Geochemical Fingerprints: Implications for Provenance and Depositional Settings

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ABSTRACT

Geochemical fingerprinting plays a pivotal role in sedimentary geology by offering insights into the provenance, transport history, and depositional environments of clastic sediments. This article explores the theoretical background, methods, and practical implications of geochemical signatures in sediments, with a specific focus on how these fingerprints help reconstruct tectonic settings, source rock composition, and sedimentary processes. This study highlights the technique which integrates the analysis of major, trace, and rare earth elements (REEs), as well as isotopic ratios, to reconstruct the geological evolution from source to sink. Elemental concentrations such as SiO_2, Al_2O_3, Fe_2O_3, K_2O, and TiO_2, alongside isotopic systems like ^87Sr/^86Sr and ^143Nd/^144Nd, are used to characterize distinct depositional settings. For instance, fluvial environments exhibit high SiO_2 due to quartz enrichment and mechanical sorting, deltaic environments show elevated Al_2O_3 and K_2O reflecting fine-grained aluminosilicate input, while marine settings are marked by high Fe_2O_3 and TiO_2 content, indicating longer transport, biogenic input, and diagenetic modifications. Despite its robustness, geochemical fingerprinting is not without limitations. Diagenetic alterations and post-depositional processes can obscure primary chemical signatures, particularly in carbonate-rich or hydrothermally altered sediments. Additionally, sediment mixing from multiple sources may complicate interpretation, requiring integrated approaches that combine petrography, mineralogy, and geochronology with geochemistry. Nonetheless, when carefully applied, geochemical signatures offer a powerful toolkit to distinguish felsic versus mafic source rocks, infer tectonic settings (e.g., passive versus active margins), and reconstruct paleoenvironments and sediment transport pathways. Advances in analytical precision and data processing continue to enhance the reliability of geochemical fingerprinting, reinforcing its central role in unravelling Earth's sedimentary and tectonic history, and in understanding landscape evolution across geological timescales. Over all, by integrating major, trace, and rare earth element (REE) analyses, researchers can draw comprehensive conclusions about geological histories that span from source to sink.

Keywords: Geochemistry, provenance, depositional Environment, elemental Composition, sediment Analysis

INTRODUCTION

Sedimentary rocks hold a wealth of information about Earth's surface processes, from weathering and erosion of source rocks to sediment transport and eventual deposition in varied environments. In other words, sedimentary rocks serve as vital archives of Earth's geological history, encapsulating information about past environments, tectonic activities, and the processes that have shaped the planet's surface over millions of years.

Among the tools used to decode these complex histories, geochemical fingerprinting has emerged as one of the most robust and versatile techniques (Taylor & McLennan, 1985; Rollinson, 1993). By analyzing the elemental and isotopic composition of sediments, geologists can deduce the nature of source rocks (provenance), tectonic settings, and depositional environments.

The concept of geochemical fingerprinting is grounded in the principle that sediments inherit the chemical signatures of their source rocks. These signatures are preserved through various geological processes, with some modifications due to weathering, transportation, and diagenesis. The immobile nature of certain trace elements and isotopic systems makes them particularly useful in provenance studies .For instance, elements like zirconium (Zr), thorium (Th), and rare earth elements (REEs) are resistant to chemical weathering and retain their original signatures, providing insights into the composition of source rocks.

Recent advancements in analytical techniques have enhanced the precision and scope of geochemical fingerprinting. High-resolution methods such as inductively coupled plasma mass spectrometry (ICP-MS) and laser ablation ICP-MS allow for detailed elemental and isotopic analyses, enabling the discrimination of subtle variations in sediment composition. These techniques have been instrumental in studies aiming to reconstruct sedimentary processes and tectonic settings.

Provenance Analysis

Provenance analysis involves determining the origin of sediments by examining their mineralogical and geochemical characteristics. The elemental composition of sediments reflects the nature of the source rocks and the processes they have undergone. For example, high concentrations of certain trace elements can indicate derivation from specific rock types. In the study of the Wa-Lawra Belt in the southeastern margin of the West African Craton, geochemical analyses revealed that the metasedimentary rocks were derived from felsic to intermediate source rocks, with evidence of moderate weathering in the source area.

Isotopic systems, such as the samarium-neodymium (Sm-Nd) system, provide additional constraints on provenance. The Sm-Nd isotopic composition of sediments can indicate the age and evolution of the source terranes. In the Taoudeni Basin of Mauritania, Sm-Nd isotopic analyses, combined with elemental geochemistry, were used to trace the sedimentary provenance and tectonic setting of Mesoproterozoic rocks.

Depositional Settings

Geochemical fingerprinting also aids in reconstructing depositional environments by analyzing the chemical signatures of sediments .Certain elemental ratios and concentrations can indicate specific depositional conditions. For instance, the presence of redox-sensitive elements can suggest anoxic conditions, while the abundance of certain trace elements can point to marine or fluvial settings. In the Padma River sediments of Bangladesh, geochemical analyses were used to infer the depositional environment, weathering intensity, and tectonic setting, revealing a complex interplay of factors influencing sediment composition.

Moreover, the integration of geochemical data with other proxies, such as mineralogical and textural analyses, enhances the interpretation of depositional settings. In the Mamfe Basin of southwest Cameroon, a combination of major, trace, and rare earth element analyses was employed to deduce the provenance, weathering conditions, and depositional environment of Cretaceous and Neogene deposits.

The major, trace and REE signatures were effectively used in the Mamfe basin because it gives insight of sediment sources, transportation processes and depositional environment. In addition, it also provides information on bulk rock composition, magma genesis and tectonic setting of the basin.

Advancements and Applications

The application of machine learning techniques to geochemical data has opened new avenues for provenance and depositional studies .By employing algorithms such as random forests and support vector machines, researchers can classify source rocks based on trace element compositions with high level of accuracy. A study utilizing machine learning approaches demonstrated the potential of these methods in distinguishing between various Igneous, metamorphic, and hydrothermal source rocks using zircon trace element data.

Furthermore, the integration of geochemical fingerprinting with other analytical methods, such as spectroscopy and mineralogical analyses, enhances the resolution of provenance studies. In the Thio River catchment of New Caledonia, a combination of color parameters and geochemical tracers was used to improve sediment source discrimination in a mining-impacted environment.

Concept of Geochemical Fingerprints

A geochemical fingerprint refers to the unique chemical signature preserved in sedimentary deposits, representing a mixture of geological, environmental, and climatic processes acting on the parent material (McLennan et al., 1993). These fingerprints typically include concentrations of major elements (e.g., Si, Al, Fe, Mg, Ca), trace elements (e.g., Cr, Ni, Sr, Ba), and rare earth elements (REEs), which collectively reflect the mineralogical and chemical makeup of the source terrain.

Sediments retain the chemical characteristics of their source rocks to a large extent, especially in tectonically stable and relatively low-energy transport systems (Cullers, 2000). For example, felsic source rocks typically contribute sediments with high SiO_2 and low Fe_2O_3 and MgO contents, while mafic sources impart a contrasting signature with higher Fe, Mg, and compatible trace elements such as Ni and Cr (Bhatia, 1983; Garzanti et al., 2007).

Provenance Analysis

One of the principal applications of geochemical fingerprinting is provenance analysis—identifying the origin of sedimentary material. This is essential in understanding basin evolution, sediment routing systems, and tectonic settings. Major element ratios such as SiO_2/Al_2O_3, Fe_2O_3/K_2O, and Na_2O/K_2O, along with immobile trace elements like Zr, Th, Sc, and Cr, have proven effective in differentiating between felsic, intermediate, and mafic sources (Roser & Korsch, 1988).

In addition, REE patterns offer critical insights. Light REE (LREE) enrichment, flat heavy REE (HREE) patterns, and negative Eu anomalies often indicate felsic sources, while more uniform REE distributions with minimal Eu anomalies suggest mafic provenance (McLennan, 1989). These geochemical signatures are preserved even after extensive transport and weathering, making them reliable indicators of source rock composition.

Isotopic systems such as Sm-Nd and Pb isotopes further enhance provenance studies by tracing sediment origin over broader spatial and temporal scales (Goldstein et al., 1984). Nd isotopic data, for instance, can differentiate between older continental crust and younger oceanic crust contributions to sediments.

Depositional Environment and Tectonic Setting

Geochemical fingerprints also reflect depositional settings, ranging from fluvial to deep marine environments. Ratios like Th/Sc, La/Co, and Cr/Th are widely used to discriminate between passive margin, active continental margin, and oceanic island arc tectonic settings (Bhatia & Crook, 1986). For instance, sediments from oceanic island arcs tend to have higher Fe_2O_3/MgO and TiO_2 contents, while those from passive margins show elevated SiO_2 and low trace metal concentrations.

The Chemical Index of Alteration (CIA) is another useful tool that indicates the degree of chemical weathering in the source area (Nesbitt & Young, 1982). A high CIA value reflects intense weathering, often associated with warm and humid climatic conditions and long sediment transport distances.

Sediment maturity and recycling can also be inferred from geochemical trends. Highly recycled sediments exhibit increased concentrations of stable heavy minerals (e.g., zircon, rutile, monazite) and associated trace elements such as Zr, Hf, and Th (Garzanti et al., 2004). This is particularly important in complex tectonic settings where sedimentary reworking is common.

METHODOLOGICAL CONSIDERATIONS

To achieve accurate geochemical fingerprinting, it is critical to use robust sampling strategies, analytical techniques, and normalization procedures. Common analytical methods include X-ray fluorescence (XRF), inductively coupled plasma mass spectrometry (ICP-MS), and instrumental neutron activation analysis (INAA), each offering different levels of sensitivity and elemental coverage (Potts, 2012).

Normalization to standard reference materials such as chondrite or upper continental crust values is essential to interpret REE patterns and trace element concentrations accurately (Taylor & McLennan, 1985). Multivariate statistical analyses, such as principal component analysis (PCA) and cluster analysis, are also increasingly used to classify samples and identify compositional trends (Viers et al., 2009).

Furthermore, the specific advanced statistical approach such as unmixing algorithms and machine learning helps in complex sediment source identification. These approaches can handle large data sets and their relationships for improved accuracy and handling of uncertainties in complex data sets.

Elemental composition across different depositional settings

The elemental composition across different depositional settings (Fluvial, Deltaic, and Marine) is shown in Figure 1. It helps illustrate how geochemical fingerprints can vary by environment, aiding in the interpretation of provenance and depositional conditions.

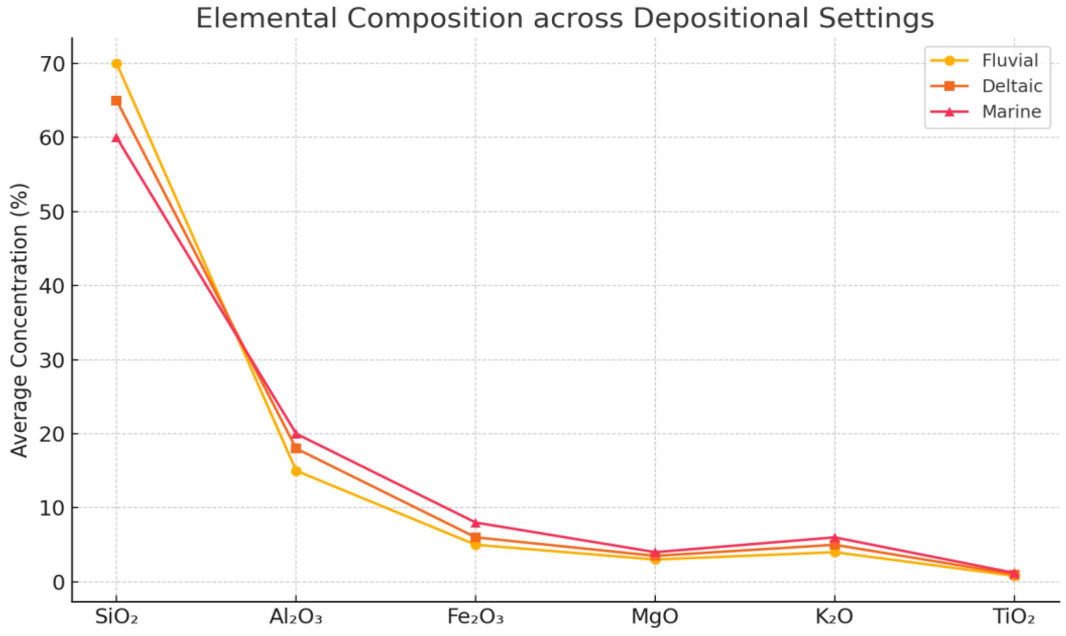

Figure 1 Visual Chart showing the Elemental Composition across different Depositional Settings

The chart in Figure 1, explains the geochemical signatures across depositional settings, comparing the average concentrations of selected major and trace elements, such as SiO_2, Al_2O_3, Fe_2O_3, K_2O, and TiO_2, across three common depositional environments: Fluvial, Deltaic, and Marine. These elements are key indicators used in geochemical fingerprinting to infer provenance (source rock type), tectonic setting, and sedimentary processes.

Figure 1, shows Silicon Dioxide (SiO_2) as highest in Fluvial settings. High SiO_2 suggests quartz-rich detritus, commonly from continental crustal sources or recycled sediments. Fluvial environments tend to have well-sorted, quartz-dominated sediments due to mechanical weathering and reworking (Valloni & Maynard, 2021). On the other hand, SiO_2 is shown to be lower in Marine settings. Marine deposits often contain more clay minerals and biogenic components (like carbonates), reducing the relative proportion of SiO_2.

Aluminium Oxide (Al_2O_3) is indicated as elevated in Deltaic environments. This reflects the presence of fine-grained aluminosilicate minerals (e.g., clays). Deltaic settings typically accumulate mudstones and siltstones, rich in weathered products of feldspars and micas (Zaid et al., 2020). Al_2O_3 is indicated as lower in Fluvial settings. The coarser grain size and mechanical sorting lead to reduced alumina content.

Iron Oxide (Fe_2O_3) is shown to be highest in Marine settings. This indicates the presence of iron-bearing minerals like hematite and goethite, and possibly authigenic iron minerals. In marine basins, reducing conditions may enhance Fe preservation (Liu et al., 2023). It was also shown to be intermediate in Deltaic, lowest in Fluvial. This indicates that Iron can be oxidized and leached more easily in fluvial environments.

Potassium Oxide (K_2O) correlates with feldspars and micas, which are more stable in lower-energy environments like Deltaic and Marine. Higher K_2O levels in Deltaic settings suggest minimal transport or weathering.On the other hand, it is indicated as depleted in Fluvial. Feldspars and micas tend to break down in fluvial systems due to prolonged mechanical abrasion.

Titanium Dioxide (TiO_2) is common in all settings but slightly elevated in Marine sediments, indicating the presence of heavy minerals like rutile and ilmenite. TiO_2 is often used as a provenance indicator due to its immobility during weathering (Garzanti et al., 2022).

Interpretative Insights and Implications for Provenance Studies

The chart indicates geochemical patterns confirming that different depositional environments leave distinct chemical signatures. Fluvial sediments show evidence of significant mechanical sorting, typical of higher-energy river systems. Deltaic sediments suggest intermediate conditions with moderate weathering and fine-grained deposition. Marine settings exhibit chemical features indicative of longer transport, biological activity, and possible diagenetic modification.

This geochemical differentiation can be used to identify source rock types (felsic vs. mafic origins), understand tectonic settings (passive vs. active margins), and reconstruct paleoenvironments and sediment transport histor**y**. Other geochemical indicators (REEs, Trace Metals, and Isotopic Ratios) **a**cross three depositional settings are represented in Figure 2.

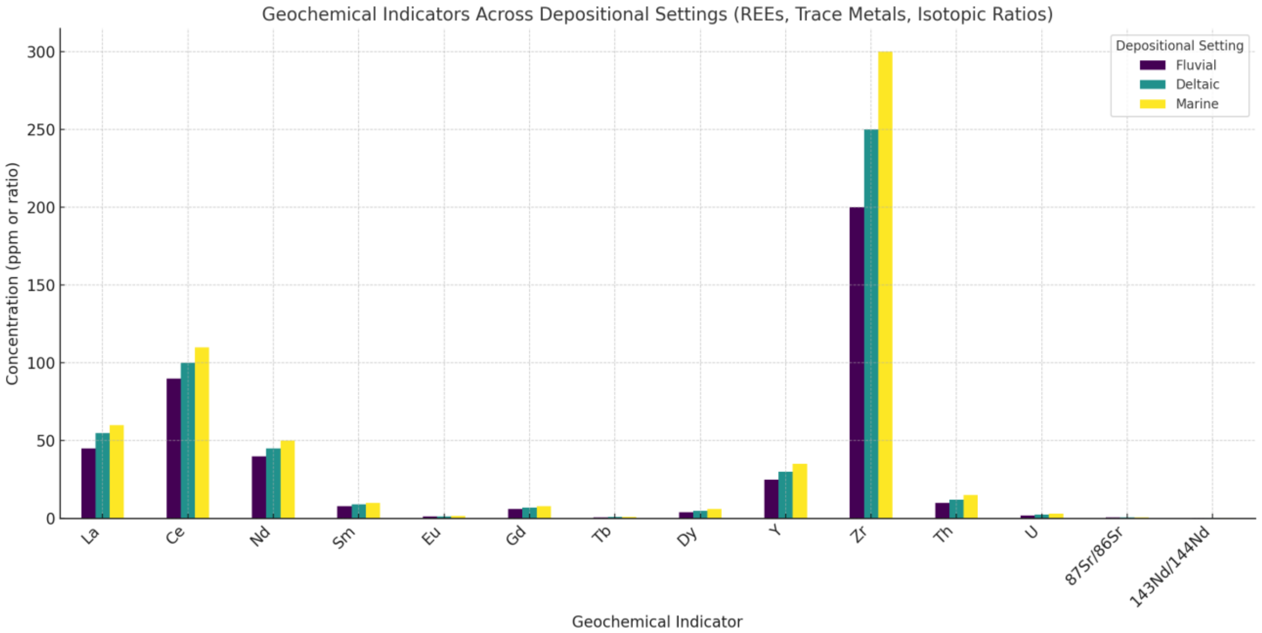

Figure 2. Chart showing Geochemical Indicators

Figure 2 presents a chart that illustrates the distribution of key geochemical indicators—specifically Rare Earth Elements (REEs), trace metals, and isotopic ratios—across three distinct depositional settings: fluvial, deltaic, and marine. These indicators include elemental concentrations such as lanthanum (La), cerium (Ce), neodymium (Nd), yttrium (Y), zirconium (Zr), and thorium (Th), alongside isotopic ratios like ^87Sr/^86Sr and ^143Nd/^144Nd. The integrated analysis of these geochemical parameters provides a comprehensive approach for interpreting sediment provenance and depositional environments.

The variation in REEs and trace metal concentrations across the three environments reflects differences in sediment source, transport processes, and geochemical fractionation. For instance, higher concentrations of light REEs (e.g., La, Ce) in fluvial settings may indicate direct input from continental sources, whereas marine settings might display a more homogenized geochemical signature due to prolonged transport and mixing. The presence of Zr and Th, often associated with heavy minerals like zircon and monazite, can also serve as robust provenance indicators due to their resistance to weathering.

Isotopic ratios further enhance the resolution of provenance studies. The ^87Sr/^86Sr ratio is sensitive to the age and type of source rocks, particularly differentiating between old continental crust and younger volcanic arcs. Similarly, the ^143Nd/^144Nd ratio provides information about mantle-derived versus crustal materials, offering insights into tectonic settings and crustal evolution. When interpreted in conjunction, these isotopic systems can trace sediment pathways over vast distances and identify tectonic events such as orogeny or rifting.

Overall, the chart in Figure 2 highlights how combining elemental and isotopic geochemistry enables a nuanced understanding of sedimentary processes and environmental changes. This integrative approach is vital for reconstructing paleo-environmental conditions and understanding the geological history of sedimentary basins.

Table 1 Summary of Geochemical Indicators Relevant to Provenance and Depositional Settings

Geochemical Indicator	Relevance to Provenance	Relevance to Depositional Setting
Rare Earth Elements (REEs): La, Ce, Nd	Helps to identify source rock types. LREE enrichment suggests felsic sources; flat REE patterns suggest mafic origins.	Reflect sorting, diagenesis, or redox conditions in different depositional environments.
Yttrium (Y)	Associated with heavy minerals; elevated in felsic terrains.	Indicates chemical weathering and hydraulic sorting, especially in fluvial settings.
Zirconium (Zr)	Linked to zircon content, common in granitic/metamorphic rocks.	High values suggest sediment recycling and high maturity of sediment.
Thorium (Th)	Indicative of crustal (felsic) sources and resistant heavy minerals.	High concentrations reflect multiple sedimentary cycles.
87Sr/86Sr Ratio	Indicates age and type of source rock; higher values mean older continental crust.	Useful for tracing marine incursions and freshwater mixing.
143Nd/144Nd Ratio	Radiogenic ratios point to younger mantle sources; less radiogenic to older continental sources.	Helps reconstruct sediment dispersal and paleogeography when combined with Sr isotopes.

Challenges and Limitations

Table 2. Summary of the Challenges and Limitations of Geochemical Fingerprinting in provenance and depositional studies

Challenge / Limitation	**Description**	**Reference(s)**
Post-Depositional Alteration (Diagenesis)	Geochemical signatures can be altered by diagenetic processes such as compaction, cementation, and fluid interactions, complicating provenance interpretations.	Kabir et al., 2023; Gani et al., 2022
Weathering Effects	Chemical weathering can mobilize or concentrate certain elements, potentially obscuring original geochemical signals of the source rock.	Mondal et al., 2021; Roy & Sharma, 2020
Sediment Recycling	Multi-cycle sedimentation can lead to mixed or homogenized signatures, making it difficult to determine the primary source.	Wang et al., 2024; Bhattacharya & Saha, 2020
Analytical Precision and Instrumental Bias	Variations in laboratory equipment calibration and protocols can lead to inconsistent data across different studies.	Arhin & Yidana, 2023; Ganne et al., 2021
Complex Source Terranes	Presence of multiple lithologies within a source region complicates the fingerprinting process, especially in tectonically active areas.	Singh et al., 2020; Mbeng et al., 2022

Element Mobility	Mobile elements (e.g., Na, K, Ca) may be redistributed during weathering and diagenesis, limiting their reliability in provenance studies.	Pal & Chakraborty, 2021; Mungall & Brenan, 2023
Sampling Bias	Inadequate or unrepresentative sampling strategies can misrepresent the true geochemical variability of a sedimentary unit.	Zou et al., 2021; Uche & Nwosu, 2024
Data Interpretation Complexity	Large geochemical datasets require robust statistical and multivariate methods, which may not always be correctly applied or interpreted.	Jebreen et al., 2022; Daneshvar & Amini, 2020
Overlap Between Provenance Signatures	Similar geochemical patterns among different source rocks can lead to ambiguity in identifying specific sources.	Hasan et al., 2023; Adekeye et al., 2022
Lack of Modern Analogues for Calibration	In ancient sedimentary records, lack of modern equivalents can limit the ability to validate geochemical interpretations.	Ojo et al., 2023; Bassey & Essien, 2020

Despite its broad applicability and effectiveness, geochemical fingerprinting is not without limitations. One of the primary challenges lies in the alteration of original geochemical signatures due to diagenetic processes and post-depositional changes. These processes, which include chemical reactions occurring after sediment deposition—such as recrystallization, cementation, and dissolution—can significantly modify the original elemental and isotopic composition of sediments. This is particularly problematic in carbonate-rich or hydrothermally altered environments, where fluids can introduce or remove elements, leading to misleading geochemical profiles that no longer reflect the initial provenance or depositional setting.

Another major limitation is the complexity introduced by sediment mixing from multiple sources. In many depositional environments, sediments are not derived from a single homogeneous source but rather from a variety of lithologies and geographic origins. This mixing can obscure distinct geochemical signatures and make it difficult to confidently attribute sediments to specific sources or tectonic settings. As a result, interpretations based solely on geochemistry may be oversimplified or inaccurate if the potential for mixed inputs is not adequately accounted for.

To overcome these limitations, integrated approaches are essential. Combining geochemical data with complementary techniques—such as petrography (the microscopic examination of mineral textures), mineralogical analysis (to identify source-specific minerals), and geochronology (dating of detrital minerals like zircon)—can significantly enhance interpretation accuracy. These multi-proxy strategies allow for cross-validation of provenance indicators and improve the robustness of geological reconstructions (Weltje & von Eynatten, 2004).

Nonetheless, when applied with care and in conjunction with other analytical methods, geochemical fingerprinting remains a powerful tool. It provides valuable insights into sedimentary processes, Earth's tectonic evolution, paleoclimate variations, and long-term landscape dynamics. By carefully accounting for potential biases and using a multidisciplinary framework, researchers can continue to extract meaningful information from complex sedimentary records.

CONCLUSION

Geochemical fingerprinting stands as a robust and versatile tool in sedimentary geology, offering insights into the provenance and depositional settings of sedimentary rocks. The integration of elemental and isotopic analyses, coupled with advancements in analytical techniques and data processing methods, has significantly enhanced the capability to reconstruct Earth's geological history. As research continues to evolve, the application of geochemical fingerprinting will undoubtedly play a pivotal role in unraveling the complexities of sedimentary processes and tectonic evolution.

However, the use of advanced analytical techniques in developing more sensitive and efficient methods to analysing geochemical signatures in sediments can further enhance research in this regard. Advanced statistical techniques can be applied to handle large geochemical data sets. Environmental monitoring(pollution sources), quantification of sediment sources and provenance/sediment transport histories are some of this research application direction.

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