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Review article

Assessing Paleoclimate through Major and Trace Element Concentrations: 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

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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 [1-3]. (2) Fossil content [4-6]. (3) Chemical composition [7-9]. (4) Geophysical properties [10]. Elements and isotopes that record environmental data are among the geochemical markers [11,12]. 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 [13-17]. In this work, the authors reviewed methods for evaluating paleoclimate based on the concentration of major and trace elements.

Paleoclimate Markers

Chemical Index of Alteration

Numerous authors [e.g., 18 and 19] have extensively evaluated paleoclimatic conditions using the chemical index of alteration (CIA = $(Al_2O_3/(Al_2O_3+CaO^*+Na_2O+K_2O))100$, [20]). There are three methods to calculate the concentration of calcium oxide (CaO^*) in the silicate fraction:

(1) $CaO^* = CaO–CO_{2(calcite)}–0.5 \times CO_{2(dolomite)}–10/3 \times P_2O_{5(apatite)}$ [21].
(2) $CaO^* = CaO−P_2O_5$, if $Na_2O>CaO−P_2O_5$, or $CaO^* = Na_2O$, if $Na_2O<CaO−P_2O_5$ [22].
(3) $CaO^* = CaO–SO_{3(anhydrite/gypsum)}$ [23].

Arid, semi-arid to semi-humid, and humid climates are characterized by CIA values of <70%, 70-80%, and 80-100%, correspondingly [20]. [24] 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, [25] demonstrated a positive correlation between land surface temperatures and CIA on a global scale. The surface temperature can be ascertained using the following equation: $T(°C) = 0.56 \times CIA - 25.7$ [26]. 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 [26]. A correlation between CIA and mean annual precipitation (MAP) without K (CIA-K) was suggested by [27]: $MAP^{CIA\text{-}K} = 221e^{0.0197(CIA\text{-}K)}$. This correlation was modified by [28] as follows: $MAP^{CIA} = 169e^{0.0271(CIA)}$.

Climatic Index

The climatic index (C.I = (Fe+Mn+Cr+Ni+V+Co)/(Ca+Mg+Sr+Ba+K+Na), [15]) 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 [7 and 15]. 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 [8 and 29].

K_2O/Al_2O_3 Ratio

Feldspars and clay minerals can be distinguished using the K_2O/Al_2O_3 ratio. Feldspars have a higher ratio (0.3-0.9) compared to clay minerals (0-0.3, [30]). Furthermore, the ratio in illite (0.2-0.3, [31]) is higher than that in kaolinite, smectite, and vermiculite (nearly zero, [30]). Accordingly, humid conditions are characterized by low K_2O/Al_2O_3 ratios (<0.2), while the ratios are high in arid climates (>0.2, [32]).

Fe/Mn Ratio

The Fe/Mn ratio can be used to provide paleoclimatic evidence [33 and 34]. 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) [33].

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 [33].

Mg/Ca Ratio

The Mg/Ca ratio is frequently used as a paleoclimate proxy in clastic rocks [33 and 35]. High ratios are generally indicative of arid climates, whereas low ratios are characteristically reflective of humid climates [33].

Rb/Sr Ratio

The Rb/Sr ratio is a significant index of paleoclimate [36]. 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) [36].

Sr/Cu Ratio

Paleoclimate studies have used the Sr/Cu ratio as a reliable indicator [37]. 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 [37].

Ga/Rb ratio

The paleoclimate system is often constrained by the Ga/Rb ratio [32]. In general, Ga is more abundant in kaolinite, suggesting humid conditions, whereas Rb is more commonly found in illite, signifying an arid environment [38]. Consequently, the Ga/Rb ratio is high in humid conditions (>0.21), while arid climates show low ratios (<0.21) [32].

Sr/Ba Ratio
Paleoclimate can be assessed based on the Sr/Ba ratio [34 and 39]. Climate has an impact on the Sr/Ba ratio; high ratios (>1) represent arid conditions, while low ratios (<1) indicate humid climates [39].

Rare Earth Elements
REE are very sensitive to variations in the paleoclimate [40-42]. The most important parameters are ΣREE [42] and Eu anomaly [40]. Eu anomaly can be calculated using the following equation: $Eu_{found}/Eu^*_{expected} = Eu_N/(Sm_N \times Gd_N)^{0.5}$. The REE values used in this equation are shale normalized. For normalization, the Post Archean Australian Shale (PAAS, [43]) and the North American Shale Composite (NASC, [44]) are utilized. Generally, humid climates display high ΣREE [42] and large negative Eu anomaly [40]. According to [41], weak weathering of REE-bearing minerals would result in weak secondary LREE-carrying product development and a drop in the $(La/Yb)_N$ ratio.

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 K_2O+Na_2O+Al_2O_3 versus SiO_2 (Fig. 1), CIA versus C.I (Fig. 2), K_2O/Al_2O_3 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).

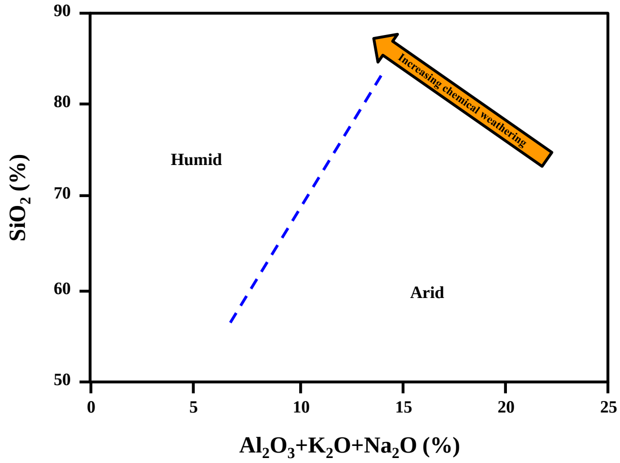

Figure 1. Binary plot of CIA vs. C.I [after 8, 20, and 29].

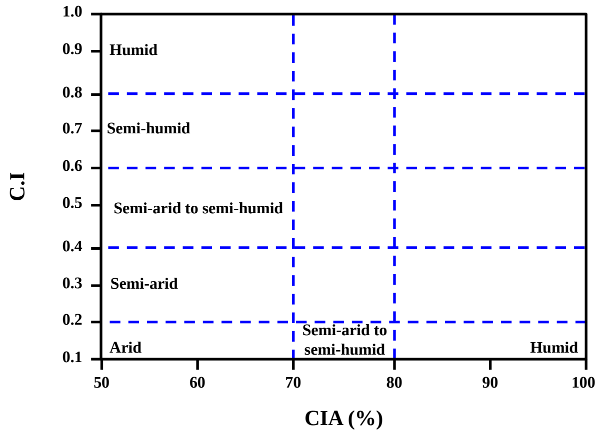

Figure 2. Binary plot of CIA vs. C.I [after 8, 20, and 29].

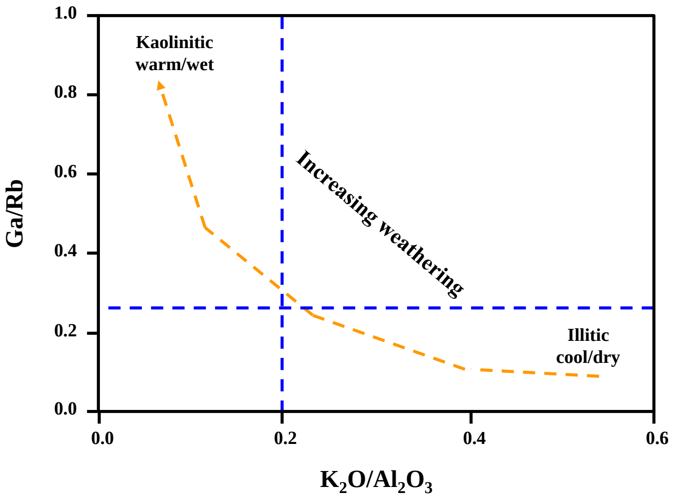

Figure 3. Binary plot of K2O/Al2O3 vs. Ga/Rb [32].

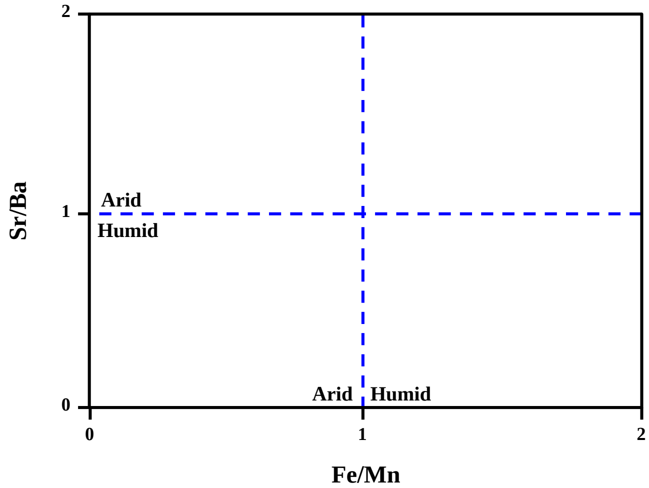

Figure 4. Binary plot of Fe/Mn vs. Sr/Ba [after 33 and 39].

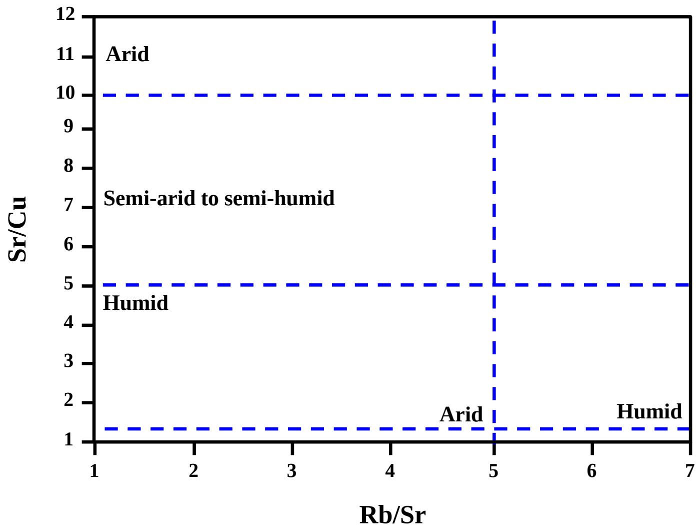

Figure 5. Binary plot of Rb/Sr vs. Sr/Cu [after 36 and 37].

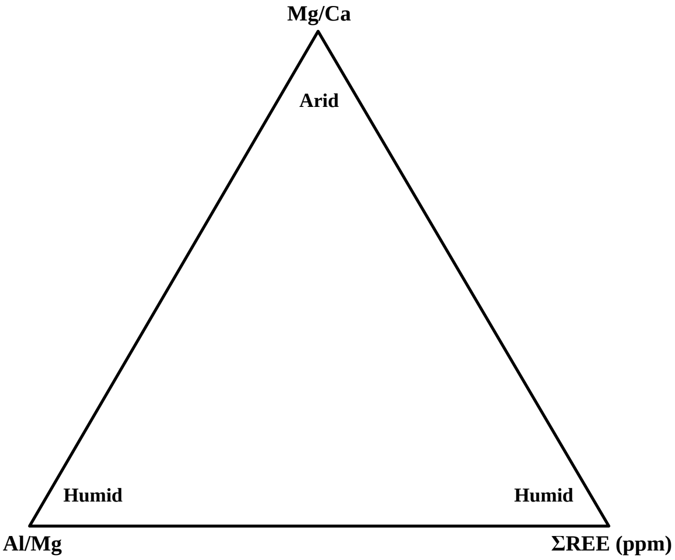

Figure 6. Triplot of Mg/Ca-Al/Mg-ΣREE [after 33 and 42].

CONCLUSION

Two conclusions can be drawn from this work: (1) Numerous markers, including CIA, C.I, K_2O/Al_2O_3, 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 $K_2O+Na_2O+Al_2O_3$ versus SiO_2, CIA versus C.I, K_2O/Al_2O_3 versus Ga/Rb, Fe/Mn versus Sr/Ba, Rb/Sr versus Sr/Cu, and Mg/Ca- Al/Mg-ΣREE.

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تقييم المناخ القديم من خلال تركيزات العناصر الرئيسية والعناصر النزرة: مراجعة

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الملخص
في علم الأرض، من الممكن استنتاج المناخ القديم للرواسب من خلال خصائصها الصخرية أو محتواها الأحفوري أو تركيبها الكيميائي أو خصائصها الجيوفيزيائية. في هذه الورقة، استعرض المؤلف استخدام تركيز العناصر الرئيسية والعناصر النزرة لاستنتاج المناخ القديم. لهذا الغرض، تم استخدام مجموعة متنوعة من العلامات في الدراسات السابقة، مثل **CIA** و **C.I** و **K2O/Al2O3** و **Al/Mg** و **Mg/Ca** و **Fe/Mn** و **Rb/Sr** و **Sr/Cu** و **Ga/Rb** و **Sr/Ba** و **ΣREE** وشذوذ **Eu.** تجدر الإشارة إلى أنه من أجل تقييم أكثر دقة للمناخ القديم، فإن مخططات التمييز (مخططات **K2O+Na2O+Al2O3** مقابل **SiO2** ، و **CIA** مقابل **C.I** ، و **K2O/Al2O3** مقابل **Ga/Rb** ، و **Fe/Mn** مقابل **Sr/Ba**، و **Rb/Sr** مقابل **Sr/Cu** ، و **Mg/Ca-Al/Mg-ΣREE)** هي التقنية الموصى بها

الكلمات المفتاحية. المناخ القديم، العناصر الرئيسية، العناصر النزرة.