Rare Earth Elements Proxies of Early Diagenesis and Oxygenation Conditions in Distal Carbonate Ramps: Vaca Muerta Formation Unconventional Reservoir Subsurface Study Case

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Abstract

Rare earth elements plus yttrium (REY) hosted in marine carbonates provide valuable constraints on seawater chemistry, redox conditions, and basin restriction. However, their application to mixed carbonate–siliciclastic successions remains challenging due to potential contamination by detrital phases, phosphates, and Fe–Mn oxides, particularly in organic-rich epicontinental basins. This study investigates the reliability of carbonate-hosted REY proxies in the Late Jurassic–Early Cretaceous Vaca Muerta Formation (Neuquén Basin, Argentina), deposited in a stratified deep-ramp system characterized by strong lateral paleoenvironmental gradients. Petrography, X-ray diffraction (XRD), bulk-rock geochemistry (XRF), and carbonate-selective REY analyses were integrated across three subsurface sections spanning marginal deep-ramp to depocentral settings. Two selective leaching protocols (HNO_3 and acetic acid) were compared to assess methodological effects. Despite systematic differences in absolute REY concentrations, strong correlations between Y/Ho ratios and Ce anomalies obtained by both methods demonstrate that they isolate the same environmental signal. Carbonate-hosted REY patterns record predominantly oxic to mildly suboxic surface and intermediate waters and reveal a clear lateral redox gradient, from well-ventilated marginal areas to a persistently suboxic depocenter. This redox gradient is interpreted as primarily reflecting lateral variations in water-mass circulation across the ramp, rather than vertical redox stratification or direct freshwater input. These results confirm the robustness of Y/Ho and Ce anomaly as paleoenvironmental proxies in mixed lithologies.

Introduction

Rare earth elements and yttrium in marine carbonates commonly preserve seawater-like signatures that reflect redox-sensitive fractionation and water-mass evolution (Elderfield et al., 1990; Bau & Dulski, 1996). Among these, the Ce anomaly and Y/Ho ratio are particularly sensitive to oxidation–reduction processes and basin restriction (German & Elderfield, 1990; Bau et al., 1997; De Baar et al., 1985). However, in mixed carbonate–siliciclastic mudrocks, REY signals may be modified by detrital input and early diagenetic processes, complicating paleoenvironmental interpretations (Lanz et al., 2021; Zhang & Shields, 2023).

The Vaca Muerta Formation (VMF) represents one of the most extensive organic-rich marine successions of the Late Jurassic–Early Cretaceous and constitutes a world-class unconventional system (Askenazi et al., 2013). Deposited under greenhouse climatic conditions, the VMF records the interaction between carbonate productivity, siliciclastic dilution, and redox-controlled organic matter preservation (Demaison & Moore, 1980; Weissert & Erba, 2004). While previous studies have addressed redox evolution using bulk geochemical proxies (Spalletti et al., 2014; Gómez-Dacal et al., 2019), carbonate-hosted REY signatures in subsurface mixed mudrocks remain poorly constrained.

Geological Setting

The Neuquén Basin is a back-arc basin developed along the western margin of Gondwana, with a sedimentary record exceeding 7 km in thickness (Yrigoyen, 1991; Vergani et al., 1995; Howell et al., 2005). During the Late Jurassic–Early Cretaceous, thermal subsidence and marine flooding led to the development of a broad carbonate–siliciclastic ramp system (Spalletti et al., 2000). The Vaca Muerta Formation was deposited during the Tithonian–Berriasian and consists of fine-grained limestones, marls, and mudstones with minor volcaniclastic input (Leanza et al., 2011; Kietzmann et al., 2016).

The analyzed subsurface sections are located within the Neuquén Embayment and capture a paleogeographic transect from marginal deep-ramp settings to the basin depocenter (Figure 1), allowing evaluation of lateral gradients in sediment composition and redox conditions under broadly coeval stratigraphic conditions.

Methodology

Cutting samples were selected from three subsurface sections. Petrographic observations and XRD analyses were conducted to characterize mineralogical composition and assess the relative contributions of carbonate and siliciclastic components (Lazar et al., 2015). Major and trace elements were determined by XRF to evaluate bulk compositional variability and identify potential contaminant phases.

Carbonate-hosted REY were extracted using two selective leaching protocols: low-molarity HNO_3 (Tostevin et al., 2016) and acetic acid (Hac - Zhang & Shields, 2023). REY concentrations were measured by ICP-MS and normalized to PAAS (Taylor & McLennan, 1985). The Ce anomaly and Y/Ho ratio were used as primary paleoenvironmental proxies.

Results

Lithological and mineralogical data indicate that the VMF is dominated by mixed carbonate–siliciclastic mudrocks, with calcite and quartz as the main mineral phases (Figure 2). Marginal sections display higher carbonate contents, whereas the depocentral section is enriched in siliciclastic material and clay minerals (Figure 3), consistent with previous regional studies (Spalletti et al., 2014).

Shale-normalized REY patterns of carbonate leachates show depletion in light REY and enrichment in middle to heavy REY, consistent with marine carbonate signatures (Figure 4). Ce anomalies range from ~0.65 to ~1.05, and Y/Ho ratios vary between ~22 and 34, defining systematic lateral trends across the basin. Although total REY concentrations correlate locally with SiO_2 (Figure 5), neither Ce anomaly nor

Y/Ho shows significant relationships with SiO_2, P_2O_5, Fe, or Mn (Figures 6-7), indicating minimal contamination effects. On the other hand, comparisons among REY proxies (total REY, Y/Ho, and Ce anomaly) reveal that both Y/Ho and Ce show no significant correlation with total REY, except in Section A where display a low correlation (r=-0.46) with total REY. Additionally, a great correlation between Y/Ho and Ce anomaly is observed in Sections A and C (Figure 8).

Comparison between leaching methods shows higher total REY concentrations, higher Ce anomaly and Lower Y/Ho ratio in HNO_3 extracts relative to HAc, but strong correlations between Y/Ho and Ce anomaly obtained by both methods (Figures 9) confirm that they capture the same variability paleoenvironmental signal.

Discussion and Concluding Remarks

Carbonate-hosted REY signatures indicate predominantly oxic to mildly suboxic conditions in surface and intermediate waters, supporting a persistently stratified water column (Spalletti et al., 2014). A clear lateral paleoenvironmental gradient is evident, from well-ventilated marginal deep-ramp areas to a persistently suboxic depocenter. The strong internal consistency of Y/Ho ratios and Ce anomalies confirms their reliability for reconstructing subtle redox gradients in mixed carbonate–siliciclastic successions and highlights their applicability to paleoceanographic reconstructions in stratified epicontinental basins.

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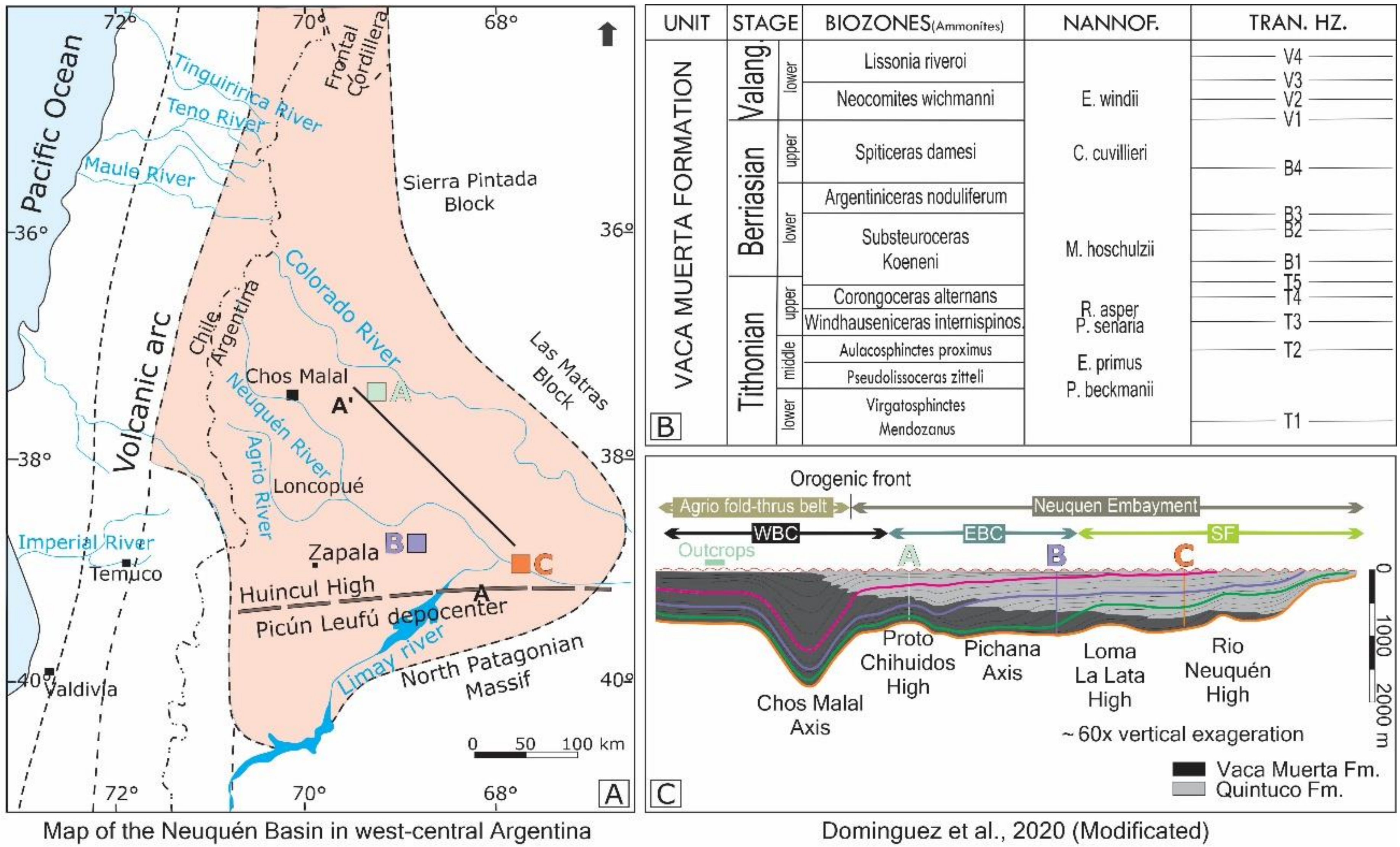

Figure 1. (A) Location map of the Neuquén Basin, showing the position of the three studied subsurface sections (A, B, and C). (B) Chronostratigraphic framework of the Vaca Muerta Formation (VMF) with ammonite and calcareous nannofossil zonations. (C) Simplified SE–NW cross-section of the Vaca Muerta and Quintuco formations (modified from Domínguez et al., 2020).

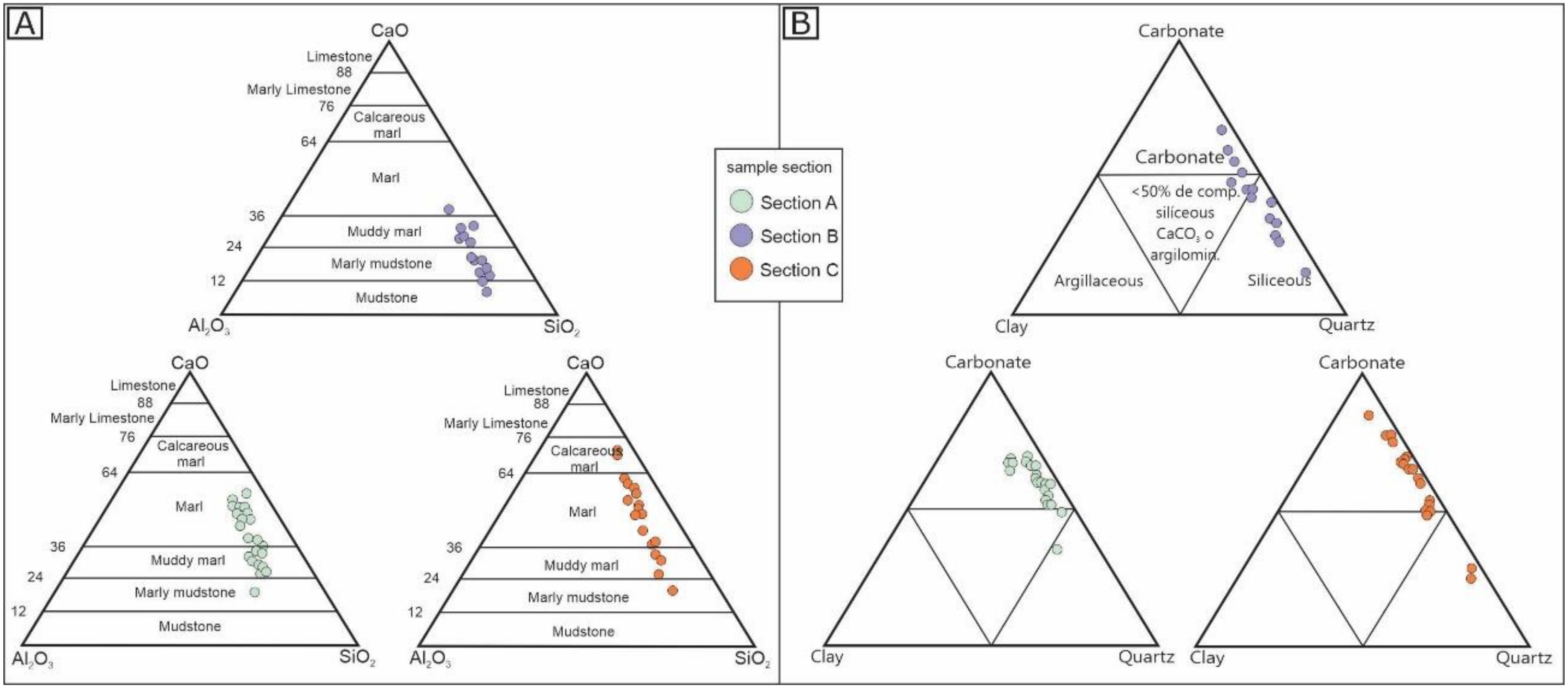

Figure 2. (A) Geochemical classification of samples based on major oxides (after Spalletti et al., 2014). (B) Mineralogical classification derived from XRD analyses (after Lazar et al., 2015). Both datasets show consistent trends, confirming the reliability of compositional interpretations.

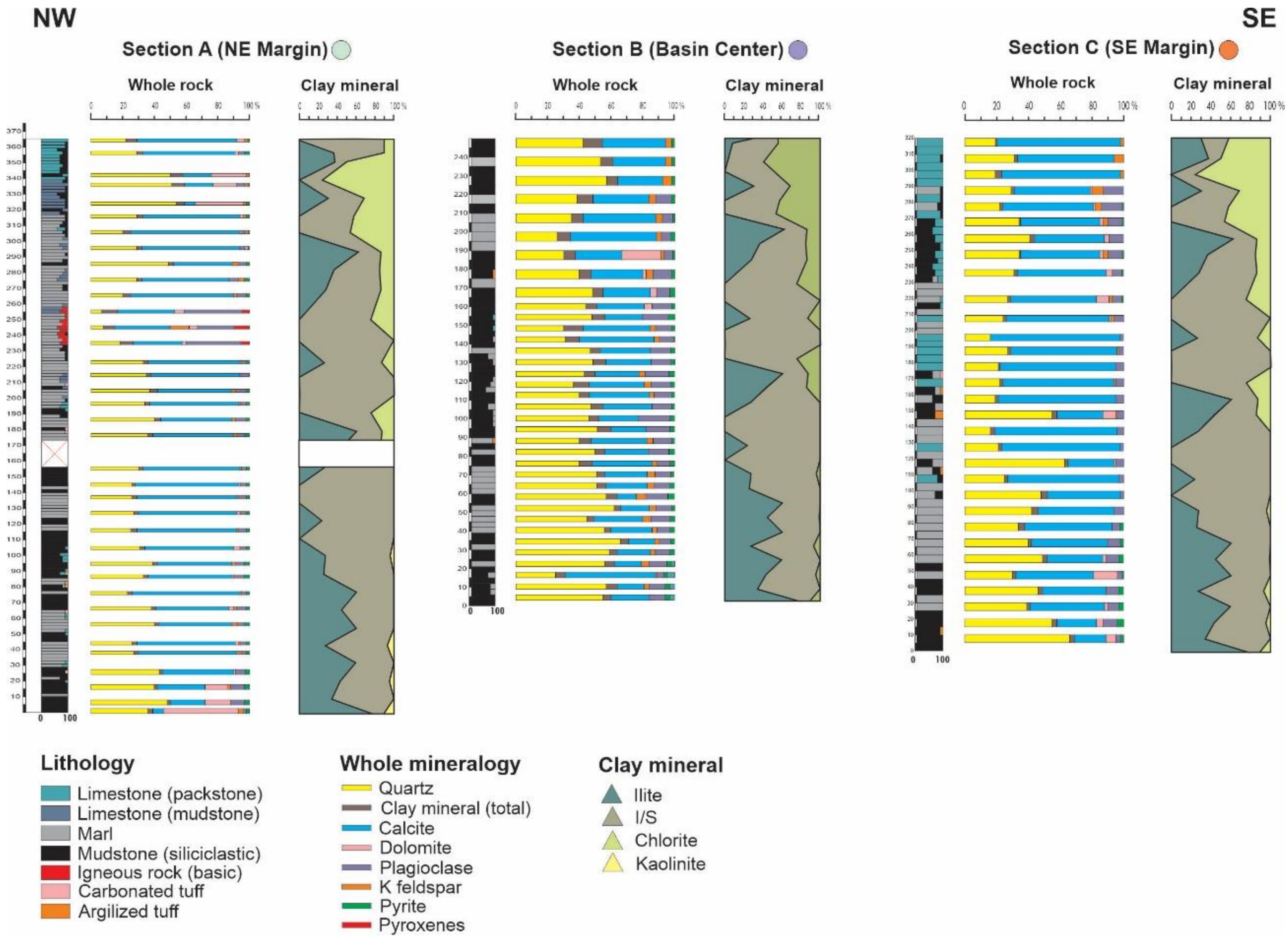

Figure 3. Vertical distribution of main mineral phases obtained from whole-rock and clay-fraction XRD analyses in sections A, B, and C. The two dominant phases are calcite and quartz, which vary inversely. Minor phases include plagioclase, feldspar, clays, dolomite, and pyrite. Note the higher carbonate content in marginal sections (A, C) and increased siliciclastic input toward the depocentral section (B).

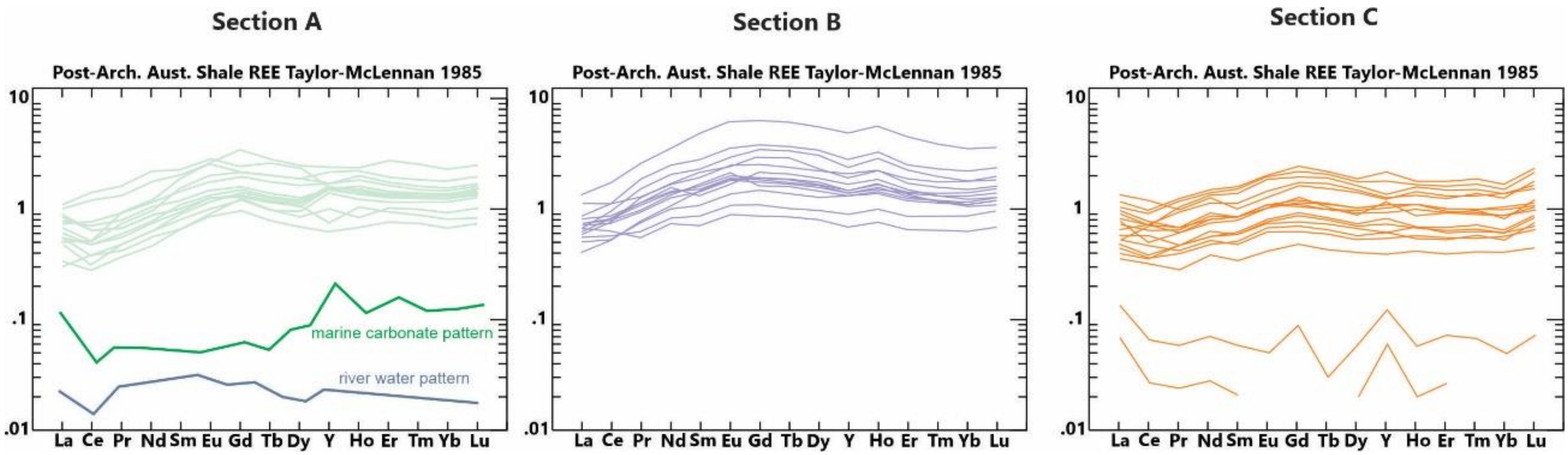

Figure 4. Shale-normalized rare earth element and yttrium (REY) patterns of carbonate fractions from sections A, B, and C of the Vaca Muerta Formation. Normalization is to PAAS (Taylor and McLennan, 1985). The patterns show depletion in light REY and enrichment in middle to heavy REY, consistent with marine carbonate signatures.

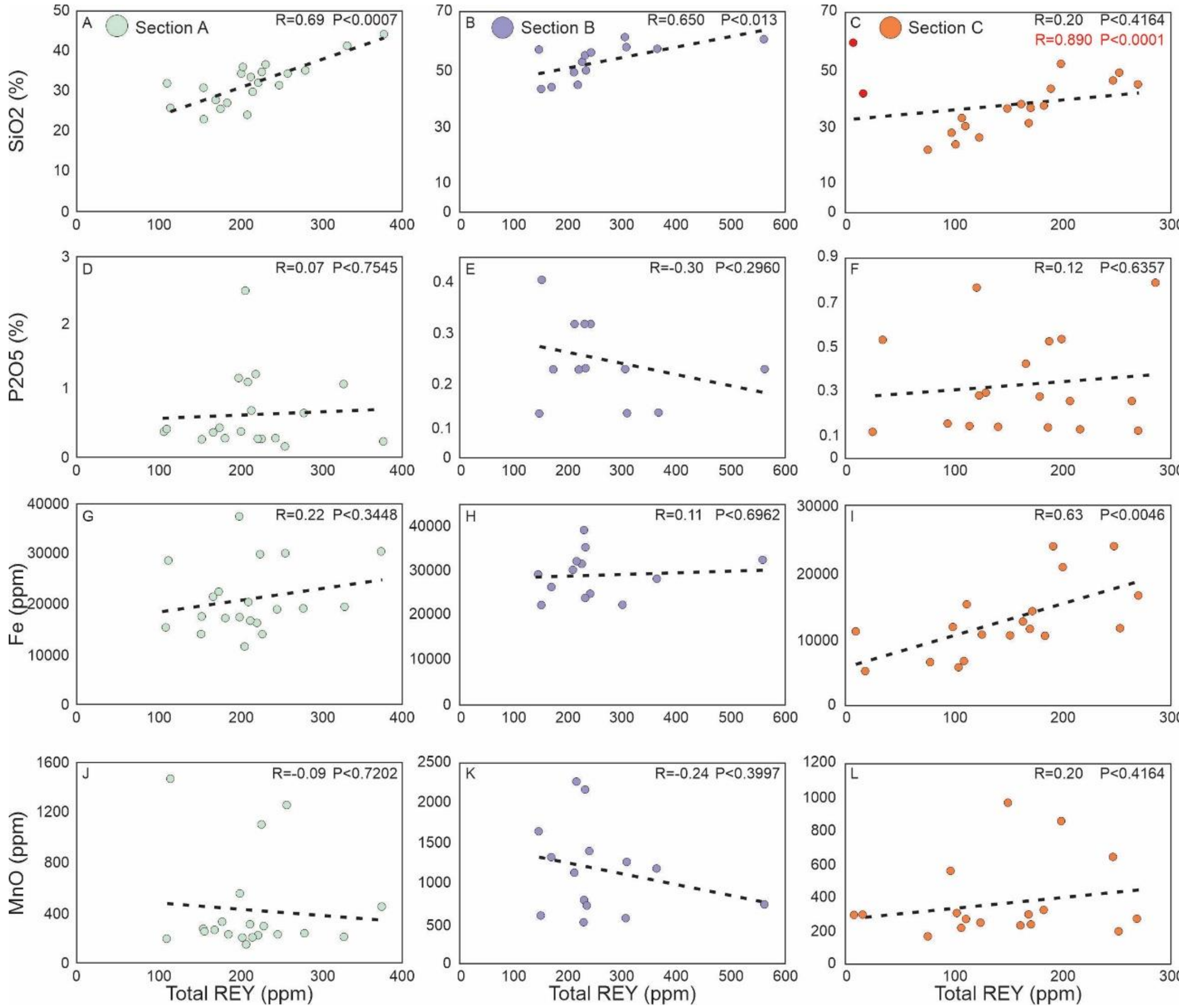

Figure 5. Relationships between total REY content and potential contaminant indicators. (A–C) SiO_2 (detrital input), (D–F) P_2O_5 (phosphatic component), (G–I) Fe (iron oxides), and (J–L) Mn (manganese oxides). Significant correlations with SiO_2 in sections A and C suggest minor detrital control, whereas other proxies show negligible influence.

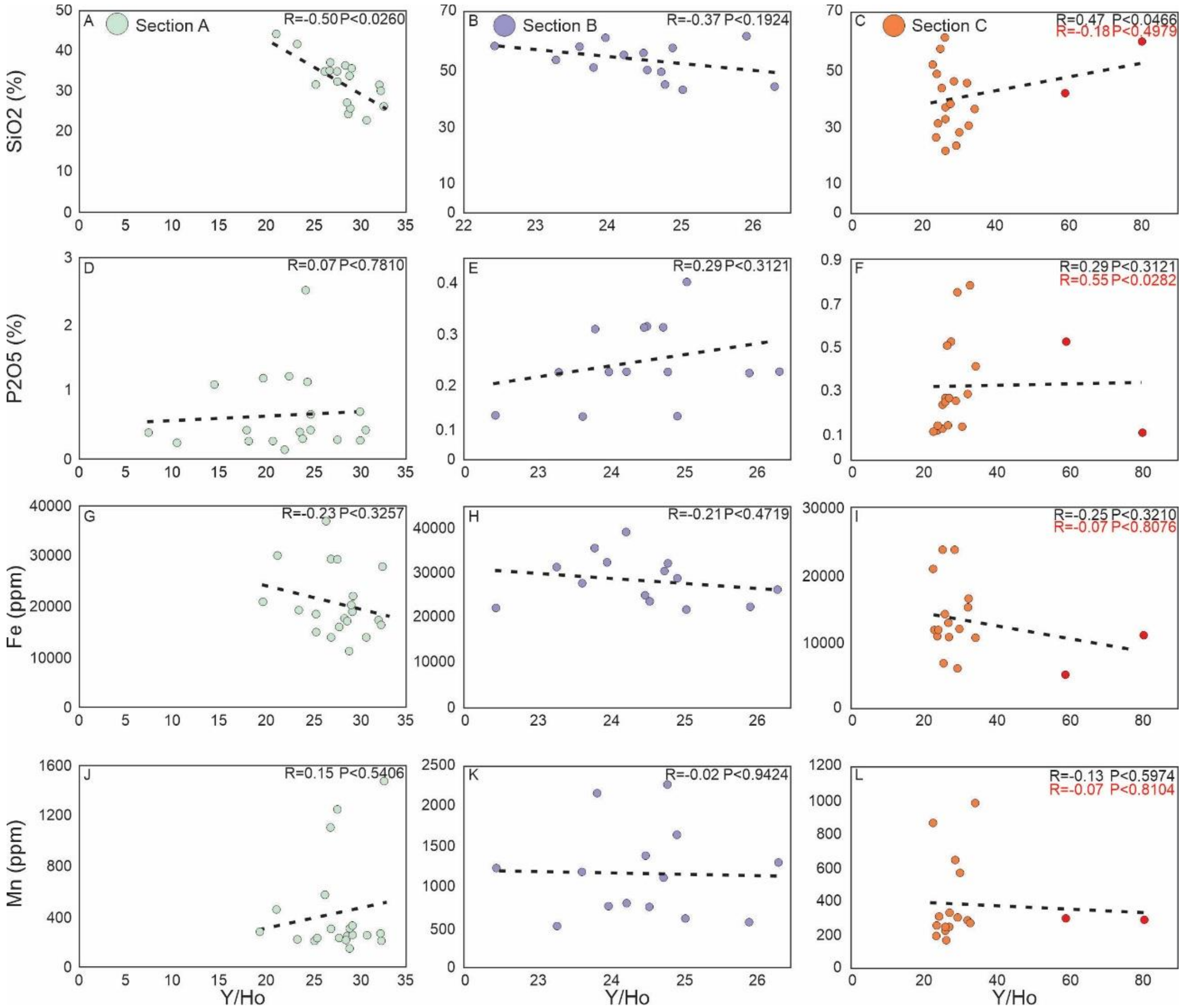

Figure 6. Y/Ho ratio plotted against potential contaminant proxies for each section: (A–C) SiO_2, (D–F) P_2O_5, (G–I) Fe, (J–L) Mn. The absence of strong correlations indicates that Y/Ho variations are largely independent of detrital or oxide contributions, supporting its reliability as a seawater-derived proxy.

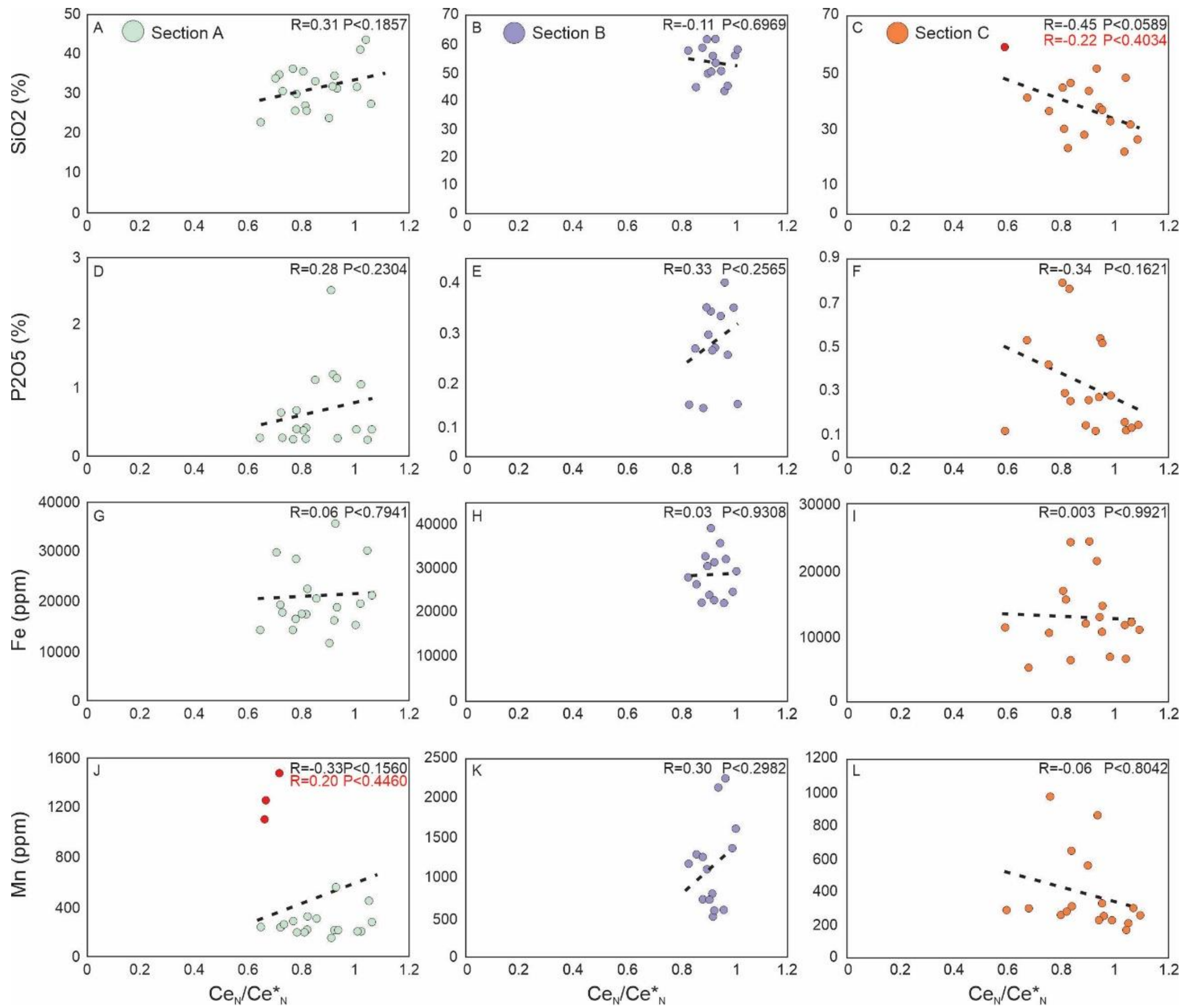

Figure 7. Ce anomaly (CeN/Ce*N) compared with potential contaminant proxies: (A–C) SiO_2, (D–F) P_2O_5, (G–I) Fe, (J–L) Mn. No significant correlations are observed, suggesting that the Ce anomaly primarily reflects paleo-redox conditions rather than contamination effects.

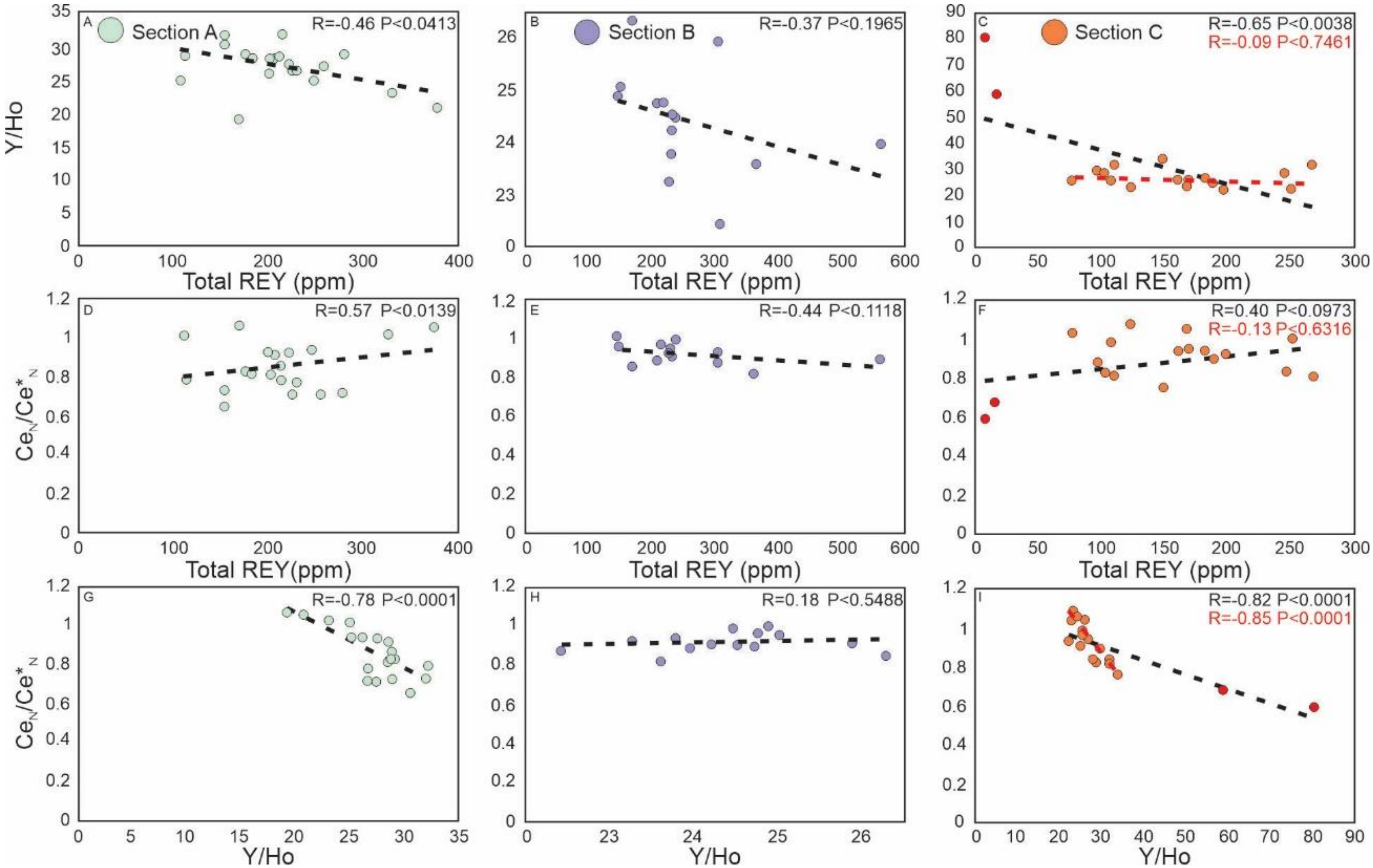

Figure 8. Internal control plots between REY proxies in carbonate leachates. (A–C) Total REY vs Y/Ho, (D–F) Total REY vs Ce anomaly, and (G–I) Y/Ho vs Ce anomaly for sections A, B, and C, respectively. The strong correlation between Y/Ho and Ce anomaly in marginal sections (A, C) supports a coherent paleoenvironmental signal, while the lack of correlation with total REY indicates minimal contamination.

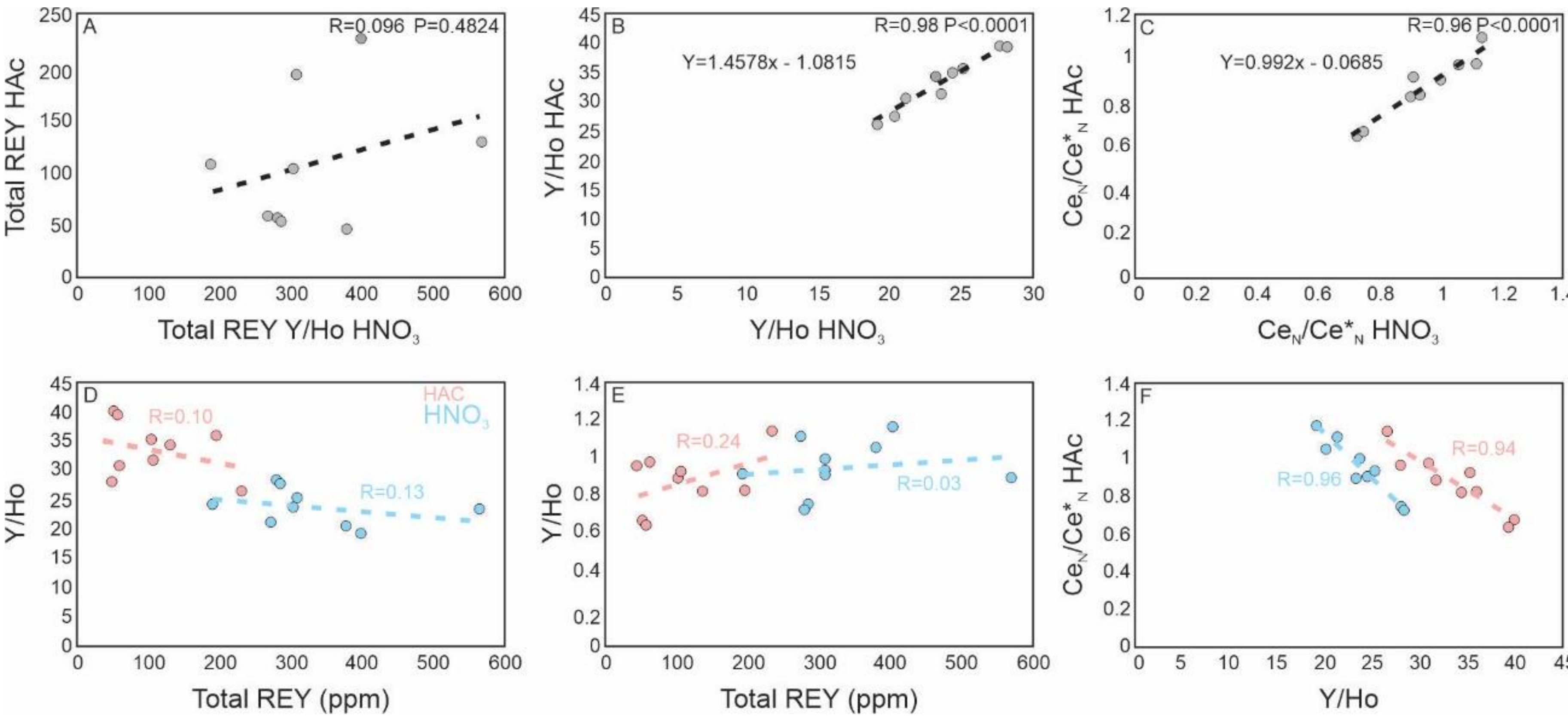

Figure 9. Comparison of REY proxies obtained using nitric acid (HNO_3) and acetic acid (HAc) leaching methods. (A) Total REY concentrations, (B) Y/Ho ratios, and (C) Ce anomalies between both methods. (D–F) Within-method relationships between total REY, Y/Ho, and Ce anomaly. Regression equations (y = ax + b) and correlation coefficients (r) are indicated for each comparison. High correlation coefficients (r = 0.92–0.95) between Y/Ho and Ce anomaly confirm the robustness of these proxies and their independence from leaching artifacts.