks (Gieré, 1996; Williams-Jones et al., 2012). The
19 source of fluids involved is variable from purely magmatic (fluids exsolved from melts
20 predominantly at late stages) to metamorphic (fluids released by dehydration decarbonation
21 of country rocks). Surface-derived fluids (of marine or continental origin) may be introduced
22 in the systems, especially if emplacement occurred at shallow depth..

23 As a general rule, alkaline massifs display a magmatic zonation at the scale of the
24 pluton, with, from the edge to the centre, saturated series (granites and syenites),

1 undersaturated series (foidal syenites, ijolites) and often a carbonatite body (e.g., Platt, 1996).
2 Because the emplacement of these massifs is commonly atectonic, i.e. they emplace in areas
3 devoid of regional deformation, their cartographic contour and the contact between the
4 magmatic units are generally circular (e.g. Andersson et al., 2013; Bonin and Giret, 1985;
5 Bowden, 1985).

6 The Upper Ruvubu Alkaline Plutonic Complex (URAPC, Burundi) displays a
7 classical magmatic assemblage but can be distinguished from other alkaline massifs by two
8 geometric features: its outstanding dimensions (~25x10 km) and its elliptic map contour
9 (Tack et al., 1984; Midende et al., 2014). Here we argue that these characteristics relate to the
10 syntectonic emplacement of the URAPC, which was accommodated by the development of
11 large shear zones, in the overall extensional tectonic regime occurring at that time in Central
12 Africa and related to the Rodinia breakup (Burke et al., 2003; Hanson, 2003; Tack et al.,
13 1996).

14 In this paper, together with structural description, we provide (1) a petrographic study
15 of the Matongo carbonatite samples, including those showing evidences of fluid-rock
16 interaction (with the occurrence of calcitic veins), (2) in situ geochemical analysis of the
17 mineral phases representative of the alteration and mineralization events, using electron
18 microprobe and laser ablation LA-ICP-MS (REE signatures) and (3) C and O isotope
19 compositions of these mineral phases as well as of the Matongo primary carbonatites. We
20 show that the Matongo carbonatite experienced interaction with fluids of variable origins,
21 focused in shear zones on a kilometeric scale, which resulted in the mobility of elements, some
22 of which possibly leading to economic concentrations. More precisely, this paper will focus
23 (1) on exceptional mineralization features, i.e. several cm-wide zircon and ilmenite
24 megacrysts (HFSE enriched), which are hosted within a kaolinite deposit (and the overlying
25 laterite) in the vicinity of the Matongo carbonatite, and (2) on REE mineral occurrences

1 found in association with carbonatitic dykes, at ~3-4 km to the north of the Matongo
2 carbonatite. Besides, the URAPC also hosts economic phosphate deposits (occurring at the
3 top of the Matongo carbonatite), of which the reserves were estimated at 40 Mt, with an
4 average grade of 4.6% P₂O₅, and with 17.3 Mt of richer ore averaging 11% P₂O₅ (considering
5 a cut-off grade at 5% and 1.5 m of minimum thickness; Notholt, 1999, in DFID report 2002).
6 Moreover, at the scale of the massif, pyrochlore showings have been recognized in the
7 feldspathoidal syenite (that constitutes the undersaturated series), and large idiomorphic
8 crystals of monazite - up to 2 cm have been found in alluvial deposits of the Tshogo area
9 **(Fig. 1A)**.

10

11 **2. Geological setting**

12 The Neoproterozoic URAPC is located along the western branch of the East African
13 Rift in Burundi. It is emplaced in Mesoproterozoic metasedimentary rocks (Akanyaru
14 Supergroup) of the Karagwe-Ankole Belt (KAB; Fernandez-Alonso et al., 2012). Three
15 generations of granite intrude the rocks of the Akanyaru Supergroup, respectively at ~ 1375
16 Ma, ~1205 Ma and ~ 986 Ma (Tack et al., 2010).

17 At ~750 Ma, about twenty alkaline plutons – including the URAPC - were emplaced
18 along lithosphere-scale shear zones, located on both sides of the present-day Western Rift
19 (Tack et al., 1996). They seem to reflect uprise of mantle-derived magmas along lithospheric
20 weakness zones in relation with the breakup of Rodinia (Burke et al., 2003; Hanson, 2003;
21 Kampunzu et al., 1997; Tack et al., 1984, 1996). In such scheme, the URAPC corresponds to
22 one of the last episodes of the magmatic activity associated with Rodinia breakup, before the
23 “renewal” of alkaline/carbonatitic activity during the Cretaceous in Central Africa (e.g.,

1 Chilwa in Malawi; Simonetti and Bell, 1994), in relation with the development of the East
2 African rift system (Midende et al., 2014).

3 The URAPC is made up of two major bodies (units) of silicate rocks and one
4 subsurface carbonatite body, with a lens shape, the Matongo carbonatite (**Fig. 1A**). The NW-
5 SE elongated “outer unit” of the URAPC comprises an intimate association of saturated
6 plutonic rocks, ranging in composition from olivine-bearing gabbro and diorite to granite and
7 quartz syenite. The N-S trending ellipsoidal inner unit cross-cuts the contact between the
8 outer unit and the country rocks (**Fig. 1A**), and thus emplaced (even slightly) after the outer
9 unit. It is mostly composed of feldspathoidal syenite. Numerous dykes of feldspathoidal
10 syenite intrude the “outer unit”, especially in its western part (where they are oriented N40).
11 In the central part of the URAPC, the Matongo carbonatite has been recognized by drilling. A
12 phosphate-rich horizon caps the carbonatite (Kurtanjek and Tandy, 1989). The Matongo
13 carbonatite has a lens shape with a long axis roughly oriented N10°.

14 For the “outer magmatic unit”, U-Pb on zircon fraction and zircon Pb-evaporation
15 ages at 748 ± 2 Ma and 741 ± 2 Ma respectively (Tack et al., 1995) have been obtained. Rb-
16 Sr whole rock isochron on the same unit yielded an age of 707 ± 17 Ma (Tack et al., 1984).
17 This age is, within uncertainty, undistinguishable from the Rb-Sr isochron age of the “inner
18 magmatic unit” (699 ± 13 Ma; Tack et al., 1984) and with the Pb-Pb isochron of the
19 carbonatite body (690 ± 32 Ma; Demaiffe, 2008). U-Pb on bulk zircon on the “inner unit” of
20 the URAPC however gave an age of 739 ± 7 Ma (Tack et al., 1984).

21 Obviously, there are important age discrepancies (30-40 Ma) relating the
22 emplacement of the URAPC. The data presented in this paper support a syntectonic
23 emplacement of the URAPC massif, what is hardly compatible with a ~30 Ma time span.
24 Most of the ages obtained on the URAPC are seemingly not accurate and do not allow to
25 interpret properly the magmatic history of the complex in terms of timing. Nevertheless, a

1 LA-ICP-MS U-Pb age on the zircon megacrysts, at 705.5 ± 4.5 Ma (obtained by Midende et
2 al., 2014; see below), constitutes a reliable milestone for the URAPC emplacement.

3 The Sr and Nd isotope compositions obtained on the Matongo carbonatites, fenites
4 ($^{87}\text{Sr}/^{86}\text{Sr}$: 0.7028 - 0.7040, initial eNd values: +0.2 - +5.2; Demaiffe, 2008) and a few rocks
5 from the inner and outer units (with initial eNd values varying between $+1.7 \pm 1$ and $+2.3 \pm$
6 1.5, and initial $^{87}\text{Sr}/^{86}\text{Sr}$ comprised between 0.7025 and 0.7030; Tack et al., 1984) point to a
7 cogenetic relation between the Matongo carbonatite and the URAPC feldspathoidal syenites
8 (Tack et al., 1984). They also strongly support a mantle origin for the parental magma of the
9 URAPC rocks (mantle source intermediate between the DM and the EM I and II; Demaiffe,
10 2008), without any evidence for significant assimilation of crustal material (Tack et al.,
11 1984). Further studies are however needed to reinterpret the genetic history of this complex
12 massif. About 3.5 km to the north of the carbonatite body, carbonatitic dykes (overprinted by
13 a hydrothermal event) made up of calcite, apatite and biotite cut across the deformed
14 feldspathoidal syenite body, and are supposed to be linked to the main carbonatite body
15 (Tack et al., 1984). This suggests that the carbonatitic activity is terminal compared to syenite
16 emplacement in the building of the URAPC massif.

17 In addition, in the Inamvumvu area (located between the subsurface carbonatite body
18 and the carbonatitic dykes (**Fig. 1B**), numerous megacrysts of idiomorphic zircon (up to 6
19 cm) and tabular ilmenite (up to 10 cm) are disseminated in a lateritic crust and kaolinized
20 zones developed on the quartz syenite. The zircon megacrysts are thought to result from the
21 circulation of alkaline pegmatitic fluids associated with the emplacement of the carbonatite-
22 feldspathoidal syenite (Fransolet and Tack, 1992). Trenching during carbonatite exploration
23 works in the 1980s (British Sulphur Company, unpublished internal report), exposed zircon
24 megacrysts in “pegmatitic-like” dyklets intruding supergene weathered rock with preserved
25 original coarse-grained “granitic” texture (Nkurikiye, 1989; Tack, unpublished data). These

1 zircon crystals have been dated at 705.5 ± 4.5 Ma (U–Pb concordant age, Midende et al.,
2 2014) and can be related to the carbonatite late magmatic or magmato-hydrothermal
3 evolution. Indeed, the ubiquitous primary calcite, magnesian calcite, and nahcolite inclusions
4 present in these zircon megacrysts (Burke, 1998) argue for the carbonatitic affinity of these
5 minerals (Fransolet and Tack, 1992).

6

7 **3. Sampling and analytical techniques**

8 Several types of samples have been studied. Whole rocks carbonatite (21 samples)
9 were collected in the 1980ies's by Tack and stored at the Royal Museum for Central Africa
10 (RMCA), Tervuren (Belgium). Five other samples were collected in the carbonatitic dyke
11 zone (RG 144739, RG 144742, RG 144748, RG 144751 and RG 144752). An additional
12 sample was collected in the field in February 2014. Five drill cores (MAT 1 to 5) from the
13 Matongo carbonatite body were selected among 9 drill cores (56 to 291 m depth) obtained
14 from an exploration campaign (British Sulphur) in the 1980's. These cores come from the
15 rock collection of the RMCA, Tervuren. Boreholes for the 10 drill cores (S1 to S8, and ITS 3,
16 4 and 5) are localized on Figure 1B. Two zircon (Zr1 and Zr2) and ilmenite (Ilm1 and Ilm 2)
17 megacrysts were collected in the Inamvumvu kaolin quarry and in the Inamvumvu laterite.

18 The petrographic description is based on optical microscopy and scanning electron
19 microscopy (SEM) with energy-dispersive spectroscopy (EDS). Cathodoluminescence (CL)
20 was performed at the University of Mons (Belgium) using a cold-cathode CL unit model Mk5
21 operated at 15 kV beam voltage and 500 μ A current (Cambridge Image Technology
22 Limited). CL spectra were recorded with a CITL optical spectrometer model COS8200
23 allowing acquisition from 380 to 1100 nm at 3.7 nm resolution. SEM-CL micrographs and
24 spectra were acquired with a cooled-CCD camera and a spectrometer mounted on the optical

1 block of a Cameca SX51 Electron Probe Micro-Analyzer (EPMA) operated at 15 kV and 20
2 nA.

3 Mineral compositions were measured by EPMA at University of Mons and by LA-
4 ICP-MS at the RMCA, Tervuren. Quantitative mineral EPMA analyses were acquired using a
5 Cameca SX51 electron microprobe operated at 15 kV and 20 nA (**Tables 1-6 in**
6 **supplementary material**). This microprobe is equipped with four wavelength-dispersive
7 (WDS) spectrometers and standard LiF, PET, TAP and PCs crystals. The laser ablation ICP-
8 MS measurements (**Tables 2-7 in supplementary material**) were performed at the RMCA,
9 Tervuren. A New-Wave UP-193 FX fast excimer (193nm) laser coupled with a Thermo
10 Scientific X-Series2 quadrupole ICP-MS was used. The laser was run at 50 Hz and a fluence
11 of 10 J/cm² for 100 µm or 30 µm spot size. He gas at a flow rate of 0.65 l/min was flushed
12 into the ablation cell and was mixed after the cell with Ar carrier gas at a flow rate of 0.76
13 l/min. Several internal standards have been used for correcting instrumental drift and ablation
14 rate, depending on the analysed mineral phases: ⁴³Ca for carbonates and fluorapatite, ²⁹Si for
15 zircon, ⁴⁷Ti for ilmenite and ¹⁴⁰Ce for monazite and ancylite-(Ce). The NIST SRM 614, 612
16 and 610 were used as external standards and were measured frequently during the course of
17 the analyses. The precision at 1 sigma level on the NIST SRM 612 is ~ 10% RSD. The
18 ablation patterns were smooth, except for ilmenite that contains inclusions.

19 The C and O isotope compositions (**Table 8 in supplementary material**) have been
20 obtained at the University of Rennes 1 (France) and at the University of Lausanne
21 (Switzerland). At Rennes, the oxygen isotope compositions of silicates and oxides were
22 obtained by the conventional fluorination method (after Clayton and Mayeda, 1963).
23 Representative samples of large populations of zircon and ilmenite megacrysts were selected,
24 cleaned, washed and crushed into a fine-grained powder. O isotope values thus correspond to
25 whole grains compositions. The powder was reacted with BrF₅ at 680 – 700°C for 12 hours

1 and the liberated O₂ converted into CO₂ by reaction with hot graphite. C and O isotope
2 compositions of carbonates were measured on whole rocks powders (21 samples of
3 carbonatite) and on powders recovered by micro-drilling on drilled cores (micro-drillings are
4 shown by red lines in Fig. 4). Carbonate powders were reacted with anhydrous
5 orthophosphoric acid in vessels at 50°C. CO₂ isotope compositions were measured on a VG
6 SIRA 10 triple collector mass spectrometer. The analytical uncertainty is ±0.2‰ for O in
7 silicates, oxides and carbonates, and ±0.1‰ for C in carbonates; it was estimated using
8 replicate analysis of some samples and reproducibility of standards, both international (NBS
9 28 and NBS 19) and in-house (Prolabo Rennes and A1113) standards. At Lausanne, the C
10 and O isotope composition of the carbonates (20 to 40 mg of rock powder) was there
11 measured with a GasBench II connected to a Finnigan MAT DeltaPlus XL mass
12 spectrometer, using a He- carrier gas system according to a method adapted after Spoetl and
13 Vennemann (2003). Sample values were normalized using an in-house Carrara Marble
14 standard calibrated against V_{PDB} for both carbon and oxygen isotope compositions and
15 recalculated to the V_{SMOW} scale for δ¹⁸O values of carbonates standard calibrated against δ¹³C
16 and δ¹⁸O values of NBS-19 (+1.95‰ and 2.20‰, relative to Vienna Pee Dee Belemnite
17 (VPDB)). External reproducibility estimated from replicate analyses of the in-house standard
18 (n=11) is ±0.1 ‰ for both δ¹³C and δ¹⁸O.

19

20 **4. Structure of the URAPC**

21 The Upper Ruvubu Alkaline Plutonic Complex (URAPC) defines an elliptic map
22 contour, with a long axis oriented NW-SE. This shape corresponds actually to the outer unit,
23 the inner unit being more N-S orientated. The Matongo carbonatite is located at the contact
24 between the inner unit and the host metasediments that form a N-S to N10° indentation on the

1 eastern edge of the carbonatite (**Fig. 1**). The carbonatite body itself has an elliptic shape, with
2 a long axis oriented N10°.

3 The regional foliation is globally vertical. It is overall parallel to the long axis of the
4 elliptic-shaped outer unit, striking NW-SE along the south-western edge of the Massif.
5 Within the URAPC, the foliation of the outer unit is parallel to the regional foliation. This is
6 also the case for the inner unit but solely in the southern part (south of Kiziba, **Fig. 1A**). In
7 the northern part of the inner unit, foliation planes display a curved pattern, parallel to the
8 external contact.

9 To the south, close to the Matongo carbonatite, the intrusion is hidden by
10 metasediments that form a N-S to N10° elongated cartographic shape. The intrusive contact
11 between metasediments and the Buraniro Granite (**Fig. 2A**, location on **Fig. 1A**) is well
12 exposed on the field. It is marked by a strain gradient in the granite, with undeformed granite
13 about 100m away from the contact, remarkable C/S fabrics 20 m away from the contact (both
14 shear and foliation planes are vertical) and mylonitic fabrics at the contact. The stretching
15 lineation is plunging to the north, between 30° in the C/S structure facies to vertical in the
16 mylonite. Kinematics criteria point to a dextral component in the horizontal plane (**Fig. 2A**,
17 second photo) and sagging of the metasedimentary block (**Fig. 2B**, third photo). In the
18 metasediments close to the contact, sediment layering is parallel to the foliation which is
19 vertical and parallel to the contact. The stretching lineation, marked notably by andalusite
20 grains (**Fig. 2B**), is vertical. At 300 m westward within the metasedimentary unit, foliation is
21 oblique to sediment layering. From these structural and metamorphic features, we infer that
22 the contact between sediments and the outer unit is a large zone of deformation that was
23 active during magmatic emplacement.

24 Other areas of high strain zones have been observed in the field, and are indicated in
25 **Fig. 1A** together with the sense of shear in the horizontal plane. In the deformed zones, which

1 commonly display a mylonitic fabric, the stretching lineation constantly plunges towards the
2 north at about 30° , reaching locally a vertical dip locally similar to that observed at the
3 intrusive contact. These deformed zones are mostly present in the outer unit and locally in the
4 eastern part of the inner unit, north and north-east of Kiziba. In the outer unit, along the road
5 between Matongo and Kayanza, a strong kaolinization of quartz syenite has developed in the
6 mylonitic zones.

7 In the north-western part of the outer unit, numerous meter-large dykes outcrop in the
8 host metasediments; they are oriented $N30^\circ$ to $N50^\circ$. One of these dykes is folded with nearly
9 vertical fold axes. The internal schistosity of the dyke defines a fan-like pattern (**Fig. 2C**)
10 around the general NW-SE direction.

11

12 **5. Evidence for fluid-rock interactions in the URAPC**

13 5.1. Field observations

14 Besides the variety of magmatic rocks occurring in the URAPC, the massif comprises
15 several features testifying for magmato-hydrothermal fluid circulations.

16 In the south-western part of the outer unit, north-east of Buraniro, a large quartz vein
17 outcrops. It is oriented $N40^\circ$ and is at least 100 m long and about 20 meters wide. Quartz
18 grains within the vein are fractured but no particular fractures orientation or fabrics can be
19 measured. About 6km NE of Matongo, quartz blocks disseminated by the local population
20 along the roads for building purpose, display a remarkable deformation with hematite crystals
21 growing along shear planes during deformation (**Figs. 3A,B**). The two types of quartz veins
22 formed syn-tectonically, and display a geometric and genetic affinity with the silica-saturated
23 outer unit.

1 Albite veins (**Fig. 3C**) and carbonatitic dykes, overprinted by a hydrothermal
2 alteration, are present at about 3.5 km north of the Matongo carbonatite body, in the
3 feldspathoidal syenite (**Fig. 1B**). They are usually present as pluridecimeteric to metric lenses
4 (**Figs. 3D, E**). They are hosted in highly deformed feldspathoidal syenite and have an
5 orientation roughly perpendicular to the foliation and the stretching lineation in the syenite.
6 Thus, they can be interpreted as tension gashes. The host feldspathoidal syenite is locally Na-
7 fenitized (transformation of nepheline into albite; as shown in Drüppel et al., 2005) and
8 brecciated close to the carbonatite injections. The carbonatitic dykes, which are cm- to dm-
9 large, contain variable amounts of angular to sub-rounded clasts, which gives a breccia
10 texture to the dykes. They are whitish or pinkish in color and predominantly made up of Na-
11 fenitized wall-rock (**Fig. 3E**). The dyke matrix predominantly comprises carbonates, biotite,
12 albite and Fe-sulfides (pyrite and pyrrhotite).

13 In the vicinity of the carbonatitic dykes (**Fig. 1B**), pegmatoid dykes made up of
14 nepheline, sodalite and cancrinite are located within deformed zones of the feldspathoidal
15 syenite. These pegmatoidic dykes correspond also to tension gashes in the zones of high
16 strain (**Fig. 3F**). Similar mineral assemblage (with Ti-magnetite) is present in mylonitic zones
17 located within the nearby quartz syenite as infillings of en-echelon sigmoidal tension gashes
18 (up to 30cm in length, **Fig. 3H**). These dykes/veins point to fluid circulation during both
19 magmatism (they have a clear genetic affinity with the under-saturated inner unit considering
20 the similar mineral assemblage) and deformation (they occur as tension gashes within zones
21 of high strain). Finally, the zircon and ilmenite megacrysts (**Figs. 3I-K**), which occur in
22 “pegmatitic-like” veinlets/dycklets crosscutting the quartz syenite also testify for magmato-
23 hydrothermal circulations. The strong development of kaolinization (mostly due to the
24 transformation of orthoclase: $3\text{KAlSi}_3\text{O}_8 + 2\text{H}^+ = 3\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{K}^+$; Manning, 1995) is
25 documented in mylonitic zones. This is consistent with mineralogical criteria that point to an

1 initial kaolinite crystallization under hydrothermal conditions (Nkurikiye, 1989), even though
2 such an early kaolinization can be debated. At the least, the present kaolinization emphasizes
3 an earlier phase of K-fenitization, with subsequent formation of orthoclase, which is easily
4 transformed into kaolinite later on. Thus, as a whole, regardless of the nature of the magmatic
5 fluid (genetically related to the saturated outer unit, to the under-saturated inner unit or to the
6 carbonatite body), magmato-hydrothermally derived fluid circulation was synchronous to
7 regional deformation.

8 9 5.2. Fluid-rock interactions in the Matongo carbonatite

10 The petrographic and mineralogical characteristics of the different facies of the
11 Matongo carbonatite body have been described by Midende et al. (2014). Coarse- and fine-
12 grained calciocarbonatite (sövite I and II, respectively), which contains vanadiferous aegirine
13 (partly transformed in amphibole) and apatite in various amounts (up to cumulates), and
14 ferrocarnatite have been identified. Calcite veinlets that crosscut the coarse-grained altered
15 calciocarbonatite have been interpreted as representing a late hydrothermal event, compared
16 to the magmatic activity (Midende, 1984; Midende et al., 2014). K-fenitization, resulting in
17 the transformation of the host rock in a dominant K-feldspar and biotite mineral assemblage,
18 is also well developed in the external part of the carbonatite (Midende, 1984).

19 In the studied drill-cores, a dense network of calcite veins is visible (**Fig. 4**). These
20 veins are variable in colour, from clear white to grey. They are mostly calcitic, but locally
21 iron oxides and euhedral dolomite crystals are present (see bottom of the large white vein in
22 core MAT 3, **Fig. 4**). The veins draw complex cross-cutting relationships (e.g. core MAT 1a,
23 **Fig. 4**), which attests of superposed fluid activities under brittle conditions. Interestingly, core

1 MAT 3 displays a well-defined foliation that results from ductile deformation of the
2 carbonatite. On the contrary, magmatic fabric is visible in core MAT 2 (**Fig. 4**).

3

4 6. Petrographic and mineralogical description

5 6.1. Carbonatitic dykes and breccia

6 In the carbonatitic dykes, the matrix predominantly comprises carbonates (generally
7 as euhedral crystal aggregates, described below), biotite (as laths up to 1cm in length),
8 euhedral albite crystals (up to 2 mm in size) and Fe-sulfides (pyrite and pyrrhotite). These
9 dykes are locally brecciated and contain clasts of more or less deeply metazomatized
10 (=finitized) former feldspathoidal syenite. A detailed description of the most finitized clasts
11 and of the complex breccia matrix in which they are embedded is given below.

12 6.1.1. Clasts

13 The most finitized clasts consist mainly of albite, variably invaded by carbonates. Albite
14 grains present fine- to coarse-grained textures (with euhedral crystals up to 500 μm) and are
15 locally cloudy (slightly silicified, **Fig. 5A**). Euhedral laths of Ba-rich muscovite (1.3-2 %
16 BaO, **Table 1**) are present as tiny veins (from 100 μm to 3 mm width) crosscutting the clasts
17 (**Figs. 5A, B**). These veins are commonly surrounded by a Fe oxide-rich halo. Muscovite also
18 replaces biotite (with the following reaction: $\text{KMg}_3(\text{AlSi}_3\text{O}_{10}) (\text{OH})_2 + 2 \text{Al}^{3+} =$
19 $\text{KAl}_2(\text{AlSi}_3\text{O}_{10}) (\text{OH})_2 + 3\text{Mg}^{2+}$; Stoch and Sikora, 1976), with a Ba-rich biotite (1.3 % BaO,
20 **Table 1**) as an intermediate product (**Fig. 5C**). In the clasts, biotite laths (up to 200 μm in
21 length) occur as complex aggregates interstitial between albite and a Fe-Mn-rich calcite,
22 named calcite 1 hereafter. Biotite is frequently associated with (1) ilmenite and rutile
23 intergrowths (**Fig. 5C**), (2) euhedral zoned and blue-luminescing fluorapatite (typically
24 several hundreds of μm in section; **Fig. 5D**), (3) euhedral, blue-green luminescing zircons

1 (from several μm to 1 mm in size), slightly enriched in Hf, Ta, Th and U (**Table 5**), and (4)
2 small (up to several μm in size) betafite grains. The CL of apatite is activated mainly by the
3 LREE Sm^{3+} , Nd^{3+} and Eu^{2+} together with Mn^{2+} (Kempe and Götze, 2002; Waychunas, 2002).
4 Ilmenite and zircon are also found as isolated crystals in the clasts. Small barite aggregates
5 (up to a few tens of μm in size) and euhedral pyrite crystals (up to 1 mm in section) are
6 observed in the most fenitized clasts.

7 *6.1.2. Matrix*

8 The matrix of the carbonatitic dykes predominantly consists of microgranular (up to
9 several mm in size) calcite 1 (2-2.4 % FeO; **Table 2**) with minor ferroan dolomite (27.5 %
10 CaO, 13.3 % FeO, 11.2 % MgO, **Table 2**). The calcite 1 is partly replaced by a nearly pure
11 calcite - named calcite 2 hereafter (see analyses **Table 2**) - associated with μm -wide
12 strontianite grains. This replacement is particularly well highlighted by CL images (**Fig. 5D**):
13 orange calcite 2 replaces a dull-luminescent calcite 1 at the edges of the crystals and along
14 cleavages. Calcite 1 and ferroan dolomite are intimately associated with subhedral crystals of
15 albite (up to 1 mm), which is pink/red under CL (**Fig. 5D**). The dominant red emission is
16 commonly observed in feldspars occurring in fenitized rocks (Marshall, 1988). As in the
17 clasts, biotite lath aggregates (up to several cm in size) seem interstitial between albite and
18 calcite 1. They are also intimately associated with ilmenite and rutile intergrowths, zircon and
19 betafite grains. In the breccia matrix, euhedral and blue-luminescing zoned fluorapatite (**Fig.**
20 **5D**), enriched in Sr (0.3-1.2 % SrO, **Table 2**), apparently formed contemporaneously or
21 slightly later than biotite.

22 *6.1.3. REE-bearing crystals*

23 In the carbonatitic dykes, monazite is the most abundant REE-bearing mineral phase.
24 It typically shows a significant enrichment in Th (ranging from 1.5 to 8.3 % ThO_2 , **Table 3**)

1 and a slight enrichment in Ca, Fe, Sr and F (0.1-0.8 % CaO, up to 0.6 % FeO, up to 1.8 %
2 SrO and 0.5-0.8 % F, **Table 3**). Monazite is usually present either as an interstitial phase
3 between the biotite lath aggregates (**Figs. 5C**), in association with the calcite 1, or as
4 subhedral crystals (up to 150 μm in length) and needle-like crystal aggregates (up to 300 μm
5 in size), replacing albite in the clasts. Under CL, monazite exhibits a weak but distinct deep-
6 blue luminescence (**Fig. 5E**). The matrix of the brecciated dykes also include ancylite-(Ce),
7 which is enriched in Sr, Th, Fe and F, (2.1-19.8 % SrO, 1.4-3.7 % ThO_2 , up to 2.8 % FeO,
8 and 0.6-0.9 % F; **Table 4**). Such enrichments have been documented in the carbonatitic
9 complex at Khibini and Sokli (Zaitsev et al., 1998; Al Ani and Sarapää, 2009). In the studied
10 carbonatitic breccias, this mineral phase is present as euhedral or subhedral crystals (several
11 tens of μm in length) or needle-like crystal aggregates, commonly in association with calcite
12 2 (**Fig. 5F**) and strontianite. Ancylite-(Ce) replaces albite and mucovite in the clasts (**Fig. 5B**)
13 or occurs as interstitial phase of the biotite aggregates (**Fig. 5G**).

14

15 6.2. Matongo carbonatite drill cores

16 The calcite veins that form the dense network observed in the drill cores (**Fig. 4**)
17 mostly comprise orange-luminescing calcite (**Fig. 6A-C**), generally slightly enriched in Mn
18 (mean value of 0.5 % MnO, **Table 2**) even though it can locally show a moderate enrichment
19 in Mn, Fe or Sr (up to 2.1 % MnO, 1.2 % FeO, and 0.8 % SrO). Red-luminescing dolomite
20 (**Fig. 6B, D**), K-feldspar, albite and fluorapatite are accessory minerals commonly associated
21 with calcite in the drill core veins.

22 In the MAT 3 core, affected by ductile deformation (**Fig. 6c**), fluorapatite occurs as
23 subhedral/ovoid crystals (several tens of hundreds μm in size) aligned parallel to the
24 mylonitic foliation marked by carbonate twins. Under CL, a light blue rim of fluorapatite is

1 visible around the deep-blue fluorapatite cores and develops especially on the crystal faces
2 perpendicular to the foliation. This feature indicates that the apatite overgrowth formed
3 during ductile deformation and being developed in pressure-shadow around fluorapatite
4 crystals. Locally, some apatite crystals embedded in the mylonitic carbonates are fractured, a
5 qualitative record of the large intensity of the deformation during the ductile to brittle
6 deformation.

7

8 6.3. HFSE mineralization – Zircon and ilmenite megacrysts

9 Megacrysts of zircon (a few mm up to six cm) exhibit growth zoning that relates to
10 the variation of Th content (up to 0.6 % ThO, **Table 5**). Zircon is also slightly enriched in Hf
11 (ranging from 0.4 to 0.8 % HfO₂, **Table 5**) with very little (if any) enrichment in U (up to 0.1
12 % UO₂, **Table 5**).

13 Ilmenite is generally well crystallized with tabular shape and can be several cm wide.
14 The ilmenite from the Inamvumvu kaolin quarry is commonly weathered and pervasively
15 replaced by iron oxides/hydroxides associated to pseudorutile/leucoxene, what is usually
16 observed in case of supergene alteration (Grey and Reid, 1975; Pownceby, 2010). This
17 explains its high Ti (53.6-74.9 % TiO₂; **Table 6**) and low Fe and Mn contents (17.1-36.3 %
18 FeO, 0.1-0.6 % MnO, **Table 6**) compared to the ilmenite megacrysts from the laterite (35.5-
19 49.9 % FeO, 43-53.1 % TiO₂, 0.1-1.3 % MnO; **Table 6**). The Nb content varies from ~450 to
20 ~2000 ppm (**Table 6**) and seems independent of the ilmenite weathering degree.

21

22 7. REE characteristics

23 7.1. Minerals from the carbonatitic dykes

1 Regarding the REE contents (LA-ICP-MS data, see Supplementary material), the
2 carbonates (calcites 1 and 2) from the carbonatitic dykes are significantly different from the
3 whole rock carbonatite facies from the main intrusion (**Fig. 7A**). Despite an overall
4 enrichment in REE (ΣREE from 326 up to 830 ppm) and a moderate LREE enrichment ($3 <$
5 $\text{La}_\text{N}/\text{Yb}_\text{N} < 5$), the calcite from the breccia exhibits variable MREE depletion (**Fig. 7A**), with
6 no significant Ce anomaly ($0.8 < \text{Ce}/\text{Ce}^* < 1.1$) and a slight positive Eu anomaly ($1.1 <$
7 $\text{Eu}/\text{Eu}^* < 1.5$). The calcite representative of sample RG 144.739 is obviously less MREE-
8 depleted than those of sample RG 144.752 (**Table. 2**). The most MREE depleted calcite
9 patterns seem to mirror (or present opposite patterns) the one of the “late” hydrothermal
10 calcite.

11 Fluorapatite is strongly enriched in REEs (ΣREE from 7300 up to 11375 ppm, **Table**
12 **2, Fig. 7A**), with high $\text{La}_\text{N}/\text{Yb}_\text{N}$ ratios, ranging from 20 to 54, and neither significant Ce nor
13 Eu anomalies ($0.9 < \text{Ce}/\text{Ce}^* < 1.2$, $1 < \text{Eu}/\text{Eu}^* < 1.1$).

14 Monazite grains from the carbonatitic breccias (**Fig. 7B**) are characterized by a very
15 strong REE enrichment ($49.5 < \Sigma\text{REE} < 61.8$ %, with an extreme $\text{La}_\text{N}/\text{Yb}_\text{N}$ ratio, up to
16 107000 (**Table 3**). Their patterns present moderate Ce and Eu anomalies ($0.6 < \text{Ce}/\text{Ce}^* < 0.9$,
17 $0.6 < \text{Eu}/\text{Eu}^* < 0.8$). Ancylyte-(Ce) is also enriched in REE (ΣREE ranges from 35.4 to 39.6
18 %; **Table 4**), especially in LREEs (**Fig. 7B**) but the fractionation varies largely ($1203 <$
19 $\text{La}_\text{N}/\text{Yb}_\text{N} < 33029$), from grain to grain. They do not exhibit large Ce and Eu ($0.7 < \text{Ce}/\text{Ce}^* <$
20 1 , $0.5 < \text{Eu}/\text{Eu}^* < 0.8$) anomalies.

21

22 7.2. Veins from the drill cores

23 The REE data obtained on the calcite of the veins (**Figs 7C-E**) are compared to the
24 patterns of several fluorapatite and host calciocarbonatite (**Fig. 7E**).

1 It appears that calcite from a single drill core can exhibit highly variable REE
2 signatures from grain to grain. In the MAT 1 drill core, a first calcite type (type 1 in **Fig. 7C**)
3 presents a LREE enrichment ($5 < La_N/Yb_N < 37$; **Table 7**), while a second type (type 2 in
4 **Fig. 7C**) is characterized by concave-upward pattern, with La_N/Yb_N ratios varying from 0.8
5 to 5. Both calcite types display comparable and low total REE contents (1-86 ppm for type 1,
6 3-77 ppm for type 2), with negative Ce and positive Eu anomalies ($0.2 < Ce/Ce^* < 1$, $2.8 <$
7 $Eu/Eu^* < 4.4$, **Table 7**). Similarly, in the MAT 2 drill core, two calcite types can be
8 distinguished. Type 1 (**Fig. 7D**) is depleted in REE ($1 < \Sigma REE < 9$), mostly in LREE
9 (La_N/Yb_N ratios ranging from 0.1 to 0.5), while type 2 (**Fig. 7D**) is characterized by MREE
10 enriched/HREE depleted patterns ($1.2 < La_N/Yb_N < 68.2$). Both types display negative Ce
11 anomalies (Ce/Ce^* from 0.1 to 1) and positive Eu anomalies ($3.4 < Eu/Eu^* < 5.1$, **Table 7**).
12 In the MAT 3 drill core, only one pure calcite has been analyzed (**Fig. 7E**). It presents a
13 LREE-rich and MREE-depleted (concave-upward) pattern ($\Sigma REE = 144$ ppm, $La_N/Yb_N =$
14 22.2), with negative Ce and positive Eu anomalies ($Ce/Ce^* = 0.7$, $Eu/Eu^* = 2.6$, **Table 7**). On
15 the contrary, fluorapatite from the same vein is enriched in REE ($4011 < \Sigma REE < 5996$ ppm,
16 $90 < La_N/Yb_N < 137$), with negative Ce ($Ce/Ce^* = 0.9$) and positive Eu anomalies (Eu/Eu^*
17 ranging from 3 to 3.2, **Table 7**).

18 Calcite from the host calciocarbonatite does not present the strong enrichment in
19 LREE (ΣREE from 17 up to 122 ppm, $1 < La_N/Yb_N < 9$) that is common for primary
20 carbonatites (e.g., Pell, 1996) (**Fig. 7E**). It shows variable Ce anomalies ($0.2 < Ce/Ce^* < 2.2$)
21 and positive Eu anomalies ranging from 3.2 to 4.4 (**Table 7**).

22

23 7.3. Zircon and ilmenite megacrysts from Inamvumvu

1 The REE patterns of the zircon megacrysts show HREE enrichment ($\text{La}_N/\text{Yb}_N < 0.01$
2 to 0.08), with a pronounced positive Ce anomaly ($1.3 < \text{Ce}/\text{Ce}^* < 6.7$) and no significant Eu
3 anomaly ($0.6 < \text{Eu}/\text{Eu}^* < 1$). The zircon crystals from the kaolin deposit have significantly
4 higher REE contents (ΣREE from 449 ppm to 1855 ppm, with two exceptions at 41 and 144
5 ppm, **Fig. 7F, Table 5**) than those from the laterite ($39 \text{ ppm} < \Sigma\text{REE} < 706 \text{ ppm}$), but the
6 patterns are quite similar.

7 Ilmenite from the Inamvumvu kaolin quarry is moderately enriched in REE (ΣREE :
8 0.4 to 64 ppm), with a LREE enrichment (**Fig. 7G**, La_N/Yb_N : 3 to 7), positive Ce anomaly
9 ($1.3 < \text{Ce}/\text{Ce}^* < 1.8$) but no significant Eu anomaly ($0.7 < \text{Eu}/\text{Eu}^* < 1.3$). This REE
10 enrichment is seemingly related to the abundance of iron (hydr-)oxide inclusions in this
11 weathered ilmenite. Indeed, the non-weathered ilmenites from the Inamvumvu laterites show
12 significantly lower REE contents (**Fig. 7G**, ΣREE from 0.1 to 2 ppm), with higher La_N/Yb_N
13 ratios (from 1 to 26) (**Table 6**), generally positive Ce anomalies ($0.8 < \text{Ce}/\text{Ce}^* < 7.6$) and
14 variable Eu anomalies ($0.6 < \text{Eu}/\text{Eu}^* < 2.8$).

15

16 8. Stable isotopes

17 8.1. Matongo carbonatite and calcite veins

18 Many of the oxygen and carbon isotope compositions of the various facies of the
19 Matongo carbonatite body (facies described in Midende et al. (2014)) are typical of magmatic
20 carbonatites (“Taylor box”; Taylor et al., 1967; **Fig. 8A**): $\delta^{18}\text{O}$ values are between 7.2 and
21 8.5‰ and $\delta^{13}\text{C}$ values are between -4.7 and -5.4‰, **Table 8**). Nevertheless, several samples
22 show a significant increase of their $\delta^{18}\text{O}$ value, up to 11‰, irrespective of their petrographic
23 nature, but their $\delta^{13}\text{C}$ remain unmodified. The altered coarse-grained sövite (sövite I) is
24 significantly displaced towards higher $\delta^{18}\text{O}$ values (20.3 and 21.0 ‰) with almost unmodified

1 $\delta^{13}\text{C}$ values (-4.8 and -4.0 ‰). The “late” hydrothermal calcite has an extreme $\delta^{18}\text{O}$ value of
2 21.6‰, with a corresponding higher $\delta^{13}\text{C}$ value of -1.1‰.

3 In the MAT1-5 drill cores (the location of micro-sampling is indicated by purple lines
4 in **Fig. 4C**), the calciocarbonatite samples have high $\delta^{18}\text{O}$ values, above 16‰, the highest
5 value (close to 25‰) being recorded by mylonitic samples of core 3 (dots 19 and 20 on Fig.
6 3c and Table 8). There is a general tendency in this population to display an increase in $\delta^{13}\text{C}$
7 values together with the $\delta^{18}\text{O}$ values increase.

8 This tendency is clearer for the calcite veins population, which shows an increase in
9 both the $\delta^{18}\text{O}$ values (from 16.3 to 25.3‰) and the $\delta^{13}\text{C}$ values (from -5.5 to 0.22‰). Only
10 three samples (1 calciocarbonatite and 2 calcite veins) significantly plot outside the array and
11 deviate from it by a marked increase in $\delta^{13}\text{C}$ for a given $\delta^{18}\text{O}$ value.

12

13 8.2. Carbonatitic dykes

14 The $\delta^{18}\text{O}$ values of the carbonatitic dykes are between 7.3 and 12.5 ‰, with
15 corresponding $\delta^{13}\text{C}$ values from -5.7 to -5.0‰ (**Table 8**). Some of these values plot in the
16 Taylor primary carbonatite box, while others are somewhat displaced towards higher $\delta^{18}\text{O}$
17 values. Sample RG 144 739, which consists almost exclusively of calcite 1 (early calcite)
18 plots in the Taylor box ($\delta^{18}\text{O} = 9.7\text{‰}$ and $\delta^{13}\text{C} = -5.6\text{‰}$), while sample RG 144 752,
19 comprising the second calcite generation (calcite 2) replacing calcite 1, shows a distinct
20 signature ($\delta^{18}\text{O} = 12.5\text{‰}$ and $\delta^{13}\text{C} = -5.0\text{‰}$)

21

22 8.3. Zircon and ilmenite megacrysts

1 The zircon megacrysts have $\delta^{18}\text{O}$ values between 4.0 and 4.7‰, regardless of their
2 host rock (kaolinite or laterite; **Table 8**). The measured range is slightly below the average
3 value for mantle zircons ($\delta^{18}\text{O}_{\text{Zr}} = 5.3 \pm 0.3\text{‰}$; Valley, 2003). However, it compares well with
4 the theoretical value of zircon in equilibrium with magmatic calcite from the carbonatite
5 ($\delta^{18}\text{O}_{\text{Cal}}$ between 7 and 8‰), which is estimated between 3.6 and 5.7‰ using the calcite-
6 zircon fractionation factor of Zheng, 1993 and a temperature of equilibration between 400
7 and 600°C. This temperature range has been previously used to calculate mineral-fluid
8 oxygen isotope composition for late-stage fluids from hydrothermal veins and pegmatite
9 related to carbonatite-syenite complex (Tamazeght complex, Morocco; Marks et al., 2009).
10 Ilmenite shows more widespread $\delta^{18}\text{O}$ values between -1.5 and -4.3‰, with the lowest value
11 at -4.3‰ obtained in ilmenite from Kaolin and the highest values at -1.5 and -1.7‰ obtained
12 in two grains from the ferriferous laterite (**Table 8**) respectively. The theoretical value of
13 ilmenite in equilibrium at 400-600°C with the carbonatite body ($\delta^{18}\text{O}_{\text{Cal}} = 7$ to 8‰) is
14 between -5.1 and -0.5 ‰ (estimate made using the calcite-H₂O and ilmenite-H₂O
15 fractionation factors of Zheng, 1999 and 1991, respectively).

16

17 **9. Discussion**

18 9.1. Architecture of the URAPC

19 Contrary to most alkaline complexes worldwide, the Upper Ruvubu Alkaline Plutonic
20 Complex has an elliptic map contour. In Central Africa, 23 Neoproterozoic alkaline plutonic
21 massifs are distributed over a distance of 1700 km along the present-day Western Rift (i.e.
22 the western branch of the East African Rift; Tack et al., 1984). Their emplacement in
23 interpreted to reflect ascent of mantle-derived magmas along lithospheric weakness zones in
24 relation with the breakup of Rodinia (Burke et al., 2003; Hanson, 2003; Kampunzu et al.,

1 1997; Tack et al., 1984, 1996). This breakup is recorded at ca. 705 Ma at Matongo by the
2 LA-ICP-MS age of the zircon megacrysts (Midende et al., 2014), even though diachronous
3 reactivation in response to differential intraplate stress related to geodynamic processes
4 invoked by Li et al. (2008) and Eyles (2008) cannot be ruled out.

5 From structural evidence the URAPC was emplaced syntectonically, with NW-SE
6 oriented stretching parallel to the long axis of the elliptical shape - consistent with the NW-SE
7 trending regional foliation - and NE-SW oriented shortening. Numerous zones of high strain
8 where foliation is vertical have been observed in the field, essentially in the outer saturated
9 unit, but also in the inner unit. These zones can be interpreted as shear zones (**Fig. 9**). On the
10 horizontal plane, their kinematics indicates either dextral or sinistral movement (**Fig. 9**). The
11 largest shear zones occur near the centre of the Complex and display dextral kinematics,
12 indicative of shortening in the NE-SW direction. Even if the angle between dextral and
13 sinistral shear zones is relatively low, it is possible that they represent conjugated shear
14 zones. Alternatively, they could represent deformed zones accommodating ballooning of the
15 pluton in a pure shear regime. The schematic cross-section drawn in Figure 9B highlights the
16 vertical displacement associated with the shear zones. This is especially visible for the shear
17 zones limiting the roof pendant of metasediments close to the Matongo carbonatite. This zone
18 thus appears as a graben located near the roof of the Complex. In addition, both contact
19 metamorphism and deformation were synchronous (see section 4), which is a strong
20 argument in favour of a syntectonic emplacement of the URAPC.

21 Magmatic dykes in the north-west region are globally oriented N30°-N50°, as is the
22 large quartz vein, of magmato-hydrothermal affinity that crops out in the south-east region,
23 near Buraniro. Both structures are indicative of a NW-SE oriented stretching, consistent with
24 the NE-SW shortening direction deduced above. The fan-like pattern of the internal foliation

1 observed in one of these dykes (**Fig. 2C**) also pleads for emplacement under a regime of
2 regional deformation.

3 The Matongo carbonatite does not outcrop. Nevertheless, some core samples
4 described in this study show a well-defined foliation of probable mylonitic origin developed
5 at magmatic temperatures. Indeed, the foliation is marked notably by the alignment of apatite
6 grains, some of them being fractured in a carbonated well-recrystallized matrix. We thus
7 propose that the elongated cartographic appearance of the carbonatite is due to its
8 emplacement along a sub-vertical shear zone. As a consequence, if most of the deformation
9 affected the outer unit of the URAPC, the latest stages of carbonatitic magmatism were still
10 syntectonic.

11 The shear zones may have acted as a preferential pathway for the carbonatitic magma
12 ascent. This also is also probably the case for the associated fluids, either coming from the
13 source mantle (as depicted by Nadeau et al., 2014) or from the surface, large permeabilities
14 being maintained in zones of deformation (e.g. Gapais et al., 2014). The fluid-rock
15 interactions observed in the field (see section 5.1) point to a long-lived hydrothermal system
16 initiated during magma emplacement and which survived magmatic activity. The geometry of
17 this system is controlled by the shear zones, which allowed fluids to circulate several
18 kilometres apart from the Matongo carbonatite body. Consequences of element mobility thus
19 occur at a large scale.

20

21 9.2. Origin of the carbonatitic dykes and their relationships with the Matongo carbonatite

22 The carbonatitic dykes of the URAPC show albitized material invaded by carbonates,
23 with fenitized margins at the contact with the deformed host rocks. This type of carbonatite,
24 displaying magmatic injection associated with brecciation and fenitization, occurs worldwide

1 (e.g. Mountain Pass; Castor, 2008). It is particularly abundant in Central and Southern Africa
2 (e.g. carbonatitic system in the Itete and Mbeya Range area, Tanzania; Brown, 1964; in
3 Kirumba, DRC; Denayer, 1966; and at Swartbooisdrift, Namibia; Drüppel et al., 2005).

4 In the URAPC, the invasion of albitized clasts by carbonates suggests that brecciation
5 and fenitization slightly predate carbonatite injection (as testified by the magmatic C and O
6 isotopic signature obtained on several invading carbonates from the carbonatitic
7 breccias/dykes). The early character of fenitization/albitization and brecciation is commonly
8 observed in carbonatitic breccias (e.g. at Mbeya Range, in Tanzania; Brown, 1964; in
9 Tundulu, Malawi; Ngwenya, 1994; and in Mountain Pass, U.S.A.; Castor, 2008).

10 Since the carbonatitic dykes of the URAPC were emplaced in an alkaline silicate
11 complex that also comprises a carbonatite body (Matongo), it is reasonable to consider that
12 both types of magmatic carbonates are related to each other, although significant differences
13 exist between them. The Matongo carbonatite body presents a typical suite from sövite to
14 ferrocarbonatite (Midende et al., 2014), while the carbonatitic dykes are merely characterized
15 by ferrocarbonatite and late calcite. In addition, the two carbonatite occurrences differ in
16 terms of fenitization : (1) a typical K-rich assemblage, comprising K-feldspar and biotite,
17 developed around the carbonatite body in the quartz syenite (Midende et al., 2014). Laterally,
18 this zone evolves, without clear continuity because of the lack of field evidence, towards (2)
19 an area where the carbonatite dykes are associated with Na-fenitisation (albitization). The
20 latter is less developed in the wall-rock than in the xenoliths of the carbonatitic matrix. The
21 presence of a K- and Na- zonation in the metasomatic aureole around carbonatites can be
22 explained by two distinct mechanisms (Le Bas, 1989): (1) the expulsion of different pulses of
23 alkali-rich fluids from the parental carbonatite magma at different depths or (2) the variable
24 Na:K ratio of the parental carbonatite, from which the fluids are expelled. On the other hand,
25 the different Na:K ratios of the different fluid pulses could derive from variation in pressure

1 at which immiscible melts separate or from the evolution of a K-rich carbonatite magma from
2 an original primary Na-rich carbonatitic magma (Le Bas, 1989). Moreover, since the minerals
3 formed during the fenitization process are directly related to the wall-rock minerals (e.g.
4 albite is thought to be the result of the transformation of plagioclase, K-feldspar and
5 nepheline in a feldspathoidal syenite; Drüppel et al., 2005), an additional control of the wall-
6 rocks geochemistry cannot be ruled out. Consistently, the Matongo carbonatite body
7 predominantly intrudes quartz syenites (~ 5.3 wt% K_2O , ~ 4.6 wt% Na_2O), while the
8 carbonatitic dykes are mainly intruding feldspathoidal syenites, which are significantly richer
9 in Na (~ 5.1 wt% K_2O , ~ 8.3 wt% Na_2O).

10 Another notable fact is that the lateral extension of the K-fenitization affecting the
11 quartz syenites is quite large compared to the relative small volume of carbonatite in the
12 URAPC (**Fig. 1A**). This could be the witness of a larger carbonatitic system at-depth, as
13 proposed for the Copperhead albitite in Australia (Rugless and Pirajno, 1996) and at Mbeya
14 Range (Brown, 1964). In that scheme, (1) the Matongo carbonatite body would represent an
15 intermediate-depth intrusion, with typical high-level K-fenitization, which evolved from a
16 deeper Na-rich carbonatitic magma by the fractional crystallization, and (2) the carbonatitic
17 dykes could be the result of the injection of residual magmatic solutions from this body,
18 releasing Na-rich fluids and inducing Na-fenitization.

19

20 9.3. Pervasive alteration of the Matongo carbonatite

21 Most samples from the Matongo carbonatite body (sövites, ferrocarbonatites and
22 fenites) as well as many carbonatitic dykes show oxygen and carbon isotope compositions
23 that are typical of primary, magmatic, carbonatites (Taylor et al., 1967; **Fig. 8A**): the $\delta^{18}O$
24 values are between 7.2 and 8.5‰ (vs. SMOW), the $\delta^{13}C$ values are between -4.7 and -5.4‰

1 (vs. PDB). Several carbonatitic dykes (RG 144739, RG 144742, RG 144748) also have a
2 signature ($7.9 < \delta^{18}\text{O} < 9.75\text{‰}$ and $-5.60 < \delta^{13}\text{C} < -5.52\text{‰}$) close to the magmatic one; the
3 slightly higher $\delta^{18}\text{O}$ values might be the sign of crystallization at a somewhat lower
4 temperature.

5 However, some sövites, ferrocarnatites and fenites show evidence of secondary
6 alteration due to interactions with fluids, as shown by their shift to higher $\delta^{18}\text{O}$ values (trend
7 1 in **Fig. 8A**). This shift is also highlighted in the RG 144751 and RG 144752 carbonatitic
8 dykes s. As a whole, the range of $\delta^{18}\text{O}$ values from typical magmatic values at 7 - 8‰ to the
9 high values (between 20 and 22‰) in the altered samples likely corresponds to varying
10 fluid/rock ratios during hydrothermal alteration. The fact that the $\delta^{13}\text{C}$ values remain rather
11 constant (-4.7 to -5.4 ‰) over the range of $\delta^{18}\text{O}$ values indicates that the involved fluids were
12 H_2O -rich (i.e. CO_2 -poor, $\sim X\text{CO}_2 < 0.05$). The most elevated $\delta^{18}\text{O}$ values are those obtained
13 under infinite fluid/rock ratios, conditions under which the fluid imposes its isotopic
14 signature to the rock. Indeed, it has been shown that under open system conditions fluids
15 buffer rocks when the fluid/rock mass ratio is higher than 2 to 3 (e.g. Boulvais et al., 1998).

16 Interestingly, the samples with the highest $\delta^{18}\text{O}$ values – i.e. the coarse-grained sövite
17 (sövite I) and the “late” hydrothermal calcite (occurring as vein infillings; Midende et al.,
18 2014) – show the most disturbed REE patterns (**Fig. 7A**). In **Figure 8B**, the intra-REE
19 fractionation resulting from the interaction with fluids is expressed by the ratio
20 $(\text{La}_N * \text{Sm}_N) / (\text{Ce}_N * \text{Nd}_N)$, proposed by Irber (1999) to quantify the so-called tetrad effect (Bau,
21 1996). The observed correlation indicates that the oxygen isotope shift and the REE
22 disturbance are likely related to the same fluid-rock interaction. Obviously, REE, if mobile,
23 are much less efficiently transported than ^{18}O in aqueous fluids, so that the first stages of
24 alteration (low fluid/rock ratios) are not accompanied by REE disturbance, contrarily to the
25 most altered stages. The final result on the REE budget is an interne leaching of REEs from

1 the sövite I (as also observed on **Fig. 8C**), showing that carbonatites with uncommon REE
2 patterns are also depleted in REE. In terms of pattern shape, late hydrothermal calcite,
3 occurring as thin veins crosscutting the sövite I, shares common characteristics with the host
4 coarse-grained sövite I. This suggests that the metasomatic fluids that invaded the carbonatite
5 body to form the carbonate veins were able to mobilize and fractionate the REEs. At
6 hydrothermal conditions between 150 and 300°C, one can estimate the origin of the fluid by
7 calculating its $\delta^{18}\text{O}$ value in equilibrium with the most altered samples ($\delta^{18}\text{O} = 20$ to 22‰),
8 provided that the fluid:rock ratio was high enough so that the invading fluid kept its original
9 signature. Using the calcite-H₂O fractionation factor of Zheng (1999), one obtains a wide
10 range of $\delta^{18}\text{O}$ values for the hydrothermal aqueous fluid between 7 and 16‰. These values
11 point to a metamorphic fluid or, more generally, to fluids equilibrated with the surrounding
12 continental crust. More specifically, the high $\delta^{13}\text{C}$ values of the most altered rocks ($\delta^{13}\text{C} = -$
13 4.7 to 0.2‰) suggest the involvement of marine-derived carbon ($\delta^{13}\text{C}$ close to zero), likely
14 incorporated in the hydrothermal fluid through its interaction with carbonated lithologies
15 during its migration in the country rocks around the URAPC. The Mesoproterozoic
16 metasedimentary rocks (Akanyaru Supergroup), in which the URAPC emplaced, is made up
17 of phyllites, graphitic schists, metaquartzites, interbedded metavolcanics and dolomite lenses
18 (Tack et al., 1984, Fernandez et al., 2012). This bedrock constitutes a possible source for
19 metamorphic fluids and interactions with Proterozoic carbonates ($\delta^{13}\text{C}_{\text{PDB Proterozoic marine}}$
20 carbonates: -2 to +10‰; Bell and Simonetti, 2010). The comparable shift in terms of Sr isotope
21 composition (**Fig. 8D**) (DemaiFFE, 2008; see the **Supplementary material**) could also reflect
22 this interaction. Indeed, most of the carbonatites (from the Matongo intrusion and the
23 carbonatitic dykes) display $^{87}\text{Sr}/^{86}\text{Sr}$ ratios comprised between 0.7028 and 0.7064, while the
24 Sr isotopic ratios of the altered sövite I and “late” hydrothermal calcite are significantly
25 higher, ranging from 0.7128 to 0.7142.

1 Compared to this first alteration trend (trend 1 on **Fig. 8A**), the calcite veins occurring
2 in the Matongo carbonatite and host carbonatites sampled in the drill cores MAT1-5 display a
3 second trend (trend 2), which is characterized by an increase in both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values
4 (for $\delta^{18}\text{O}$ values above 16.3‰, **Fig. 8A**). This suggests that the carbonatites were affected by
5 two alteration events recorded by the two trends (1 and 2) in the $\delta^{13}\text{C} - \delta^{18}\text{O}$ diagram.

6 Calcite - that materializes this second alteration event in the drill cores - is
7 characterized by strong variations in terms of REE distribution. Such variations are observed
8 within a same drill core, suggesting that this alteration induced element (REE) mobilization
9 and redistribution, at least at a small scale.

10 11 9.4. General implications for fluid circulations and potential mineralizations in the URAPC

12 This study highlights the intimate association of deformation, magmatic emplacement
13 and hydrothermal activity in the URAPC. These processes have induced element
14 mobilization and reconcentration at the scale of the massif, thanks notably to the large extent
15 of shear zones. Element mobility is recorded for instance by the HFSE-rich megacrysts at
16 Inamvumvu and the REE mineral occurrences in the carbonatitic dykes.

17 The O isotope signatures of the zircon and ilmenite megacrysts from Inamvumvu
18 suggest a high temperature magmato-hydrothermal origin in equilibrium with the carbonatitic
19 reservoir. High-temperature processes are also responsible for REE concentration in the
20 carbonatitic dykes. Indeed, monazite is cogenetic with the early calcite (calcite 1), which has
21 a magmatic signature ($\delta^{18}\text{O} = 9.75\text{‰}$ and $\delta^{13}\text{C} = -5.60\text{‰}$ in sample RG 144739). This
22 suggests that primary monazite has a late magmatic origin. Evidence of primary monazite in
23 carbonatites has been encountered - amongst others - at Kangankunde Hill (Malawi; Deans,
24 1966), at Mountain Pass (USA; Castor, 2008), and at Montviel (Canada; Nadeau et al.,
25 2015)..

1 In the carbonatitic dykes overprinted by a hydrothermal event, the highest $\delta^{18}\text{O}$ value
2 ($\delta^{18}\text{O} = 12.5\text{‰}$) is recorded by sample RG 144752, which contains ancylite-(Ce) coeval with
3 the predominant calcite 2 (second generation of calcite), suggesting circulation of “late”
4 hydrothermal fluids. The $\delta^{18}\text{O}$ values measured on carbonatitic dykes were obtained on
5 “whole rock samples”, and thus correspond to a mixture between several generations of
6 carbonates, some with low $\delta^{18}\text{O}$ values, some with high $\delta^{18}\text{O}$ values, possibly as high as the
7 value reached by the altered facies of the Matongo carbonatite ($\delta^{18}\text{O} = 20$ to 22‰). It is
8 therefore possible that the REEs gained in the carbonatitic dykes could be due to the leaching
9 of the sövite I facies of the Matongo intrusion. Alternatively, the REE-carbonate of the
10 carbonatitic dykes could originate from evolved fluids directly derived from the carbonatite
11 magma and enriched in LREE, Sr (and F). A contribution from both sources cannot be ruled
12 out.

13 In addition, it is worth mentioning that the mineralization – HFSE and REE – seems
14 to be spatially associated with the different fenitization types. Indeed, (1) in the vicinity of the
15 Matongo carbonatite body, where most of the late-magmatic HFSE mineralization occurs
16 (megacrysts of zircon and ilmenite), the K-fenites are prominent, while (2) Na-fenites relate
17 to the presence of carbonatitic dykes, associated with magmato-hydrothermal REE-
18 mineralization. At the scale of the URAPC massif, the close spatial association between Na-
19 fenites, carbonatitic dykes and REE-mineralization could likely be related to the channeling
20 of magmatic and metasomatic/hydrothermal fluids to near-surface levels into the same
21 conduits. Examples of carbonatitic systems showing spatial relationship between Na-fenites,
22 (ferro)carbonatitic dykes and REE mineral occurrences include : (1) the Mesoproterozoic
23 Swartbooisdrift alkaline complex (Namibia), in which the Na-fenites are restricted to
24 ferrocarbonatitic dykes/breccias that comprise a REE-Sr mineralization (Drüppel et al.,
25 2005); (2) the Neoproterozoic alkaline complex of Kirumba (DR Congo), in which ankerite

1 dykes invade fractured and albitized country rocks (Denayer, 1966), albite being frequently
2 associated with REE-minerals (Denayer, 1959). In addition to the fenitization, the
3 hydrothermal activity and associated mobility of elements are preferentially located in large
4 ductile shear-zones, which have been active during magma emplacement and cooling at sub-
5 solidus temperatures. Additional structural mapping of the URAPC is needed to obtain a 3D
6 geometry of the shear zones array and associated metallogenic system of the URAPC.

7

8 **Conclusion**

9 The large Neoproterozoic Upper Ruvubu Alkaline Plutonic Complex (URAPC),
10 located in Burundi along the western branch of the East African Rift, hosts carbonatites (as
11 intrusive body and dykes) and REE and HFSE mineral occurrences.

12 Syntectonic emplacement of the URAPC is revealed by its elliptic map contour. The
13 deformation was accommodated by large shear zones, one of them controlling the
14 emplacement of the Matongo carbonatite body. The shear zones array controlled the
15 geometry of the hydrothermal system associated with magmatic emplacement.

16 The C and O isotope compositions of the Matongo carbonatite body, of the zircon and
17 ilmenite megacrysts and of the carbonatitic dykes highlight the involvement of (1) late
18 magmatic-(carbonatitic) fluids in the formation of HFSE mineralizations and monazite, (2)
19 hydrothermal fluids (mostly metamorphic or - more generally - equilibrated with the
20 surrounding continental crust, with a contribution of the late-magmatic fluids) in the
21 deposition of ancylite-(Ce), and (3) late metamorphic fluids derived from the country rocks.
22 All these fluids induced – at least partly – the alteration and leaching of the REEs from the
23 primary carbonatite facies (sövite I) and their transport to form REE mineral occurrences,

1 likely in the carbonatitic dykes. A contribution of REE from at deep-seated « parental »
2 carbonatitic magma is likely.

3 This study emphasizes the relationships between alkaline magmatism, carbonatite,
4 fluid circulations and REE-HFSE mineral occurrences at the scale of the URAPC. It also
5 indicates that these relationships are intimately associated with the regional deformation and
6 tectonic setting during the Neoproterozoic, seemingly related – at a much larger scale - to the
7 Rodinia breakup. Thus, insights from the URAPC give new keys to understand the geometric,
8 magmatic and metallogenic characteristics of other alkaline plutonic massifs, amongst others,
9 those distributed along the present-day western branch of the East-African Rift.

10

11 **Acknowledgments**

12 This study is part of the GECO project (Belgian Federal Public Service for Foreign
13 Affairs). Field work has been partly funded by the program of the Belgian development
14 agency, BTC, dedicated to the digitizing of the Burundi geological map. The author would
15 like to warmly thank the MRAC for providing the study samples. Luc André and Laurence
16 Monin are also thanked for their role in providing LA-ICP-MS analyses. The authors are also
17 grateful to Randall Parrish, editor, and Olivier Nadeau and Olivier Vanderhaeghe, reviewers,
18 for the helpful remarks on the manuscript. These comments have contributed to significantly
19 improve the quality of this paper.

20

21 **References**

22 Andersson, M., Malehmir, A., Troll, V. R., Dehghannejad, M., Juhlin, C., Ask, M., 2013. Carbonatite
23 ring-complexes explained by caldera-style volcanism. Nature Scientific reports 3, 1-9.

- 1 Bau, M., 1996. Controls on the fractionation of isovalent trace elements in magmatic and aqueous
2 systems: Evidence from Y/Ho, Zr/Hf, and lanthanide tetrad effect. *Contribution to Mineralogy and Petrology*
3 123, 323-333.
- 4 Bell, K., Simonetti, A., 2010. Source of parental melts to carbonatites—critical isotopic constraints.
5 *Mineralogy and Petrology* 98, 77-89.
- 6 Bonin, B., Giret, A., 1985. Contrasting roles of rock-forming minerals in alkaline ring complexes.
7 *Journal of African Earth Sciences* 3, 41-49.
- 8 Boulvais, P., Fourcade, S., Gruau, G., Moine, B., and Cuney, M., 1998. Persistence of premetamorphic
9 C and O isotopic signatures in marbles subject to Pan-African granulite-facies metamorphism and U-Th
10 mineralization (Tranomaro, southeast Madagascar). *Chemical Geology* 150, 247-262.
- 11 Bowden, P., 1985. The geochemistry and mineralization of alkaline ring complexes in Africa (a
12 review). *Journal of African Earth Sciences* 3, 17-39.
- 13 Brown, P.E., 1964. The Songwe scarp carbonatite and associated feldspathization in the Mbeya Range,
14 Tanganyika. *Geological Society of London, Quarterly Journal of the Geological Society* 120, 223-240.
- 15 Burke, E.A.J., 1998. New data on zircon from Matongo (Burundi). *Aardk. Mededel.* 8, 1-4.
- 16 Burke, K., Ashwal, L.D., Webb, S.J., 2003. New way to map old sutures using deformed alkaline rocks
17 and carbonatites. *Geology* 31, 391-394
- 18 Castor, S.B., 2008. The Mountain Pass rare-earth carbonatite and associated ultrapotassic rocks,
19 California. *Canadian Mineralogist* 46, 779-806.
- 20 Chakhmouradian, A. R., 2006. High-field-strength elements in carbonatitic rocks: geochemistry, crystal
21 chemistry and significance for constraining the sources of carbonatites. *Chemical Geology* 235, 138-160.
- 22 Chakhmouradian, A. R., Zaitsev, A. N., 2012. Rare earth mineralization in igneous rocks: sources and
23 processes. *Elements* 8, 347-353.
- 24 Clayton, R.N., Mayeda, T.K., 1963. The use of bromine pentafluorine in the extraction of oxygen from
25 oxides and silicates for isotopic analysis. *Geochimica et Cosmochimica Acta* 27, 43-52.
- 26 Deans, T., 1966. Economic mineralogy of African carbonatites, in: Tuttle, O.F., Gittins, J., (Eds.),
27 *Carbonatites*. Interscience, Wiley publishers, New-York, pp. 385-413.

- 1 Demaiffe, D., 2008. Le magmatisme alcalin et carbonatitique: synthèse sur la province paléozoïque de
2 Kola (Russie) et caractéristiques générales du massif protérozoïque de Matongo (Burundi). Bulletin de Séances
3 de l'Académie royale des Sciences d'Outre-Mer 54, 171-196.
- 4 Denayer, M.E., 1959, Les syénites métasomatiques du massif de Kirumba : Mémoires de l'Académie
5 Royale des Sciences Coloniales, Classe des Sciences Techniques NS 9 (2), 234 p.
- 6 Denaeyer, M.E., 1966. Sur la présence d'une carbonatite ankéritique (rauhaugite) en bordure du
7 complexe alcalin de Kirumba (Kivu). Comptes Rendus de l'Académie des Sciences de Paris 263 (D), 9-12.
- 8 DFID, 2002. Local phosphate resources for sustainable development in sub-Saharan Africa. Economic
9 Minerals and geochemical Baseline Programme. Report CR/02/121/N. British Geological Survey.
10 http://www.bgs.ac.uk/research/international/dfid-kar/CR02121N_col.pdf.
- 11 Drüppel, K., Hoefs, J., and Okrusch, M., 2005. Finitizing processes induced by ferrocarnatite
12 magmatism at Swartbooisdrif, NW Namibia. *Journal of Petrology* 46, 377-406.
- 13 Eyles, N., 2008. Glacio-epochs and the supercontinent cycle after ~3.0 Ga: Tectonic boundary
14 conditions for glaciation. *Palaeogeography, Palaeoclimatology, Palaeoecology* 258, 89-129.
- 15 Fernandez-Alonso, M., Cutten, H., De Waele, B., Tack, L., Tahon, A., Baudet, D., and Barritt, S.D.,
16 2012. The Mesoproterozoic Karagwe-Ankole Belt (formerly the NE Kibara Belt): The result of prolonged
17 extensional intracratonic basin development punctuated by two short-lived far-field compressional events.
18 *Precambrian Research* 216, 63-86.
- 19 Fransolet, A.M., and Tack, L, 1992. Les zircons de Matongo (Burundi) et leur signification. *Annales de*
20 *la Société géologique de Belgique* 115, 113-118.
- 21 Gapais, D., Jaguin, J., Cagnard, F., Boulvais, P., 2014. Pop-down tectonics, fluid channelling and ore
22 deposits within ancient hot orogens. *Tectonophysics* 618, 102-106.

- 1 Gieré, R., 1996. Formation of rare earth minerals in hydrothermal systems, in: Jones, A.P., Wall, F.,
2 Williams, C.T. (Eds.), Rare Earth minerals, The Mineralogical Series, 7. Chapman & Hall, London, UK, pp.
3 105-150.
- 4 Grey, I.E., Reid, A.F., 1975. The structure of pseudorutile and its role in the natural alteration of
5 ilmenite. *American Mineralogist* 60, 898-906.
- 6 Hanson, R.E., 2003. Proterozoic geochronology and tectonic evolution of southern Africa, in: Yoshida,
7 M. et al. (Eds.), Proterozoic East Gondwana: Supercontinent assembly and breakup. Geological Society,
8 London, Special Publications, 206, pp. 427-463.
- 9 Irber, W., 1999. The lanthanide tetrad effect and its correlation with K/Rb, Eu/Eu*, Sr/Eu, Y/Ho, and
10 Zr/Hf of evolving peraluminous granite suites. *Geochimica et Cosmochimica Acta* 63, 489–508.
- 11 Kampunzu, A.B., Kramers, J., and Tembo, F., 1997. Neoproterozoic alkaline and carbonatite
12 magmatism along the western rift in Central-Eastern Africa: Break-up of Rodinia supercontinent and
13 reconstruction of Gondwana. *Gondwana Research* 1, 155-156.
- 14 Kempe, U., Götze, J., 2002. Cathodoluminescence (CL) behaviour and crystal chemistry of apatite from
15 rare-metal deposits. *Mineralogical Magazine* 66, 151-172. Kurtanjek, M.P., Tandy, B.C., 1989. The igneous
16 phosphate deposits of Matongo-Bandaga, Burundi, in: Notholt, A.J.G., Sheldon, R.P., Davidson, D.F. (Eds.),
17 Phosphate deposits of the world. Vol. 2. Phosphate rock resources. Cambridge University Press, Cambridge,
18 UK, pp. 262-266.
- 19 Le Bas, M.J., 1989. Diversification of carbonatite, in: Bell, K. (Ed.), Carbonatites: Genesis and
20 Evolution. London, Unwin Hyman, pp. 428-447.
- 21 Li, Z.X., Bogdanova, S.V., Collins, A.S., Davidson, A., De Waele, B., Ernst, R.E., Fitzsimons, I.C.W.,
22 Fuck, R.A., Gladkochub, D.P., Jacobs, J., Karlstrom, K.E., Lu, S., Natapov, L.M., Pease, V., Pisarevsky, S.A.,
23 Thrane, K., Vernikovsky, V., 2008. Assembly, configuration, and break-up history of Rodinia: A synthesis.
24 *Precambrian Research* 160, 179-210.
- 25 McDonough, W.F., 1990. Constraints on the composition of the continental lithospheric mantle. *Earth
26 and Planetary Science Letters* 101, 1-18.
- 27 Manning, D.A.C., 1995. Introduction to industrial minerals. Springer, 277 p.

- 1 Marks, M.A.W., Neukirchen, F., Venneman, T., Markl, G., 2009. Textural, chemical, and isotopic
2 effects of late-magmatic carbonatitic fluids in the carbonatite-syenite Tamazeght complex, High Atlas
3 Mountains, Morocco. *Mineralogy and Petrology* 97, 23-42.
- 4 Marshall, D.J., 1988. *Cathodoluminescence of Geological Materials*. Unwin Hyman, Boston. 146 p.
- 5 Midende, G. 1984. *La carbonatite de Matongo (Burundi)*. Unpublished PhD thesis, Université Libre de
6 Bruxelles, Bruxelles, 288 p.
- 7 Midende, G., Boulvais, P., Tack, L., Melcher, F., Gerdes, A., Dewaele, S., Demaiffe, D., Decrée, S.,
8 2014. Petrography, geochemistry and U-Pb zircon age of the Matongo carbonatite Massif (Burundi): implication
9 for the Neoproterozoic geodynamic evolution of Central Africa. *Journal of African Earth Sciences* 100, 656-
10 674.
- 11 Mitchell, R.H., 2014. Primary and secondary niobium mineral deposits associated with carbonatites.
12 *Ore Geology Reviews* 64, 626-641.
- 13 Nadeau, O., Stevenson, R., Jébrak, M., 2014. The Archean magmatic-hydrothermal system of Lac
14 Shortt (Au-REE), Abitibi, Canada: Insights from carbonate fingerprinting. *Chemical Geology* 387, 144-156.
- 15 Nadeau, O., Cayer, A., Pelletier, M., Stevenson, R., Jébrak, M., 2015. The Paleoproterozoic Montviel
16 carbonatite-hosted REE–Nb deposit, Abitibi, Canada: Geology, mineralogy, geochemistry and genesis. *Ore
17 Geology Reviews* 67, 314-335.
- 18 Ngwenya, B., 1994. Hydrothermal rare-earth mineralization in carbonatites of the Tundulu Complex,
19 Malawi – Processes at the fluid-rock interface. *Geochimica Cosmochimica Acta* 58, 2061-2072.
- 20 Nkurikiye, L., 1989. *Le kaolin au Burundi: Contribution à sa caractérisation, sa genèse et son
21 utilisation*. Unpublished M. Sc. Thesis, Burundi University. Notholt, A.J.G., 1999. *Phosphate: a world
22 monograph* (A compilation of unfinished paper). British Geological Survey.
- 23 Pell, J., 1996. Mineral deposits associated with carbonatites and related alkaline igneous rocks, in:
24 Mitchell, R.H. (Ed.), *Undersaturated alkaline rocks: Mineralogy, petrogenesis, and economic potential*. Short
25 Course Series 24, Mineralogical Association of Canada, Winnipeg, pp. 271-310.

- 1 Platt, R.G., 1996. Nepheline-syenite complexes – an overview, in: Mitchell, R.H. (Ed.), Undersaturated
2 alkaline rocks: Mineralogy, petrogenesis, and economic potential. Short Course Series 24, Mineralogical
3 Association of Canada, Winnipeg, pp. 63-100.
- 4 Pownceby, M.I., 2010. Alteration and associated impurity element enrichment in detrital ilmenites from
5 the Murray basin, southeast Australia: a product of multistage alteration. *Australian Journal of Earth Sciences*
6 *57*, 243-258.
- 7 Rugless, C.S., Pirajno, F., 1996. Geology and geochemistry of the Copperhead Albitite 'Carbonatite'
8 Complex, east Kimberley, Western Australia. *Australian Journal of Earth Sciences* *43*, 311-322.
- 9 Simonetti, A., Bell, K., 1994. Isotopic and geochemical investigation of the Chilwa Island carbonatite
10 complex, Malawi: evidence for a depleted mantle source region, liquid immiscibility, and open-system
11 behaviour. *Journal of Petrology* *35*, 1597-1621.
- 12 Spoetl, C., Vennemann, T. W., 2003. Continuous-flow isotope ratio mass spectrometric analysis of
13 carbonate minerals. *Rapid Communications in Mass Spectrometry* *17*, 1004–1006.
- 14 Stoch, L., Sikora, W., 1976. Transformation of micas in the process of kaolinitization of granites and
15 gneisses. *Clay and Clay Minerals* *24*, 156-162.
- 16 Stormer, J. C., Pierson, M. L., Tacker, R. C., 1993. Variation of F and Cl X-ray intensity due to
17 anisotropic diffusion in apatite. *American Mineralogist* *78*, 641-648.
- 18 Sun, S.S., 1982. Chemical composition and origin of the Earth's primitive mantle. *Geochimica*
19 *Cosmochimica Acta* *46*, 179–192.
- 20 Tack, L., De Paepe, P., Deutsch, S., Liégeois, J.P., 1984. The alkaline plutonic complex of the Upper
21 Ruvubu (Burundi): geology, age, isotopic geochemistry and implications for the regional geology of the
22 Western rift, in: Klerkx, J., and Michot, J. (Eds.), *African Geology: Tervuren*, pp. 91-114.
- 23 Tack, L., Liégeois, J.P., André, L., Navez, J., 1995. The Upper Ruvubu alkaline plutonic complex
24 (Burundi). *Annual Report of the Royal Museum for Central Africa, Tervuren*, p. 9.
- 25 Tack, L., Deblond, A., De Paepe, P., Duchesne, J.C., Liégeois, J.P., 1996. Proterozoic alignments of
26 alkaline plutons revealing lithospheric discontinuities: evidence from Eastern Africa, in: Demaiffe, D. (Ed.),
27 *Petrology and Geochemistry of magmatic suites of rocks in the continental and oceanic crusts. A volume*
28 *dedicated to Professor Jean Michot. Université Libre de Bruxelles, Bruxelles, Belgium*, pp. 219-226.

- 1 Tack, L., Wingate, M.T.D., De Waele, B., Meert, J., Belousova, E., Griffin, A., Tahon, A., Fernandez-
2 Alonso, M., 2010. The 1375 Ma “Kibaran event” in Central Africa: prominent emplacement of bimodal
3 magmatism under extensional regime. *Precambrian Research* 180, 63–84.
- 4 Taylor, H.P.Jr, Frechen, J., Degens, E.T., 1967. Oxygen and carbon isotope studies of carbonatites
5 from Laacher See district, West Germany and Alnø district, Sweden. *Geochimica et Cosmochimica Acta* 31,
6 407-430.
- 7 Valley, J.W., 2003. Oxygen isotopes in zircon. *Reviews in mineralogy and geochemistry* 53, 343-
8 385. Wall, F., Mariano, A. N., 1996. Rare earth minerals in carbonatites: a discussion centred on the
9 Kangankunde Carbonatite, Malawi, in: Jones, A.P., Wall, F., Williams, C.T. (Eds.), *Rare Earth minerals, The*
10 *Mineralogical Series*, 7. Chapman & Hall, London, UK, pp. 193-226.
- 11 Waychunas, G.A., 2002. Apatite luminescence. In: Kohn MJ, Rakovan J, Hughes JM (eds) *Reviews in*
12 *Mineralogy and Geochemistry Volume 48 – Phosphates*. Mineralogical Society of America, Washington DC,
13 pp. 701-742.
- 14 Williams-Jones, A. E., Migdisov, A. A., Samson, I. M., 2012. Hydrothermal mobilisation of the rare
15 earth elements—a tale of “ceria” and “yttria”. *Elements* 8, 355-360.
- 16 Wyllie, P.J., Jones, A.P., Deng, J., 1996. Rare earth elements in carbonatite-rich melts from mantle to
17 crust, in: Jones, A.P., Wall, F., Williams, C.T. (Eds.), *Rare Earth minerals, The Mineralogical Series*, 7.
18 Chapman & Hall, London, UK, pp. 77-107.
- 19 Zaitsev, A., Wall, F., Le Bas, M.J., 1998. REE-Sr-Ba minerals from the Khibina carbonatites, Kola
20 Peninsula, Russia: their mineralogy, paragenesis and evolution. *Mineralogical Magazine* 62, 225-250.
- 21 Zheng, Y.F., 1991. Calculation of oxygen isotope fractionation in metal oxides. *Geochimica et*
22 *Cosmochimica Acta* 55, 2299-2307.
- 23 Zheng, Y.F., 1993. Calculation of oxygen isotope fractionation in anhydrous silicate minerals.
24 *Geochimica et Cosmochimica Acta* 7, 1079-1091.
- 25 Zheng, Y.F., 1999. Oxygen isotope fractionation in carbonate and sulfate minerals. *Geochemical*
26 *Journal* 33, 109-126.

27

1

2 **Figure and Table captions**

3 **Figure 1.** (A) Geological sketch map of the studied area (modified and redrawn from Tack et al.,
4 1984, and after Fernandez-Alonso et al., 2012), with an insert showing the alkaline complexes
5 along the western branch of the East African Rift system (redrawn from Tack et al., 1984).
6 (B) location of the showings/deposits, samples (RG 144739, RG 144752, GPS74) and
7 boreholes (from S1 to S8, from ITS3 to ITS5) mentioned in the text (see also Table 8 in the
8 Supplementary material for the correspondence between samples and drill cores).

9 **Figure 2.** Field pictures showing the intrusive contact between the Buraniro Granite (A) and the
10 metasediments (B). The evolution of the deformation within the granite and the contact
11 metamorphism are illustrated (presence of andalusite “And.” on the figure). See text for
12 further explanations and Figure 1A for the location of the contact. Field picture of an aplitic
13 dyke (quartz syenite) with internal schistosity defining a fan-like pattern (C), as highlighted
14 on the drawing. The host rocks are of medium- to high-grade metapelites, some of them being
15 garnet-bearing.

16 **Figure 3.** Field pictures (A-E) and mineral occurrences (F-H) showing the relationships between
17 magmatism, deformation and hydrothermal fluid circulation within the URAPC. (A)
18 Deformed quartz + hematite vein in the quartz syenite, (B) Slickenslide lineation on hematite
19 in the shear plane of the quartz+hematite vein shown in figure A. (C) Carbonatitic venue
20 emphasized by the presence of an albite vein in a fenitized feldspathoidal syenite. (D)
21 Representative outcrop of a deformed and fenitized feldspathoidal syenite comprising a
22 carbonatite vein. (E) Carbonatitic dykes with albitized clasts and the invading carbonatite
23 (Carb) in the felspathoidal syenite (sample RG 144752). (F) Deformed felspathoidal syenite
24 (the foliation is parallel to the pen) cross-cut by a dyke comprising feldpathoids and oxides.
25 (G) Highly mylonitized quartz syenite. (H) Tension gashes filled with feldpathoid (sodalite in
26 blue) in a mylonitized quartz syenite. (I-J): Euhedral zircon megacrysts originating from the

1 Inamvumvu hill and set in a lateritic crust. (K) Euhedral ilmenite megacryst from the
2 Inamvumvu hill.

3 **Figure 4.** Pictures of the Matongo drill cores, which are strongly invaded by calcite veins. The
4 numbers and pink lines correspond to the micro-drill sampling for the stable isotope study.

5 **Figure 5.** Photomicrographs of the carbonatitic dykes (sample RG 144.752) in transmitted light (A),
6 cathodoluminescence (D-E), and backscattered electron images (B-C, F-G). Abbreviations are
7 as follows: Calc 1 for the first generation of Fe-Mn-rich calcite, Calc 2 for the second
8 generation of calcite, Ilm for ilmenite, Fluorap for fluorapatite, Rut for rutile and Str for
9 strontianite. (A) Muscovite vein in an albitized clast, partly slightly silicified (leading to
10 cloudy albite). (B) Muscovite vein in an albitized clast. Ancylyte-(Ce) replacing a muscovite
11 lath in this vein. (C) Biotite aggregates within albitized clast; rims of biotite laths are
12 transformed into a Ba-rich biotite and occur in association with euhedral zircon and ilmenite-
13 rutile intergrowths; monazite occurs as interstitial phase of biotite. (D) Assemblage
14 comprising pink albite, biotite, dull luminescent calcite 1 and blue apatite in the matrix of the
15 carbonatitic dykes; late calcite (orange in Cl) and bright strontianite replace earlier calcite 1
16 (see text for further comments). (E) Blue-luminescing monazite. (F) Biotite, calcite 1 and
17 fluorapatite invading an albitized clasts; insert shows ancylyte-(Ce) associated with calcite 2
18 replacing albite. (G) Assemblage of biotite, late calcite 2 and strontianite in the matrix of the
19 carbonatitic dykes. Monazite seems associated with biotite, while ancylyte-(Ce) is interstitial
20 to biotite laths.

21 **Figure 6.** Photomicrographs of the Matongo drill cores in transmitted light (A) and
22 cathodoluminescence (B-C). Abbreviations are as follows: Felds for K-feldspar and Fluorap
23 for fluorapatite. (A) Typical vein, where calcite is associated with fluorapatite and oxides in
24 the MAT 1a drill core. (B) Vein comprising dolomite and fluorapatite within the host
25 calciocarbonatite, which is associated with K-feldspar (MAT 3 drill core). (C) Alignment of
26 fluorapatite parallel to the foliation (MAT 3 drill core). See text for further explanation.

1 **Figure 7.** Chondrite-normalized REE abundance patterns of the minerals from the carbonatitic dykes
 2 (A-B), from the Matongo drill cores (C-E) and of the megacrysts from the Inamvumvu laterite
 3 and kaolin (F-G) (LA-ICP-MS analyses). (A) Fluorapatites and calcites from the carbonatitic
 4 dykes and comparison with whole-rock analyses of various facies of the Matongo carbonatite
 5 (sövite I, sövite II and late hydrothermal calcite; Midende et al., 2014). (B) REE-minerals -
 6 monazite and ancylite-(Ce) - from the carbonatitic breccias. (C) Two calcite types from veins
 7 of the MAT 1 drill core. (D) Two calcite types from veins of the MAT 2 drill core. (E)
 8 Fluorapatites and calcite from veins of the MAT 3 drill core. Host calciocarbonatite analyses
 9 are given for comparison purposes. (F) Zircons megacrysts from the laterite and kaolin
 10 deposit. (G) Ilmenite megacrysts from the laterite and kaolin deposits. (Normalization values
 11 to the chondrites from Sun (1982) and McDonough (1990).

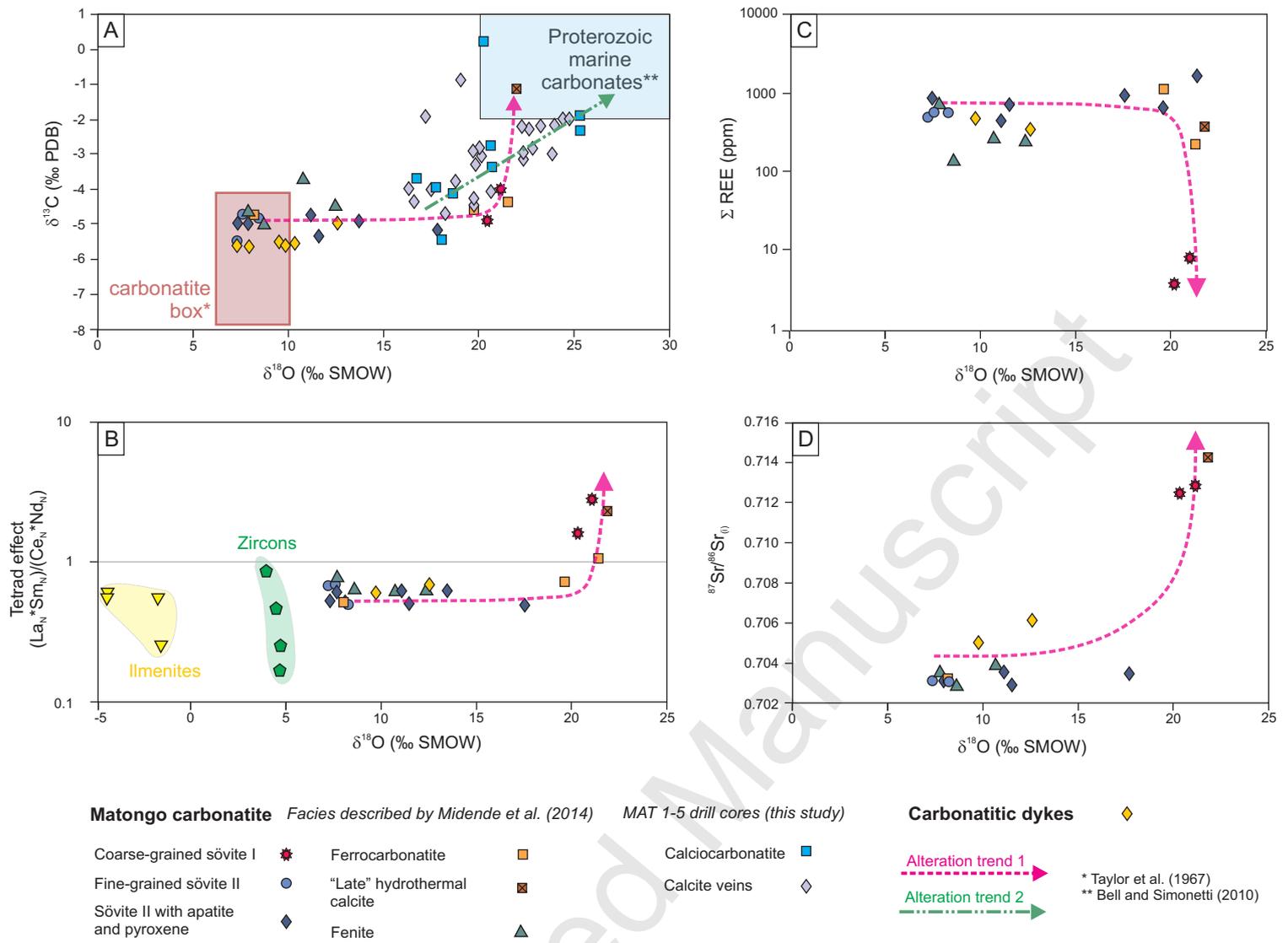
12 **Figure 8.** (A) $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ isotopic diagram for the various facies of the Matongo carbonatite and
 13 for the carbonatitic dykes. The carbonatite box corresponds to the isotopic signature of the
 14 primary (=magmatic) carbonatites (Taylor et al., 1967). See the text for explanations about
 15 trends 1 & 2. (B) Correlation between the oxygen isotopic composition and the tetrad effect.
 16 Data relating the zircon and ilmenite megacrysts from the Inamvumvu hill are also plotted in
 17 this diagram. (C) Correlation between the oxygen isotopic composition and the sum of REE.
 18 (D) $^{87}\text{Sr}/^{86}\text{Sr}$ (initial recalculated ratios) versus $\delta^{18}\text{O}$ isotopic diagram for several facies of the
 19 Matongo carbonatite and for the carbonatitic breccias.

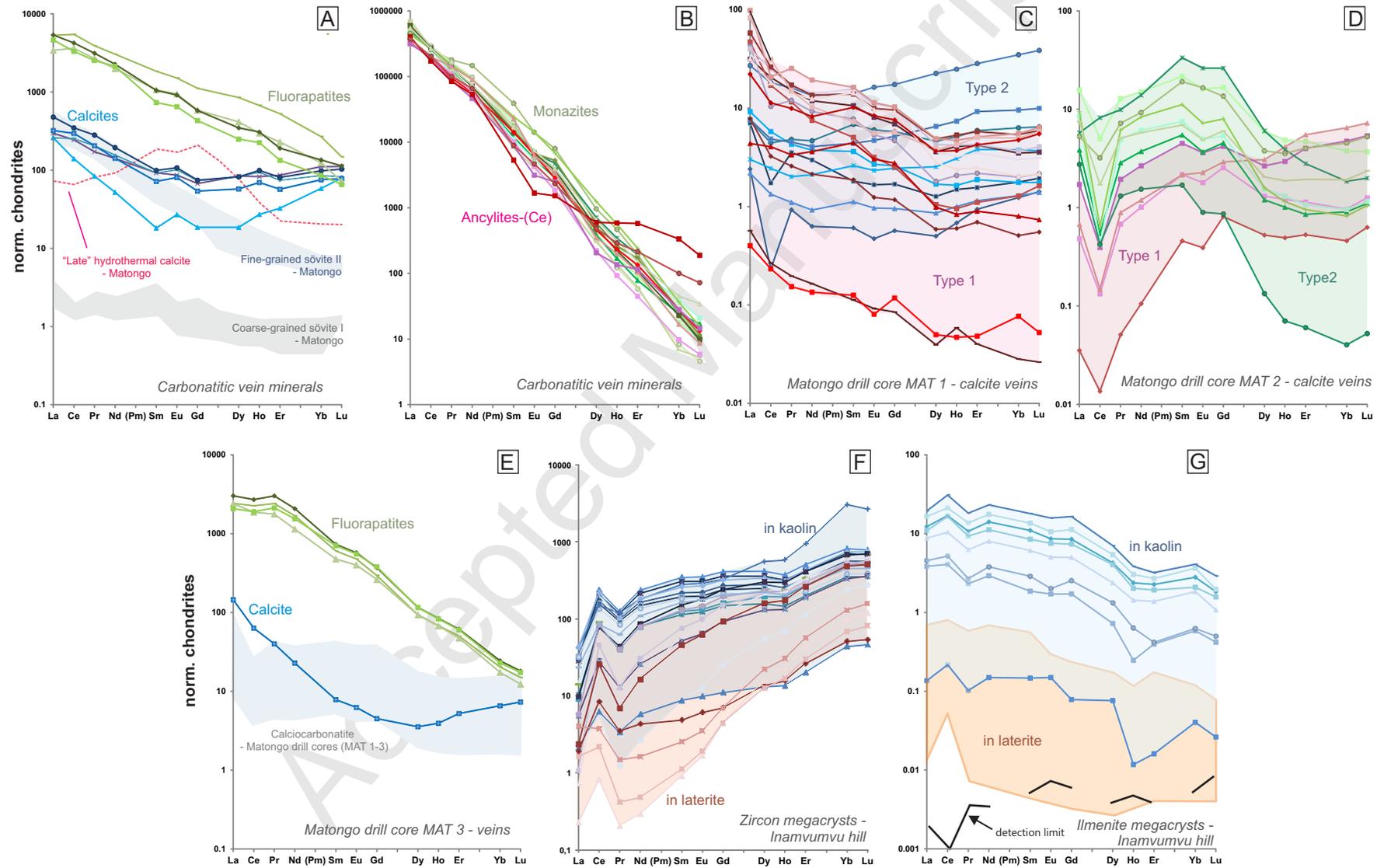
20 **Figure 9.** Schematic structural map and cross-section of the URAPC highlighting the role of shear
 21 zones in controlling the geometry of the Complex. Some shear zones have been observed on
 22 the field (they are marked by an asterisk on the cross-section), some others have been inferred
 23 from the global geometry.

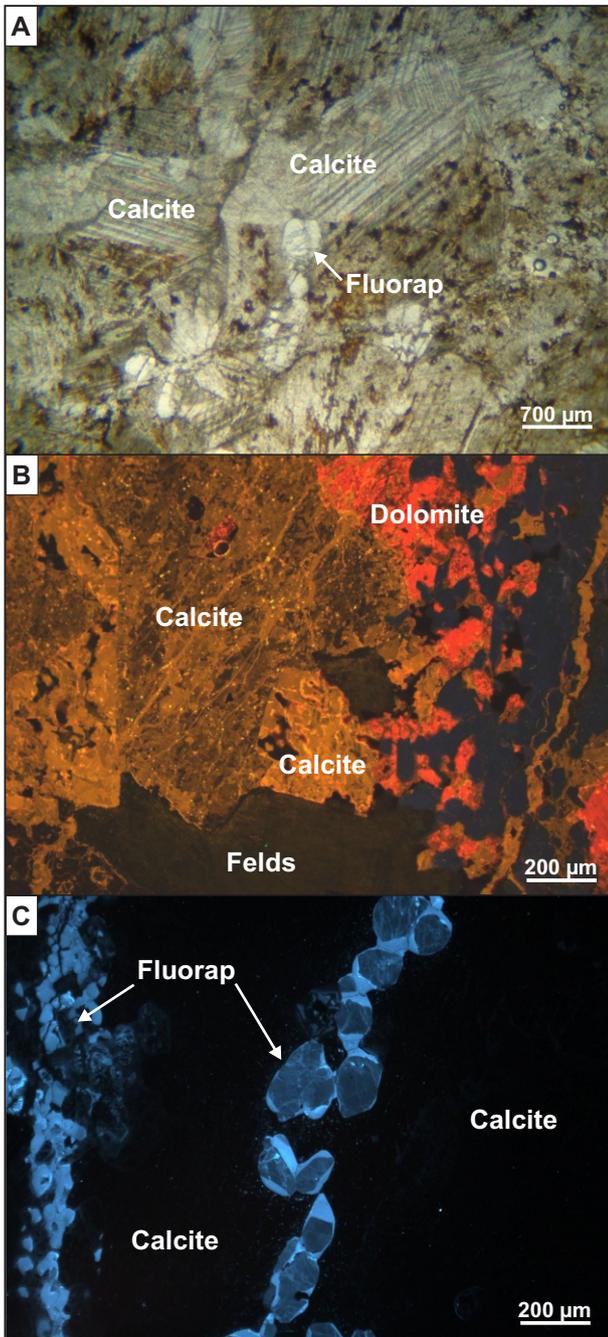
24

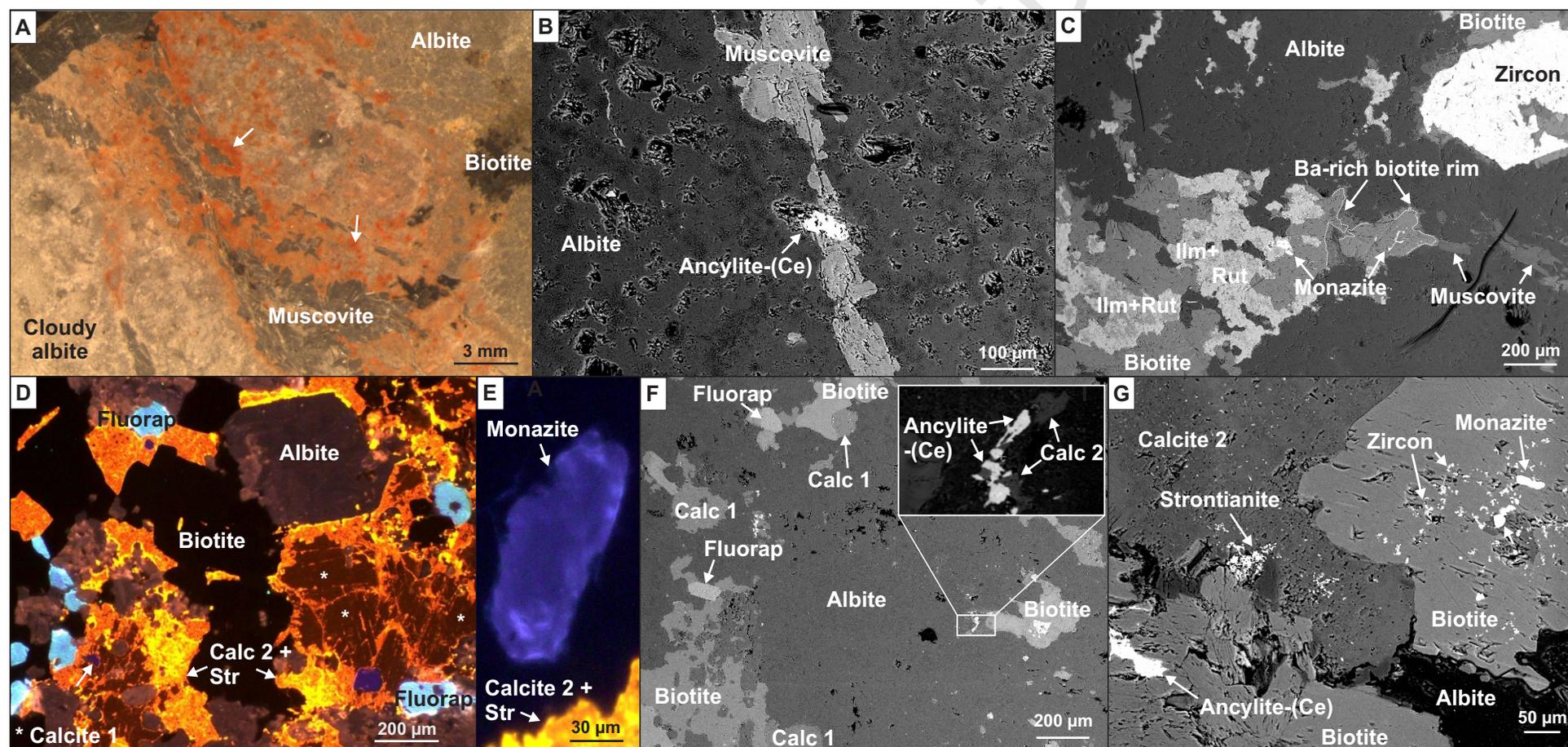
- 1 - This study focuses on a Neoproterozoic syntectonic alkaline complex in Burundi
- 2 - Field observations evidence fluid-rock interactions in relation with deformation
- 3 - Petrographic and geochemical data testify for different fluid circulations
- 4 - HFSE and REE mobilizations/mineral occurrences are related to these circulations
- 5

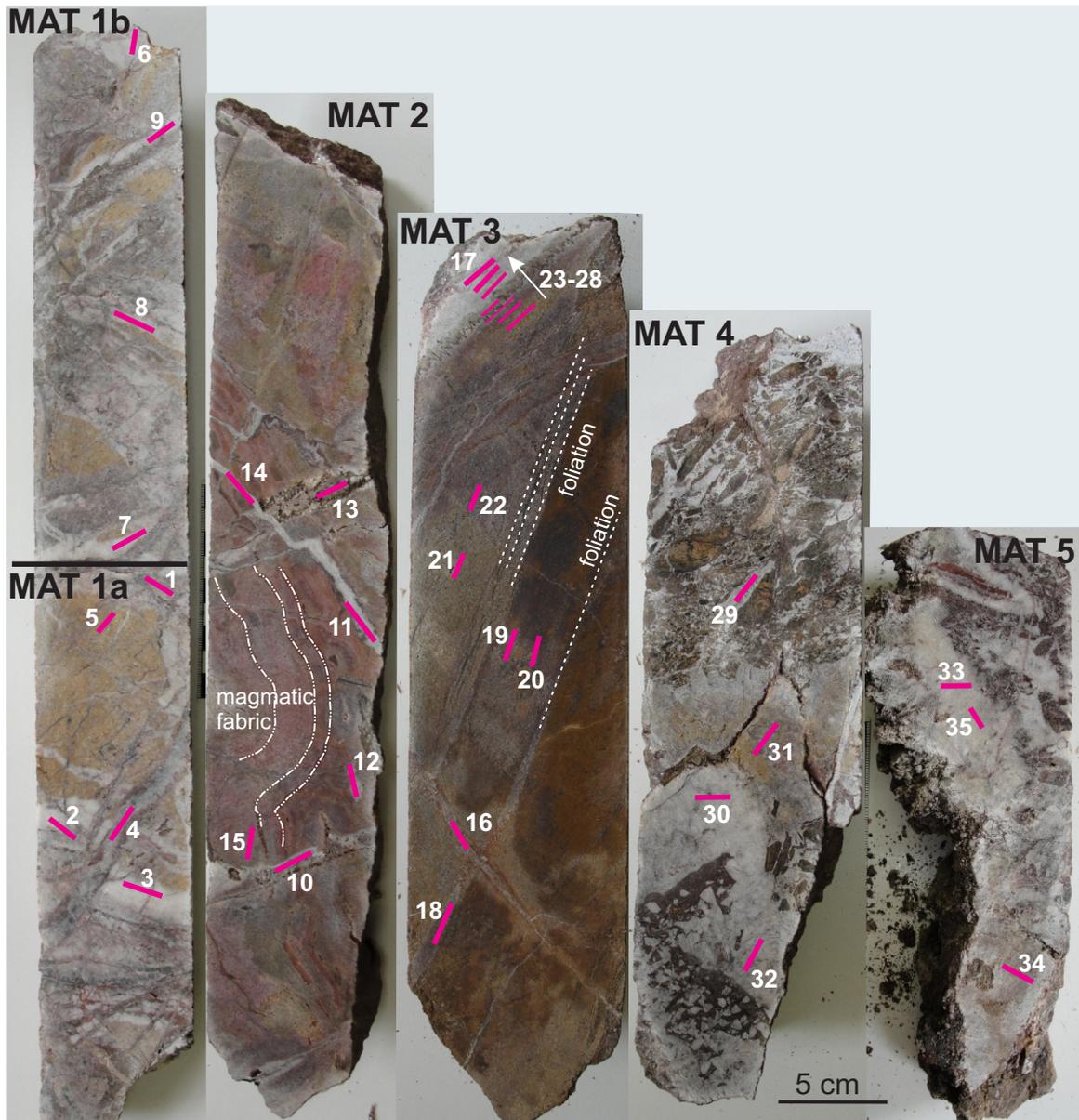
Accepted Manuscript

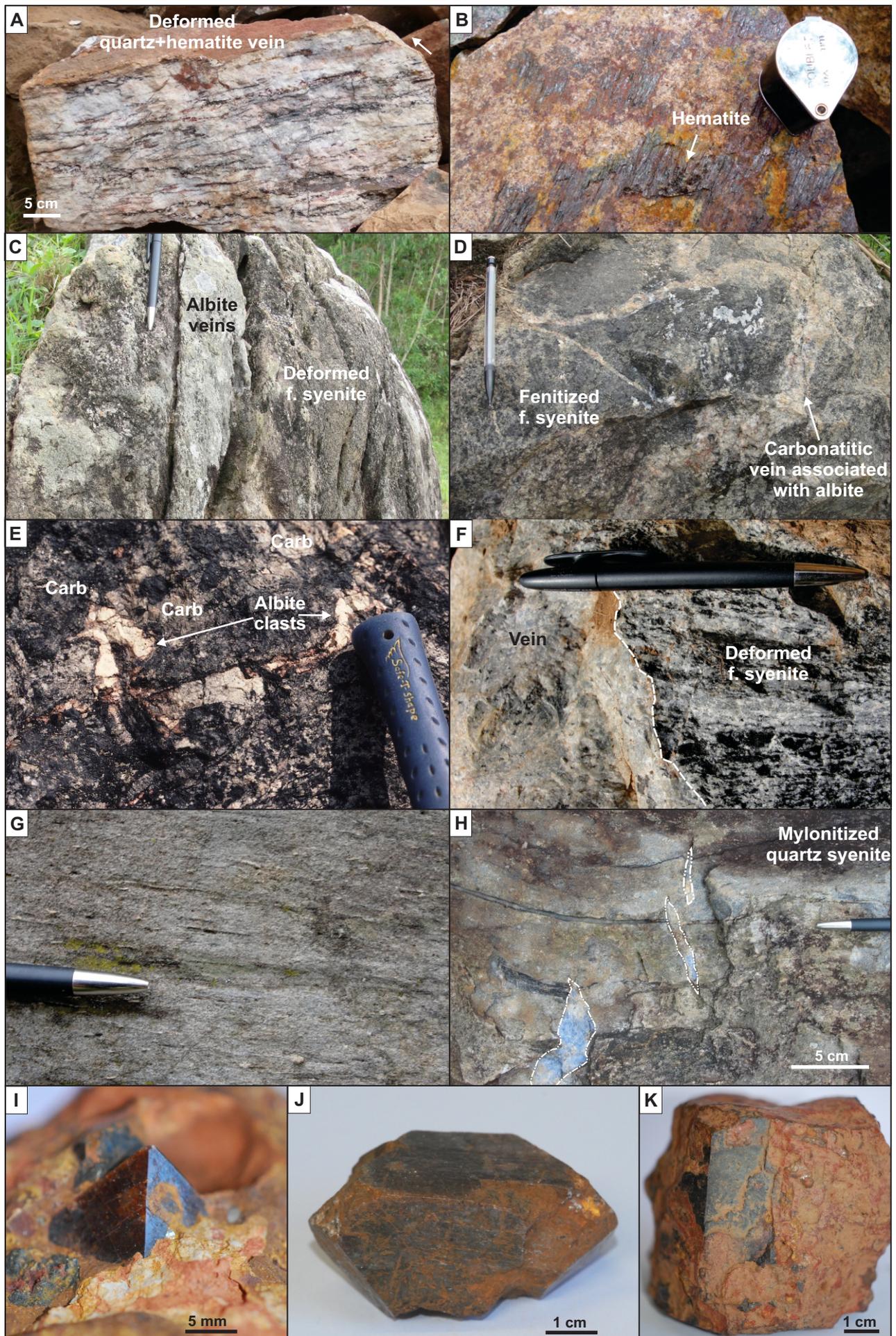








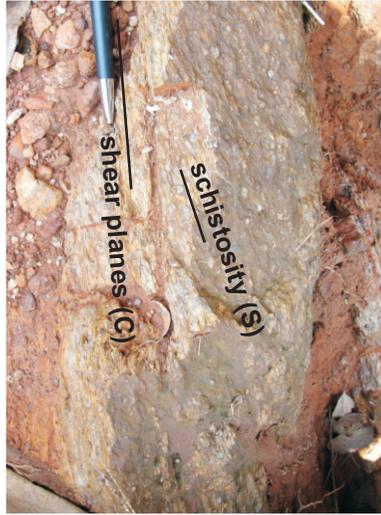




A. GRANITE



1 m



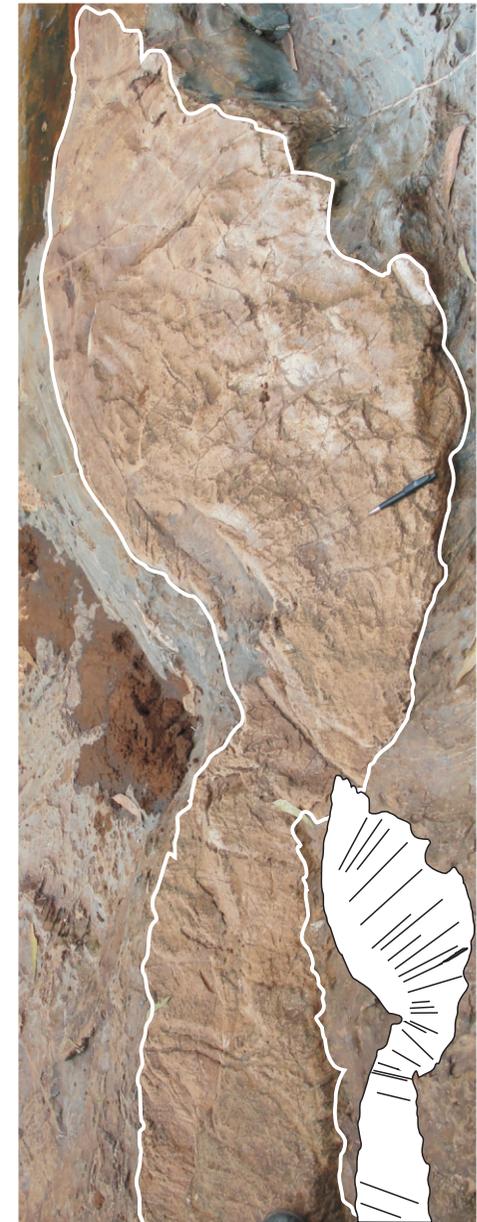
20 m



100 m



C. Qz SYENITE



B. MICASCHISTES

