**ASSESSING THE PALEOCLIMATE BASED ON THE CONCENTRATION OF MAJOR AND TRACE ELEMENTS – A REVIEW**

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**Abstract**

In geoscience, it is possible to deduce the paleoclimate of sediments from their lithology, fossil content, chemical composition, or geophysical characteristics. In this paper, the author reviewed the use of the concentration of major and trace elements to infer the paleoclimate. For this purpose, a variety of markers have been used in the previous studies, such as CIA, C.I, K2O/Al2O3, Al/Mg, Mg/Ca, Fe/Mn, Rb/Sr, Sr/Cu, Ga/Rb, Sr/Ba, ΣREE, and Eu anomaly. It should be noted that, for a more accurate evaluation of paleoclimate, discrimination diagrams (the plots of K2O+Na2O+Al2O3 versus SiO2, CIA versus C.I, K2O/Al2O3 versus Ga/Rb, Fe/Mn versus Sr/Ba, Rb/Sr versus Sr/Cu, and Mg/Ca-Al/Mg-ΣREE) are the recommended technique.

Keywords: Paleoclimate, Major Elements, Trace Elements.

**1. Introduction**

The climate of a former geological era is known as the paleoclimate. There are three distinct periods of paleoclimate that correspond to different geological ages: Precambrian, Phanerozoic, and Quaternary. Global paleoclimate markers are the proxies that are susceptible to changes in the global paleoclimatic condition. The majority of their origins are in marine sediments. Conversely, paleoclimate markers obtained from terrestrial sediments are frequently impacted by local tectonic shifts and paleogeographic fluctuations. Plate tectonics, which regulates the arrangement of continents, the interaction between the atmosphere and ocean, and the properties of Earth's orbit (Milankovitch cycles) are some of the factors that affect the climate system on Earth. Based on data gleaned from the examination of geologic materials global paleoclimate markers are developed. Generally, there are four types of paleoclimate markers: (1) Lithology (e.g., Noble et al., 2016; Fedorchuk et al., 2019; Gao et al., 2024); (2) Fossil content (e.g., Luoto et al., 2012; Kim et al., 2019; Korasidis et al., 2023); (3) Chemical composition (e.g., Tao et al., 2017; Awan et al., 2020; Shaltami, 2024); and (4) Geophysical properties (e.g., Peng et al., 2024).

Elements and isotopes that record environmental data are among the geochemical markers (e.g., Tao et al., 2017; Zhang et al., 2020; Platt and Smith, 2024). Geochemists employ these markers to interpret paleoclimate environments. Concentrations of Si, Al, K, Na, Mg, Ca, Fe, Mn, Ga, Cr, Ni, V, Co, Sr, Ba, Cu, Rb, and REE can be used to determine paleoclimate (Suttner and Dutta, 1986; Beckmann *et al.,* 2005; Cao et al., 2012; Tao et al., 2017; Zhang et al., 2021; Xiao et al., 2024). In this work, the author reviewed methods for evaluating paleoclimate based on the concentration of major and trace elements.

**2. Paleoclimate Markers**

**2.1. Chemical Index of Alteration**

Numerous authors (e.g., El Mourabet et al., 2018; Khan et al., 2023) have extensively evaluated paleoclimatic conditions using the chemical index of alteration (CIA = (Al2O3/(Al2O3+CaO\*+Na2O+K2O))100, Nesbitt and Young, 1982). There are three methods to calculate the concentration of calcium oxide (CaO\*) in the silicate fraction: (1) CaO\* = CaO–CO2(calcite)–0.5 x CO2(dolomite)–10/3 x P2O5(apatite) (Fedo et al., 1995); (2) CaO\* = CaO−P2O5, if Na2O>CaO−P2O5, and CaO\* = Na2O, if Na2O<CaO−P2O5 (McLennan et al., 1993); and (3) CaO\* = CaO–SO3(anhydrite/gypsum) (Scheibe, 2021). Arid, semi-arid to semi-humid, and humid climates are characterized by CIA values of <70%, 70-80%, and 80-100% correspondingly (Nesbitt and Young, 1982). Goldberg and Humayun (2010) pointed out the limitations of the CIA, despite its usefulness in interpreting paleoclimatic conditions. They believed that the existence of carbonate-rich sediments, post-depositional potassium addition, and the hereditary of clays from the source area could restrict the reliance on the CIA as a paleoclimate parameter. They suggested that the CIA is a valuable resource for determining paleoclimate conditions, if used with the proper caution. In order to estimate climate changes, Yang et al., (2014) demonstrated a positive correlation between land surface temperatures and CIA on a global scale. The surface temperature can be ascertained using the following equation: T(°C) = 0.56 × CIA−25.7 (Cao et al., 2019). The correlation held true with an uncertainty of approximately ±5 °C when CIA and T ranged from ~50 to 90% and ~3 to 25 °C, correspondingly (Cao et al., 2019). A correlation between CIA and mean annual precipitation (MAP) without K (CIA-K) was suggested by Sheldon et al., (2002): MAPCIA-K = 221e0.0197(CIA-K). This correlation was modified by Perri (2020) as follows: MAPCIA = 169e0.0271(CIA).

**2.2. Climatic Index**

The climatic index (C.I = (Fe+Mn+Cr+Ni+V+Co)/(Ca+Mg+Sr+Ba+K+Na), Cao et al., 2012) is utilized as a paleoclimate reference. C.I also referred to as C-value. The underlying suggestion for C.I is that, there is an increase in Fe, Mn, Cr, Ni, V, and Co in humid environments; while in arid environments, saline minerals precipitate as water alkalinity increases due to evaporation, resulting in the enrichment of Ca, Mg, K, Na, Sr, and Ba (Cao et al., 2012; Tao et al., 2017). Humid, semi-humid, semi-arid to semi-humid, semi-arid, and arid climates are represented by C.I values of >0.8, 0.6-0.8, 0.4-0.6, 0.2-0.4, and <0.2, respectively (Ding et al., 2018; Awan et al., 2020).

**2.3. K2O/Al2O3 Ratio**

Feldspars and clay minerals can be distinguished using the K2O/Al2O3 ratio. Feldspars have a higher ratio (0.3-0.9) compared to clay minerals (0-0.3, Cox et al., 1995). Furthermore, the ratio in illite (0.2-0.3, Zhou et al., 2015) is higher than that in kaolinite, smectite, and vermiculite (nearly zero, Cox et al., 1995). Accordingly, humid conditions are characterized by low K2O/Al2O3 ratios (<0.2), while the ratios ​​are high in arid climates (>0.2, Roy and Roser, 2013a).

**2.4. Fe/Mn Ratio**

The Fe/Mn ratio can be used to provide paleoclimatic evidence (Yan et al., 2021; Eric et al., 2023). Mn concentration is low in humid conditions where Fe is rapidly precipitated from colloidal iron hydroxides, whereas Mn content is typically high in arid climates. Therefore, humid climates are linked to high Fe/Mn ratios (>1), whereas arid environments are characterized by low ratios (<1) (Yan et al., 2021).

**2.5. Al/Mg Ratio**

The Al/Mg ratio can reveal information about the paleoclimate during deposition; low ratios suggest an arid environment, while high ratios indicate a humid climate (Yan et al., 2021).

**2.6. Mg/Ca Ratio**

The Mg/Ca ratio is frequently used as a paleoclimate proxy in clastic rocks (Deng et al., 2019; Yan et al., 2021). High ratios are generally indicative of arid climates, whereas low ratios are characteristically reflective of humid climates (Yan et al., 2021).

**2.7. Rb/Sr Ratio**

The Rb/Sr ratio is a significant index of paleoclimate (e.g., Zou et al., 2021). During weathering, Sr is depleted through leaching, whereas Rb remains relatively stable. Sr is depleted and the Rb/Sr ratio rises (>0.5) as a result of increased precipitation and increased weathering in humid climates. Since there is less precipitation, less weathering, and more Sr-rich rocks in arid climates, the Rb/Sr ratio would be relatively low (<0.5) (Zou et al., 2021).

**2.8. Sr/Cu Ratio**

Paleoclimate studies have used the Sr/Cu ratio as a reliable indicator (e.g., Lerman, 1978; Tao et al., 2017; Zhang et al., 2020). Similar to Rb, Cu does not change during weathering. The typical Sr/Cu ratios for humid, semi-arid to semi-humid, and arid climates are 1.3-5, 5-10, and >10, correspondingly (Lerman, 1978).

**2.9. Ga/Rb ratio**

The paleoclimate system is often constrained by the Ga/Rb ratio (Xie et al., 2018). In general, Ga is more abundant in kaolinite, suggesting humid conditions (Beckmann et al., 2005; Roy and Roser, 2013b), whereas Rb is more commonly found in illite, signifying an arid environment (Roy and Roser, 2013b). Consequently, the Ga/Rb ratio is high in humid conditions (>0.21), while arid climates show low ratios (<0.21) (Roy and Roser, 2013a).

**2.10. Sr/Ba Ratio**

Paleoclimate can be assessed based on the Sr/Ba ratio (Dai et al., 2020; Eric et al., 2023). Climate has an impact on the Sr/Ba ratio; high ratios (>1) represent arid conditions, while low ratios (<1) indicate humid climates (Dai et al., 2020).

**2.11. Rare Earth Elements**

REE are very sensitive to variations in the paleoclimate (Condie, 1991; Yang et al., 2014; Ma et al., 2021; Xiao et al., 2024). The most important parameters are ΣREE (Ma et al., 2021) and Eu anomaly (Condie, 1991). Eu anomaly can be calculated using the following equation: Eufound/Eu\*expected = EuN / (SmN × GdN)0.5. The REE values used in this equation are shale normalized. For normalization, the Post Archean Australian Shale (PAAS, Taylor and McLennan, 1985) and the North American Shale Composite (NASC, Gromet et al., 1984) are utilized. Generally, humid climates display high ΣREE (Ma et al., 2021) and large negative Eu anomaly (Condie, 1991). According to Yang et al., (2014), weak weathering of REE-bearing minerals would result in weak secondary LREE-carrying product development and a drop in the (La/Yb)N ratio.

**2.12. Discrimination Diagrams**

Discrimination diagrams are the preferred method for more accurate paleoclimate evaluation. There are many discrimination diagrams that depend on the paleoclimate markers, such as the binary plots of K2O+Na2O+Al2O3 versus SiO2 (Fig. 1), CIA versus C.I (Fig. 2), K2O/Al2O3 versus Ga/Rb (Fig. 3), Fe/Mn versus Sr/Ba (Fig. 4), and Rb/Sr versus Sr/Cu (Fig. 5), and the triplot of Mg/Ca-Al/Mg-ΣREE (Fig. 6).

**3. Conclusions**

Two conclusions can be drawn from this work:

1) Numerous markers, including CIA, C.I, K2O/Al2O3, Al/Mg, Mg/Ca, Fe/Mn, Rb/Sr, Sr/Cu, Ga/Rb, Sr/Ba, ΣREE, and Eu anomaly, can be used to determine the paleoclimate of sediments.

2) The best approach for a more precise assessment of paleoclimate is to use discrimination diagrams such as the plots of K2O+Na2O+Al2O3 versus SiO2, CIA versus C.I, K2O/Al2O3 versus Ga/Rb, Fe/Mn versus Sr/Ba, Rb/Sr versus Sr/Cu, and Mg/Ca- Al/Mg-ΣREE.

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Fig. 1: Binary plot of Al2O3+K2O+Na2O vs. SiO2 (after Suttner and Dutta, 1986).



Fig. 2: Binary plot of CIA vs. C.I (after Nesbitt and Young, 1982; Ding et al., 2018; Awan et al., 2020).



Fig. 3: Binary plot of K2O/Al2O3 vs. Ga/Rb (after Roy and Roser, 2013a).



Fig. 4: Binary plot of Fe/Mn vs. Sr/Ba (after Dai et al., 2020; Yan et al., 2021).



Fig. 5: Binary plot of Rb/Sr vs. Sr/Cu (after Lerman, 1978; Zou et al., 2021).



Fig. 6: Triplot of Mg/Ca-Al/Mg-ΣREE (after Ma et al., 2021; Yan et al., 2021).

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