See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/332085754>

Nb-Ta-Sn-W distribution in granite-related ore systems: fractionation mechanisms and examples from the Karagwe-Ankole Belt of Central Africa

Chapter · May 2019

DOI: 10.1002/9781119290544.ch4

CITATIONS

2

READS

520

1 author:

Niels Hulsbosch

KU Leuven

23 PUBLICATIONS 148 CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:

Chemical fractionation in granite-related ore systems: evidence from Nb-Ta-Sn pegmatite-type and Sn-W quartz vein-type mineralisation in the Karagwe-Ankole Belt (Rwanda). [View project](#)

The influence of P, B and Cl on the evolution of LCT pegmatites and rare-metal mineralisation processes: the example of the Buranga pegmatite, Rwanda [View project](#)

4

Nb-Ta-Sn-W Distribution in Granite-related Ore Systems: Fractionation Mechanisms and Examples from the Karagwe-Ankole Belt of Central Africa

Niels Hulsbosch

ABSTRACT

Tantalum, niobium, tin, and tungsten mineralization typically occurs worldwide in close proximity to fractionated peraluminous leucogranites. These granite-related ore deposits show a diversity of mineralization modes, ranging from plutonic-hosted breccia and hydrothermal vein-stockwork systems to (peri)batholithic greisens, skarns, pegmatites, and hydrothermal veins. In the Mesoproterozoic Karagwe-Ankole orogenic belt (KAB) of Central Africa, numerous early Neoproterozoic Nb-Ta-Sn-W rare-metal deposits formed as primary mineralization in hydrothermal quartz veins, magmatic lithium-cesium-tantalum (LCT) family pegmatites and associated intrapegmatitic greisens. This chapter reviews the petro- and metallogensis of Nb-Ta-Sn-W granite-related ore deposits, as they occur in the Rwandese part of the KAB, and provides a general overview of the geochemical mechanisms behind the formation of pegmatite- and quartz vein-hosted deposits and the distribution and enrichment of the ore elements Nb, Ta, Sn, and W in the different metallogenic subsystems (i.e., granites, pegmatites, and veins). Moreover, this chapter assesses the observed close spatiotemporal association between leucogranites, pegmatites, and quartz veins in terms of a direct genetic link between the mineralization and the felsic magmatism. Based on this review and element distribution calculations, an integrated orthomagmatic metallogenic model for Nb-Ta-Sn-W mineralization in the KAB is demonstrated. This model can form a major tool in the exploration for granite-related ore deposits in general.

4.1. INTRODUCTION

Granites are able to concentrate a large number of chemical elements, such as Li, Rb, Cs, Be, Cu, Mo, Sn, Zr, Th, U, Nb, Ta, W, Au, and rare earth elements, several order of magnitude above their respective crustal abundances (Černý et al., 2005; Taylor & McLennan, 1985). This chapter will mainly focus on rare-element mineralization associated with peraluminous granites, pegmatites, and related quartz veins, which are typically enriched in Li,

Rb, Cs, Ta, Nb, Ta, Sn, and W (Linnen & Cuney, 2005; Raimbault et al., 1995). Rb and Cs are geochemically classified as large-ion lithophile element (LILE) because of their small charge to ionic radius ratios. Gast (1972) also included Li as a LILE since it has a large radius to charge ratio, despite its small radius. Nb, Ta, W, and probably Sn are High Field Strength Elements (HFSE) with high charge-to-ionic-radius ratios. Both LILE and HFSE do not substitute into common rock-forming minerals and thus behave incompatibly during the crystallization of silicate melts (e.g., Breiter et al., 2007; Linnen & Cuney, 2005). Except for Sn, these metals have been classified based on their economic importance and supply risk as critical raw materials for the high-tech industry (EC, 2017).

*KU Leuven, Geodynamics and Geofluids Research Group,
Department of Earth and Environmental Sciences, Leuven,
Belgium*

Ore Deposits: Origin, Exploration, and Exploitation, Geophysical Monograph 242, First Edition.

Edited by Sophie Decrée and Laurence Robb.

© 2019 American Geophysical Union. Published 2019 by John Wiley & Sons, Inc.

Figure 4.1 (a) Overview of major W-Sn provinces in the world in relationship to Nb-Ta-Sn pegmatite provinces. 1: North American Cordillera; 2: Colorado Plateau; 3: Appalachian; 4: Bolivian; 5: east Brazilian; 6: Iberian-Panasqueira; 7: Massif Central; 8: Cornwall; 9: Erzgebirge/Krušné Hory; 10: east African; 11: Kibara Metallogenic; 12: Nigerian; 13: north Caucasian; 14: east Uralian; 15: central Kazakhstan; 16: Gorno-Altai; 17: Kalba-Naryn; 18: south Tien Shan; 19: Mongolian Transbaikalian; 20: Verkhoyansk-Kolyma; 21: Chukotka; 22: Sikhote-Alyn; 23: Japanese; 24: southeast China; 25: Myanmar-Thailand-Malaysia; and 26: east Australian province (after Taylor, 1979; Beus, 1986; Romer and Kroner, 2016; and Melcher et al., 2017). (b) Schematic diagram illustrating primary granite-related W-Sn deposit styles in combination with their type-localities. Styled partly after Baker et al. (2005).

Three major categories of granite-related ore deposits - sensu stricto- could develop in the vicinity of granite intrusions and are observed worldwide (Fig. 4.1): (1) disseminated magmatic mineralization in granites themselves, (2) mineralization in late-magmatic pegmatites intruding as endo- and exodikes, and (3) mineralization in magmatic-hydrothermal or metasomatic deposits imprinted on the granites, pegmatites, or on the immediate host rocks (i.e., veins, greisens or skarn; Baker et al., 2005; Beus, 1986; Černý et al., 2005;

Štemprok, 1987; Taylor, 1979). Peraluminous rare-metal granites with magmatic disseminated mineralization are locally associated with vein- and greisen-type mineralization (Breiter et al., 1999), both requiring water saturation and under hydrostatic regime (Černý et al., 2005). However, significant hydrothermal deposits are generated from granites that lack magmatic disseminated ore bodies or show no direct relationships with a parental granite (Audétat et al., 2000a; Pettke et al., 2005). Reciprocally, most evolved

Figure 4.2 Conceptual outline of the geographical and geological setting of the major rare-metal deposits of the Karagwe-Ankole (KAB) and Kibara (KIB) belts in the Kibara Metallogenic Province of the Central African Great Lakes region; B: Bujumbura; BB: Bengo-Biri; Bi: Bisesero; Bk: Bukavu; Bu: Busanga; Bug: Bugarama; GG: Gatumba-Gitarama pegmatite field; Gi: Gifurwe; K: Kigali; Ka: Kampala; Kaa: Kabaya; Kab: Kabunga; Kai: Kailo; Kal: Kalanda; Kas: Kasese; Kl: Kalima; Ki: Kivuvu; Kib: Kibungo; KaM: Kamituga-Mobale; KM: Kirundo-Muyinga; KY: Kabambare – Yungwe; L: Lowa; Kis: Kiseke; M: Maniema; Ma: Matala; Mi: Mitwaba; MK: Manono-Kitotolo; MN: Musha-Ntungwa; Mu: Mulehe; Mua: Muana; Mui: Muika; Mw: Mwenga; N: Nyakabingo; Ny: Nyangulube; P: Punia; R: Rutongo; Ru: Ruhembe; Rw: Rwinkwavu; S: Sasa (after Dewaele et al., 2015; Fernandez-Alonso et al., 2012; Koegelenberg et al., 2015; Pohl et al., 2013).

granites are not associated with W-Sn mineralization (Romer & Kroner, 2015; Romer & Kroner, 2016). In addition, pegmatites are often not associated with disseminated magmatic or hydrothermal mineralization (Černý et al., 2005).

The co-occurrence of Nb-Ta-Sn pegmatite-type and Sn-W quartz vein-type mineralization in the Karagwe-Ankole Belt

(KAB) region of the Kibara Metallogenic Province in Central Africa (Fig. 4.2) provides a first-class and, moreover, relatively rare opportunity to investigate the geochemical evolution of a global granite-related ore system and to evaluate the element distribution in space and time between pegmatites and quartz veins during the magmatic-hydrothermal transition. Another example of granite-related, rare-element

mineralization in cogenetic pegmatites and quartz veins is described for the Neo-Archean Preissac-Lacorne batholith (Superior Province, Canada; Mulja et al., 1995b).

The Rwandan part of the KAB is well known for its richness in granite-related ore deposits spatiotemporally associated to the barren early Neoproterozoic Kibara Sn granites or locally named G4 granites of Rwanda (Figs. 4.2 and 4.3; Pohl, 1994; Pohl et al., 2013; Tack et al., 2010), for example, the Nb-Ta-Sn Gatumba-Gitarama pegmatite field, the Ntungwa Nb-Ta-Sn pegmatite, the Nyakabingo W quartz vein, the Rutongo Sn quartz vein, and the Musha Sn quartz vein type localities (Fig. 4.3). An important feature of the Kibara Sn granites (G4) in the KAB is their frequent occurrence in well-defined composite plutons dominantly composed of an older generation (~1375 Ma) of granites (Pohl, 1994). This work will provide a review, discussion, and interpretation of the metallogensis of Nb-Ta-Sn-W granite-related ore deposits based on the example of the KAB. Main fractionation processes responsible for element enrichment will be discussed. As a conclusion, a general orthomagmatic metallogenic model will be presented.

4.2. ORTHOMAGMATIC OR RECYCLED METAL ORIGIN

Nb, Ta, Sn, and W deposits typically occur worldwide in close proximity to differentiated, late- to post-orogenic granites mainly peraluminous in composition (Baker et al., 2005; Černý et al., 2005; Melcher et al., 2015; Melcher et al., 2017; Romer & Kroner, 2016). One of the major research axes on these deposits is focused around the question of whether a close spatiotemporal association implies a direct genetic link between the mineralization and the granitic magmatism, especially for the case of peribatholithic deposits (Černý et al., 2005; Förster et al., 2009; Harlaux et al., 2017a; Wilkinson, 1990). This debate opposes two end-member models as conceptualized in Figure 4.4: (1) the granitic magma acted as the direct source of the ore metals and the fluids (i.e., the orthomagmatic hypothesis: Audétat et al., 2000b; Moura et al., 2014; Reyf, 1997; Varlamoff, 1972; Webster, 2004), or (2) the intrusion induced thermal convection of metamorphic fluids, which extracted ore metals from surrounding rocks, mainly metasediments, within the circulation cell (i.e., recycling hypothesis: Linnen & Williams-Jones, 1995; Marignac & Cuney, 1999; Marignac & Cathelineau, 2010; Vindel et al., 1995). Mixing and cooling of the magmatic fluid with (preheated) meteoric water, circulating in the upper parts of the granite cupola, has been proposed by Audétat et al. (2000b) at the Mole Granite (Australia) and led toward precipitation of W in intragranitic or perigranitic quartz veins. While Nb-Ta-oxide mineralization in pegmatites is generally accepted to be formed

cogenetic with magmatic granite-pegmatite differentiation (Breiter et al., 2007; Černý et al., 2005; Linnen et al., 2014; London, 2008), the contribution of granite-derived fluids as direct W and Sn metal sources is still debated for peribatholithic quartz-wolframite-cassiterite veins (Hulsbosch et al., 2016; Marignac & Cathelineau, 2010).

In order to relate the Kibara Sn granites as potential sources to the pegmatite- and quartz vein hosted rare metal mineralization, the geochemical distribution of elements among the different deposit styles should be evaluated. Previous metallogenic research in the Kibara Metallogenic Province, applying petrographical, geochemical, and fluid inclusion studies, focused mainly on the W and Sn quartz vein deposits (e.g., Dewaele et al., 2010; Pohl, 1994; Pohl & Günther, 1991). This has led to contrasting interpretations concerning the metal source for W and Sn mineralization in the quartz veins (see discussion in De Clercq, 2012; Hulsbosch et al., 2016). For example in the case of the Rutongo Sn and Nyakabingo W quartz veins deposits, the pristine signatures were overprinted by fluid-rock reactions during mineralization at the deposit site, as indicated by studies of fluid inclusions (aqueous-gaseous $\text{H}_2\text{O}-\text{CO}_2-\text{CH}_4-\text{N}_2$ -NaCl fluids), minerals, and bulk rocks (intense wall-rock interaction), and isotopes ($\delta^{18}\text{O}_{\text{quartz}}$: between 13.6 and 15.6‰ V-SMOW; highly variable $\delta\text{D}_{\text{quartz}}$: between -47 and -64‰ V-SMOW) (see details in sections 4.3. & 4.4.). This was interpreted as a metamorphic origin for these quartz veins (De Clercq et al., 2008; Dewaele et al., 2010) as opposed to a magmatic-hydrothermal origin (Pohl, 1994; Pohl et al., 2013). Overprinting of the source signature record of Sn-W hydrothermal quartz-vein deposits by fluid-rock interactions is common and also observed elsewhere (see e.g., Chicharro et al., 2016; Heinrich, 1990; Polya et al., 2000; Wood & Samson, 2000). These difficulties imply that genetic metal source studies of Sn-W deposits cannot be firmly based on the investigation of individual quartz-vein systems only.

4.3. ANATECTIC ORIGIN OF PEGMATITES

One of the current discussions in pegmatite research is centered around the question of whether the formation of pegmatites is mainly driven via granitic differentiation or anatectic processes (Simmons & Webber, 2008). Many pegmatite fields worldwide are known to form by differentiation from granitic melts (Černý, 1991c; London, 2008; London, 2014). In many cases, the connection of pegmatites with a parent pluton is inferred from spatial relationships, age determinations, and geochemical characteristics (e.g., London, 2008; Mulja et al., 1995a; Mulja et al., 1995b). However, there is a renewal of interest for the nongranitic or anatectic origin of some pegmatite fields because these pegmatites seem not to be

Figure 4.3 Geological map of Rwanda and the Karagwe-Ankole belt (KAB). The most important granite-related ore deposits of Rwanda are indicated. B: Bugarama; Bu: Bugalula; ED: eastern domain; G: Gifurwe; GG: Gatumba-Gitarama; K: Kigali; Ka: Kabaya; Ku: Kuluti; L: Lutsiro; M: Mwaka; MN: Musha-Ntunga; N: Nyakabingo; R: Rutongo; Rw: Rwinkwavu; WD: western domain. After Fernandez-Alonso (2007) and Koegelenberg et al. (2015). Geochronological data from (1) Buchwaldt et al. (2008), (2) Tack et al. (2010), (3) Deblond et al. (2001), (4) Mäkitie et al. (2014), (5) Fernandez-Alonso et al. (2012), (6) Westerhof et al. (2014), (7) Maier et al. (2007).

Figure 4.4 End-member metallogenic models for the development of granite-related Nb-Ta-Sn pegmatite-type and Sn-W quartz vein-type deposits. (a) The orthomagmatic hypothesis in which the granitic magma acted as the direct melt/fluid source of the ore metals. A continuous genetic relation can exist from a differentiated granite and pegmatite system towards the quartz veins (e.g., Varlamoff, 1972; Webster et al., 1997). Alternatively, the pegmatite and quartz vein systems could form disconnected but were both derived from a common granite source system (e.g., Audétat et al., 2000b; Chicharro et al., 2015; Hulsbosch et al., 2016; Moura et al., 2014). (b) The recycling hypothesis in which convection of external metamorphic fluids extracted ore metals from igneous and metasedimentary rocks within the circulation cell (e.g., Dewaele et al., 2010; Marignac & Cuney, 1999; Vindel et al., 1995).

associated with potential parental granites, or when they are, granite and pegmatites are slightly diachronous (Černý, 1991b; Müller et al., 2017; Shaw et al., 2016). In high-grade metamorphic areas, low-degree partial melting of quartzo-feldspathic or amphibolitic rocks can produce pegmatitic melts in the absence of felsic magmatism or generate pegmatites, which do not demonstrate a genetic relationships with spatially associated granitic plutons (Müller et al., 2015; Roda Robles et al., 1999; Shearer et al., 1992; Simmons & Webber, 2008). For example, in the Late-Proterozoic Sveconorwegian pegmatite province of southern Norway and southwest Sweden, more than 5000 rare-element pegmatites with a dominant niobium-yttrium-fluorine (NYF) signature are not related to a parental granite generation. Instead, they occur in areas of high-grade metamorphism and are the result of migmatization (Müller et al., 2017). In granitic

source models, dominantly metasedimentary sequences are partially melted and the containing incompatible elements ultimately end up in a granitic melt which, in turn, can form a pegmatitic melt by extreme melt differentiation processes (e.g., > 99% of fractional crystallization; Černý, 1991c). In the anatectic source models, the same fluxing components and incompatible elements will be preferentially partitioned into a silicate melt derived from low-degree partial melting and that can directly form a pegmatite (Simmons & Webber, 2008; Turlin et al., 2017). Because the granites and pegmatites of the Kibara metallogenic province meet the criteria pointing toward a granitic source model (e.g., spatial relationships, age determinations, and chemical characteristics; see discussion in the following section 4.4), this chapter will not further discuss the specifics of anatectic source models for pegmatites in detail.

4.4. CASE STUDY: THE KIBARA METALLOGENIC PROVINCE

The Great Lakes region in Central Africa is marked by abundant Sn, W, Nb, and Ta deposits related to prominent granitic intrusions (Varlamoff, 1972). Geographically, this giant granite-related metallogenic province extends through the Katanga and Kivu-Maniema provinces of the Democratic Republic of Congo (DR Congo) in the southwest, over Rwanda and Burundi, up to southwest Uganda and northwest Tanzania in the northeast (Figs. 4.2 and 4.3). The Great Lakes region is known as the Kibara Metallogenic Province (Pohl et al., 2013) and comprises the Mesoproterozoic Karagwe-Ankole orogenic belt (KAB) in the northeast and the Kibara orogenic belt (KIB) in the southwest, both separated by the northwest-trending Paleoproterozoic Rusizian basement units of the Ubende belt (Figs. 4.2 and 4.3) (for a detailed discussion of the basement units, see Fernandez-Alonso et al., 2012; Tack et al., 2010).

Two contrasting tectono-magmatic models currently exist for the KAB and KIB region. The first set of models places the region in an intracratonic geodynamic setting. In this view, the KAB has been kinematically affected by different periods of extension and compression (Cahen et al., 1984; Klerkx et al., 1984; Klerkx et al., 1987) or alternatively by extensional detachments conditioned by transtensional strike-slip reactivations of shear zones in the Paleoproterozoic basement (Fernandez-Alonso & Theunissen, 1998). The most prominent tectono-magmatic event has set as a short-lived anorogenic event at 1375 Ma (Tack et al., 2010). The compressional deformation in the KAB is in this model set at ~1 Ga and interpreted as a far-field effect of the Irumide Orogen (Tack et al., 2010). The second set of models interprets the KAB region around 1375 Ma as an active margin, related to the Congo Craton–Tanzania/Bangweulu Block convergence, with localized extension in a back arc setting. The Kibara Sn (G4) granite magmatism at 1 Ga in the KAB suggests a renewed convergence and associated deformation, potentially related to the Rodinia amalgamation (Debruyne et al., 2015; Kampunzu et al., 1986; Koegelenberg & Kisters, 2014; Koegelenberg et al., 2015; Kokonyangi et al., 2004; Kokonyangi et al., 2007; Rumvegeri, 1991).

The primary rare metal mineralization of the Kibara Metallogenic Province is hosted in magmatic Nb-Ta-Sn pegmatites and magmatic-hydrothermal Sn or W quartz veins associated with the regionally defined “Kibara Sn granites” of an early Neoproterozoic age (Cahen et al., 1984; Fig. 4.2). Generally, Sn granites represent specialized granitic intrusions with high content of Sn (>15 ppm Sn; Barsukov, 1957), and spatially associated to Sn deposits (Lehmann, 1987). The mineralized systems consist of

swarms of pegmatite dykes or quartz veins emplaced in the metasedimentary host rocks, or at the granitic cupola level, structurally situated above these Sn granites. Endogranitic deposits, such as breccia pipes, greisens, intragranitic veins, or stockscheider pegmatites, have not been described in the region. Estimates of historical mining concentrates are about 800,000 t cassiterite (SnO_2), 30,000 t Ta-Nb oxide ($(\text{Nb,Ta})_2\text{O}_5$), 30,000 t wolframite ($(\text{Fe,Mn})\text{WO}_4$), and 600 t gold. Pohl et al. (2013) report grades of 153 g/t Sn, 70 g/t Ta, and 82 g/t Nb for pegmatite deposits (i.e., Gatumba, Rwanda); 4.7 kg/t Sn for Sn quartz veins (Rutongo, Rwanda); and 1.5 to 2.3 g/t Au for Au quartz veins (Twangiza, DR Congo). Grades for W in quartz veins (Nyakabingo, Rwanda), are currently not published. At times, bismuth (Bi), molybdenite (MoS_2), beryl ($\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$), and amblygonite ($(\text{Li,Na})\text{AlPO}_4(\text{F,OH})$) were by-products of mining (Pohl et al., 2013).

Individual pegmatite or quartz vein deposits of the Kibara Metallogenic Province have been intensely studied, especially at their type-localities in Rwanda; Gatumba-Gitarama, Rutongo, Nyakabingo, Musha, and Ntunga (Figs. 4.2, 4.3, and 4.5), which led to a vast amount of literature concerning the paragenesis, metallogenesis, and alteration of the ore bodies on a deposit scale (De Clercq et al., 2008; Dewaele et al., 2016a; Dewaele et al., 2010; Dewaele et al., 2016b; Dewaele et al., 2011; Günther & Ndutiye, 1990; Lehmann & Lavreau, 1987; Melcher et al., 2015; Pohl, 1994; Pohl & Günther, 1991; Pohl et al., 2013; Varlamoff, 1948, 1954, 1969, 1972). The evolution of the granite-pegmatite system and, especially, the pristine source of the mineralizing fluids and the metals for the peribatholithic quartz-vein deposits has been studied recently in depth (Dewaele et al., 2016b; Hulsbosch, 2016; Hulsbosch et al., 2016; Hulsbosch et al., 2014). Recent work suggests that the Kibara Sn granites, pegmatites, and quartz veins evolved spatiotemporally as one integrated metallogenic system operating at ca. 980 ± 20 Ma (Dewaele et al., 2016b; Hulsbosch et al., 2016; Hulsbosch et al., 2014; Lehmann et al., 2014; Pohl et al., 2013).

4.4.1. Kibara Sn (G4) Parental Granites

Major ilmenite-series, S-type granitic magmatism intruded the KAB (Günther et al., 1989; Lehmann & Lavreau, 1987; 1988) at 986 ± 10 Ma (SHRIMP U-Pb on zircon; Tack et al., 2010). Spatially, the rare-metal pegmatites and Sn-W vein systems are related to this granite event (Günther & Ndutiye, 1990; Lehmann & Lavreau, 1987; Pohl et al., 2013; Varlamoff, 1954). These Kibaran Sn granites (also called G4 granites in Rwanda) are leucocratic and show a typically equigranular and unfoliated texture (Cahen & Ledent, 1979). Their mineralogical composition consists of quartz, microcline, albite, and

Figure 4.5 Geological map of central Rwanda with localization of the Gatumba-Gitarama, Nyakabingo, and Rutongo type-localities for Kibaran granite-related deposit. Profile A-B refers to Figure 4.13 (after Fernandez Alonso, 2007).

muscovite, with accessory apatite, garnet (almandine-spessartine), zircon, monazite, xenotime, and tourmaline (Cahen & Ledent, 1979). Many Kibara Sn granites exhibit aplitic and pegmatitic textures, and miaroles or veinlets of tourmaline and quartz or amethyst. Postsolidus hydrothermal alteration (albitization: see also Fig. 4.6d, muscovite/sericite formation, tourmalinization, and kaolinization) and poor exposure caused by deep lateritic weathering are characteristic (Günther et al., 1989; Pohl, 1994; Pohl et al., 2013).

Geochemically, the Kibara Sn granites can be classified as dominantly alkali-calcic to calc-alkalic, peraluminous leucogranites (Fig. 4.6a, b, c, and e). Their geochemical

composition has been interpreted being a function of the variable degree of differentiation (Lehmann & Lavreau, 1988). The Kibara Sn granites are typically enriched in lithophile elements, such as Li, B, Rb, Cs, Nb, Ta, Th, U, Ga, Y, and W, and depleted in elements that are compatible, such as Sr, Ba, Ti, Co, Ni, Zr, and Eu (Pohl et al., 2013; see also Fig. 4.6f). A compilation of reported geochemical data of Kibara Sn granites in Rwanda (regionally called G4 granites), Burundi (regionally called Gr5 granites), and DR Congo (regionally called E-group granites) is given in Figure 4.6. They are characterized by high B ($n=50$; 5–60 ppm; average 40 ppm) and relatively low F concentrations ($n=50$: 315–2400 ppm; average

Figure 4.6 Compilation of reported geochemical data of G1-3 granites (blue; $n=51$) and Kibara Sn granites (G4; red; $n=69$) in Rwanda, Burundi, and DR Congo. (a) SiO_2 versus $\text{Na}_2\text{O} + \text{K}_2\text{O}$ variation diagram (after Wilson, 1989); (b) SiO_2 versus $\text{Na}_2\text{O} + \text{K}_2\text{O} - \text{CaO}$ variation diagram of Frost et al. (2001); (c) A/CNK versus A/NK variation diagram (after Shand, 1943), (d) and (e) P - Q and B - A variation diagrams of Debon and Le Fort (1983); and (f) Upper Continental Crust of Taylor and McLennan (1985) normalized multielement diagram. The colored fields correspond to reported ranges in elemental concentrations. Geochemical data compiled from Fernandez-Alonso (1981), Fernandez-Alonso et al. (1986), Lehmann and Lavreau (1987), Lehmann and Lavreau (1988), Günther (1990), and Hulsbosch et al. (2014).

1020 ppm) (De Clercq, 2012; Lehmann & Lavreau, 1988; Pohl et al., 2013) compared with average barren low-Ca granite abundances (B: 10 ppm; F: 850 ppm) (Turekian & Wedepohl, 1961). Sn concentrations in the Kibara Sn granites are between 4 and 80 ppm with an average of 19 ppm. The majority of the granite samples analyzed previously (24 out of 38 samples with reported Sn concentrations) are not enriched in Sn as typically observed for rare element granites (i.e., >15 ppm; De Clercq, 2012; Lehmann, 1990b). This has been ascribed to redissolution and redistribution of Sn during later hydrothermal/metasomatic events (Lehmann, 1990a). Reported W concentrations in the Kibara Sn granites are between 1.5 ppm and 11 ppm (Günther, 1990; Hulsbosch et al., 2014). The geochemical specialization of the Kibara Sn granites has been ascribed to prolonged magmatic differentiation (Lehmann, 1987) combined with hydrothermal fluid interaction (Lehmann & Lavreau, 1987) and fractional crystallization at depth (Lehmann & Lavreau, 1988) by crustal thickening and remelting of restites of older (1373 ± 6 Ma; SHRIMP U-Pb zircon; Tack et al., 2010) G1-3 peraluminous S-type granites (Günther et al., 1989; Pohl, 1994) and ~2 Ga Rusizian basement rocks (Tack et al., 2010). The widely distributed Kibara Sn granite magmatism occurs mainly as composite intrusions into the foliated batholiths of the G1-3 generation (Muechez et al., 2014; Pohl, 1994). The geochemistry of the G1-3 generation granites is variable, but within rather narrow limit, they are dominantly calc-alkalic to alkali-calcic, peraluminous, S-type, biotite-muscovite granites (Fig. 4.6a, b, c, d, and e; Fernandez-Alonso & Theunissen, 1998; Fernandez-Alonso et al., 1986). Their variable geochemical compositions have been interpreted to reflect the effects of partial melting of variably proportions of supracrustal metasedimentary rocks and crystalline basement rocks of presumably Paleoproterozoic age (i.e., Rusizian basement rocks), differentiation by fractional crystallization, and high degrees of contamination (Fernandez-Alonso et al., 1986; Tack et al., 2010). A geochemical comparison of the G1-3 granites with the Kibara Sn (G4) granites is given in Figure 4.6.

In certain regions of Rwanda, for example in the north-eastern part of the Gitarama batholith (Fig. 4.5), G1-3 granitic and Kibara Sn (i.e., G4) granitic pluton types can be observed (Muechez et al., 2014). The G1-3 granites are characterized by a fine-grained quartz, plagioclase, K-feldspar, and biotite compositions that show a well-developed foliation. The Kibara tin granites outcrop as leucogranites with centimeter- to decimeter-size (pegmatitic) quartz, feldspar crystals. These leucogranites contain pods (up to meter-scale) of quartz-feldspar graphic intergrowths. The leucogranites and pods clearly cross-cut and thus postdate the foliated granite (Muechez et al., 2014). Reported Sn concentrations in the older G1-3 granites are

~2 ppm, that is, about the Clarke value of the Upper Continental Crust (Fig. 4.6f) (Lehmann & Lavreau, 1988).

The depth of emplacement of the Kibara Sn granites is constrained by metamorphic contact aureoles, which are characterized by andalusite, indicating a pressure of ≤ 4 kbar, and the presence of spodumene in the associated pegmatites, indicating a pressure of ≥ 2.5 kbar, which defines a depth range of 10 to 16 km under lithostatic regime (Lehmann et al., 2014). Pohl and Günther (1991) constrained the emplacement of the Kibara Sn granites at shallower depths of 6 to 12 km (1.6 to 3.2 kbar) based on fluid inclusion work. The depth of emplacement of the older G1-3 granites is estimated at a minimum of 16 km by metamorphic contact aureoles of quartz-kyanite-staurolite-garnet-chlorite-biotite-muscovite (≥ 4 kbar under lithostatic pressure; Lehmann et al., 2014). These pressure ranges correspond to the 2–5 kbar range of Fernandez-Alonso et al. (1986) derived from normative composition.

4.4.2. Nb-Ta-Sn Pegmatites (Gatumba-Gitarama)

The regional occurrence and mineralogy of the pegmatites of the KAB in Rwanda, Burundi, and the DR Congo have been studied in detail by N. Varlamoff (Varlamoff, 1954, 1960, 1961, 1963, 1969, 1972). These studies identified that the striking feature of these pegmatites is their well-developed regional zoning around the Kibara Sn granites. This regional zoning is defined as a succession of seven well-defined pegmatite types differing in their size and their mineral composition (Varlamoff, 1972). The regional pegmatite classification of Varlamoff (1972) is mainly based on minerals that can be easily identified in the field, such as quartz, micas, tourmalines, beryl, spodumene, amblygonite, apatite, cassiterite, columbite-group minerals, and pyrochlore, in combination with textures (e.g., graphic structures and crystal size).

The regional pegmatite zonation of the Gatumba-Gitarama type-locality has been mapped in detail by Hulsbosch et al. (2014) and Muechez et al. (2014) who showed that four major regional mineralogical zones could be identified in the field: (1) biotite, (2) biotite-muscovite (or two-mica), (3) muscovite, and (4) mineralized pegmatite zone. Zones 1 to 3 are common pegmatites belonging to the muscovite-rare-element class, while zone 4 is classified as rare-element class pegmatites (cf. classification of Černý & Ercit, 2005). The regional pegmatite zonation sequence can be observed starting from leucogranite feeder zones with Kibara Sn granite affinity evolving proximally in common pegmatites (zone 1 to 3) and culminating most distally in the mineralized pegmatites of zone 4. Regionally, the pegmatites of zones 1–3 occur both as intrabatholithic pegmatites and as exopegmatites in a 4.5 km wide aureole around the batholith at Gatumba-Gitarama. The mineralized

pegmatites belonging to zone 4 at Gatumba-Gitarama occur only as exopegmatites in the most outward aureole of the pegmatite zonation sequence. (Hulsbosch et al., 2014). The regional zonation sequence is in fact a complex, superimposed distribution of individual pegmatite zonations starting from leucogranite extrusion sources. The magmatic crystallization age of the Gatumba-Gitarama pegmatites has been interpreted at ~975 Ma: 975 ± 29 Ma (Rb-Sr on muscovite of zone 4; Cahen, 1964) and 975 ± 8 Ma (U-Pb on columbite-tantalite of zone 4; Dewaele et al., 2011).

Biotite pegmatites (zone 1) are dominantly composed of microcline, plagioclase, biotite, and small amounts of quartz; and can developed abundant quartz-feldspar and quartz-tourmaline graphic textures. Biotite-muscovite pegmatites (zone 2) are also dominantly composed of quartz, microcline, plagioclase, biotite-muscovite intergrowths, in combination with quartz-tourmaline-(muscovite) graphic textures. Muscovite pegmatites (zone 3) show abundant muscovite, quartz, microcline, small and rare prisms of beryl, and a weak development of secondary albitization. Assemblages of quartz-tourmaline-(muscovite) graphic textures are often observed. Mineralized pegmatites (zone 4) are made up of pink K-feldspar (orthoclase), microcline, albite-oligoclase, quartz, Li-rich muscovite, spodumene, and elbaite. Accessory minerals include cassiterite, lepidolite, apatite, multicolored and white beryl, columbite-tantalite, rare phosphates, and other accessory phases (e.g., Daltry & Von Knorring, 1998). A famous example of a phosphate-rich

pegmatite dyke in the Gatumba-Gitarama region is the Buranga pegmatite, which contains over one hundred mineral species, of which more than half are phosphates (Bertossa, 1965, 1968; Daltry & Von Knorring, 1998). The phosphates gatumbaite ($\text{CaAl}_2(\text{PO}_4)_2(\text{OH})_2 \cdot \text{H}_2\text{O}$), burangaite ($\text{NaFe}^{2+}\text{Al}_3(\text{PO}_4)_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}$), and bertossaite ($(\text{Li},\text{Na})_2(\text{Ca},\text{Fe}^{2+},\text{Mn}^{2+})\text{Al}_4(\text{PO}_4)_4(\text{OH},\text{F})_4$) have been first described in the Buranga dyke. At Buranga, the phosphates occur in an isolated zone next to the quartz core (Dewaele et al., 2011; Varlamoff, 1963). These mineralized pegmatites have been metasomatized (25–90 vol%), causing a large part of the primary mineralogy of the pegmatites to be altered to muscovite-quartz-(cassiterite) greisens (Varlamoff, 1963). Dewaele et al. (2008) and Dewaele et al. (2011) concluded, based on petrographic, fluid inclusion and stable oxygen and hydrogen isotope studies, that the Ta-Nb and cassiterite mineralization mainly formed during two distinct stages: the Ta-Nb and some of the cassiterite formed during an earlier stage of crystallization of the pegmatites prior to the albitization, while the major part of the cassiterite formed in quartz-muscovite-cassiterite greisen pockets during the later metasomatic-hydrothermal overprint. The greisen-hosted cassiterite is paragenetically associated with sericitization and muscovitization of the zone 4 pegmatites (Fig. 4.7). Nb and Ta mineralization in the pegmatites of the Kibara Metallogenic Province is regionally known as “coltan,” but covers in fact a wide array of Ta-Nb oxide (TNO) mineralogical compositions. Most

Figure 4.7 Paragenetic sequence of the pegmatite-hosted Nb-Ta-Sn mineralization at Gatumba-Gitarama (after Dewaele et al., 2011).

TNO mineralization in Rwanda (and KAB) comprises a solid solution of the columbite group minerals (CGM), that is, columbite-(Fe), columbite-(Mn), tantalite-(Fe), except for pure tantalite-(Mn) and the miscibility gap to tapiolite (Melcher et al., 2015). Apart from CGM (comprising on average 91% of the TNO), tapiolite (3% to 78%), wodginite-ixiolite (2% to 35%), pyrochlore supergroup minerals (mainly microlite; average 3% to 86%), and Ta-Nb rutile (1% to 40%) are reported by Melcher et al. (2015). Nb-Ta mineralization within the Gatumba-Gitarama pegmatites has been dated around 975 ± 8 Ma (LA-ICP-MS U-Pb on columbite-tantalite; Dewaele et al., 2011). On the basis of scanning electron microscope/mineral liberation analysis techniques, the non-TNO fraction of concentrates of the Gatumba-Gitarama mineralized pegmatites dominantly contains cassiterite and accessory ilmenite, zircon, monazite, xenotime, apatite, garnet, and wolframite, all in variable proportions (total fraction non-TNO: 5% up to 75%; Melcher et al., 2015).

The magmatic evolution of the four pegmatite zones at Gatumba-Gitarama from a leucogranitic Kibara Sn granite (G4) source has been successfully reconstructed by means of alkali metal and rare earth element (REE) geochemical modeling of rock-forming minerals (feldspars, micas, and tourmaline) sampled from dykes belonging to the four pegmatites zones (Hulsbosch et al., 2013, 2014). Fractionation modeling shows that the pegmatites adjacent to the parental Kibara Sn granite pluton are the least fractionated, and the distal pegmatites are the most fractionated. Biotite pegmatites (zone 1) form from 0% to 69% crystallization, two-mica pegmatites (zone 2) between 69% and 92% crystallization, and muscovite pegmatites (zone 3) from 92% crystallization onward. The extreme differentiation as observed in the rare-element pegmatites (zone 4) requires at least 98% fractionation of the initial Kibara Sn granite composition (Hulsbosch et al., 2014). Consequently, trace element modeling indicates that Rayleigh fractional crystallization governs the regional mineralogical and geochemical evolution from a granite source to muscovite-rare-element class and eventually rare-element class pegmatites. This mechanism shows that granitic pegmatites of the KAB are extremely fractionated melts, which are genetically and temporally connected to a main Kibara Sn granite body (Hulsbosch et al., 2014). During the end-stages of crystallization of individual dykes of zones 1–3 pegmatites of the Gatumba-Gitarama field, residual melt pools with a boro-aluminosilicate composition developed and caused the formation of mineralogical zonations within dyke, such as schorl-quartz-(muscovite) assemblage (Hulsbosch et al., 2017a).

Primary fluid inclusions in tourmaline of these less-differentiated pegmatites (zones 1–3) demonstrate the

presence of low- to moderate-salinity, H_2O -NaCl-KCl-MgCl₂-complex salt (e.g., Rb-, Cs-salt) fluids, which started to exsolve at the Kibara Sn granite-pegmatite transition stage. LA-ICP-MS analysis of these primary fluid inclusions show significant W enrichment in these fluid phases (5–500 ppm) (Hulsbosch et al., 2016). The general absence of W mineralization in this magmatic suite, including the most differentiated columbite-tantalite mineralized pegmatites of the Gatumba-Gitarama area, emphasizes the efficiency of fluid saturation to extract crystal-melt incompatible W from the differentiating melt phase as tungstate species in aqueous solutions (Hulsbosch et al., 2016).

4.4.3. W Quartz Veins (Nyakabingo)

The Nyakabingo deposit (Figs. 4.3 and 4.5) has been studied as a representative locality for W quartz veins in the KAB (De Clercq, 2012; De Clercq et al., 2008; Dewaele et al., 2016b; Goldmann et al., 2013; Pohl & Günther, 1991; Pohl et al., 2013). The quartz vein system is typically located in the cores and flanks of second- to fourth-order complex anticlinal folds of the regional Bumbogo anticline (Fig. 4.5). Recent dating of selvage muscovite from the Nyakabingo W quartz veins provided an age of 992.4 ± 1.5 Ma, which has been interpreted as the formation age of the veins (Ar-Ar on muscovite; Dewaele et al., 2016b). The veins are hosted in sandstones and black, organic-rich metapelitic rocks of the Nduba-Shyorongi and Bumbogo formation belonging to the Gikoro Group (Fig. 4.8; Dewaele et al., 2016b). Two types of W-mineralized quartz veins are exposed in the field: bedding-parallel veins with a thickness between 0.1 and 2 m (exceptionally up to 9 m thick) and bedding-crosscutting quartz veins that are at a high angle to the bedding, and which have a thickness of a few centimeters up to several meters (Dewaele et al., 2016b). Metapelitic host rock around the veins has been altered to muscovite, tourmaline, and minor biotite early during vein opening and fluid-rock interactions. Centimeter large muscovite sheets precipitated in this contact zone between the veins and the surrounding metapelitic host rock during early vein formation (Fig. 4.9). During the main vein stage, the first quartz phase precipitated together with euhedral arsenopyrite, pyrite, scheelite, massive ferberite, and molybdenite (De Clercq, 2012; Goldmann et al., 2013). Often, the massive ferberite contains aligned scheelite inclusions, indicating ferberite after scheelite (Fig. 4.9). Subsequently, the scheelite crystals recrystallized and ferberite pseudomorphs (i.e., reinite variant) formed. The reinite pseudomorphs have been fractured and filled by an assemblage of quartz, muscovite, and xenotime (De Clercq, 2012; Goldmann et al., 2013). Afterward, the quartz veins have been crosscut by a sulfide phase

Figure 4.8 Synthetic litho- and chronostratigraphic reconstruction of sedimentation and magmatism in the western domain of the Karagwe-Ankole Belt (after Fernandez-Alonso et al., 2012).

Figure 4.9 Simplified paragenetic sequences of the vein-hosted W and Sn mineralization at Nyakabingo and Rutongo, respectively (after De Clercq, 2012).

consisting of galena, cosalite, bismuth and bismuthite, and siderite and a late oxide phase (De Clercq, 2012).

The W ore minerals are interpreted to have precipitated from an aqueous-gaseous $\text{H}_2\text{O}-\text{CO}_2-\text{CH}_4-\text{N}_2-\text{NaCl}-(\text{KCl})$ fluid, with a low to moderate salinity (0.6–13.8 eq. wt% NaCl) and minimal trapping temperatures between 247 and 344°C based on fluid inclusion studies (Dewaele et al., 2016b). Based on LA-ICP-MS analyses of individual fluid inclusions by De Clercq (2012), the composition of the mineralizing fluid is characterized as dominantly Na rich, with lesser amounts of Mg (220–3800 ppm), K (850–1700 ppm), Ca (930–4710 ppm), Mn (230–1030 ppm), and Fe (160–1080 ppm). Trace amounts of Sr (10–180 ppm), Cs (20–50 ppm), Ba (300–1300 ppm), W (50 ppm), and Pb (10–160 ppm) were also measured (De Clercq, 2012). Intense fluid–host rock interactions controlled the scheelite-ferberite precipitation during vein formation and caused the associated selvage contact alteration by muscovitization and tourmalinization reactions (see also Lecumberri-Sanchez et al., 2017). This alteration overprinted the fluid composition, causing a change in the gaseous composition with enrichment in N_2 and CH_4 likely derived from the host rock (6–44 mol% N_2 and 5–10 mol% CH_4 ; Dewaele et al., 2016a). Moreover, the quartz stable isotope record, with $\delta^{18}\text{O}_{\text{quartz}}$ values of +14.4‰ to +15.6‰ V-SMOW and $\delta\text{D}_{\text{quartz}}$ values of –33‰ to –64‰ V-SMOW, would favor a dominant “metamorphic” signature of the mineralizing fluid, which is, however, likely caused by intense fluid–metapelite interactions (Fig. 4.12 in Dewaele et al., 2016b; Hulsbosch et al., 2016). This is supported by the typical association of the tungsten vein-type deposits with organic-rich black shales (Dewaele et al., 2016b). The latter are typically altered to a tourmaline-muscovite-(biotite) selvage at the contact with the quartz vein. These black shales acted also as a source of iron and calcium for the formation of tungstate minerals (Dewaele et al., 2016b; Lecumberri-Sanchez et al., 2017). For example, De Clercq (2012) and Günther and Ndutiye (1990) reported abundant cubic cavities (2–3 mm) of boxwork pyrite in the black shales and sandstones of Nyakabingo indicating Fe leaching. Sulfide dissolution is also observed on the vein selvages at contact with the enclosing metapelite. Additionally, during fluid–metapelite interaction, the mineralizing fluid could have been mixed with diluted “metamorphic” fluids, which could have caused a decrease in chloride concentration of the mineralizing fluid and induced a substantial decrease in the W solubility (Hulsbosch et al., 2016). The $^{40}\text{Ar}-^{39}\text{Ar}$ age of vein muscovite from Nyakabingo (992 ± 2 Ma; Dewaele et al., 2016b) overlaps with the 986 ± 10 Ma intrusion age of the Kibara Sn granites (SHRIMP U-Pb on zircon; Tack et al., 2010). At the deposit scale, there are no field observations indicating a direct spatial link between the W-bearing veins and the Kibara Sn granites.

However, based on magnetometric data, a hidden granitic body is inferred to be present at an estimated depth of 0.5–2 km (Günther & Ndutiye, 1990).

4.4.4. Sn Quartz Veins (Rutongo)

One of the largest Sn districts of the KAB, reasonably covered by more recent scientific studies (Dewaele et al., 2007; Dewaele et al., 2010; Günther, 1990; Pohl, 1994; Pohl & Günther, 1991; Pohl et al., 2013), is the Rutongo mining district in central Rwanda (Figs. 4.3 and 4.5). The Rutongo Sn veins are also located in secondary anticlinal structures of the regional Rutongo anticline (Fig. 4.5). In contrast to the W deposits, the Sn deposits are typically hosted in a number of massive sandstone and/or quartzite units that are separated by units of alternating metapelitic rocks and sandstones (De Clercq, 2012; Pohl et al., 2013). The Sn deposits are mainly hosted in metasediments, which belong to the Gikoro Group (Fig. 4.8; Baudet et al., 1988). The Sn-mineralized quartz veins occur in swarms of several hundreds of subparallel crosscutting veins that are oriented perpendicular to the fold axes. The individual quartz veins have a thickness that varies between a few cm to several meters (more than 5 m), with an average between 0.5 and 1 m. They can be several hundred meters long (Dewaele et al., 2010).

The emplacement age of the Rutongo veins is estimated at 965 ± 29 Ma by muscovite Rb-Sr age dating (muscovite associated with cassiterite; Monteye-Poulaert et al., 1962). Recent dating of cassiterite from the Rutongo Sn quartz veins provided ages of 957 ± 21 Ma (U-Pb; Zhang et al., 2016), that is, within the same time interval uncertainty as the Rb-Sr age of Monteye-Poulaert et al. (1962). Structural analysis indicated a relatively late formation of the Sn-mineralized veins in the general evolution of the Rutongo anticline (De Clercq, 2012). More specifically, in the southeastern part of the Rutongo anticline, granitic rocks of the Kigali granite can be found. This muscovite-bearing leucogranite is interpreted to be a Kibara Sn granite (Bertossa et al., 1964). In the contact zone between the Kigali granite intrusion and the Rutongo host rocks, it is reported that the intrusion postdates microfolds in the host rocks (Lhoest, 1957a, b). The Kigali granite is as such interpreted to have been emplaced during a late phase or postfolding of the rocks (Lhoest, 1957a; b; Peeters, 1956; Pohl, 1974). Consequently, the Rutongo Sn veins are interpreted to be formed syn- to post-Kigali granite emplacement.

The quartz veins are associated with intense wall-rock alteration, comprising silicification, tourmalinization, muscovitization, and precipitation of biotite (Fig. 4.9; De Clercq, 2012; Dewaele et al., 2010). These reactions are typical for the Sn vein-type deposits in the central part of Rwanda (Dewaele et al., 2010). Cassiterite formed in a

late stage of the evolution of the mineralized veins and is intimately associated with muscovite crystals in fractures in the quartz veins. Afterward, the quartz veins were crosscut by a sulfide phase, consisting of arsenopyrite, galena, and chalcopyrite, and late Fe oxides (De Clercq, 2012). Cassiterite is interpreted to have precipitated from an aqueous-gaseous fluid with a low to moderate salinity (6.2–15.4 eq. wt% NaCl) and a minimal trapping temperature between 225°C and 349°C, based on fluid inclusion studies (De Clercq, 2012). The gas phase is composed of CO₂ (50–78 mol%), N₂ (11–40 mol%), and smaller amounts of CH₄ (10–15 mol%). Na is the dominant cation in solution, with lesser amounts of K (1444–3377 ppm), Li (149–284 ppm), and Cs (446 ppm) (De Clercq, 2012). The $\delta^{18}\text{O}_{\text{quartz}}$ values of the Sn-mineralized quartz veins are +13.6 and +14.1‰ V-SMOW. The $\delta\text{D}_{\text{quartz}}$ show a large spread between -47 and -67‰ V-SMOW. The oxygen and deuterium isotopic values of the fluids are interpreted to reflect metamorphic, possibly magmatic signatures (De Clercq, 2012; Fig. 4.5 in Dewaele et al., 2010). Both oxygen and deuterium isotopic values of cassiterite are relatively homogeneous (7.5 and 7.9‰ V-SMOW $\delta\text{D}_{\text{quartz}}$, and -90 and -105‰ $\delta^{18}\text{O}_{\text{quartz}}$) and indicate that the Sn-mineralizing fluid interacted with metamorphic rocks (De Clercq, 2012). As for the W vein-type deposits, intense water-rock interactions have overprinted the pristine source signature.

4.5. NB-TA-SN-W FRACTIONATION MECHANISMS

The co-occurrence of Nb-Ta-Sn pegmatite-type and Sn-W quartz vein-type mineralization at multiple locations in the KAB region of the Kibara Metallogenic Province provides a first-class and, moreover, relatively rare opportunity to investigate the geochemical evolution of a global granite-related ore system and to evaluate the element distribution between pegmatites and quartz veins during the magmatic-hydrothermal transition. The next sections provide a discussion and interpretation of the metallogensis of the Nb-Ta-Sn-W granite-related ore deposits and its application on the Rwandese, and to some extent the Kibara Metallogenic Province, granite-related ore deposits. Main fractionation processes responsible for element enrichment will be discussed. As a conclusion, a general granite-related metallogenic model will be presented for the B-rich, F-poor KAB metallogenic system.

4.5.1. Processes Related to Disseminated Magmatic Mineralization

4.5.1.1. Generalities

Disseminated rare-metal, Nb-Ta-Sn-W-Li-Be-(Zr-U-REE), mineralization is restricted to shallow albite-rich, peraluminous granites (Černý et al., 2005). The crustal

emplacement is generally from subvolcanic to miarolitic (<5 km) and mineralization occurs often in isolated bodies, or rhyolitic to microgranitic dykes (Cuney et al., 1992; Raimbault et al., 1995). Albite-rich granites represent most-fractionated end members of layered sequences in upwardly differentiated plutons (Candela, 1992, 1997).

Various classifications of rare-metal granites have been proposed based on their geochemistry. However, only the peraluminous, high phosphorus rare-metal granite type is associated with Nb-Ta-Sn-W mineralization (Černý et al., 2005; Linnen & Cuney, 2005). A well-studied example is the Sn-Ta-Nb-Rb-Cs-Li-rich, late-Variscan Beauvoir granite in the French Massif Central (Cuney et al., 1992; Raimbault et al., 1995), which has been interpreted to be intruded at a pressure range of 1.0 to 1.2 kbar, which corresponds to emplacement depths of <4.5 km. (Aissa et al., 1987). In general, these low-seated peraluminous rare-metal granites are spatially associated with large muscovite-biotite leucogranite plutons at depth that formed during postorogenic relaxation in continental collisions (Bouchot et al., 2005). Lenharo et al. (2003) constrained the PT evolution of several granite types associated with disseminated rare-metal mineralization in Pitinga, Amazonas, Brazil. Parental, barren quartz monzonites have been interpreted to intrude at ~930°C and 5 kbar while the last and mineralized albite granite formed below 650°C and 1 kbar. This suggests that (1) initial crystallization of the early intrusive phases occurred at around 15 km depth under lithostatic regime and (2) the final emplacement of the more differentiated rare-metal granites took place at a depth of 0.5–1 km (Lenharo et al., 2003).

In general, these peraluminous granites are mineralized in the form of microlite, CGM, or Ta-rich cassiterite (Linnen et al., 2014). They are characterized by low concentrations of REE (close to chondritic values) and contain Li-rich muscovite, amblygonite, or lepidolite (Cuney et al., 1992; Kovalenko & Yarmolyuk, 1995). P, Rb, and Cs levels are generally high (Černý et al., 2005). Most metallogenic studies identified that disseminated mineralization in rare-metal granites is the product of primary magmatic crystal-melt fractionation processes (Candela, 1997; Černý et al., 2005; Kovalenko & Yarmolyuk, 1995; Linnen, 1998; Webster et al., 2004) due to the (very) low crystal/melt distribution coefficients of Nb (0.05–0.09), Ta (0.02–0.05), W (0.04–0.4), and Sn (~0.3) (Antipin et al., 1981; Bartels et al., 2010; Candela, 1992; Kovalenko et al., 1988; Lehmann, 1990b; Linnen, 1998; Linnen & Cuney, 2005; Linnen et al., 2014; Raimbault et al., 1995). However, extensive hydrothermal reworking of the magmatic mineralization is documented by the formation of Li-rich, Sn-W greisens (Webster et al., 2004). Based on bulk Ta enrichment trends from increasingly more fractionated granite batches, that is,

≤ 1 ppm in less-fractionated up to >100 ppm in the most fractionated units, Černý et al. (2005) proposed a degree of fractionation ≥ 0.99 of the parental melt. The associated enrichment of the crystal-incompatible fluxes, such as F, Li, B, and P, during fractionation causes modification of the physicochemical properties of the melt (lowering of the viscosity and solidus temperature), which facilitates crystal-melt separation and favors protracted crystal-melt fractionation, promoting extreme rare-metal enrichment (Bartels et al., 2013; Černý et al., 2005; Dingwell, 1988; Linnen, 1998; Pichavant, 1981). In addition, Raimbault et al. (1995) proposed that melt-melt and melt-aqueous fluid exsolution processes can occur as additional enrichment mechanisms, superimposed on the general crystal-melt fractionation trends. These processes can potentially lead to a immiscible hydrosaline liquid that could transport elements such as Li, Rb, Cs, Sn, W, Nb, and Ta upward through the magma toward the roof of the granite bodies (Badanina et al., 2004; Harlaux et al., 2017b; Reyf et al., 2000; Thomas et al., 2000; Veksler et al., 2002). However, the process of liquid-liquid immiscibility in the formation of orthomagmatic deposits, such as the composition and dynamics of liquid-liquid immiscibility or the metal distribution and solubility in immiscible phases, is not well understood (cf. Černý et al., 2005; Kamenetsky & Kamenetsky, 2011; Linnen et al., 2014).

4.5.1.2. Consequences for the KAB

The B and Cl-rich, F-poor leucocratic and calc-alkaline, peraluminous Kibara Sn granites are spatiotemporally related to the rare-metal pegmatites and Sn-W vein mineralization systems in the KAB (operated in a ca. 980 ± 20 Ma range; Lehmann & Lavreau, 1988; Pohl, 1994; Pohl et al., 2013; Tack et al., 2010). These major ilmenite-series granites are, however, reported as barren (Günther et al., 1989; Lehmann & Lavreau, 1987, 1988). The depth of emplacement is interpreted at 10–16 km (Lehmann et al., 2014) (see section 4.4.1). The depth of emplacement of the Kibara Sn granites appears in contrast with the shallow rare-metal granites, which are generally emplaced at ~ 4 km (e.g., Aissa et al., 1987; Lenharo et al., 2003).

The Kibara Sn granites are mainly derived by anatexis of supracrustal metasedimentary rocks and crystalline basement rocks (Fernandez-Alonso et al., 1986; Pohl, 1994; Tack et al., 2010) and such granitic melts are, in general, hydrated (water-saturated) and can contain water in the range of 7–8 wt% H_2O (Burnham, 1997). Typically, these peraluminous S-type magmas, like the Kibara Sn system, can maximally rise upward in the crust until they intersect the water-saturated granite solidus (cf. Holtz et al., 2001). By this time, typically at 15–18 km (4–5 kbar under lithostatic pressure), they would have become completely solid and could not intrude upward

any farther (Robb, 2013; Strong, 1988). H_2O -fluid saturation in these magmas at these crustal levels will eventually occur by second boiling and eventually yield to the formation of pegmatites and associated hydrothermal systems like quartz veins (e.g., Strong, 1988). In addition, F-enriched granitic magmas have the potential to rise upward to higher crustal levels in comparison to F-poor systems due to the positive effective of F in reducing the viscosity and the minimum liquidus temperature of granitic melts (Manning, 1981; Pichavant & Manning, 1984). F also significantly delays fluid/vapor saturation of granitic melts (Holtz et al., 1993; Manning, 1981; Strong, 1988). The absence of F in the Kibara Sn granite could also explain its more deep-seated nature compared with granites with disseminated rare-metal mineralization. Consequently, the deeper-seated nature of the Kibara Sn granites, at crustal depths of ~ 10 –16 km, is probably caused by the high initial water content, and by the exsolution of a magmatic aqueous fluid phase by second boiling during crystallization until solidus conditions (cf. Whitney, 1988), that is, at the granite-pegmatite transition stage in case of the Gatumba-Gitarama pegmatites (Hulsbosch et al., 2016).

Rare elements Nb, Ta, Sn, and W are generally incompatible in peraluminous melt systems (Linnen et al., 2014). The lack of magmatic disseminated mineralization in Kibara Sn granites can be consequently interpreted to result from “an unsuccessful alignment and combination” (cf. Richards, 2013) of magmatic to hydrothermal fractionation processes. A competing interplay can be expected in a differentiating magma system with an exsolved fluid phase between (1) the enrichment of an incompatible ore element in the melt phase up to ore mineral saturation and precipitation, versus (2) the fractionation of the incompatible but soluble ore element and partition into the exsolved fluid phase. At each infinitesimal step of melt differentiation, there is as a result a competition between the further enrichment of the incompatible element in the melt versus the depletion of the element in the melt due to the combination of its soluble behavior and the dominance of the fluid phase in the system (i.e., mass fraction of fluid, which is related to the water content of the melt). For example, solubility data of Sn in silicic melts strongly suggest that crystallization of magmatic cassiterite from a melt containing Sn at the ppm level is unlikely (Lehmann, 1990c). This is particularly unlikely for reduced, peraluminous granites, such as the Kibara Sn granites, even with their Sn content at the 100 ppm level (Štemprok, 1990). These estimated values are exceedingly lower than the Sn saturation value for peraluminous melts, which ranges between ca. 0.4 and 0.8 wt% Sn (Linnen et al., 1996). However, cassiterite saturation may occur in extremely fractionated pegmatite phases (Štemprok, 1990). Experimental W solubility studies by

Che et al. (2013) show that the crystallization of magmatic wolframite is possible in flux-rich subaluminous to peraluminous melts, such as Kibara Sn granites, at approximately 500°C. The lack of magmatic wolframite in the Kibara Sn granites and associated pegmatites has been correlated to the exsolution of a mobile fluid phase and the subsequent fractionation of soluble W toward this fluid phase (Hulsbosch et al., 2016). Fractionation of W toward an early aqueous fluid phase hampers further enrichment of incompatible W in the melt phase because the W content of the melt is depleted by fluid scavenging of W. If the felsic magma system is not fluid saturated, incompatible W concentrates in the melt and is forced to saturate at the appropriate W-mineral solubility products (e.g., Che et al., 2013). Based on average W concentrations in magmatic muscovite from the Gatumba-Gitarama pegmatites, which range from ~30 ppm in the pegmatites of zone 2 to ~7 ppm in the pegmatites of zone 3 and 4 (Hulsbosch et al., 2013, 2014), and the W muscovite-melt distribution coefficient (i.e., 1.6; Kovalenko et al., 1988), calculated W melt concentration decreases from 18 ppm to 4 ppm in the pegmatites of zone 2 to zone 4. These W melt concentrations are well below experimentally derived solubility products for wolframite in peraluminous melts, for example, ~4600 ppm W for ferberite and ~1100 ppm for hubnerite at 800°C (calculated from data of Che et al., 2013). The solubility behavior of Nb and Ta in peraluminous melts is probably related to the formation of bonds with Al; Ta is preferentially bonded to nonbridging oxygens with Al as first neighbors (Van Lichtervelde et al., 2010). In sub- and peraluminous melts tantalite solubility is higher than that of columbite resulting in a systematic decrease of Nb/Ta during the crystallization of these melts (Linnen et al., 2014; Van Lichtervelde et al., 2010). The effect of fluxing compounds on Nb-Ta-solubilities is somewhat controversial (Linnen et al., 2014): Li increases the solubility of columbite and tantalite (Linnen, 1998) while F does not increase its solubility (Fiege et al., 2011). Notwithstanding, flux-rich granitic melts can dissolve weight percent levels of Nb and Ta (Bartels et al., 2010). As with the rare elements W and Sn, the solubility of columbite and tantalite is strongly temperature dependent, especially in the case of peraluminous melt compositions (Linnen & Keppler, 1997; Linnen & Cuney, 2005; Van Lichtervelde et al., 2010). Experimental Ta solubilities systematically decrease from ~25000 ppm at 1050°C to ~8000 ppm at 800°C (at an ASI of 1.0; Linnen & Keppler, 1997). Taking the above-mentioned fractionation experiments into account, Nb-Ta and Sn magmatic disseminated mineralization can be expected only at magmatic end-stages (Linnen & Cuney, 2005) characterized by very high degrees of crystal-melt fractionation ($F \geq 0.99$), such as observed in the mineralized pegmatites of the Gatumba-Gitarama area. In contrast, the (early) magmatic disseminated W mineralization can be more easily

expected in flux-rich, volatile undersaturated subaluminous to peraluminous melts, which are characterized by significant degrees of crystal-melt saturation in the absence of a mobile aqueous fluid phase (Hulsbosch et al., 2016).

4.5.2. Processes Related to Pegmatitic Rare-Element Mineralization

4.5.2.1. Generalities

Generally, the granite intrusions generating rare-element class pegmatites range in morphology from small stocks and sheets to medium-sized plutons and diapiric cupolas up to batholithic masses (Černý, 1991a,b). Intrusion depths for the granite and pegmatite aureoles have been estimated at 5 to 2 kbar (London, 2008). Homogenous biotite to two-mica granites have been identified to be spatially associated with low- to medium-fractionated pegmatites (Beus, 1966; Černý et al., 2005). However, granites parental to highly fractionated pegmatites are leucocratic and heterogeneous two-mica granites with local pods of graphic-textured pegmatitic leucogranites (Beus, 1966). Older studies have unsuccessfully attributed fractionation processes such as the Soret effect (i.e., thermogravitational diffusion: heavy elements migrate toward the colder end and lighter ones to the hotter end of the melt gradient), differential breakdown of divers complexes, aqueous fluid separation, and late aqueous fluid overprint for the extensive fractionation of Nb and Ta (and other HFSE) in pegmatitic melts (cf. review in Beus, 1966). Recent experiments, however, confirmed that crystal-melt fractionation and differential solubility of Nb and Ta are mainly responsible for rare-metal fractionation in pegmatitic melts, in combination with depolymerization of the fluxed melt (review in Linnen et al., 2014). The extreme solubility of rare metals particularly in conjugate/immiscible peralkaline melt fractions is also demonstrated for Ta by melt inclusions studies (Thomas et al., 2011a; Thomas et al., 2011b). The systematics of rare-metal solubility and melt fractionation in the case of peraluminous lithium-cesium-tantalum (LCT family) pegmatite melts is in concept similar to the behavior in granitic systems, in particular in high P peraluminous granites (section 4.5.1).

4.5.2.2. Consequences for the KAB

The regional pegmatite zonation in Gatumba-Gitarama is mineralogically characterized by an evolution from muscovite-rare-element class (zone 1 to 3) to rare-element class pegmatites (zone 4), which is generated by magmatic crystal-melt differentiation from parental leucocratic Kibara Sn granite (Hulsbosch et al., 2014). Moreover, the four pegmatite zones intruded metasedimentary units of relatively low-pressure, greenschist metamorphic facies (cf. Gérards, 1965), which is above the regional depth for an anatectic origin (i.e., upper amphibolite facies, cf.

Brown, 1994). The culmination of Li-Be-Cs-Ta-Nb mineralization in pegmatites of zone 4 (i.e., end-member units of fractional crystallization of Kibara Sn source granites) is in line with the most recent experimental work, which showed that crystal-melt fractionation and differential solubility of Nb and Ta are the main differentiation processes acting in crystallizing pegmatitic melts (Linnen et al., 2014). Extreme crystal-melt fractionation of peraluminous granitic melt system ($F > 98\%$; Hulsbosch et al., 2014) caused (1) the large-scale, regional pegmatite melt evolution and (2) the magmatic enrichment of incompatible Nb, Ta, Sn, and W at the Gatumba-Gitarama pegmatite field. Phase separation by aqueous fluid immiscibility is observed in the mineral and inclusion record (e.g., Hulsbosch et al., 2016; Sirbescu & Nabelek, 2003; Thomas & Davidson, 2013; Thomas et al., 2012) and can cause fluid partitioning of fluid soluble elements, like W, which can form tungstate species in aqueous solutions (Wood & Samson, 2000). Fluid immiscibility processes become increasingly more important at high degrees of fractional crystallization of B-rich, F-poor hydrous granite-pegmatite melts (Hulsbosch et al., 2017a).

4.5.3. Processes Related to Hydrothermal/ Metasomatic Mineralization

4.5.3.1. Generalities

Hydrothermal vein and greisen systems are, in contrast to disseminated magmatic rare-metal mineralization in granites and pegmatites, dominantly driven by fluid-melt equilibria, fluid mixing, and aqueous geochemistry (Černý et al., 2005; Heinrich, 1990; Wood, 2005; Wood & Samson, 2000). The Kibara Sn magmatic system is distinctly F-poor, B- and Cl-rich (Pohl et al., 2013), consequently fluid-melt partitioning will be mainly discussed for B- and Cl-dominated fluid-peraluminous melt systems. Moreover, F partitions generally in favor of the melt (Carroll & Webster, 1994) with reported fluid/melt distribution coefficients of < 0.5 for peraluminous granite-pegmatite systems (London et al., 1988). In addition, the solubility of water increases with increasing B content (Pichavant, 1981), an effect also observed with increasing Al content in peraluminous melts (Dingwell et al., 1984).

Fluid distribution of Nb and Ta is very low with experimental fluid-melt partition coefficients ranging from ~ 0 to 0.1, and from ~ 0.001 to 0.08, respectively (Borodulin et al., 2009; Chevychev et al., 2004; Linnen & Cuney, 2005). However, it has been demonstrated that Nb and Ta can be soluble as hydroxyl-fluorine species in concentrated fluoride solutions ($(\text{HF}) > 10^{-3}$ mol/kg) under reducing conditions (Timofeev et al., 2015; Zarausky et al., 2010). Chloride and carbonate hydrothermal solutions are ineffective in transporting Ta and Nb and are not

capable of transferring these metals in the amounts sufficient for the formation of economic viable ore deposits (Zarausky et al., 2010). The lack of Nb or Ta enrichment in geochemical aureoles above most rare-element granite and pegmatite cupolas (e.g., the Beauvoir granite or KAB system), except for some Li-F type granites and pegmatites (Zarausky et al., 2010), supports an extremely low-fluid affinity of these elements in Cl-dominated magmatic fluids (cf. Cuney et al., 1992; Pohl, 1994; Varlamoff, 1972).

Experimental determination of Sn fluid-partitioning is problematic due to the reaction of cassiterite with precious metals making up the experiment capsule, especially at reduced conditions (Linnen et al., 1995). At oxygen fugacities near the NNO buffer and with a fluid chlorinity less than $1 \text{ mol} \cdot \text{l}^{-1}$, Sn partitions experimentally in favor of the melt (Taylor, 1988 as cited in Linnen & Cuney, 2005). Keppler and Wyllie (1991) report lower fluid-melt partition coefficients ranging from 0.005 to 0.08 for fluid HCl concentrations of 0 to $2 \text{ mol} \cdot \text{l}^{-1}$. Experimental data of Hu et al. (2008) and Hu et al. (2016) constrained the influence of melt composition on the fluid partitioning of Sn. They showed that the fluid-melt partition coefficient increases with increasing aluminum saturation index, $K_{fm,Sn} = 0.1886 \cdot ASI - 0.1256$, giving absolute coefficients for peraluminous melts alike to the Kibara Sn granites between 0.06 and 0.18 ($ASI = 1.0\text{--}1.6$; Fig. 4.6c). Given that Sn is readily complexed by Cl in aqueous solutions (Wilson & Eugster, 1990), it is expected that Sn will partition more preferentially in favor of the fluid at very high Cl concentrations (Linnen & Cuney, 2005). However, experiments of Wilson and Eugster (1990) and Taylor and Wall (1993) showed that significant amounts of Sn can partition into the chloride-bearing acidic magmatic fluid phase (100s–10,000s ppm Sn; Taylor & Wall, 1993). Based on Sn partitioning between coexisting fluid and silicate melt inclusions, Zajacz et al. (2008) found no systematic variation of the fluid-melt partition coefficients of Sn with the chlorinity of the fluid. In the low chlorinity range ($1\text{--}3 \text{ mol} \cdot \text{kg}^{-1}$), partition coefficients vary between 1.5 and 6.7. A contrasting behavior is observed in high chlorinity fluids with reported partition coefficients ranging from 0.26 and 2.11, up to ~ 42 (Zajacz et al., 2008).

W fluid distribution differs from Sn in that W forms oxyacid complexes like HWO_4^- , and as such, complexes with alkalis, such as NaHWO_4 (Wood & Samson, 2000). As a consequence, the observed positive correlation between the W fluid-melt partition coefficient and the NaCl content of the fluid may be caused by Na ion pairing rather than Cl complexes (cf. Linnen & Cuney, 2005). There is, as such, some variation in experimental fluid-melt partition coefficients. For halogen-free experiments, fluid-melt partition coefficients range from ~ 0.1

(Manning & Henderson, 1984) to ~4 (Schäfer et al., 1999) and ~5 (Keppler & Wyllie, 1991). For low-salinity (NaCl) fluids, fluid-melt partition coefficients of ~0.3 to 1.0 have been derived (Chevychelov & Chevychelova, 1997, as stated in Linnen & Cuney, 2005). For HCl-rich fluids, coefficients of ~0.4 to 1.0 have been reported (Keppler & Wyllie, 1991). Natural fluid-melt partition coefficients of W show a positive correlation with the chlorinity of the fluid phase between 1 and 3 mol·kg⁻¹ (Zajacz et al., 2008). For high-chlorinity natural fluids, the scatter of the natural data is high (Zajacz et al., 2008). Variations in W fluid-melt partition coefficients with chlorinity have been interpreted on the basis of different mass transfer reactions of W from the silicate melt to the exsolved aqueous fluid (Keppler & Wyllie, 1991; Manning & Henderson, 1984; Zajacz et al., 2008):

Fractionation according to reaction 1 would result in a positive correlation between the chlorinity of the fluid phase and W fluid-melt partition coefficient, while reaction 2 would probably result in a negative correlation due to decreasing water activity with increasing salinity. Also fractionation according to reaction 3 would result in a positive correlation between the salinity of the fluid and the fluid-melt partition coefficient (Zajacz et al., 2008). Gibert et al. (1992) demonstrated that the presence of volatiles (N₂, CH₄, CO₂) in W mineralizing fluids have an effect on W speciation and scheelite solubility. Their modeling showed that the addition of N₂ (≤10 mol %) to the mineralizing fluids results in an increase in H₂WO₄⁰ and HWO₄⁻ concentrations relative to WO₄⁻ and in a decrease in scheelite solubility. This mechanism favors scheelite precipitation and illustrates the commonly observed association of W deposits with black shales, which generates mixed volatile fluids and acts as sources for Fe (e.g., ferberite) or Ca (e.g., scheelite) during host-rock interaction and W mineralization (Chicharro et al., 2016; Dewaele et al., 2016b; Hulsbosch et al., 2016; Lecumberri-Sanchez et al., 2017; Polya et al., 2000).

4.5.3.2 Consequences for the KAB

Magmatic Nb-Ta and Sn mineralization in the KAB is only observed at the magmatic end-stages of melt

differentiation ($F \geq 0.98$; i.e., the pegmatites of zone 4). Based on primary fluid inclusions analyses in tourmaline, Hulsbosch et al. (2016) observed that magmatic-hydrothermal fluids, originating from the differentiating Kibara Sn granite-pegmatite system, contain both W (~5–500 ppm) and Sn (~10–400 ppm). Depending on the host-rock lithology, these fluids can exclusively precipitate W or Sn in hydrothermal quartz veins. W mineralization exclusively occurs in the KAB in the peribatholithic quartz vein hosted in black shales (e.g., Nyakabingo) while hydrothermal Sn-mineralization is observed in quartz-muscovite veins hosted in muscovite-feldspar-rich quartzites (e.g., Rutongo). Dewaele et al. (2016b) and Hulsbosch et al. (2016) demonstrate that in case of W mineralization in the KAB, the black shale host rocks are typically altered to a tourmaline-muscovite-(biotite) selvage at the contact with the quartz vein. During host-rock interaction, the black shales acted as a source of iron and calcium for the formation of tungstate minerals (Dewaele et al., 2016b). For example, De Clercq (2012) reported abundant leaching of pyrite in the black shales and sandstones of Nyakabingo. Additionally, during fluid-black shale interaction, the mineralizing fluid could have been mixed with diluted “metamorphic” fluids causing a decrease in chloride concentration of the mineralizing fluid and inducing a substantial decrease in the W solubility (Hulsbosch et al., 2016). Selective cassiterite precipitation from a W- and Sn-containing hydrothermal fluid is favored by oxidation (with H₂ consumption), acid neutralization, or decreasing salinity (Heinrich, 1990). H₂ is consumed by vapor separation and in reactions of the mineralizing fluids with aluminosilicate host rocks. Acidity is consumed during interaction of the mineralizing fluid with host rocks rich in feldspars, which results in the formation of muscovite and quartz assemblages. Cassiterite and cogenetic muscovite occur mainly at the contact zone between the quartz vein and the quartzite host rock due to the selective precipitation mechanism of Sn by acid-consuming induced by feldspar consumption. As such, in the KAB, a magmatic-hydrothermal fluid containing both W and Sn, which originated from the differentiating Kibara Sn granite-pegmatite system, can exclusively precipitate W or Sn depending on the host-rock lithology and associated host-rock reactions (Hulsbosch et al., 2016).

In the Kibara Sn granite-pegmatite system, only Sn can precipitate from these fluids due to the oxidation of Sn²⁺ to Sn⁴⁺ by hydrolysis during greisenization reactions in the zone 4 pegmatites (see also reactions 6 and 7). This general behavior is in line with the experimentally derived fluid-melt partition coefficients stated above: extremely low fluid affinity for Nb and Ta (i.e., retained generally in the melt), insoluble behavior for Sn (i.e., dominantly retained in the melt), and moderately insoluble to soluble

Figure 4.10 Comparison of reported fluid-melt partition coefficient (K_{fm}) for both Sn and W as a function of the molinity of Cl in the fluid phase (moles of Cl/kg of solution). (a) Experimental partitioning in haplogranitic-H₂O-HCl system at 2 kbar, 750°C and NNO buffer conditions (adapted and recalculated from Keppler & Wyllie, 1991). (b) Natural partitioning based on LA-ICP-MS analysis of coexisting fluid and silicate melt inclusions in various granitic systems (peralkaline to peraluminous in composition) at oxygen fugacities ranging from NNO-1.7 to NNO+4.5 (adapted from Zajacz et al., 2008). Grey shaded areas correspond to calculated molinity of Cl in the fluid phase of type I and type II fluid inclusions in the pegmatites of Gatumba-Gitarama (Hulsbosch et al., 2016). Black lines correspond to calculated ratios of the W over Sn fluid-melt partition coefficients.

behavior for W (i.e., partitioning into the aqueous fluid). Notwithstanding the high melt affinity for Sn, magmatic cassiterite is observed only as an accessory mineral phase in the biotite to muscovite pegmatites of zone 1 to 3 have been calculated to vary between 7 and 62 ppm (at 580°C) and between 30 and 270 ppm (at 720°C), which are all significantly lower than the cassiterite saturation limit of Ryabchikov et al. (1978) and Bhalla et al. (2005). In order to evaluate consistently the hydrothermal-metasomatic mineralization potential for both Sn and W, data from studies that determined fluid-melt partition coefficient for Sn and W will be applied. However, studies reporting coefficients for both Sn and W are scarce, with the exception of the experimental study of Keppler and Wyllie (1991) and the natural study of Zajacz et al. (2008). Although, absolute values for fluid-melt partition coefficients can vary over more than one order in magnitude between these studies, overall general conclusions for hydrothermal element fractionation can still be drawn (Fig. 4.10).

Based on the literature review above and the experimental and natural fluid partitioning data of Sn and W in Figure 4.10, the metallogenic processes for hydrothermal Sn and W quartz vein-hosted deposits of an orthomagmatic origin for the KAB can be proposed. (1) A first stage of enrichment of Sn and W in the Kibara Sn granitic up to the initial pegmatitic melt stages by incompatible crystal-melt fractionation. (2) The highly differentiated peraluminous B-rich, F-poor Kibara Sn granite systems will reach

behavior for W (i.e., partitioning into the aqueous fluid). Notwithstanding the high melt affinity for Sn, magmatic cassiterite is observed only as an accessory mineral phase in the biotite to muscovite pegmatites of zone 4. The high solubility of Sn²⁺ in these reduced peraluminous melts (cf. Johnston, 1965; Lehmann, 1990b) is surmounted only by extreme degrees of melt fractionation ($F > 0.98$; Hulsbosch et al., 2014). In these highly fractionated pegmatites of zone 4, oversaturation relatively to SnO₂ can cause direct cassiterite precipitation from the melt when high solubility limits have been exceeded (1000–2000 ppm Sn at the NNO buffer, and at 1.5 kbar and 750°C; Ryabchikov et al., 1978). Bhalla et al. (2005) determined for an H₂O-saturated peraluminous melt (~1 wt% F and at the NNO buffer) the following relationship: $C_{SnO_2} = 3.17 - \frac{3.51 \cdot 10^3}{T}$ for the temperature-dependent (T , Kelvin) cassiterite saturation (C_{SnO_2} , wt%). For a peraluminous melt, cassiterite solubility at 750°C amounts ~5500 ppm SnO₂ (Bhalla et al., 2005). Based on Sn concentrations in magmatic muscovite from zone 4 pegmatites, which range from ~600 to ~1000 ppm (Hulsbosch et al., 2013; 2014), and Sn muscovite-melt distribution coefficients (1.1 at 720°C and 4.9 at 580°C; Kovalenko et al., 1988), calculated Sn concentration in the highly fractionated pegmatitic melt ($F > 0.98$) are between 125 and 204 ppm (at 580°C) and between 545 and 909 ppm (at 720°C). Sn melt contents for the Kibara Sn granites have been estimated between 4–80 ppm

(concentrations can be affected by hydrothermal redistribution; Lehmann & Lavreau, 1987), and Sn melt contents in the biotite to muscovite pegmatites of zone 1 to 3 have been calculated to vary between 7 and 62 ppm (at 580°C) and between 30 and 270 ppm (at 720°C), which are all significantly lower than the cassiterite saturation limit of Ryabchikov et al. (1978) and Bhalla et al. (2005).

In order to evaluate consistently the hydrothermal-metasomatic mineralization potential for both Sn and W, data from studies that determined fluid-melt partition coefficient for Sn and W will be applied. However, studies reporting coefficients for both Sn and W are scarce, with the exception of the experimental study of Keppler and Wyllie (1991) and the natural study of Zajacz et al. (2008). Although, absolute values for fluid-melt partition coefficients can vary over more than one order in magnitude between these studies, overall general conclusions for hydrothermal element fractionation can still be drawn (Fig. 4.10).

Based on the literature review above and the experimental and natural fluid partitioning data of Sn and W in Figure 4.10, the metallogenic processes for hydrothermal Sn and W quartz vein-hosted deposits of an orthomagmatic origin for the KAB can be proposed. (1) A first stage of enrichment of Sn and W in the Kibara Sn granitic up to the initial pegmatitic melt stages by incompatible crystal-melt fractionation. (2) The highly differentiated peraluminous B-rich, F-poor Kibara Sn granite systems will reach

water saturation at relative deeper crustal levels in comparison with F-dominated and/or metaluminous melts (see section 4.5.1.). First indications of fluid saturation are observed just prior to or at the granite-pegmatite transition stage. The relative late-stage fluid saturation of the Kibara Sn system is particularly beneficial for hydrothermal W enrichment because it enables sufficient accumulation of the otherwise highly soluble W in the melt phase. (3) Based on the overall high W to Sn fluid-melt partition coefficient ratio ($k_{\text{fm,W/Sn}} > 1$; Fig. 4.10), the coexisting aqueous fluid phase will preferentially be enriched in W compared to Sn. However, absolute fluid concentrations depend also on the concentration in the Kibara Sn melt systems, which have been estimated between 4 and 80 ppm for Sn (bulk rock data; Lehmann & Lavreau, 1987) and 7.5 ppm for W (Hulsbosch et al., 2016). (4) In the case of W, the high fluid affinity ($K_{\text{fm}} = 1-5$) (i.e., natural systems; Hulsbosch et al., 2016; Zajacz et al., 2008) in combination with the moderately incompatible melt affinity ($K_{\text{cm}} \sim 0.4$) (Hulsbosch et al., 2016) causes preferential enrichment in the coexisting fluid phase during melt differentiation. However, based on W concentrations in primary pegmatitic fluid inclusions and melt-fluid-crystal fractionation calculations (Hulsbosch et al., 2016), W fluid concentrations do not demonstrate a typical exponential enrichment trend during melt differentiation. This is a direct consequence of the depletion of W in the melt phase during differentiation by the dominant partitioning of W into the fluid phase ($K_{\text{fm}} > 1$) (Hulsbosch et al., 2016). As a result, the mineralization potential of W from hydrothermal fluids can be expected already high at the initial stages of magmatic fluid saturation. Protracted melt fractionation in equilibrium with an exsolved fluid phase will only further deplete W from the melt. The lithological control of black shales (e.g., Fe-source; Dewaele et al., 2016b; Hulsbosch et al., 2016) on W precipitation is, moreover, a critical factor for hydrothermal W mineralization in quartz veins (reactions 4 and 5).

with $\text{M} = (\text{Fe}, \text{Mn})^{2+}$ derived from black shales
 $n = 0$ to 2.

(5) In the case of Sn, it preferentially partitions into the melt phase ($k_{\text{fm,W/Sn}} > 1$; Fig. 4.10) and gets more enriched toward the latest magmatic units of the zone 4 pegmatites where melt oversaturation relatively to SnO_2 may cause cassiterite precipitation. In combination with incompatible crystal-melt fractionation, Sn also (but not preferential;

$K_{\text{fm}} < 1$) enriches in the coexisting fluid phase. Due to its highly incompatible behavior (cf. Taylor, 1979), Sn melt concentrations should describe an exponential enrichment trend during melt differentiation, which in turn, should cause an exponential fluid enrichment trend in the cogenetic fluid phase due to the relatively low fluid affinity (compared to W; e.g., Fig. 4.10). Ultimately, in H_2O -saturated peraluminous melt systems, very high Sn fluid concentrations should be expected at high ($F > 0.98$) degrees of melt differentiation. However, verification is, up to now, hampered because no LA-ICP-MS compositional analyses of the inclusions in minerals from the highly fractionated, Nb-Ta-Sn pegmatites of zone 4 could not be performed due to the overprinting of the inclusion record by secondary fluids (cf. Dewaele et al., 2008). As a result, the mineralization potential of Sn from hydrothermal fluids can be expected to increase with melt differentiation in equilibrium with an exsolved fluid. Hydrothermal Sn mineralization is consequently expected to culminate at the highest degrees of melt differentiation. Moreover, due to the capability of both pegmatites and sandstones/quartzites to act as lithologically controlled precipitation horizons by feldspar hydrolysis reactions (reactions 6 and 7; Dewaele et al., 2016b; Hulsbosch et al., 2016) and due to the higher Sn/W ratios in Kibara Sn granites (e.g., ~ 16 based on data of Lehmann & Lavreau, 1987), Sn mineralization is more widespread in the KAB granite-related ore system.

4.6. W-SN ORE POTENTIAL OF GRANITE-RELATED SYSTEMS

In section 4.5.3., it is concluded that W and Sn have an opposing hydrothermal mineralization potential in water-saturated, peraluminous granite-related ore systems. The potential of W to form hydrothermal deposits can be expected already optimally high at the initial stages of magmatic fluid saturation (i.e., a melt at relatively lower degrees of differentiation). Protracted melt fractionation in equilibrium with an exsolved fluid phase will only further deplete W in the melt and in turn in the coexisting fluid phase due the partitioning of W into the fluid phase. The mineralization potential of Sn from hydrothermal fluids increases with melt differentiation in equilibrium with an exsolved fluid. Hydrothermal Sn mineralization is consequently expected to culminate at the highest degrees of melt differentiation. In order to conceptualize

this opposing fractionation behavior, two theoretical parameters are proposed to quantify the potential from magmatic and hydrothermal Sn and W ores, that is, the Magmatic Ore Potential (MOP) and Hydrothermal Ore Potential (HOP), shown in equations (4.1)–(4.4):

$$MOPW = \frac{C_{m,W}}{C_{m,Sn}} = C_{m,W/Sn}^0 \frac{\left(\frac{f_m}{f_m^0}\right)^{K_{cm,W}\left(1-\frac{K_{fm,W}}{K_{cm,W}}\right)\Phi_{H_2O}+K_{cm,W}-1}}{\left(\frac{f_m}{f_m^0}\right)^{K_{cm,Sn}\left(1-\frac{K_{fm,Sn}}{K_{cm,Sn}}\right)\Phi_{H_2O}+K_{cm,Sn}-1}} \quad (4.1)$$

$$MOPSn = \frac{C_{m,Sn}}{C_{m,W}} = C_{m,Sn/W}^0 \frac{\left(\frac{f_m}{f_m^0}\right)^{K_{cm,Sn}\left(1-\frac{K_{fm,Sn}}{K_{cm,Sn}}\right)\Phi_{H_2O}+K_{cm,Sn}-1}}{\left(\frac{f_m}{f_m^0}\right)^{K_{cm,W}\left(1-\frac{K_{fm,W}}{K_{cm,W}}\right)\Phi_{H_2O}+K_{cm,W}-1}} \quad (4.2)$$

$$HOPW = \frac{C_{f,W}}{C_{f,Sn}} = C_{m,W/Sn}^0 \frac{K_{fm,W}\left(\frac{f_m}{f_m^0}\right)^{K_{cm,W}\left(1-\frac{K_{fm,W}}{K_{cm,W}}\right)\Phi_{H_2O}+K_{cm,W}-1}}{K_{fm,Sn}\left(\frac{f_m}{f_m^0}\right)^{K_{cm,Sn}\left(1-\frac{K_{fm,Sn}}{K_{cm,Sn}}\right)\Phi_{H_2O}+K_{cm,Sn}-1}} \quad (4.3)$$

$$HOPSn = \frac{C_{f,Sn}}{C_{f,W}} = C_{m,Sn/W}^0 \frac{K_{fm,Sn}\left(\frac{f_m}{f_m^0}\right)^{K_{cm,Sn}\left(1-\frac{K_{fm,Sn}}{K_{cm,Sn}}\right)\Phi_{H_2O}+K_{cm,Sn}-1}}{K_{fm,W}\left(\frac{f_m}{f_m^0}\right)^{K_{cm,W}\left(1-\frac{K_{fm,W}}{K_{cm,W}}\right)\Phi_{H_2O}+K_{cm,W}-1}} \quad (4.4)$$

With C_m = trace element concentration in the melt phase, C_f = trace element concentration in the fluid phase, C_m^0 = initial trace element concentration in the parental melt, K_{fm} = bulk fluid-melt partition coefficient, K_{cm} = bulk crystal-melt partition coefficient, f_m = mass fraction of melt, $f_m^0 = 1$ = melt is water-saturated at the liquidus, Φ_{H_2O} = the negative of the solubility of water in the melt (see details in Spera et al., 2007).

In Equations (4.1) to (4.4), the partitioning of the ore elements among coexisting crystals, melt, and supercritical fluid melt (i.e., C_m and C_f) during crystallization are calculated on the basis of equations of Spera et al. (2007) (see also Fig. 4.11). The MOP and HOP parameters

Figure 4.11 Conceptual sketch demonstrating the partitioning of trace elements among coexisting crystals, melt, and fluid, and illustrating the chemical behavior of compatible versus incompatible, and soluble versus insoluble elements as quantified by their crystal-melt and fluid-melt partition coefficients. The distribution of elements among these three phases forms the backbone of the Magmatic Ore Potential (MOP) and Hydrothermal Ore Potential (HOP) calculation.

express the normalized (i.e., $C_{m,W}^0 = C_{m,Sn}^0 = 1$ at $f_m = 1$) potential of a melt or hydrothermal fluid to be relatively enriched in W or Sn in function of melt differentiation (i.e., the mass fraction of melt f_m). The evolution of the adimensional MOP or HOP parameters in function of mass fraction of melt provides a semiquantitative evaluation of the ore elements Sn and W and their potential to form magmatic or hydrothermal granite-related deposits with protracting fractionation of the melt. In the case of magmatic deposits (cf. section 4.5.1, i.e., MOP), enrichment of an incompatible element in the melt and subsequent saturation-precipitation of the respective ore mineral are the main mineralization processes while for hydrothermal deposits fluid-mineral fractionation, solubility in aqueous phase, and precipitation processes dominate (cf. section 4.5.3, i.e., HOP).

By applying the Spera et al. (2007) formulation to calculate the melt (C_m) and fluid (C_f) concentrations, the essential role of the fluid phase is considered by implementing a mass-balance expression of water (ϕ_{H_2O}) to the traditional fractional crystallization expressions. This is the only valid procedure for multiphase crystal-fluid-melt systems, especially if water solubilities exceed ~5 wt%

H₂O (cf. Spera et al., 2007). Ignoring the mass-balance expression of water and consequently the partitioning of soluble elements, like W, into the fluid phase leads to significant miscalculation of the melt concentrations.

The MOP and HOP of the Kibara Sn granite ore systems have been evaluated using the method explained above. In order to calculate the necessary partition coefficients, the Kibara Sn system has been simplified to a water-saturated, peraluminous haplogranitic melt (i.e., 47.5% Kfs, 23.8% Pl, 23.8% Qz, and 5% Ms; ASI = 1.5) with following system parameters:

$f_m^0 = 1$ = water saturation at the liquidus

$K_{cm,W} = 0.4$ (value from Hulsbosch et al., 2016)

$K_{cm,Sn} = 0.3$ = calculated from the Sn crystal-melt partition coefficients for Kfs, Pl, Qz, and Ms of Kovalenko et al. (1988)

$K_{fm,W} = 2.5$ (value from Hulsbosch et al., 2016)

$K_{fm,Sn} = 0.16$ = calculated from the correlation between the Sn fluid-melt partition coefficient and aluminum saturation index of Hu et al. (2008)

The MOP and HOP parameters of W and Sn for the peraluminous and water-saturated Kibara Sn granite are given in Figure 4.12. Based on the MOP and HOP parameters of W (Fig. 4.12 a and b), a distinct preference of W to fractionation toward the immiscible fluid phase is observed at the expense of the melt with an approximate factor of 10 ($HOP \gg MOP$). With protracted melt fractionation, both the MOP and HOP decrease due to high solubility of W. This behavior can especially be noticed by evaluating the MOP and HOP parameters calculated for different water solubilities (Fig. 4.12 a, b: 5, 10, and 15 wt% H₂O) showing a general decrease with increasing water solubilities. The potential to form magmatic or hydrothermal deposits decrease over several orders of magnitude with melt differentiation from $f_m = 1$ to $f_m = 0.01$. The MOP and HOP parameters quantify and visualize the proposed fractionation behavior of W in sections 4.5.1 and 4.5.3: the potential of W to form magmatic disseminated and hydrothermal deposits decreases exponentially with protracted melt differentiation and is

Figure 4.12 The relative Magmatic Ore Potential (MOP) and Hydrothermal Ore Potential (HOP) parameters for W (a) and (b), and Sn (c) and (d) versus the mass fraction of melt (f_m), respectively, and for different water solubilities (5, 10, 15 wt.%). Calculations stopped at $f_m = 0.01$. For calculation and interpretation see text.

negatively affected by protracted W fluid fractionation. The potential for hydrothermal deposits is high at relatively low degrees of melt differentiation (f_m between 1 and 0.25).

A contrasting evolution can be deduced from the MOP and HOP parameters of Sn (Fig. 4.12 c and d). A general preference of Sn for the melt phase is observed (MOP > HOP). Due to the incompatibility and insolubility of Sn, both the melt and coexisting fluid phase show an increasing potential to form Sn mineralization with protracted melt differentiation. The amount of exsolved fluids (Fig. 4.12 c and d: 5, 10, and 15 wt% H₂O) is a less crucial factor for Sn mineralization due to the low Sn solubility. Again, the MOP and HOP parameters quantitatively describe the fractionation behavior of Sn as proposed in sections 4.5.1 and 4.5.3. Magmatic disseminated Sn mineralization can occur only at very high degrees of melt differentiation (i.e., oversaturation) and the potential to form hydrothermal or metasomatic deposits exponentially increase with protracted melt differentiation. Consequently, for the KAB, the MOP and HOP parameters explain the formation of only hydrothermal mineralization in quartz veins for W, whereas Sn can form both magmatic and hydrothermal/metasomatic mineralization in pegmatites and quartz veins.

4.7. KIBARA METALLOGENIC MODEL

Based on the presented results of this study, an integrated metallogenic model is proposed for the granite-related ore deposits in the KAB. The model is based on four evolutionary stages (a to d, see also Figs. 4.13 a–d) and focused on the three main deposit types of the KAB as they occur in Central Rwanda: the Nb-Ta-Sn Gatumba-Gitarama pegmatite field, the Nyakabingo W quartz vein, and the Rutongo Sn quartz-vein localities (Figs. 4.5 and 4.8). This generic model can be applied to all ore deposit types associated with B-rich, F-poor granite systems (Fig. 4.13).

1. Intrusion and crystallization of barren G1-3 granitic magmas at ca. 1.375 Ga (Tack et al., 2010) in a basin sequence composed of Akanyaru Supergroup metasediments (see also Fig. 4.8; see also Fig. 4.7; Fernandez-Alonso et al., 2012).

2. Regional intrusion of the late-orogenic Kibara Sn or so-called G4 granite generation at ~986 Ma (Tack et al., 2010) as composite intrusions within the G1–3 generation in a folded and foliated basin sequence. Initial differentiation due to Rayleigh fractionation causes incompatible elements Sn, W, Nb, and Ta to progressively concentrate in the melt (Hulsbosch et al., 2014). Subsequent second boiling of this relatively deep-seated system (≤ 4 kbar; Lehmann et al., 2013) initiated saturation of a magmatic medium saline fluid (Hulsbosch et al.,

2016). W partitions strongly into the fluid phase as (alkali-) tungstate complexes. Especially the lack of F in this specific granite system delays the exsolution of the W-bearing fluid phase. Moreover, Sn is retained preferentially in the melt at these conditions and will selectively partition only into the fluid phase at elevated Cl concentrations. Notwithstanding that this magmatic fluid will contain W and Sn, the fluid's ore potential for W will decline with protracting melt differentiation and fluid exsolution, while the fluid's ore potential for Sn will exponentially increase. Magmatic fluid expulsion and fluid flow will occur along pre-existing planes of structural weakness like bedding, cleavage, and fractures (Hulsbosch et al., 2017b; Muchez et al., 2014). Once these initial W-(Sn) magmatic fluids are channeled out of the differentiating Kibara Sn granite system, the fluid source signature is modified due to mixing with external meteoric or "metamorphic" fluid reservoirs and overprinting by fluid–host rock interactions (e.g., De Clercq, 2012). More specifically, black shales controlled the scheelite-ferberite precipitation in hydrothermal quartz veins (992.4 ± 1.5 Ma at Nyakabingo; ^{40}Ar – ^{39}Ar on muscovite) by a combination of decreasing temperature, addition of volatiles, an increase in pH through wall-rock reaction, and wall-rock element leaching. Hydrothermal cassiterite-containing quartz veins will occur in quartzite-sandstone units by feldspar hydrolysis reaction. However, based on the exponentially increasing MOP and HOP parameters for Sn with melt differentiation, a culmination of hydrothermal Sn mineralization in quartz veins is expected near the end-stage of the magmatic Kibara Sn system (965 ± 29 Ma at Rutongo; Rb-Sr on muscovite; Montey-Poulaert et al., 1962). Both the lithological control of different host-rock units and contrasting fluid evolution of W and Sn will cause a decoupling of these elements during hydrothermal ore formation.

Contemporaneous and cogenetically with the formation of a W-enriched fluid phase, the residual melt-fluid system becomes more and more differentiated by Rayleigh fractionation processes (Hulsbosch et al., 2016). Eventually, expulsion of the highly evolved pegmatite-forming melts is triggered. The magmatic crystallization age of the Gatumba-Gitarama pegmatites has been determined at ca. 975 Ma (i.e., zone 4): 975 ± 29 Ma (Rb-Sr on muscovite; Cahen, 1964) and 975 ± 8 Ma (U-Pb on columbite-tantalite; Dewaele et al., 2011). The residual pegmatitic melt is extremely enriched in incompatible melt structure modifiers (e.g., Nb, Ta, Sn B, P, alkali metals, carbonates, sulfates, borates, phosphates, and H₂O), causing the melt viscosity to be several orders of magnitude lower than the crystal mush matrix (Thomas & Davidson, 2013). These chemical and physical conditions between a low-viscous, residual melt and its parental melt are favorable conditions to extract the

pegmatitic liquid from the granitic system. The pegmatite-forming melt system will increasingly become more differentiated by Rayleigh fractionation processes with the formation of biotite, biotite-muscovite, muscovite, and mineralized pegmatite zones. Eventually Ta-Nb oxide and cassiterite saturation initiates at the most differentiated and late magmatic end-stages, that is, the mineralized pegmatite zone, and a magmatic Nb-Ta and Sn mineralization forms in the residual pegmatite system (ages between 975 ± 8 Ma and 966 ± 9 Ma; U-Pb on CGM) (Dewaele et al., 2011; Melcher et al., 2015).

3. Late-stage reduced acidic and saline magmatic fluids in both the granitic and pegmatitic system (Thomas & Davidson, 2013; Veksler, 2005) transported Sn as Sn^{2+} -chloride complexes (Černý et al., 2005). Intra- and peribatholithic Sn deposits form by the interaction of this Sn-bearing fluid with host (pegmatite) and wall rock (sandstone-quartzite), triggering acid-consuming reactions (cf. muscovitization), and eventually precipitation of the major phase of cassiterite.

4.8. CONCLUSION

The results of this study strongly suggest an orthomagmatic origin for granite-related Nb-Ta-Sn-W mineralization, especially at their type-localities in Central Rwanda. It classifies the KAB as a granite-related ore system genetically related to Kibara Sn granites (i.e., G4 granites). Rayleigh-type fractional crystallization acted as the main mechanism by which pegmatitic magmas differentiate from a parental leucogranitic melt and by which incompatible elements Nb, Ta, Sn, and W initially are enriched. However, early aqueous fluid immiscibility has been identified to occur during differentiation of this B-rich, F-poor melt system, which greatly affects further W enrichment in the melt by preferential partitioning of W into the mobile fluid phase. Element-specific melt-fluid-crystal fractionation together with element-specific and lithological-controlled precipitation conditions are the key enrichment processes and are all responsible for the decoupling of Nb-Ta, Sn, and W and their subsequent precipitation in pegmatite, hydrothermal quartz vein, and greisen deposits.

ACKNOWLEDGMENTS

Sincere thanks to Philippe Muchez and Stijn Dewaele for all their advice, guidance, and insights. Research of the author is funded by a postdoctoral fellowship of the Research Foundations–Flanders (FWO). Helpful comments to the manuscript made by two AGU reviewers are greatly appreciated. Last, thanks to editors Sophie Decrée and Laurence Robb for the opportunity to write this chapter and for their editorial handling.

REFERENCES

- Aissa, M., Weisbrod, A., & Marignac, C. (1987). Caractéristiques chimiques et thermodynamiques des circulations hydrothermales du site d'Echassières. *Géologie de la France*, 2–3, 335–350.
- Antipin, V. S., Kovalenko, V. I., Kuznetsova, A. I., & P. L. A. (1981). Tin and tungsten behavior in ore-bearing acidic magmatic rocks according to analyses of the partition coefficients. *Geokhimiya*, 2, 163–177.
- Audétat, A., Günther, D., & Heinrich, C. A. (2000a). Magmatic-hydrothermal evolution in a fractionating granite: A microchemical study of the Sn-W-F-mineralized Mole Granite (Australia). *Geochimica et Cosmochimica Acta*, 64(19), 3373–3393.
- Audétat, A., Gunther, D., & Heinrich, C. A. (2000b). Causes for large-scale metal zonation around mineralized plutons: Fluid inclusion LA-ICP-MS evidence from the Mole Granite, Australia. *Econ. Geol. Bull. Soc. Econ. Geol.*, 95(8), 1563–1581.
- Badanina, E. V., Veksler, I. V., Thomas, R., Sryitso, L. F., & Trumbull, R. B. (2004). Magmatic evolution of Li-F, rare-metal granites: a case study of melt inclusions in the Khangilay complex, Eastern Transbaikalia (Russia). *Chemical Geology*, 210(1–4), 113–133.
- Baker, T., Pollard, P. J., Mustard, R., Markl, G., & Graham, J. L. (2005). A comparison of granite-related tin, tungsten, and gold-bismuth deposits: Implications for exploration. *SEG Newsletter*, 61, 5–17.
- Barsukov, V. L. (1957). The geochemistry of tin. *Geochemistry*, 1, 41–52.
- Bartels, A., Holtz, F., & Linnen, R. L. (2010). Solubility of manganotantalite and manganocolumbite in pegmatitic melts. *American Mineralogist*, 95(4), 537–544.
- Bartels, A., Behrens, H., Holtz, F., Schmidt, B. C., Fechtelkord, M., Knipping, J., Crede, L., et al. (2013). The effect of fluorine, boron and phosphorus on the viscosity of pegmatite forming melts. *Chemical Geology*, 346(0), 184–198.
- Baudet, D., Hanon, M., Lemonne, E., Theunissen, K., Buyagu, S., Dehandschutter, J., Ngizimana, W., et al. (1988). Lithostratigraphie du domaine sédimentaire de la chaîne Kibarienne au Rwanda. *Annales de la Société Géologique de Belgique*, 112, 225–246.
- Bertossa, A. (1965). La pegmatite de Buranga. *Bulletin de la Société belge de Rwanda*, 2, 1–5.
- Bertossa, A. (1968). Inventaire des minéraux du Rwanda. *Bulletin du Service Géologique de Rwanda*, 4, 25–46.
- Bertossa, A., Gérards, J., & Petricec, V. (1964). Géologie de la région de Kigali. *Bulletin du Service Géologique de Rwanda*, 1, 3–12.
- Beus, A. A. (1966). *Geochemistry of Beryllium And Genetic Types of Beryllium Deposits*. W. H. Freeman, San Francisco.
- Beus, A. A. (1986). *Geology of Tungsten*. UNESCO Publishing.
- Bhalla, P., Holtz, F., Linnen, R. L., & Behrens, H. (2005). Solubility of cassiterite in evolved granitic melts: effect of T, fO₂, and additional volatiles. *Lithos*, 80(1–4), 387–400.
- Borodulin, G. P., Chevychelov, V. Y., & Zaraysky, G. P. (2009). Experimental study of partitioning of tantalum, niobium, manganese, and fluorine between aqueous fluoride fluid and granitic and alkaline melts. *Doklady Earth Sciences*, 427(1), 868–873.

- Bouchot, V., Ledru, P., Lerouge, C., Lescuyer, J. L., & Milesi, J. P. (2005). Late Variscan mineralizing systems related to orogenic processes: The French Massif Central. *Ore Geology Reviews*, 27(1–4), 169–197.
- Breiter, K., Forster, H. J., & Seltmann, R. (1999). Variscan silicic magmatism and related tin-tungsten mineralization in the Erzgebirge-Slavkovsky les metallogenic province. *Mineralium Deposita*, 34(5–6), 505–521.
- Breiter, K., Škoda, R., & Uher, P. (2007). Nb-Ta-Ti-W-Sn-oxide minerals as indicators of a peraluminous P- and F-rich granitic system evolution: Podlesí, Czech Republic. *Mineralogy and Petrology*, 91(3–4), 225–248.
- Brown, M. (1994). The generation, segregation, ascent and emplacement of granite magma: the migmatite-to-crustally-derived granite connection in thickened orogens. *Earth-Science Reviews*, 36(1–2), 83–130.
- Buchwaldt, R., Toulkeridis, T., Todt, W., & Ucakuwun, E. K. (2008). Crustal age domains in the Kibaran belt of SW-Uganda: Combined zircon geochronology and Sm-Nd isotopic investigation. *Journal of African Earth Sciences*, 51(1), 4–20.
- Burnham, C. W. (1997). *Magma and hydrothermal fluids*, 3rd ed. John Wiley & Sons.
- Cahen, L. (1964). État de la géochronologie du Rwanda. *Bulletin du Service Géologique de Rwanda*, 1, 35–38.
- Cahen, L., & Ledent, D. (1979). Précisions sur l'âge, la pétrogénèse et la position stratigraphique des granites à étain de l'est de l'Afrique Centrale. *Bulletin de la Société belge de Géologie*, 88, 33–49.
- Cahen, L., Snelling, N. J., Delhal, J., Vail, J. R., Bonhomme, M., & Ledent, D. (1984). *The Geochronology and Evolution of Africa*. Oxford University Press.
- Candela, P. A. (1992). Controls on ore metal ratios in granite related ore systems: an experimental and computational approach. *Transactions of the Royal Society of Edinburgh: Earth Sciences*, 83, 317–326.
- Candela, P. A. (1997). A Review of Shallow, Ore-related granites: textures, volatiles, and ore metals. *Journal of Petrology*, 38(12), 1619–1633.
- Carroll, M. R., & Webster, J. D. (1994). Solubilities of sulfur, noble gases, nitrogen, chlorine, and fluorine in magmas. *Volatiles in Magmas*, 30, 231–279.
- Černý, P. (1991a). Rare-element granitic pegmatites. Part I. Anatomy and internal evolution of pegmatite deposits. *Geoscience Canada*, 18, 49–67.
- Černý, P. (1991b). Fertile granites of Precambrian rare-element pegmatite fields: Is geochemistry controlled by tectonic setting or source lithologies? *Precambrian Research*, 51(1–4), 429–468.
- Černý, P. (1991c). Rare-element granitic pegmatites. Part II. Regional to global environments and petrogenesis. *Geoscience Canada*, 18, 68–81.
- Černý, P., & Ercit, T. S. (2005). The classification of granitic pegmatites. *The Canadian Mineralogist*, 43(6), 2005–2026.
- Černý, P., Blevin, P. L., Cuney, M., & London, D. (2005). Granite-Related Ore Deposits. *Economic Geology 100th Anniversary volume*, 337–370.
- Che, X. D., Linnen, R. L., Wang, R. C., Aseri, A., & Thibault, Y. (2013). Tungsten solubility in evolved granitic melts: An evaluation of magmatic wolframite. *Geochimica et Cosmochimica Acta*, 106, 84–98.
- Chevychelov, V., Zarskiy, C., Borisovsky, S., & Borkov, D. (2004). Partitioning of Ta and Nb between magmatic melt and aqueous (K,Na,H)F-containing fluid. Effects of temperature and chemical composition of the melt. *Lithos*, 73(1–2), S17–S17.
- Chicharro, E., Boiron M.-C., López-García, J. Á., D. N. Barfod, & Villaseca, C. (2016). Origin, ore forming fluid evolution and timing of the Logrosán Sn–(W) ore deposits (Central Iberian Zone, Spain). *Ore Geology Reviews*, 72, Part 1, 896–913.
- Chicharro, E., Martín-Crespo, T., Gómez-Ortiz, D., López-García, J. Á., Oyarzun, R., & Villaseca, C. (2015). Geology and gravity modeling of the Logrosán Sn–(W) ore deposits (Central Iberian Zone, Spain). *Ore Geology Reviews*, 65, Part 1(0), 294–307.
- Cuney, M., Marignac, C., & Weisbrod, A. (1992). The Beauvoir topaz-lepidolite albite granite (Massif Central, France); the disseminated magmatic Sn-Li-Ta-Nb-Be mineralization. *Economic Geology*, 87(7), 1766–1794.
- Daltry, V. D. C., & Von Knorring, O. (1998). Type-mineralogy of Rwanda with particular reference to the Buranga pegmatite. *Geologica Belgica*, 1, 9–15.
- De Clercq, F. (2012). *Metallogenesis of Sn and W vein-type deposits in the Karagwe-Ankole belt (Rwanda)*, KU Leuven, Department of Earth and Environmental Sciences.
- De Clercq, F., Muchez, P., Dewaele, S., & Boyce, A. (2008). The tungsten mineralisation at Nyakabingo and Gifurwe (Rwanda): Preliminary results. *Geologica Belgica*, 11(3–4), 251–258.
- Deblond, A., Punzalan, L. E., Boven, A., & Tack, L. (2001). The Malagarazi supergroup of southeast Burundi and its correlative Bukoba supergroup of northwest Tanzania: neo- and mesoproterozoic chronostratigraphic constraints from Ar-Ar ages on mafic intrusive rocks. *Journal of African Earth Sciences*, 32(3), 435–449.
- Debon, F., & Le Fort, P. (1983). Chemical-mineralogical classification of common plutonic rocks and associations. *Transactions of the Royal Society of Edinburgh: Earth Sciences*, 73, 135–149.
- Debruyne, D., Hulsbosch, N., Van Wilderode, J., Balcaen, L., Vanhaecke, F., & Muchez, P. (2015). Regional geodynamic context for the Mesoproterozoic Kibara Belt (KIB) and the Karagwe-Ankole Belt: Evidence from geochemistry and isotopes in the KIB. *Precambrian Research*, 264, 82–97.
- Dewaele, S., Muchez, P., Burgess, R., & Boyce, A. (2015). Geological setting and timing of the cassiterite vein type mineralization of the Kalima area (Maniema, Democratic Republic of Congo). *Journal of African Earth Sciences*, 112, 199–212.
- Dewaele, S., Tack, L., Fernandez, M., Boyce, A., & Muchez, P. (2007). *Cassiterite mineralization in vein-type deposits of the Kibara orogen (Central Africa): Nyamiumba (Rutongo area, Rwanda)*, 1007–1010.
- Dewaele, S., Hulsbosch, N., Cryns, Y., Boyce, A., Burgess, R., & Muchez, P. (2016a). Geological setting and timing of the world-class Sn, Nb-Ta and Li mineralization of Manono-Kitotolo (Katanga, Democratic Republic of Congo). *Ore Geology Reviews*, 72, Part 1, 373–390.

- Dewaele, S., De Clercq, F., Muchez, P., Schneider, J., Burgess, R., Boyce, A., & Fernandez Alonso, M. (2010). Geology of the cassiterite mineralisation in the Rutongo area, Rwanda (Central Africa): current state of knowledge. *Geologica Belgica*, 13(1–2), 91–111.
- Dewaele, S., De Clercq, F., Hulsbosch, N., Piessens, K., Boyce, A., Burgess, R., & Muchez, P. (2016b). Genesis of the vein-type tungsten mineralization at Nyakabingo (Rwanda) in the Karagwe–Ankole belt, Central Africa. *Mineralium Deposita*, 51(2), 283–307.
- Dewaele, S., Tack, L., Fernandez Alonso, M., Boyce, A., Muchez, P., Schneider, J., Cooper, G., & Wheeler, K. (2008). Geology and mineralisation of the Gatumba area, Rwanda: present state of knowledge. *Etudes Rwandaises*, 16, 6–24.
- Dewaele, S., Henjes-Kunst, F., Melcher, F., Sitnikova, M., Burgess, R., Gerdes, A., Fernandez, M. A., Clercq, F. D., Muchez, P., & Lehmann, B. (2011). Late Neoproterozoic overprinting of the cassiterite and columbite-tantalite bearing pegmatites of the Gatumba area, Rwanda (Central Africa). *Journal of African Earth Sciences*, 61(1), 10–26.
- Dingwell, D. B. (1988). The structure and properties of fluorine-rich magmas: a review of experimental studies, in R. P. Taylor & D. F. Strong, *Recent advances in the geology of granite-related mineral deposits* (pp. 1–12). Canadian Institute of Mining and Metallurgy.
- Dingwell, D. B., Harris, D. M., & Scarfe, C. M. (1984). The solubility of H₂O in melts in the system: SiO₂–Al₂O₃–Na₂O–K₂O at 1 to 2 Kbars. *Journal of Geology*, 92(4), 387–395.
- EC (2017). *Study on the review of the list of critical raw materials: Critical raw materials factsheets*, European Commission, Directorate-General for Internal Market, Industry, Entrepreneurship and SMEs.
- Fernandez-Alonso, M. (1981). Données préliminaires sur la géochimie de granites protérozoïques du Rwanda et du Burundi. *Rapport Annuel de la Musée royal de l'Afrique Centrale*, 195–207.
- Fernandez-Alonso, M., & Theunissen, K. (1998). Airborne geophysics and geochemistry provide new insights in the intracratonic evolution of the Mesoproterozoic Kibaran belt (Central Africa). *Geological Magazine*, 135(2), 203–216.
- Fernandez-Alonso, M., Lavreau, J., & Klerkx, J. (1986). Geochemistry and geochronology of the Kibaran granites in Burundi, Central Africa: Implications for the Kibaran orogeny. *Chemical Geology*, 57(1–2), 217–234.
- Fernandez-Alonso, M., Cutten, H., De Waele, B., Tack, L., Tahon, A., Baudet, D., & Barritt, S. D. (2012). The Mesoproterozoic Karagwe–Ankole Belt (formerly the NE Kibara Belt): The result of prolonged extensional intracratonic basin development punctuated by two short-lived far-field compressional events. *Precambrian Research*, 216–219, 63–86.
- Fernandez-Alonso, M. (2007). *Geological Map of the Mesoproterozoic Northeastern Kibara Belt*, Royal Museum for Central Africa, Tervuren, Belgium.
- Fiege, A., Kirchner, C., Holtz, F., Linnen, R. L., & Dziony, W. (2011). Influence of fluorine on the solubility of manganotantalite (MnTa₂O₆) and manganocolumbite (MnNb₂O₆) in granitic melts: An experimental study. *Lithos*, 122(3–4), 165–174.
- Förster, H. J., Romer, R. L., Gottesmann, B., Tischendorf, G., & Rhede, D. (2009). Are the granites of the Aue-Schwarzenberg Zone (Erzgebirge, Germany) a major source for metalliferous ore deposits? A geochemical, Sr–Nd–Pb isotopic, and geochronological study. *Neues Jahrbuch für Mineralogie, Abhandlungen*, 186(2), 163–184.
- Frost, B. R., Barnes, C. G., Collins, W. J., Arculus, R. J., Ellis, D. J., & Frost, C. D. (2001). A geochemical classification for granitic rocks. *Journal of Petrology*, 42(11), 2033–2048.
- Gast, P. W. (1972). The chemical composition and structure of the moon. *The Moon*, 5(1), 121–148.
- Gérards, J. (1965). Géologie de la région de Gatumba. *Bulletin du Service Géologique Rwandaise*, 2, 31–42.
- Gibert, F., Moine, B., Schott, J., & Dandurand, J.-L. (1992). Modeling of the transport and deposition of tungsten in the scheelite-bearing calc-silicate gneisses of the Montagne Noire, France. *Contributions to Mineralogy and Petrology*, 112(2), 371–384.
- Goldmann, S., Melcher, F., Gäbler, H.-E., Dewaele, S., Clercq, F., & Muchez, P. (2013). Mineralogy and Trace Element Chemistry of Ferberite/Reinite from Tungsten Deposits in Central Rwanda. *Minerals*, 3(2), 121–144.
- Günther, M. A. (1990). Flüssigkeitseinschlüsse und geologisches Umfeld zentralafrikanischer Sn-, W- und Au-Lagerstätten (Rwanda und Burundi), technischen Universität Carolo-Wilhelmina zu Braunschweig, Braunschweig.
- Günther, M. A., & Ndutiye, W. (1990). The tungsten deposit of Nyakabingo, Rwanda. *International Geological Correlation Programme, Project n° 255, TU Braunschweig-MRAC Tervuren*, 3, 31–36.
- Günther, M. A., Dulski, P., Lavreau, J., Lehmann, B., Möller, P., & Pohl, W. (1989). The Kibaran tin granites: Hydrothermal alteration versus plate tectonic setting. *International Geological Correlation Programme, Project n° 255, TU Braunschweig-MRAC Tervuren*, 2, 21–27.
- Harlaux, M., Romer, R. L., Mercadier, J., Morlot, C., Marignac, C., & Cuney, M. (2017a). 40 Ma of hydrothermal W mineralization during the Variscan orogenic evolution of the French Massif Central revealed by U–Pb dating of wolframite. *Mineralium Deposita*.
- Harlaux, M., Mercadier, J., Bonzi, W., Marc-Emile, D., Kremer, V., Marignac, C., & Cuney, M. (2017b). Geochemical Signature of Magmatic-Hydrothermal Fluids Exsolved from the Beauvoir Rare-Metal Granite (Massif Central, France): Insights from LA-ICPMS Analysis of Primary Fluid Inclusions. *Geofluids*, 2017, 25.
- Heinrich, C. A. (1990). The chemistry of hydrothermal tin(tungsten) ore deposition. *Economic Geology*, 85(3), 457–481.
- Holtz, F., Dingwell, D. B., & Behrens, H. (1993). Effects of F, B₂O₃ and P₂O₅ on the solubility of water in haplogranite melts compared to natural silicate melts. *Contributions to Mineralogy and Petrology*, 113(4), 492–501.
- Holtz, F., Johannes, W., Tamic, N., & Behrens, H. (2001). Maximum and minimum water contents of granitic melts generated in the crust: a reevaluation and implications. *Lithos*, 56(1), 1–14.
- Hu, X., Bi, X., Hu, R., Shang, L., & Wenling, F. (2008). Experimental study on tin partition between granitic silicate melt and coexisting aqueous fluid. *Geochemical Journal*, 42(2), 141–150.

- Hu, X., Bi, X., Hu, R., Cai, G., & Chen, Y. (2016). Tin partition behavior and implications for the Furong tin ore formation associated with peralkaline intrusive granite in Hunan Province, China. *Acta Geochimica*, 35(2), 138–147.
- Hulsbosch, N. (2016). Chemical fractionation in granite-related ore systems: evidence from Nb-Ta-Sn pegmatite-type and Sn-W quartz vein-type mineralisation in the Karagwe-Ankole Belt (Rwanda). University of Leuven, KU Leuven, Leuven.
- Hulsbosch, N., Boiron, M.-C., Dewaele, S., & Muchez, P. (2016). Fluid fractionation of tungsten during granite-pegmatite differentiation and the metal source of peribatholithic W quartz veins: Evidence from the Karagwe-Ankole Belt (Rwanda). *Geochimica et Cosmochimica Acta*, 175, 299–318.
- Hulsbosch, N., Hertogen, J., Dewaele, S., André, L., & Muchez, P. (2013). Petrographic and mineralogical characterisation of fractionated pegmatites culminating in the Nb-Ta-Sn pegmatites of the Gatumba area (western Rwanda). *Geologica Belgica*, 16(1–2), 105–117.
- Hulsbosch, N., Hertogen, J., Dewaele, S., André, L., & Muchez, P. (2014). Alkali metal and rare earth element evolution of rock-forming minerals from the Gatumba area pegmatites (Rwanda): Quantitative assessment of crystal-melt fractionation in the regional zonation of pegmatite groups. *Geochimica et Cosmochimica Acta*, 132, 349–374.
- Hulsbosch, N., Thomas, R., Boiron, M.-C., Dewaele, S., & Muchez, P. (2017a). Direct Observation of Boro-Aluminosilicate Melt Compositions: Insights From Raman Spectroscopy of Melt Inclusions In Pegmatitic Tourmaline of the Gatumba-Gitarama Area (Rwanda). *The Canadian Mineralogist*, 55(3), 377–397.
- Hulsbosch, N., Van Daele, J., Reinders, N., Dewaele, S., Jacques, D., & Muchez, P. (2017b). Structural control on the emplacement of contemporaneous Sn-Ta-Nb mineralized LCT pegmatites and Sn bearing quartz veins: Insights from the Musha and Ntunga deposits of the Karagwe-Ankole Belt, Rwanda. *Journal of African Earth Sciences*, 134, 24–32.
- Johnston, W. D. (1965). Oxidation-reduction equilibria in molten Na₂O-SiO₂ glass. *Journal of the American Ceramic Society*, 48, 184–190.
- Kamenetsky, V. S., & Kamenetsky, M. B. (2011). Magmatic fluids immiscible with silicate melts: examples from inclusions in phenocrysts and glasses, and implications for magma evolution and metal transport, in B. Yardley, C. Manning, & G. Garven, *Frontiers in Geofluids* (pp. 293–311). Wiley-Blackwell.
- Kampunzu, A. B., Rumvegeri, B. T., Kapenda, D., Lubala, R. T., & Caron, J. P. H. (1986). Les Kibarides d'Afrique centrale et orientale: Une chaîne de collision. *UNESCO. Geology for Development Newsletter*, 5, 125–137.
- Kepler, H., & Wyllie, P. (1991). Partitioning of Cu, Sn, Mo, W, U, and Th between melt and aqueous fluid in the systems haplogranite-H₂O–HCl and haplogranite-H₂O–HF. *Contributions to Mineralogy and Petrology*, 109(2), 139–150.
- Klerkx, J., Liégeois, J. P., Lavreau, J., & Theunissen, K. (1984). Granitoides kibariens précoces et tectonique tangentielle au Burundi: magmatisme bimodal lié a une distention crustale, in J. Klerkx & J. Michot, *African Geology, a Volume in Honour of L. Cahen* (pp. 29–46). Royal Museum for Central Africa, Tervuren.
- Klerkx, J., Liégeois, J. P., Lavreau, J., & Claessens, W. (1987). Crustal evolution of the northern Kibaran Belt, eastern and central Africa, in A. Kröner, *Proterozoic Lithospheric Evolution* (pp. 217–233). American Geophysical Union and the Geological Society of America.
- Koegelenberg, C., & Kisters, A. F. M. (2014). Tectonic wedging, back-thrusting and basin development in the frontal parts of the Mesoproterozoic Karagwe-Ankole belt in NW Tanzania. *Journal of African Earth Sciences*, 97(0), 87–98.
- Koegelenberg, C., Kisters, A. F. M., Kramers, J. D., & Frei, D. (2015). U-Pb detrital zircon and ³⁹Ar-⁴⁰Ar muscovite ages from the eastern parts of the Karagwe-Ankole Belt: Tracking Paleoproterozoic basin formation and Mesoproterozoic crustal amalgamation along the western margin of the Tanzania Craton. *Precambrian Research*, 269, 147–161.
- Kokonyangi, J., Armstrong, R., Kampunzu, A. B., Yoshida, M., & Okudaira, T. (2004). U-Pb zircon geochronology and petrology of granitoids from Mitwaba (Katanga, Congo): Implications for the evolution of the Mesoproterozoic Kibaran belt. *Precambrian Research*, 132(1–2), 79–106.
- Kokonyangi, J. W., Kampunzu, A. B., Armstrong, R., Arima, M., Yoshida, M., & Okudaira, T. (2007). U-PbSHRIMP dating of detrital zircons from the Nzilo Group (Kibaran belt): Implications for the source of sediments and mesoproterozoic evolution of central Africa. *Journal of Geology*, 115(1), 99–113.
- Kovalenko, V. I., & Yarmolyuk, V. V. (1995). Endogenous rare metal ore formations and rare metal metallogeny of Mongolia. *Econ. Geol. Bull. Soc. Econ. Geol.*, 90(3), 520–529.
- Kovalenko, V. I., Ryabchikov, I. D., & Antipin, V. S. (1988). Temperature dependence of the distribution coefficients for Sn, W, Pb, and Zn in magmatic systems. *Geochemistry International*, 25(1), 1–10.
- Lecumberri-Sanchez, P., Vieira, R., Heinrich, C. A., Pinto, F., & Walle, M. (2017). Fluid-rock interaction is decisive for the formation of tungsten deposits. *Geology*, 45(7), 579–582.
- Lehmann, B. (1987). Tin granites, geochemical heritage, magmatic differentiation. *Geologische Rundschau*, 76(1), 177–185.
- Lehmann, B. (1990a). Regional element distribution patterns and the problem of pregranitic tin enrichments, in *Metallogeny of Tin*. Springer, Berlin-Heidelberg-New York.
- Lehmann, B. (1990b). Magmatic enrichment of tin, in *Metallogeny of Tin*, 45–85. Springer, Berlin-Heidelberg-New York.
- Lehmann, B. (1990c). Model of tin ore formation, in *Metallogeny of Tin*. Springer, Berlin-Heidelberg-New York.
- Lehmann, B., & Lavreau, J. (1987). Tin granites of the northern Kibaran belt, Central Africa (Kivu/Zaire, Rwanda, Burundi), in G. Matheis & H. Schandelmeier, *Current Research in African Earth Sciences* (pp. 33–36). Balkema, Rotterdam.
- Lehmann, B., & Lavreau, J. (1988). Geochemistry of the tin granites from Kivu (Zaire), Rwanda and Burundi. 255 *Newsletter/Bulletin*, 1, 43–46.
- Lehmann, B., Halder, S., Ruzindana Munana, J., de la Paix Ngizimana, J., & Biryabarema, M. (2013). The geochemical signature of rare-metal pegmatites in Central Africa: Magmatic rocks in the Gatumba tin-tantalum mining district, Rwanda. *Journal of Geochemical Exploration*.
- Lehmann, B., Halder, S., Ruzindana Munana, J., de la Paix Ngizimana, J., & Biryabarema, M. (2014). The geochemical signature of rare-metal pegmatites in Central Africa: Magmatic rocks in the Gatumba tin-tantalum mining district, Rwanda. *Journal of Geochemical Exploration*, 144, Part C, 528–538.

- Lenharo, S. L. R., Pollard, P. J., & Born, H. (2003). Petrology and textural evolution of granites associated with tin and rare-metals mineralization at the Pitinga mine, Amazonas, Brazil. *Lithos*, 66(1–2), 37–61.
- Lhoest, A. (1957a). Les différents types de filons de la concession Somuki à Rutongo. *Annales de la Société Géologique de Belgique*, 80, 503–530.
- Lhoest, A. (1957b). Note préliminaire sur la géologie de la région Kigali-Rutongo dans le Ruanda. *Bulletin de la Société belge de Géologie*, 66, 190–198.
- Linnen, R. L. (1998). The solubility of Nb-Ta-Zr-Hf-W in granitic melts with Li and Li + F: Constraints for mineralization in rare metal granites and pegmatites. *Econ. Geol. Bull. Soc. Econ. Geol.*, 93(7), 1013–1025.
- Linnen, R. L., & Williams-Jones, A. E. (1995). Genesis of a Magmatic Metamorphic Hydrothermal System: The Sn-W Polymetallic Deposits at Pilok, Thailand. *Economic Geology*, 90, 1148–1166.
- Linnen, R. L., & Keppler, H. (1997). Columbite solubility in granitic melts: consequences for the enrichment and fractionation of Nb and Ta in the Earth's crust. *Contributions to Mineralogy and Petrology*, 128(2–3), 213–227.
- Linnen, R. L., & Cuney, M. (2005). Granite-Related Rare-Element Deposits and Experimental Constraints on Ta-Nb-W-Sn-Zr-Hf, in R. L. Linnen & I. M. Samson, *Rare-Earth Geochemistry and Mineral Deposits* (pp. 45–68). Geological Association of Canada.
- Linnen, R. L., Pichavant, M., & Holtz, F. (1996). The combined effects of $f(\text{O}_2)$ and melt composition on SnO_2 solubility and tin diffusivity in haplogranitic melts. *Geochimica Et Cosmochimica Acta*, 60(24), 4965–4976.
- Linnen, R. L., Pichavant, M., Holtz, F., & Burgess, S. (1995). The effect of $f\text{O}_2$ on the solubility, diffusion, and speciation of tin in haplogranitic melt at 850°C and 2 kbar. *Geochimica et Cosmochimica Acta*, 59(8), 1579–1588.
- Linnen, R. L., Samson, I. M., Williams-Jones, A. E., & Chakhmouradian, A. R. (2014). Geochemistry of the Rare-Earth Element, Nb, Ta, Hf, and Zr Deposits, 543–568.
- London, D. (2008). *Pegmatites*. Mineralogical Association of Canada.
- London, D. (2014). A petrologic assessment of internal zonation in granitic pegmatites. *Lithos*, 184–187, 74–104.
- London, D., Hervig, R., & Morgan, G. V. I. (1988). Melt-vapor solubilities and elemental partitioning in peraluminous granite-pegmatite systems: experimental results with Macusani glass at 200 MPa. *Contributions to Mineralogy and Petrology*, 99(3), 360–373.
- Maier, W. D., Peltonen, P., & Livesey, T. (2007). The ages of the Kabanga North and Kapalagulu intrusions, Western Tanzania: A Reconnaissance Study. *Economic Geology*, 102(1), 147–154.
- Mäkitie, H., Data, G., Isabirye, E., Mänttari, I., Huhma, H., Klausen, M. B., Pakkanen, L., & Virransalo, P. (2014). Petrology, geochronology and emplacement model of the giant 1.37Ga arcuate Lake Victoria Dyke Swarm on the margin of a large igneous province in eastern Africa. *Journal of African Earth Sciences*, 97, 273–297.
- Manning, D. A. C. (1981). The effect of fluorine on liquidus phase relationships in the system Qz-Ab-Or with excess water at 1 kb. *Contributions to Mineralogy and Petrology*, 76(2), 206–215.
- Manning, D. C., & Henderson, P. (1984). The behaviour of tungsten in granitic melt-vapour systems. *Contributions to Mineralogy and Petrology*, 86(3), 286–293.
- Marignac, C., & Cuney, M. (1999). Ore deposits of the French Massif Central: insight into the metallogenesis of the Variscan collision belt. *Mineralium Deposita*, 34(5–6), 472–504.
- Marignac, C., & Cathelineau, M. (2010). *The Nature of Ore-forming Fluids in Peri-Batholithic Sn-W Deposits and a Classification*. James Cook University, Townsville, 245–247.
- Melcher, F., Graupner, T., Gäbler, H.-E., Sitnikova, M., Henjes-Kunst, F., Oberthür, T., Gerdes, A., & Dewaele, S. (2015). Tantalum–(niobium-tin) mineralization in African pegmatites and rare metal granites: Constraints from Ta-Nb oxide mineralogy, geochemistry and U-Pb geochronology. *Ore Geology Reviews*, 64(0), 667–719.
- Melcher, F., Graupner, T., Gäbler, H.-E., Sitnikova, M., Oberthür, T., Gerdes, A., Badanina, E., & Chudy, T. (2017). Mineralogical and chemical evolution of tantalum-(niobium-tin) mineralisation in pegmatites and granites. Part 2: Worldwide examples (excluding Africa) and an overview of global metallogenetic patterns. *Ore Geology Reviews*, 89, 946–987.
- Monteye-Poulaert, G., Delwiche, R., & Cahen, L. (1962). Âges de minéralisations pegmatitiques et filoniennes du Rwanda et du Burundi. *Annales de la Société Géologique de Belgique*, 71, 210–221.
- Moura, A., Dória, A., Neiva, A. M. R., Gomes, C. L., & Creaser, R. A. (2014). Metallogenesis at the Carris W-Mo-Sn deposit (Gerês, Portugal): Constraints from fluid inclusions, mineral geochemistry, Re-Os and He-Ar isotopes. *Ore Geology Reviews*, 56, 73–93.
- Muchez, P., Hulsbosch, N., & Dewaele, S. (2014). Geological mapping and implications for Nb-Ta, Sn and W prospecting in Rwanda. *Mededelingen Zittingen Koninklijke Academie Overzeese Wetenschappen*, 60(3–4), 515–530.
- Mulja, T., Williams-Jones, A. E., Wood, S. A., & Boily, M. (1995a). The rare-element-enriched monzogranite-pegmatite-quartz vein systems in the Preissac-Lacorne Batholith, Quebec. II. Geochemistry and Petrogenesis. *Can. Mineral.*, 33, 817–833.
- Mulja, T., Williams-Jones, A. E., Wood, S. A., & Boily, M. (1995b). The rare-element-enriched monzogranite-pegmatite-quartz vein systems in the Preissac-Lacorne Batholith, Quebec. I. Geology and Mineralogy. *Can. Mineral.*, 33, 793–815.
- Müller, A., Romer, R. L., & Pedersen, R.-B. (2017). The Sveconorwegian Pegmatite Province—Thousands of pegmatites without parental granites. *The Canadian Mineralogist*, 55(2), 283–315.
- Müller, A., Ihlen, P. M., Snook, B., Larsen, R. B., Flem, B., Bingen, B., & Williamson, B. (2015). The Chemistry of Quartz in Granitic Pegmatites of Southern Norway: Petrogenetic and Economic Implications. *Economic Geology*, 110(7), 1737–1757.
- Peeters, L. (1956). Contribution à la géologie des terrains anciens du Ruanda-Urundi et du Kivu. *Annales du Musée Royale du Congo belge, Tervuren, série in 8°. Sciences Géologiques*, 16, 1–197.
- Pettke, T., Audétat, A., Schaltegger, U., & Heinrich, C. A. (2005). Magmatic-to-hydrothermal crystallization in the

- W-Sn mineralized Mole Granite (NSW, Australia). *Chemical Geology*, 220(3–4), 191–213.
- Pichavant, M. (1981). An Experimental Study of the Effect of Boron on a Water Saturated Haplogranite at 1 Kbar Vapour Pressure: Geological Applications. *Contributions to Mineralogy and Petrology*, 76(4), 430–439.
- Pichavant, M., & Manning, D. (1984). Petrogenesis of tourmaline granites and topaz granites; the contribution of experimental data. *Phys. Earth Planet. Inter.*, 35(1–3), 31–50.
- Pohl, W. (1974). *Rapport préliminaire: Mission géologique Rutongo*.
- Pohl, W. (1994). Metallogeny of the northeastern Kibara belt, Central Africa: Recent perspectives. *Ore Geology Reviews*, 9(2), 105–130.
- Pohl, W., & Günther, M. A. (1991). The origin of Kibaran (late Mid-Proterozoic) tin, tungsten and gold quartz vein deposits in Central Africa: a fluid inclusions study. *Mineralium Deposita*, 26(1), 51–59.
- Pohl, W. L., Biryabarema, M., & Lehmann, B. (2013). Early Neoproterozoic rare metal (Sn, Ta, W) and gold metallogeny of the Central Africa Region: a review. *Applied Earth Science*, 122(2), 66–82.
- Polya, D. A., Foxford, K. A., Stuart, F., Boyce, A., & Fallick, A. E. (2000). Evolution and paragenetic context of low δD hydrothermal fluids from the Panasqueira W-Sn deposit, Portugal: new evidence from microthermometric, stable isotope, noble gas and halogen analyses of primary fluid inclusions. *Geochimica et Cosmochimica Acta*, 64(19), 3357–3371.
- Raimbault, L., Cuney, M., Azencott, C., Duthou, J. L., & Joron, J. L. (1995). Geochemical Evidence for a Multistage Magmatic Genesis of Ta-Sn-Li Mineralization in the Granite at Beauvoir, French Massif Central. *Econ. Geol. Bull. Soc. Econ. Geol.*, 90(3), 548–576.
- Reyf, F. G. (1997). Direct evolution of W-rich brines from crystallizing melt within the Mariktikan granite pluton, west Transbaikalia. *Mineralium Deposita*, 32(5), 475–490.
- Reyf, F. G., Seltmann, R., & Zarskiy, G. P. (2000). The role of magmatic processes in the formation of banded Li,F-enriched granites from the Orlovka tantalum deposit, Transbaikalia, Russia: Microthermometric evidence. *Can. Mineral.*, 38, 915–936.
- Richards, J. P. (2013). Giant ore deposits formed by optimal alignments and combinations of geological processes. *Nature Geosci.*, 6(11), 911–916.
- Robb, L. (2013). *Introduction to Ore-Forming Processes*, Wiley.
- Roda Robles, E., Pesquera Perez, A., Velasco Roldan, F., & Fontan, F. (1999). The granitic pegmatites of the Fregeneda area (Salamanca, Spain); characteristics and petrogenesis. *Mineralogical Magazine*, 63(4), 535–558.
- Romer, R., & Kroner, U. (2015). Sediment and weathering control on the distribution of Paleozoic magmatic tin-tungsten mineralization. *Mineralium Deposita*, 50(3), 327–338.
- Romer, R. L., & Kroner, U. (2016). Phanerozoic tin and tungsten mineralization—Tectonic controls on the distribution of enriched protoliths and heat sources for crustal melting. *Gondwana Research*, 31, 60–95.
- Rumvegeri, B. T. (1991). Tectonic significance of Kibaran structures in Central and eastern Africa. *Journal of African Earth Sciences*, 13(2), 267–276.
- Ryabchikov, I. D., Durasova, N. A., Barsukov, V. L., & Efimov, A. S. (1978). Redox potentials as a factor of metalliferous ability of acid magmas. *Geokhimiya*(6), 832–834.
- Schäfer, B., Frischknecht, R., Gunther, D., & Dingwell, D. B. (1999). Determination of trace-element partitioning between fluid and melt using LA-ICP-MS analysis of synthetic fluid inclusions in glass. *European Journal of Mineralogy*, 11(3), 415–426.
- Shand, S. J. (1943). *The Eruptive Rocks*. John Wiley, New York.
- Shaw, R. A., Goodenough, K. M., Roberts, N. M. W., Horstwood, M. S. A., Chenery, S. R., & Gunn, A. G. (2016). Petrogenesis of rare-metal pegmatites in high-grade metamorphic terranes: A case study from the Lewisian Gneiss Complex of north-west Scotland. *Precambrian Research*, 281, 338–362.
- Shearer, C. K., Papike, J. J., & Jolliff, B. L. (1992). Petrogenetic links among granites and pegmatites in the Harney Peak rare-element granite-pegmatite system, Black Hills, South Dakota. *The Canadian Mineralogist*, 30(3), 785–809.
- Simmons, W. B. S., & Webber, K. L. (2008). Pegmatite genesis: state of the art. *European Journal of Mineralogy*, 20(4), 421–438.
- Sirbescu, M.-L. C., & Nabelek, P. I. (2003). Crystallization conditions and evolution of magmatic fluids in the Harney Peak Granite and associated pegmatites, Black Hills, South Dakota: Evidence from fluid inclusions. *Geochimica et Cosmochimica Acta*, 67(13), 2443–2465.
- Spera, F. J., Bohrsen, W. A., Till, C. B., & Ghiorso, M. S. (2007). Partitioning of trace elements among coexisting crystals, melt, and supercritical fluid during isobaric crystallization and melting. *American Mineralogist*, 92(11–12), 1881–1898.
- Štemprok, M. (1987). Greisenization (A Review). *Geologische Rundschau*, 76(1), 169–175.
- Štemprok, M. (1990). Solubility of tin, tungsten and molybdenum oxides in felsic magmas. *Mineralium Deposita*, 25(3), 205–212.
- Strong, D. F. (1988). A review and model for granite-related mineral deposits, in R. P. Taylor & D. F. Strong, *Recent Advances in the Geology of Granite-related Mineral Deposits* (pp. 424–445). Canadian Institute of Mining Metallurgy.
- Tack, L., Wingate, M. T. D., De Waele, B., Meert, J., Belousova, E., Griffin, B., Tahon, A., & Fernandez-Alonso, M. (2010). The 1375 Ma “Kibaran event” in Central Africa: Prominent emplacement of bimodal magmatism under extensional regime. *Precambrian Research*, 180(1–2), 63–84.
- Taylor, J. R., & Wall, V. J. (1993). Cassiterite solubility, tin speciation, and transport in a magmatic aqueous phase. *Economic Geology*, 88(2), 437–460.
- Taylor, R. G. (1979). *Geology of tin deposits*. Elsevier, Amsterdam, Oxford and New York.
- Taylor, S. R., & McLennan, S. M. (1985). *The Continental Crust: Its Composition and Evolution*. Blackwell Scientific Publication, Carlton.
- Thomas, R., & Davidson, P. (2013). The missing link between granites and granitic pegmatites. *Journal of Geosciences*, 183–200.
- Thomas, R., Webster, J. D., & Heinrich, W. (2000). Melt inclusions in pegmatite quartz: complete miscibility between silicate melts and hydrous fluids at low pressure. *Contributions to Mineralogy and Petrology*, 139(4), 394–401.
- Thomas, R., Davidson, P., & Beurlen, H. (2011a). Tantalite-(Mn) from the Borborema Pegmatite Province, northeastern

- Brazil: Conditions of formation and melt- and fluid-inclusion constraints on experimental studies. *Mineralium Deposita*, 46(7), 749–759.
- Thomas, R., Davidson, P., & Schmidt, C. (2011b). Extreme alkali bicarbonate- and carbonate-rich fluid inclusions in granite pegmatite from the Precambrian Rønne granite, Bornholm Island, Denmark. *Contributions to Mineralogy and Petrology*, 161(2), 315–329.
- Thomas, R., Davidson, P., & Beurlen, H. (2012). The competing models for the origin and internal evolution of granitic pegmatites in the light of melt and fluid inclusion research. *Mineralogy and Petrology*, 106(1–2), 55–73.
- Timofeev, A., Migdisov, A. A., & Williams-Jones, A. E. (2015). An experimental study of the solubility and speciation of niobium in fluoride-bearing aqueous solutions at elevated temperature. *Geochimica et Cosmochimica Acta*, 158(0), 103–111.
- Turekian, K., & Wedepohl, K. H. (1961). Distribution of the Elements in Some Major Units of the Earth's Crust. *GSA Bulletin*, 72(2), 175–192.
- Turlin, F., André-Mayer, A.-S., Moukhsil, A., Vanderhaeghe, O., Gervais, F., Solgadi, F., Groulier, P.-A., & Poujol, M. (2017). Unusual LREE-rich, peraluminous, monazite- or allanite-bearing pegmatitic granite in the central Grenville Province, Québec. *Ore Geology Reviews*, 89, 627–667.
- Van Lichtervelde, M., Holtz, F., & Hanchar, J. M. (2010). Solubility of manganotantalite, zircon and hafnon in highly fluxed peralkaline to peraluminous pegmatitic melts. *Contributions to Mineralogy and Petrology*, 160(1), 17–32.
- Varlamoff, N. (1948). Gisements de cassitérite de la région de Kalima (Maniema, Congo belge). *Annales de la Société Géologique de Belgique*, 71, 194–237.
- Varlamoff, N. (1954). Répartition des types de pegmatites autour de la partie nord-ouest du grand massif granitique de Nyanza. *Annales de la Société Géologique de Belgique*, 78, 1–21.
- Varlamoff, N. (1960). Habitus des cristaux de cassitérite des pegmatites stannifères de Kirengo (région de Katumba, Ruanda). *Annales de la Société Géologique de Belgique*, 84, 169–177.
- Varlamoff, N. (1961). Pegmatites à amblygonite et à spodumène et pegmatites fortement albitisées à spodumène et à cassitérite de la région de Katumba (Ruanda). *Annales de la Société Géologique de Belgique*, 84, 257–278.
- Varlamoff, N. (1963). Les phénomènes de greisenification, d'albitisation et de lépidolitisation et leurs relations spatiales avec les granites et les pegmatites granitiques d'Afrique. *Annales de la Société Géologique de Belgique*, 86, 285–322.
- Varlamoff, N. (1969). Transitions entre les filons de quartz et les pegmatites stannifères de la région de Musha-Ntungwa (Ruanda). *Annales de la Société Géologique de Belgique*, 92, 193–213.
- Varlamoff, N. (1972). Central and West African Rare-Metal Granitic Pegmatites. Related Aplites, Quartz Veins and Mineral Deposits. *Mineralium Deposita*, 7(2), 202–216.
- Veksler, I. A. (2005). Element Enrichment and Fractionation by Magmatic Aqueous Fluids: Experimental Constraints on Melt-Fluid Immiscibility and Element Partitioning in R. L. Linnen & I. M. Samson, *Rare-Earth Geochemistry and Mineral Deposits* (pp. 69–85). Geological Association of Canada.
- Veksler, I. V., Thomas, R., & Schmidt, C. (2002). Experimental evidence of three coexisting immiscible fluids in synthetic granitic pegmatite. *American Mineralogist*, 87(5–6), 775–779.
- Vindel, E., Lopez, J. A., Boiron, M. C., Cathelineau, M., & Prieto, A. C. (1995). P-V-T-X-fO₂ evolution from wolframite to sulphide depositional stages in intragranitic W-veins. An example from the Spanish Central System. *European Journal of Mineralogy*, 7(3), 675–688.
- Webster, J. (2004). The exsolution of magmatic hydrosaline chloride liquids. *Chemical Geology*, 210(1–4), 33–48.
- Webster, J., Thomas, R., Förster, H.-J., Seltmann, R., & Tappen, C. (2004). Geochemical evolution of halogen-enriched granite magmas and mineralizing fluids of the Zinnwald tungsten mining district, Erzgebirge, Germany. *Mineralium Deposita*, 39(4), 452–472.
- Webster, J. D., Thomas, R., Rhede, D., Forster, H. J., & Seltmann, R. (1997). Melt inclusions in quartz from an evolved peraluminous pegmatite: Geochemical evidence for strong tin enrichment in fluorine-rich and phosphorus-rich residual liquids. *Geochimica Et Cosmochimica Acta*, 61(13), 2589–2604.
- Westerhof, A. B., Härmä, P., Isabirye, E., Katto, E., Koistinen, T., Kuosmanen, E., Lehto, T., et al. (2014). Geology and geodynamic development of Uganda with explanation of the 1: 1,000,000 scale geological map. *Geological Survey of Finland Special Paper*, 55.
- Whitney, J. A. (1988). The origin of granite: The role and source of water in the evolution of granitic magmas. *GSA Bulletin*, 100(12), 1886–1897.
- Wilkinson, J. J. (1990). The role of metamorphic fluids in the development of the Cornubian orefield: fluid inclusion evidence from south Cornwall. *Mineralogical Magazine*, 54, 219–230.
- Wilson, G. A., & Eugster, H. P. (1990). Cassiterite solubility and tin speciation in supercritical chloride solutions, in R. J. Spencer & I. M. Chou, *Geochemical Society Special Publication* (pp. 179–195).
- Wilson, M. (1989). *Igneous Petrogenesis*. Springer, Dordrecht.
- Wood, S. A. (2005). The Aqueous Geochemistry of Zirconium, Hafnium, Niobium and Tantalum, in *Rare-Element Geochemistry and Mineral Deposits*, edited by R. L. Linnen & I. M. Samson, pp. 217–268, Geological Association of Canada.
- Wood, S. A., & Samson, I. M. (2000). The Hydrothermal Geochemistry of Tungsten in Granitoid Environments: I. Relative Solubilities of Ferberite and Scheelite as a Function of T, P, pH, and mNaCl. *Economic Geology*, 95(1), 143–182.
- Zajacz, Z., Halter, W. E., Pettke, T., & Guillong, M. (2008). Determination of fluid/melt partition coefficients by LA-ICPMS analysis of co-existing fluid and silicate melt inclusions: Controls on element partitioning. *Geochimica et Cosmochimica Acta*, 72(8), 2169–2197.
- Zaraisky, G. P., Korzhinskaya, V., & Kotova, N. (2010). Experimental studies of Ta₂O₅ and columbite-tantalite solubility in fluoride solutions from 300 to 550°C and 50 to 100 MPa. *Mineralogy and Petrology*, 99(3–4), 287–300.
- Zhang, R.-Q., Sun, W.-D., Lehmann, B., Seltmann, R., & Li, C. Y. (2016). Multiple tin mineralization events in Africa: Constraints by in-situ LA-ICPMS cassiterite U-Pb ages in P. N. 2798. *35th International Geological Congress*, Cape Town, South Africa.

REVISED PROOFS