

Introduction

Discovered in 1982, the Maw Zone is a REE-rich breccia located in the southeastern corner of the Athabasca Basin, northern Saskatchewan (Fig. 1). The occurrence consists of highly silicified, hematitized, dravitic tourmaline-rich rocks with high contents of REE (up to 8.1 wt% as total REE oxides; Agip Canada Ltd, 1985). The zone is located ca. 4 km SW from the south end of Phoenix U deposits (Fig. 2) and is exposed on surface for 300 by 200 m. Despite exhibiting some features in common with the Athabasca unconformity-related U deposits, the zone does not contain significant U contents (< 7.8 ppm U, Denison Mines Corp., 2006). In the Athabasca unconformity-related deposits, it is recognized that U is accompanied by REE enrichment (Fayek and Kyser, 1997), but the relationship between two styles of mineralization are uncertain. MacDougall (1990), Quirt et al. (1991) and Hanly (2001) suggested similar fluid histories based on mineral paragenesis and mineral chemistry. Following our principal component analysis (PCA) of sandstones overlying the Phoenix deposits (Chen et al., 2014a), we conducted PCA of the REE rich Maw Zone (Chen et al., 2014b) in order to evaluate the relationship between the two different styles of mineralization.

Objectives

1. To study elemental assemblages associated with REE mineralization in the Maw Zone.
2. To identify minerals hosting REEs in the Maw Zone.
3. To evaluate the relationship between REEs and U in the Maw Zone.

Methodology

PCA is a multivariate procedure to reduce the dimensionality of a dataset with a large number of variables, while retaining the variation in the variables (Jolliffe, 1986). The raw data was transformed to log-ratios and elemental assemblages were evaluated using simultaneous RQ-mode PCA. This study applied methods developed by Grunsky (2001) in the R statistical environment to a dataset containing 545 sandstone samples with data for 43 elements, obtained by near-total three acid digestion. After the examination of drill cores and outcrops, polished thin sections were made to identify minerals with an optical microscope and a JEOL 6610 LV scanning electron microscope (SEM) equipped with an EDS at the University of Ottawa.

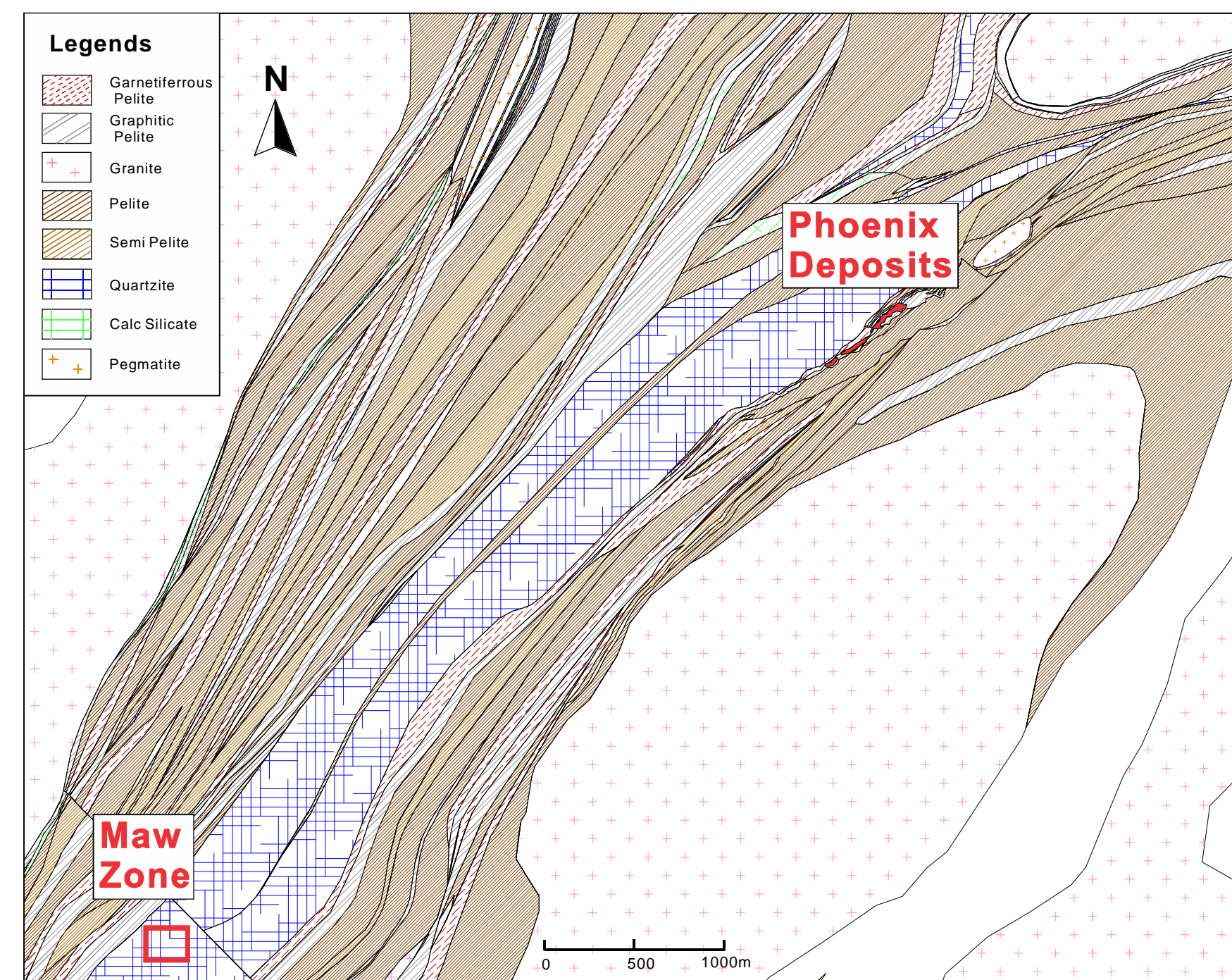


Fig 2: Geological map of the Denison Mines' Wheeler River property. The Maw Zone is 4 km SW from Phoenix Deposit B (after Denison Mines, 2014).

Fig 3: Hematite altered and brecciated sandstones from the largest outcrop in the Maw Zone (Easting: 6370502, Northing: 0472848, NAD83 Zone 13N). The sandstones exhibit intense pre-brecciation hematite alteration and silicification. The breccia fragments contain diagenetic illite, hematite and quartz. Hematite is ubiquitous imparting a dark red to pink colouration to the rocks.

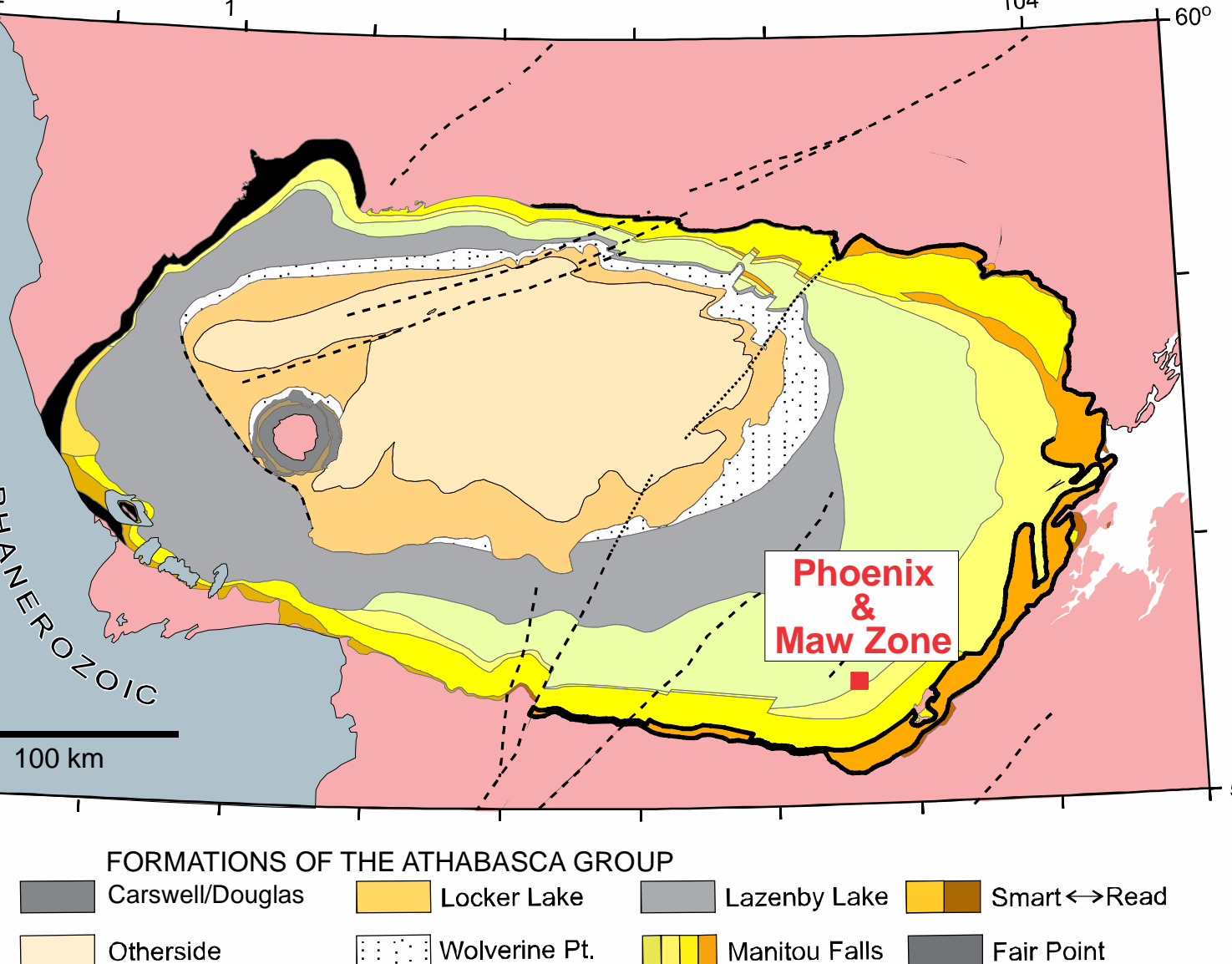


Fig 1: Location of Maw Zone and Phoenix Deposits within the Athabasca Basin, northern Saskatchewan, Canada



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Principal Component Analysis

Eigenvalues of the first six components are above 1, indicating that they represent more information than original variables. They account for 65.4% of the total variation in the data. The PC1-6 communalities of REEs, Y and U show high values (not shown), indicating these six capture the variability of those elements.

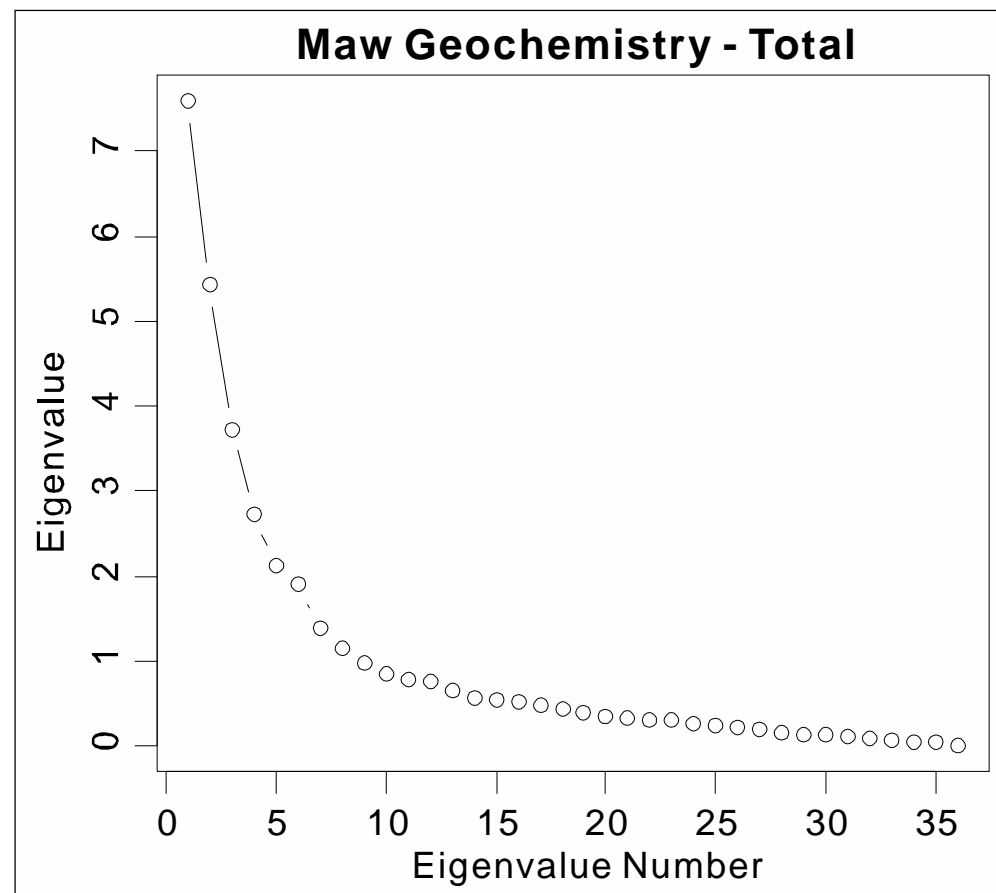


Fig. 4: Screeplot of sandstone data from the Maw Zone.

Relative enrichment of HREEs and Y is observed along the negative PC2 axis in samples from the MFb, MFC and MFD (Fig. 5). HREEs are separated from LREEs, and Eu is fractionated from the rest of LREEs along PC1. The position of P between HREEs and LREEs suggests at least two phosphate phases: one with HREEs and one with LREEs; HREEs are likely hosted by xenotime and the LREEs by monazite or/and aluminum phosphate-sulphate (APS) minerals. Chondrite-normalized REE patterns (not shown) display negative Eu anomalies and high ratios of LREEs to HREEs in sandstones, suggesting sourcing of REE from felsic rocks. Hematite is abundant in most rocks. Therefore, the enrichment of Fe is attributed to oxidized environments. Since Fe is plotted in the upper left, sandstone samples plotted towards the direction are interpreted to be more oxidized.

The biplot of PC3 vs. PC4 shows a relative enrichment in U, LREEs, P along the positive axis of PC3 (Fig. 6), indicating the likely association of LREEs with monazite and/or APS minerals. Uranium may be in monazite as it commonly contain significant amounts of U (Hecht and Cuney, 2000). Iron, Cr and V are in the upper right quadrant, indicating that MFD and RD are more oxidized than MFb and MFC. This feature also can be observed in PC1-PC2 biplot (Fig. 5).

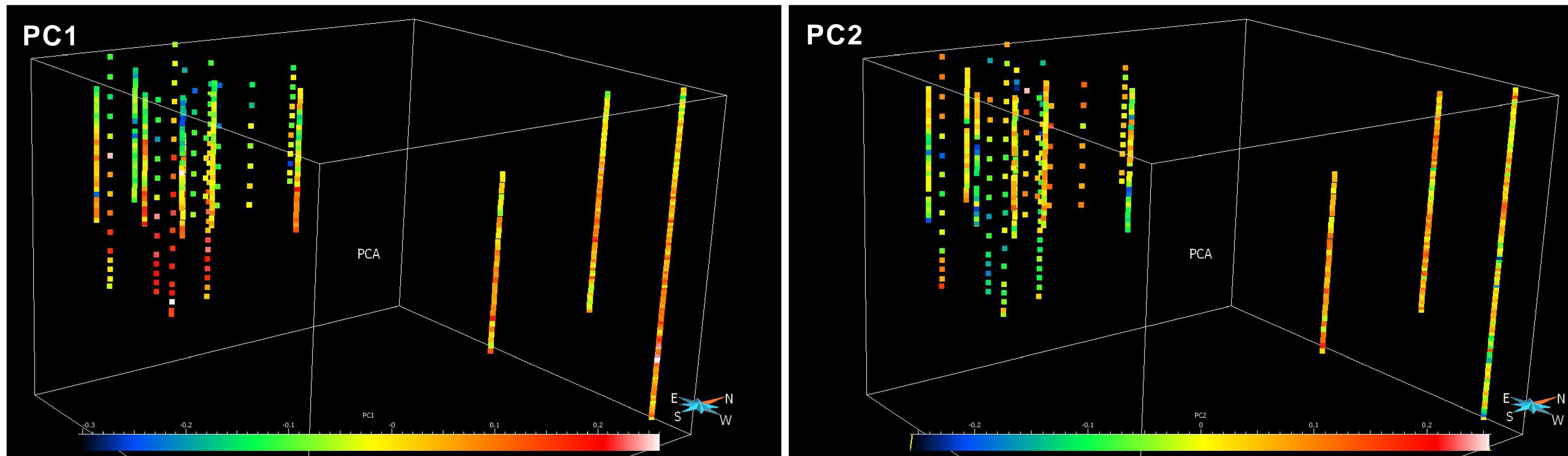


Fig. 7: 3D diagrams showing scores of PC1 (Left) and PC2 (Right) in drill cores. Strontium, U, Th, LREEs, Ti, V and Y account for most of the total variation of PC1 and Y, HREEs, Eu, Li, P and Ba for PC2. Negative scores of PC1 and PC2 appear in the upper part, reflecting the enrichment of xenotime because HREEs show strongly negative scores in PC1 and PC2.

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Petrography

The REEs are correlated with P in PCA, indicating that hosts are monazite and/or APS for LREEs and xenotime for HREEs. Back scattered electron (BSE) images of xenotime show two different forms. Subhedral to euhedral grains of xenotime rim detrital zircon grains (Fig. 8B). The second form occurs interstitial to detrital quartz grains, associated with magnesio-foitite (Fig. 8D). The fine-grained xenotime appears to be late hydrothermal product.

BSE imaging revealed that bastnäsite [(Ce,La,Y)(CO₃)F] occurs along fractures within and crystallizes around detrital zircon grains (Fig. 9B). Semi-quantitative analysis of bastnäsite using SEM-EDS shows no P but very high Y. The ratios of Y/HREE are higher for bastnäsite than those of xenotime.

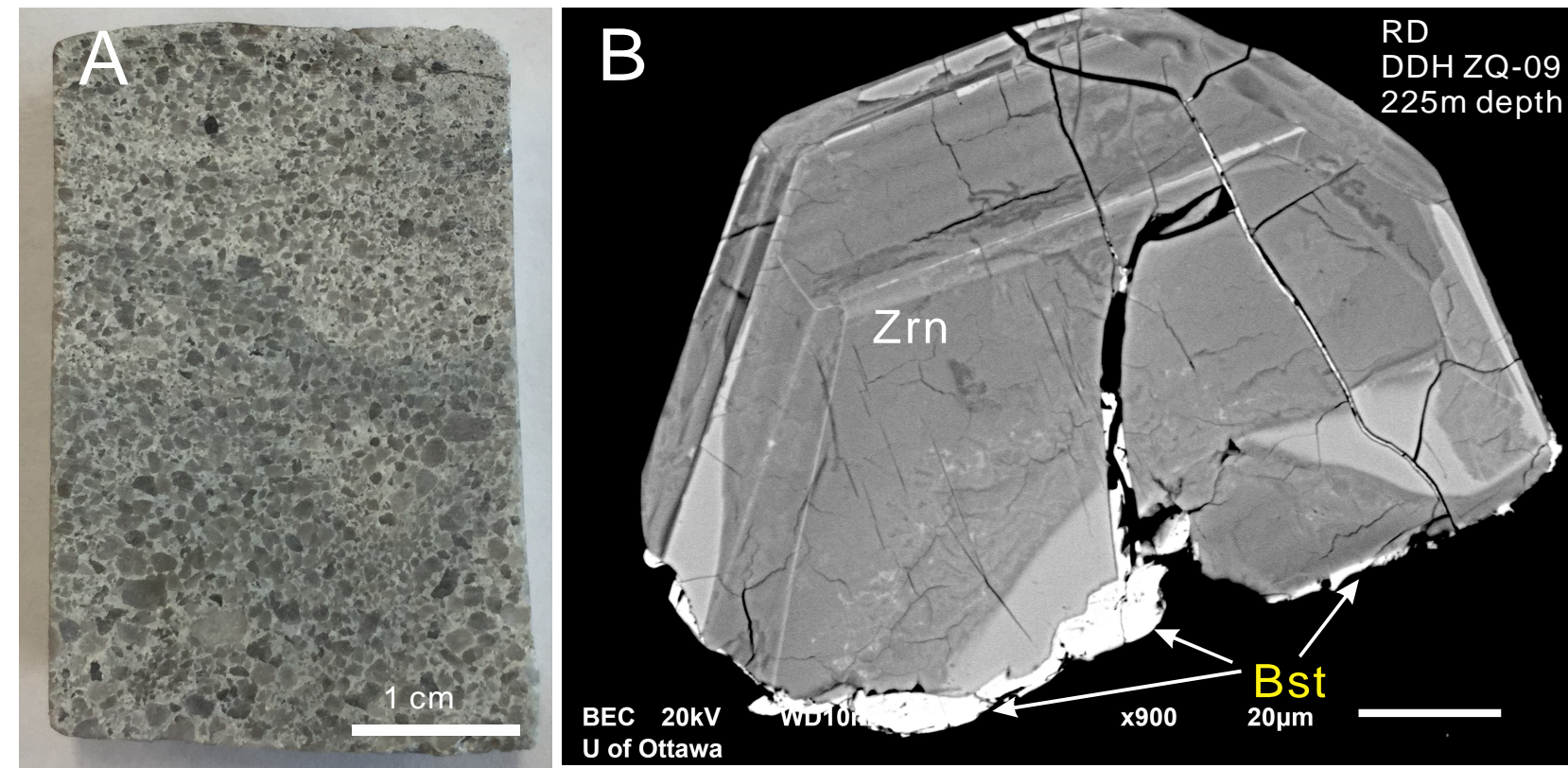


Fig. 9: (A) a buff-colored sample from DDH ZQ-09 at 225 m depth; (B) BSE image of bastnäsite (Bst) from the sample.

APS minerals are the primary host of LREE and occurs disseminated in a matrix of magnesio-foitite, sudoite and illite (Fig. 10). Detrital grains of monazite were reported by Quirt et al. (1991) and Hanly (2001) but not found in our samples. SEM-EDS analysis shows that they contain high Sr and LREEs and significant SO₄²⁻, suggesting that the APS minerals are a solid solution series of svanbergite-florenceite. The presence of SO₄²⁻ confirms oxidized conditions. APS minerals are known to contain high Th (Mwenifumbo and Bernius, 2007), consistent with the association of Th and LREEs in PCA (Fig. 5).

Summary

1. **PCA combined with the mineralogical study suggests xenotime as the host of HREEs in upper sandstone units, and APS minerals for the carrier of LREEs.**
2. **U is correlated with V, Cr, Fe, Ni, Cu, Cd, Na, Li and Ba, but very weakly correlated with HREEs-Y, and inversely with LREEs and P. The assemblages are different from those of the Phoenix dataset where U is associated with REEs and Pb and inversely correlated with Ti, Zr, Th and Al (Chen et al., 2014a);**
3. **REEs were introduced later by reduced fluids. This is reflected by inverse correlation between REEs and Fe and V.**
4. **There are two possible explanations for the lack of U mineralization in the Maw Zone: a) fluids did not contain U, as suggested by Pan et al (2013); and b) the oxidizing fluids did not encounter reducing media to precipitate U.**
4. **REEs show strong negative values in PC1 and PC2. These findings may be useful in assessing the potential for REE mineralization in the area by mapping the principal component scores of the rocks.**

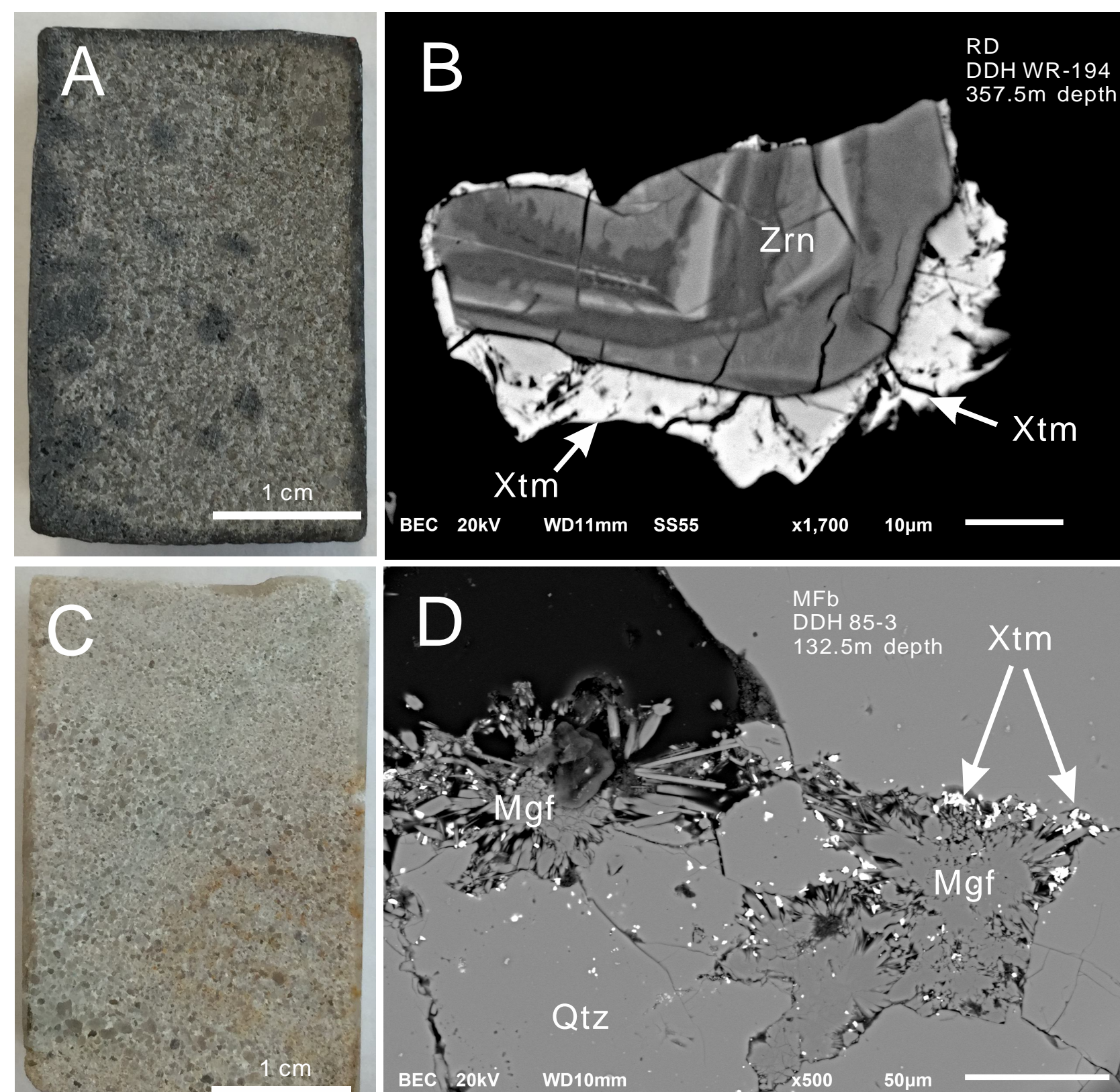


Fig. 8: Samples from DDH WR-194 at 357.5 m depth (A, B) and DDH 85-3 at 132.5 m depth (C, D). B & D: BSE images of xenotime forms. Mgf = magnesio-foitite (alkali-deficient dravitic tourmaline), Qtz = quartz, Xtm = xenotime, and Zrn = zircon

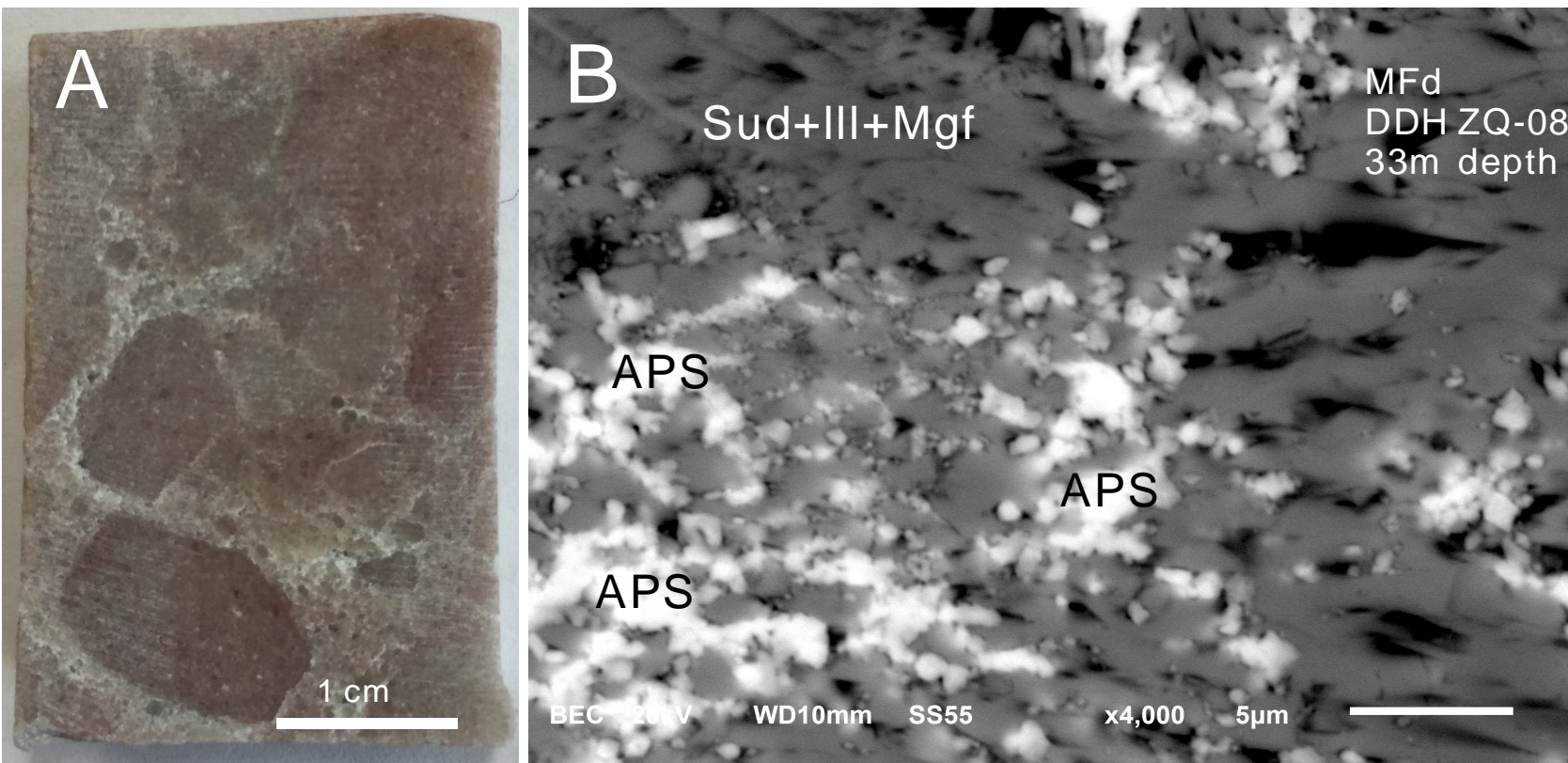


Fig. 10: (A) Sample from DDH ZQ-08 at 33 m depth, (B) BSE image of bastnäsite (Bst) from the sample. Ill = illite, Mgf = magnesio-foitite, and Qtz = quartz.