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Trace elements in corundum, chrysoberyl, and zircon: Application to mineral exploration and provenance study of the western Mamfe gem clastic deposits (SW Cameroon, Central Africa)

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A B S T R A C T

Trace element abundances in three indicator minerals (corundum, chrysoberyl, and zircon grains) from the western Mamfe gem placers, as determined by LA-ICP-MS analytical techniques, are shown to be sensitive to their crystallization conditions and source rock types.

Corundum is dominantly composed of Al (standardized at 529,300 ppm), Fe (2496–12,899 ppm), and Ti (46–7070 ppm). Among element ratios, Fe/Mg (73–1107), Fe/Ti (0.5–245.0), Ti/Mg (1–175), and Ga/Mg (4–90) are generally higher whereas, Cr/Ga (<0.072) is low. The Fe (≤12,899), Ga (≤398), Mg (2–62), Cr (1.1–33.0), and V (3.0–93.0) contents (in ppm) mostly typify corundum grains formed in magmatic rocks, although some are metamorphic affiliated. A very higher Ti and significantly low Ga, Ta and Nb contents in some blue grains, suggest interesting concentrations of those high-tech metals in their source rocks.

Chrysoberyl is dominantly composed of Al (standardized at 425,000 ppm) and Be (62701–64371 ppm). Iron (7605–9225 ppm), Sn (502–3394 ppm), and Ti (33–2251 ppm) contents are high, whereas Ga (333–608 ppm), Ta (<456.0 ppm), and Nb (<3.0 ppm) are significantly low. The high (Be and Sn) and significantly low Ga–Rb abundances, and Ta > Nb in the western Mamfe chrysoberyls show that they were crystallized in granitic pegmatites, with some of those source rocks being enriched in Ta and Sn.

Zirconium oxide (ZrO_2: standardized at 66.1 wt.%)) is the only major oxide in analysed coarse-grained zircons. Within the minor elementary suites: Hf (4576–12,565 ppm) and Y (48–2805 ppm) contents are significantly high. The trace element suites include: Th (7–1565 ppm), U (13–687 ppm), and ∑REE (50–2161 ppm), whose values are significantly low. The $(Yb/Sm)_N$, Ce/Ce*, and Eu/Eu* anomalies range from 1.0 to 227.0, 0 to 308, and 0.08 to 1.7 respectively. They are Hf-Y-HREE enriched and depleted zircons mainly crystallized in magmatic oxidized environments. They were mainly sorted from granitoids, syenites and kimberlites.

1. Introduction

Indicator minerals are generally heavy minerals of some importance sorted from a weathered host rock of magmatic and metamorphic crystallization (McClenaghan, 2011). They can be

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recovered from a variety of sample media, including stream, alluvial, glacial, beach or eolian sediments and residual soils (McClenaghan, 2011; Kanouo, 2014). Indicator minerals have been found associated with lighter minerals in lithified clasts (e.g. Hodireva and Korpechkov, 2011; Kanouo, 2014). This shows the heterogeneity of their occurrence environment, and makes it difficult to study the displaced grains. The study of indicator minerals and their use as a tool for mineral exploration is widely known in locating the primary source of economically viable gem variety minerals (Lehtonen et al., 2005; Kepezhinskas, 2011; Kanouo, 2014). Application of indicator mineral methods to mineral exploration that was commonly used in diamond exploration, has expanded and significantly improved. It is now used around the world to explore kimberlites (diamonds: Kepezhinskas, 2011; Ushkov et al., 2011), magmatic Ni–Cu deposits (McClenaghan et al., 2011), and pebble porphyry Cu–Au–Mo deposits (Eppinger et al., 2011). It is also used to search for porphyry Cu, U, Sn, W, and rare metals deposits (Averill, 2001), and as an exploration means for REE and other high-tech metals (Ga, Ge, In, Li, Nb, Ta, and Ti) (Lehtonen et al., 2011).

The western Mamfe gem placers are heterogeneous unlithified clastic deposits occurring along Asenem River (Fig. 1) in the south western region of Cameroon. These placer deposits have been subject of mostly unpublished research studies since November 1964 to May 1965 and December 1965 to April 1966 G.M.R.B "Geology and Mining Research Office" field research surveys. The results of G.M.R.B surveys led to the location of more than sixty lead and zinc mineral occurrences in the clayish sandstones of the Manyu and Cross River Formation; sapphires, diamond and ruby grains in Nsanaragati and Munaya (Laplaine and Soba, 1967; Lettermann, 1967). These earlier workers found the corundum grains, mostly rounded with no well-defined shape. Study of mineral inclusions in some of the corundum grains suggests that they were sourced from pegmatites (Laplaine and Soba, 1967). Kanouo (2008) determined the field relationships and petrographic features of some of those placers. The mineralogical features of the western Mamfe gem placers were determined by Kanouo et al. (2012a). The geochemical features of found coarse-grained rutiles and of some blue corundums from Nsanaragati were obtained by Kanouo et al. (2012b, 2012c) respectively. The coarse-grained rutiles were Nb-rich rutiles mainly sorted from metapelitic rocks, whereas the blue corundums mainly grew in alkaline magmatic rocks. U–Pb dating of coarse-grained zircons, found to be associated with the above mentioned minerals, shows that they were sorted from Cenozoic, Cretaceous, Neoproterozoic, and Paleoproterozoic age rocks (Kanouo et al., 2012a, 2014, 2015).

The presence of diamond mentioned in Laplaine and Soba (1967) is not yet confirmed, although some kimberlite indicator minerals (Kepezhinskas, 2011; Ushkov et al., 2011), such as corundum, garnet and spinel were found in those placers (Kanouo, 2008, 2014; Kanouo et al., 2012a, c). Not all the indicator minerals found in those placers are characterized. Information on yellow and greyish-green corundums and newly analysed blue sapphires are still unpublished, and the geochemical data for the coarse-grained zircons is still to be completed. In this paper, we update some published data in Kanouo et al. (2012a, c, 2015), and present new geochemical data for three indicator minerals (corundum, chrysoberyl, and zircon) from the western Mamfe gem placers. The results are used to understand the history of genesis of these minerals and also as tools for mineral exploration.

2. Geological settings

The Mamfe Sedimentary Basin hosting the studied gem placers lay on basement rocks of assumed Precambrian age, made up of granites, syenites, gneisses, mica-schists, and migmatites (Wilson, 1928; Dumort, 1968; Regnoult, 1986; Kanouo, 2014). Most of those rocks were affected by post-emplacement tectonic and magmatic events (Kanouo, 2014). Some are cross-cut by mafic or felsic dykes (e.g. Ajayuk–Ndip, Nkogho and Kembong granites and Araru mica-schists) or overlain by mafic flows (e.g. in Ossing and Kembong) (Kanouo, 2014). Many mafic volcanic materials are found spotted within the sedimentary rocks in Ekok and Otu (Kanouo, 2014). Mafic dykes cross-cut coarse-grained sandstones in River Munaya (NW of Ajayuk–Ndip village). At the SE of the basin, precisely in Mount Nda Ali, volcanic rocks (e.g. trachytes and phonolites) underlay undated gabbros, diorites, syenites, and monzonites. Skarn-type rocks (hornfels) are also found in Mount Nda Ali (Njonfang and Moreau, 1996).

Field observations and polarizing microscopic studies carried out by Kanouo (2014) on some basement rocks (e.g. Kembong and Nkogho granites, Nkogho syenite, Otu granitic pegmatite, Babi micaschist and gneiss, and Araru gneiss) show that they enclose polycrystalline and fractured quartz. The Babi micaschist in particular, shows deformed features in most minerals found: kinked biotite and folded muscovite, recrystallized and fractured quartz giving a polycrystalline and mylonitic to porphyroblastic texture to the mica-schist.

The western Mamfe gem placers from which the studied indicator minerals (corundum, chrysoberyl, and zircons) were sampled, are mixture of different source materials, including rock fragments (mafic pyroclasts, sandstones, gneisses, and quartzites), light and heavy minerals (e.g. quartz, magnetite, ilmenite, rutile, biotite, garnet, spinel, zircon, and muscovite) (Laplaine and Soba, 1967; Kanouo, 2014; Kanouo et al., 2015). They are underlain by lithified clasts (Fig. 2) composed of immature mudstones, sandstones, conglomerates, and conglomeratic sandstones (Le Fur, 1965; Eyong, 2003; Kanouo, 2014). The colour of the sandstones is variable, ranging from grey to whitish grey, yellow to pinky. The mudstones are greenish-grey or pinky, and the conglomeratic rocks mainly found in Ekok are whitish-grey. Brine springs are found in some localities (e.g. Nsanakang, Mbakang, Mbenyan, Ayukaba German) (Wilson, 1928; Dumort, 1968; Eseme et al., 2002). U–Pb dating of zircon grains found in these sediments shows that they are clastic materials mainly of a post-Serravallian, post-Cretaceous, and post-Precambrian deposition (Kanouo et al., 2012a, 2014, 2015). The Cenozoic zircons were mainly sorted from the Cameroon Volcanic Line, whereas Cretaceous grains were probably eroded from the Benue Trough, and Precambrian zircons from the southern Mamfe basement (Kanouo et al., 2012a, 2015; Kanouo, 2014).

3. Materials and methods

A total of fourteen blue corundums with eleven grains from Kanouo et al. (2012c), and three recently analysed, two yellow and one greyish-green corundums, four yellow chrysoberyls, and forty six coloured coarse-grained zircons were analysed to determine their geochemical composition at the University of Tasmania (Australia) and China University of Geosciences (Wuhan, China). The results were acquired using LA-ICP-MS analytical techniques at the ARC Centre of Excellence in Ore Deposits and State Key Laboratory of Geological Processes and Mineral Resources.

Analytical procedures used to obtain results for corundum and chrysoberyl grains at the University of Tasmania are same as those presented in Kanouo et al. (2012c). Each mounted grain is polished (Fig. 3) and analysed following standard procedures using a New Wave UP-213Nd: YAG Q-switched Laser Ablation system coupled with the Agilent HP 4500 Quadrupole ICP-MS. Element abundance was determined by NIST 612, which was also used as the primary standard to correct ablation depth. BCR-2 basaltic glass was used as