

TRANSFER OF RARE EARTH ELEMENTS FROM NATURAL METALLIFEROUS SOILS INTO PLANT SHOOT BIOMASS OF METALLOPHYTES FROM KATANGA

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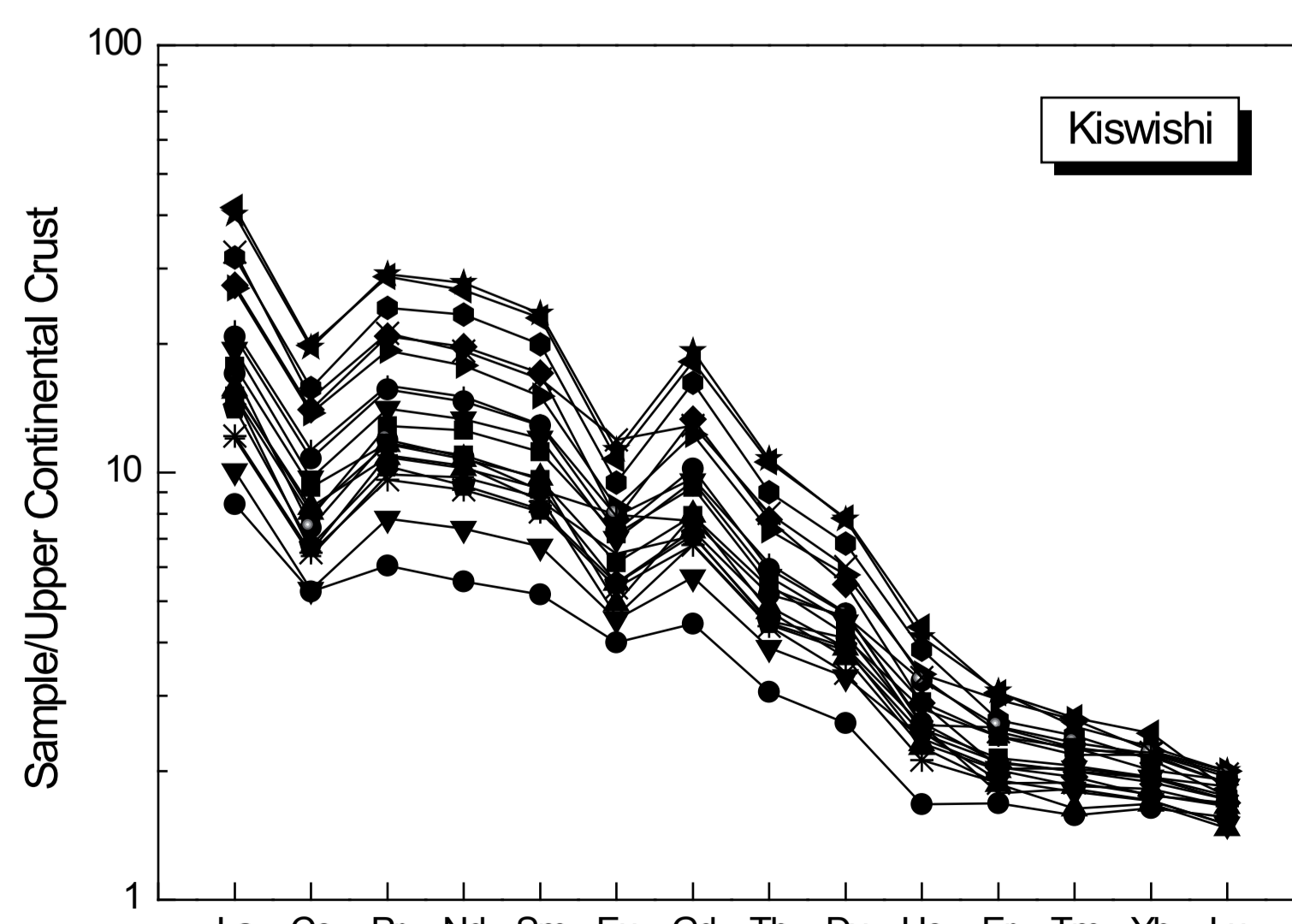
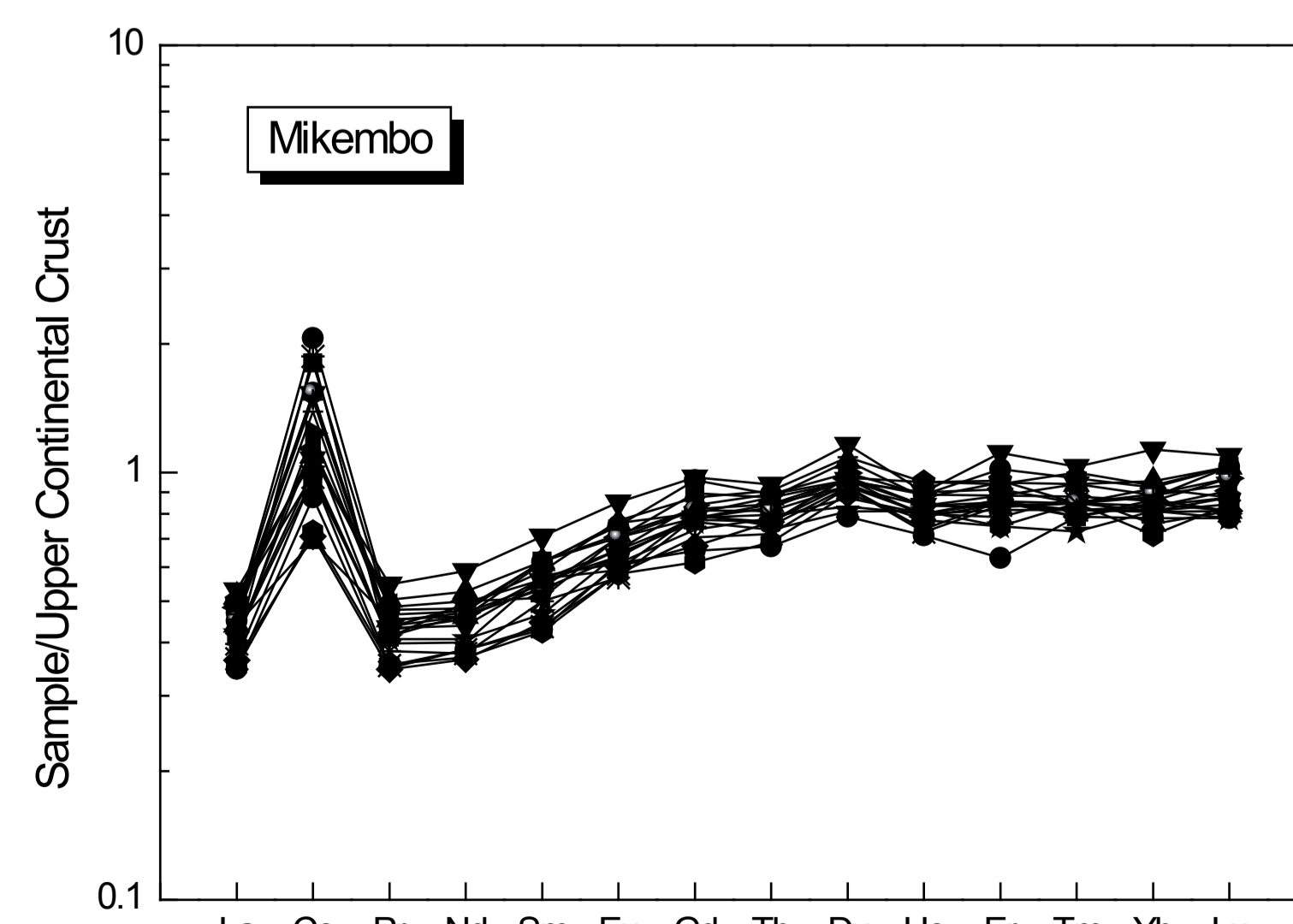
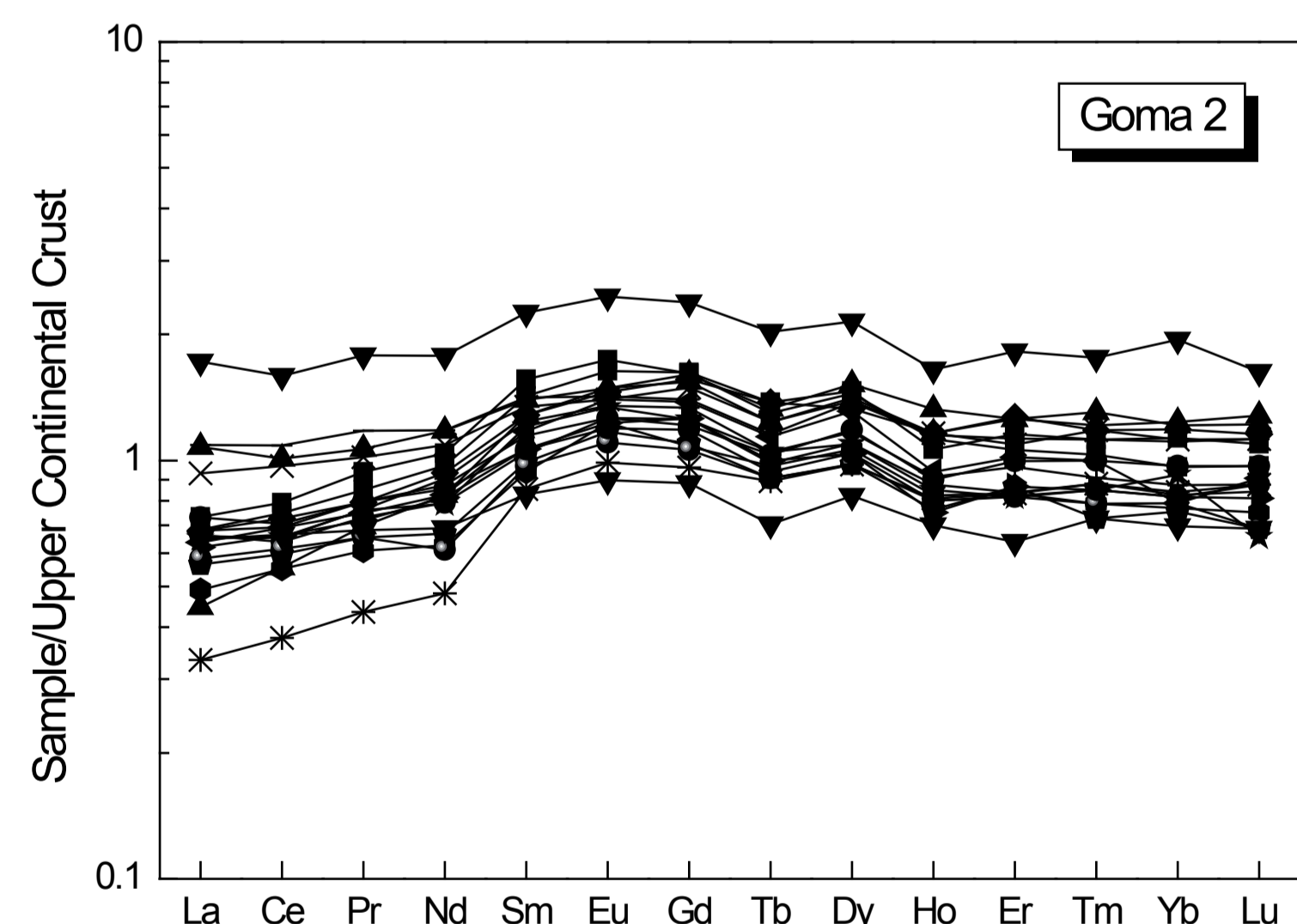
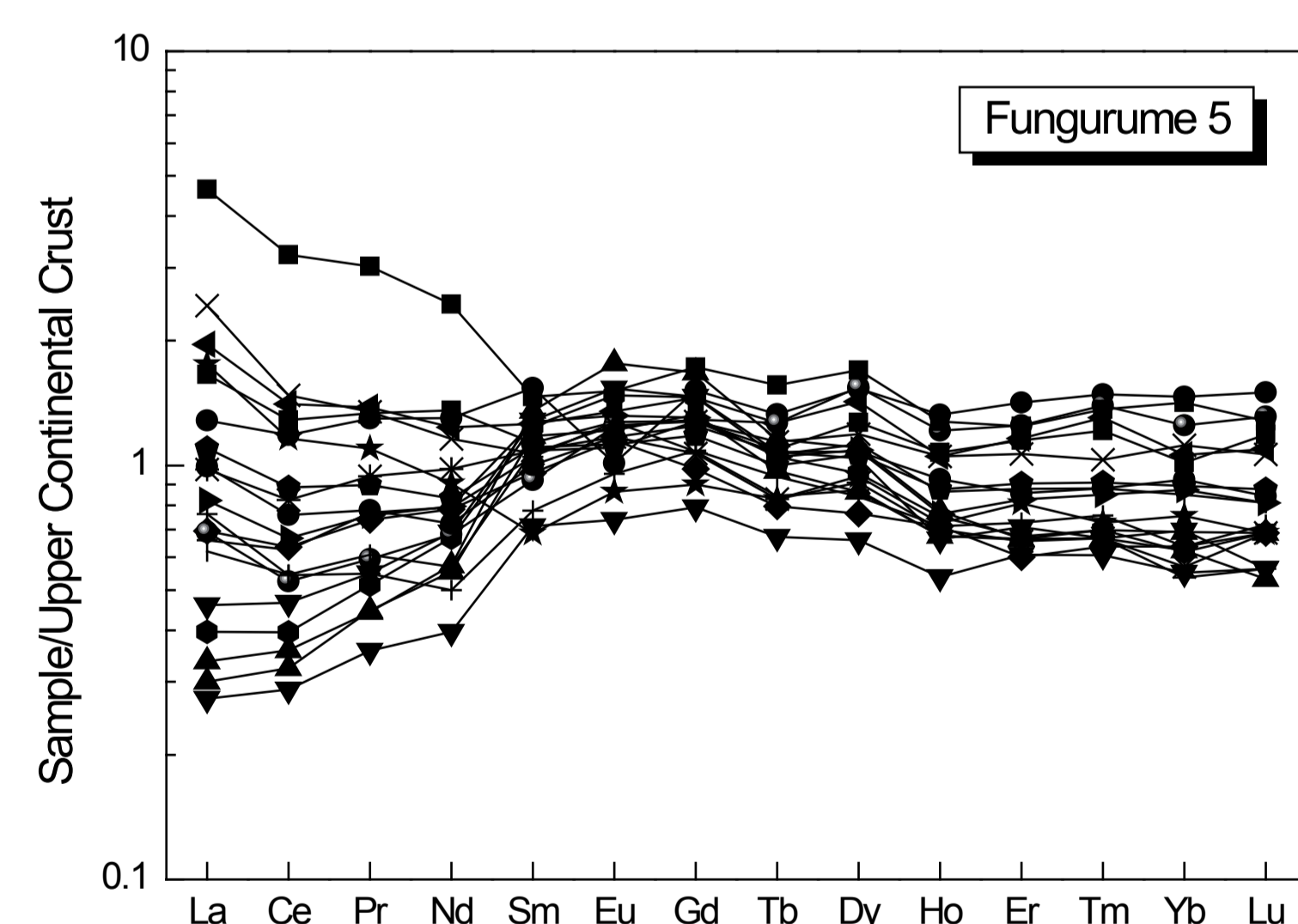
1/ Scope of the study

The geochemical behavior of rare earth elements (REE) is generally assessed for the characterization of the geological systems where these elements represent the best proxies of processes involving the occurrence of an interface between different media. REE behavior is investigated according to their concentrations normalized with respect to the upper continental crust. In this study, the geochemical fingerprint of REE in plant shoot biomass of an unique metallic flora (i.e., *Anisopappus chinensis*) was investigated. The plants originate from extremely copper and cobalt rich soils, deriving from Cu and Co outcrops in Katanga, Democratic Republic of Congo. Species investigated in this study is able to accumulate high amounts of Cu and Co in shoot hence being considered as Cu and Co hyperaccumulators (Lange et al., 2014). Therefore, assessing the behavior of REE may lead to a better understanding of the mechanisms of metal accumulation by this flora.

2/ Rare earth elements in soils

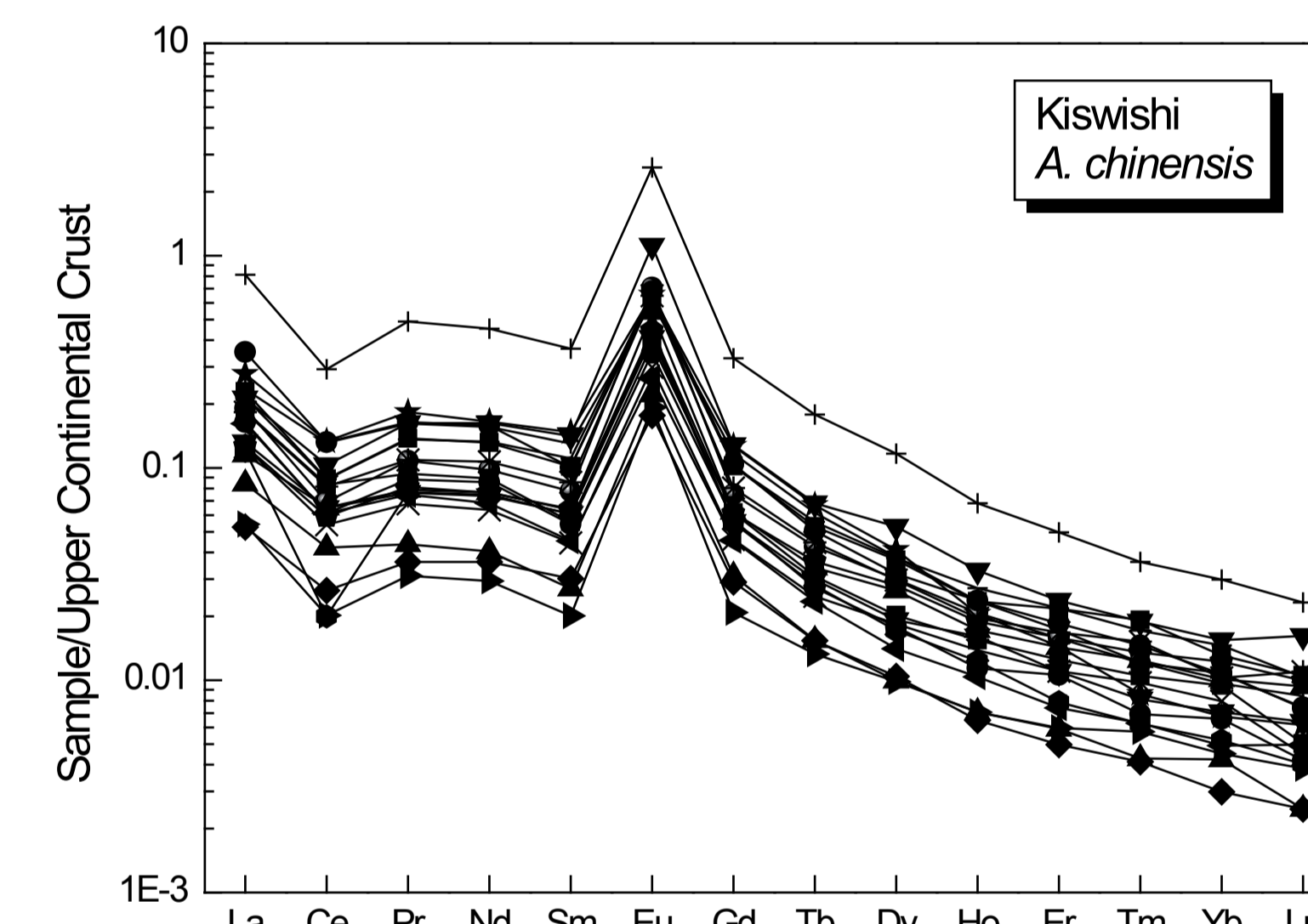
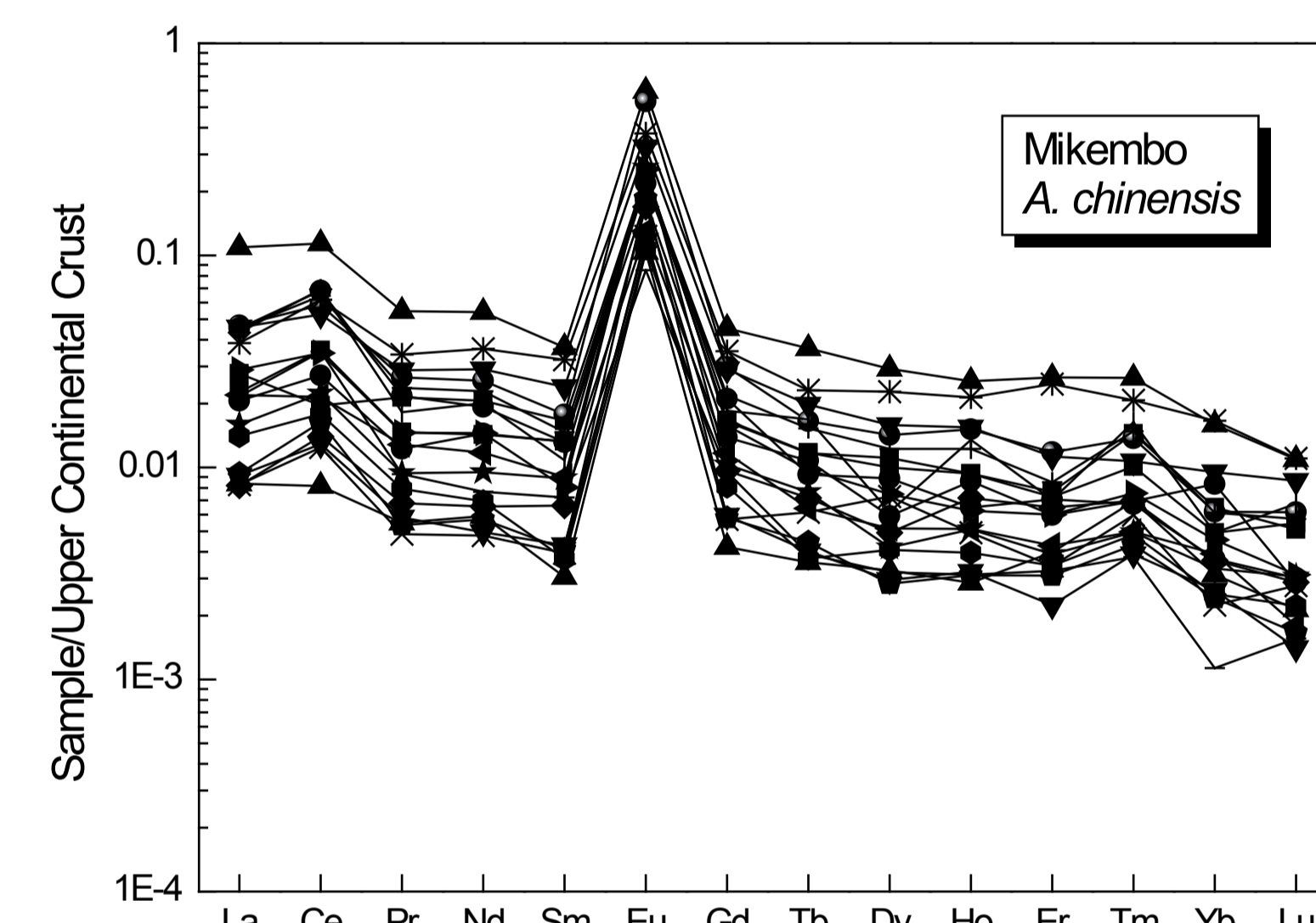
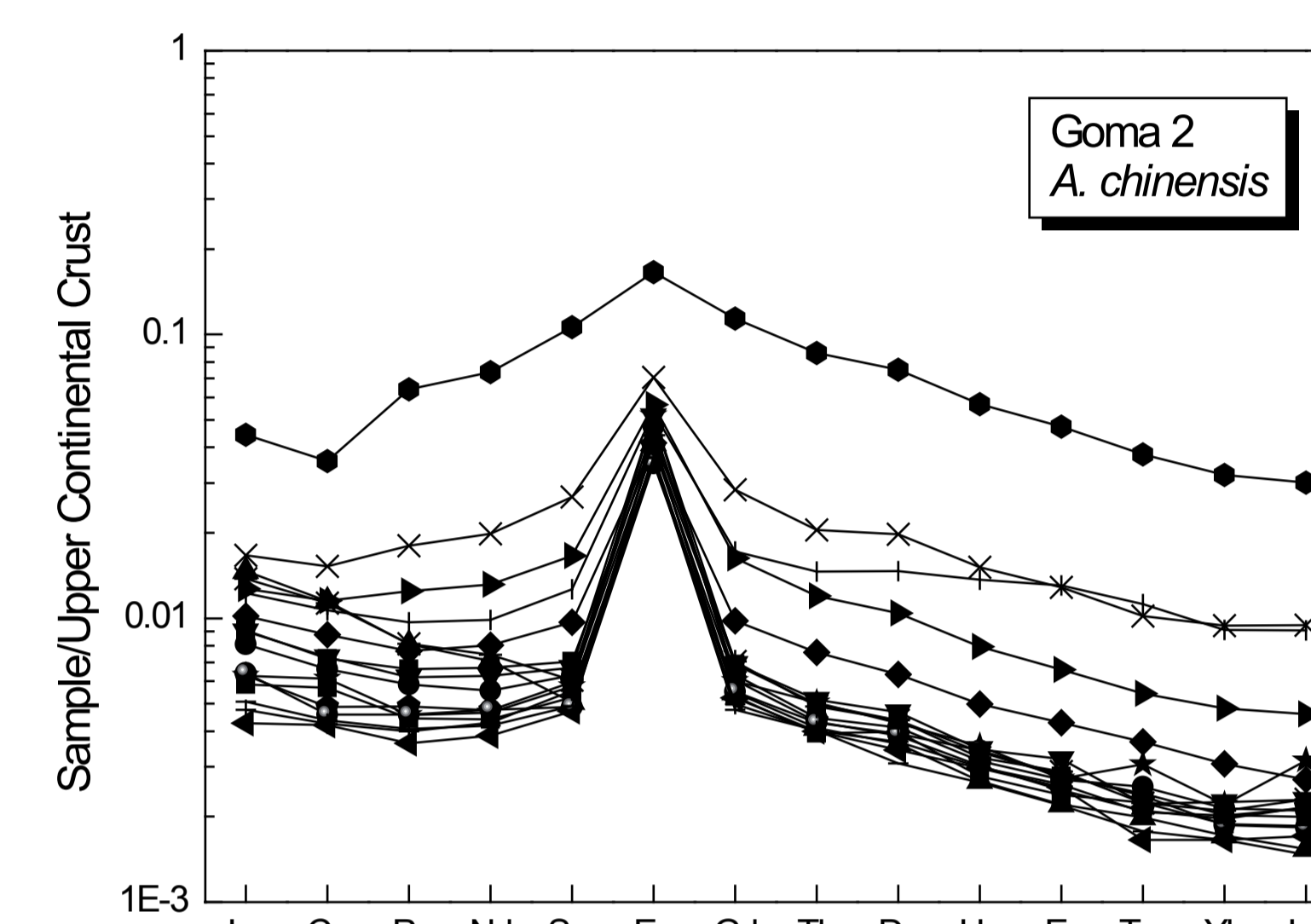
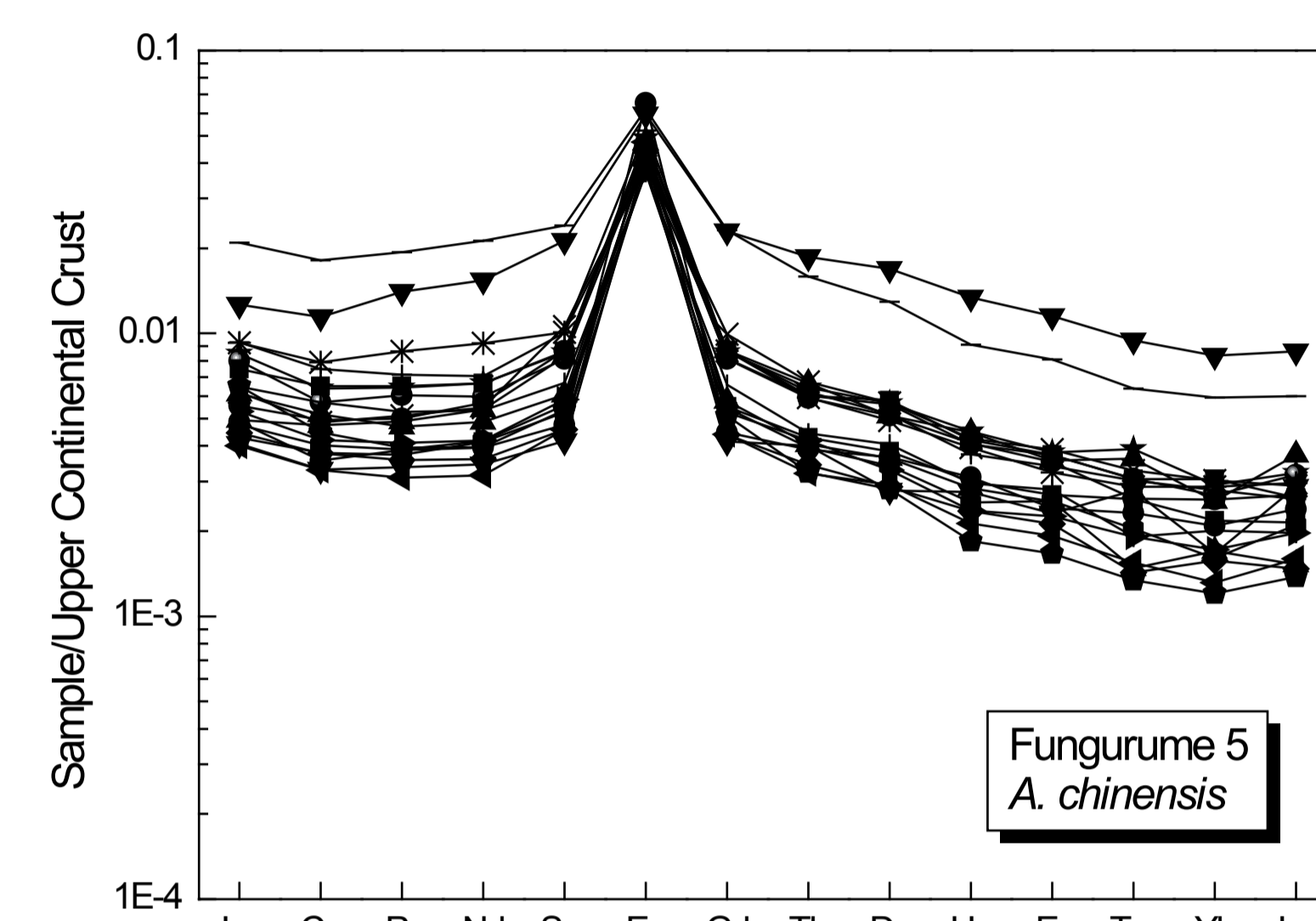
Soil samples (organic layer; 0-10 cm) have been collected on four various sites: two natural Cu-Co undisturbed hills (Ca poor, 0.14 wt % < Ca < 0.27 wt %) from the Tenke-Fungurume region: Fungurume 5 and Goma 2; and two Miombo woodlands, both Cu-Co poor and Ca very poor (<0.04 wt %), and Fe rich for Mikembo and alkaline rich (carbonatite derived soil) for Kiswishi. REE elements patterns for Fungurume 5 and Goma 2 displays relatively flat, middle REE (MREE) enriched patterns, that can be interpreted as organic controlled. Mikembo samples display heavy REE (HREE) enriched patterns with positive Ce anomaly, interpreted as controlled by Fe-rich soils. Kiswishi samples display light REE (LREE) enrichment with both Ce and Eu anomaly; apparently resulting from carbonatite oxidation.

Tenke-Fungurume hills

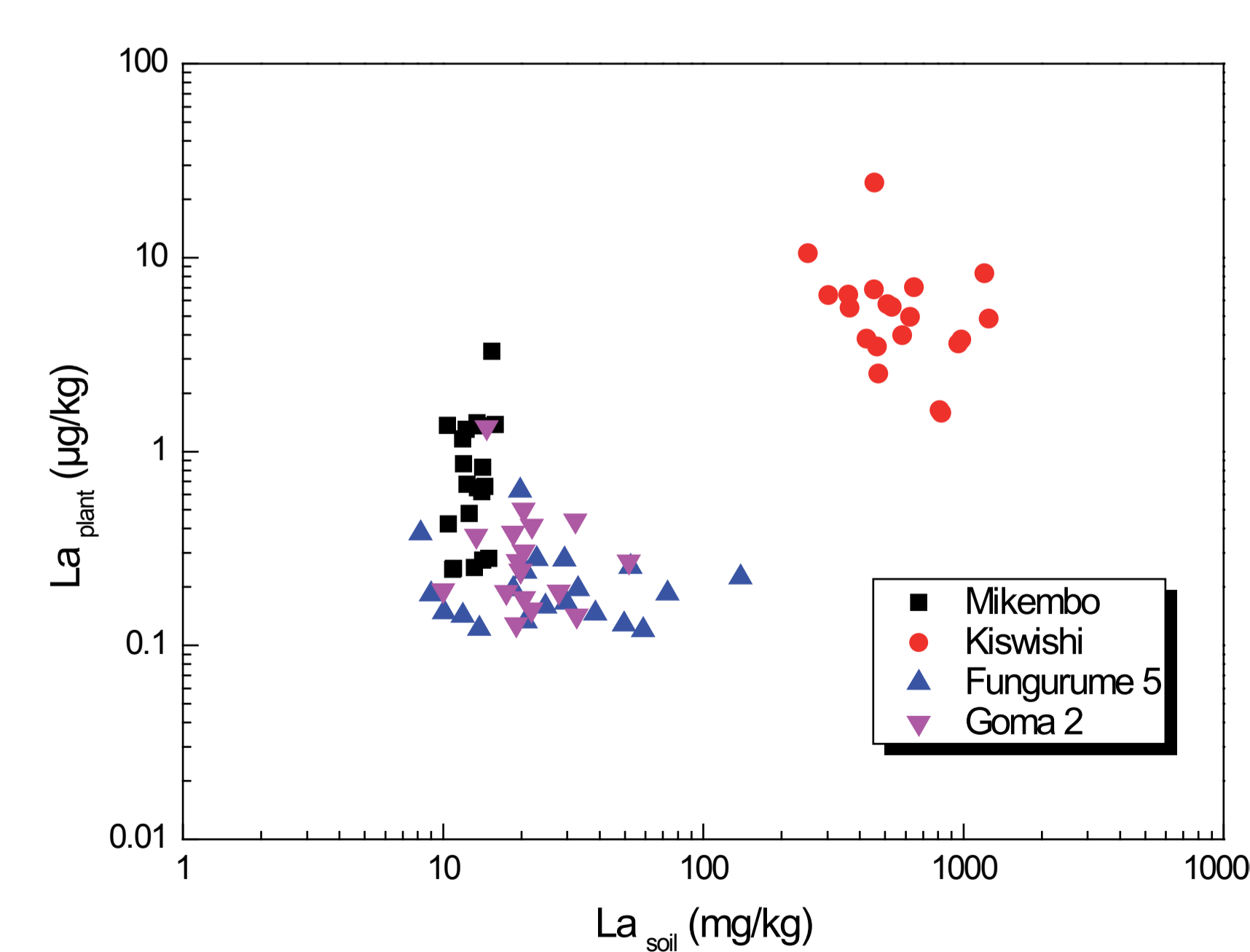


3/ Rare earth elements in plants

Whole shoots from *A. chinensis* developed on previous sites were sampled and analyzed. REE patterns display relatively LREE enrichment and huge Eu anomaly for all samples. Shoots REE patterns do not mimic soil REE patterns except for positive and negative Ce anomaly, for Mikembo and Kiswishi, respectively.



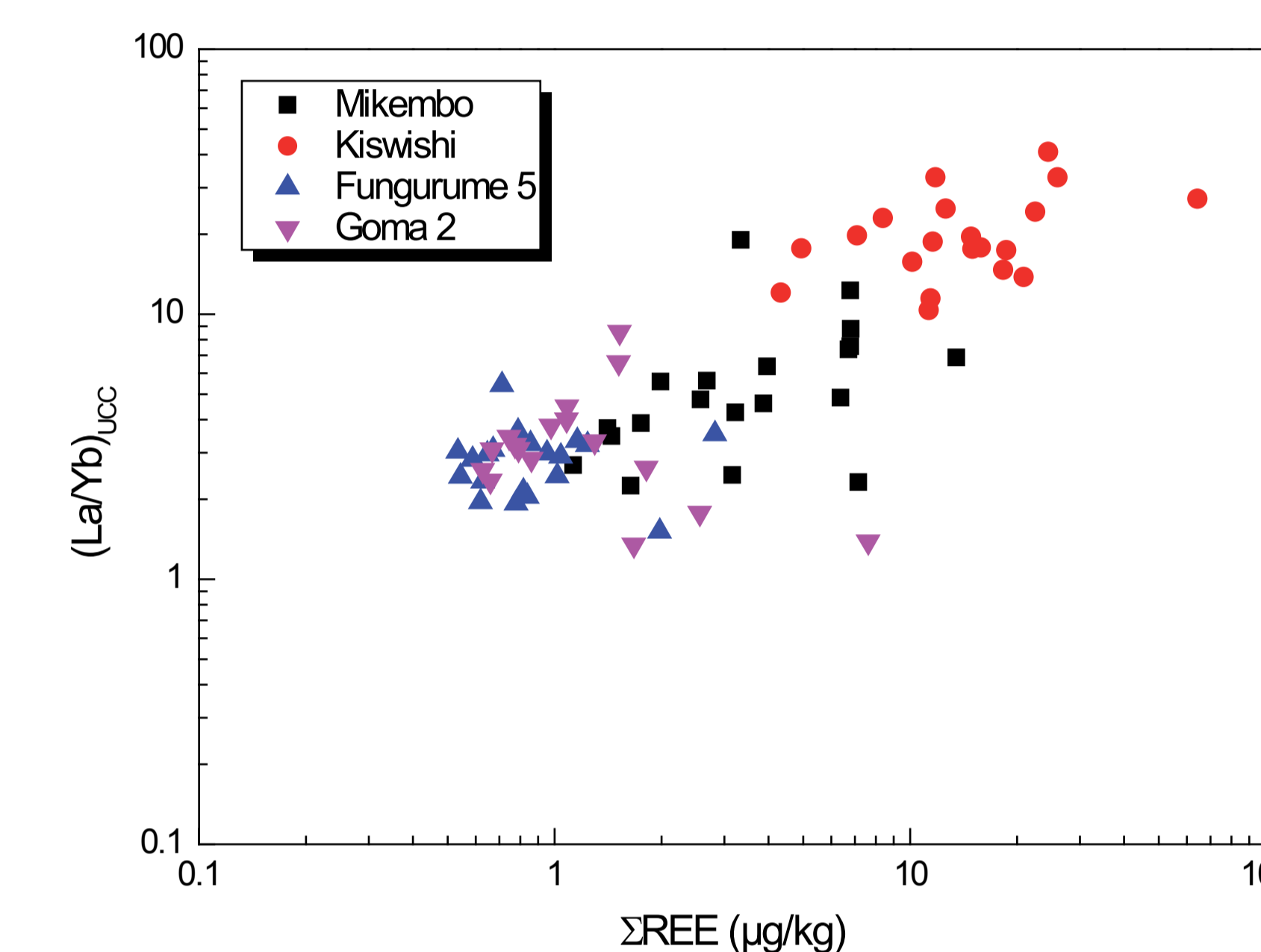
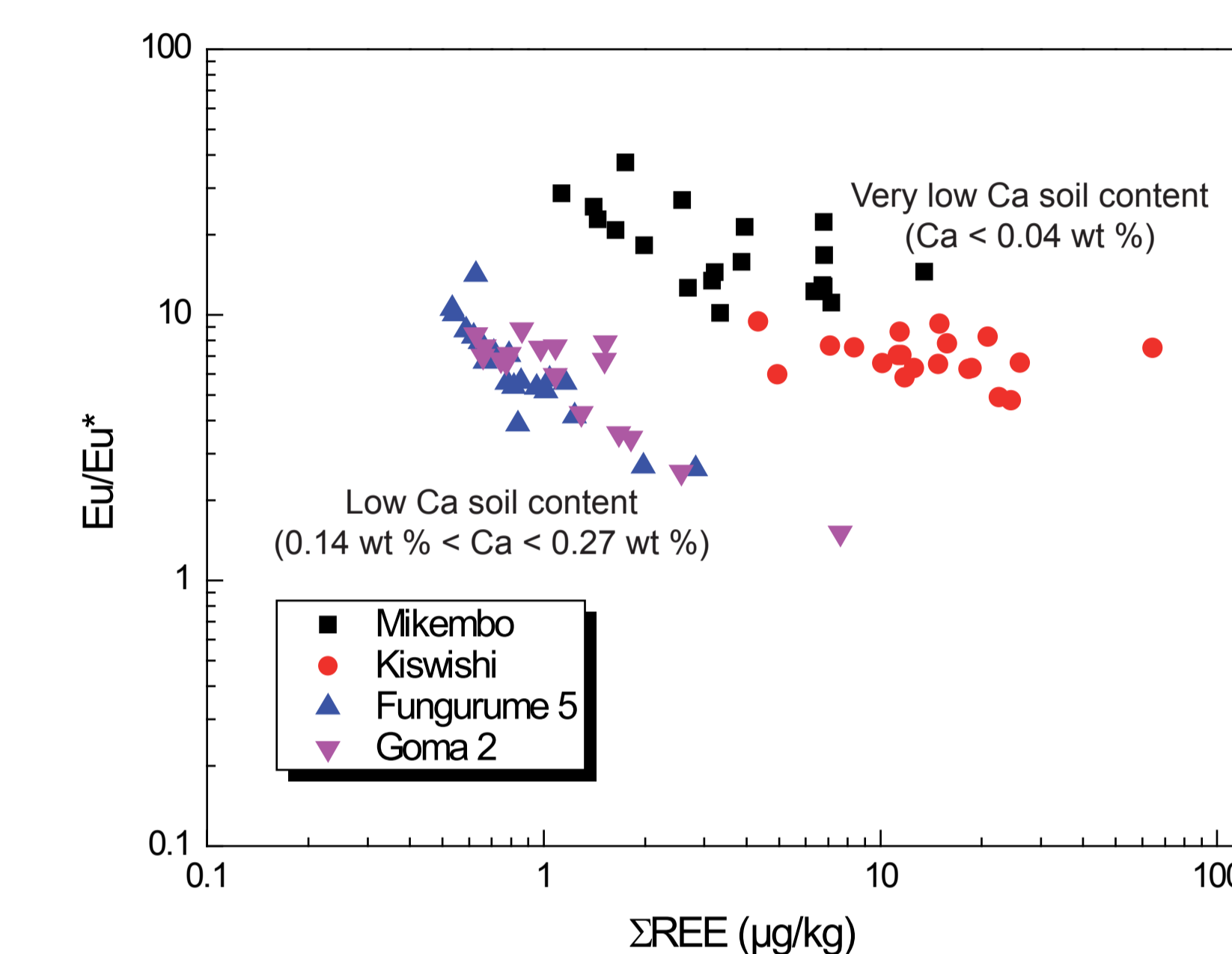
Anisopappus chinensis



The results from study this indicate that REE uptake by plants is not primarily controlled by REE speciation in soil as *A. chinensis* displays relatively the same REE patterns whereas the soil is. Moreover, Eu enrichments occur in aerial parts. Eventually, soil concentration only have an impact at high level (i.e., for Kiswishi site) as previously shown in the literature (e.g., Brioschi et al., 2013 and reference therein).

4/ Specific behavior of europium

REE concentrations decrease simultaneously with the appearance of a strong Eu anomaly as previously illustrated by Stille et al. (2006). This general trend suggests that REE fractionation is controlled by metabolic processes within the plant. Indeed, important similitude exist between Eu^{3+} and Ca^{2+} in their atomic radius and structures of the valence electron; Eu^{3+} might replace Ca^{2+} in plants and promote calcium transportation across plasma membrane. This general trend can be view separately for low Ca soil content and very low Ca soil content. Additionally, while REE concentrations increase a LREE enrichment can be observed as expressed by La/Yb ratio.



Positive Eu anomalies in shoots suggest that Eu^{3+} can form stable organic complexes in place of Ca^{2+} in several biological processes as in xylem fluids associated with the general nutrient flux. The possibility that Eu mobility in these fluids can be enhanced by its reductive speciation as Eu^{2+} cannot be ruled out.

5/ Concluding remarks

The geochemical behavior of REE illustrates that metals accumulation in aerial parts of *A. chinensis* is mainly driven by dissolved complexation. Light REE are preferentially uptake by plant shoots. The transport of REE within the plant is associated with the general nutrient flux and well illustrated by the substitution between Ca and Eu. Eventually, speciation modeling will shed more light on the bioavailable REE fraction transferred from soil to plant.

6/ References

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