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Citation for final published version:

Al Bahri, Jalila, Bankole, Olabode, Muir, Duncan, El Albani, Abderrazzak, Oldroyd, Anthony, Contreras, Diana, Andersen, Morten and Chi Fru, Ernest 2024. Clay mineral geochemistry and paleoenvironmental reconstruction across the Cryogenian Sturtian Snowball glaciation. *Precambrian Research* 410 , 107498. 10.1016/j.precamres.2024.107498

Publishers page: <http://dx.doi.org/10.1016/j.precamres.2024.107498>

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**Clay mineral geochemistry and paleoenvironmental reconstruction across the
Cryogenian Sturtian Snowball glaciation**

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Highlights

Clay mineralogy reflects climatic conditions before, during and after the Sturtian Snowball Earth glaciation.

Detrital and diagenetic illite is common across all three climatic intervals.

Predominance of detrital chlorite in the glaciogenic tillites plus weak chemical weathering of source rocks is consistent with strong continental erosion by melting ice sheets.

Detrital clay minerals modulated nutrient supply to marginal seawater across the Sturtian Snowball Earth glaciation.

Abstract

Recent evidence from marine sedimentary rocks suggests that clay minerals were important in the supply of bioessential nutrients to seawater at the end of the Sturtian Snowball Earth glaciation that occurred ~717-660 million years ago. However, little is known about the identity of these clay minerals, their abundance and distribution in the pre-glacial, glacial and post-glacial deposits. Here, high resolution petrographic scanning electron microscopy-energy dispersive x-ray spectroscopy, combined with bulk and <2 μ clay-size fraction X-ray diffraction mineralogical analysis and trace and major element geochemistry, point to dominant enrichment of illite in shallow marine platform sediments preserved across Sturtian Snowball Earth facies on Islay and the Garvellachs Island, Scotland. The glacial till is enriched with detrital chlorite, while pore-filling authigenic kaolinite is observed in the pre-glacial and post-glacial greenhouse facies, but scarce in the glaciogenic tillites. Discriminant binary plots of Th/Sc vs Zr/Sc ratios, indicative of insignificant modification of primary sediment composition by hydraulic sorting and recycling processes, together with chemical weathering indices, point to moderate to intense chemical weathering of the pre-glacial and post-glacial source rocks. Low Chemical Index of Alteration (CIA) values, coupled to the distinct chlorite composition of the glacial till, is consistent with mechanical tillage of continental landmass by the terminal Snowball melting ice sheets. The moderate to intense chemical weathering indices in the pre- and post-glacial deposits correspond with greenhouse conditions of elevated atmospheric CO₂ content and temperature. Overall, the predominantly detrital origin of the clay minerals implies enhanced post-glacial nutrient supply bound to clay minerals in lower pH river water during transportation, followed by release in higher pH saline seawater.

Key words: Weathering; tillites; Neoproterozoic; nutrients; climate

1. Introduction

Clay mineral assemblages preserved in ancient and modern sedimentary rocks are commonly used as proxies for paleo-environmental reconstruction due to their ability to record sediment and fluid histories during geological processes, including transport, deposition and post-depositional modification by diagenesis and metamorphism (Singer, 1980; Bristow et al., 2009; Ngombi-Pemba et al., 2014; Wallmann et al., 2023). While primary detrital clays are important tracers of provenance and pre-depositional sedimentary drivers (Baldermann et al., 2020), secondary diagenetic clays are excellent for tracking post-depositional changes associated with chemical, physical and fluid modification of the primary sediments (Baldermann et al., 2015; Isson and Planavsky, 2018; Isson & Rauzi, 2024). Further, detrital clays have been proposed as key vectors of bioessential nutrients to seawater (e.g., Hao et al., 2020; Hao et al., 2021a; Chi Fru et al., 2023), suggesting that marine sedimentary clay minerals may represent critical archives of past seawater nutrient budgets, with direct implications for reconstructing marine primary productivity, ocean-atmosphere oxygenation and climate perturbations (Hao et al., 2021a; Chi Fru et al., 2023; Krause et al., 2023).

Clay minerals are the products of weathering and soil formation processes, and are strongly associated with biological activity, but with less contribution from soil and biological activity during Precambrian times because of limited land colonisation by life. It is therefore thought that in modern soils, life is central to clay mineral production through promoting weathering, the elevation of ionic pore water fluid chemistry, enhancement of soil water retention capacity and the production of organic acids and chelating ligands (Singer, 1979; Rafiei and Kennedy, 2019). Geological marine records are usually more or less altered during post-burial diagenesis and metamorphism, requiring an assessment of these effects on primary sedimentary signals before any information about paleoenvironment or paleoclimate conditions can be deduced from such data, especially in the clay-fraction assemblage (Thiry, 2000). The use of clay minerals as paleoclimatic and provenance proxies is based on the assumption that they are conservatively delivered into the basin without undergoing any significant modifications after deposition. However, the change in the physio-chemical conditions, temperature, pressure, and other kinetically controlled processes immediately after sediment deposition may trigger chemical, structural, and physical changes in detrital clay minerals and pseudomorphic or direct recrystallization of new ones during sediment burial.

Here, ‘clay minerals’ are defined as hydrated phyllosilicates of any size often formed by silicate mineral weathering (Berner and Berner, 2004; Warr, 2022). Once formed, clay minerals modulate aqueous bioessential ion concentrations due to their varying cation exchange capacity

and pH-dependent surface charge area affinity for trace elements (Garrels and Mackenzie, 1971; Froelich, 1988; Berner and Berner, 2004; Gerard, 2016; Hao et al., 2019, 2021a; Baldermann et al., 2022; Warr, 2022). For example, clay minerals have been shown to regulate the seawater content of bioessential phosphorus (P) and the concentration of various redox sensitive trace metals and metalloids (e.g., Violante and Pigna, 2002; Hao et al., 2020; Hao et al., 2021a, 2021b; Chi Fru et al., 2023). In addition, clay composition and abundance influence the burial efficiency of organic carbon in continental margin platforms (Tosca et al., 2010; Kennedy and Wagner, 2011; Keil and Mayer, 2014), again pointing to their importance as archives of past seawater biogeochemical elemental cycles and ocean-atmosphere redox history (e.g., Frei et al., 2009; Jeandel and Oelkers, 2015; Chi Fru et al., 2016, 2019; Ramos et al., 2018; Abbott et al., 2019; Hao et al., 2021a; Baldermann et al., 2022; Wei et al., 2024) and climate (Warr, 2022; Krause et al., 2023;).

From modern evidence, sedimentary clay minerals inherited from weathered parent rocks and soils constitute up to 8.6% of the total clay mineral inventory on the modern Earth, where they are deposited primarily through detrital inheritance (Warr, 2022). In contrast, authigenic clays are formed either by direct precipitation from solution in sediment pore spaces or from the replacement of precursor detrital minerals during and after sediment burial (Furquim et al., 2008). Authigenic clays can also be formed *in situ* by ‘reverse silicate weathering’ within the sedimentary basin, often present as sediment pore-lining filling material (Isson and Planavsky, 2018). Nonetheless, the large reservoir of clay minerals, making up to 12.9 wt.% of the upper continental crust, UCC (Warr, 2022), suggests that marine sediments represent a significant sink when this material is eroded on land and delivered by riverine detritus to continental margin seawater.

Physical erosion of continental land mass by melting glaciers (Bland and Rolls, 2016) forms glacial till or tillites composed of grains of various sizes of the same mineralogical and chemical composition as the parent rocks. Chemical weathering on the other hand, which often correlates with the amount of CO₂ in the atmosphere and temperature (Isson et al., 2020; Kump et al., 2000; Krause et al., 2023), dissolves and transforms rock silicates to more stable minerals like clays under surface conditions (Fedo et al., 1995), with the resulting chemical leaching producing Al-rich clays like kaolinite and gibbsite (Tosca et al., 2010). During this process, mobile alkali and alkaline earth metals such as Na, K, Ca and Mg as well as bioessential and redox sensitive elements like P, Ni, Co, Cu, Mo, V, As and Cr are dissolved from the parent rock matrix to form soluble aqueous ions, while immobile elements like Al, Ti, Sc, Zr, Hf, Th,

Y, and various REEs are retained in the solid parent residue (e.g., Tosca et al., 2010; Fedo et al., 1995).

In oxidising conditions, ferrous (Fe^{2+}) Fe is oxidised to solid phase Fe oxyhydr(oxides) and incorporated with the clay minerals. Based on these predictable behaviours, several weathering indices have been developed (e.g., Nesbitt and Young, 1984; Fedo et al., 1995; Fedo and Babechuk, 2023) to track variations in chemical weathering intensities in fine-grained sedimentary rocks and as proxies for inferring deep-time climate dynamics (e.g., Rieu et al., 2007) and environmental redox histories (e.g., Tribovillard et al., 2006). However, the Chemical Index of Alteration (CIA), which considers the distribution of poorly mobile Al relative to mobile Ca, Na and K in sediments, is the most widely applied measure for constraining the degree of chemical weathering associated with sedimentary deposits (Nesbitt and Young, 1982; Rieu et al., 2007; Wei et al., 2020; Fedo and Babechuk, 2023).

Of particular relevance, the Neoproterozoic Earth witnessed major global glaciations that may have covered the Earth with kilometre-thick ice sheets from pole to pole (Hoffman et al., 1998, 2017). As the landmass is protected by a thick ice sheet cover from atmospheric agents of chemical weathering, such icy conditions that lasted millions of years are thought to severely curtail chemical weathering rates. Consequently, marine sediments deposited at this time are expected to contain weak CIA values relative to greenhouse intervals. This would also have affected type of clay formation, nutrient supply to seawater and by extension redox variation and ocean-atmosphere oxygen content (Planavsky et al., 2010; Brocks et al., 2017; Chi Fru et al., 2023). Gaining insights into Cryogenian clay mineralogy and geochemistry is therefore crucial for high-resolution reconstruction of a broad range of environmental processes in which the Cryogenian world operated, including deciphering proposed connections to post-glacial nutrient enrichment dynamics and relevance to the Neoproterozoic rise of atmospheric oxygen content and the emergence of metazoan life.

This paper couples high-resolution clay mineralogy and geochemistry to interpret paleoenvironmental conditions across the Cryogenian Sturtian Snowball Earth. A detailed understanding of clay composition, mineralogy and abundance, coupled to geochemistry and formation mechanism, is investigated to explore principal pathways for nutrient supply to seawater before, during, and after the Sturtian Snowball glaciation – the first of two major Neoproterozoic Snowball glaciations, lasting from ~717 to 660 million years ago (Ma) (Hoffman et al., 1998, 2017).

2. Geological setting

The Cryogenian samples studied here belong to the same set reported in Chi Fru et al. (2023). They correspond to well-described shallow marine sedimentary rocks deposited before, during and after the melting phase of the Sturtian Snowball glaciation on the Isles of Islay and the Garvellachs, Scotland (e.g., Prave et al., 2009; Rooney et al., 2011; Sawaki et al., 2010; Arnaud et al., 2011; Tanner et al., 2013; Parnell and Boyce, 2017; Fairchild et al., 2018; Shuster et al., 2018). As part of the Dalradian Supergroup, the sampled section is subdivided into the Grampian, Appin and Argyll groups (Fig. 1). The Appin and Argyll group sediments formed on the palaeo-ocean continental shelf margin and later in the open ocean, with a shift in depositional style linked to the initial rifting of the Rodinia supercontinent at ~840 Ma and the opening of the Iapetus Ocean shortly after 600 Ma (Tanner et al., 2013; Parnell and Boyce, 2017; Fairchild et al., 2018; Shuster et al., 2018). The studied interval includes the Tonian Lossit Limestone Formation (LLF), belonging to the 4 km thick Appin Group and precipitated from warm tropical shallow marine waters (Fairchild et al., 2018). The LLF contains organic-rich mudstones, sandstones and a variety of carbonate lithologies with some hosting stromatolites. The upper layer is part of the overlying 1.1 km-thick Port Askaig Tillite Formation (PATF) associated with the melting stages of the Sturtian Snowball glaciations. The PATF comprises a sequence of alternating layers of coarse-grained and poorly sorted diamictite or tillites interbedded with sandstone, mudstone, conglomerate and megaclast. The overlying post-glacial Bonahaven Dolomite Formation (BDF) consists of an estimated 300 m-thick fine-grained clastic sequence made up predominantly of dolostones and evaporite minerals (Prave et al., 2009; Sawaki et al., 2010; Arnaud et al., 2011; Tanner et al., 2013; Parnell and Boyce, 2017; Fairchild et al., 2018; Shuster et al., 2018).

3. Materials and methods

3.1. Sample collection and preparation

The location, stratigraphy and lithologies of the sampled outcrop are described in Figure 1, and as mentioned above, belong to the sample set analysed in Chi Fru et al. (2023). Before sampling, weathered and metamorphosed lithologies were carefully screened in the field, while the outer exposed parts of selected samples were chipped off with a saw prior to geochemical and mineralogical analyses. A portion of the fresh surface rocks was milled into fine powder for geochemical and mineralogical analyses using standard methods. Polished thin sections of selected samples were prepared from slices of the whole rock samples for mineralogical and

textural observations with a scanning electron microscope (SEM) coupled with a -energy dispersive spectrometer (EDS).

3.2. X-Ray Diffraction (XRD) analysis

XRD analysis on whole rock samples and the 2- μm clay fraction was conducted in the X-Ray Diffraction Laboratory in the School of Earth and Environmental Sciences, Cardiff University with a Philips PW1710 Automated diffractometer and a Bruker D8 ADVANCE diffractometer at the Institute de Chimie des Milieux et Matériaux de Poitiers (IC2MP), University of Poitiers, France. The samples were analysed with an automatic divergence slit and a Cu-K α radiation at 35 kV and 40 mA. For the whole rock analysis, the powdered samples were packed into aluminium holders, and analysed between 2 and 70 $^{\circ}2\theta$ angular range at a scan speed of 0.04 $^{\circ}2\theta/\text{s}$. The <2 μm clay-size fraction was separated by sedimentation and centrifugation at 20 $^{\circ}\text{C}$ with a Sorvall LEGEND XRF centrifuge at a rotating speed of 1000 rpm for 2 minutes 30 seconds at the University of Poitiers. Oriented mounts of the <2 μm fractions were prepared by settling on glass slides and analysed after air-drying (AD) at room temperature overnight and after saturation with ethylene-glycol (EG). The oriented AD and EG mounts were scanned from 2 $^{\circ}$ to 35 $^{\circ}$ 2θ angular range at a scan speed of 0.02 $^{\circ}2\theta/3\text{s}$. The minerals were identified based on their principal peak positions and comparison with International Centre for Diffraction Data (ICDD) files (Moore and Reynolds Jr, 1989) using X'pert Highs core software. Semi-quantitative analyses of the relative abundance of the mineral assemblages were made using the area ratios of the principal peaks after decomposition by the Fityk program (Wojdyr, 2010).

3.3. Scanning electron microscopy (SEM)

Samples were further characterised by SEM-EDS for detailed mineral mappings, mineral chemistry, and textural relationships to distinguish detrital and authigenic mineral phases. Polished thin sections of selected samples were prepared using diamond saws following standard preparation techniques for producing 48 $\times$ 28mm polished thin sections. The polished thin-sections were then carbon-coated to a thickness of $\sim$ 14 nm with BIO-RAD SC5 and examined in back-scattered electron (BSE) imaging mode using a high-resolution FEI-XL30 field emission SEM fitted with an EDS detector at Cardiff University. Mineral mapping and semi-quantitative EDS chemical analyses were performed at 15 kV accelerating voltage, probe current of 1 nA, 50 s counting time and 8.9 mm working distance.

Mineral identification was achieved by a combination of morphology, shape, elemental composition, comparison of EDS spectra against references for known mineral standards and by independent XRD-based mineral identification following the approach of Reed (2005). In general, coarse (sub)angular particles such as mica, quartz and feldspar with discrete grain boundaries characteristic of physical transportation were classified as primary minerals. Secondary, diagenetic and neoformed minerals were identified by their hairy, fibrous morphology in the case of illite and chlorite, blocky kaolinite, and as randomly oriented intergranular and intragranular pore space fillings (Rafiei et al., 2020).

3.4. Bulk rock geochemical analysis

The bulk major and trace element compositions in the samples were performed at the *Pôle Spectrométrie Océan, Institut Universitaire Européen de la Mer* (PSO/IUEM) Brest, France, following the analytical procedure of Cotten et al. (1995). About 250 mg of powdered samples were dissolved with concentrated 3 ml 40% HF, 3 ml 32% HCl and 1 ml of 65% HNO₃ in screw-capped Teflon Savillex vessels at 90°C for 24 hrs. The excess HF in the aliquots was neutralised with 93 ml 20 g/L H₃BO₃ aqueous solution. The major elements were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and the trace elements by inductively coupled plasma mass spectroscopy (ICP-MS) on a Horiba Jobin Yvon® Ultima 2 spectrometer with a boron solution as internal standard. The solutions were calibrated with ACE, JB2, and WSE international standards and the relative standard deviation was estimated to be ≤1% for SiO₂ ≤2% for the major elements and ≤5% for the trace elements.

The degree of chemical weathering, expressed by the chemical index of alternation [CIA = $\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO}^*) \times 100$], where elemental abundances are expressed in molar proportions, was calculated assuming CaO* represents the amount of CaO associated with silicate minerals (Nesbitt and Young, 1984; Fedo et al., 1995). First, we corrected for CaO in apatite as $\text{CaO}^+ = \text{CaO} - \frac{10}{3} \times \text{P}_2\text{O}_5$ and we assumed that moles of silicate $\text{CaO}^* = \text{Na}_2\text{O}$ if $\text{CaO}^+ > \text{Na}_2\text{O}$ and $\text{CaO}^* = \text{CaO}^+$ if $\text{CaO}^+ \leq \text{Na}_2\text{O}$ to correct for CaO in carbonates (McLennan et al., 1993; Fedo et al., 1995; Jian et al., 2013; Fedo and Babechuk, 2023). Typically, unweathered to weakly weathered rocks associated with cold/dry temperate climates have CIA values of ~50%, moderately weathered rocks between 60-80% and highly weathered rocks linked to humid/warm tropical climates being >80% (Nesbitt and Young, 1984; Fedo et al.,

1995). The calculated CIA values were visualised on the $\text{Al}_2\text{O}_3 - (\text{CaO}^* + \text{Na}_2\text{O}) - \text{K}_2\text{O}$ ternary diagram (A-CN-K) to monitor the addition of K during weathering and/or illitization (Fedo et al., 1995; Fedo and Babechuk, 2023).

4. Results

4.1. Bulk-Rock Mineralogy

The bulk XRD mineralogical and SEM-EDS mineral data indicate that non-clay minerals are mainly composed of quartz, feldspar (K-feldspar and albite), muscovite, carbonate dolomite and calcite, while illite, kaolinite and chlorite are the main clay minerals (Figs. 2-4a & Tables S1, S2). The framework detrital grains in the pre-Sturtian Snowball facies are composed of poorly to moderately sorted subangular to subrounded $>10\ \mu\text{m}$ quartz and feldspar grains dispersed in a dominant dolomite cement (Figs. 2a & 3a). The overlying tillites are dominated by poorly sorted fine-grained quartz, albite, and platy micaceous muscovite and biotite within illitic matrix and Fe/Mg-rich dolomite cement, with occasional pore-filling framboidal to subhedral/euhedral pyrite crystals, together with Fe-rich clay minerals (Figs. 2b, 3b & S1a-b). Disseminated magnetite grains are observed in a few of the mudstones up section of the immediate post-Sturtian Snowball interval (Figs. 2c, 3c & S1c-d). The upper part of the post-Sturtian Snowball (late post-Snowball) mudstones consist mainly of fine-grained quartz dispersed in illite and a carbonate (calcite and dolomite) dominated matrix (Figs. 2c-d & 3c-d). Hematite occurs in a few pre-/post-Snowball samples as well as trace amounts of magnetite (Figs. 3c; Table S1).

The bulk XRD data show that quartz is the dominant mineral in most of the samples. It is present across the whole section with concentrations varying from 2.0 to 93.0 wt.%, whereas feldspars (Na-/Ca-rich plagioclases and alkali feldspar minerals) and K-rich muscovite, although prevalent, are absent in some samples (Fig. 4a & Tables S1, S2). The Na-rich plagioclase (albite) is common across all three climatic intervals compared to the Ca-rich plagioclase (anorthite) that is detected in only one pre-Snowball sample (Fig. 4a & Table S1). Trace amounts of microcline is the main alkali K-feldspar in most of the samples, while orthoclase was identified in one post-Snowball sample (Table S1). Muscovite, the dominant platy micaceous mineral, is present across the studied section, with averages of 2.8 wt.%, 1.0 wt.% and 0.9 wt.% in the studied post-Snowball, tillite and pre-Snowball samples, respectively (Fig. 2-4a & Table S2), while biotite is common only in the tillite facies (Fig. 3b). Carbonate minerals, mostly present as dolomite and as calcite in a few instances (Figs. 2-4a), predominate the pre-Snowball and late post-Snowball successions compared to the immediate post-

Snowball lithologies. The amount of carbonate minerals is significantly lower in the tillites compared to the overlying and underlying post-Snowball and pre-Snowball samples, respectively (Figs. 2 & 4a). Dolomite in the tillites is Fe/Mg-rich, with the Fe-rich variety being the most common, while EDS analysis show that dolomite in the pre-Snowball and late post-Snowball successions is mainly non-ferroan (Fig. S1b). Illite was observed in varying amounts across all the three distinct climatic intervals with an average of 0.63 wt.% (n=8), 1.75 wt.% (n=4), and 2.1 wt.% (n=10) in the post-Snowball, tillite and pre-Snowball samples, respectively (Fig. 4a). Kaolinite makes up 0.25 wt.%, 0.75 wt.% and 0.7 wt.% of analysed post-Snowball, tillite and pre-Snowball samples, respectively (Fig. 4a & Table S2). Combined, clay minerals constitute up to 3.68 wt.%, 3.5 wt.% and 3.7 wt.% in the post-Snowball, tillite and pre-Snowball facies, respectively, which are significantly lower than the estimated global 8.6 wt.% inventory for the modern oceanic crust and sediments (Warr, 2022).

4.2. Bulk rock geochemistry

Bulk SiO₂, Fe₂O₃, K₂O, MgO, CaO, P₂O₅ and MnO concentrations (Fig. 4b-e and Tables S3 & S4), major elements considered essential to clay mineral formation and distribution, generally track average upper continental crust (UCC) trends (Fig. S2). Sustained enrichment of SiO₂, Fe₂O₃, K₂O and P₂O₅ in the tillite and immediate post-Snowball samples, is counterbalanced by a persistent MgO and CaO decline across this interval (Fig. 4b-e). The corresponding Ni, V, Cr and Co trace element concentrations display multiple peaks along the studied succession, recording sustained enrichment across the tillite-immediate post-Snowball interval (Fig. 4f-g). Comparative bivariate plots and Pearson correlation analysis indicate that Al₂O₃ correlates positively with SiO₂, Fe₂O₃, TiO₂, K₂O, Na₂O, P₂O₅, V, Ni and Cr and K₂O with V, Ni and Cr concentrations, suggesting the dominant control and supply of these elements by associated detrital silicate minerals (Figs. 5-6 & Table S5), including clays, micas, and feldspars into the basin. However, MgO, CaO and MnO display negative correlations with Al₂O₃, indicating likely enrichment by the non-silicate carbonate minerals that are of a chemical rather than detrital origin. Bioessential V, Cr, Ni and Co display strong positive correlations with the detrital indicators TiO₂ and Al₂O₃, including Fe₂O₃ and negative correlations with MgO, CaO and MnO, especially for the pre-/late post-Snowball samples (Table S5).

These bioessential and/or redox sensitive trace metals also correlate positively with P₂O₅ in the pre-/late post-Snowball samples, except for Co in the late post-Snowball interval. V is positively correlated with TiO₂ and Fe₂O₃, Cr with Al₂O₃ and TiO₂ and Co with Al₂O₃ in the immediate post-Snowball samples. A weak positive correlation is observed for V and Ni,

together with a strong negative correlation for Cr and Co with P_2O_5 in the immediate post-Snowball interval. In the tillites V and Ni, together with redox sensitive Cr, are positively correlated with TiO_2 and Fe_2O_3 . While Co is not correlated to these major elements in the tillites and with Al_2O_3 , a stronger positive association is instead suggested with MgO and CaO (Table S5) and mainly V and Cr show a strong positive correlation with P_2O_5 in the tillites. Further, the strong Pearson linear correlation of these trace elements with K_2O in the pre-/late post-Snowball interval suggests a potential association with K-rich illitic phases as shown in Figure 6.

The calculated CIA values for the studied samples range from 44-92, 42- 59, 62-64 and 51-66 for pre-Snowball, tillite, immediate post-Snowball and the late post-Snowball intervals, respectively (Figs. 4h, 7 & Table S3).

4.3. Clay mineralogy and chemistry

SEM-EDS and XRD analysis of the $<2\ \mu m$ clay-sized fractions corroborate the bulk XRD analysis, showing illite, chlorite and kaolinite as the main clay minerals in the studied samples (Fig. 8 & Table S6). Our SEM results demonstrate persistent occurrence of detrital and authigenic clay minerals formed mainly by diagenetic transformation of detrital minerals in the studied samples (Fig. 9). Minor neoformed authigenic clays, precipitated either directly from seawater or porewater, were detected for some clay minerals such as kaolinite (Figs. 9g & S3). Illite, identified by its characteristic basal $9.97\ \text{\AA}$ (001) and $4.99\ \text{\AA}$ (002) peaks is unaffected by ethylene glycol treatment (Fig. 8). The symmetrical and Gaussian shape of the peaks in both the air-dried and ethylene glycol treatment indicate dominance of well crystallised illite and the absence of smectite and illite-smectite mixed layers in the samples (Fig. 8). The characterized detrital and diagenetic clay minerals, together with their EDS spectra are shown in Figure 9 & 10. These observations show that illite is present either as pore filling or diagenetic replacement of detrital muscovite and K-feldspar grains (Figs. 9 & S4). Particularly, the occurrence of flaky and well-crystallised tiny micaceous materials, point to the presence of detrital illite in the samples (Fig. 9). These well crystallised illitic minerals have well-defined boundaries and elongated crystal shapes with no preferred direction or orientation (Figs. 9e & S4). The detrital illite phase is marked by a distinct higher enrichment of Al compared to the authigenic illite phase (Table S7) and they all fall in the illite field on the $4Si-M^+-R^{2+}$ chemographic projection (Fig. 11a).

Chlorite is identified by its characteristic $14.2\text{\AA}$ (001), $7.10\text{\AA}$ (002), $4.74\text{\AA}$ (003), and $3.55\text{\AA}$ (004) peaks, which are equally unaffected by ethylene glycol treatment (Fig. 8). Chlorite

is observed mainly in both the glaciogenic tillites at the top of the LLF and the overlying PATF in the tillite succession (Fig. 8b). The higher intensities of the even 002 and 004 peaks compared to the odd 001 and 003 peaks (Fig. 8b) suggests the dominance of Fe(II)-rich chlorites (Moore and Reynolds, 1989) in the tillites. Chlorites are present mainly in the tillite samples filling the pore spaces and along the cleavages of biotite as a pseudomorphic replacement mineral as well as well-crystallised discrete detrital particles with well-defined boundaries dispersed within matrix (Fig. 9f).

EDS point chemical analyses show that the pore filling, grain replacement, and detrital chlorites are Fe-rich and have similar composition with Fe/(Fe+Mg) ratios >0.3 (Fig. 11b) and they all plot in the chlorite field on the 4Si-M⁺-R²⁺ chemographic projection (Fig. 11a; Meunier and Velde, 2004). Kaolinite was identified by its 7.16Å (001) and 3.58Å (002) peaks that were also unaffected by ethylene glycol treatment (Fig. 8). Kaolinite sparsely occurs in some of the PATF tillites overlying the LLF, in the pre-Snowball and post-Snowball lithologies (Figs. 4a), defined by its booklet morphologies and EDS spectra, filling both primary and secondary pores of dissolving detrital grains (Figs. 9g & 3S).

5. Discussion

5.1. Post-depositional mineral alteration and preservation of primary signatures

The abundance of detrital framework grains and micaceous minerals indicate the samples analysed in this study are largely composed of continental detritus (Figs. 2-4a & Fig. 9). However, the presence of dissolving detrital minerals (e.g., feldspars), filling of primary and secondary pores by authigenic carbonates and diagenetic clay minerals (Figs. 2 & 9), and pseudomorphic replacements of muscovite and biotite along their cleavages by illite and chlorite, respectively (Fig. 9), demonstrate that the sediments have undergone some degree of post-depositional diagenetic modifications.

The occurrence of pyrite in the tillite and post-Sturtian samples is associated with high continental silicate weathering, which drives up the concentration of (Fe²⁺) ferrous Fe (Parnell and Boyce, 2017). When combined with sulphide produced by the metabolic respiration of sulphate by the sulphate-reducing microorganisms, dissolved ferrous Fe is transformed to pyrite in anoxic bottom waters/sediment pore water settings (Hoffman et al., 2017; Parnell and Boyce, 2017; Wei et al., 2020). Therefore, the observed framboidal pyrite grains in the tillite samples are probably an early diagenetic mineral phase. Pyrite framboids (Fig. S1a) precipitate when both dissolved Fe²⁺ and Fe mono-sulphides are supersaturated in pore waters, while euhedral pyrite (Fig. S1a) is formed in pyrite oversaturated and Fe monosulphide

undersaturated pore waters, during early diagenesis (Roberts and Turner, 1993; Rickard, 1997). The overgrowth of magnetite grains in some instances on pyrite grains suggests that in some cases, diagenetic magnetite formed from the oxidative weathering of pre-existing pyrite grains in the immediate post-Snowball interval (Fig. S1d). Iron-rich and Fe-poor (non-ferroan) dolomite cement, a common feature in Neoproterozoic sedimentary deposits (Hood et al., 2011), occurs locally as rhombic crystals (Figs. S1b) in primary pore spaces, indicating that they precipitated directly from seawater and/or pore water fluids. Contact with meteoric water may lead to the dissolution and re-precipitation of secondary Fe-rich dolomite carbonate phases (Stern and Miller, 2021).

However, the bulk composition of dolomite in the non-tillite samples is Fe-poor. The non-ferroan dolomite is thus suggested to pre-date the Fe-rich equivalent. During deglaciation, intense weathering of lithogenic silicates, by up to ~350 times more carbon dioxide present in the atmosphere at the end of Snowball Earth glaciations (Fabre and Berger, 2012; Huang et al., 2016), would have promoted the rapid precipitation of carbonate minerals in the post-Sturtian Snowball ocean (Fairchild and Spiro, 1990; Hoffman et al., 2017). This is depicted in the sedimentary record as cap carbonates (Hood et al., 2021) that usually overly the tillites formed during the deglaciating phase. In Scotland, although present, the carbonate content in the immediate post-Sturtian Snowball is sparse before intensifying up section. Recently, it was revealed that siliciclastic deposits overlying Sturtian Snowball tillites, are indicative of post-Snowball intense chemical weathering of continental rocks resulting in marine precipitation of quartz (Zhu et al., 2024). Similarly, the immediate post-Snowball samples investigated in this study are dominated by quartz, with a distinct subordinate carbonate content (Fig. 4a). The low carbonate-high quartz concentration in the immediate post-Snowball interval, is therefore likely coupled to increased continental silicate weathering leading to initial preferential quartz precipitation (Zhu et al., 2023), before switching to enhanced marine carbonate deposition up sequence.

Although it is difficult to establish the timing of dolomitisation with certainty, its massive filling of pore spaces and presence between detrital grains suggests direct precipitation from seawater during early diagenesis (Tucker, 1982). This is consistent with suggestions that dolomite in Precambrian sediments is generally the result of primary marine dolomitisation (e.g., Hood and Wallace, 2014; Shuster et al., 2018). Importantly, Li et al (2021) showed that dolomite can be of syngenetic origin in anoxic waters. It has also been pointed out that Fe-dolomite in the Port Askaig Formation has an authigenic origin (Spence et al., 2016). In this regard, the occurrence of Fe-dolomite in the tillites, which also coincides with the enrichment

of Fe-rich chlorites, may result from remobilisation of Fe^{2+} from dissolving Fe^{2+} -bearing minerals like biotite and precipitation of authigenic Fe-rich carbonates during deglaciation. It is also likely that the Fe was sourced through the erosional activity of melting glaciers on the local bedrock (e.g., Bhatia et al., 2013; Hawkins et al., 2014, 2016, 2020; Hopwood et al., 2014; Hodson et al., 2017). Similarly, the persistently high P_2O_5 content of the immediate post-Snowball facies may reflect the production and delivery of detritus-rich phosphate load to seawater by the melting ice sheets, as observed in modern glaciated polar regions (e.g., Hawkins et al., 2016; Chi Fru et al., 2023).

The main composition of Neoproterozoic clay minerals is believed to have derived primarily from the physical and chemical weathering of primary rock minerals, as opposed to a significant contribution by soils (Kennedy et al., 2006; Wei et al., 2024). For example, even in the absence of strong biological processes involved in clay mineral production on land, variable quantities of detrital and diagenetic clay minerals dominated mostly by illite, illite/smectite [I/S] and chlorite, have been reported for Paleoproterozoic marine shales (Baruch et al., 2015).

Clay mineral texture and relationships with detrital grains, crystal shapes, primary and secondary pore space filling and replacement of detrital grains, reflect a mixture of abundant detrital and subordinate authigenic clay minerals (Figs. 3, 9 & S1, S4). It is possible that marine clay mineral authigenesis resulting from continental silicate weathering could have initiated direct clay mineral precipitation from seawater and sediment porewater (Yin et al., 2023; Li et al., 2021). However, XRD mineralogical analysis, together with high-resolution SEM petrology, point to a dominant detrital composition of identified clay minerals, with most authigenic clays formed mainly by diagenetic transformation of detrital grains. It is also possible that the lower carbonate content in the immediate post-Snowball interval could have been generated by acidity produced during reserve weathering enabling authigenic clay mineral formation at the expense of carbonate deposition (Isson and Planavsky, 2018; Li et al., 2021). However, quartz is abundant in this interval, and Al_2O_3 exhibits a generally positive correlation with SiO_2 (Figs. 4a & 5a) while the negative correlation with CaO and MgO (Figs. 4d, 5e & 5h), hints on dominant detrital supply of SiO_2 and chemical precipitation of sparse carbonate.

Kaolinite is typically formed under warm climatic conditions characterised by intense chemical weathering (Nesbitt and Young, 1984; Fedo et al., 1995). However, the presence of kaolinite within the secondary pores of albite and absence between grain boundaries, suggest an authigenic origin (Fig. 9g), with the conspicuous lack of well-crystallised blocky stable authigenic dickite kaolin polytype morphologies indicating association with low-temperature

alteration and absence of deep burial diagenetic and hydrothermal influence (Lanson et al., 2002; Aubineau et al., 2021). Therefore, the authigenic kaolinites were likely derived from alteration of detrital feldspar in a warm climate.

However, kaolinite is also found in XRD spectra obtained for the tillite succession formed during the deglaciating Snowball phase (Table S6). Detrital kaolinite associated with this interval could have resulted from mechanical tillage of old sedimentary rock deposits by the melting ice, and from increasing chemical weathering of silicate rocks by carbonic acid in the CO₂-rich deglaciating atmosphere. For example, kaolinite content in the post-Snowball deposit is consistent with increasing CIA values. Additionally, the degradation of organic matter through sulphate reduction produces organic acids within pore waters, as indicated by deposition of authigenic pyrite (Fig. S1a), would favour authigenic precipitation of kaolinite from porewater (Hao et al., 2021a). However, previous studies do not indicate widespread distribution of kaolinite in Precambrian sedimentary rocks (Tosca et al., 2010), possibly because of transformation of primary kaolinite to illite during diagenetic illitisation (Meunier and Velde, 2004).

Chlorite is stable in modern marine sediments formed in cold regions marked by strong physical and weak chemical weathering (Darby, 1975; Hallam et al., 1991; Ehrmann et al., 1992; Wahsner et al., 1999; Worden et al., 2020) and can be preserved after glacial erosion of country rocks (Föllmi et al., 2009; Shi et al., 2018), including detrital kaolinite supplied by continental shales and soils (Darby, 1975). Further, early Oligocene transition to illite-/chlorite-rich marine sediments has been interpreted to indicate a change from warm-humid chemical weathering conditions to a cool greater physical weathering state (e.g., Ehrmann et al., 1992; Wahsner et al., 1999). Our observations show a dominance of chlorite in the glaciogenic tillites. As depicted in Figure 9f, the alteration and replacement of ferromagnesian biotite is also suggested as a potential source of diagenetically formed authigenic chlorite (Weaver, 1989; Jinag and Peacor, 1994; Worden et al., 2020). An examination of the Fe/(Fe+Mg) content of putative chlorite grains prevalent in the tillites by SEM-EDS, indicates a mainly chamosite composition characterised by $\text{Fe}/(\text{Fe}+\text{Mg}) > 0.3$ as shown in Table S7 (Bozkaya et al., 2017). Direct precipitation of chlorite cements is commonly observed in the sediment pore spaces, implying, as discussed above, Fe enrichment within the basin during the deglaciation phase. Taken together, the abundance of detrital chlorite in the tillites (Fig. 9) is consistent with the expected strong physical weathering associated with the grinding of continental landmass by the end-Snowball melting ice sheets (Paige-Green, 1980; Chamley, 1989). On the other hand, illite forms under a variety of conditions and tends to crystallise in different forms (Środoń et

al., 1984). In this study, illite is detected in all the three distinct lithologies, including cold climate deposits (Darby 1975; Ehmann et al., 1992; Wahsner et al., 1999). Petrographic observation shows the presence of detrital illite derived from the physical weathering of mica (e.g., muscovite). Besides detrital illite, authigenic or diagenetic illite was observed as pore-filling and pore-lining material (Fig. 9).

The studied samples are completely devoid of smectite and mixed-layer clay mineral assemblages. Smectite is considered to be inherited from continental weathering (Tosca et al., 2010). Thus, its absence across the sampled lithologies is most likely due to burial diagenesis, leading to the formation of illite. For instance, while detrital illite grains are apparent in the samples, additional illite formation is suggested to have formed via the transformation of micaceous minerals like K-rich muscovite, as indicated by their association with illite. Overall, the above observations hint that the studied samples have not undergone significant metamorphic alteration, consistent with previous studies (Thomas et al., 2004; Arnaud and Fairchild, 2011; Skelton et al., 2015).

5.1.2. Clay mineral illitization

During burial diagenesis, potassium metasomatism (K-metasomatism) may strongly change sediments bulk composition and, consequently, the CIA index (Fedo et al., 1995). K-metasomatism leads to the conversion of plagioclase to K-feldspar and/or Al-rich clay minerals (e.g., kaolinite) to illite (Fedo et al., 1995; Tosca et al., 2010). This illitization process has been widely reported in many Precambrian sediments (Fedo et al., 1995; Rieu et al., 2007; Tosca et al., 2010; Rafiei and Kennedy 2019).

The influence of K-metasomatism is visualised by the Al_2O_3 –($\text{CaO}^* + \text{Na}_2\text{O}$)– K_2O (A–CN–K) ternary diagram (Fig. 7), according to Fedo et al. (1995). Theoretically, the chemical weathering trend without K-metasomatism should be distributed along an ideal line that runs parallel to the A–CN boundary axis, which reflects concurrent loss of Na, Ca, and K, while deviations towards the K- apex indicate significant K addition by K-metasomatism (Fedo et al., 1995; Tosca et al., 2010). However, most samples deviate from the ideal weathering curve (Fig. 7). Particularly, the pre-/post-glacial samples are suggested by the A–CN–K plot to have experienced K addition, which is common for aluminous clays through the growth of authigenic illite (Nesbitt and Young, 1984; Fedo et al., 1995). The corrected CIA value (CIA_{corr}), which minimizes the interference of K-metasomatism on the CIA, has been corrected through backward projection to the predicted weathering trend (Fedo et al., 1995; Tosca et al., 2010), leading to the corrected CIA values (CIA_{corr}) exhibiting a linear trend similar to the

predicted ideal weathering line of granodiorite, with no shift towards the K endpoint (Fig. 7). To allow for a maximum possible effect of K-metasomatism on CIA values, we applied a correction assuming that the ideal weathering trend originated from granite and a granodioritic source rock composition (Fig. 7). Whereas the absence of a similar observation for the tillite succession implies insignificant K enrichment (Fig. 7).

5.2. Weathering conditions, sediment maturity and sediment recycling

Climate change has been linked to variations in siliciclastic rock compositions, related to the vulnerability of rock silicates to chemical weathering induced by atmospheric CO₂ in the form of acidic rain (e.g., Gaillardet et al., 1999; Zhai et al., 2018). In this regard, CIA indices have been widely used to determine the degree of chemical weathering of glacial sediments (Nesbitt and Young, 1984; McLennan and Taylor, 1991; Rieu et al., 2007; Scheffler et al., 2003, 2006). Particularly, the effects of chemical weathering on sedimentary rock composition are dependent on climatic conditions and the residence time of material exposed to chemical weathering while stored in continental basins (Rieu et al., 2007). Hence, to determine climate change patterns from calculated weathering indices, it is necessary to address the effects of sedimentary processes such as sediment sorting, recycling and diagenesis, from those due to the character of the protolith (McLennan et al., 1993).

Sedimentary recycling is likely to be accompanied by the enrichment of poorly mobile heavy minerals, notably zircon because the elemental composition of zircon is dominated by trace elements that track sedimentary cycling processes (e.g., Zr). Therefore, to uncouple potential variations in the CIA values caused by transport sorting and possible recycling during deposition, Zr/Sc vs. Th/Sc cross plots were adopted (McLennan et al., 1993). Th and Sc are immobile and therefore do not undergo significant fractionation during transport and deposition (McLennan et al., 1993). In addition, Zr is highly stable throughout the sedimentary cycle, so the Zr/Sc ratio increases with the enrichment of zircon during the process of transportation and sedimentation, while Th/Sc ratios remain relatively unchanged during the sedimentary cycle (McLennan et al., 1993). The plot of Th/Sc versus Zr/Sc suggests that the studied samples were derived mainly from intermediate igneous rocks and that they experienced insignificant sediment recycling. Most of the analysed samples cluster close to the UCC values, and the provenance-dependent compositional variation trend on the Th/Sc vs Zr/Sc binary diagram (Fig. 12a) shows that Zr/Sc ratios are positively correlated with Th/Sc ratios. This correlation does not support Zr enrichment by sediment recycling processes. Therefore, the studied samples are considered the result of first order cycling of eroded

continental rocks, exempting polycyclic reworking (Rieu et al., 2007). The low Zr/Sc ratios of <35 across the successions further indicate that sediment deposition was primarily controlled by the composition of the source rocks, and that sediment recycling did not significantly influence the chemical composition of the samples (Fig. 12a). Moreover, Th/Sc (provenance indicator) vs. CIA had no discernible covariance (Fig. 12c), implying that the first order change in CIA reflects weathering processes and that the CIA values are not influenced by changes in the source rock composition (Taylor and McLennan, 1985; McLennan et al., 1993; Rieu et al., 2007).

Based on mineralogical mapping (Fig. 2), the tillites are compositionally dominated by less mature sheet silicate mineral components like muscovite and biotite compared to the pre-/post-Snowball successions.

5.3. Provenance interpretation

Provenance analysis is important for determining the origin and evolution of sediments. Source rock identification and provenance was therefore investigated based on assessing facies chemical composition using major and trace elements to retain source rock compositions (Cullers, 2000). The analysis relied on elements that have low immobility and are resistance to alteration during weathering and sedimentary processes and believed to be transported specifically on the terrigenous component of sediments. These elements which are thought to reflect the chemistry of the source rocks, include Al, Fe, Ti, Th, Sc, Co, Zr and rare earth elements (Taylor and McLennan, 1985; Cullers, 2000).

In weathered igneous rocks, Al is hosted primarily in mica and clays and residual feldspars, whereas Ti is hosted chiefly by mafic minerals like pyroxene, biotite and ilmenite. Therefore, the $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio was used to broadly predict the source rock composition, since these two oxides do not experience strong fractionation during weathering and diagenesis, where $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios <8, 8-21 and >21, approximate a mafic, intermediate and felsic igneous source rock composition, respectively (e.g., Hayashi et al., 1997). The $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios (Table S3) of the studied samples are broadly homogeneous, indicating a relatively uniform source provenance. The $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios of the studied samples range from 16.7-24 across the section — averaging 16.7 ± 2.3 for the pre-Snowball, 24.0 ± 4.7 for the tillites, 19.1 ± 0.9 for the immediate post-Snowball and 23 ± 1.6 for the late post-Snowball facies. These values suggest that the source area was potentially dominated by intermediate igneous and felsic rocks.

In addition, the composition of high field-strength elements (HFSE) Th, La and Sc was used to further assess the source provenance (McLennan et al., 1993). Moreover, incompatible trace elements are more enriched in UCC felsic rocks compared to compatible elements which are more abundant in mafic and ultramafic rocks (McLennan et al., 1993). Consequently, the compositional ratios of the incompatible element (Th) and the compatible element (Sc) were also used to discriminate primary sediment provenance (Condie, 1993). The La–Th–Sc ternary diagram (Fig. 12b) places all samples close to the La apex, far away from Sc, which implies a predominant felsic source composition, since Sc is enriched in mafic igneous rocks (Taylor and McLennan, 1985; McLennan et al., 1993). Most of them fall into the area between granite and granodiorite indicating the potential mixture of these rocks in the source area and a mainly felsic parent rock composition. This further agrees with the dominance of albite, muscovite and quartz rich content of the studied facies and, to a lesser extent, the presence of orthoclase in some samples.

The inferred granodiorite source for most samples is also supported by the relatively high Th/Sc ratios (Table S4). The Th/Sc ratio was applied to distinguish between felsic and mafic contribution to facies composition when Th/Sc ratios are >0.4 for felsic and <0.2 for mafic lithologies, because Th tends to be enriched in felsic rocks and Sc in mafic rocks. The variable enrichments and depletions in incompatible and compatible elements in the studied samples (Fig.12a & b) point to a predominantly felsic source for the post-Snowball lithology. In contrast, the tillite and pre-Snowball facies are more associated with a dominant intermediate igneous rock source as they are mostly enriched in incompatible elements and depleted in compatible elements with respect to UCC (Fig.12a). Taken together, the major elements and incompatible trace elements geochemical data suggest that the source rocks were mainly felsic and/or intermediate igneous.

A low Th/Sc ratio across the succession, together with ternary A-CN-K versus corrected CIA variations indicate a felsic source for the sedimentary rocks (Fig. 12c), consistent with their strong UCC-like profile (Fig. S2). Moreover, Th/Sc versus Zr/Sc ratios plot along the expected compositional array of primary sediments that have experienced insignificant recycling and sorting effects (Fig. 12a). This, together with the La, Th and Sc ternary diagram associate the primary sediments with a felsic provenance (Fig. 12b).

5.4.Weathering and paleoclimate variations

By excluding the potential effects of post-depositional diagenesis, sedimentary recycling, and provenance, the corrected CIA values and sediment composition can therefore be used to

evaluate climate fluctuations and chemical weathering intensities in the source area. Climate exerts a strong influence on bulk sediment chemistry, with greater leaching of cations under warm and humid climates. Significant changes in chemical weathering intensity, as recorded by the CIA values pre-Snowball, during deglaciation and post-Snowball phases, are believed to have occurred over the studied interval. First, association of the A-CN-K data for the glaciogenic tillite deposits with feldspar indicate that their primary composition experienced negligible chemical alternation, as reflected by low CIA values in the range of 42-59%. Further, clay mineralogy is sensitive to variations in weathering, sediment source area, transport processes and regime over time, and thus careful study of the clay mineralogy provides some insights into paleoclimate variability across the section.

In this regard, mica and chlorite are considered common by-products of chemical weathering reactions linked with the low hydrolysis typical of cool to temperate and/or dry climates. This agrees with the cold/dry climatic conditions expected to have been prevalent during the glaciating interval (Chamley, 1989). These values hint that physical weathering was dominant over chemical weathering at this time, consistent with the expected physical weathering of country rocks by the thawing ice sheets (Rieu et al., 2007; Ding et al., 2016; Wang et al., 2020). Moreover, evidence for this conclusion is provided by the SEM data (Fig. 2), which shows the dominant deposition of sheet silicates (Chi Fru et al., 2023). Whereas the CIA values of pre-/post-Snowball facies (Fig. 4h & 7), point to intensification of chemical weathering as would be expected for interglacial periods with warmer and more humid conditions (Rieu et al., 2007; Ding et al., 2016; Wang et al., 2020).

The variations in CIA recorded in the studied facies correspond well with major climatic changes (glacial versus non-glacial) inferred from independent paleoenvironmental interpretations (Rieu et al., 2007). Our results are, thus, in agreement with a number of studies that report paleo-CIA values for siliciclastic sediments of a similar age (Fedo et al., 1995; Rieu et al., 2007; Tosca et al., 2010; Ding et al., 2016; Zhu et al., 2020; Du et al., 2021). In addition, our CIA data is consistent with the detrital composition as shown by SEM-EDS mineral mapping and strong correlation of various major and trace elements with detrital indicators like TiO_2 and Al_2O_3 . Below, the observed changes in the degree of chemical weathering of source rocks before, during and after the Sturtian Snowball are explored to gain insights into nutrient supply from land to the seawater and potential impact on marine primary productivity.

5.5. Implications for marine nutrient concentrations

Clay minerals, through their physical and chemical properties, have been identified as potentially important bioessential trace element transporters, including phosphorus (P), from land to the ocean (Uncles et al., 2006; Zhao et al., 2018; Hao et al., 2021a, 2021b; Chi Fru et al., 2023). Their pH and ionic strength-dependent high affinity for ions, due to their large surface area and charge, results in a high capacity for adsorptive accumulation of a variety of bioessential elements (Landry et al., 2009; Hao et al., 2019; Hao et al., 2021a, 2021b). Particularly, the surface charge of clay minerals like illite and kaolinite identified in this study, varies with solution pH and ionic strength (Gu and Evans, 2007; Bradbury and Baeyens, 2009; Hao et al., 2019). Accordingly, as clay minerals are transported from land to the oceans by rivers, the change from freshwater and slightly acidic to saline-alkaline pH conditions, impact clay mineral surface properties, which in turn affects their ability to effectively bind and adsorbed trace metals and P (e.g., Hao et al. 2021a and 2021b).

Because different clay minerals have different P and trace element binding capacities (Hao et al., 2019, 2020, 2021a, 2021b), it is therefore expected that changes in detrital clay supply and composition across the sequence would have influenced seawater P and trace element content accordingly. Although, the present study did not quantify the amount of P and trace elements associated with specific clay mineral phases, previous analysis of these samples by Chi Fru et al. (2023), show that P is preferentially enriched in the chlorite-rich tillites, as are the representative trace elements Co, Ni, V and Cr (Fig. 4). This observation points to a likely association between detrital chlorite enrichment, P and trace element supply to seawater at this time. Moreover, the predominance of illite across the sampled succession further represents a likely constant pathway for nutrient delivery to seawater.

Bioessential trace element nutrients and P are integral to the functioning of biogeochemical processes at the Earth's surface and play an important role in supporting marine biological productivity and seawater-atmosphere oxygenation (e.g., Hopwood et al., 2014; Partin et al., 2013; Twinning et al., 2013; Reinhard et al., 2017; Lohan, 2018). Particularly, the fertilisation of seawater with particulate and dissolved Fe and P by glacial till in modern glaciated environments has been recognised (e.g., Bhatia et al., 2013; Hawkings et al., 2014, 2016, 2020; Hopwood et al., 2014; Hodson et al., 2005, 2017). This process affects seawater chemistry through a combination of inputs and outputs where adsorption/desorption and dissolution/precipitation reactions linked to the exchange of ions on clay minerals and Fe oxyhydr(oxides) surfaces for example, are the main mechanisms involved in the transfer of nutrients from land to oceans (Jeandel and Oelkers, 2015; Large et al., 2015; Hao et al., 2020, 2021b). In this regard, the moderate to strong co-variation of most of the whole-rock elements,

including bioessential V, Ni, Co and P, with the Al_2O_3 detrital tracer and K_2O (Figs. 5-6), indicate that the detrital fluxes, including the clay minerals and their precursors, were predominantly responsible for the bulk supply of nutritious elements to the basin. The behavior of key bioessential and redox sensitive trace elements, based on correlation coefficients, reveals the crucial role played by Al and clay minerals in the fixation and regulation of seawater elemental composition.

Interestingly, the positive correlation between Al_2O_3 and Fe_2O_3 as well as with P_2O_5 and representative trace elements, with persisting elevated records encountered in the immediate post-Snowball samples (Figs. 4b-e & 5), indicate that the physical weathering processes that accompanied the melting ice sheets, were a likely contributor to seawater and primary sediment P, Fe and trace metal enrichment, similar to reports for modern glaciated seawater margins (e.g., Bhatia et al., 2013; Hawkings et al., 2014, 2016, 2020; Hopwood et al., 2014; Hodson et al., 2005, 2017), as well as trace element supply. The well described release of Fe(II) by glacial weathering in these cold climate environments to seawater, is consistent with the Fe-chlorite and Fe-dolomite enrichment in the tillites and potential formation of magnetite/hematite in the immediate aftermath of the Snowball (Chi Fru et al., 2023). Moreover, given that kaolinite forms under extreme humid greenhouse chemical weathering conditions, the lack of strong chemical weathering in the tillites, suggest that if not produced diagenetically, kaolinite could have been eroded from land, where it formed during the high chemical weathering conditions of the pre-Snowball Earth greenhouse state, into the sedimentary basin. In such conditions kaolinite may have played a crucial role in the delivery of P to seawater from land during the melting of the Snowball ice sheets, together with detrital illite to a lesser extent (Hao et al., 2021b).

6. Conclusion

The clay minerals reported in this study carry valuable paleoenvironmental and paleoclimatic information, including the potential to unlock their role in nutrient delivery to seawater and sediments, recycling in sediment pore waters and back to seawater. Their diversity, the presence of significant compositional variations and the bulk sediment CIA values across the studied successions, reasonably track changing climatic cycles before, during and after the Sturtian Snowball. This is interpreted to imply that the switch in clay mineralogy from pre-Sturtian Snowball times to the deglaciation phase, reflects a change in paleoenvironmental conditions rather than post-depositional primary sediment alteration. Collectively, the data

agree with the independent study by Tosca et al. (2010), suggesting that clay minerals are a consistent weathering product associated with changing Neoproterozoic Cryogenian climates. Based on modern evidence and experimental data linking clay mineralogy and seawater nutrient content, we propose that abundant clay mineral production by the Cryogenian Snowball glaciations, coupled to end-Snowball intensification of chemical weathering, likely played a fundamental role in the fertilisation of post-Snowball seawater with key bioessential nutrients, contributing eventually to the Neoproterozoic Oxygenation Event.

Acknowledgements

This project was funded by the Omani government as part of the PhD project of Jalila Al Bahri. We also acknowledge funds from the European Research Council (ERC) Seventh Framework (F7) program, grant No: 336092 to Ernest Chi Fru that enabled sample collection and generation of the geochemical data.

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Author statement

Ernest Chi Fru, Morten Andersen: Conceptualization, Methodology. **Jalila Al Bahri, Ernest Chi Fru, Anthony Oldroyd, Duncan Muir, Diana Contreras, Olabode Bankole, Abderrazzak El Albani:** Investigation and visualization. **Jalila Al Bari:** Original draft preparation. **Ernest Chi Fru, Olabode Bankole, Abderrazak El Albani, Duncan Muir, Diana Contreras, Morten Andersen:** Writing-reviewing and editing.

Figure legends

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Figure 4. Variation of key major and trace elements with sequence stratigraphy. **a**, Semi-quantitative XRD bulk mineralogy of the analyzed samples grouped into quartz, carbonates (dolomite and calcite), feldspars (K-feldspars and plagioclase), Fe-oxides, muscovite, and clay minerals (kaolinite, chlorite, illite). Stratigraphic variation of major element oxides. **b**, SiO₂ and Al₂O₃. **c**, K₂O and Fe₂O₃. **d**, MgO and CaO. **e**, MnO and P₂O₅. **f**, CIA – chemical index of alteration. See Table S2 for detailed mineral and elemental evolution/distribution with stratigraphy.

Figure 5. Major elements cross plots with Al₂O₃ content.

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Figure 7. Ternary A-CN-K (Al₂O₃-CaO* + Na₂O-K₂O) diagram in molar proportions according to Nesbitt & Young (1984) for the studied samples. Data for basalt, granite, and granodiorite are from Condie (1993). The arrows 1, 2, and 3 indicate possible weathering trends for unmetasomatized basalt, granodiorite, and granite, respectively.

Figure 8. XRD patterns of the air-dried (black) and glycolated (red) for the studied samples. **a**, Pre-Snowball (LL-16-D). **b**, Tillite sample (LL-16-A1). **c**, Immediate post-Snowball (BH-16-03). **d**, Post-Snowball sample (PS-16-12). Q, Quartz; M, Muscovite; Alb, Albite; Do, Dolomite, KF, K-feldspar; Ch, Chlorite; K, Kaolinite; Py, Pyrite; I/M, Illite/Muscovite; Ch/I/M, Chlorite/Illite/Muscovite.

Figure 9. Backscatter (BSE) photomicrographs showing exemplary mineral phases across the studied sequence. **a-b**, Late post-Snowball (PS-16-00). **c-d**, Early post-Snowball. **e-f**, Tillites (LL-16-A1); **g-h**, pre-Snowball (LL-16-d). Dotted White dotted lines in panels a, c, e and g show selected areas amplified in panels b, c, f and h to show specific details of key clay mineral phases. Dotted red lines show distinct boundaries of primary minerals phases that have been diagenetically transformed to secondary clay minerals.

Figure 10. Examples of SEM-EDS spectra of chlorite, illite and kaolinite clay minerals. **a**, Detrital chlorite. **b**, Diagenetic chlorite. **c**, Detrital illite. **d**, Diagenetic illite. **e**, Detrital kaolinite. **f**, Diagenetic Kaolinite. Chlorite and illite spectra – sample LL-16-a1. Kaolinite spectra – sample LL-16-d.

Figure 11. **a**, Chemographic projection of illite and chlorite chemistry on the 4Si-M+-R2 ternary diagram (Meunier and Velde, 2004). **b**, Co-variation of octahedral Fe/(Fe+Mg) index and Al(VI) cations of chlorites (Velde, 1985). Mu- muscovite, Bei – beidellite, Mont – montmorillonite, Ce – celadonite, Ch – chlorite, Ph – phengite, Bio – biotite

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Figure 1

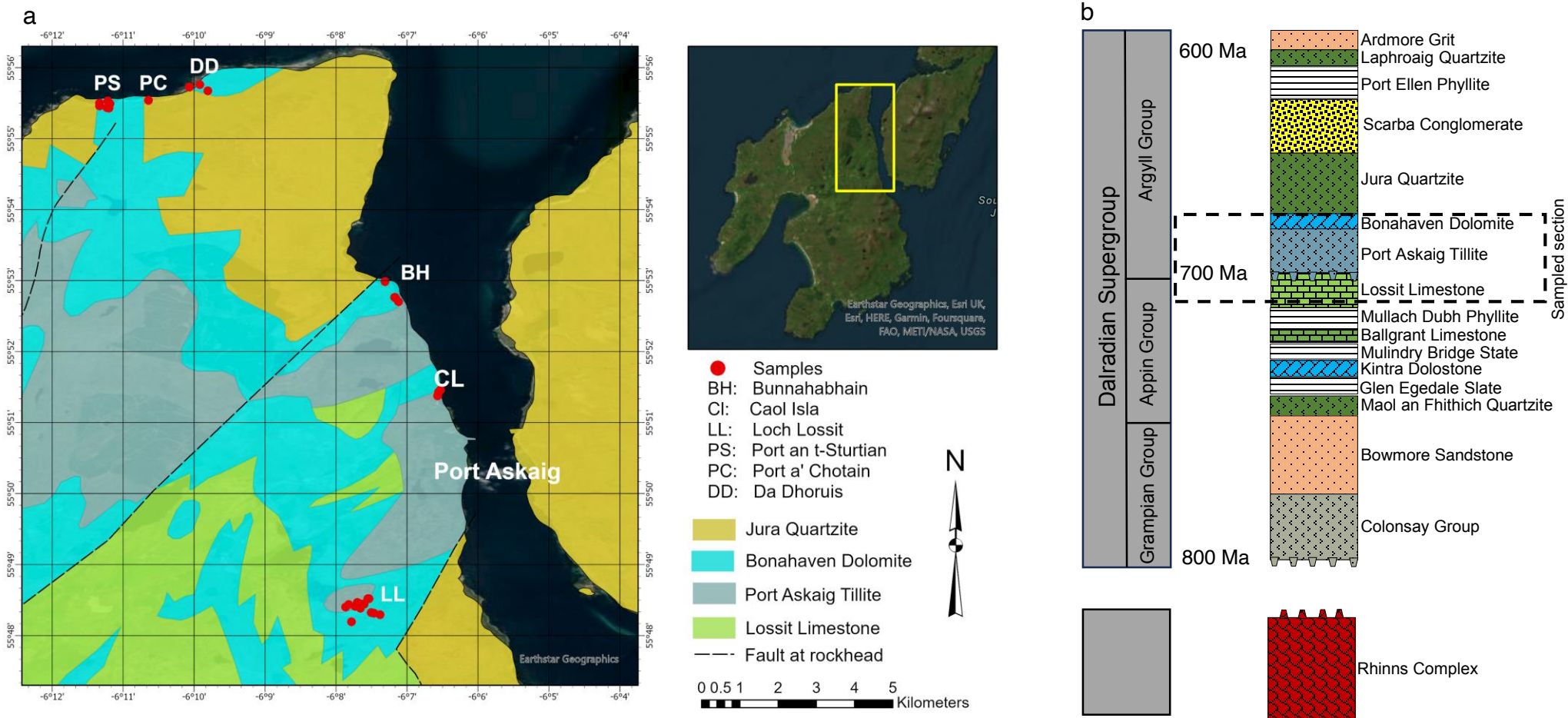


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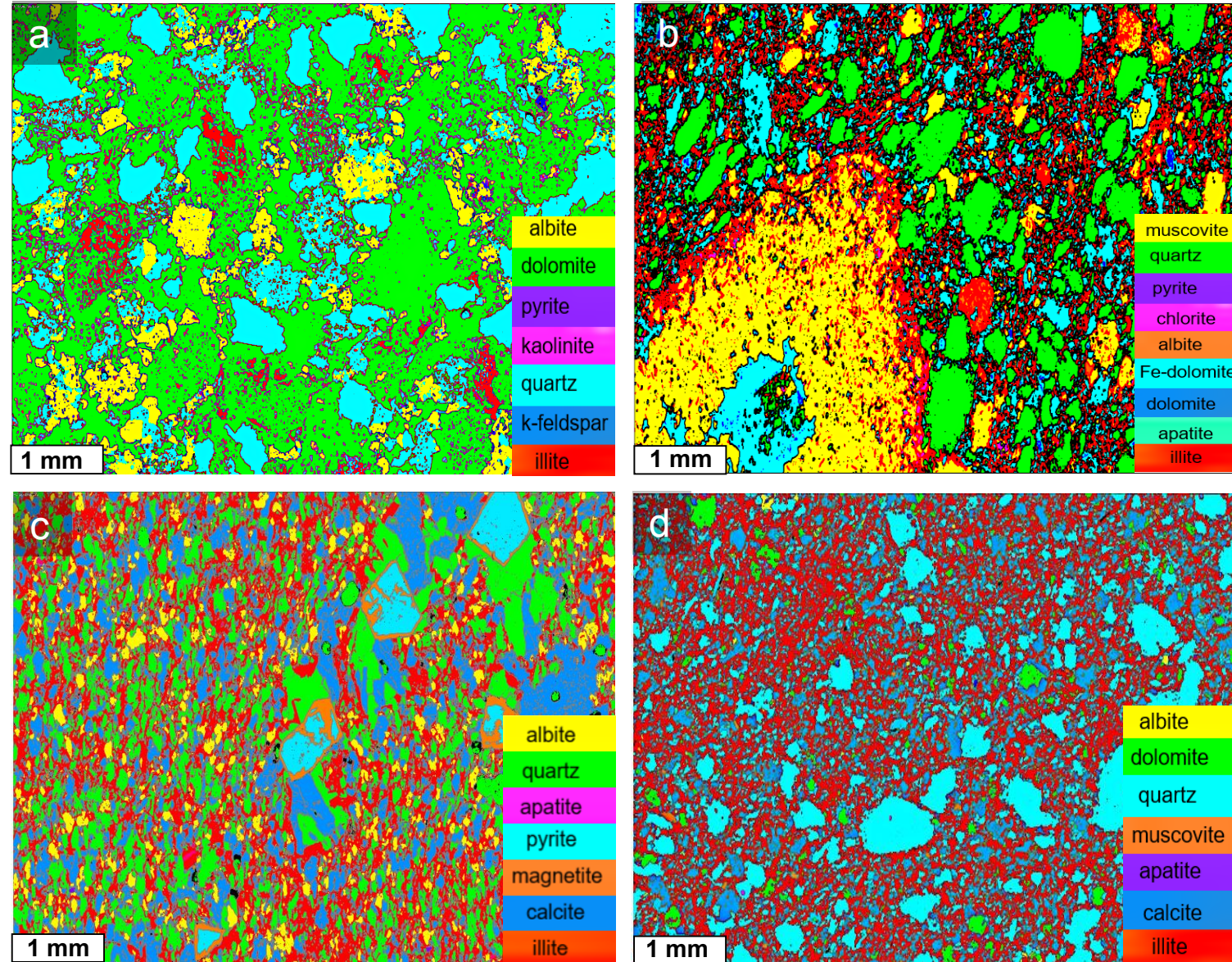


Figure 3

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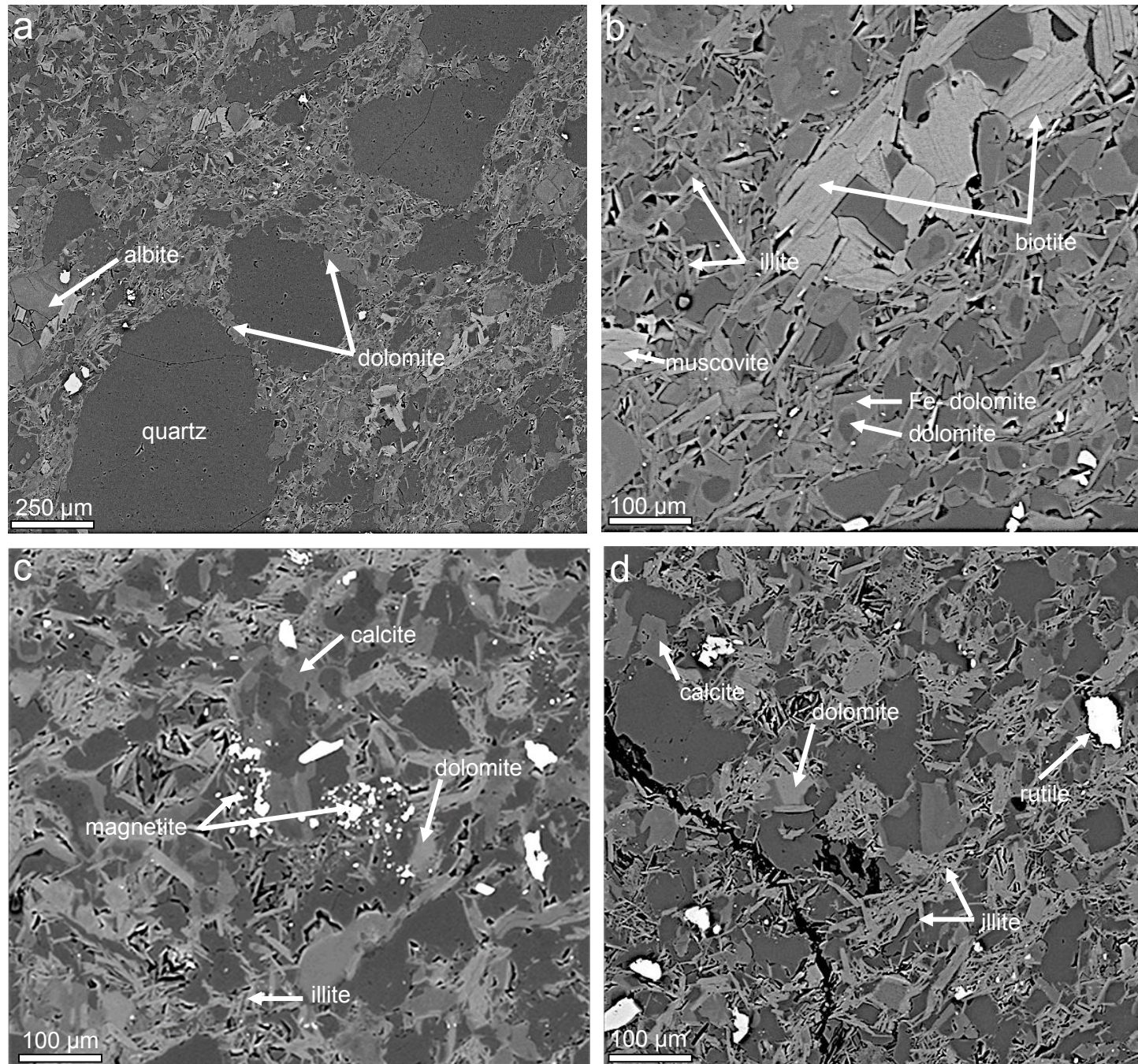


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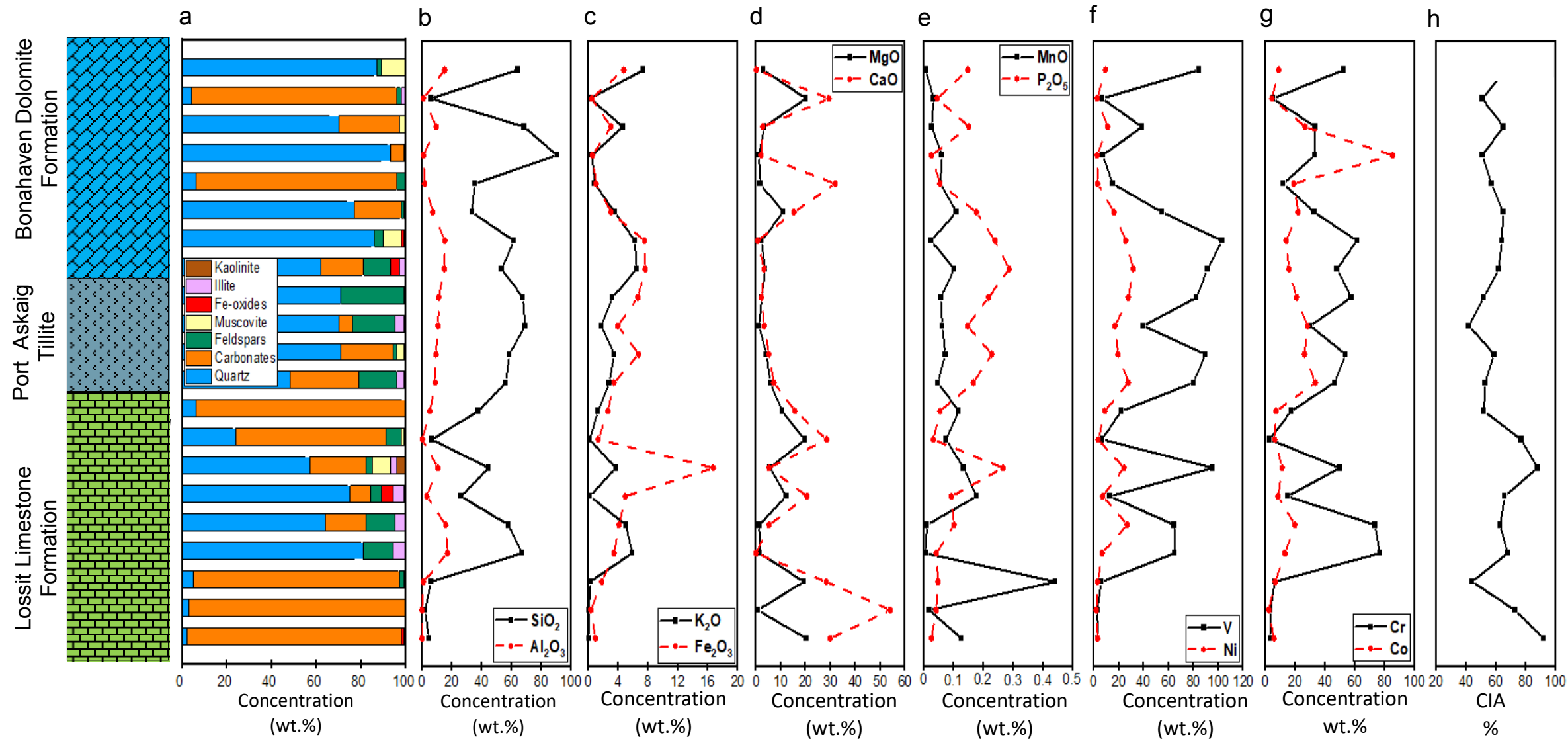


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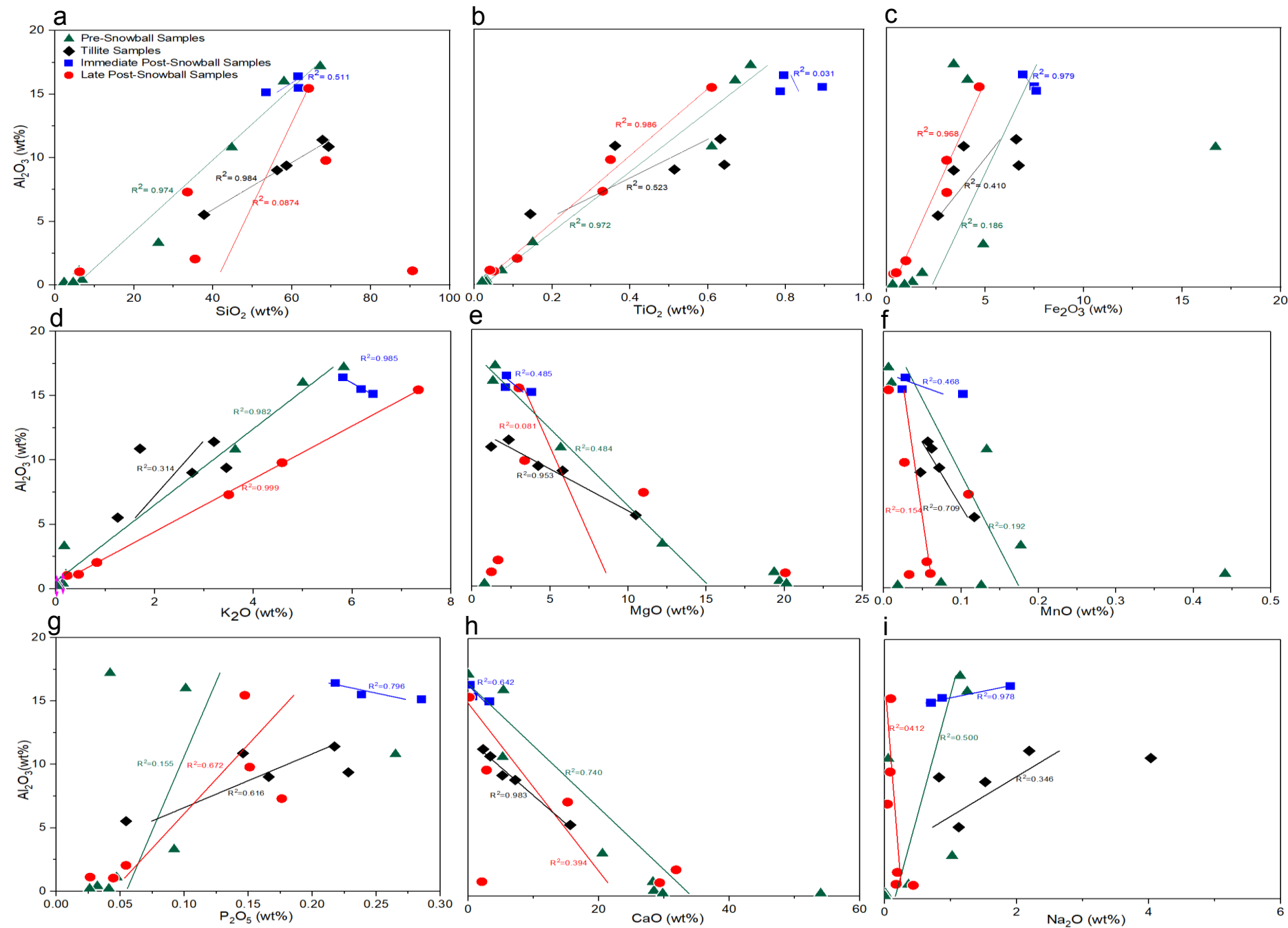
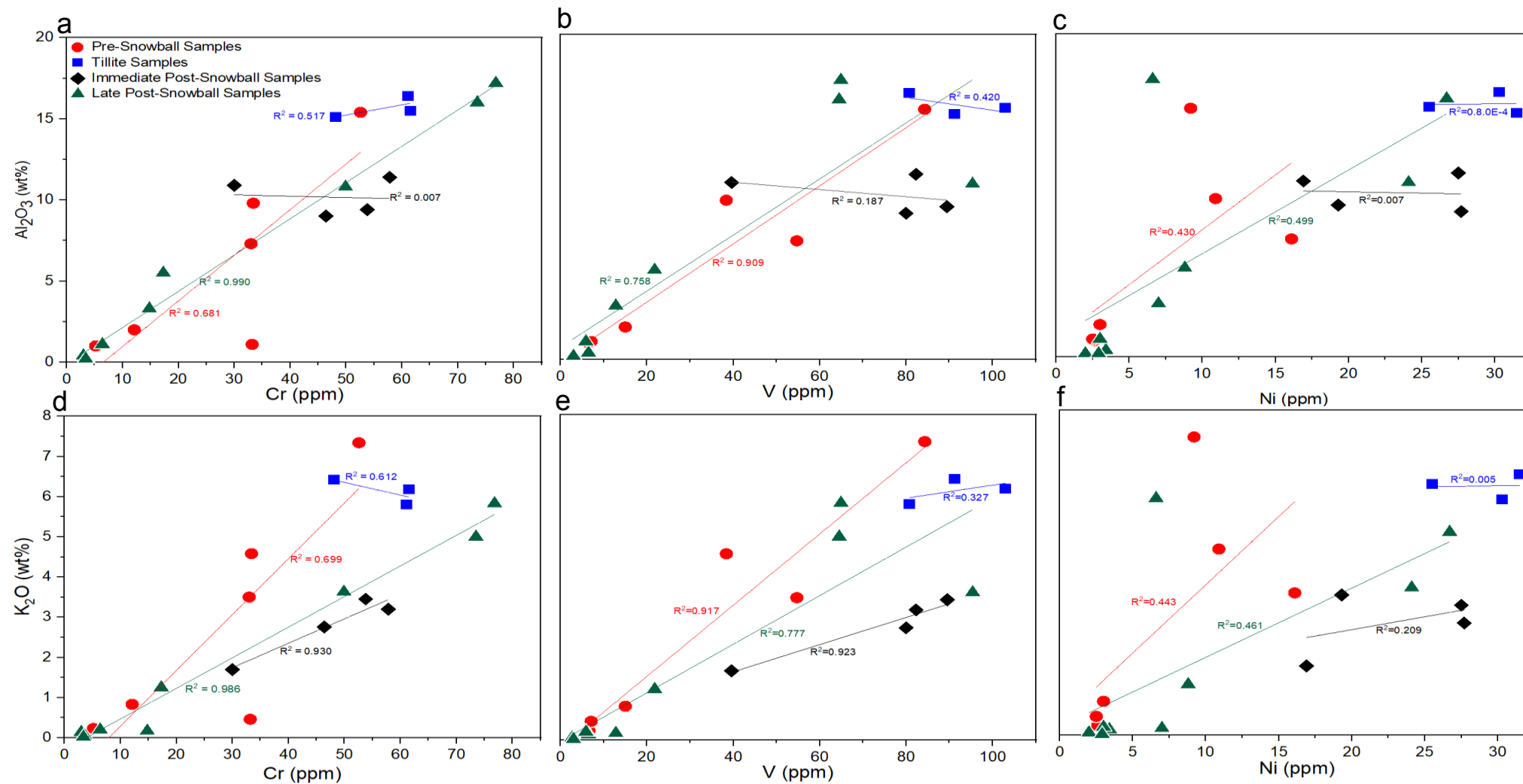
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Figure 6



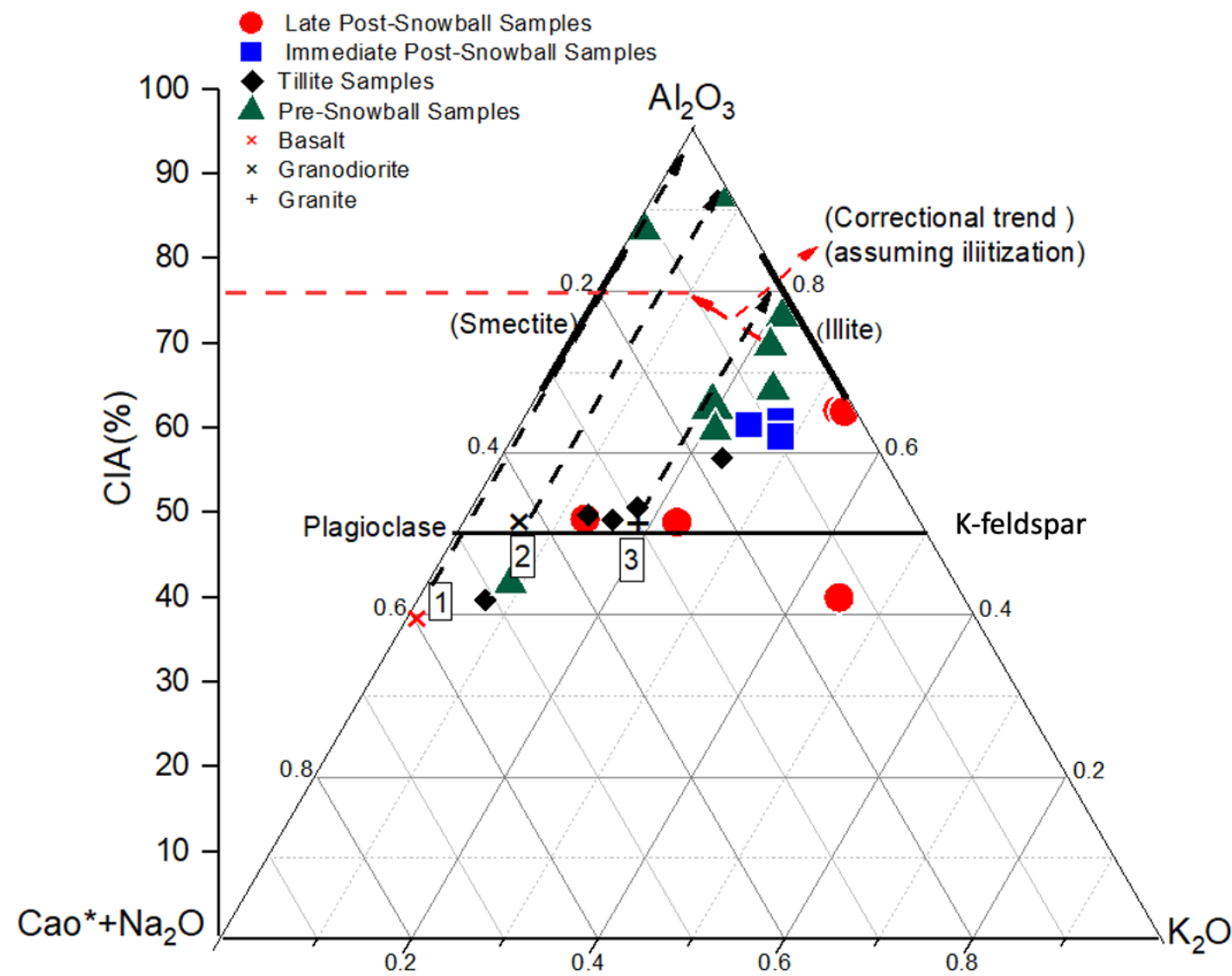


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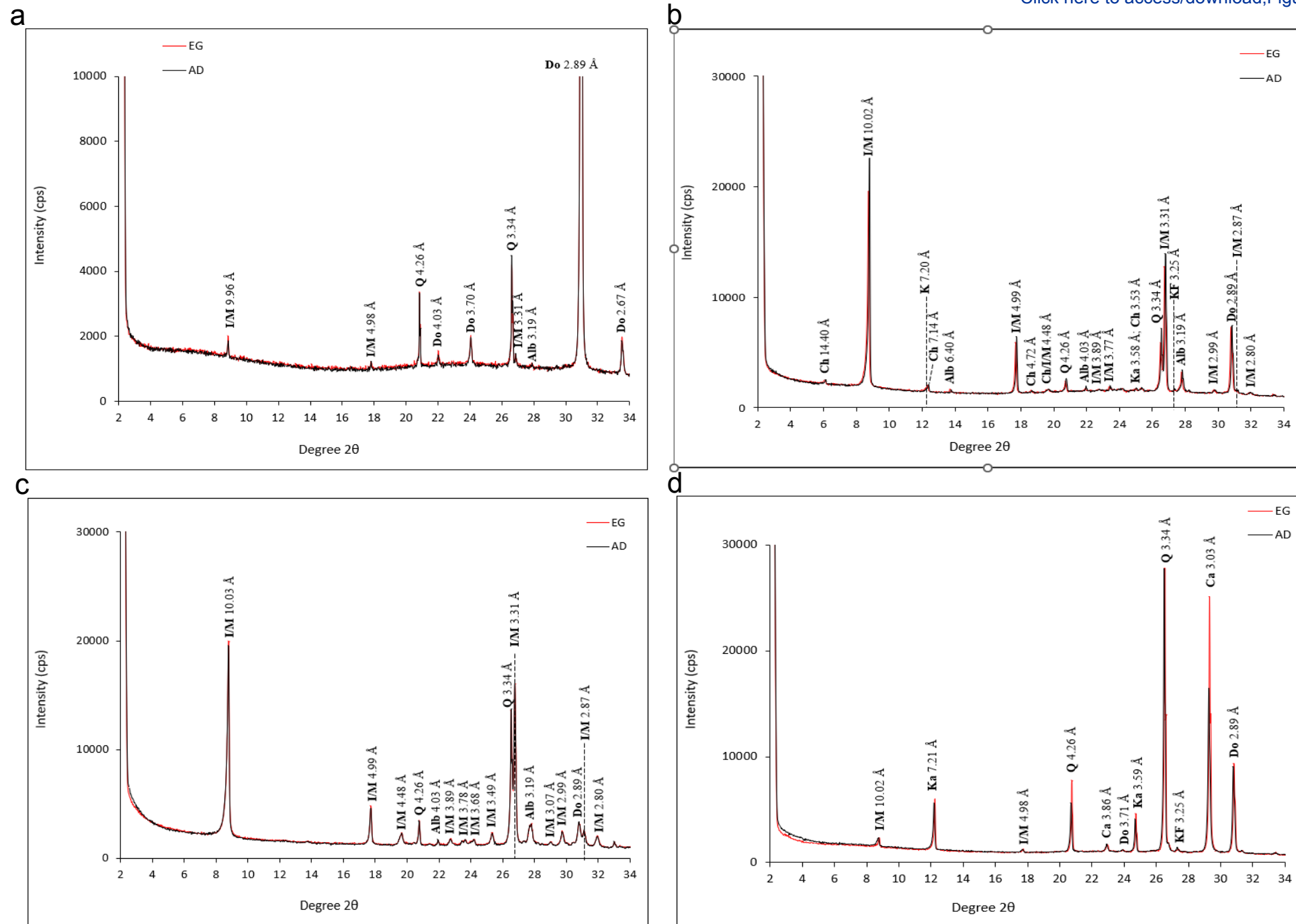
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Figure 9

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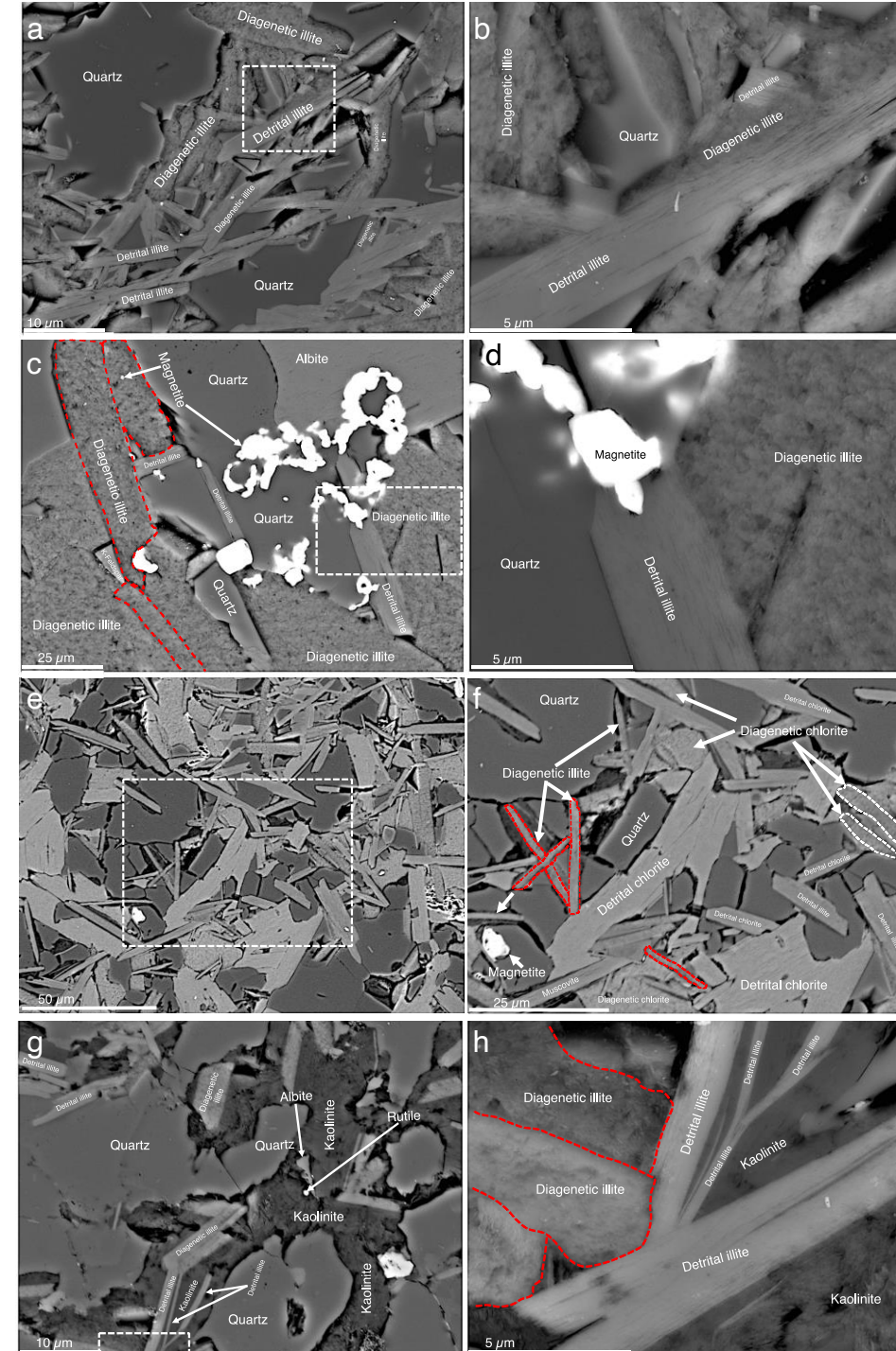


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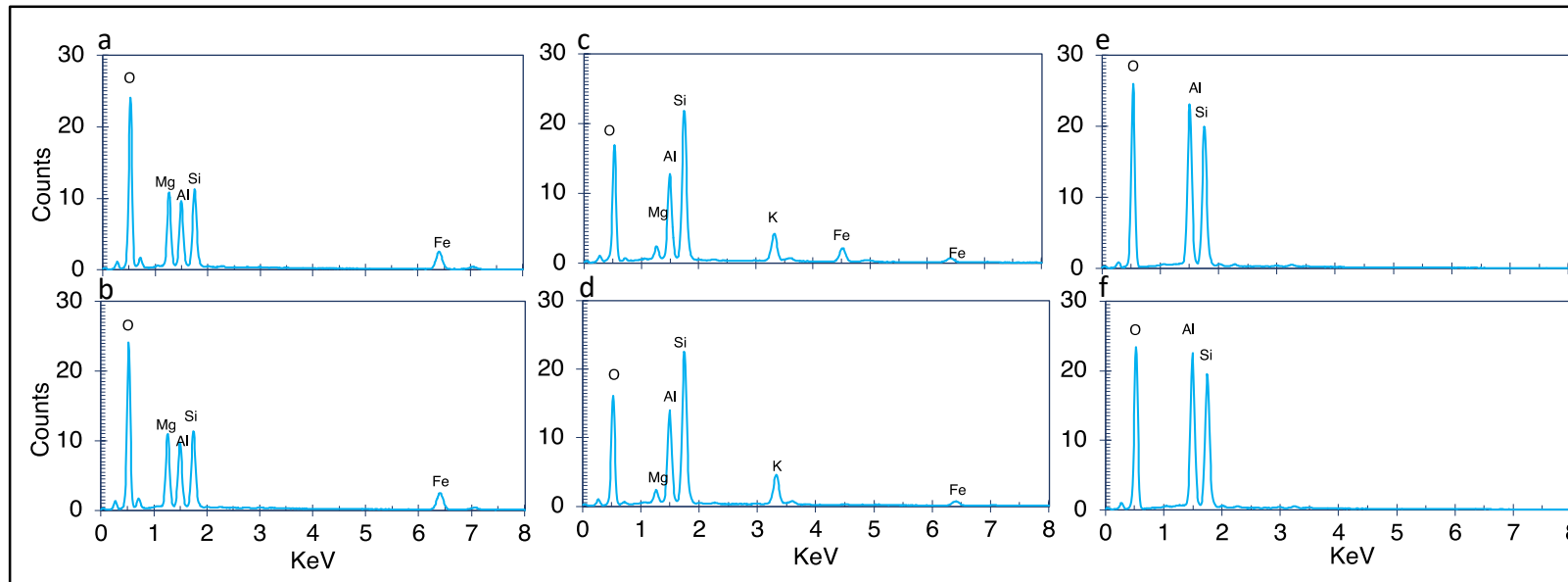


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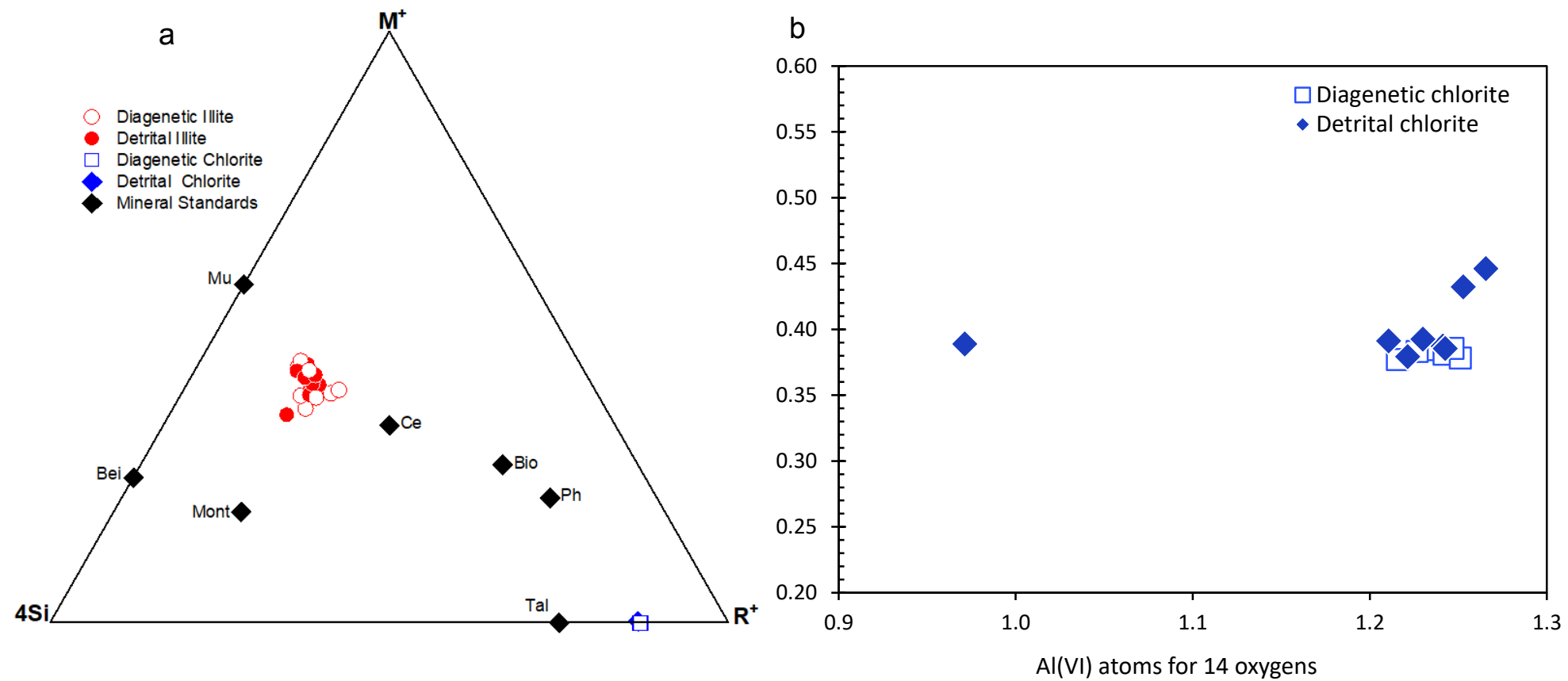
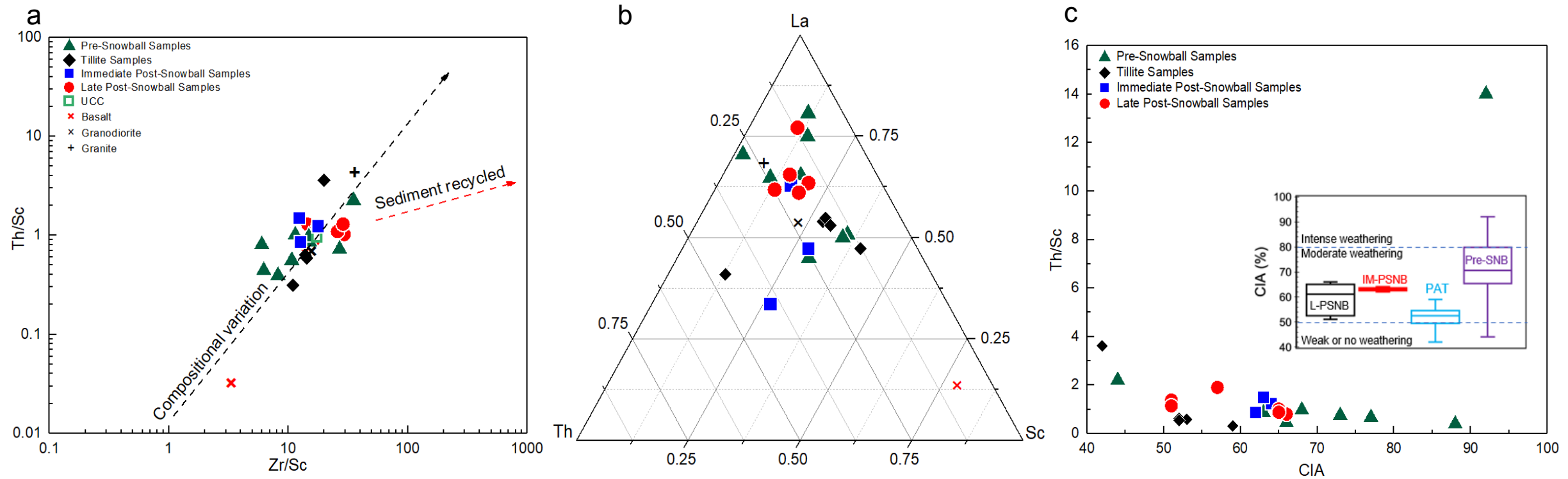
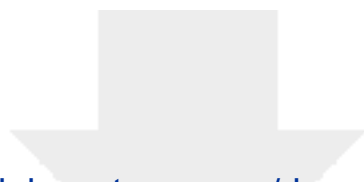


Figure 12







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Supplementary Material

[illite and Chlorite chemical composition.xlsx](#)

