

# **Jurassic Limestone-Marl Sequences in Northern Spain: Detecting Diagenetic Signals Using Rare Earth and Minor Trace Elements\***

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## **Abstract**

Mesozoic rhythmically bedded limestone and marl sequences have been traditionally interpreted to be the result of eustatic sea-level changes related to Milankovitch cycles. An alternative interpretation supports the idea that these calcareous alternations are a product of diagenetic bedding. Stratigraphic analysis is typically used to determine the extent of diagenesis and to detect any primary depositional signal in limestone-marl rhythmites. Rare earth and minor-trace element geochemistry is an overlooked method to disentangle the presence of a primary signal from a diagenetic one. Both rare earth and minor trace elements can substitute for more common elements, such as calcium during active deposition; however, unlike calcium, the heavier trace and rare earth elements will remain immobile during diagenesis. Data will be presented from the application of this geochemical approach, in conjunction with stratigraphic analysis, to Jurassic limestone-marl sequences along the coast of Asturias in northern Spain. These calcareous rhythmites are part of the Rodiles Formation (Pliensbachian, Lower Jurassic), a ramp carbonate deposited in a shallow epicontinental sea; the rhythmites previously were interpreted to be the result of diagenetic bedding. As a result, these deposits represent an ideal example to test the validity of using rare earth and minor-trace elements as a method for determining diagenesis in carbonate sequences.

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# Jurassic Limestone-Marl Sequences in Northern Spain: Detecting Diagenetic Signals Using Rare Earth and Minor Trace Elements

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# Geologic Background

- Limestone-marl sequences are rhythmically bedded calcareous units.
- Carbonate platforms/ramps shallow, epicontinental seas.
- Prevalent throughout Jurassic-Cretaceous.
- Potential source rocks for hydrocarbon exploration



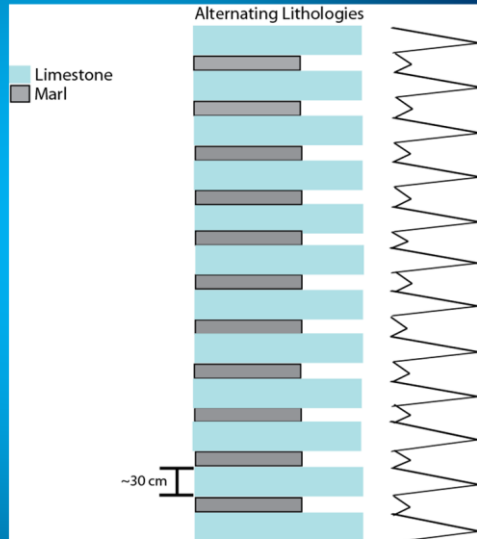
Belemnite Marl, Dorset coast  
Weedon & Jenkyns, 1999

Presenter's notes: Marls are approximately 35-65% clay / 65 -35% carbonate.

Pictured: Classic outcrop of rhythmites along the Dorset coast, southern England. Geologist for scale. Weedon and Jenkyns (1999) used strontium isotope, total organic carbon (TOC) and weight percent carbonate (wt%) cyclostratigraphy to determine if the Belemnite Marl was influenced by eustatic sea-level change due to Milankovitch cycle. (Milankovitch Cycle: Precession (21-24 ka); obliquity (40 ka); eccentricity (120 ka or 405 ka).) This is part of a large correlatable unit and a source rock.

# Primary Signal

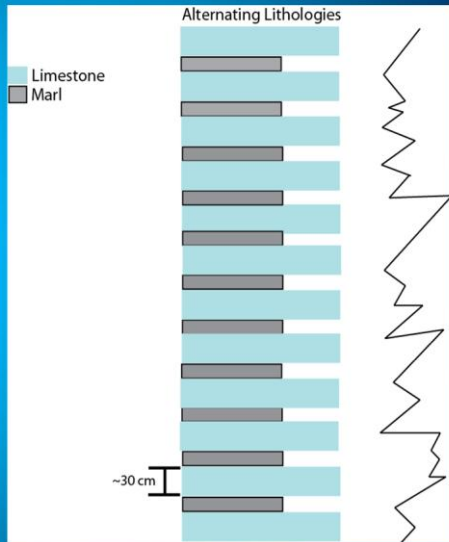
- Primary signal refers to an external factor during active deposition and then recorded in the stratigraphy.
- Eustatic (global) sea-level change due to Milankovitch cyclicity.
- Sea-level change caused facies shift with limestones representing shallower depths and marls deeper depths in a carbonate ramp



Presenter's notes: Stratigraphic column tuned using Ar40/Ar39 decay data (Kupier et al, 2008). Tuned to Milankovitch eccentricity cycles. Produced sine curves are called primary signals. Approximate thicknesses based on Arzani (2006). Image after Kuiper et al. (2008) and Arzani (2005).

# Diagenesis

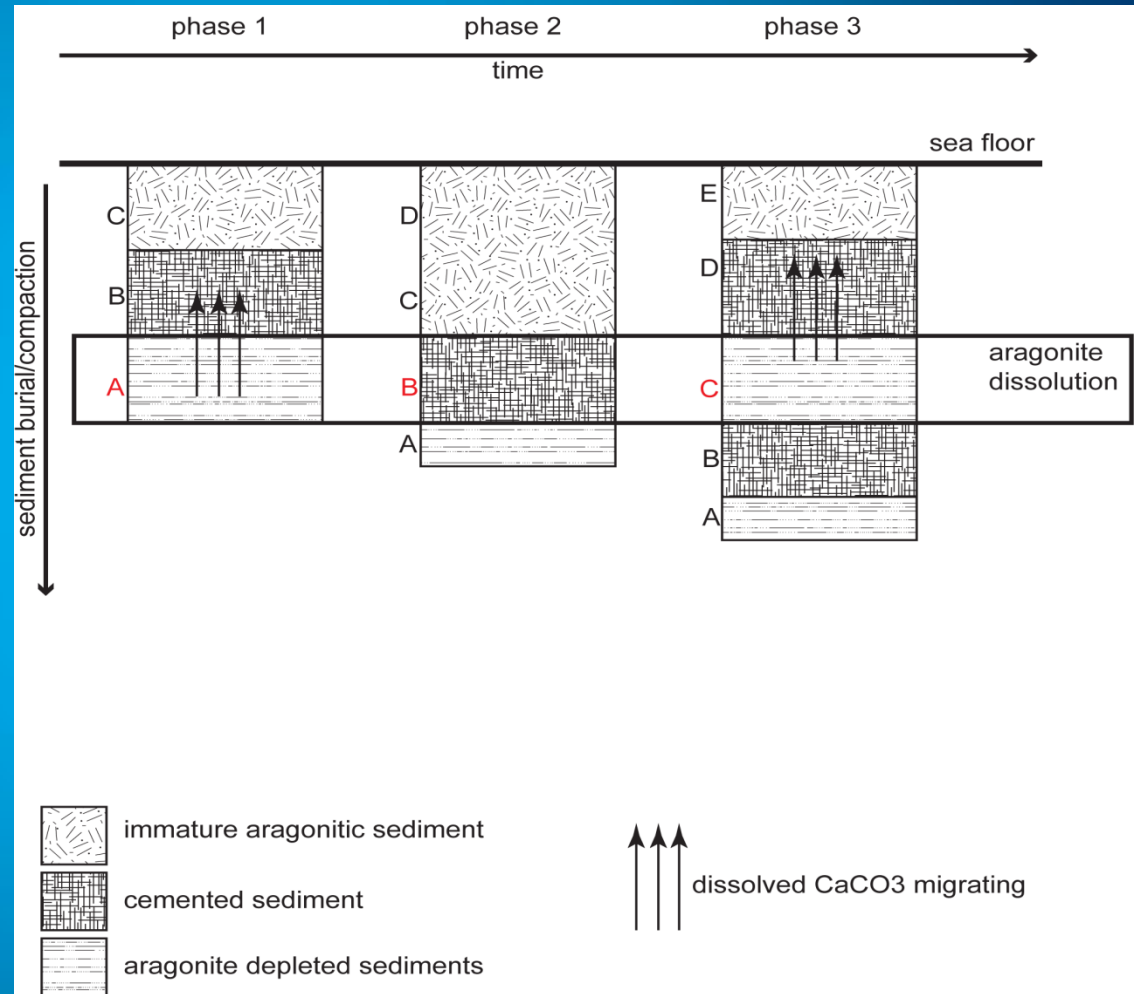
- Diagenesis is processes that alter sedimentary rocks after deposition and burial.
- Diagenetic bedding are zones of repeated carbonate dissolution and cementation.
- Diagenesis will destroy or distort primary signals.



Presenter's notes: Diagenesis generally manifests itself as geochemical changes in mineralogy and texture.

# Diagenetic Bedding

- Aragonite dissolution from macro/micro-fossils is hypothesized to be the source of the needed carbonate to produce diagenetic bedding.
- Common methods for determining diagenetic bedding includes total weight percent carbonate and stable isotopes.

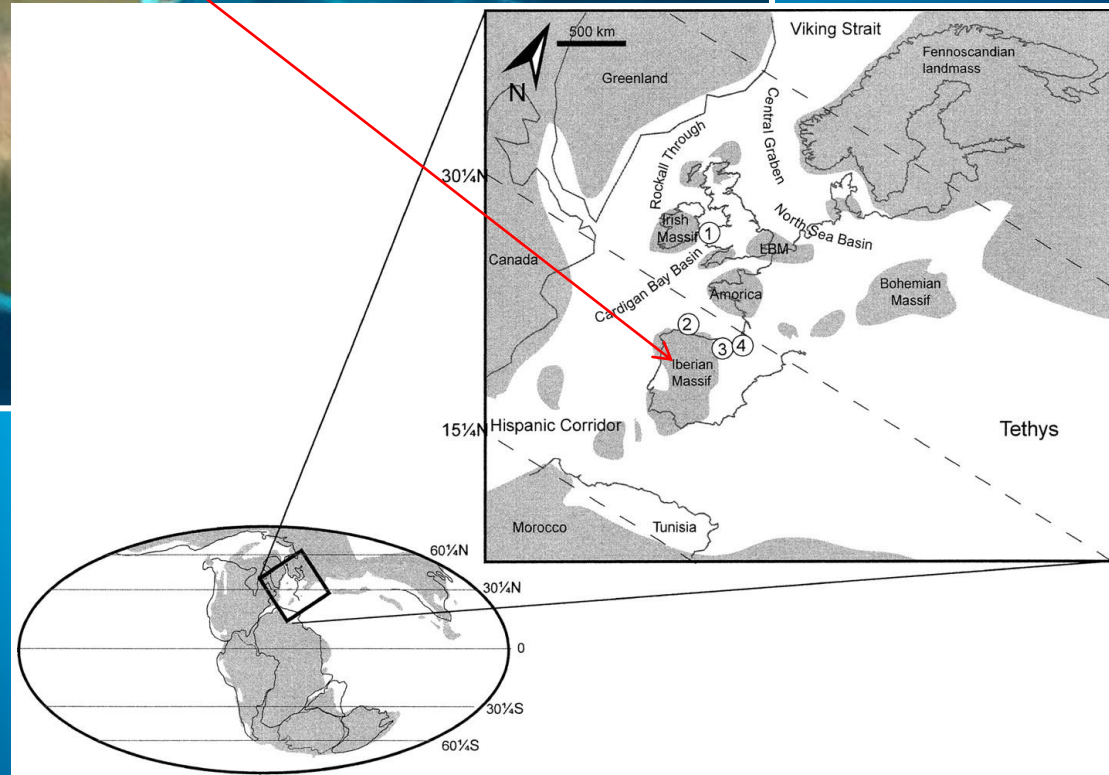
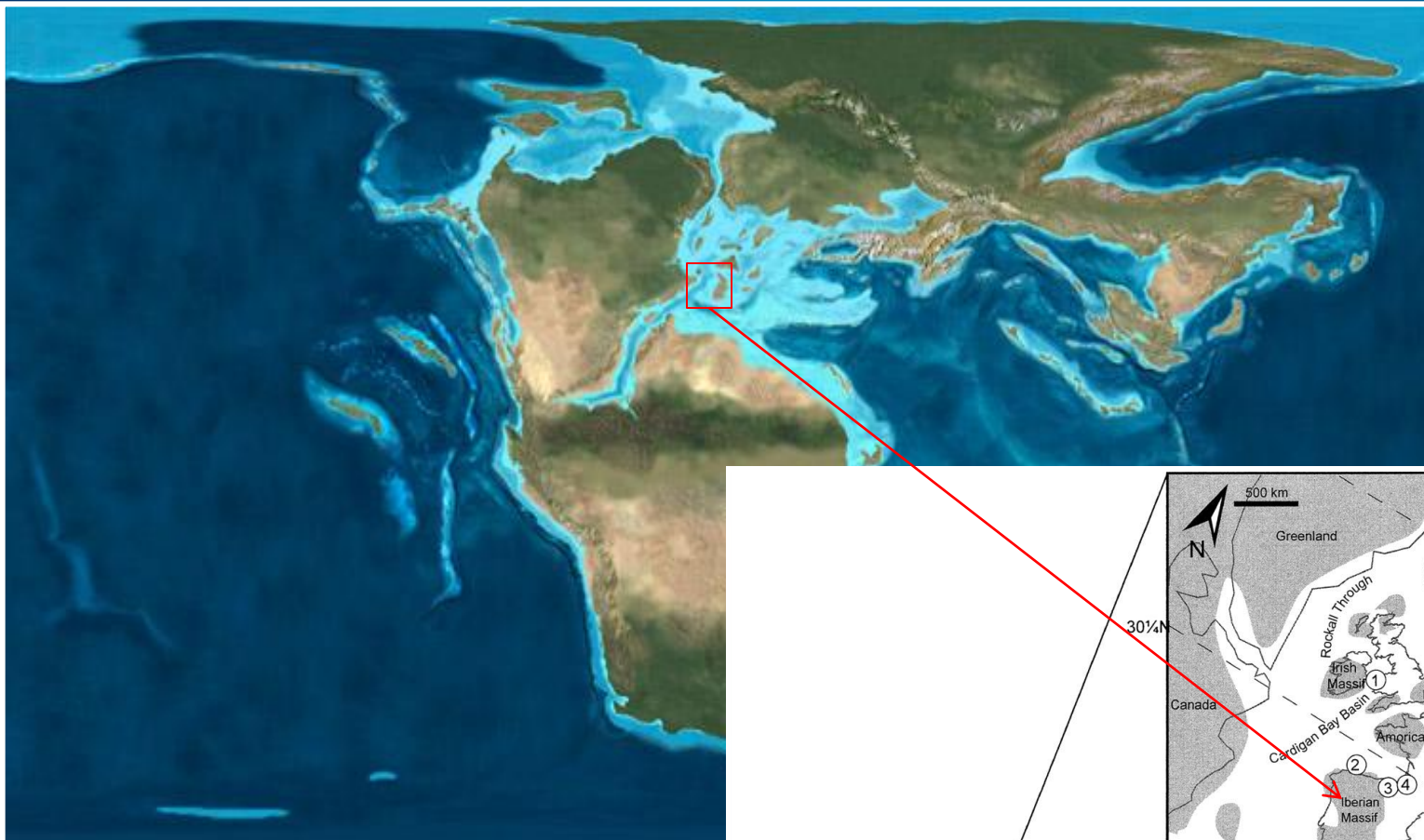


# Objectives

- Test the use of REE to detect diagenesis in rhythmic carbonate sequences
- Apply this geochemical approach to Lower Jurassic rhythmic sequences in northern Spain.
- Constrain through petrography and major/minor element geochemistry.



# Early Jurassic (201.6 – 176 m.y.a)

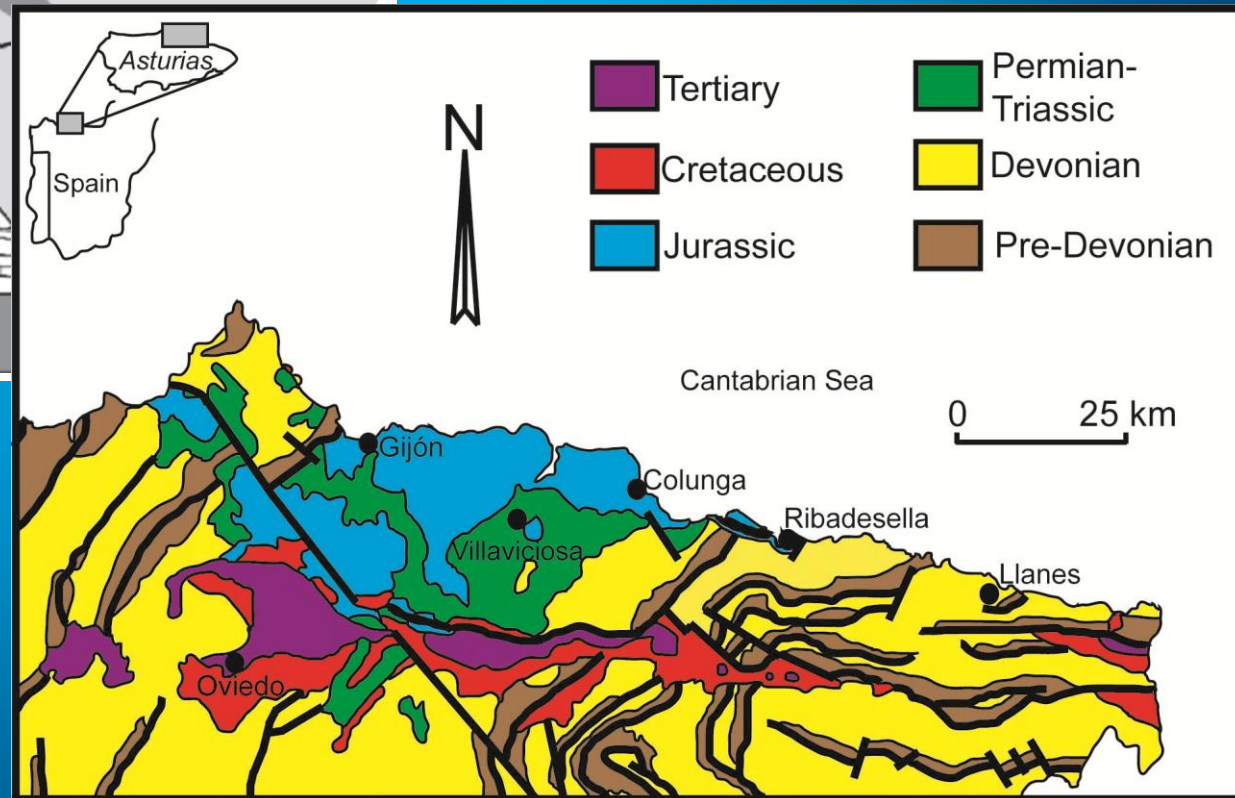
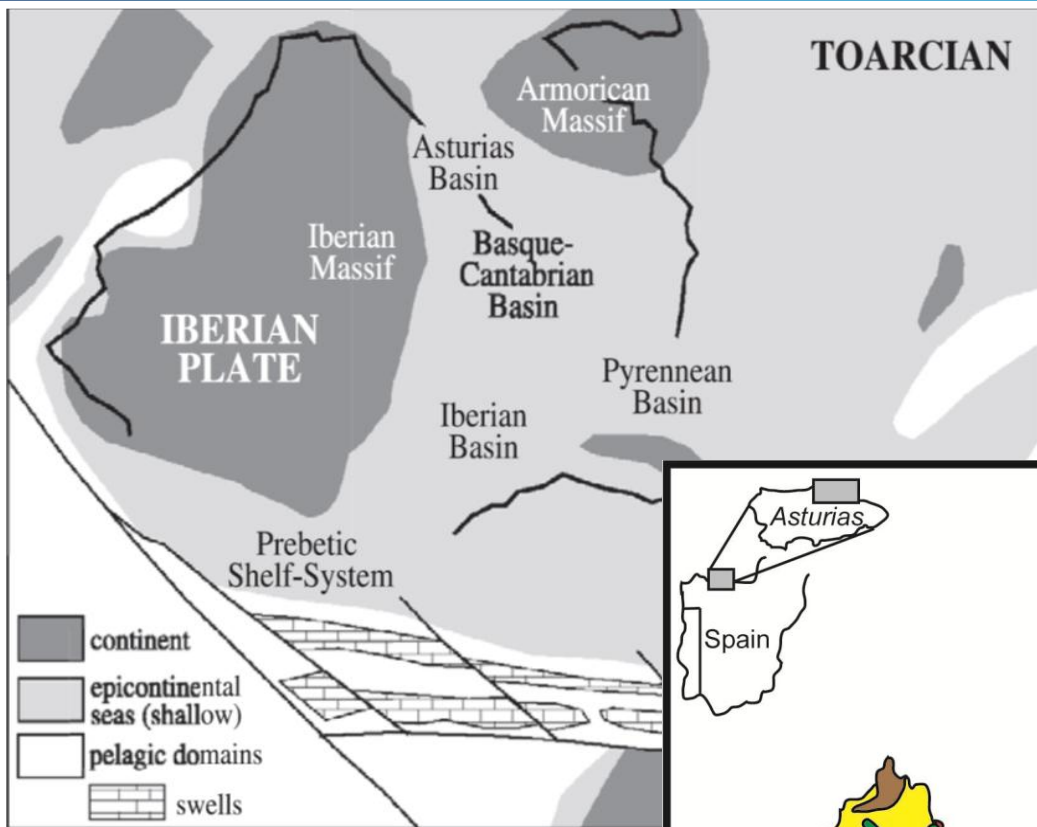


Blakey, 2011

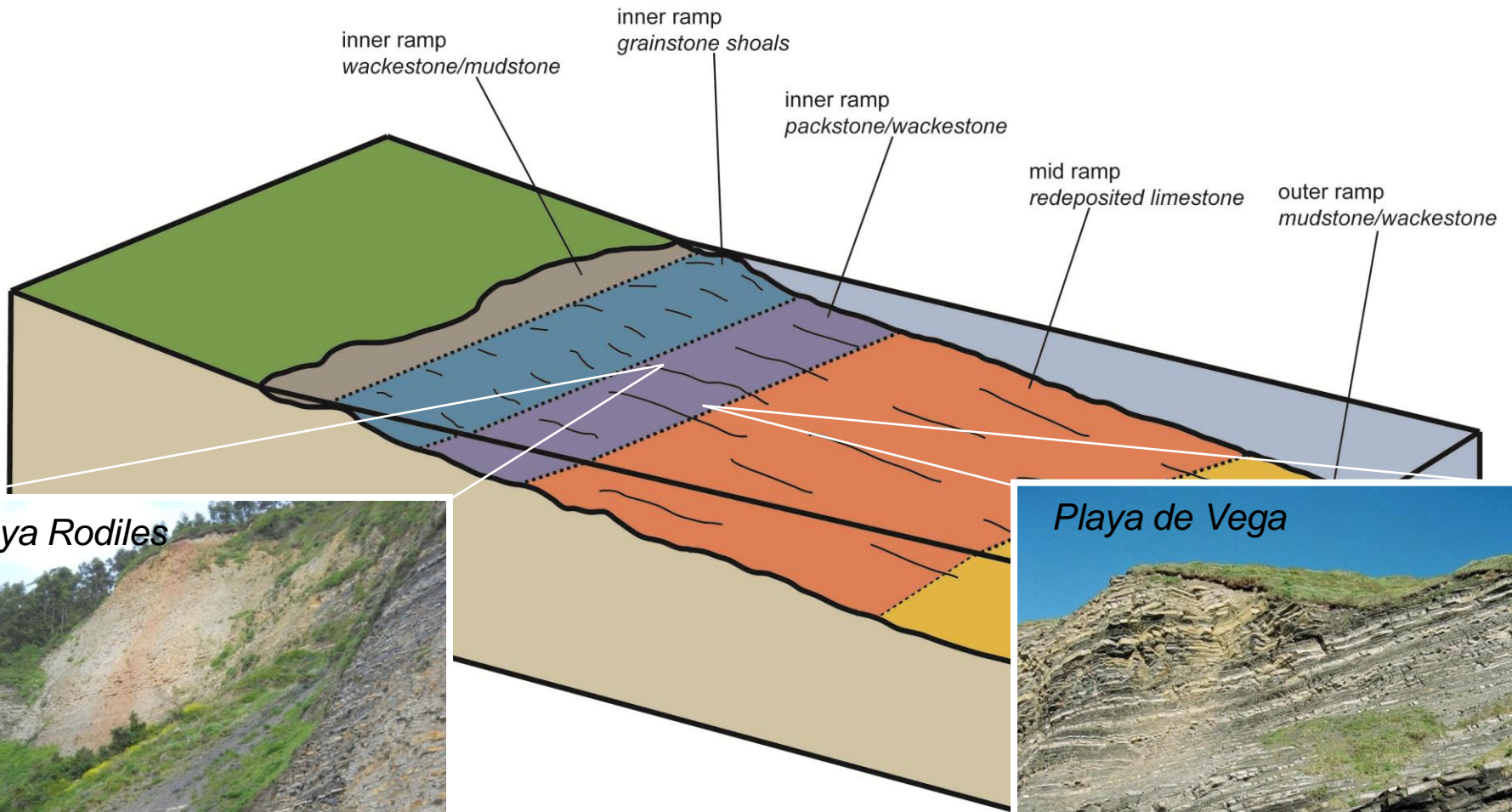
Schootbrugge, 2005

# Asturias, Spain

Aurell et al., 2003



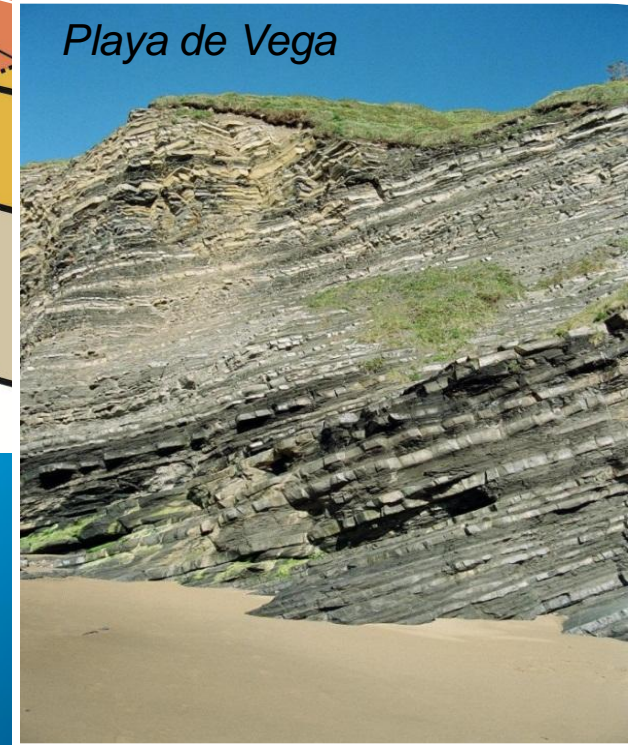
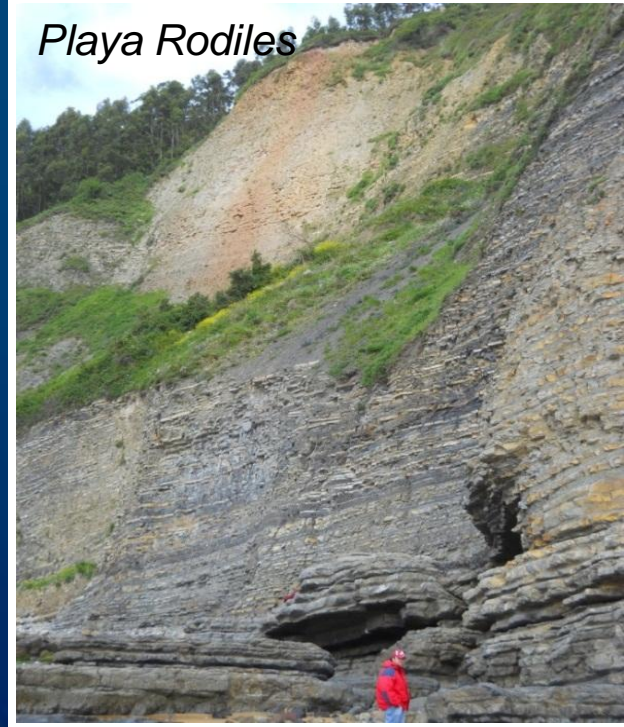
Modified from Avanzini et al., 2005



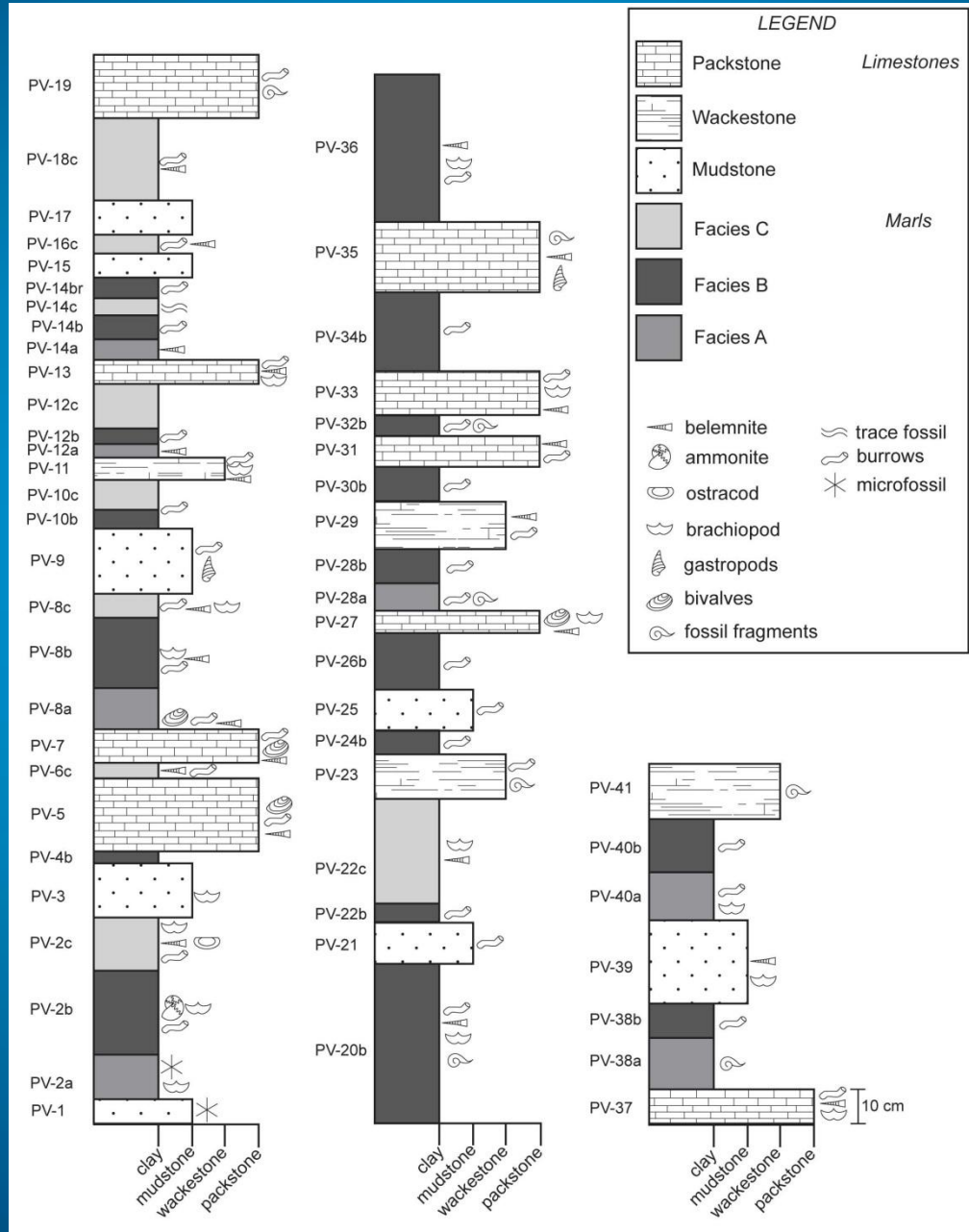
*Playa Rodiles*

*Playa de Vega*

# Ramp Setting



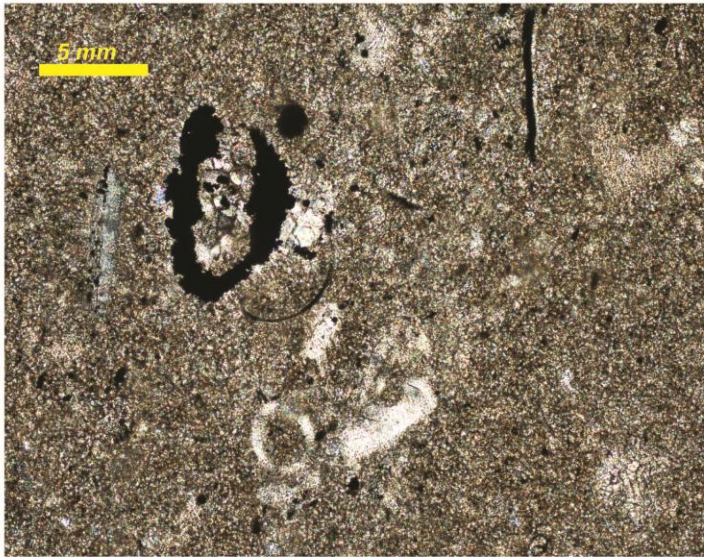
# Playa de Vega Stratigraphy



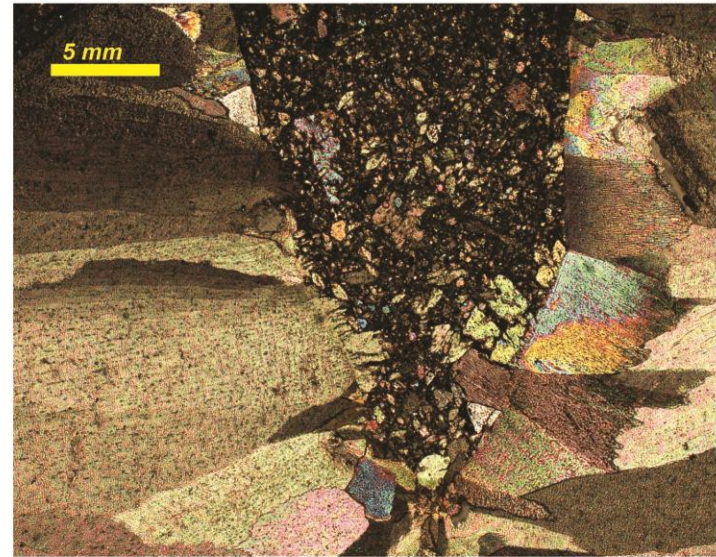
# Playa de Vega Outcrop



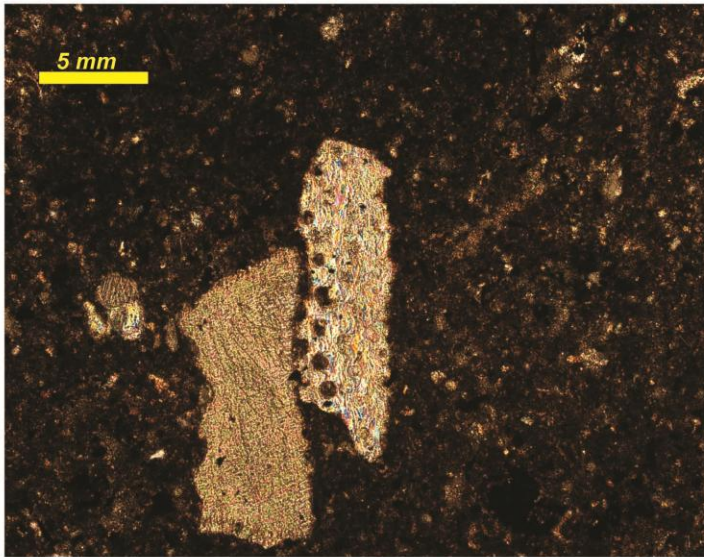
# Petrography



**PV-1**



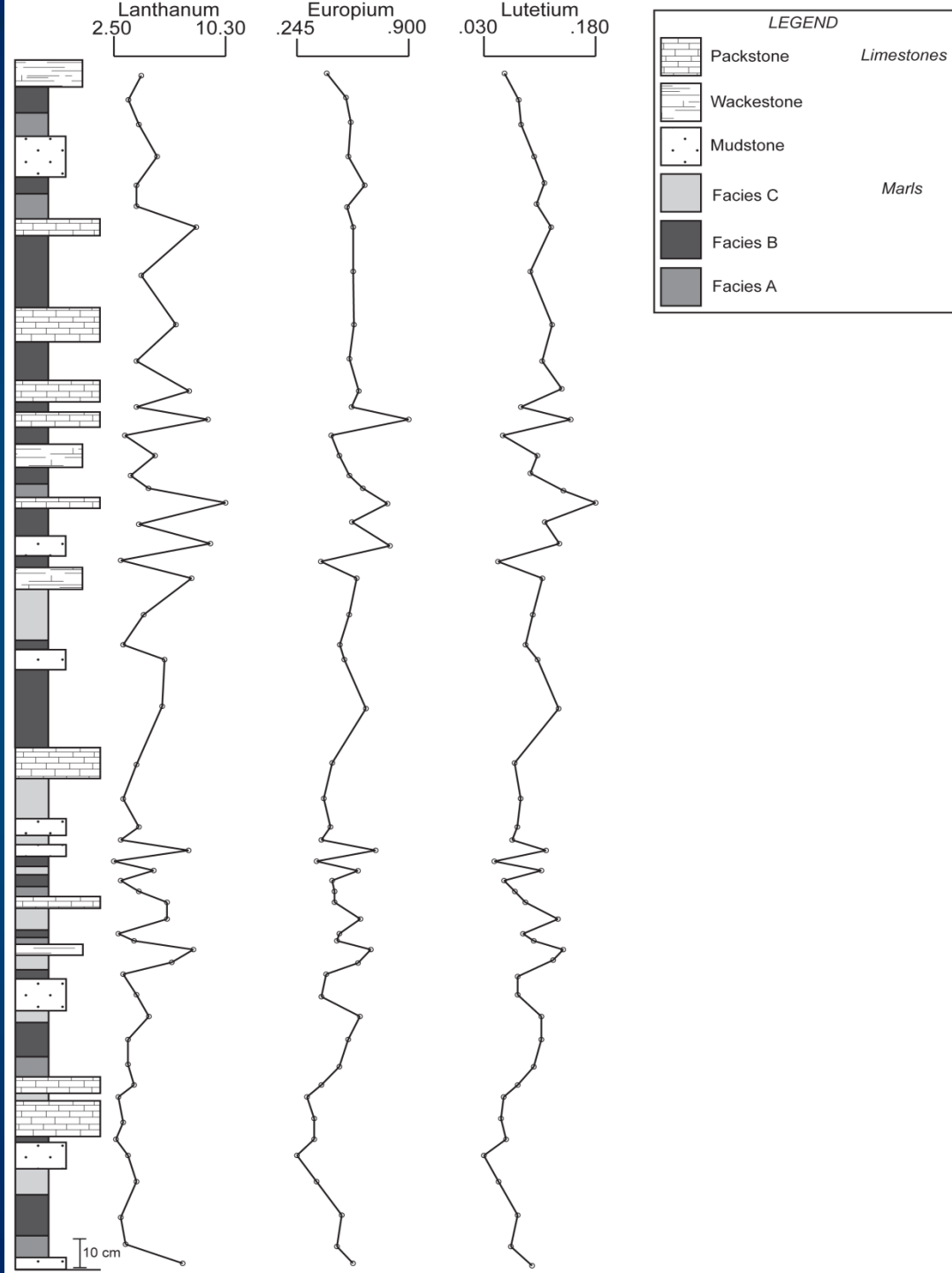
**PV-2a**



**PV-2b**



**PV-2c**



# REE Chemostratigraphy

Elements analyzed include:

## *Light Rare Earths:*

Lanthanum, Praseodymium, Cerium, Neodymium

## *Middle Rare Earths:*

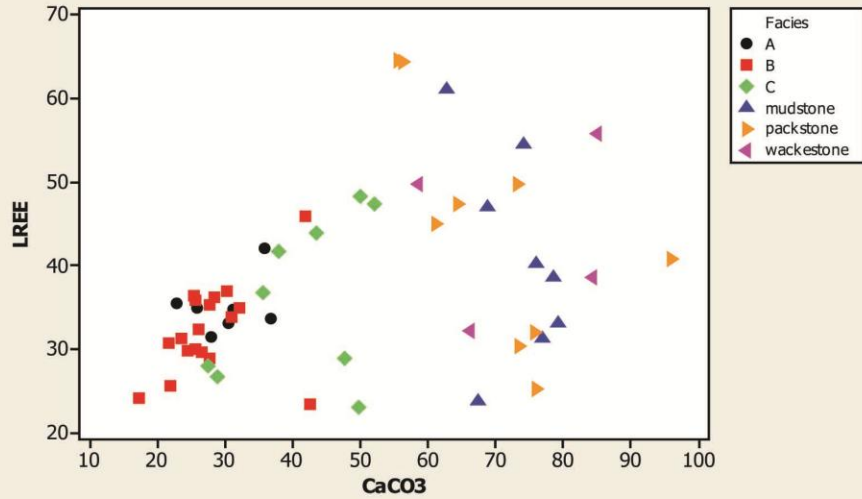
Samarium, Europium, Gadolinium, Terbium, Dysprosium

## *Heavy Rare Earths:*

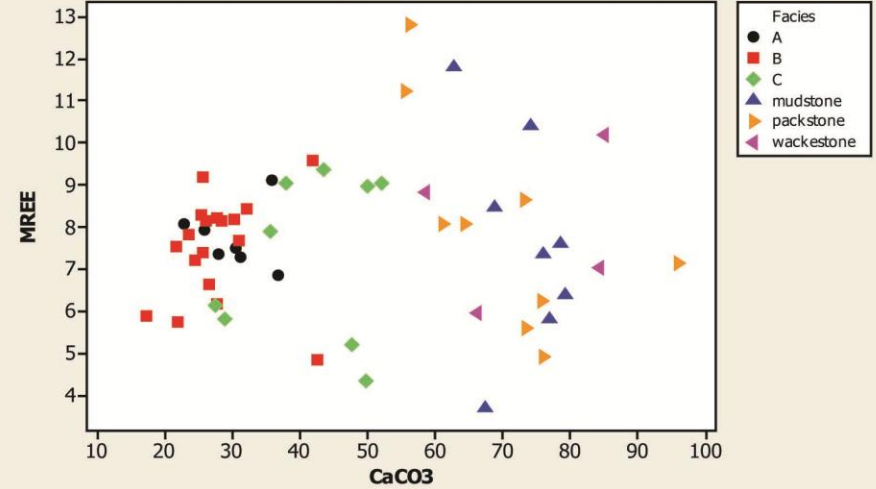
Holmium, Erbium, Thulium, Ytterbium, Lutecium

# REE Facies Distribution

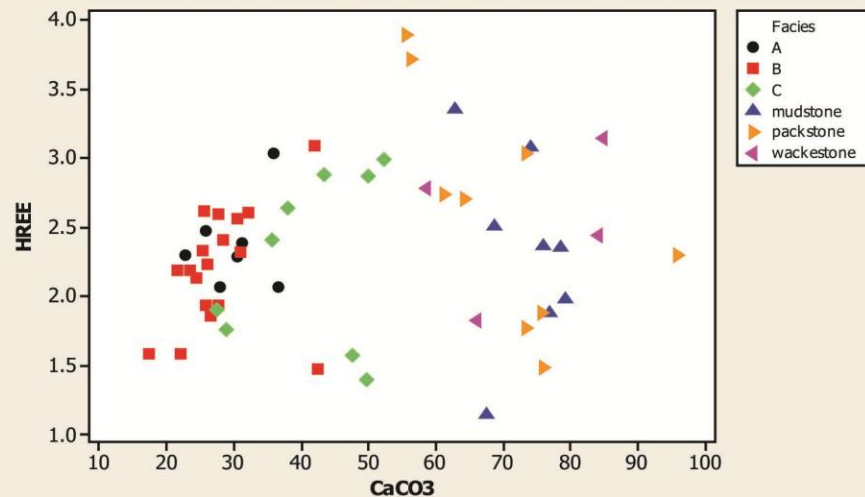
Scatterplot of LREE vs CaCO<sub>3</sub>



Scatterplot of MREE vs CaCO<sub>3</sub>

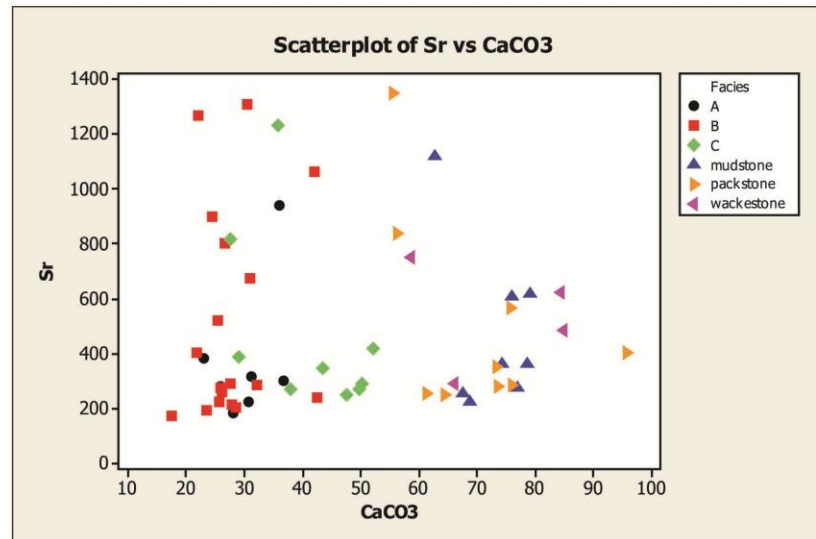
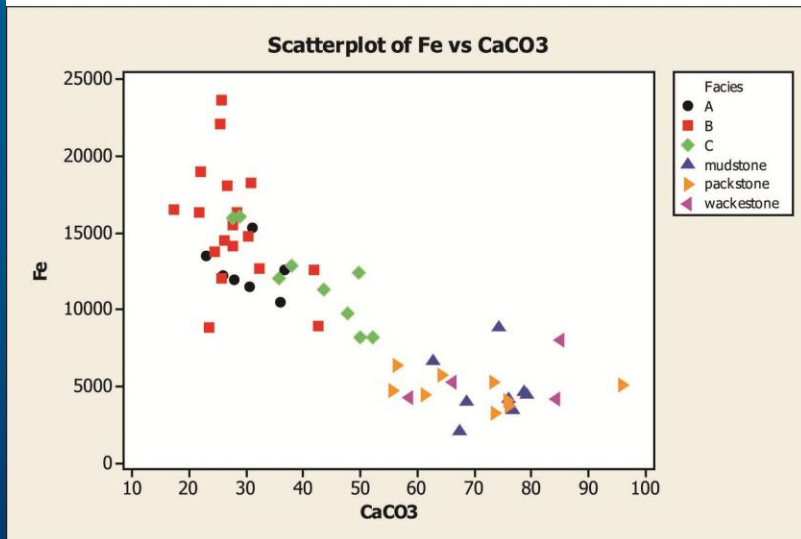
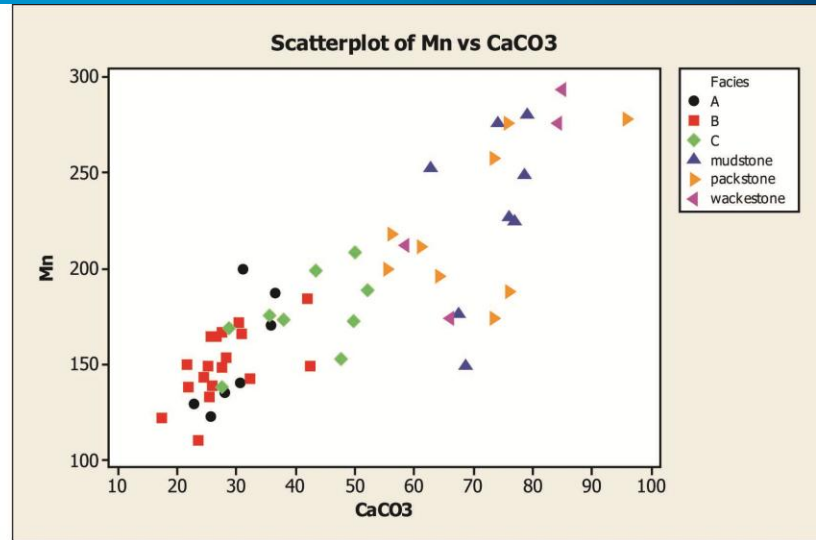
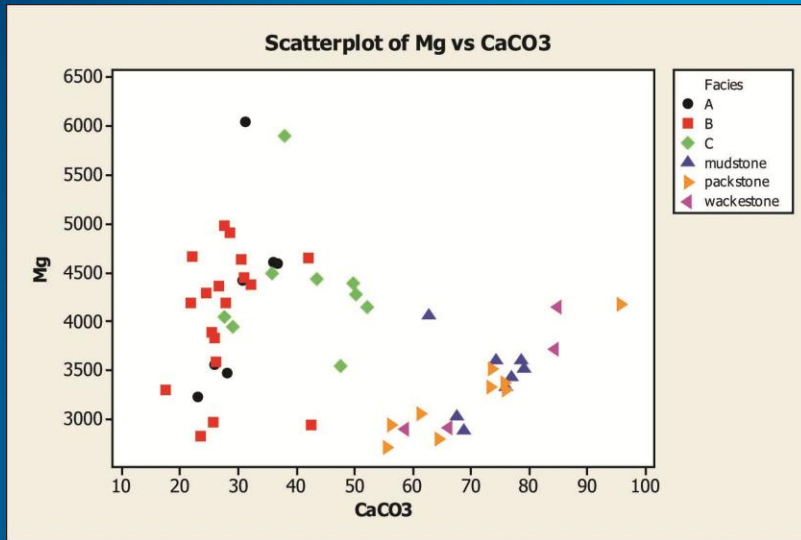


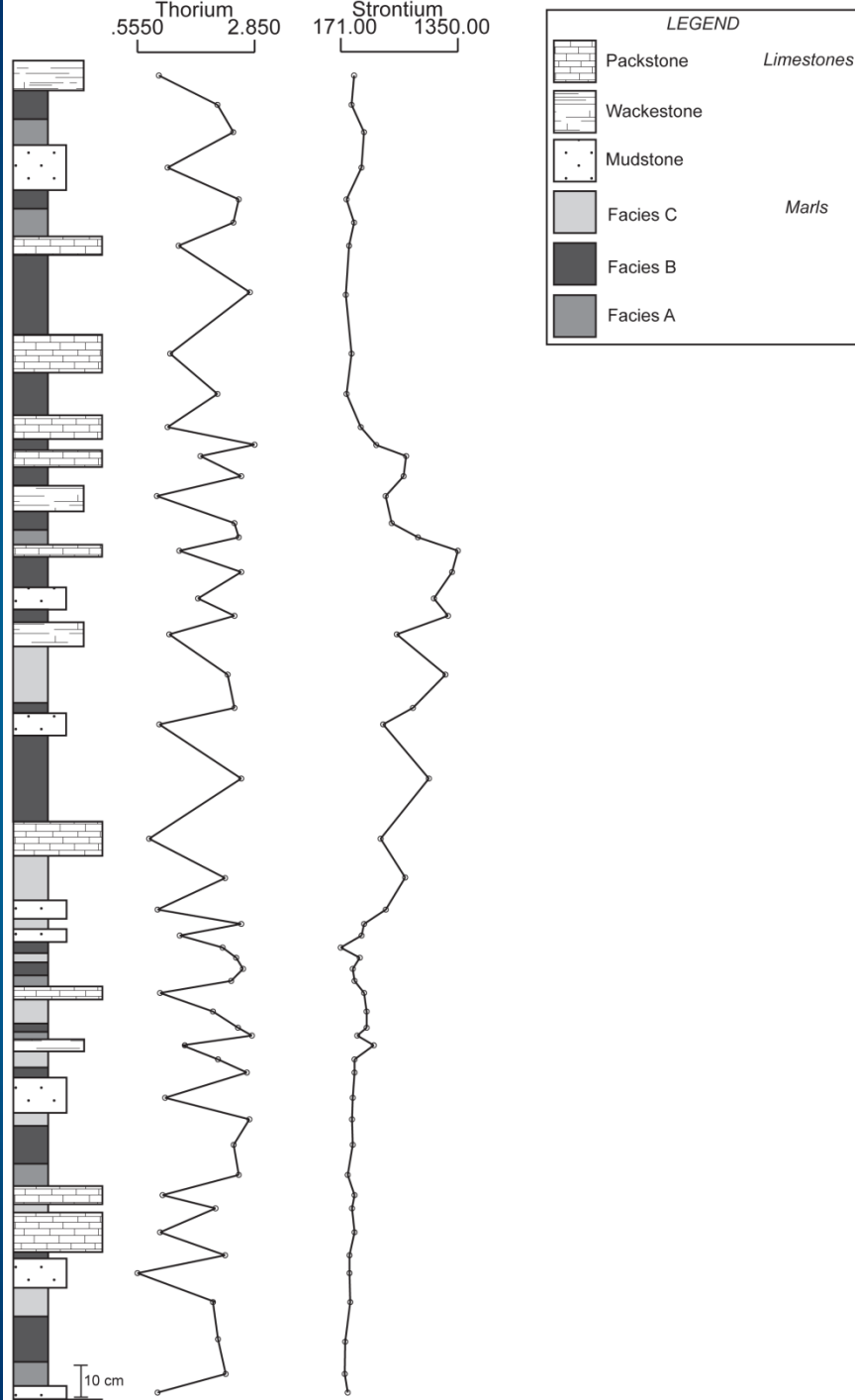
Scatterplot of HREE vs CaCO<sub>3</sub>





# Major Element Facies Distribution





# Strontium-Thorium

- Thorium-232 enters the ocean as continental detritus and dissolves in the water column.
- Thorium is particle reactive and readily sorbs onto clay sediments settling into basins.
- Strontium can be an indicator of an increase in continental weathering.
- Strontium commonly substitutes for calcium, particularly in aragonite.

# Conclusions

- Minor  $\text{CaCO}_3$  dissolution indicates minimal diagenetic influence. However, high Mg also indicates diagenesis.
- Rare earth elements are probably being controlled by both lattice substitution and adsorption. Not best to use because of unclear results.
- Fe and Mn are classic indicators of diagenesis but are not applicable due to being facies-controlled rather than chemically controlled.
- Thorium is the best overall proxy for the determination of a remnant, eustatically controlled signal.

# Acknowledgments

## Committee Members:

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Questions?