In-situ multiple-trace element analyses as a tool for investigating the petrogenesis of phoscorite-carbonatite associations, as exemplified by the Phalaborwa Complex, South Africa

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The Palaeoproterozoic (2.06 Ga) Phalaborwa Complex in the Limpopo Province of South Africa hosts one of the largest copper mines in Africa. It represents the only economic occurrence of this commodity mined in carbonatite rocks, and important aspects of petrogenetic relationship between Ca-rich silicatic phoscorite and carbonatite remain poorly understood.

We investigated the main mineral phases through in-situ laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). This technique, combined with electron microprobe (EMP), has become an important tool in recent times for deciphering petrogenetic conditions, in particular for exploration of ore deposits. Analyses were carried out on magnetite, ilmenite, apatite, calcite, dolomite, olivine and phlogopite.

According to the systematics of the elements behaving as strongly compatible during magmatic oxide formation, two different generations of magnetite have been traced. A first magmatic stage, developing towards hydrothermal conditions (with variable Ti-V content), pre-dates the sulfide mineralization, and was followed by a second low-temperature, late-hydrothermal event, mostly post-dating sulfide formation. Combining geochemical data and geothermo-oxysterometry calculations on magnetite-ilmenite pairs indicates that the most primitive magnetite likely formed at oxygen fugacity above the nickel nickel oxide (NNO) buffer, revealing an evolutionary trend of decreasing temperature and oxygen fugacity.

Overall, there is a remarkable similarity in the Fe-Ti-oxide geochemistry from the silicate and carbonatite melts. Such uniformity among the rock types is confirmed also from textural and compositional observations regarding all the other mineral phases. EMP analyses on fluorapatite suggest that the phase is primary magmatic at Phalaborwa, and largely unaffected by metasomatic mineral-fluid interaction.

Rare Earth Element (REE) distribution in the phoscorite-carbonatite association can be traced through the light REE systematics in fluorapatite and calcite, as these phase minerals sequester the bulk of the LREE budget in these types of rocks. LREE binary plots for the two mineral phases show a cross correlation among the different carbonatite samples, which rules out a complex crystallization history involving multiple magma batches.
LREE systematics were also used to model fractionation paths, and equilibrium and fractional crystallization among the carbonates were tested. Modelling results cannot be adequately ascribed to crystallization models, and a simple mixing mechanism appears to better reconcile the geochemistry of the carbonatite types at Phalaborwa. A mixing model is consistent with previously reported mineral isotope systematics that requires an open-system behaviour.