Analytical fingerprint of columbite-tantalite (coltan) mineralisation in pegmatites - Focus on Africa

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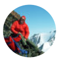

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Analytical Fingerprint of Columbite-Tantalite (Coltan) Mineralisation in Pegmatites – Focus on Africa

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ABSTRACT

Following the United Nations initiative to fingerprint the origin of conflict materials, the German Federal Ministry for Economic Cooperation and Development has decided to fund a pilot study on coltan ores. Since 2006, our working group has been investigating columbite-tantalite (coltan) mineralisation, especially in Africa, also within the wider framework of establishing certified trade chains.

More than 300 samples were obtained from the world's major coltan producing areas. Special attention is, however, directed to samples and concentrates from Ta-Nb-Sn provinces in Africa: Democratic Republic of the Congo, Rwanda, Mozambique, Ethiopia and Namibia. Using state of the art analytical tools, we investigate mineralogical and chemical parameters obtained from columbite-tantalite ores and concentrates in order to distinguish between ore provinces, likely even down to the deposit scale. Methods employed include fully automated electron microscopy (mineral liberation analysis), electron microprobe analysis (major and minor elements), laser ablation plasma-source mass spectrometry (trace elements and U-Pb dating), X-ray fluorescence spectroscopy (bulk major and trace elements), X-ray diffraction analysis (mineralogy and structure) and thermal-ionisation mass-spectrometry (U-Pb dating).

Major and trace element concentration patterns, mineral assemblages in the ore concentrates, and zoning characteristics in the different pegmatites from Africa distinctly differ from each other. Furthermore, the following age populations are evident:

- Archaean (>2.6 Ga);
- Palaeoproterozoic (1.9 - 2.1 Ga);
- early Neoproterozoic ('Kibaran'; 0.98 - 0.93 Ga); and
- late Neoproterozoic to early Palaeozoic (ca 0.5 Ga).

Currently, we focus on the resolution of the fingerprinting system from region via ore province down to deposit scale. Our preliminary analytical results indicate that a certification scheme including fingerprinting of sources of coltan ores is feasible.

INTRODUCTION

The chemical properties of tantalum are increasingly used in various technological developments. Tantalum capacitors are invaluable in the production of mobile phones, digital cameras, computers and cars. Tantalum is almost exclusively mined from rare-element pegmatites and a few specialised granites, with minor production coming from niobium-rich carbonatites and residues of tin smelting. Annually, approximately 1300 tonnes of Ta metal is mined in Western Australia, Brazil, Canada, China and numerous African countries. Future mines will eventually open up in Egypt, Saudi Arabia, Russia, Finland and Greenland. Today, Talison (Australia) produces in excess of 50 per cent of the world production from its Wodgina mine. However, increasing pressure on the world market has initiated and renewed extensive exploration in many African countries, in the hope that ore may be produced at a lower price. In most African countries, tantalum is mined by artisanal miners from eluvial and alluvial deposits: miners produce 'coltan', which is the Central African trade name for concentrates containing minerals of the columbite-tantalite solid solution series (abbreviated CGM, columbite-group minerals). Such concentrates contain from ten to 40 per cent Ta_2O_5, in addition to Nb, Sn, W, Ti, U, Th, REE, Zr and other metals.

Coltan has been identified as one of several raw materials that were used to finance the civil wars in central Africa. The term 'blood coltan' was coined in the Congolese civil wars as the sale of this mineral powered the fighting, especially in the eastern provinces of the Democratic Republic of the Congo (DRC). The various armies in this war-torn region, both official and amateur, moved in to take over the trade. A sharp price increase for tantalum on the market at the beginning of the century caused by speculation (from US$60 to US$480/kg Ta_2O_5) made this trade highly profitable. After the 'coltan boom' in 2000, large quantities of coltan were smuggled from the DRC into the neighbouring countries to be sold illegally on the black market.

The United Nations took the initiative and an expert group proposed that measures should be taken to certify tantalum-bearing mineral products along their trade chain. Analytical schemes should be worked out that allow distinguishing mineral matter produced within regions affected by the civil war from other sources. Results of a pilot study funded by the German Federal Ministry for Economic Cooperation and Development (BMZ) are presented here.

TANTALUM PRODUCTION IN AFRICA

Tantalum mineralisation has been reported from many countries in Africa (Fetherston, 2004). Central African countries such as the DRC, Uganda, Burundi and Rwanda have been significant suppliers of tantalum concentrates for at least 40 years. Other

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tantalum producing countries include Mozambique, Nigeria, Ethiopia, Namibia and Zimbabwe. Recently, the largest single producers are the Kenticha mine, Ethiopia and Marropino, Mozambique, which are both mined in a semi-industrial way. In all other areas, tantalum mining continues as small-scale, artisanal mining.

According to the USGS Mineral Commodity Summaries, African countries have a share of ~20 per cent of the world tantalum production. That production developed from low quantities (<100 tonnes of Ta metal) – before a dramatic price increase in 2000 (the 'coltan boom') – to 350 tonnes in 2000, and has stayed above 250 tonnes per annum since then. The major share of the production was reported from the DRC and Rwanda in 2000 - 2001, but since then has shifted to Rwanda (2001 - 2002), Zimbabwe (2002 - 2003), and Mozambique (2003 - 2004). These 'official' numbers suggest significant transfer of Congolese material into neighbouring countries (Figure 1). In contrast, the Ethiopian production (Kenticha mine) steadily increased its output since 1995. Mozambique did not contribute significantly to the world market before 2007.

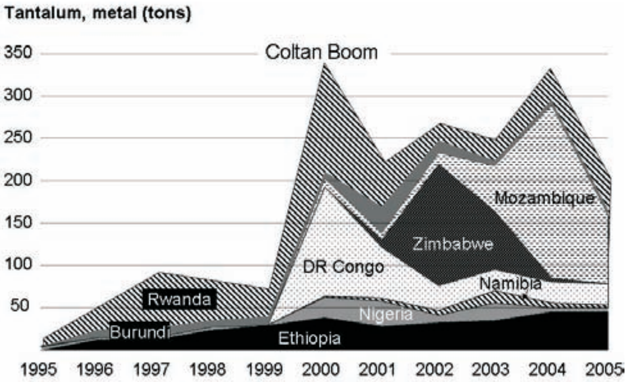

FIG 1 - Mine production of tantalum metal from African countries. Sources: USGS Mineral Commodity Summaries, BGR mineral database.

Almost all tantalum deposits in Africa appear to be related to granitic rare-metal pegmatites or their regolith derivatives, such as deeply weathered deposits, or to eluvial and alluvial placer deposits (Varlamoff, 1972; Fetherston, 2004). At least five periods of tantalum mineralisation are identified in Africa (Figure 2):

1. Late Archaean to early Palaeoproterozoic pegmatites host tantalum mineralisation on the Zimbabwe and northern DRC-Central African Republic (DRC-CAR) cratons.
2. The Palaeoproterozoic granite-greenstone belt terranes of the Eburnean Province in West Africa carry small rare-metal pegmatite deposits, eg in the Ivory Coast (Allou *et al*, 2005) and Ghana (Kokobin near Oda).
3. A major period of rare-element granite emplacement is manifested in the Kibaran Belt of central Africa. Mineralisation is slightly younger than 1.0 Ga (billion years). Identical ages are found in the Tantalite Valley pegmatite field, Namaqualand Province of southern Namibia and South Africa.
4. The Neoproterozoic to early Palaeozoic 'Panafrican' mobile belts, especially along the eastern coast of Africa, are locally highly endowed with rare-metal granites (Egypt) and pegmatites (Ethiopia, Mozambique, Madagascar). Intrusion ages range from 0.45 to 0.6 Ga. Pegmatites of similar ages are known from the Central Zone of the Damara orogen in central Namibia, and from the Panafrican basement in Nigeria.

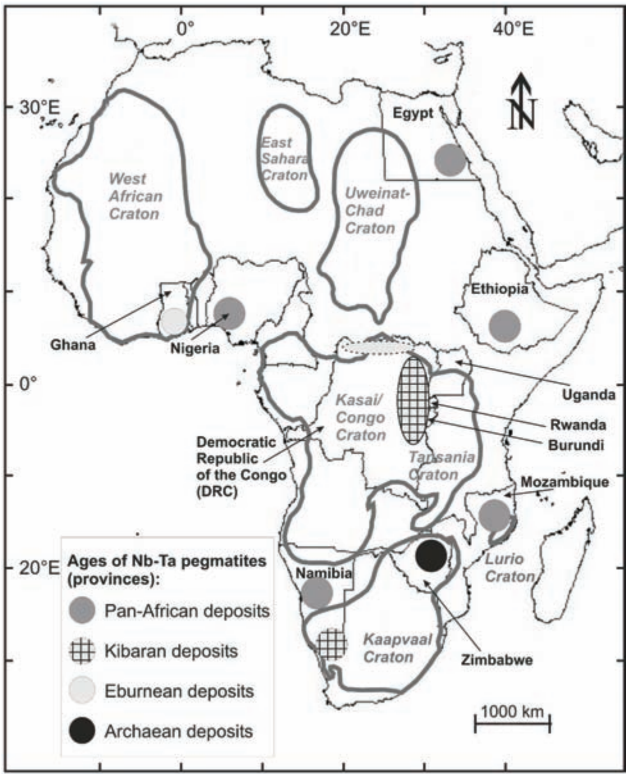

FIG 2 - Location of important ore provinces with Nb-Ta mining activities in Africa. See text for discussion of the ages. The position of the Archaean to Palaeoproterozoic craton areas in Africa is added for illustration (modified from Schlüter, 2006).

5. The youngest tantalum mineralisation in Africa appears to be related to the Jurassic granitic ring complexes of the Jos Plateau in central Nigeria.

Areas of the pilot study

Democratic Republic of the Congo, Rwanda, Burundi and Uganda

Tantalum-rich placer deposits have been intermittently mined in the Ituri Province (DRC), within the 'northern DRC-CAR craton'. However, the Kibaran Belt (DRC, Rwanda, Burundi and Uganda) is the major producer of Ta-Nb, Sn, W, REE (monazite) and Au. The world's largest reserves of tantalum are probably contained in the Kivu Province of the eastern DRC. Mining took place from about 1910 into the Mobutu era. The largest single pegmatite body in the Kibaran Belt (Manono-Kitotolo; Katanga Province, DRC) hosted total reserves of ~100 million tonnes of eluvial/alluvial and primary ore (Bassot and Morio, 1989). With the outbreak of the Congolese war in 1998, mining, distribution and sale of coltan in the Kivu Province came under the control of the Rwandan-backed rebel army, which was not withdrawn before mid-2002 (Fetherston, 2004). Recently, mining licenses have been granted to internationally operating mining companies. However, the artisanal miners are out of control in most areas, and industrial production of coltan is not likely to restart in the very near future. In Rwanda, the state-owned Régie d´Exploitation et de Developpement des Mines (REDEMI) still controls many concessions, but has also granted licenses to mining companies that produce cassiterite and coltan concentrates in cooperation with the local artisanal miners. Historical productions of cassiterite and coltan of Rwanda from 1958 to 2005 are ~60 000 and 5000 tonnes, respectively (BRGM, 1987; USGS Mineral Commodity Summaries 1990 - 2005).

The NNE-SSW-oriented Kibaran Belt extends from Uganda via Rwanda and finally into the Katanga region of the DRC (Pohl, 1994; Dewaele *et al*, in press). Palaeo- and Mesoproterozoic clastic sediments are ubiquitous, and have been intruded by three generations of granites. The oldest granites have been dated at 1.38 Ga, whereas the youngest are slightly younger than 1.0 Ga. The Ta-Nb, Sn and W ores are exclusively connected with the youngest post-orogenic 'tin granites' (Late-Kibaran), also called G4 granites. Mineralisation is developed in quartz veins, greisens and small pegmatitic bodies that are sometimes zoned, in some distance to the G4 granites (Varlamoff, 1972). The rare-metal pegmatites are of the lithium-caesium-tantalum type (LCT; Černý, 1991) and intrude metasediments, basic intrusive rocks (metadiorites) or rarely older granites. They generally carry Sn, and many contain Ta-Nb, in addition to locally abundant Li, Be and phosphate mineralisation. Cassiterite is also abundant in veins that are locally spatially related to pegmatites. However, cassiterite-bearing veins are usually devoid of tantalum mineralisation. The quartz-wolframite veins are usually free of Sn and Ta.

Ethiopia

All production of Ta comes from the Kenticha pegmatite in the Oromia Regional State, which is presently mined by the Ethiopian Mineral Development Share Company (EMDSC). It produces 70 tonnes Ta metal per annum (120 tonnes of concentrate at 60 per cent Ta_2O_5). The probable reserve of primary ore is 17 000 tonnes Ta_2O_5 at a grade of 0.017 per cent Ta_2O_5, whereas the reserve of Ta_2O_5 in the weathered zone was calculated to 2400 tonnes at 0.015 per cent Ta_2O_5.

The pegmatites in the Oromia Regional State intruded into a Precambrian terrane that is dominated by granitoids and ophiolites emplaced between 0.9 and 0.7 Ga. Collisional granitic magmatism occurred between 0.7 and 0.55 Ma. The pegmatites were classified as barren, beryl-columbite, complex spodumene and albite-spodumene types (Desta, Garbarino and Valera, 1995; Tadesse and Desta, 1996). In the zoned Kenticha LCT rare-metal granite pegmatite, the tantalum mineralisation is hosted by post-tectonic alaskite and associated granitic pegmatite within fractured and partly sheared serpentinite along a regional-scale thrust fault separating the low-grade Kenticha greenstone belt from medium- to high-grade gneisses.

Mozambique

From the 1950s until the civil war, various rare-element pegmatite deposits in the Alto Ligonha region have been mined for gemstones, industrial minerals and rare metals (REE, Be, Nb-Ta, Li, U-Th). After the civil war, mining and exploration licences have been granted to several mining companies, including NOVENTA. About 81 tonnes of Ta were produced from the Marropino deposit in 2006 (Mining Journal Supplement, 2007).

The pegmatites are part of the Zambesia Province in NE Mozambique. The Marropino pegmatite, ca 0.48 Ga old, is a deeply weathered, kaolinitised, zoned LCT rare-metal pegmatite that intruded mafic gneiss and schist of the Proterozoic Morrua Formation. The main orebody extends for 1 km in ENE-WSE direction and is up to 80 m thick. The pegmatites at Morrua, ca 50 km north of Marropino, are less altered. Drilling has indicated six pegmatite bodies each >3 m thick, and extending up to 1 km along strike (Cronwright, 2005). Tantalite (1900 tonnes concentrate) has been mined at Morrua from 1957 to 1979, besides spodumene, beryl and gold. At Mutala, 90 km north of Marropino, zoned pegmatites form up to 50 m thick bodies intruded into mica- and amphibole-schist of the Morrua Formation. Ancient mines have been reactivated by local garimpeiros to produce tantalite (Munhamola, Moneia).

Namibia

Lithium-beryllium and tin-columbite-tantalite occurrences are associated with rare-metal pegmatites in the Central Zone of the Damara orogenic belt in central Namibia. The tin pegmatites of Uis are historically the most important Ta producers of Namibia. Ta_2O_5 resources are estimated at 7.2 million tonnes (at 0.05 per cent) and 2.0 million tonnes (at 0.024 per cent; Fetherston, 2004). At present, coltan is only produced by local artisanal miners. Tin-bearing pegmatites are concentrated in four broad belts. The Cape Cross-Uis belt is a narrow NE-trending belt of up to 8 km in width and 100 km in length, and contains both zoned and unzoned cassiterite-bearing pegmatites. Most pegmatites are unzoned and up to 50 m thick. CGM, ixiolite, tapiolite and wodginite have been identified as Ta minerals.

Mining of the Tantalite Valley pegmatites of southernmost Namibia took place up to the 1970s and early during this century, but is closed at the moment. Reserves are estimated at 0.74 million tonnes at 0.043 per cent Ta_2O_5 (Fetherston, 2004). The pegmatites are part of the Mesoproterozoic Tantalite Valley Basic complex, which is composed of olivine gabbro and gneisses. Up to 1 km long and >10 m thick rare metal pegmatites of the LCT type intruded along a shear zone 0.93 to 0.88 Ga ago (Diehl, 1992). Pegmatites commonly show symmetrical zonation. The major minerals are quartz, K-spar, albite and white mica, accompanied by spodumene, lepidolite, amblygonite, beryllium and bismuth minerals, CGM and phosphates.

THE ANALYTICAL FINGERPRINT

The focus of this study is to develop a methodological approach that is capable of identifying the origins of tantalum ore concentrates. There are a number of factors which have to be taken into consideration.

1. The analytical time and effort have to be kept at a reasonable level. The costs for the certification should not raise the price for coltan unreasonably (eg application of a two-step procedure).
2. The quality and composition of the coltan ore concentrates available on the market may vary considerably depending on the technical equipment used for ore processing and the experience of the miners.
3. The mineralogical and chemical composition of Ta-Nb ores is extremely complex, based on the wide range of minerals of the columbite-tantalite solid solution series (CGM) and the ability of CGM to incorporate a large number of additional elements. Furthermore, coltan ores may also contain other tantalum-bearing mineral phases, like tapiolite ($FeTa_2O_6$), wodginite [$(Mn,Sn,Fe,Ti,Li)Ta_2O_8$], ixiolite [$(Nb,Ta,Sn,Fe,Mn,Ti)_4O_8$], bismutotantalite [$Bi(Nb,Ta)O_4$], stibiotantalite [$Sb(Nb,Ta)O_4$], minerals of the pyrochlore group such as microlite [$(Ca,Na)_2Ta_2O_6(O,OH,F)$], and further minerals of the complex fergusonite, aeschynite and euxenite mineral groups. Although confusing at first, these large variations in Ta-Nb minerals and ores also offer chances for a scheme of fingerprinting.

In this study we demonstrate the usefulness of a combined mineralogical-geochemical approach to distinguish the origin of coltan concentrates from five African countries; namely the DRC, Rwanda, Mozambique, Ethiopia and (southern) Namibia. This approach is based on an extensive database acquired and compiled for samples obtained from Africa's major coltan producing areas. Most data have been acquired from concentrates sold by artisanal miners, or recovered on site from mineral concentration plants. Most samples from the DRC, however, are from the Mineralogical Collection of the Museum for Central Africa in Tervuren.

Methodological approach

Coltan concentrates are studied in a step-by-step mode (Figure 3) subdivided into three different 'paths', which evolve from:

1. bulk methods to,
2. single grain, and
3. *in situ* methods.

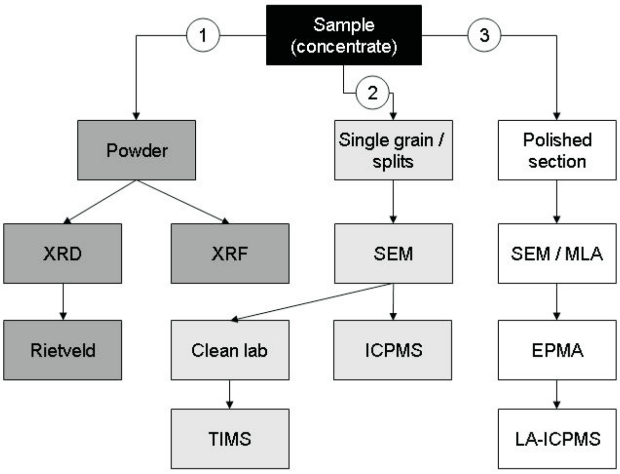

FIG 3 - Methods used for characterisation of the mineralogical parameters and geochemical compositions of Ta-Nb concentrates. Abbreviations: EPMA – electron probe microanalysis; ICPMS – inductively coupled plasma mass spectrometry; LA-ICP-MS – laser ablation ICPMS; MLA – mineral liberation analysis; SEM – scanning electron microscopy; TIMS – thermal ionisation mass spectrometry; XRD – X-ray diffractometry; XRF – X-ray fluorescence spectrometry. Analytical paths 1 to 3 are discussed in the text.

In first approximation, this sequence also coincides with increases in time and costs involved, but also with an enhanced knowledge on the grain-scale. Which path is followed depends on the information needed, questions asked, and also on the analytical equipment available, if the fingerprint will be applied by other laboratories in the future.

The first path (1; Figure 3) comprises bulk analysis of sample powders. Major and trace element concentrations are obtained by wavelength-dispersive-X-ray fluorescence analysis (XRF) on bulk samples (PANAlytical Axios and Philips PW2400). XRF on fused glass discs provides fast and cheap average concentration data of major and most relevant trace elements, except Li, Be, B and some of the REE. Due to the heterogeneous nature of the concentrates (sampling approaches; preconcentration techniques), comparison of the data is not easily possible. However, the method provides important data on the quality of a concentrate. The mineralogical composition of bulk samples is determined by X-ray diffraction analysis (XRD; Philipps PW 3710).

Analyses performed following the second path (2; Figure 3) include major and trace element analysis, including U-Pb dating, of single grains or fragments of single grains, requiring a minimum size of the grains used, and careful pre-examination by scanning electron microscopy (SEM). For major and trace element analysis by magnetic sector ICP-MS (Element 1) and ICP-OES one or several hand-picked grains (5 to 100 mg of sample material) are ground and dissolved in a mixture of hydrofluoric acid 48 per cent (20 - 200 µl) and nitric acid 65 per cent (200 µl). After complete dissolution deionised water is added to bring the volume to 20 ml. Aliquots from this solution are diluted by 0.15 M nitric acid and analysed by ICP-OES (Nb, Ta, Mn, Fe, Sn) and magnetic sector ICP-MS (32 trace elements including the REE). The dilution factors depend on the sample weight and the applied instrument and vary between 2.5 and 50. Analyses of CGM grains (or fragments of grains) that have been carefully selected from concentrates provide a reasonably fast and cheap method to chemically characterise single grains. Weighted sample portions are smaller, and detection limits are lower compared to XRF. However, contribution from mineral inclusions and the effects of zoning are neglected. The method provides quantitative major and trace element data of single grains. However, only a limited number of grains (about five to ten grains) from a concentrate can be analysed in a reasonable time interval. Nevertheless, the results agree well with *in situ* methods such as electron probe microanalysis and laser ablation ICP-MS, with the exception of some more mobile trace elements (eg Rb, LREE) that may be present in secondary phases, which are avoided during *in situ* analyses.

Following path 3 (Figure 3), polished sections are prepared and investigated by quantitative mineralogical analysis using the mineral liberation analysis software (MLA; JK Tech Pty Ltd, Australia) on a Quanta 600 FEG scanning electron microscope (FEI company), equipped with an EDAX 32 module. The MLA software combines backscattered electron (BSE) images with EDX spectra. For the MLA a series of BSE images including an X-ray spectrum for each mineral particle is collected. The offline processing routine compares the measured mineral spectra with known mineral standards to determine the mineral identity for each grain. The MLA is a fast and accurate method for quantitative determination of all particles in a sample, and is particularly well suited for mineral concentrates.

CGM and other Ta-Nb-bearing mineral phases are analysed for major and trace elements by electron microprobe (CAMECA SX100), with detection limits (LOD) of 200 ppm for trace elements. The advantages of wavelength-dispersive electron microprobe analysis (EPMA) of Ta-bearing phases are the high spatial resolution (ca 1 µm), the non-destructive nature of the method, simple analytical procedures including standardisation (against natural CGM and pure metallic standards), and the possibility of automatisation. The major disadvantages are long counting times for trace elements at reasonable LODs. In order to collect a representative number of analyses from a tantalum concentrate, ~100 - 150 grains are analysed; taking abundant zoning into account, between 200 and 500 analyses are carried out, consuming altogether ~50 to 125 hours. The results are populations, or fields of analytical data in binary diagrams which, in principle, represent fractionation and post-magmatic evolution trends of CGM (Figure 4; eg Černý and Ercit, 1985; Černý, 1989). Often, plots of the major element ratios XMn (100 × Mn/(Mn+Fe)) and XTa (100 × Ta/(Ta+Nb)) enable discrimination of different ore provinces even down to a deposit scale. Many trace elements also follow fractionation trends with XMn and/or XTa. Others, however, do not show coherent behaviour and may be used to discriminate the origin of the sample. EPMA is the only method available to date to quantitatively resolve complex zoning patterns of CGM (eg Lahti, 1987). Many zones are less than a few micrometres wide (Figure 5) and cannot be measured by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Chemical variation within zoned grains is substantial, and in some cases as large as the overall variation of all CGM. Possibilities for discrimination of tantalum pegmatite sources based on EPMA thus include variations of major and trace element concentrations (>200 ppm) in a population of grains, and in single crystals. Both are considered viable fingerprints to their source.

For determination of low levels of trace elements the LA-ICP-MS technique (Nd:YAG laser – 266 nm New Wave Merchantek LUV 266x; Agilent 7500i quadrupole ICP-MS; University of Würzburg) is applied. Thirty-seven trace elements including the REE are determined. Argon is used as the carrier

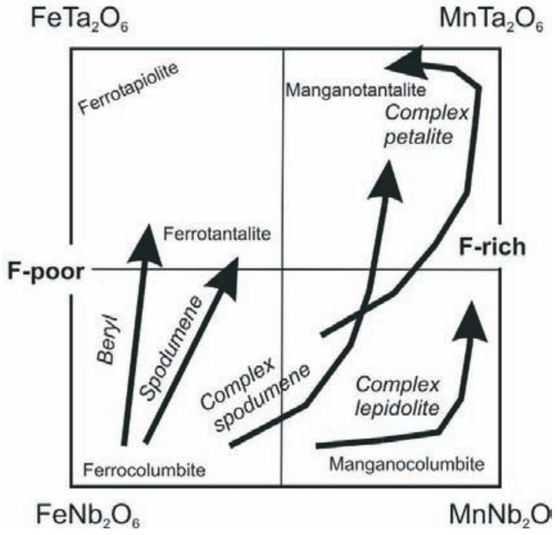

FIG 4 - General fractionation trends of CGM in the columbite quadrilateral (after Černý, 1989).

gas. The spot size varies from 30 to 50 µm. The glass reference materials NIST SRM 610 and 612 with the values of Pearce *et al* (1997) are used for external calibration and calculation of trace elements by the GLITTER Version 3.0 (Macquarie Research Ltd, 2000). Advantages of the LA-ICPMS method are the significantly lower detection limits for trace elements (maximum LOD values are mostly ≤1 ppm; higher maximum values for Mg, Al, Si, Ca, Ti, As and Sn) compared to the analysis by EPMA. Disadvantages include the destructive nature of the method and its lower spatial resolution compared to EPMA. Possible contamination of the analysis by micromineral inclusions ablated at depth during single spot analysis is generally easily recognised and can be eliminated in most cases.

Uranium-lead dating is carried out both on crystal fragments using conventional thermal ion mass spectrometry (TIMS; BGR and University of Toronto), and *in situ* using a Thermo-Scientific Element II sector field ICP-MS coupled to a New Wave UP213 ultraviolet laser system with low-volume ablation cell (University of Frankfurt). Spot size varies from 30 to 60 µm. Raw data are corrected for background signal, common Pb, laser induced elemental fractionation, instrumental mass discrimination, and time-dependant elemental fractionation (Gerdes and Zeh, 2006).

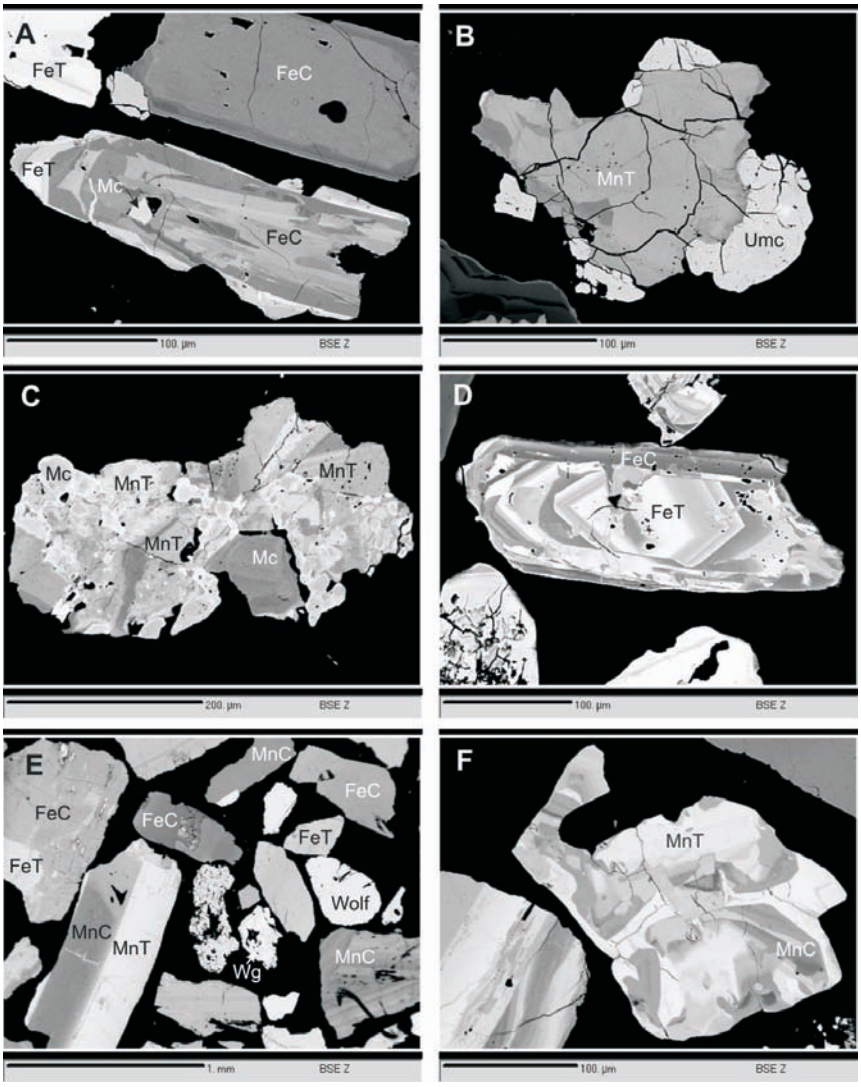

FIG 5 - Backscatter electron images (CAMECA SX 100 electron microprobe) of coltan concentrates from (A) Gatumba, Rwanda; (B) Ruhanga, Rwanda; (C) Nyarigamba, Rwanda; (D) Nyambisindu, Rwanda; (E) Yubili mine, Kivu Province, DRC; (F) Manono, Katanga, DRC. Abbreviations: FeC, ferrocolumbite; FeT, ferrotantalite; MnC, manganocolumbite; MnT, manganotantalite; Mc, microlite; Umc, Uranmicrolite; Wg, wodginite; Wolf, wolframite.

The analytical reproducibility (eg GJ-1 reference zircon) of the $^{206}Pb/^{238}U$ and $^{207}Pb/^{206}Pb$ is commonly about 0.8 and 0.5 per cent, respectively. No matrix dependent U/Pb fraction has been observed.

The chemical procedures to separate U and Pb for TIMS analysis are adapted from Romer and Wright (1992) and Romer and Smeds (1994). U and Pb are measured in multicollector mode on a MM354 TIMS (University of Toronto) and a ThermoFinnigan Triton (BGR). Isoplot (Ludwig, 2003) is used for graphical presentation of U-Pb isotope data and age calculation. U-Pb dating can yield highly precise and concordant mineral ages provided CGM grains free of inclusions or alteration phenomena are selected. However, this is nearly impossible due to the opaque nature of the CGM. Thus, U-Pb dating of CGM often yields complex and discordant ages. To minimise the effects of disturbance of the U-Pb isotopic system in CGM, strong HF leaching of the grains prior to dissolution has been proposed (Romer and Wright, 1992). At the University of Toronto, individual fragments (<100 µm; <1 mg) not leached in HF are analysed separately ('single-grain method'). This allows careful inspection of the quality of the fragments to be dated. However, variations in age within a concentrate cannot be detected by this method. At the BGR, fragments from different grains (fragment size 0.8 - 0.16 mm; mass 1 - 4 mg) are investigated ('multigrain method'). The fragments are leached in several steps using warm diluted HF, HCl and HNO_3 prior to dissolution. Both approaches of U-Pb TIMS dating are time consuming because many steps of quality controlling pre-analytical preparation, chemical dissolution, chemical U-Pb separation and mass-spectrometric U-Pb isotopic measurements are required. In addition, chemical processing of the grains and subsequent handling of the U-Pb element fractions have to be performed under clean-air conditions. On the other hand, TIMS dating is the state-of-the-art method to obtain precise U-Pb dates and useful for discrimination of sources with small (< 10 Ma) differences in age as are present in the Kibaran province of central Africa.

RESULTS AND DISCUSSION

Tantalum-enriched pegmatites are found in the intermediate to outermost parts of zoned pegmatite aureoles surrounding parental granites (Černý, 1989). Granitic pegmatites are grouped into five classes, namely the:

1. abyssal;
2. muscovite;
3. muscovite-rare element;
4. rare-element; and
5. miarolitic classes (Černý *et al*, 2005; Ercit, 2005).

The LCT (Li, Cs, Ta) and NYF (Nb, Y, F) petrogenetic families within the rare-element class are important hosts to Ta-Nb mineralisation. Based on their mineral parageneses, rare-element pegmatites may be further subdivided into five pegmatite types: the rare earth, beryl, complex (with spodumene, petalite, amblygonite, lepidolite and elbaite subtypes), albite-spodumene and albite types (Černý *et al*, 2005).

No matter which classification is adhered to, the chemical composition of CGM, and other Ta-bearing phases systematically varies according to the pegmatite type (Figure 4). In beryl pegmatites, CGM are Fe-Nb dominated, mostly ranging from ferrocolumbite to ferrotantalite, whereas in highly fractionated pegmatites of the complex type, CGM are commonly Mn- and Ta-rich and display fractionation trends from manganocolumbite to manganotantalite. Large compositional variations within distinct pegmatites are rather common.

Up to date, a vast amount of electron microprobe data on CGM has accumulated in the literature. The XMn (100 × Mn/(Mn+Fe), atomic ratio) versus XTa (100 × Ta/(Ta+Nb), atomic ratio) diagram identifies a pegmatite type or subtype (eg, Breaks, Selway and Tindle, 2005), and discrimination of different pegmatites might be achieved in cases as well. Most data sets contain concentrations of Ti, Sn, rarely of W, Zr, U, Sc, Y, Mg and other elements substituting into the CGM structure. Černý *et al* (2007) investigated the role of Zr and Hf in CGM and wodginite. The trace element composition of CGM in the ppm range has not been investigated previously.

The possibility to use major and trace element compositions to fingerprint the origin of Ta concentrates from unknown locations has not been taken into account. During the Congolese wars, problems arose with coltan that was illegally mined from the Kahuzi-Biega National Park in the DRC, which is a major habitat of lowland gorillas. Poirier and Lastra (2002) postulated that coltan concentrates derived from the National Park may be distinguished from coltan concentrates from other parts of the DRC and of Rwanda based on their mineralogical composition (ie the presence or absence of cassiterite) and microprobe major element data (XMn versus XTa diagram). However, this study was based on seven CGM-bearing samples only and, therefore, does not fulfil any statistical criteria. In the following, we will demonstrate that major element chemistry of CGM and mineralogical composition of concentrates in most cases does not unequivocally discriminate between different mining areas within a given region of interest. This will be demonstrated using a sample set comprising 151 samples, including 86 concentrate samples, from pegmatite deposits in the DRC, Rwanda, Ethiopia, Mozambique and southern Namibia (Tantalite Valley Complex). Data are grouped according to their country of origin: this is a prerequisite for the fingerprint of minerals from conflict areas.

The fields defined by the major element compositions of the CGM overlap to a large extent (Figure 6a). It is hardly possible to prove or disprove the origin of a group of CGM grains, especially when samples plot within an area of XMn ratios between 40 and 100 and XTa ratios between ten and 70. The presence of ferrotapiolite discriminates concentrates from the DRC and Rwanda, because this phase has not been identified so far in samples from the other countries. Fe-rich ferrocolumbite to ferrotantalite (XMn <40) is also restricted to the DRC and Rwanda.

Better discrimination of overlapping fields is achieved using minor elements such as W, Sn, Ti, Zr, Hf and U that are routinely measured by EPMA if concentrations exceed 200 ppm. Although, in many cases, these elements will be present in lower concentrations, they may be used for further discrimination (Figure 6b). Tungsten concentrations are highest in CGM from the DRC (up to four weight per cent WO_3), whereas CGM from other countries rarely exceed 0.6 weight per cent WO_3. Populations from Mozambique and Ethiopia will follow different fractionation trends, especially in the XTa versus WO_3 diagram. The manganotantalite from southern Namibia plots in a distinct field to rather high WO_3 concentrations. The XMn and XTa versus WO_3 diagrams will allow identification of concentrates from the DRC only at high W concentrations. Low tungsten concentrations, which are also present in some DRC samples within the data set, will not be unequivocally discriminated using this approach.

As a next step, a quantitative measurement of the mineralogical composition is used to further discriminate samples that plot at WO_3 concentrations <0.6 weight per cent. Using the presence of minor phases such as tapiolite, cassiterite or bismutotantalite discriminates concentrates from:

- Mozambique (bismutotantalite present, cassiterite and tapiolite absent);
- Ethiopia and southern Namibia (bismutotantalite, cassiterite and tapiolite largely absent); and

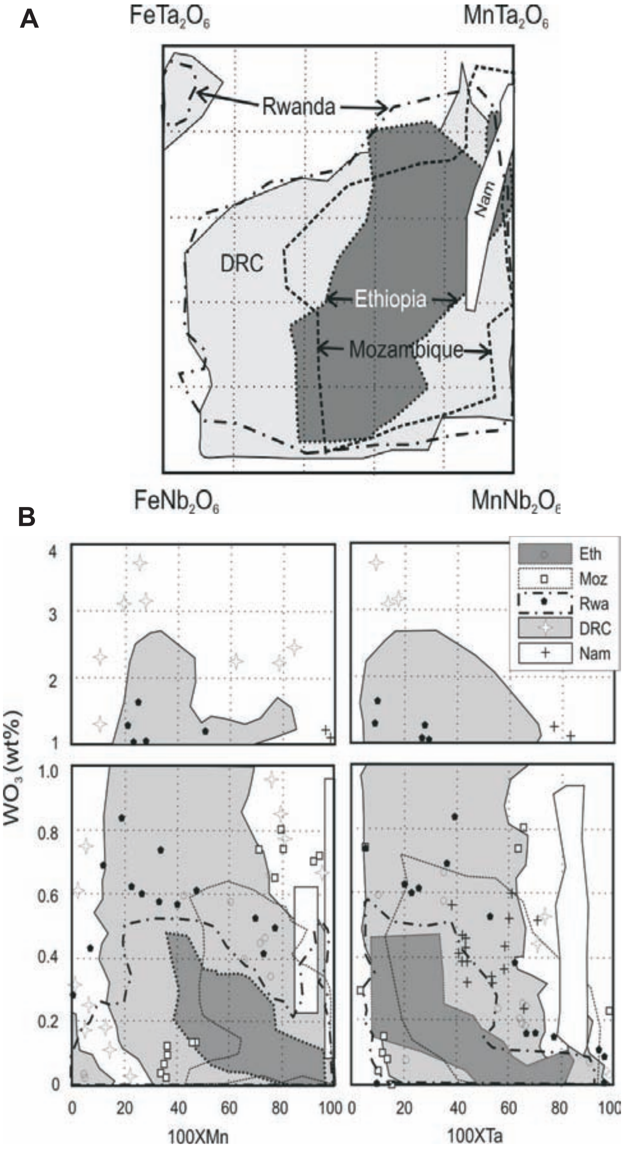

FIG 6 - Electron microprobe analyses of CGM from African coltan areas. Individual point analyses are grouped according to their countries of origin. Numbers of analyses used for constructing the fields are as follows: DRC (Kibaran occurrences only) 1383, Rwanda 1962, Ethiopia 473, Mozambique 585, Namibia 538. Note that both columbite-tantalite and ferrotapiolite data are plotted. (A) XMn versus XTa diagram; (B) XMn and XTa versus WO_3 (wt per cent); note different scaling on y-axis. XMn = 100 × Mn/(Mn+Fe), XTa = 100 × Ta/(Ta+Nb), both in atomic per cent.

- DRC and Rwanda (bismutotantalite absent, cassiterite and tapiolite commonly present) (Table 1).

In case 2, age determination will unequivocally discriminate Ethiopia (ca 530 Ma; Küster *et al*, 2007) from southern Namibia (ca 980 Ma; Melcher *et al*, 2008). In case 3, age determination will not be able to discriminate concentrates originating from Kibaran-age (ca 930 - 1000 Ma) pegmatites of the DRC and Rwanda (Figures 7c and 7d). However, CGM originating from the northern Congo craton (Ituri Province, DRC) will be easily depicted due to their significantly older ages (2000 - 2500 Ma; Figure 7b).

Manganotantalites with moderate to low tungsten concentrations from concentrates lacking cassiterite, tapiolite and bismutotantalite may originate from southern Namibia, the DRC, Rwanda or Mozambique. Mozambique will yield

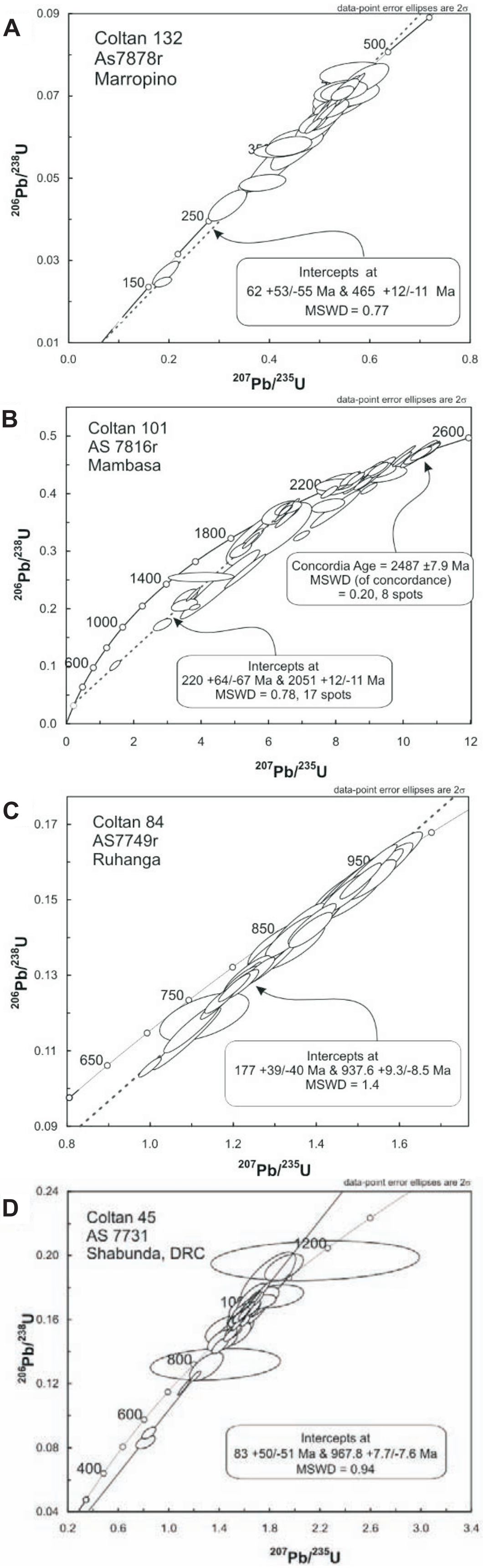

FIG 7 - U-Pb isochron diagrams for coltan concentrates from (A) Marropino, Mozambique; (B) Mambasa, Ituri Province, DRC; (C) Ruhanga, Rwanda; (D) Shabunda, Kivu Province, DRC; LA-ICPMS data; each ellipse corresponds to one CGM grain.

TABLE 1

Frequencies of minerals in coltan ore concentrates from pegmatite provinces in Africa as determined by MLA.

	Critical concentration (%)	DR Congo/ Kibaran	Mean	DR Congo/ Eburnean	Mean	Rwanda	Mean	Mozambique	Mean	Ethiopia	Mean
Ferrocolumbite	5.0	xx	19.70	xx	4.82	xx	9.15		0.06		0.22
Ferrotantalite	5.0	x	5.33	xxx	26.80	xx	10.90		0.14		0.10
Manganocolumbite	5.0	xxx	18.30	xxx	20.00	xxx	15.30	x	0.97	xx	9.84
Manganotantalite	5.0	xxx	20.90	xxx	28.00	xxx	18.70	xxx	17.50	xxx	67.80
Ferrotapiolite	1.0	x	4.81	xxx	11.40	(x)	2.77		0.06		<0.01
Microlite	0.5		0.04		0.03	(x)	2.95	xxx	8.68		
Uranmicrolite	0.2		0.02		0.01	(x)	0.87	xxx	0.61	x	1.22
Wodginite	0.5	(x)	1.64		<0.01	x	2.00		0.06		0.17
Bismutotantalite	0.2		<0.01		<0.01		<0.01	xx	0.55		<0.01
Cassiterite	1.0	xx	7.36		<0.01	xxx	16.80		<0.01		<0.01
Haematite/magnetite	1.0	x	6.09		<0.01	x	4.69	xx	8.46	x	6.19
Ilmenite	1.0	xx	4.53	xx	0.90		0.89	x	5.25		0.68
Monazite	0.2	x	0.27		<0.01		0.13	xx	6.56		0.03
Rutile	0.5		0.43	xx	5.46		0.44		0.30		0.05
Zircon	0.2		0.27		0.05	xx	1.56	xx	0.44	x	0.23
Number of samples		20		2		30		7		5	

Legend: Fraction of samples with higher concentrations of a mineral than the defined critical concentration for the respective mineral phase: xxx – ~75 - 100 per cent; xx – about 50 - 75 per cent; x – about 25 - 50 per cent; (x) – individual samples with high concentrations of the mineral occur.

a younger age (eg 450 - 500 Ma; Figure 7a), whereas the remaining locations will give similar ages (930 - 1000 Ma). In this case, trace element diagrams will help unravel their origin. We find rare earth element concentrations and patterns to be very useful to discriminate Kibaran samples from nearly all other coltan pegmatite areas. Kibaran samples usually lack Eu anomalies, or have small negative Eu anomalies (Eu*, calculated as $(0.5 \times (Sm_N+Gd_N))/Eu_N$), 0.5 to 10) and low to moderate $MREE_N/HREE_N$ ratios (0.1 - 10). Manganotantalite from southern Namibia is characterised by strong negative Eu anomalies (Eu* > 20) and high $MREE_N/HREE_N$ ratios (>10). Using a trace element such as Bi, fields might be constructed that overlap only to a small degree (Figure 8).

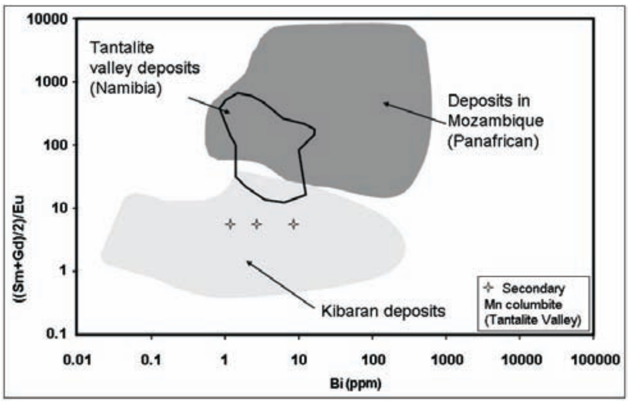

FIG 8 - Diagram of Bi concentration (ppm) versus Eu anomaly of CGM from the central African Kibaran Province, the Tantalite Valley Complex in southern Namibia and Panafrican pegmatites from Mozambique.

Having excluded southern Namibia as the origin of a concentrate, we still have to resolve a possible origin from the DRC and Rwanda. Analysis of many concentrates from different areas within the Kibaran Province has yielded amazing differences of major and trace element compositions. In most cases, microprobe data of a large number of CGM in a given concentrate will define a field at low, intermediate or high XMn values, with zoning trends in XTa in individual crystals (Figure 9). These reflect the general fractionation trends of beryl pegmatites (low XMn), spodumene pegmatites and various complex rare-element pegmatite groups (intermediate to high XMn) (Černý, 1989). Within such groups, further discrimination is possible using trace element ratios (Figure 10). This last step will finally enable to discriminate the origin of a sample even down to the deposit scale.

A schematic flow chart illustrates the general options to distinguish coltan concentrates from ore provinces of similar geological age (Figure 11), arranged in a step-by-step mode from modal mineralogy to major and trace element chemistry of CGM.

CONCLUSIONS

Without doubt, there are regional and local variations in the composition of coltan. These are due to differences in geological age and mineralogical and chemical composition of host pegmatites and their derivative heavy mineral concentrates. Zoned CGM crystals perfectly mimic the chemical evolution of pegmatitic melts and can thus be used as monitors of the fractionation stage of the source rocks. This allows distinction of locations even in districts and provinces of similar geological ages, similar host rocks or similar parental melt compositions. Each tantalum deposit has its unique characteristics. Therefore, a fingerprint of samples of suspect or unknown origin should be possible when a large and high-quality analytical database is available.

However, it takes appreciable analytical efforts and time to completely characterise a concentrate. In the future, methods will be developed that allow fast screening based on modal mineralogy and trace element and/or isotope geochemistry.

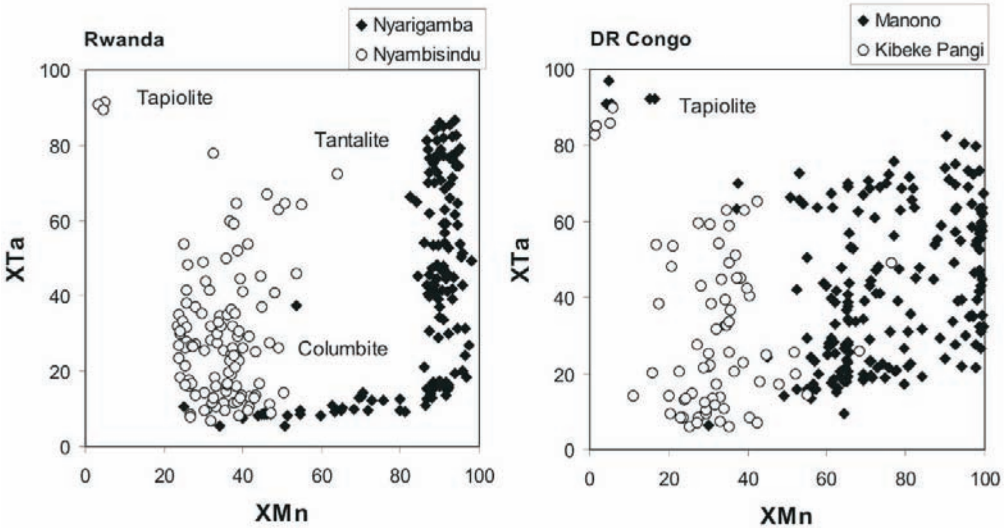

FIG 9 - Variation of XMn and XTa in CGM and tapiolite in four coltan concentrates from Rwanda and the DRC.

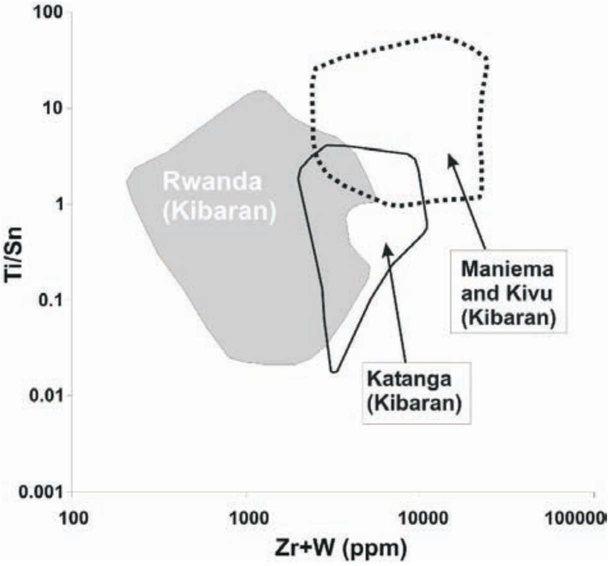

FIG 10 - Zr+W (ppm) versus Ti/Sn for CGM from the central African Kibaran Province, discriminating different geographical regions.

Minerals are traded on an open global market. However, the public is increasingly aware of 'clean' products, which are mined in an environmentally sound and socially tolerable way in countries which accept the rules of good governance. This is true especially for minerals imported from conflict areas. The worldwide implementation and acceptance of the 'Kimberley Process' for diamonds proves that the international community is no longer willing to accept materials from conflict areas or materials produced under criminal circumstances. The analytical fingerprint of 'coltan' may assist in the establishment of a control instrument in an envisaged certification of the production and trade chain of coltan.

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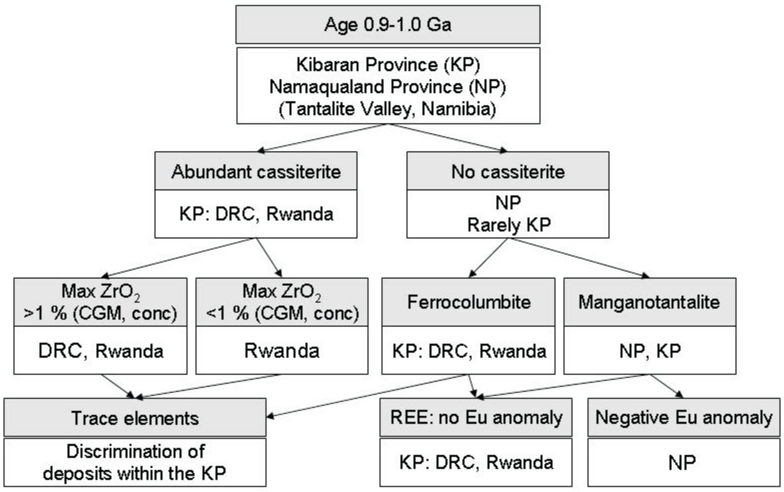

FIG 11 - Flow chart exemplifying the discrimination of tantalum concentrates (0.9 - 1.0 Ga old) from central and southern Africa. CGM = columbite-group minerals; conc = concentrate.

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