

CARBONATITES, RARE EARTHS AND THE LESSONS WE LEARN FROM PETROGRAPHY AND TRACE-ELEMENT GEOCHEMISTRY

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Synopsis

Carbonatites are carbonate-dominant igneous rocks, which are commonly affected by subsolidus re-equilibration processes. These rocks reach extreme levels of REE enrichment ($n \times 10^4$ mantle values), yet are not known for the same spectacular diversity of REE minerals as undersaturated alkaline rocks, for example. (Only some 40 REE minerals have been reported from carbonatites worldwide, and fewer than 10 are reasonably common.) One of the reasons for this, of course, is the abundance of Ca minerals in these rocks, which provide a perfect alternative host for REE and thus affect the metallogenic aspects of carbonatite evolution. For example, apatite-group minerals can incorporate up to 15 wt.%, calcite up to 2,000 ppm and amphiboles up to 1,000 ppm REE. Despite the importance of carbonatites as a commercial source of REE, the effect of different rock-forming minerals on the trace-element budget of carbonatitic magmas and fluids is poorly understood. Preliminary economic assessments typically report bulk-rock values and disregard this REE dispersal effect. Microbeam trace-element analysis is now increasingly used for this purpose, but a thorough understanding of paragenetic constraints, based on careful petrographic studies, is required to map the distribution of REE among different constituent minerals in a time-resolved fashion. These data can be used in conjunction with the theory of trace-element partitioning to unravel the pathways of carbonatite evolution and to refine the as-yet underdeveloped metallogenic models. Some of the challenges facing researchers in this field include (i) element-partitioning phenomena that do not agree well with the theory, (ii) quasi-equilibrium growth, (iii) experimental oversimplification of natural systems, leading to partitioning data that cannot be feasibly applied to real rocks, and (iv) the effects of subsolidus re-equilibration obscuring primary parageneses and their interrelations.

The role of petrography and trace-element geochemistry in REE deposit research: a case study

The Devonian Aley intrusion in British Columbia (Canada) comprises a wide variety of carbonatites, many of which were produced by subsolidus processes which accompanied deformation and ductile mobilization of these rocks during the Laramide orogeny (CHAKHMOURADIAN *et al.*, 2015, 2016). A wide variety of minerals (rock-forming carbonates, mafic silicates and magnetite) were replaced by dolomite. This process was accompanied by the

pseudomorphization of phlogopite by chlorite and of pyrochlore by fersmite (CaNb_2O_6) and, to a lesser extent, ferrocolumbite (FeNb_2O_6). The igneous carbonates and secondary dolomite differ in morphology, isotopic and trace-element composition, indicating that these processes involved re-equilibration of the primary paragenesis with an externally derived fluid. For structural reasons, dolomite has a much lower tolerance for REE than calcite: up to ~700 and 1,600 ppm with median values of 63 and 510 ppm, respectively. In areas of pervasive dolomitization, igneous apatite also shows evidence of chemical re-equilibration, i.e. its peripheral and fractured areas are depleted in REE and characterized by lower $(\text{La}/\text{Yb})_{\text{CN}}$ ratios (typically, < 5,000 ppm and 75, respectively) than the unaltered material (up to 13,500 ppm and 210, respectively). Primary pyrochlore, containing 7,000–40,000 ppm REE, is replaced by fersmite with comparable levels of REE (3,000–57,000 ppm). However, the latter mineral is notably richer in Y and heavy lanthanides relative to its precursor [median $(\text{La}/\text{Yb})_{\text{CN}} = 2.4$ vs. 68, respectively]. Our data show that the process of hydrothermally induced dolomitization resulted in the release of REE and, in particular, the less-compatible light lanthanides into the fluid and their sequestration in the secondary paragenesis (monazite, bastnäsite, parisite, euxenite, xenotime). Our calculations show that dolomitization of a calcite carbonatite intrusion the size of Aley (~7 km²) would lead to the release of $n \times 10^5$ tons of each La, Ce, Nd and Y. Late-stage mineralization associated with dolomitization is found in intimate association with chlorite, quartz, secondary rhombohedral dolomite, barite, and other minerals filling fractures and voids. One important geochemical characteristic of this late assemblage of minerals is size-driven fractionation between light and heavy REE and relatively low mobility of the latter, which lead to the precipitation of secondary Y-rich minerals with very low $(\text{La}/\text{Yb})_{\text{CN}}$ (fersmite, euxenite, xenotime) close to their precursor minerals. Notably, similar carbonatite-hosted deposits are known elsewhere, but some of their key petrographic characteristics may have been overlooked or misinterpreted.

Modelling REE behaviour: recognized and emerging challenges

Yttrium-holmium decoupling is a striking example of deviation from trace-element partitioning patterns predicted by theory (e.g., KARATO, 2016). For example, perovskite (CaTiO_3) from carbonatites has

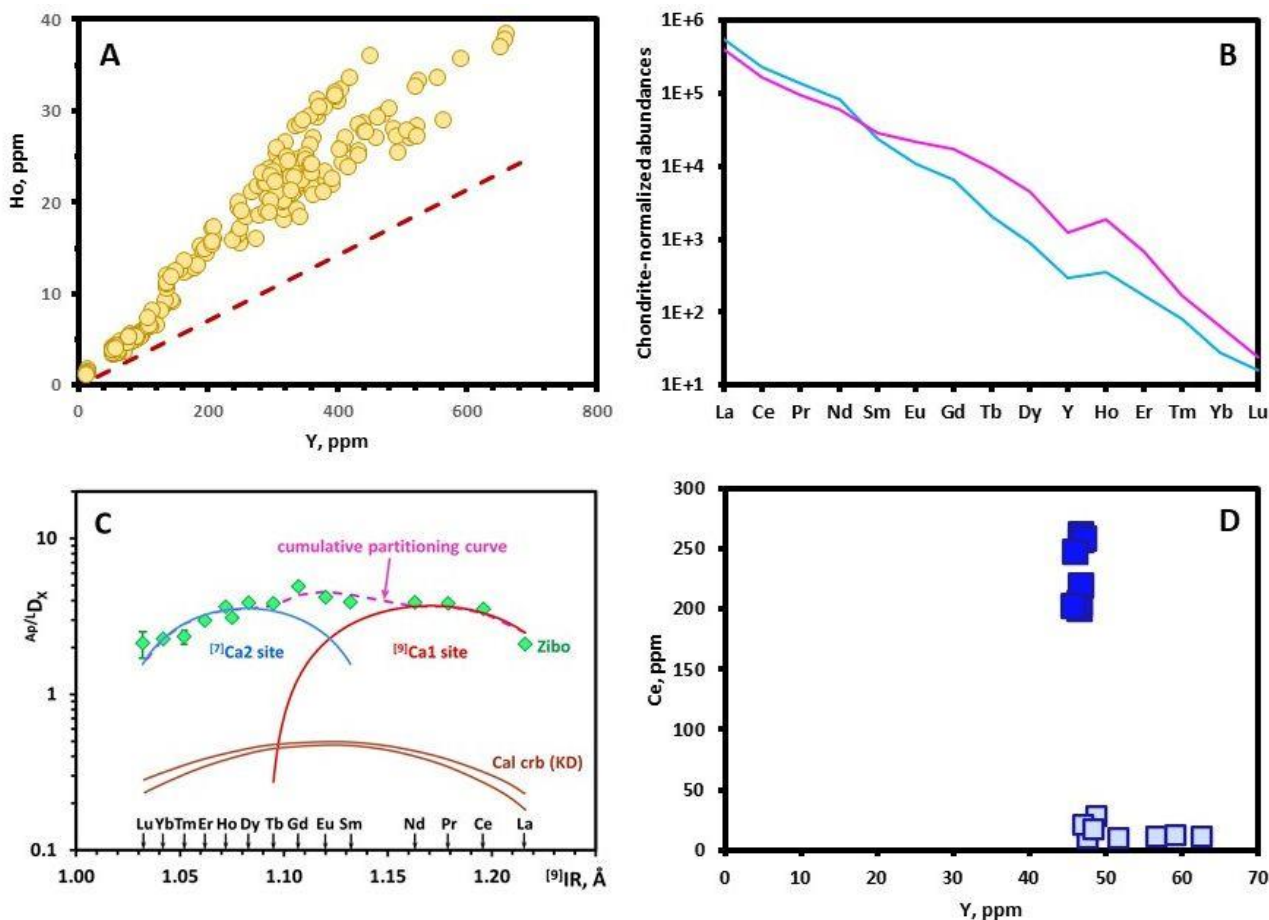


Fig. 1. Selected examples of unusual or poorly understood REE characteristics observed in carbonatites. (A) Y vs. Ho distribution in perovskite (yellow circles, global dataset) showing deviation from the correlation trend expected from ionic radii (dashed red line). (B) Chondrite-normalized REE distributions in prism and pyramid sectors (purple and blue curves, respectively) in carbocernaite from Bear Lodge, Wyoming, USA. (C) Onuma diagram showing variations in REE partition coefficients with ionic radius, calculated for apatite phenocrysts from Zibo, China (green diamonds), compared to the interpolated experimental data of KLEMME & DALPÉ (2003). (D) Y vs. Ce distribution between coarse calcite porphyroclasts (dark blue squares) and fine-grained calcite produced by dynamic recrystallization (pale blue squares).

consistently subchondritic Y/Ho values (15.3 ± 1.9), i.e., higher partition coefficients for Ho in comparison with Y (Fig. 1A). Owing to the lanthanide contraction, Y and Ho have essentially identical ionic radii, and do not readily separate in the geological environment. Yttrium-Ho decoupling has been thought to be restricted to low-T aqueous processes (BAU, 1996), but may clearly play a significant role in magmatic fractionation, as well. This “abnormal” behaviour can be explained by greater strength of Ho bond to its coordinating oxygen atoms. Because of this, the attachment of Ho cations to a growing perovskite nucleus is statistically more likely to occur, even though Y is much more common in its crystallization environment.

Crystallographically controlled REE uptake is poorly understood, but has been demonstrated for a number of minerals. For example, Ca-Sr-rich prism sectors in carbocernaite $[(\text{Na,Ca})(\text{Sr,Ca,REE,Ba})(\text{CO}_3)_2]$ exhibit a lesser degree of enrichment in light lanthanides

relative to heavy lanthanides in comparison with Na-REE-rich pyramid sectors (Fig. 1B). Clearly, REE uptake in this case was affected by the structure of growth surfaces and outpaced the attainment of equilibrium. These effects can be very significant [e.g., the $(\text{La/Yb})_{\text{CN}}$ ratio in zoned carbocernaite varies by a factor of three] and should be taken into account in trace-element modelling.

Much experimental work has been published on potential REE hosts in carbonatites. These data are of critical importance to geochemical modelling, but a careful analysis of the literature shows that caution should be exercised to avoid drawing incorrect conclusions from trace-element data acquired for real rocks. For example, the only currently available REE partitioning studies for apatite (HAMMOUDA *et al.*, 2010; KLEMME & DALPÉ, 2003) are based on the system $\text{CaCO}_3 - \text{Ca}_5(\text{PO}_4)_3(\text{F,OH})$, which does not take into account the chemical complexity of natural magmas. Further, experimental data are typically fitted

to a simplified partitioning curve that does not agree with the structural data on REE distribution between two topologically distinct Ca sites (FLEET & PAN, 1995, 1997). As a result, the experimental results poorly agree with partition coefficients calculated for real rocks (BRASSINNES *et al.*, 2005; CHAKHMOURADIAN *et al.*, 2017), which indicate greater compatibility in the middle of the lanthanide series due to overlap between REE partitioning curves representing the two different Ca sites (Fig. 1C).

Petrogenetic models rely on our ability to identify textures indicative of a specific process and to differentiate among visually similar petrographic characteristics produced by different mechanisms. This ability is diminished if the rock has been overprinted by subsolidus processes. For example, many carbonatites show preferred orientation and modal layering, but are these features a manifestation of magma flow or ductile deformation? In comparison to silicate rocks, carbonatites are far more susceptible to textural and chemical re-equilibration, grain abrasion and fragmentation, ductile flow, dissolution and other forms of chemical interaction with fluids even at relatively low pressures and temperatures. Cumulate layers within the intrusion, where REE mineralization is concentrated, have a low calcite (dolomite) content but significantly higher density than the material separating them and thus will behave very differently under stress. Deformation will not only disrupt or obliterate the pre-existing igneous features, but affect REE distribution patterns in the rock and its constituent minerals. For example, dynamic recrystallization in foliated carbonatites facilitates the removal of primary REE minerals included in calcite or dolomite (CHAKHMOURADIAN *et al.*, 2016; CHAKHMOURADIAN & DAHLGREN, 2021) and selective mobilization of certain trace elements (Fig.

1D). Clearly, metallogenic modelling or the assessment of mineral potential in these cases will require a thorough understanding of the local tectonic framework and interrelations between the observed geological structures, modal and geochemical variations in the carbonatite

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