The nature of REE mineralization in the Ashram deposit, Eldor Carbonatite Complex, Québec

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Introduction

Demand for rare earth elements (REE) has greatly increased due to their use in high technology applications, especially 'green technologies'. Carbonatites are an important source of REE. Historically, the ores have been considered to be magmatic. Recent studies, however, suggest that (carbo)hydrothermal fluids play an important role in the formation of carbonatite-hosted REE deposits. The Eldor Carbonatite Complex and its Ashram deposit provide an ideal natural laboratory in which to identify the dominant controls (magmatic and hydrothermal) on ore formation, and develop vectors to potentially economic deposits.

Summary of Ashram Geology

The Eldor Carbonatite Complex, Northern Quebec (Fig. 1) is an elliptical body, comprising a series of intrusive carbonatite events, from calcio- through magnesio- to ferrocarbonatite. The complex is subdivided into a rim and core, with the core being the Ashram REE deposit (Fig. 2). Ashram contains three main zones: BD, B, and A. The MHREO zone is considered a sub portion of the A zone. The outermost BD zone is an apatite-rich magnesiocarbonatite with rare earth fluorocarbonate (REEflc) mineralization (bastnäsite-(Ce), parisite-(Ce), synchisite-(Ce)) (Fig 3b). The B zone is also a magnesiocarbonatite, but with the dominant assemblage fluorite + monazite (Fig 3a). This assemblage continues into the A zone ferrocarbonatite. The innermost MHREO zone is also a ferrocarbonatite, crosscuts the A zone, and is thus the youngest phase of the carbonatite. This zone contains monazite-(Ce) and subordinate xenotime-(Y) and aeschynite-(Y).

The rim and BD zones are highly enriched in phosphate (up to 14 wt% P_2O_5, Fig. 4). From the rim to the BD zone, there is a transition from euhedral, discrete apatite grains (Fig 3d) to veins of fine-grained, sucrosic apatite (Fig 3c).
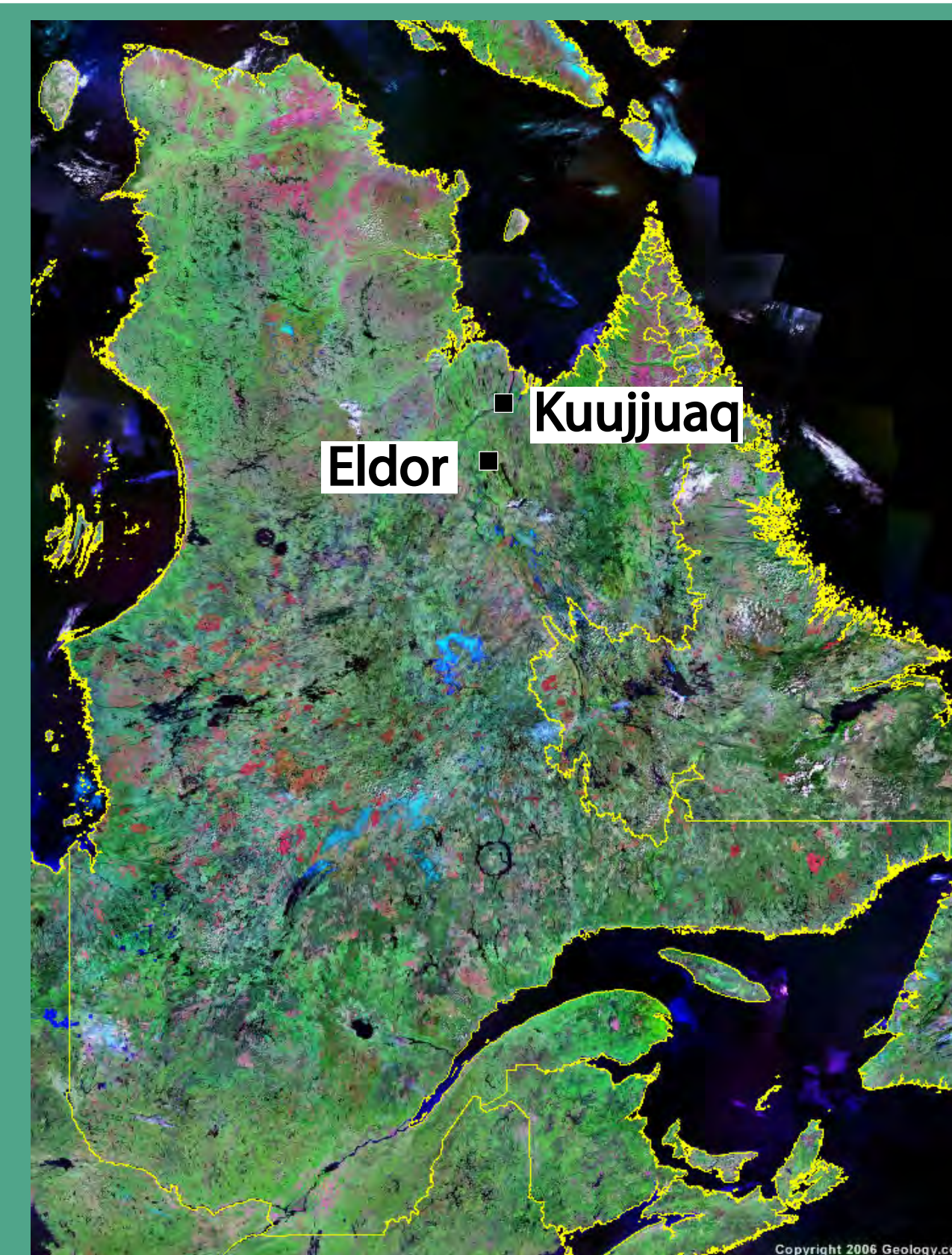

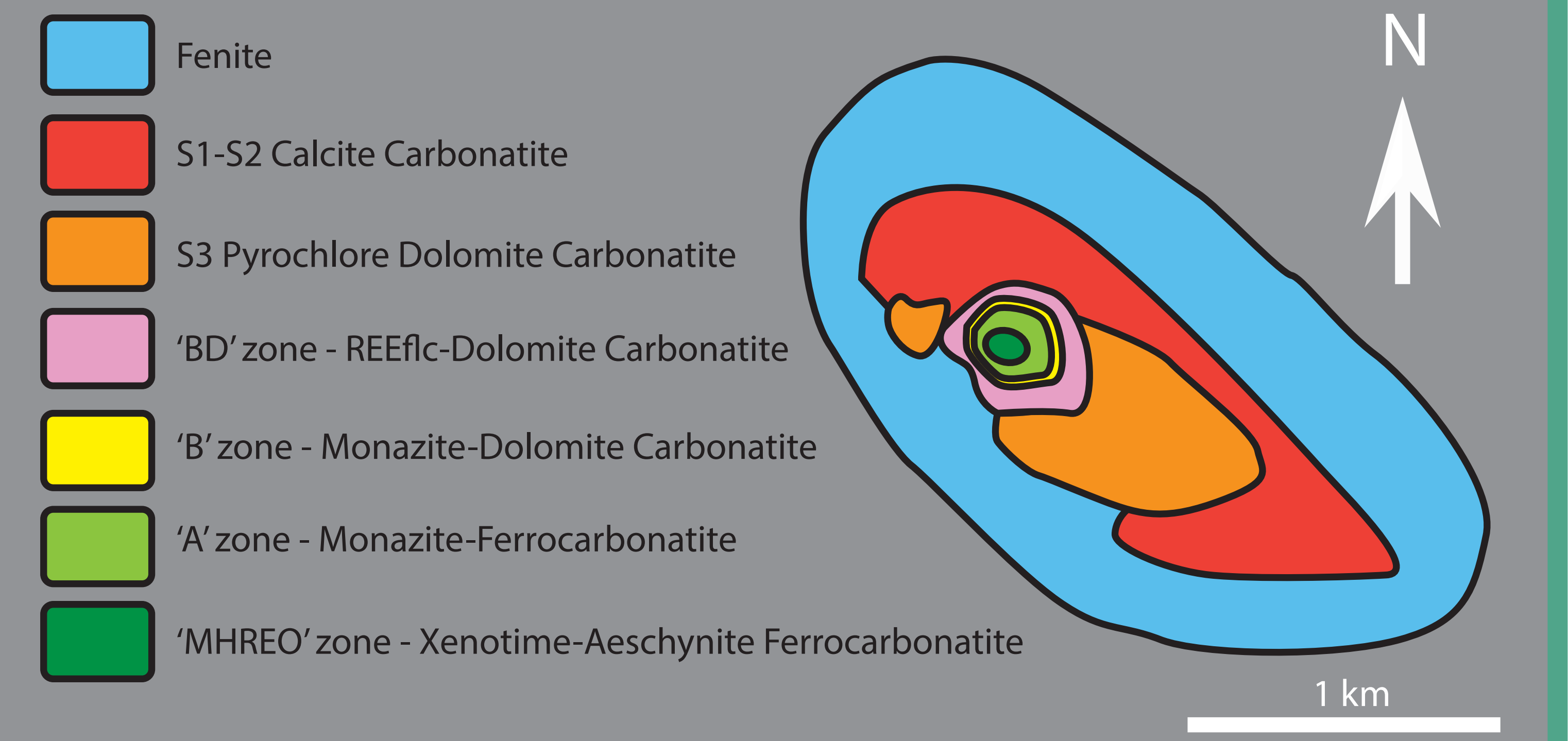**Figure 1:** The Eldor Carbonatite Complex is located in Northern Québec, approximately 130 km south of Kuujjuaq.

Legend:
- Fenite
- S1-S2 Calcite Carbonatite
- S3 Pyrochlore Dolomite Carbonatite
- 'BD' zone - REEflc-Dolomite Carbonatite
- 'B' zone - Monazite-Dolomite Carbonatite
- 'A' zone - Monazite-Ferrocarbonatite
- 'MHREO' zone - Xenotime-Aeschynite Ferrocarbonatite

Figure 2: Simplified geological map of the Eldor Carbonatite Complex [1] with the Ashram deposit at its core.
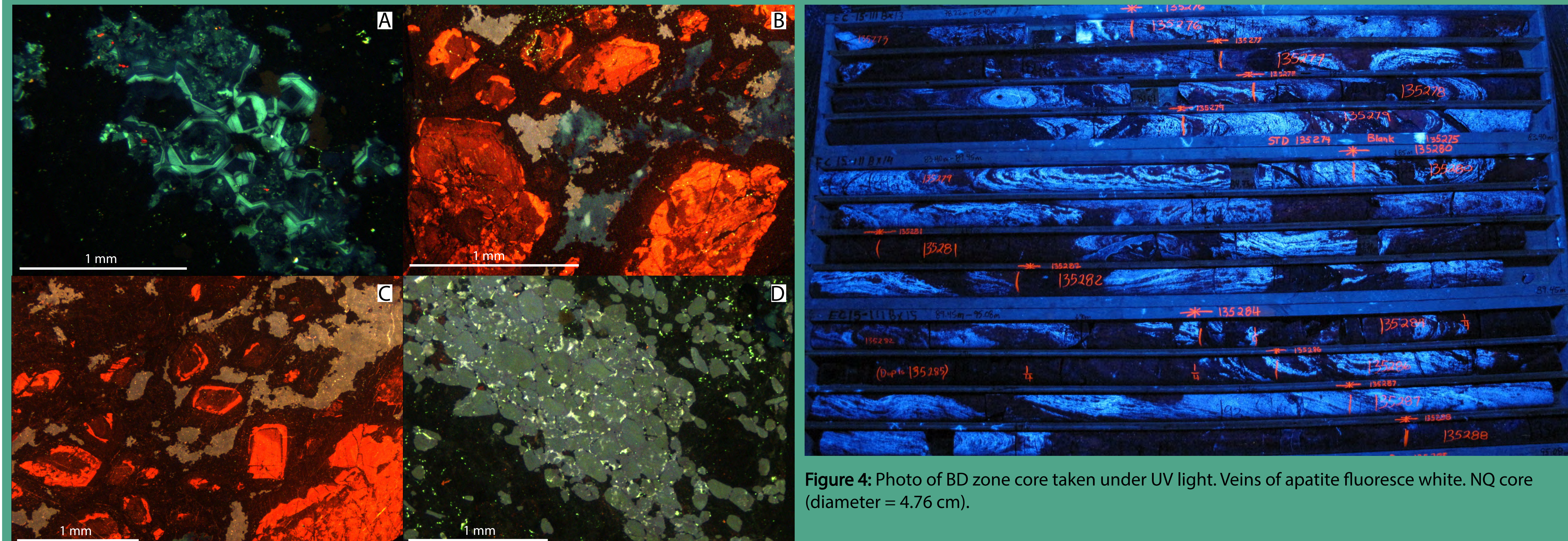

Figure 3: Cathodoluminescence images of selected samples. A) Complex zonation in blue- and green-luminescing fluorite, MHREO zone. B) Early dolomite grains (bright red) rimmed by Fe-rich dolomite (dark brown), and brecciated with an infill of apatite (white), fluorite (blue) and REEflc (deep pink), BD zone. C) Veins of white-luminescing, fine-grained and sucrosic apatite cutting the BD zone dolomite carbonatite. D) Cluster of green-luminescing, euhedral and coarse-grained apatite, characteristic of the rim units.
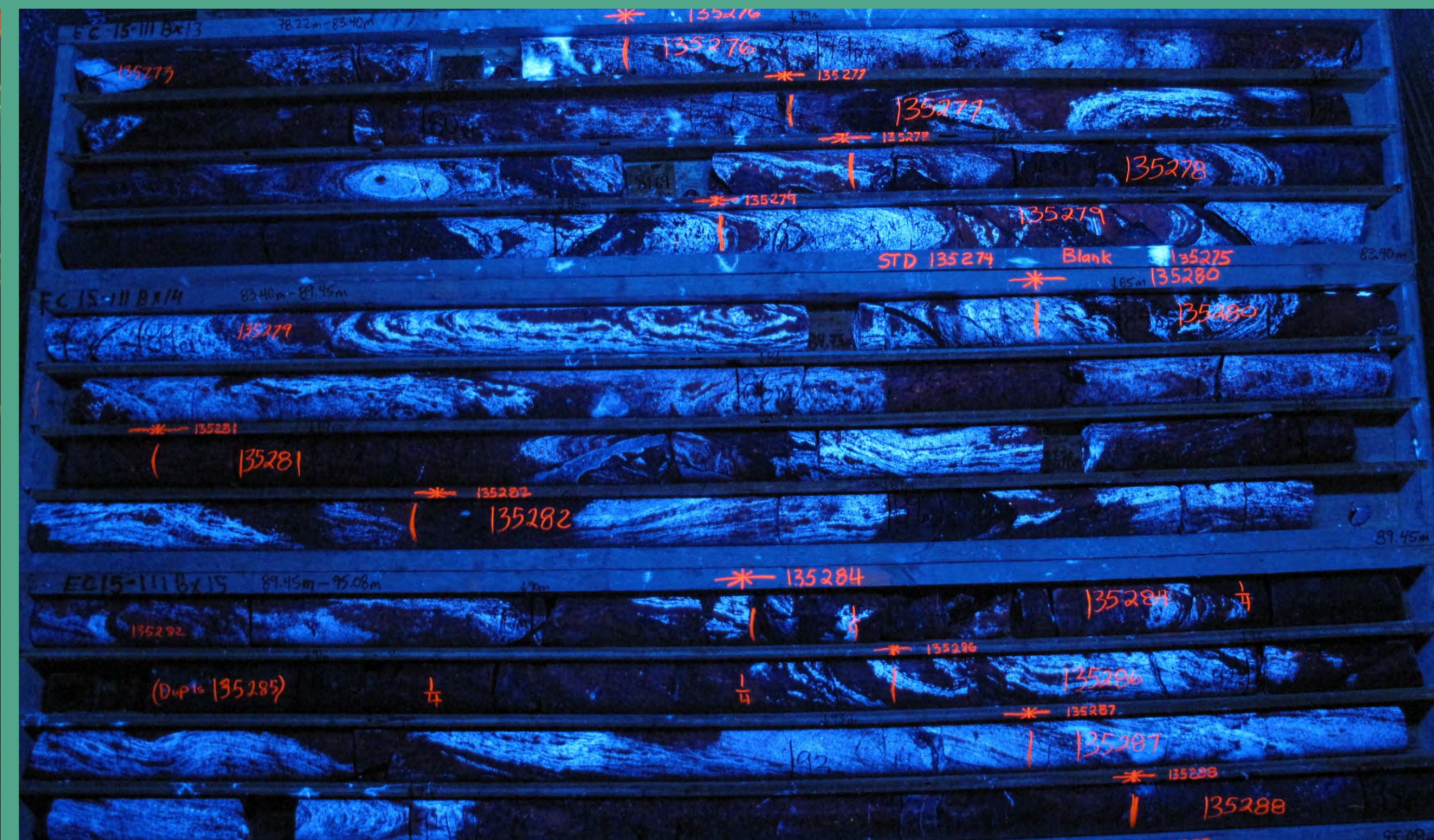

Figure 4: Photo of BD zone core taken under UV light. Veins of apatite fluoresce white. NQ core (diameter = 4.76 cm).

Textural Observations

The rare earth minerals, monazite-(Ce) ($REEPO_4$), bastnäsite-(Ce) ($REECO_3F$), xenotime-(Y) (YPO_4) and minor aeschynite-(Y) (($(Y,Ca,Fe)(Ti,Nb)_2(O,OH)_6$), occur in veins, as vug fillings, and as disseminations in breccia matrices (Fig. 5). These textural observations indicate precipitation from a hydrothermal fluid, though this does not rule out the possibility of magmatic pre-concentration.
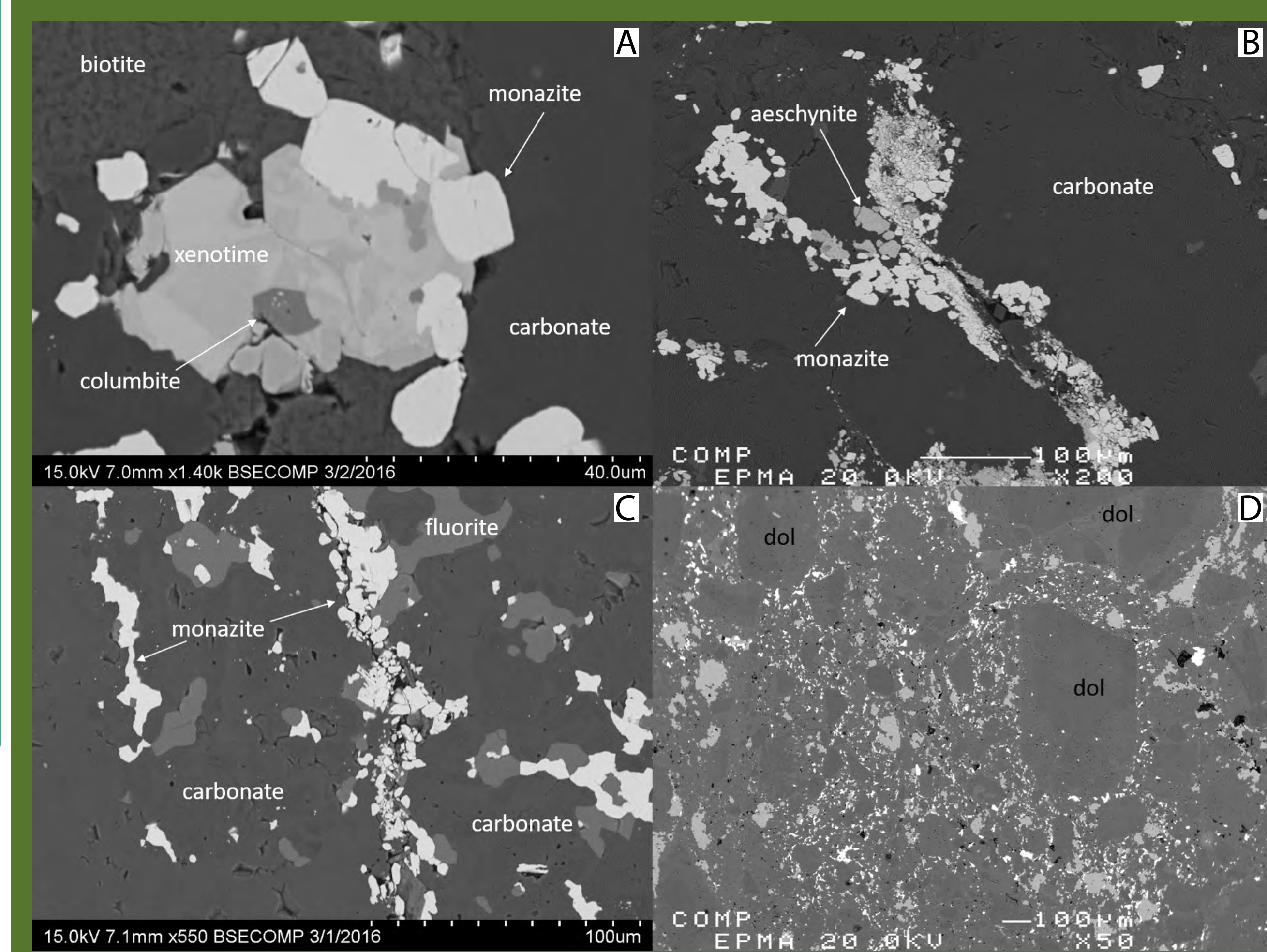

Figure 5: BSE images of rare earth minerals at Ashram. A) Xenotime-(Y) and monazite-(Ce) filling a vug in the MHREO zone. B) A vein of monazite-(Ce) and aeschynite-(Y) in the MHREO zone. C) Monazite-(Ce) ± fluorite veins in the B zone (similar veins are observed in the A zone). D) REEflc (white) and apatite (light grey) disseminated in dolomite breccia in BD zone.

Mineral Chemistry

The compositions of monazite-(Ce) and bastnäsite-(Ce) vary with location in the deposit, particularly in respect to their Nd_2O_3 and ThO_2 contents (Fig. 6,7). Monazite-(Ce) from the A and B zones can be subdivided into high- and low-Nd groups. Low-Nd monazite-(Ce) and bastnäsite-(Ce) exhibit identical trends of Nd/Th with evolution of the system (B to MHREO zone): the BD zone bastnäsite-(Ce) and high-Nd monazite-(Ce) have the same Nd and Th contents.

Three types of apatite can be distinguished on the basis of their chondrite-normalized REE profiles [2] (Fig. 8). The green-luminescing variety of apatite is LREE-enriched with a steep, negative slope, very similar to that of monazite-(Ce). White-luminescing apatite can be subdivided into two types: one with a steep REE profile, identical to that of the rim apatite, and another that has a flat MREE profile. The three types are similarly depleted in HREE.
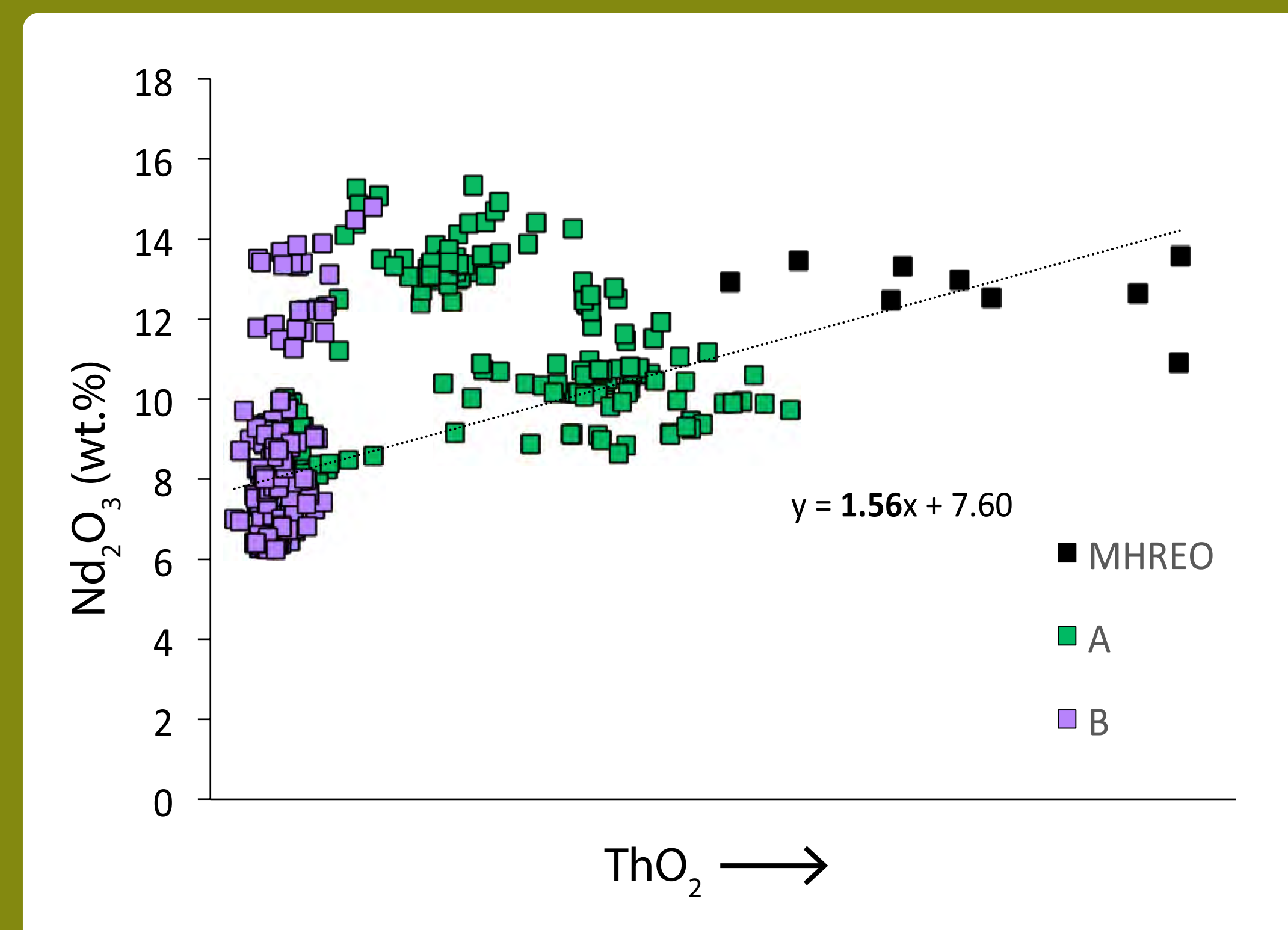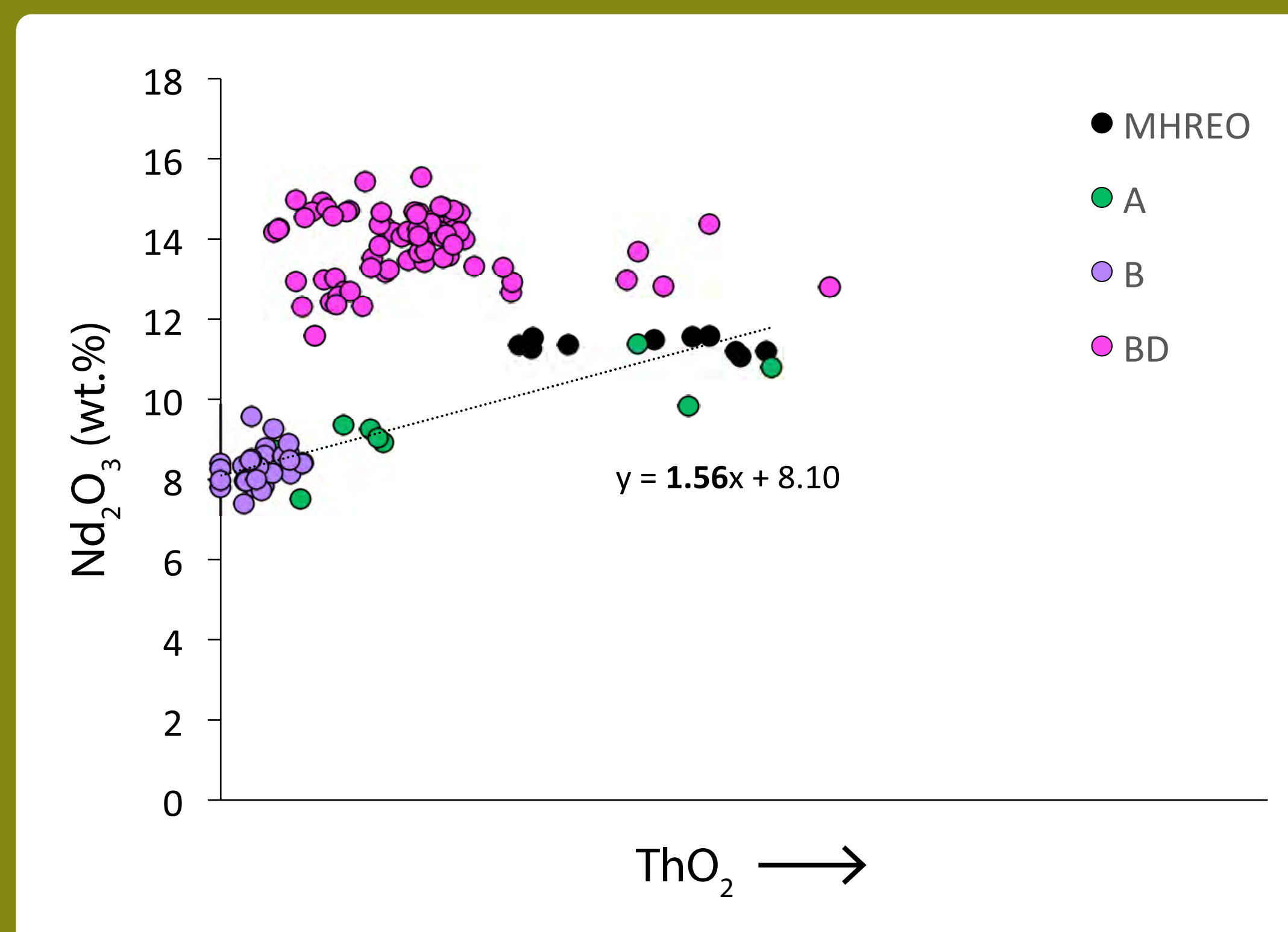

Figure 6 plot: Nd_2O_3 (wt.%) vs ThO_2. Legend: MHREO, A, B, BD. Trend line: $y = 1.56x + 8.10$

Figure 7 plot: Nd_2O_3 (wt%) vs ThO_2. Legend: MHREO, A, B. Trend line: $y = 1.56x + 7.60$

Figure 8 plot: Mineral / Chondrite. Legend: MHREO mnz, A mnz, B mnz, BD113 ap (mineralized), BD114 ap (mineralized), BD ap (barren), S3, S2, S1.

Figure 6 (top left): Bastnäsite-(Ce) from the B, A and MHREO zones define a positive linear trend of Nd_2O_3 vs ThO_2. The BD zone bastnäsite-(Ce) is richer in Nd.

Figure 7 (top right): MHREO zone monazite-(Ce) and low-Nd monazite-(Ce) of the B and A zones define a positive linear trend in Nd_2O_3 vs ThO_2. The slope of this trend is nearly identical to that for bastnäsite-(Ce) in Fig. 6. Some monazite-(Ce) from the B and A zones are more enriched in Nd.
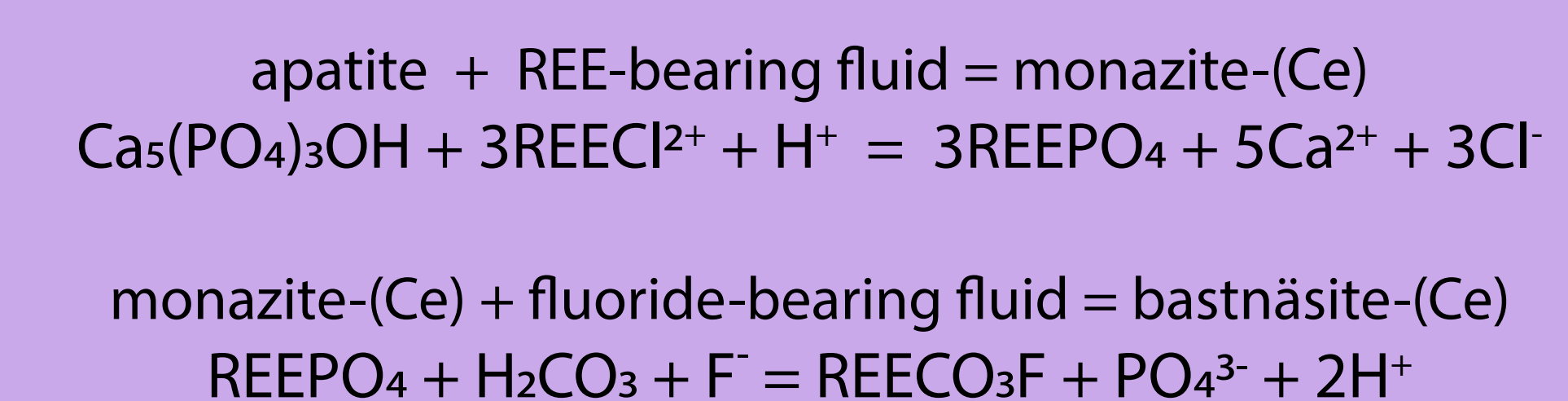
Figure 8 (bottom left): Chondrite-normalized REE profiles of monazite-(Ce) compared to apatite.
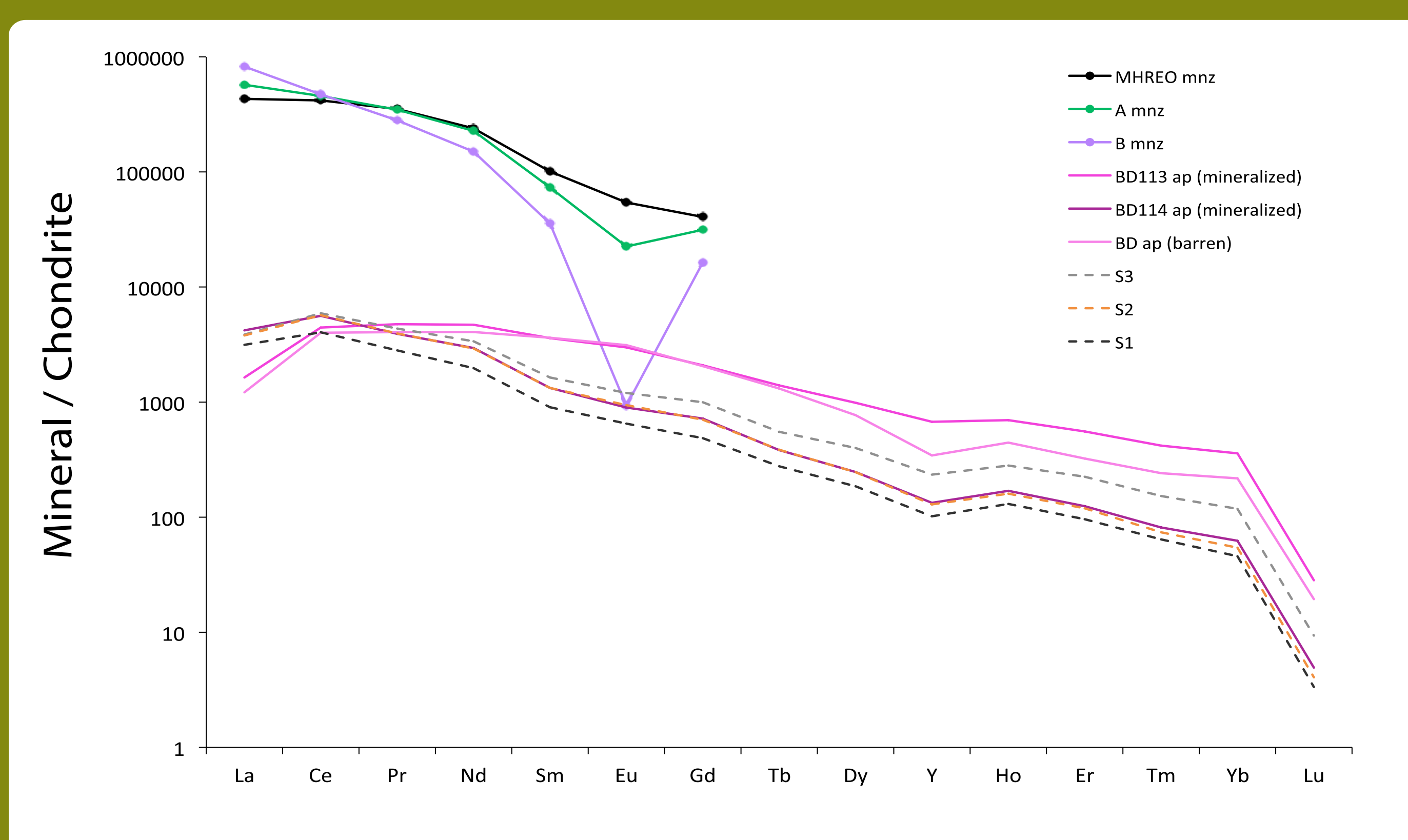
Discussion

Monazite-(Ce) was the earliest mineral to form, followed by xenotime-(Y) and bastnäsite-(Ce). Where in contact, bastnäsite-(Ce) invariably mantles monazite-(Ce) (Fig. 9). These textural observations, combined with the mineral chemistry (the similar Nd and Th contents of monazite-(Ce) and bastnäsite-(Ce)), indicate that bastnäsite-(Ce) developed as a replacement of monazite-(Ce) through ligand exchange (F^-, CO_3^{2-} for PO_4^{3-}), while preserving the original REE chemistry. Monazite-(Ce) compositions suggest that there were two mineralizing events (distinguished by Nd content). Bastnäsite-(Ce) from the B, A and MHREO zones partially replaced low-Nd monazite-(Ce), whereas the BD zone represents total replacement of high-Nd monazite-(Ce) by bastnäsite-(Ce). Similarly, where apatite and monazite-(Ce) are in contact, monazite-(Ce) occurs adjacent to or within apatite (Fig. 9), suggesting that it replaced apatite by substituting REE^{3+} for Ca^{2+}. Their very similar chondrite-normalized distributions indicate that monazite-(Ce) inherited its REE from the LREE-enriched apatite.

The proposed depositional mechanisms for monazite-(Ce) and bastnäsite-(Ce) are as follows:

$$apatite + REE\text{-}bearing\ fluid = monazite\text{-}(Ce)$$
$$Ca_5(PO_4)_3OH + 3REECl^{2+} + H^+ = 3REEPO_4 + 5Ca^{2+} + 3Cl^-$$

$$monazite\text{-}(Ce) + fluoride\text{-}bearing\ fluid = bastnäsite\text{-}(Ce)$$
$$REEPO_4 + H_2CO_3 + F^- = REECO_3F + PO_4^{3-} + 2H^+$$

Changes in system pH were important depositional controls for the Ashram REE deposit. These observations suggest that Ashram had a long-lived history in which the combination of magmatic zone-refinement and hydrothermal mobilization contributed to the formation of a carbonatite-hosted deposit with considerable potential for the exploitation of highly sought-after REE such as neodymium and dysprosium.
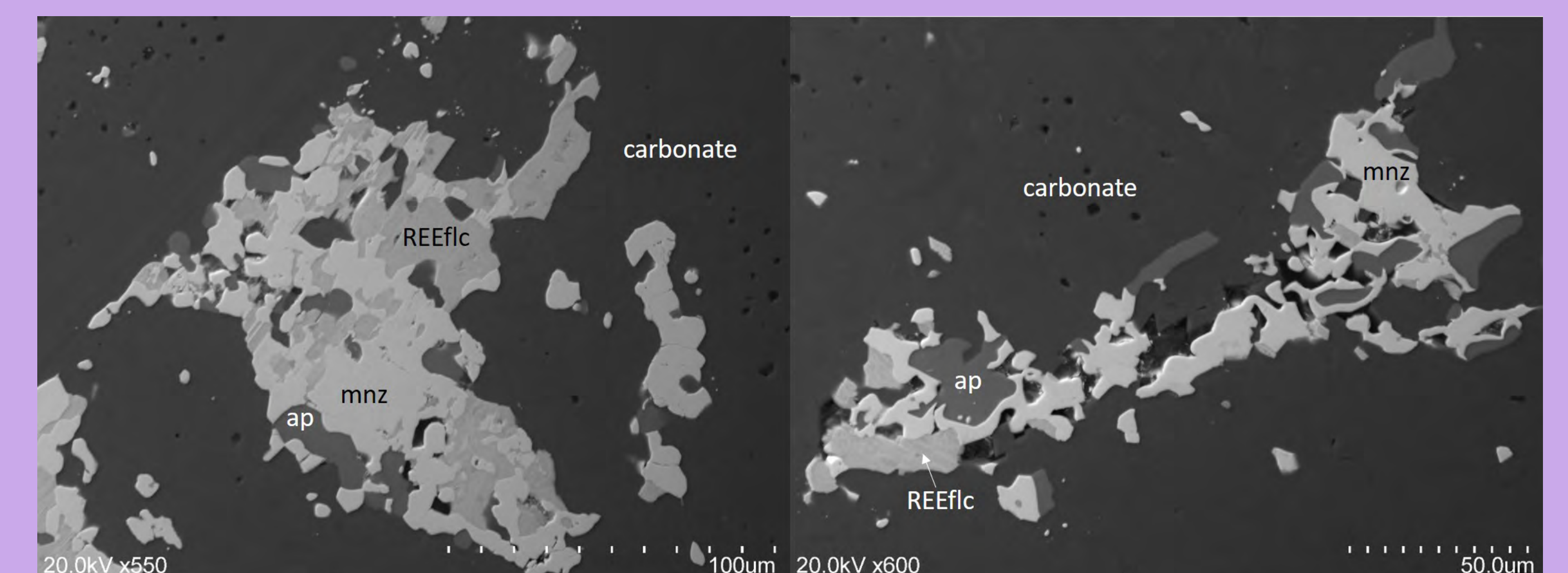

Figure 9: BSE images showing the relationship between apatite (ap), monazite-(Ce) (mnz) and the rare earth fluorocarbonates (REEflc). Apatite is mantled by monazite, which is in turn mantled by the REEflc.

Acknowledgements and References

[1] Schmidt, P. (2013). High-field-strength element distribution of the Eldor carbonatite complex, Canada. Unpublished MSc thesis, Tubingen University.
[2] McDonough, W.F. & Sun, S.-s. (1995). The composition of the Earth. Chemical Geology 120: 223-253.