Impact of green clay authigenesis on K–Mg–Fe sequestration in marine settings

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Article

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Abstract

Retrograde clay mineral reactions (i.e., reverse weathering), including glauconite formation, are first-order controls on element (re)cycling vs sequestration in modern and ancient marine sediments. Here, we report substantial K–Mg–Fe sequestration by glauconite formation in shallow marine settings from the Triassic to the Holocene, averaging $4 \pm 3 \text{ mmol K} \cdot \text{cm}^{-2} \cdot \text{kyr}^{-1}$, $4 \pm 2 \text{ mmol Mg} \cdot \text{cm}^{-2} \cdot \text{kyr}^{-1}$ and $10 \pm 6 \text{ mmol Fe} \cdot \text{cm}^{-2} \cdot \text{kyr}^{-1}$, which is ~ 2 orders of magnitude higher compared to deep-sea settings. Upscaling of glauconite abundances in shallow-water ($< 200 \text{ m}$) environments predicts a global K–Mg–Fe uptake of $\sim 0.05\text{--}0.06 \text{ Tmol K} \cdot \text{yr}^{-1}$, $\sim 0.04\text{--}0.06 \text{ Tmol Mg} \cdot \text{yr}^{-1}$ and $\sim 0.11\text{--}0.14 \text{ Tmol Fe} \cdot \text{yr}^{-1}$. We conclude that authigenic clay elemental uptake had a large impact on the global marine K, Mg and Fe cycles throughout Earth's history, in particular during 'greenhouse' periods with sea level highstand. Quantifying authigenic clay formation is key for better understanding past and present geochemical cycling in marine sediments.

Introduction

Chemical elements are supplied to the global ocean by the chemical and physical weathering of carbonate and silicate minerals on the continents, and the subsequent transport of dissolved and particulate matter by rivers, groundwater, glaciers and wind (Raiswell, 2006; Jeandel and Oelkers, 2015; Santiago Ramos et al., 2018). Hydrothermal sites of mid-oceanic ridges and flanks constitute another major source of chemical elements to the oceanic dissolved pool, but hydrothermal reactions between seawater and the oceanic crust may also result in a significant element fixation and burial (i.e., sequestration) (Huang et al., 2018; Voigt et al., 2020; Shalev et al., 2019; Laureijs et al., 2021). The dissolution of continent-derived reactive particulate matter and the subsequent uptake of dissolved elements by reverse weathering (i.e., clay mineral authigenesis), occurring in both shallow marine and deep marine settings, are other key factors that control the rate and magnitude of element cycling in marine settings (Isson and Planavsky, 2018; Abbott et al., 2019). It is thought that the mean elemental fluxes close to the sediment-seawater interface are controlled mainly by the tectonic setting, sediment provenance and climate regime prevailing on the continents (Schopka et al., 2011; Jeandel and Oelkers, 2015; Wright et al., 2020), which define sedimentation rate, composition and reactivity of the weathering influx, as well as silicate and carbonate bio-productivity, which largely depend on the ocean chemistry, and long-term variations of the atmospheric carbon dioxide (CO_2) pool (Crowley and Berner, 2001; Hoffmann et al., 2008; Arvidson et al., 2013; Homoky et al., 2016; Coogan and Gillis, 2018; Santiago Ramos et al., 2018).

The source-sink relations of the global elemental cycles are increasingly well constrained due to advances in e.g., high-precision isotope and element concentration measurements in benthic chambers, novel isotopic tracing methods and isotope-enabled earth system models combined with multivariate statistical modeling (Dale et al., 2015; Charette et al., 2016; Homoky et al., 2016; Dunlea et al., 2017; Santiago Ramos et al., 2018; Schijf et al., 2020; Sieber et al., 2021). However, there remain large gaps in

knowledge concerning the marine rare earth elements (REE), trace elements and K budgets (Cuadros et al., 2016; Haley et al., 2017; Abbott et al., 2019; Laureijs et al., 2021). Moreover, the magnitude of reverse weathering to produce authigenic (green) clay minerals on the ocean floor remains unknown and is, if ever, only indirectly accounted for in earth system models (Arvidson et al., 2013; Rahman et al., 2017; Isson and Planavsky, 2018).

The long-standing view that clay mineral reactions taking place at low to ambient temperature ($\leq 30^{\circ}\text{C}$) over much of the Earth's surface are very slow ($\sim 10^5$ up to a few 10^6 yr) has been increasingly challenged (Michalopoulos and Aller, 1995; Baldermann et al., 2013; Baldermann et al., 2015; Egli and Mirabella, 2021). Fast ($\sim 10^2$ to 10^5 yr) retrograde clay reactions occurring in hydrothermal or in deep-burial and diagenetic surroundings (Voigt et al., 2020; ; Laureijs et al., 2021), in the Amazonas deltaic sediments, in mangrove forests or estuaries (Michalopoulos and Aller, 1995; Cuadros et al., 2016), and even in the deep-sea (Baldermann et al., 2015; Homoky et al., 2016; Dunlea et al., 2017; Santiago Ramos et al., 2018) are increasingly considered critical controls on K–Fe–Mg–Si sequestration in both modern and ancient marine sediments. The mineral glauconite, $(\text{K, Na, Ca})(\text{Fe, Al, Mg})[(\text{Si, Al})_4\text{O}_{10}](\text{OH})_2$, is one such authigenic clay, commonly forming mm-scale green granules near the sediment-water interface. Glauconite forms in siliciclastic and calcareous sediments in marine and continental depositional environments and within a wide range of substrates, including faecal pellets, foraminifera chambers and lithoclasts (Odin and Matter, 1981; Amorosi, 2012; Banerjee et al., 2016; López-Quirós et al., 2019). It is thought to evolve from K-poor, but Fe(III)-rich smectite to K- and Fe(III)-rich glauconite through the formation of glauconite-smectite intermediates over a time-frame less than a few million years (Myr) after sediment deposition (Baldermann et al., 2013; Baldermann et al., 2017; Banerjee et al., 2016; López-Quirós et al., 2019). While Fe uptake by glauconite and glauconite-smectite formation in modern deep-sea settings has been shown to be significant, up to six-fold greater than Fe sequestration by pyrite formation in suboxic near-surface sediments (Baldermann et al., 2015), there has been no attempt to estimate the impact of glauconite formation on past and present marine geochemical cycles.

In this study, we fill this gap using a well-characterized glauconite-bearing sequence from Langenstein, in the Northern German basin (Germany), as representative example of Mesozoic and Cenozoic glauconite-bearing intervals, to calculate K–Mg–Fe sequestration rates related to glauconite formation in shallow-water settings, and to compare this with published estimates for the deep-sea (Baldermann et al., 2015). The sedimentary sequence from Langenstein (Fig. 1) represents an authigenic glauconite deposit on a palaeo-shelf setting (Wilmsen, 2003; Wilmsen et al., 2005; Wilmsen, 2007). Here, shallow-water carbonate or sandstone lithologies contain major glauconite, with overlying shelf sediments hosting relatively smaller quantities of glauconite. K–Ar glauconite dating indicate glauconite formation was completed within < 1 Myr close to the sediment-seawater interface (Baldermann et al., 2017). This study site is representative of many modern and palaeo-shelf settings that accumulate glauconite minerals (Odin and Matter, 1981; Baldermann et al., 2013; Banerjee et al., 2016; Bansal et al., 2017; Banerjee et al., 2020; Bansal et al., 2020a,b; Choudhury et al., 2020). Here, we highlight the significance of green clay

authigenesis on K–Mg–Fe sequestration in marine sediments that strongly impacted the marine K, Mg and Fe cycle throughout Earth's history.

Results

Glaucinite characterization. XRD analysis identifies the green grains within the sandstone lithology as glauconite with minor admixtures of glauconite-smectite based on broad reflections at 10 Å (001), 5.0 Å (002), 4.5 Å (020), 3.3 Å (003), 2.6 Å ($\overline{131}$) and 1.51 Å ($\overline{060,331}$) (Fig. 2a). The glauconite within the carbonate lithologies produces identical XRD patterns, though these rocks contain calcite and quartz impurities. Well defined reflections at 3.6 Å ($\overline{112}$) and 3.1 Å (112) and the weak 'XRD hump' between 25 to 40° 2 θ indicate the green grains are mixtures of the 1 M and 1M_d polytype structures, which correspond to ordered glauconite and disordered glauconite-smectite (Odin and Matter, 1981; Baldermann et al., 2015; Banerjee et al., 2016).

Petrographically, the green grains are dominated by glauconitized faecal pellets of dark green and medium green color (~ 85 ± 5 wt.%; insert in Fig. 2b), with subordinate light green colored glauconitized faecal pellets (~ 10 ± 5 wt.%) and greenish infills in foraminifera chambers (~ ≤ 5 wt.%). Backscattered electron imaging illustrates the micro-texture of the glauconite is made of tightly-packed, sub-micron sized crystals forming 'rosette-like' structures (Fig. 2b), whereas the high-resolution TEM lattice fringe image shows the flake-shaped particles are made of 10 Å domains (Fig. 2c and the insert). These features are indicative of 'highly evolved' glauconite (Baldermann et al., 2015; Choudhury et al., 2021).

Chemically, the vast majority (more than 95 % of the EMPA data, cf. Table S1) of the glauconite grains has K₂O contents exceeding 7 wt.%, frequently reaching up to > 9 wt.%, with averages of 8.3 ± 0.3 wt.%, 9.0 ± 0.2 wt.%, 8.7 ± 0.2 wt.% and 9.2 ± 0.2 wt.% for samples S4-S7, respectively (Fig. 2d), which is characteristic of 'evolved' to 'highly evolved' glauconites (e.g., Odin and Matter, 1981; Banerjee et al., 2016). The total Fe contents (defined here as TFe; sum of Fe₂O₃ and FeO) range from 16 to 26 wt.% (av. 21.6 ± 1.9 wt.% for S4, 24.3 ± 1.6 wt.% for S5, 23.0 ± 1.5 wt.% for S6 and 24.2 ± 1.3 wt.% for S7; Fig. 2e), which shows the glauconites are Fe-rich (Baldermann et al., 2017; Choudhury et al., 2021). The measured Al₂O₃, MgO and SiO₂ contents are in the typical range of Mesozoic and Cenozoic glauconites (Amorosi, 2012; Banerjee et al., 2016; Bansal et al., 2017; Banerjee et al., 2020; Bansal et al., 2020a), averaging 7.9 ± 1.0 wt.%, 4.1 ± 0.3 wt.% and 51.8 ± 1.5 wt.%, respectively. The Na₂O (< 0.2 wt.%) and CaO contents (< 0.2 wt.%, but up to 7.9 wt.% where hydroxyl-apatite is present) are generally low, as expected in mature glauconite (Table S1). The calculated structural formula of the glauconites varies in the range of (K_{0.75-0.82}Ca_{0.01-0.04}Na_{0-0.01})(Fe³⁺_{1.06-1.20}Fe²⁺_{0.11-0.12}Al_{0.29-0.42}Mg_{0.40-0.46})[Si_{3.65-3.73}Al_{0.27-0.35}O₁₀](OH)₂ based on averaged chemical data (cf. Fig. S2-S4). The variable composition of the glauconites, the absence of oxidized grain surfaces, the presence of cracks in the pellets and the occurrence of glauconite infillings within chambers of foraminifera indicate the authigenic nature of the glauconites.

The plot of the chemical composition data in the Al_2O_3 vs TFe and K_2O vs SiO_2 diagrams (Fig. 2d,e) indicates glauconite formation progressed through the substitution of Fe^{3+} , Fe^{2+} and Mg^{2+} ions for Al^{3+} ions in the octahedral sites and of Al^{3+} ions (and eventually Fe^{3+} ions) for Si^{4+} ions in the tetrahedral sites, which resulted in a negative layer charge that had to be balanced by the uptake of K^+ ions and minor Na^+ and Ca^{2+} ions in the interlayer sites of the glauconite (Baldermann et al., 2013). Baldermann et al. (2017) showed that the glauconites evolved in organic-rich, semi-confined micromilieus, such as in faecal pellets and in foraminifera chambers, close to the sediment-seawater interface through the reaction of Fe(III)-smectite precursors with monosilicic acid, goethite (inherited from the sediment) and seawater-derived K^+ and Mg^{2+} ions. As the mixed-layered glauconite-smectite clay transforms into glauconite, Na^+ , Ca^{2+} and H^+ ions are released from the crystal lattice, as supported by our chemical composition data (Table S1). This mode of glauconite formation is representative of many modern and palaeo-shelf environments (Banerjee et al., 2016; Bansal et al., 2017; Banerjee et al., 2020; Bansal et al., 2020a,b).

Glauconite abundance in the palaeo-depositional context. The bottom part of the Langenstein profile contains continental sandstones, which are unconformably overlain by an inner-shelf conglomerate, ~ 30 cm thick, and subsequently deposited glauconite-bearing strata (see supplementary information for details on different lithologies, stratigraphic framework and sample material). Two glauconite-bearing lithologies are recognizable across the profile (Fig. 3a): a sandstone bed rich in glauconite (up to ~ 70 wt.%), ~ 40 cm thick, and the glauconite-bearing carbonates (so-called Glauconitic Pläner Limestones). The limestones have a highly variable glauconite content, ranging from ~ 20–25 wt.% at the base (1.1–1.6 m) and ~ 5–10 wt.% in the middle part (1.6–2.5 m) to ~ 1 wt.% at the top of the profile (2.4–3.4 m) (Fig. 3b). Hence, the glauconite-bearing interval has a cumulative thickness of ~ 2.8 m (sandstone plus Pläner Limestones), reflecting the estimated sediment accumulation rate of ~ $1.3 \text{ m} \cdot \text{Myr}^{-1}$ (Wilmsen, 2007) and the absolute duration (~ 1.8 Myr) of the glauconite-bearing *Mantelliceras dixonii* Zone (henceforth called M. dixonii Zone; Gradstein et al., 2004), which lasted from ~ 97.9 Myr to ~ 96.1 Myr. However, we note that the bulk sedimentation rate was calculated on the basis of estimates of carbonate bio-productivity and that the rate is much lower compared to the distal marine sequences (glauconite-free) of Northern Germany (~ $70 \text{ m} \cdot \text{Myr}^{-1}$ at Wunstorf; Wilmsen, 2007). This is mainly because of low productivity of the carbonate factory and low clastic sedimentation on the palaeo-shelf at Langenstein. This observation agrees with the conclusions drawn by Chatteraj et al. (2016), who have argued that glauconite formation is suppressed at relatively high sedimentation rates ($> 27 \text{ m} \cdot \text{Myr}^{-1}$) and within highstand systems tracts, while transgressive systems tracts and low sedimentation rates ($< 5 \text{ m} \cdot \text{Myr}^{-1}$) favor glauconite formation and accumulation. The highly evolved nature and the high abundance of glauconite at Langenstein indicate condensed to mega-condensed sedimentation (Amorosi, 2012). Similar shallow marine mega-condensed deposits containing glauconite are reported globally from the Cenomanian (Bansal et al. 2020a).

The carbon and oxygen isotopic composition (cf. Table S2) of calcite spar within the sandstones and the conglomerate (-7.5 to -0.8‰ of $\delta^{13}\text{C}$, VPDB, and -7.5 to -5.4‰ of $\delta^{18}\text{O}$, VPDB), as well as the positive

linear correlation between the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values ($R^2 = 0.995$), suggest a continent-derived carbon source (i.e., low $\delta^{13}\text{C}$ values inherited from soil organic matter) and minor diagenetic overprinting (i.e., low $\delta^{18}\text{O}$ values inherited from the interaction with meteoric or burial fluids) (Fig. 3c,d). The calcite matrix within the glauconitic sandstone records the transition from continental influences to progressing marine sedimentation (-6.0 to 0.4‰ of $\delta^{13}\text{C}$, VPDB, and -7.3 to -5.0‰ of $\delta^{18}\text{O}$, VPDB), while the carbonate mud within the Glauconitic Pläner Limestones exhibits isotopic signatures typical for shallow marine carbonate sedimentation (1.0 to 2.1‰ of $\delta^{13}\text{C}$, VPDB, and -3.9 to -3.4‰ of $\delta^{18}\text{O}$, VPDB) (Fig. 3c,d). Calcite mud precipitation within the glauconite-bearing interval occurred at a temperature of around $26 \pm 2^\circ\text{C}$, which is typical of a 'warm' shelf environment (Banerjee et al., 2020; Gao et al., 2021). Thus, the palaeo-depositional setting at Langenstein is representative of many modern and palaeo-shelf environments.

Discussion

Rate of K–Mg–Fe sequestration by glauconite in marine settings. Reverse weathering reactions to produce authigenic clay minerals in the ocean can significantly impact the ratio of element (re)cycling vs element sequestration in marine sediments. Such element sequestration reactions are commonly slower (10^5 to 10^6 yr) compared to clay mineral formation by continental weathering (10^3 to 10^5 yr) or hydrothermal-driven fluid-rock interactions at mid-oceanic ridges (10^2 to 10^4 yr). Nevertheless, previous studies have identified 'hot spot' areas that favor clay mineral precipitation in marine sediments, such as mangrove forests, deltas and estuaries (Michalopoulos and Aller, 1995; Cuadros et al., 2016), low- to high-temperature hydrothermal sites (Huang et al., 2018; Shalev et al., 2019; Voigt et al., 2020; Laureijs et al., 2021) and shallow-water shelfal settings characterized by mega-condensed sedimentation (Baldermann et al., 2017; Bansal et al., 2020b). In such surroundings, clay retrograde reactions can behave as important controls on element sequestration and marine elemental output fluxes at or close to the sediment-seawater interface.

Herein, we focus on constraining the sequestration rates for K and Mg, as these elements are taken up directly from seawater or seawater-derived pore fluids by glauconite, and on Fe, because this element is an essential micro-nutrient in the ocean and plays a key role in the sedimentary Fe redox cycle, in particular when the rate of pyrite formation is low (Raiswell, 2006; Baldermann et al., 2013; López-Quirós et al., 2019). We do not consider Na and Ca, as they are barely incorporated in glauconite (Table S1), and also exclude Al and Si from further consideration, as these elements are virtually 'absent' in modern ocean water. This is attributed to the low solubility of most Al- and Si-bearing solids and the strong concentration limitations arising from the activity of silicifying organisms, such as radiolarians, diatoms and siliceous sponges, in particular in the surface oceans (Hoffmann et al., 2008; Kranzler et al., 2019).

Assuming (i) a sedimentation rate of $130 \text{ cm} \cdot \text{Myr}^{-1}$ for the M. dixonii Zone (Wilmsen, 2007) and (ii) a density of $2.7 \text{ g} \cdot \text{cm}^{-3}$ for the glauconitized strata (Logvinenko, 1982), and considering (iii) the K–Mg–Fe contents of the glauconites (Table S1) and (iv) the abundance of glauconite across the studied

sedimentary sequence (Fig. 3a,b), element-specific sequestration rates associated with shallow-water glauconite formation can be calculated (Fig. 3e and Table S3). The sequestration rates range from 0.7 to 42 mmol K·cm⁻²·kyr⁻¹, 0.4 to 23 mmol Mg·cm⁻²·kyr⁻¹ and 1.1 to 65 mmol Fe·cm⁻²·kyr⁻¹, reflecting the extremely low to very high abundances (1 vs 70 wt.%) of glauconite in the profile.

The 'low rate' of element sequestration may reflect reverse weathering processes taking place in depositional systems that are characterized by high sedimentation rates and a short residence time at the sediment-seawater interface. Authigenic clay precipitation is inefficient under such conditions (Amorosi, 2012; Chatteraj et al., 2016) so that element sequestration is reduced. The 'high rate' of element sequestration may represent transgressive systems that are characterized by low to close to zero overall sedimentation and a prolonged residence time at the sediment-seawater interface, which favor glauconite formation (Amorosi, 2012; Banerjee et al., 2020).

Considering an average glauconite content of 5–10 wt.% for the ~ 2.8 m thick glauconitized interval at Langenstein, which is representative of Phanerozoic glauconite deposits (7 ± 4 wt.%; Banerjee et al., 2016), the sequestration rate for glauconite formation in the palaeo-shelf environment of the Upper Cretaceous averages 7 ± 5 mmol K·cm⁻²·kyr⁻¹, 3 ± 1 mmol Mg·cm⁻²·kyr⁻¹ and 14 ± 13 mmol Fe·cm⁻²·kyr⁻¹. For comparison, the sequestration rates for glauconite-smectite and glauconite forming in the modern deep-sea sediments of the Ivory Coast (Ghana Marginal Ridge) were determined as 0.017 mmol K·cm⁻²·kyr⁻¹, 0.024 mmol Mg·cm⁻²·kyr⁻¹ and 0.080 mmol Fe·cm⁻²·kyr⁻¹ (partly recalculated from Baldernann et al., 2015), which is, on average, ~ 100-400-times lower than shelfal sequestration rates. However, the glauconite content (2.5 wt.%, on average), the K₂O concentration (2.9 wt.%, on average, reflecting the 'nascent' stage) and the rate of glauconite formation (~ 5-times lower) are substantially lower in deep-water settings than in the shelf regions. The lower rate of glauconite formation in deep-water settings is due to the low temperature (~ 5 vs ~ 25°C), the reduced supply and sedimentary reflux of Al³⁺ ions, silicic acid and organic matter, the latter controlling local redox restrictions (semi-confined micromilieu vs redoxcline) that predetermine the availability and the speciation of Fe (Fe²⁺ vs Fe³⁺), which is the rate-determining factor for glauconite formation (Baldernann et al., 2013; López-Quirós et al., 2019).

Effect of glauconite formation on global marine K–Mg–Fe palaeo-fluxes. The source-sink relations of chemical elements in the modern ocean are relatively well constrained (Raiswell, 2006; Henderson et al., 2007; Arvidson et al., 2013; Dale et al., 2015; Jeandel and Oelkers, 2015; Cuadros et al., 2016; Huang et al., 2018; Shalev et al., 2019; Somes et al., 2021). Model estimates indicate that the marine K, Mg and Fe cycle is mainly controlled by flux variations of riverine (and groundwater), atmospheric, glacial and hydrothermal inputs vs silicate and carbonate mineral deposition on the ocean floor. However, the role of authigenic clay formation on the fluxes in the marine sedimentary K–Mg–Fe budgets of the modern and ancient oceans remains enigmatic.

Although the K–Mg–Fe sequestration rates reported for glauconite formation at Langenstein (shallow-water; this study) and the Ivory Coast (deep-water; Baldernann et al., 2015) may not be directly

transferrable to all other marine settings that accumulated glauconite through time and space, (i) the mode of glauconite formation (Fe-smectite-to-glauconite reaction), (ii) the micro-environment (faecal pellets and foraminifera), (iii) the timing (10^5 - 10^6 yr), (iv) the composition (Fe-rich, highly evolved vs nascent), (v) the abundance (5–10 wt.% vs 2–3 wt.%) and (vi) the depositional environment (warm shallow shelf vs cool deep-sea; low sedimentation rate) at the two localities are representative of the range expected for many modern and past glauconite-forming environments (Odin and Matter, 1981; Baldermann et al., 2015; Banerjee et al., 2016; Baldermann et al., 2017; Bansal et al., 2017; López-Quirós et al., 2019; Banerjee et al., 2020; Bansal et al., 2020a,b; Choudhury et al., 2021). Furthermore, the Langenstein glauconites share many similarities with other Mesozoic to Cenozoic glauconite deposits, such as a similar abundance (7 ± 4 wt.% in the marine rock record from the Triassic to the Holocene time; Fig. 4a; Banerjee et al., 2016), a comparable chemical composition (7 ± 1 wt.% K_2O , 4 ± 1 wt.% MgO and 23 ± 2 wt.% TFe; Fig. 4b; Banerjee et al., 2016), and a low overall sedimentation rate (1 to 5 $m \cdot Myr^{-1}$; Fig. 4c; Chatteraj et al., 2016). If we assume that the sedimentation rate ($1.3 m \cdot Myr^{-1}$) and the sediment density ($2.7 g \cdot cm^{-3}$) on the palaeo-shelf at Langenstein are representative of the global shelf through geological time, we can compute K–Mg–Fe palaeo-sequestration rates for shallow-water glauconite formation for Mesozoic and Cenozoic times (Fig. 4d-f; Table S4).

It is evident that glauconite formation significantly contributed to K–Mg–Fe sequestration in shallow marine sediments throughout Earth's history, averaging $4 \pm 3 mmol K \cdot cm^{-2} \cdot kyr^{-1}$, $4 \pm 2 mmol Mg \cdot cm^{-2} \cdot kyr^{-1}$ and $10 \pm 6 mmol Fe \cdot cm^{-2} \cdot kyr^{-1}$, respectively. We note that K–Mg–Fe sequestration by glauconite formation also happened in the 'older' sediments of the Archaean, Proterozoic and early Cambrian, but this elemental uptake can be barely quantified given that sedimentary archives of this time are scarce and that most of the 'old' glauconites are at least partly altered to illite or chlorite minerals (Bansal et al., 2020b; Rafiei et al., 2020). K–Mg–Fe sequestration by green clay authigenesis was of minor importance in the Late Ordovician, Early Silurian and Late Devonian, which corresponded to major glacial events, where glauconite formation is inefficient (Banerjee et al., 2016). On the contrary, high glauconite abundances and related high K–Mg–Fe sequestration rates are evident, for example, in the Neogene (glauconite sands from the Chatham Rise, Southwest Pacific), at the Paleogene-Eocene Transition (glauconite sands from the continental margins of the northern hemisphere; Upper and Lower Greensands of England) and in the Cretaceous (New Jersey, Maryland and Delaware Greensands; greensand giants from the Duwi group, Egypt; Bakchar glauconite deposit, Western Siberia) (cf. Figure 4d-f). These periods record glauconite deposits of huge economic or geological value (Banerjee et al., 2016; Banerjee et al., 2020).

Using average elemental sequestration rates per geological period (Fig. 5a) and corresponding occurrences of glauconite on the shelf (Fig. 4a), as well as calculated low and high estimates of the shallow ocean areas over time (Fig. 5b; Cao et al., 2017; Scotese and Wright, 2018), we can compute K–Mg–Fe palaeo-fluxes ($Tmol \cdot yr^{-1}$) associated with green clay authigenesis that progressed on the world's shelf area (defined here as 0-200 m water depth) over time (Fig. 5c-e; Table S5). Based on comparison with global K–Mg–Fe fluxes of the modern and past ocean, we propose that the obtained 'high' K–Mg–

Fe palaeo-fluxes are overestimated (i.e., the shelf areas reported by Cao et al. (2017) are overestimated) and that the 'low' K–Mg–Fe palaeo-fluxes (i.e., the shelf areas reported by Scotese and Wright (2018)) better portray the average elemental burial related to green clay authigenesis per geological period, which averages $0.09 \pm 0.12 \text{ Tmol K}\cdot\text{yr}^{-1}$, $0.08 \pm 0.11 \text{ Tmol Mg}\cdot\text{yr}^{-1}$ and $0.20 \pm 0.28 \text{ Tmol Fe}\cdot\text{yr}^{-1}$ during the Triassic to Holocene. The ratio of the K–Mg–Fe palaeo-fluxes associated with glauconite formation in the past vs modern ocean (Fig. 5d) indicates further that the elemental fluxes were much higher from the Jurassic to the Oligocene compared to the modern ocean, averaging a factor of 2.4 ± 3.4 , which we attribute to the warm and sea level highstand 'greenhouse' conditions prior to the Eocene-Oligocene transition. The lower K–Mg–Fe palaeo-fluxes ever since the Oligocene are caused by the decrease of the shallow-water shelf areas and seawater temperature with the onset of the first Southern Hemisphere glaciation ($\sim 34 \text{ Myr}$ ago) and then Northern Hemisphere glaciation ($\sim 5 \text{ Myr}$ ago), where glauconite formation is reduced (Banerjee et al., 2016). Although these estimates have a relatively high uncertainty and need to be better constrained in future work, it is evident that green clay authigenesis greatly affected the global marine K, Mg and in particular Fe cycle throughout Earth's history.

K–Mg–Fe sequestration by green clay authigenesis in modern marine settings. To the best of our knowledge, elemental output fluxes attributed to widespread glauconite formation taking place at the shallow shelf and in the deep-sea (defined here as $> 2000 \text{ m}$ water depth) of the modern oceans have not been determined yet and are not fully accounted for in earth system models (Arvidson et al., 2013; Baldermann et al., 2015; Cuadros et al., 2016; Haley et al., 2017; Rahman et al., 2017; Isson and Planavsky, 2018; Abbott et al., 2019). We recognize that some of the glauconite deposits of the Quaternary and Holocene are of para-autochthonous or detrital origin, representing reworked glauconites of the Neogene or even older ages (Odin and Matter, 1981; Baldermann et al., 2013; Banerjee et al., 2016). As a first-order approximation to calculate the present-day global K–Mg–Fe output fluxes attributed to green clay authigenesis, we use (i) published glauconite contents in the shallow and deep-marine sediments of the Holocene (5.6 wt.% vs 2.5 wt.%; Banerjee et al., 2016; Logvinenko, 1982), (ii) the total areas of the modern shelf and deep-sea regions ($27.12 \cdot 10^{12} \text{ m}^2$ vs $302.5 \cdot 10^{12} \text{ m}^2$; Dale et al., 2015) and (iii) K–Mg–Fe sequestration rates by Holocene shallow-water and deep-water glauconite formation ($3.0\text{--}4.0 \text{ mmol K}\cdot\text{cm}^{-2}\cdot\text{kyr}^{-1}$, $2.4\text{--}4.1 \text{ mmol Mg}\cdot\text{cm}^{-2}\cdot\text{kyr}^{-1}$ and $7.4\text{--}8.8 \text{ mmol Fe}\cdot\text{cm}^{-2}\cdot\text{kyr}^{-1}$, Fig. 5d-f, vs $0.017 \text{ mmol K}\cdot\text{cm}^{-2}\cdot\text{kyr}^{-1}$, $0.024 \text{ mmol Mg}\cdot\text{cm}^{-2}\cdot\text{kyr}^{-1}$ and $0.080 \text{ mmol Fe}\cdot\text{cm}^{-2}\cdot\text{kyr}^{-1}$; Baldermann et al., 2015). Upscaling predicts global K–Mg–Fe output fluxes associated with glauconite formation of $\sim 0.05\text{--}0.06 \text{ Tmol K}\cdot\text{yr}^{-1}$, $\sim 0.04\text{--}0.06 \text{ Tmol Mg}\cdot\text{yr}^{-1}$ and $\sim 0.11\text{--}0.14 \text{ Tmol Fe}\cdot\text{yr}^{-1}$ at the shallow shelf, and of $\sim 0.001 \text{ Tmol K}\cdot\text{yr}^{-1}$, $\sim 0.002 \text{ Tmol Mg}\cdot\text{yr}^{-1}$ and $\sim 0.006 \text{ Tmol Fe}\cdot\text{yr}^{-1}$ for the deep-sea glauconites (Fig. 6). The calculated K–Mg–Fe fluxes have a relatively high uncertainty, but the estimates are well within global marine K–Mg–Fe fluxes published in the literature (Dale et al., 2015; Sun et al., 2016; Huang et al., 2018; Shalev et al., 2019). However, we assume the herein reported K–Mg–Fe fluxes are conservative estimates, if considering that the abundance of glauconite in shallow marine sediments was much higher in the majority of the Phanerozoic due to sea level lowstands and higher seawater temperatures under warm 'greenhouse' conditions vs modern 'icehouse' conditions that significantly reduce the burial fluxes linked to green clay authigenesis (Banerjee et al., 2020).

K sequestration by deep-water glauconite formation is barely significant and accounts for $\sim 0.1\%$ removal of the total dissolved riverine K influx ($\sim 1.51 \text{ Tmol}\cdot\text{yr}^{-1}$; Garrels and Mackenzie, 1971) and of the K supplied to the ocean by hydrothermal alteration of the modern oceanic crust ($\sim 1.51 \text{ Tmol}\cdot\text{yr}^{-1}$; Berner and Berner, 2012). Contrary, shallow-water glauconite formation can play an important role in the global K cycle (Fig. 6), as it fixes $\sim 3\text{--}4\%$ of the total oceanic K inventory that is sourced from riverine and hydrothermal fluxes, or $\sim 3\%$ of the K that is removed from the ocean through low-temperature alteration of ocean-floor basalts ($\sim 1.99 \text{ Tmol}\cdot\text{yr}^{-1}$; Sayles, 1979; Sun et al., 2016). Hence, K sequestration by glauconite formation at the shelf is at the same order of magnitude as K sequestration by Fe-illite formation taking place in the mangrove forests worldwide ($\sim 0.02\text{--}0.08 \text{ Tmol}\cdot\text{yr}^{-1}$; Cuadros et al., 2016). An exception to this amount of K sequestration occurs when K is available locally from e.g., a K-feldspar substrate altering to glauconite, as reported in Proterozoic oceans (Banerjee et al., 2015).

The same conclusions can be drawn for the marine Mg cycle (Fig. 6): Glauconite formation at the shelf consumes $\sim 1\%$ of the terrestrial Mg flux ($\sim 5.51 \text{ Tmol}\cdot\text{yr}^{-1}$) that is brought to the ocean via continental weathering of Mg-bearing carbonates and silicates (Fig. 6) and constitutes $\sim 1\text{--}2\%$ to the marine Mg sink that is associated with low- and high-temperature alteration of the oceanic crust ($\sim 2.71 \text{ Tmol}\cdot\text{yr}^{-1}$; Huang et al., 2018). Further, Mg sequestration by glauconite is equivalent to $\sim 1\text{--}4\%$ of the estimated Mg sink by enigmatic (yet hidden) dolomite deposits ($\sim 1.48\text{--}2.88 \text{ Tmol}\cdot\text{yr}^{-1}$; Shalev et al., 2019) or $\sim 19\text{--}29\%$ of the Mg consumption by authigenic clays forming in the Amazon deltaic sediments ($\sim 0.21 \text{ Tmol}\cdot\text{yr}^{-1}$; Sun et al., 2016). Contrary, Mg sequestration associated with deep-water glauconite formation accounts for only $\sim 0.3\%$ of the low-temperature alteration flux ($\sim 0.66 \text{ Tmol}\cdot\text{yr}^{-1}$; Higgins and Schrag, 2012; Sun et al., 2016; Shalev et al., 2019).

In addition, glauconite acts as an important sink for Fe (Fig. 6), with shallow-water glauconite formation accounting for up to $\sim 13\text{--}29\%$ removal of the dissolved and particulate riverine flux of highly reactive Fe to the ocean ($\sim 0.48\text{--}0.86 \text{ Tmol}\cdot\text{yr}^{-1}$ and $\sim 0.63 \text{ Tmol}\cdot\text{yr}^{-1}$; Raiswell, 2006). Although Fe uptake by deep-water glauconite formation is less significant (Fig. 6), it is still equivalent to $\sim 2\%$ removal by the total hydrothermal alteration flux ($\sim 0.25 \text{ Tmol}\cdot\text{yr}^{-1}$) or $\sim 3\%$ and $\sim 30\%$ removal by the glacial flux ($\sim 0.20 \text{ Tmol}\cdot\text{yr}^{-1}$) and the atmospheric dust flux ($\sim 0.02 \text{ Tmol}\cdot\text{yr}^{-1}$; Raiswell, 2006). Even though oxidation and scavenging processes are the first-order controls for the benthic Fe fluxes in the ocean (Dale et al., 2015), we conclude that glauconite formation taking place in shallow and deep marine settings is an important but currently overlooked mechanism and elemental sink. These glauconite formation settings can, at least locally, affect the pore water inventory of Fe^{2+} , K^+ and Mg^{2+} ions that might otherwise be available for biogeochemical use for the ocean and the marine sediments.

We conclude that fast retrograde clay mineral reactions, which occur to wide extent on the ocean floor, are of great significance in the marine K, Mg and in particular Fe cycle and have to be considered in earth system models of the present and past marine element cycles. The elemental burial fluxes attributed to green clay authigenesis were significantly higher under the sea level highstand and 'greenhouse' conditions in the majority of the Phanerozoic compared to the modern sea level lowstand and icehouse

conditions, which suppress glauconite formation. It is now up to future studies (i) to estimate how K–Mg–Fe sequestration through glauconite formation impacts the isotopic composition of the ocean, the pore water reservoir and the modern marine (deep-sea) sediments, and (ii) to assess the impact of climate change through time on the elemental burial fluxes attributed with reverse silicate weathering and green clay authigenesis.

Methods

X-ray diffraction (XRD) patterns were recorded on powdered bulk rocks using a PANalytical X'Pert PRO diffractometer equipped with a high-speed Scientific X'Celerator detector and operated at 40 kV and 40 mA (Co-K α radiation source). The samples were prepared using the top-loading technique (Baldermann et al., 2021). The preparations were examined in the range 4 to 85° 2 θ with a step size of 0.008° 2 θ and a scan speed of 40 s. Mineral quantification was carried out by Rietveld analysis of the XRD patterns using the PANalytical X'Pert HighScore Plus Software and the ICSD database (Baldermann et al., 2021). The analytical error is better than ± 3 wt.% (Baldermann et al., 2013; Rafiei, et al., 2020).

The micro-texture and the chemical composition of the green grains were analyzed on polished thick sections by electron microprobe analyses (EMPA) using a JEOL JXA8530F Plus Hyper Probe at Karl-Franzens-University Graz. Analytical conditions were 15 keV accelerating voltage, 15 nA beam current and defocused beam, ~ 3 μ m in size, to avoid mineral damage during the measurements. The chemical data were standardized against a range of natural and synthetic crystals, which included the following elements with their characteristic spectral lines: Al-K α , Si-K α and K-K α (microcline), Mg-K α and Ca-K α (augite), Fe-K α (ilmenite), Na-K α (tugtupite) and P-K α (LaPO $_4$). Counting times were set to 10 s on peak and 5 s on background position on each side of the element-specific peak. Only compositions with an analytical error of less than 7 wt.% off 100 wt.% were taken into further consideration (Table S1). The chemical compositions were corrected for the average Fe(II)/Fe(III) ratio of the green grains reported by Baldermann et al. (2017) based on electron energy-loss spectroscopy (EELS) analyses. Structural formulae were calculated based on 22 negative charges, assuming (i) $^{IV}\text{Si}^{4+} + ^{IV}\text{Al}^{3+}$ is equal to 4, (ii) $\text{Fe}^{2+/3+}$, Mg^{2+} , and $\text{Al}^{3+}_{\text{rest}}$ occupy the octahedral sheet, (iii) K^+ , Na^+ and Ca^{2+} are located within the interlayer sites and (iv) the P $_2$ O $_5$ contents belong to apatite impurities and not to glauconite. Furthermore, element distribution maps (Al, Fe, K, Si, Ca, Mg, F, Na, S and P) of 1200 $\times$ 1200 pixel resolution were acquired (Fig. S1-3). The analytical conditions were as follows: focused beam, 15 keV accelerating voltage, 20 nA beam current, 3 μ m pixel size and a dwell time of 13 ms·step $^{-1}$.

The particle form and the nature of the green grains were determined by transmission electron microscopy (TEM) using a FEI Tecnai F20 instrument operated at an accelerating voltage of 200 kV and fitted with a Schottky field emitter, a Gatan imaging filter and an UltraScan CCD camera. High-resolution TEM lattice fringe images were collected parallel to the (001)-plane of the clay minerals particles. Therefore, a sub-fraction of the Glauconitic Pläner Limestones was treated with 10 % acetic acid for 1 h to dissolve carbonates. The acid-insoluble residue was washed several times with ultrapure water and

subsequently the green grains were separated by hand-picking under a binocular microscope. The green grains were ultrasonically dispersed for 15 min in ethanol and prepared following standard procedures prior to the TEM analyses (Baldermann et al., 2021).

Stable carbon and oxygen isotope compositions of carbonates with calcite mineralogy only were obtained on the evolved CO₂ after the reaction of powdered whole rock sub-samples with pure H₃PO₄ at 72°C in an automated GASBENCH II preparation unit connected to a Thermo Finnigan delta plus XP mass spectrometer at the Institute for Geological and Geochemical Research (IGGR in Budapest, Hungary). The isotopic values are expressed as $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (in ‰) relative to the Vienna Pee-Dee Belemnite (VPDB) reference material (Table S2). On the basis of standard measurement, the accuracies of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are estimated to be better than $\pm 0.1\text{‰}$. Analytical details are described in Demény et al. (2019). Calcite formation temperatures (in °C) were calculated exclusively for the Glauconitic Pläner Limestones based on the measured $\delta^{18}\text{O}$ values assuming a $\delta^{18}\text{O}$ value of -1‰ (VSMOW) for Cretaceous seawater and applying the equation of Friedman and O'Neil (1977).

Declarations

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Author contributions

A.B. designed the study. A.B., S.B., S.L., U.M., E.S. and T.Z. participated in the early-stage discussion. G.C. provided the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotopic data and N.W. contributed the areas of the global shallow ocean. A.B., M.D., S.L. and J.F. calculated the K–Mg–Fe sequestration rates and the K–Mg–Fe palaeo-fluxes. A.B. U.M., E.S. and T.Z. carried out the field work. All co-authors contributed to the writing.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information. The supplementary material is attached to the article and will be made accessible via the Zenodo Data Repository.

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Figures

Figure 1

Overview of the glauconite-bearing sedimentary sequence at Langenstein. A) Google Earth view of the study site in Germany. B) Geological map of the Subhercynian Cretaceous Basin with the location of the Langenstein profile (modified from Baldermann et al., 2017). C) Lithostratigraphic log of the Langenstein profile with the glauconite-bearing interval marked with green color. The biostratigraphy is from Wilmsen et al. (2005), while the glauconite K-Ar age is from Baldermann et al. (2017) (sample position in the log is marked by the red star).

Figure 2

Glaucinite characterization. A) The XRD pattern of the glauconite-bearing sandstone identifies ordered glauconite (1 M polytype), disordered glauconite-smectite (1 Md polytype), quartz (Qz) and minor kaolinite (Kln), feldspar (Fsp), apatite (Ap) and calcite (Cal). B) The secondary electron image (SEI) shows 'rosette' structures within the dark green faecal pellets (cf. inset), which is typical for 'evolved' glauconite grains. C) The TEM images highlight the majority of 10 Å domains (cf. inset) within the lath-like

glaucinite particles. D-E) The chemical composition of the glaucinites records ‘evolved’ to ‘highly evolved’ and Fe-rich grains, which is representative of Mesozoic to Cenozoic glaucinites.

Figure 3

Glaucinite abundance, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotope profiles of calcite and K–Mg–Fe sequestration rate related to glauconite formation. A) Lithostratigraphic log of the studied profile with the glauconitized interval highlighted in green color (refer to Fig. 1C for legend). The age refers to glauconite K–Ar dating (Baldermann et al., 2017). B) Glaucinite abundance across the Langenstein profile. C–D) Carbon and oxygen isotopic profiles of calcite indicate the glauconitized interval to be deposited on a warm proximal shelf environment. E) K–Mg–Fe sequestration rates attributed to glauconite formation.

Figure 4

K–Mg–Fe sequestration rates for shallow-water glauconite formation during the Mesozoic and Cenozoic. A) Glauconite abundance on the shelf through time (total occurrence of glauconite in the rock record and the relative proportions of glauconite on the shelf are from Banerjee et al., 2016). B) Average composition (± 2 SD) of K, Mg and Fe of glauconite over time (Banerjee et al., 2016). C) Variation in overall sedimentation rate typical for glauconite formation (Chattoraj et al., 2016). D-F) Elemental sequestration rates for K, Mg and Fe associated with shallow-water glauconite formation through time (colored curves) and at Langensteen (black stars). Average sequestration rates (± 2 SD) are highlighted by the grey shaded intervals. The rate calculations are based on a low but constant sedimentation rate of 1.3 m·Myr⁻¹ and a sediment density of 2.7 g·cm⁻³ for each geological period. Thus, temporal changes in the sequestration rates illustrate the variability in glauconite composition and abundance over time.

Figure 5

K–Mg–Fe palaeo-fluxes ($\text{Tmol}\cdot\text{yr}^{-1}$) associated with green clay authigenesis taking place on the shelf during the Mesozoic and Cenozoic. A) Average K–Mg–Fe sequestration rates associated with shallow-water glauconite formation through time (cf. Fig. 4d-f). B) Estimated areas of the global shallow ocean (0-200 m water depth) over time using two different paleogeographic reconstructions. The estimate labelled as 'low' is the shelf area (average $\pm$ 2SD) that was computed from the respective contours of a series of palaeo-digital elevation models ($1^\circ \times 1^\circ$ resolution) developed by Scotese and Wright (2018) using Generic Mapping Tools (Wessel et al., 2019). The estimate labelled as 'high' is the shelf area (average $\pm$ 2SD), which was calculated by Cao et al. (2017) based on the paleogeographic model from Golonka et al. (2006) that is available as a series of polygons, reconstructed with the plate tectonic model of Matthews et al. (2016). C-E) Elemental palaeo-fluxes (average $\pm$ 2SD) associated with shallow-water glauconite formation for the 'low' vs 'high' paleogeographic reconstructions. F) Elemental palaeo-flux ratios (ancient vs modern ocean) for the 'low' shallow ocean scenario. The K–Mg–Fe palaeo-flux calculations assume a constant occurrence of glauconite (cf. Fig. 4a) for each geological period, meaning that changes in the K–Mg–Fe palaeo-flux illustrate the effects of the individual elemental sequestration rates and of the varying shelf areas over time.

Figure 6

Simplified sketch of the global K, Mg and Fe cycle with average fluxes of the main oceanic sources and sinks of K–Mg–Fe (in Tmol·yr⁻¹). The directions of the arrows refer to the net uptake or release of K, Mg and Fe for each geological process. Elemental fluxes due to phosphate and evaporate formation and/or dissolution are not considered. K fluxes: Garrels and Mackenzie (1971), Sayles (1979), Berner and Berner (2012), Cuadros et al. (2016), Sun et al. (2016); Mg fluxes: Higgins and Schrag (2012), Sun et al. (2016), Huang et al. (2018), Shalev et al. (2019); Fe fluxes (aq – aqueous/dissolved; s – solid/particulate): Raiswell (2006), Dale et al. (2015); Glaucinite K–Mg–Fe fluxes: Baldermann et al. (2015), this study; Ocean chemistry: John and Adkins (2010); Sun et al. (2016), Huang et al. (2018).

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