

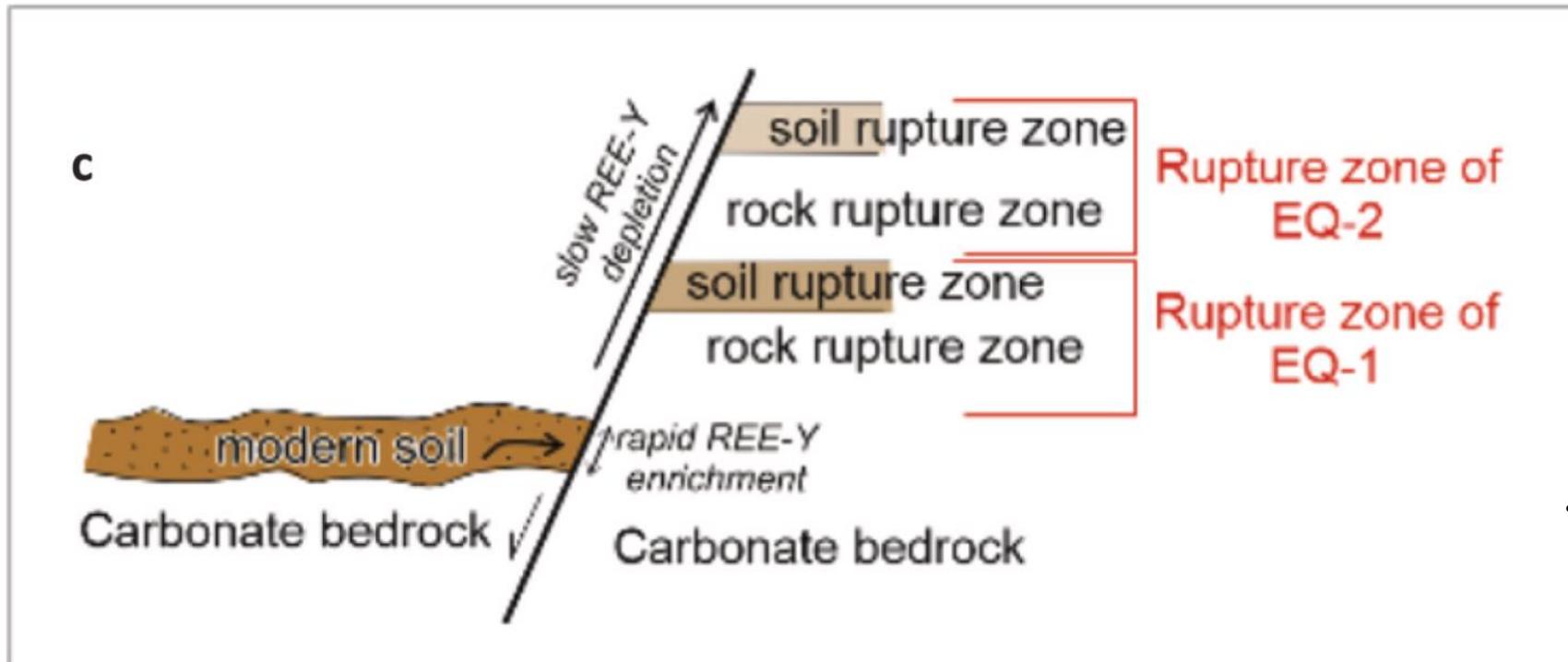
A photograph showing two researchers in safety gear (hard hats, harnesses, and ropes) climbing a steep, rocky fault line on a mountain slope. The fault line is a prominent, light-colored, linear feature cutting through the darker, more vegetated rock. The researchers are positioned on the fault line, likely collecting samples or conducting field observations. The background shows a steep, rocky slope with sparse vegetation and a clear sky.

**Rare Earth Elements on Active Faults:  
From Tracing Individual EQs to Time-  
Constrained Geochemical Signals**

# Presentation Objectives

- ▶ REE-Y cycle within fault scarp systems
- ▶ Environmental geochemical cycle of REE-Y
- ▶ Current knowledge from fault-related REE-Y studies
- ▶ Identify key challenges and open questions

# REE-Y enrichment and signal degradation across sequential earthquake rupture zones



- Mouslopoulou, V., Moraetis, D., Fassoulas, C., 2011. Earth Planet Sci. Lett. 309, 45–55. <https://doi.org/10.1016/j.epsl.2011.06.015>.

- Bello, S., Galli, P., Perna, M. G., Peronace, E., Messina, P., Rosatelli, G., et al. (2025). Geochemistry, Geophysics, Geosystems, 26, e2024GC011868. <https://doi.org/10.1029/2024GC011868>
- Carcaillet, J., Manighetti, I., Chauvel, C., Schlagenhauf, A., Nicole, J.M., 2008.. Earth Planet Sci. Lett. 271,145–158. <https://doi.org/10.1016/j.epsl.2008.03.059>.
- Mouslopoulou, V., Moraetis, D., Fassoulas, C., 2011. Earth Planet Sci. Lett. 309, 45–55. <https://doi.org/10.1016/j.epsl.2011.06.015>.
- Moraetis, D., Mouslopoulou, V., Pratikakis, A., Begg, J., & Pracejus, B. (2023). Applied Geochemistry, 155, 105703. <https://doi.org/10.1016/j.apgeochem.2023.105703>

# Current gaps-problems in REE-Y method

## Problem-1

- ▶ Current REE-Y-based models implicitly assume that REE-Y enrichment and subsequent degradation along fault scarps follow a systematic and transferable pattern linked to cumulative rupture exposure; however, we lack a consistency in the REE enrichment and depletion which have still not explain
  - ❖ This gap highlights a lack of understanding of how local physicochemical conditions (e.g., soil chemistry, redox dynamics, hydrology, lithology, and scarp microstructure) can decouple REE-Y behavior from rupture chronology

## Problem-2

- ▶ While REE-Y enrichment patterns can delineate rupture zones and relative event sequences, **there is currently no direct or indirect dating framework that links REE accumulation or depletion to absolute time**, preventing REE-Y signals from being used as standalone chronological markers.

# What should be happening to have REE signal on the fault scarp

- ▶ REE-Y Sources
- ▶ REE-Y Mobility
- ▶ REE-Y Precipitation / Adsorption



# Major rock types hosting REE (relative content)

## High REE content

- Carbonatites (up to wt% REE in extreme cases)
- Peralkaline granites & syenites
- Phosphorites
- Black shales

## Moderate REE content

- Granites (especially S-type and peraluminous)
- Basalts & gabbros
- Metamorphic equivalents (gneisses, schists)

## Low bulk REE content

- Limestones & dolostones
- Quartz-rich sandstones



Soil: 165 mg kg<sup>-1</sup> (16–700 mg kg<sup>-1</sup>)

## Igneous rocks

Average  $\Sigma$ REE: 100-300 ppm

- Basalts / gabbros: ~80-150 ppm
- Granites (average): ~150-250 ppm
- Peralkaline granites & carbonatites: >500 ppm to wt% levels (extremes)

## Sedimentary rocks

Average  $\Sigma$ REE: 150-250 ppm

- Shales / mudstones: ~200-300 ppm
- Sandstones: ~30-100 ppm
- Limestones & dolostones: 5-30 ppm
- Phosphorites: 500-2000+ ppm

## Metamorphic rocks

Average  $\Sigma$ REE: 100-250 ppm

- Gneisses (felsic protoliths): 150-300 ppm
- Schists: 120-250 ppm
- Marbles (carbonate protoliths): 5-20 ppm

# pH, CO<sub>2</sub>, Redox and humic substances



## ▶ pH

- Acidic pH (5-6) will maintain REE<sup>3+</sup> in solution but strong affinity to oxides
- Alkaline pH REE will in solution in carbonato or dicarbonato complexes or in humic and fluvic complexes

## ▶ Redox

- Oxidative conditions facilitate REE precipitation because Fe-Mn-oxides and reductive conditions are dissolving Fe<sup>2+</sup> and Mn<sup>2+</sup> which are releasing REE-Y
- Oxidation breaks down the organic matter which produces fluvic and humic substances can maintain REE in solution

## ▶ CO<sub>2</sub>

- The PCO<sub>2</sub> decreases the REE<sup>3+</sup> adsorption and maintain REE<sup>3+</sup> in solution

## ▶ Ionic strength

- Increase of ionic strength decreases REE-Y adsorption

## ▶ Humic substances

- The low pH increases humic substances adsorption onto mineral surfaces and compete to REE<sup>3+</sup> but also are deprotonated in high pH

- Tang, J., Johannesson, K.H., 2005. *Geochem. Cosmochim. Acta* 69, 5247–5261. <https://doi.org/10.1016/j.gca.2005.06.021>.
- Tang, J., Johannesson, K.H., 2006. *Chem. Geol.* 225, 156–171.
- Tang, J., Johannesson, K.H., 2010. *Chem. Geol.* 279, 120–133. <https://doi.org/10.1016/j.chemgeo.2010.10.011>.

# Speciation

## ▶ REE provenance in soil:

- ❖ Primary: Heavy minerals (anatase, ilmenite, sphene, rutile and zircon), phosphates (allanite, monazite, apatite), Fluoro-carbonates (Bastnäsite).
- ❖ Secondary minerals: clays, Fe- Mn- oxides, organic matter

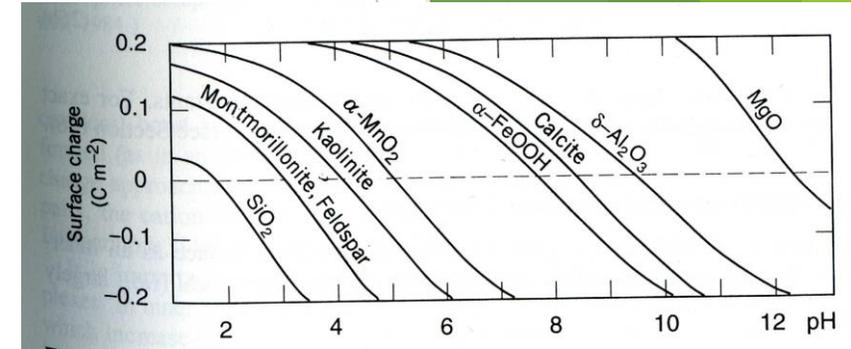
## ▶ REE-Y mobilization

- ❖ Carbonato-REE-Y and Dicarbonato-REE-Y in  $\text{pH} > 6$
- ❖ Organic matter (humic and fulvic substances) in  $\text{pH} > 6$
- ❖  $\text{REE}^{3+}$  in low  $\text{pH} < 6$

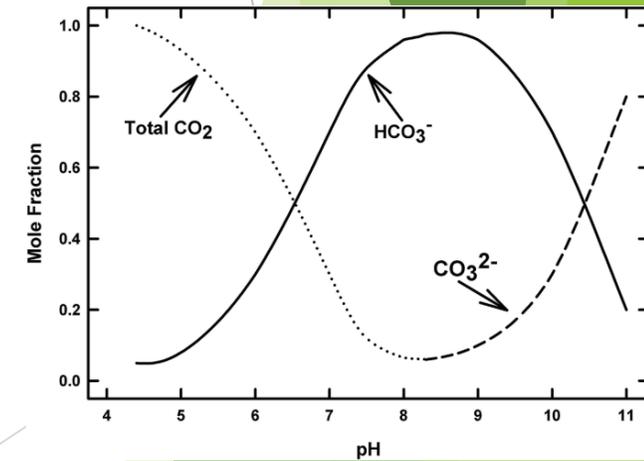
## ▶ REE-Y precipitation

Fault scarp

- ▶  $\text{REE}^{3+}$  adsorption in minerals surfaces (dominant at high pH, low alkalinity)(dominant at pH 5-7)
- ▶ Calcite precipitation scavenges REEs (surface, co-precipitation and trapping)
- ▶  $\text{REE}_2(\text{CO}_3)_3$  precipitation in extreme high pH and high alkalinity



From Stumm and Morgan, Aquatic Chemistry



- Tang, J., Johannesson, K.H., 2005. *Geochem. Cosmochim. Acta* 69, 5247–5261. <https://doi.org/10.1016/j.gca.2005.06.021>.
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- Tang, J., Johannesson, K.H., 2010. *Chem. Geol.* 279, 120–133. <https://doi.org/10.1016/j.chemgeo.2010.10.011>.

# Scenario-pH with clays, oxides and organic compounds

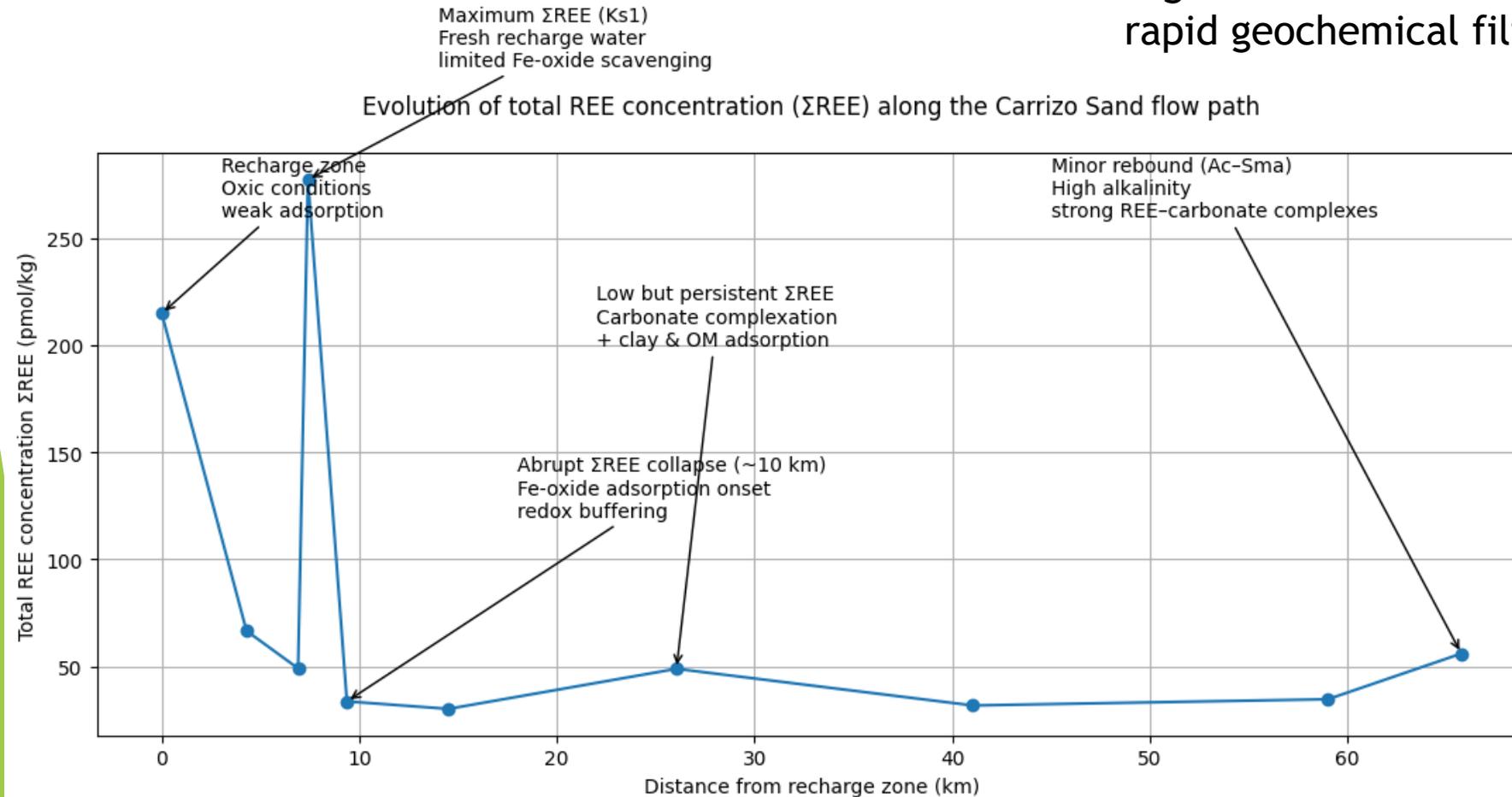
pH range	Dominant REE complexes	Clay surfaces	Fe-Mn oxides	Humic & fulvic acids	Net REE behavior
≤ 5.5	REE <sup>3+</sup> , REE-SO <sub>4</sub>	Positively charged edges → <b>strong REE adsorption</b>	Stable Fe-Mn oxides → <b>very strong REE scavenging</b>	Protonated, immobile, surface-bound	<b>REE immobilization, strong surface control</b>
5.5-7	REE <sup>3+</sup> , REE-HCO <sub>3</sub>	Increasing negative charge → <b>competitive adsorption</b>	Active Fe-oxide sorption fronts	Partial deprotonation → moderate REE binding	<b>Maximum REE partitioning sensitivity</b>
7-8	REE(CO <sub>3</sub> ) <sup>+</sup>	Negative surfaces → <b>reduced REE adsorption</b>	Fe oxides stable but less effective	HS increasingly soluble → competition with surfaces	<b>REE mobility increases</b>
≥ 8-9	REE(CO <sub>3</sub> ) <sub>2</sub> <sup>-</sup>	Electrostatic repulsion → minimal adsorption	Fe-Mn oxides may dissolve (if reducing)	Strongly deprotonated → <b>REE-DOM complexes</b>	<b>High mobility, signal smoothing</b>

# Scenario-REDOX with clays, oxides and organic compounds

Redox condition (Eh)	Dominant REE complexes (aqueous)	Clay surfaces	Fe-Mn oxides	Humic & fulvic substances	Net REE behavior
<b>Strongly oxidizing (high Eh)</b>	REE <sup>3+</sup> , REE-SO <sub>4</sub>	Edge sites active → moderate REE adsorption	<b>Fe(III)-Mn(IV) oxides stable</b> → very strong REE scavenging	Mostly oxidized, surface-bound, limited mobility	<b>REE immobilization, oxide-dominated control</b>
<b>Moderately oxidizing</b>	REE <sup>3+</sup> , weak carbonate complexes	Competitive adsorption on clay edges	Active Fe-oxide sorption fronts	Partial complexation, limited DOC	<b>Strong REE retention, high spatial sensitivity</b>
<b>Transition zone (redox boundary)</b>	Mixed REE <sup>3+</sup> / REE-carbonate	Clay control variable	<b>Fe-Mn oxides precipitate/dissolve episodically</b>	DOC pulses released	<b>Maximum REE redistribution and signal overprinting</b>
<b>Moderately reducing</b>	REE-carbonate, REE-DOM	Clay adsorption weakened	<b>Reductive dissolution of Mn oxides (first)</b>	Increasing REE-DOM complexation	<b>REE mobilization increases</b>
<b>Strongly reducing (low Eh)</b>	REE-carbonate, REE-DOM	Minimal adsorption	<b>Fe(III) oxides dissolve</b> → REE release	Strongly complexed, dissolved humic/fulvic acids	<b>High REE mobility, loss of chronological signal</b>

# REE are not conservative within an aquifer

High REEs mark recharge entry points; low REEs mark rapid geochemical filtering.

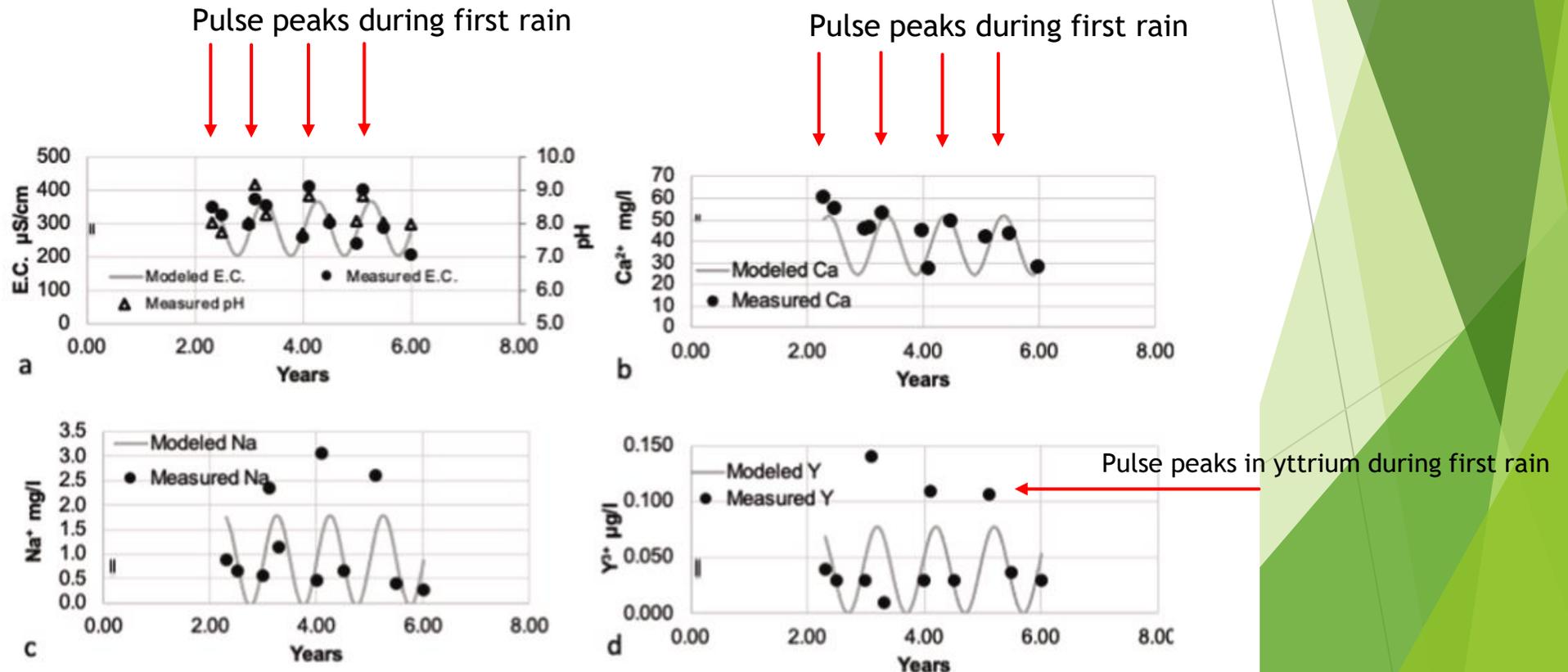


“a complex combination of adsorption reactions, changes in pH and bulk solution composition, and redox processes.”

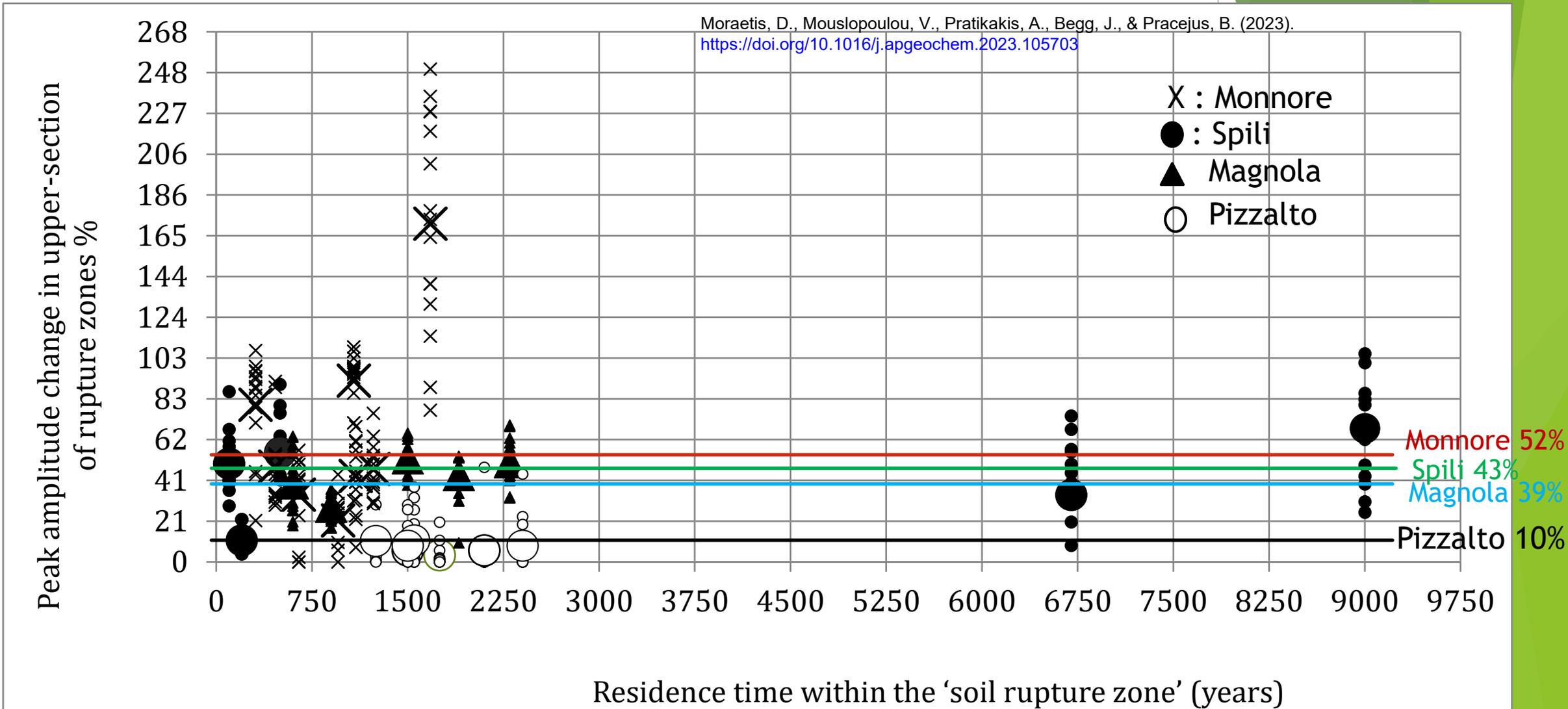
Tang, J., Johannesson, K.H., 2006. Chem. Geol. 225, 156–171

# REE are not conservative within the soil solution due to dry-wet cycles in Greece

- ▶ During summer, soils there become extremely dry, aerated, more oxidized and, in general, resemble the marginal soils in desert climates. These dry conditions decompose organic matter and increases acidity in soil. When rain comes acidity immediately interacts with carbonates with increase dissolution which is washed out like a "pulse" during the first rains after dry periods.



# REE-Y Enrichment in studied faults



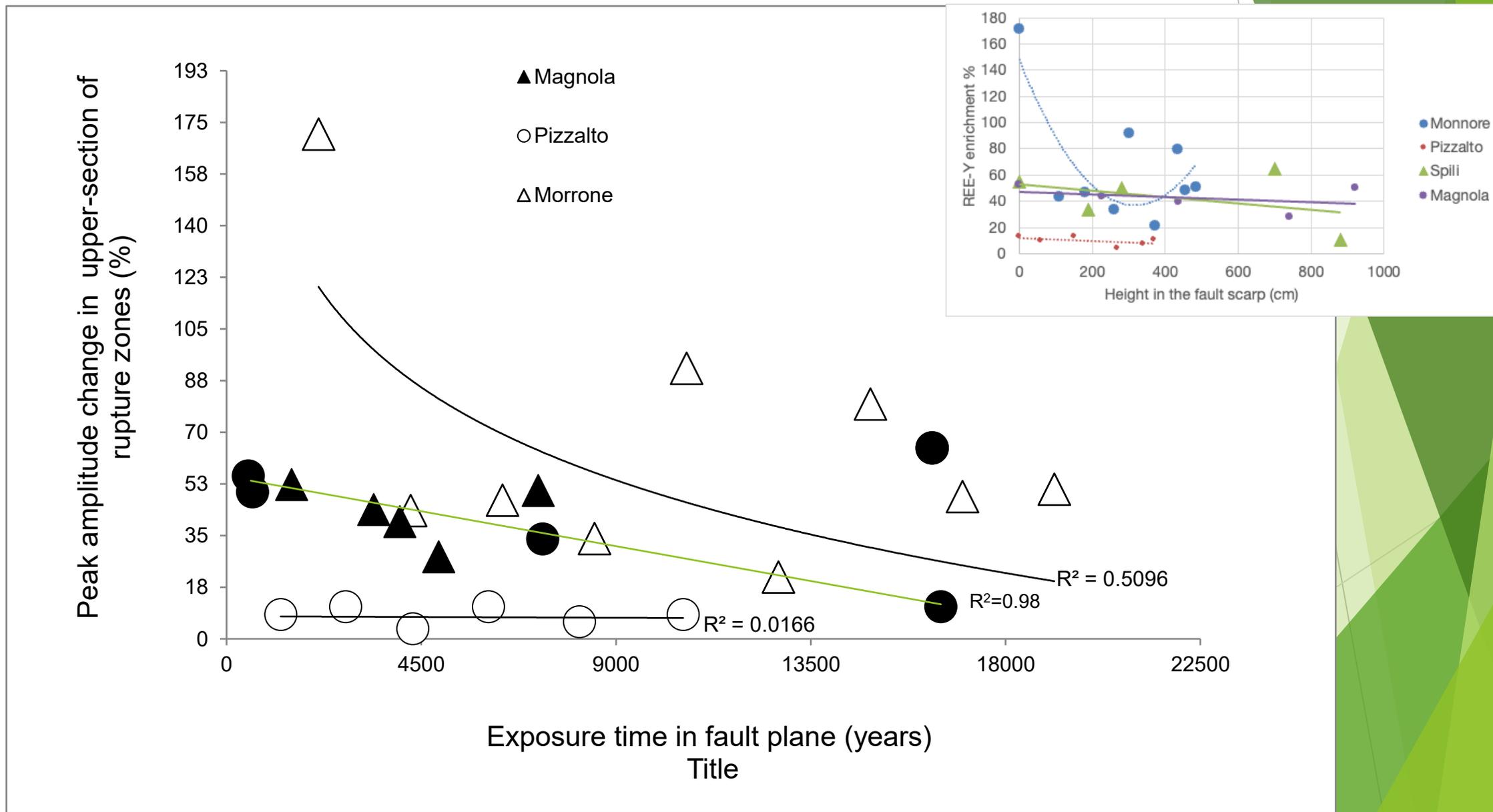
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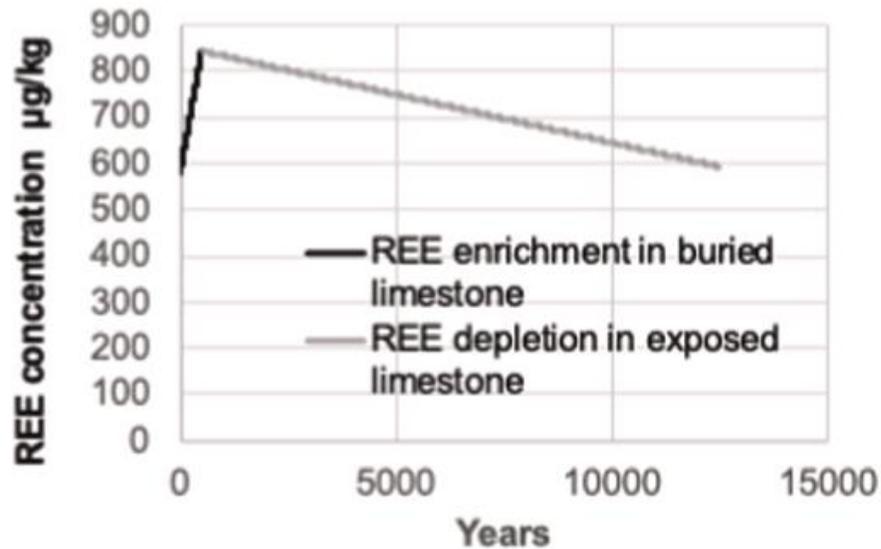
Mouslopoulou, V., Moraetis, D., Fassoulas, C., 2011. *Earth Planet Sci. Lett.* 309, 45–55. <https://doi.org/10.1016/j.epsl.2011.06.015>.

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# REE-Y depletion in studied faults



Research-Challenge: REE-Y signals within mechanistic geochemical rate laws, spatial and vertical variations in enrichment zones can be interpreted as the outcome of evolving surface reactions and exposure history, moving beyond empirical rupture identification



- Magnola and Spili fault showed an enrichment rate of (0.53 µg/kg/year) derived from the ages given by Cl36
- Depletion rate was much lower – 0.021 µg/kg/year

## Soil

- What are the prevailing REE-complexes in soil solution in different soil types
- How the climate conditions might have influence the enrichment and degradation process

## Fault scarp

- Is any of the limestone scarp sediment structure texture influence the REE hosting sites
- Is any scarp surface karst features or tectonic features facilitate or weakening the REE adsorption
- What are exactly the REE hosted-minerals and their complexation: E.J. Elzinga, R.J. Reeder, S.H. Wang, R.E. Peale, R.A. Mason, K.M. Beck, W.P. Hess, 2000, *Geochimica et Cosmochimica Acta*, Volume 66, 1-16,

# Soil



Figure-Soil sensors

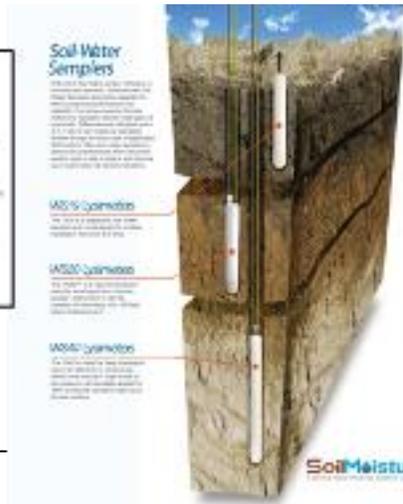
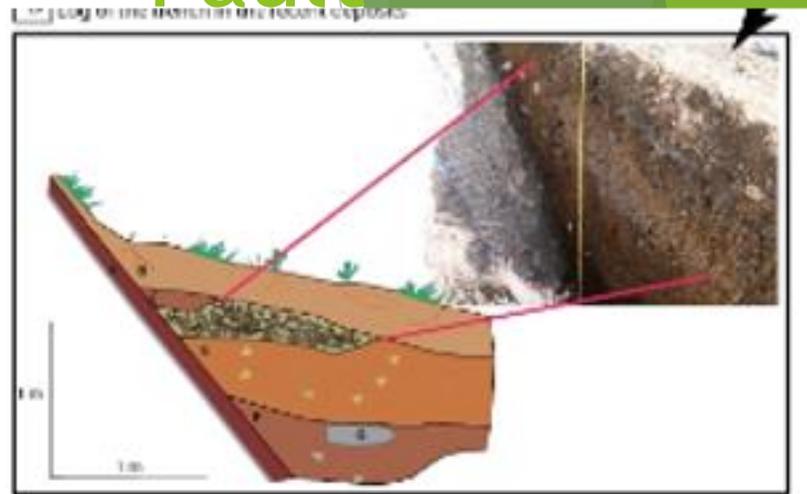


Figure 3-Lysimeters

# Fault

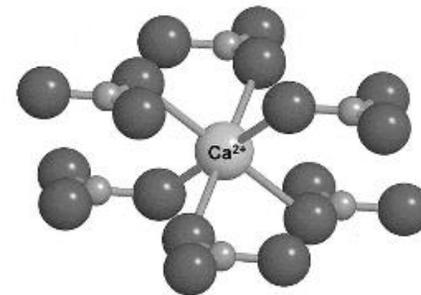


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E.J. Elzinga, R.J. Reeder, S.H. Withers, R.E. Peale, R.A. Mason, K.M. Beck, W.P. Hess, Geochimica et Cosmochimica Acta, Volume 66, Issue 16, 2002