



Multivariate statistical analysis of the REE-mineralization of the Maw Zone, Athabasca Basin, Canada



Shishi Chen^{a,*}, Keiko Hattori^a, Eric C. Grunsky^{b,1}

^a Department of Earth and Environmental Sciences, University of Ottawa, 25 Templeton Street, Ottawa, Ontario, Canada

^b Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario, Canada

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ABSTRACT

To evaluate the relationship between the enrichment of rare earth elements (REEs) and U, we carried out a principal component analysis (PCA) of sandstones in the REE-rich Maw Zone in the Athabasca Basin, Canada. The Maw Zone, a breccia pipe with surface exposure of 300 × 200 m, consists of highly silicified, hematized, tourmaline-rich rocks with high REEs (up to 8.1 wt.% as total REE oxides). It is ~4 km southwest from the south end of the Phoenix U deposits, however, rocks in the Maw Zone do not show high U (<7.8 ppm in most rocks). We used RQ-mode PCA to compute variable and object loadings simultaneously, which allows the displays of observations and the variables at the same scale. PCA biplots of the Maw Zone data show that U is strongly correlated with V, Cr, Fe, Ni, Cu, Na, Li and Ba, but very weakly correlated with heavy rare earth elements (HREEs) + Y, and inversely with light rare earth elements (LREEs) and P. Relative enrichment of HREEs, Y, and P suggests xenotime as the predominant host of the HREEs. The grouping of LREEs + Sr + Th + P suggests the probable occurrence of monazite and/or aluminum phosphate-sulfate (APS) minerals. A mineralogical study confirmed the common occurrence of xenotime and APS minerals. The positive association between U and Fe in the PCA plot in the Maw Zone suggests that U was transported by oxidized fluids. The absence of U mineralization in the Maw Zone is explained by low U in the oxidizing fluids, or a lack reducing fluids to precipitate U. The PC1 and PC2 may reflect the major element assemblages related to the REE mineralization. The comparison of the maps of PC scores and the concentrations of HREEs + Y and P shows that the scores of PCs are better indicating the hydrothermal REE mineralization. For prospecting HREEs, PC2 is more reliable than PC1 because PC2 has the largest variance of HREEs and the second largest variance of LREEs.

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1. Introduction

1.1. Rare earth elements in Athabasca Basin

The Athabasca Basin is a large Paleoproterozoic to Mesoproterozoic sandstone basin that occupies much of the northernmost quarter of the province of Saskatchewan and a smaller portion of northeastern Alberta (Fig. 1). It is the most significant U producing district in the world. Although no rare earth elements (REEs) have been produced in the past or are currently being produced in the Athabasca Basin, most U deposits contain anomalously high concentrations of REEs (Normand, 2014). REEs are mostly hosted by allanite and phosphate minerals, such as monazite, cheralite and xenotime (Normand, 2014). The earliest record of the REE mineralization in the Athabasca Basin was provided by Union Oil Company of Canada Inc. for the “Wheeler River Yttrium Prospect” (Knox, 1985, cited in Normand, 2014), which was found by AGIP Canada Ltd. and

renamed the “Maw Zone” (MacDougall, 1990; Quirt et al., 1991; Hanly, 2001). The total indicated and possible resources were estimated to be ca. 463,000 tonnes grading 0.21 wt.% Y₂O₃ equivalent (0.1 wt.% cutoff) (Knox, 1985 cited in Normand, 2014). Quirt et al. (1991) suggested that the Maw Zone is the shallow peripheral expression of U deposits that occur along the unconformity between sandstones and the basement.

1.2. Principal component analysis

Principal component analysis (PCA) is useful in describing multi-element associations of geochemical data that often reflect mineralogy. In this particular study, PCA may reveal the geological processes critical to REE mineralization or minerals hosting REEs. The objective of PCA is to reduce the dimensionality of a dataset with a large number of variables, while retaining as much as possible of the variation in the variables (Jolliffe, 1986). This reduction is carried out by transforming raw data to a set of artificial variables, principal components, which retain the variation of the original variables in decreasing order. PCA has been used in geoscientific studies to identify elemental assemblages

* Corresponding author.

E-mail address: schen162@uottawa.ca (S. Chen).

¹ Current address: Department of Earth and Environmental Sciences, University of Waterloo, 200 University Ave. W, Waterloo, Ontario, Canada.

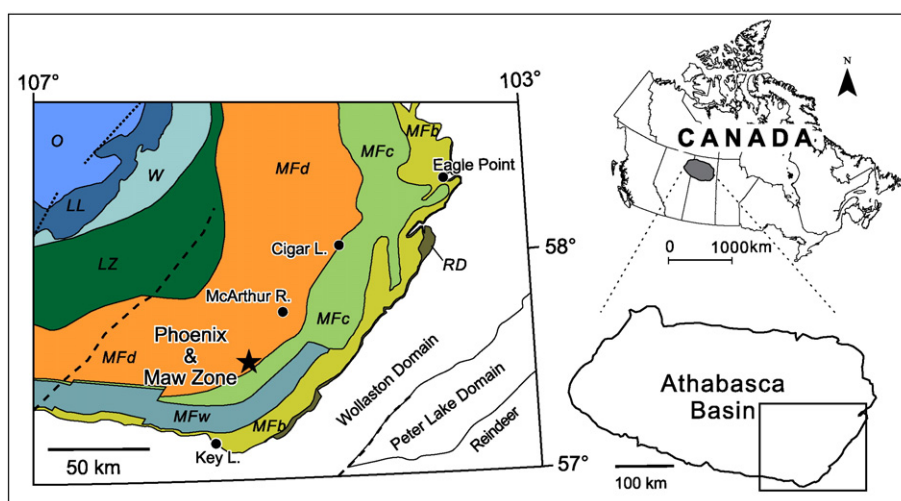


Fig. 1. General geological map of the southeast part of the Athabasca Basin, Saskatchewan, Canada (after Jefferson et al., 2007). Also shown is the position of the Phoenix U deposits and Maw Zone (solid star) and major unconformity-related uranium deposits (solid dots). RD = Read Formation; MF = Manitou Falls Formation (b = Bird Member; w = Warnes Member; c = Collins Member; d = Dunlop Member); LZ = Lazenby Lake Formation; W = Wolverine Point Formation; LL = Locker Lake Formation; O = Otherside Formation; The inserted map (upper right) shows the location of the Athabasca Basin within Canada. Boundaries of provinces are shown with thin black lines. The square in the lower right map shows the location of the main map within Athabasca Basin.

related to geological processes, such as hydrothermal alteration and mineralization (Grunsky, 1986).

1.3. The compositional nature of geochemical data

Geochemical data are reported as partial of a compositions (weight per cent, parts per million, etc.). Compositional data are unique in that the parts of a composition always sum to a constant (100%, 1,000,000 ppm). Thus for any D-part composition (x), D-1 parts are all that are required since the Dth composition is automatically defined as $(\text{constant} - \sum x_i) = x_D$. This problem was noted by Pearson (1897) and was largely ignored in the literature. Chayes (1960) attempted to deal with the problem using ratio correlations. Aitchison (1986) provided a solution to the problem by suggesting that the ratios are the most important information in any composition, and by taking the logarithms of the ratios, the values transformed range across the real number space, enabling the use of standard statistical methods to study geochemical data.

2. Study area

2.1. Geology

The Maw Zone is in the eastern part of the Athabasca Basin (Fig. 1) and ~4 km SW from the high-grade U ore of the Phoenix U deposits along the same NE-trending basement shear deformation zone (Fig. 2). AGIP Canada Ltd. (1985) discovered the enrichment in heavy REEs (HREEs) and Y in brecciated sandstones. The Maw Zone, with a surface exposure of 300×200 m, consists of highly silicified, hematitized, tourmaline-rich rocks with high REEs (up to 8.1 wt.% as total REE oxides; AGIP Canada Ltd., 1985). Tourmaline in the area has been described as dravite with varying Cr content (Quirt et al., 1991). The recent study of tourmaline chemistry in the Maw Zone suggests that it is magnesio-foitite (alkali-deficient Mg-rich tourmaline; O'Connell et al., 2015). Although the Maw Zone is close to the Phoenix U deposits, rocks do not show significantly high U (<7.8 ppm) except for one sample at a depth of 320 m in DDH WR195, which yielded 40.9 ppm U. The most prominent feature of the Maw zone is the intense hematitization and brecciation in sandstones. Some breccia fragments are large (up to 90 cm), and can retain primary sedimentary features, such as cross-bedding (MacDougall, 1990). The basement rocks in the area belong to the western Wollaston Domain of the Wollaston

Supergroup that is Paleoproterozoic in age (Quirt et al., 1991; Yeo and Delaney, 2007; Jefferson et al., 2007). They are mostly graphite-, garnet- and cordierite-bearing, biotite metapelites, semipelites and quartzite and pegmatite lenses (Barker, 2011).

2.2. Sandstone stratigraphy

The eastern part of the Athabasca Basin is underlain by sandstones of the Manitou Falls Formation and the Read Formation. The Manitou Falls Formation is subdivided into three members in the area: the Dunlop Member, the Collins Member, and the Bird Member in stratigraphic order (Ramaekers et al., 2007, Table 1). The total thickness of sandstones in the Maw Zone varies greatly, from approximately 200 m in the western part to over 300 m in the eastern and northern parts of the Maw Zone. This large difference in the sandstone thickness is partly related to the paleo-topographic high of a quartzite "ridge" and the vertical movement along basement faults during the deposition of sandstones. The lowermost sandstone unit is lacking above the quartzite ridge. A major northeast-trending basement fault directly below the Maw Zone dips moderately to steeply to the east, occurring along a graphitic rock in quartzite and shows significant vertical displacement. Sandstones and quartzite close to the fault are brecciated, suggesting the ascent of hydrothermal fluids from the basement.

3. Samples

This study is based on chemical compositions of drill core sandstones (drill-hole locations are shown in Fig. 2) determined by the Saskatchewan Research Council for Denison Mines Corp. using an inductively coupled plasma optical emission spectrometer (ICP-OES) and mass spectrometry (ICP-MS) following the near total digestion using three acids (HF-HNO₃-HCl). Details of the analysis method and the quality assurance/quality control procedures are provided by Roscoe (2014). There is a total of 545 sandstone samples in the dataset. The elements in the original dataset include Al, Ag, Ba, Be, Ca, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Fe, Ga, Gd, Hf, K, La, Li, Mg, Mo, Na, Nb, Nd, Ni, P, Pb, Pr, Sc, Sm, Sn, Sr, Ta, Tb, Th, Ti, U, V, W, Y, Yb and Zn. In this study, light REEs (LREEs) include La, Ce, Nd, Sm, and heavy REEs (HREEs), Gd, Dy, Er, and Yb. Europium is one of the LREEs, but it was not included in LREEs.

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