Impact of green clay authigenesis on element sequestration in marine settings

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Retrograde clay mineral reactions (reverse weathering), including glauconite formation, are first-order controls on element sequestration in marine sediments. Here, we report substantial element sequestration by glauconite formation in shallow marine settings from the Triassic to the Holocene, averaging 3 ± 2 mmol·cm⁻²·kyr⁻¹ for K, Mg and Al, 16 ± 9 mmol·cm⁻²·kyr⁻¹ for Si and 6 ± 3 mmol·cm⁻²·kyr⁻¹ for Fe, which is ~2 orders of magnitude higher than estimates for deep-sea settings. Upscaling of glauconite abundances in shallow-water (0–200 m) environments predicts a present-day global uptake of ≤ 0.1 Tmol·yr⁻¹ of K, Mg and Al, and ~0.1–0.4 Tmol·yr⁻¹ of Fe and Si, which is ~half of the estimated Mesozoic elemental flux. Clay mineral authigenesis had a large impact on the global marine element cycles throughout Earth’s history, in particular during ‘greenhouse’ periods with sea level highstand, and is key for better understanding past and present geochemical cycling in marine sediments.

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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, glacial, and wind.

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.

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.

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, which determine the sedimentation rate, composition, and reactivity of the continental weathering influx. This influx and the corresponding chemical evolution of the ocean, as well as long-term variations of the atmospheric carbon dioxide (CO₂) pool, subsequently influence the marine silicate and carbonate bioproducitivity.

The source-sink relations of the global elemental cycles are increasingly well constrained due to advances in 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. However, there remain large gaps in knowledge concerning, for example, the marine rare earth elements (REE), trace elements, and potassium (K) budgets.

Moreover, the magnitude of element burial attributable to reverse weathering and (green) clay mineral authigenesis on the ocean floor remains poorly constrained, except for very specific settings (e.g., well studied deltaic sediments), and is only indirectly accounted for in earth system models.

The long-standing view that clay mineral reactions taking place at low to ambient temperature (∼30°C) over much of the Earth’s surface are very slow has been increasingly challenged. Fast retrograde clay reactions occur in hydrothermal settings or in deep-burial and diagenetic surroundings, in deltaic sediments, mangrove forests or estuaries, and even in the deep-sea.

Authigenic minerals, such as green clay, are increasingly considered critical controls on element sequestration in modern and ancient marine sediments.

However, the often cryptic nature of authigenic clays, as well as their small particle size and compositional similarity to detrital clays, make it difficult to estimate their abundance in the rock record, so that the broader significance of authigenic clays in the marine geochemical cycle remains disputed.

The mineral glauconite, (K, Na, Ca)(Fe, Al, Mg)[(Si,Al)₄O₁₀](OH)₂, is one such authigenic clay, which commonly forms large (mm-scale), distinct, and easily recognized green granules near the sediment-water interface, making it a particularly important proxy to assess the broader significance of clay authigenesis in marine sediments.

Glaucinite forms in siliciclastic and calcareous sediments in marine and continental depositional environments, and within a wide range of substrates, including fecal pellets, foraminifera chambers, and lithoclasts.

It is thought to evolve from K-poor, but iron (Fe)-rich smectite to K- and Fe-rich glauconite via the formation of glauconite-smectite intermediates over a time-frame much less than a few million years (Myr) after sediment deposition.

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 near-surface sediments, there has been no attempt to estimate the broader impact of glauconite formation on past and present marine geochemical cycles.

In this study, we fill this gap using a well-characterized, Cretaceous-aged glauconite-bearing sequence from Langenstein, Northern German basin, to calculate elemental sequestration rates related to glauconite formation in shallow-water settings. The Langenstein sequence (Fig. 1) is an authigenic glauconite deposit formed in a palaeo-shelf setting. Here, shallow-water carbonate or sandstone lithologies contain abundant glauconite, with overlying shelf sediments hosting smaller quantities of glauconite (see Supplementary Fig. 1 for lithofacies analysis).

K-Ar dating indicates glauconite formation was completed within 1 Myr of deposition, close to the sediment-seawater interface.

This study site is representative of many modern and palaeo-shelf settings that accumulate glauconite minerals.

Upscaling of the Langenstein rates indicates that element sequestration through green clay authigenesis strongly impacted the marine geochemical cycle throughout Earth’s history.

Results and discussion

Characterization of Langenstein glauconite. XRD analysis identifies the green grains within the sandstone and carbonate lithologies as glauconite with minor admixtures of glauconite-smectite based on broad reflections at 10 Å (001), 5.0 Å (002), 4.5 Å (002), 3.3 Å (003), 2.6 Å (131), and 1.51 Å (060,331) (Fig. 2a). Well defined reflections at 3.6 Å (112) and 3.1 Å (112), and the weak “XRD hump” between 25 to 40° 2θ indicate the green grains are mixtures of the M1 and M2 polytype structures, which correspond to ordered glauconite and disordered glauconite-smectite.

Petrographically, the green grains are dominated by glauconitized fcel pellets of dark green and medium green color (~85 ± 5 wt%; insert in Fig. 2b), with subordinate light green colored glauconitized fcel pellets (~10 ± 5 wt%) and greenish fillins 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). The high-resolution TEM lattice fringe image shows the flake-shaped glauconite particles are made of 10 Å domains (Fig. 2c and the insert). All these features are indicative of evolved, mature glauconite.

Glaucinite commonly evolves from an authigenic Fe-smectite precursor, with glauconite maturation from a K-poor but Fe(III) rich nascent stage (~<4 wt% K₂O) to a K-rich evolved or highly evolved stage (~>8 wt% K₂O) occurring over less than a few Myr. Chemically, the vast majority (more than 95% of the chemical data, see Supplementary Table 1) of the glauconite grains has K₂O contents exceeding 7 wt%, frequently reaching up to ~9 wt% (Fig. 2d), which is characteristic of mature glauconite (i.e., reflecting the “evolved” to “highly evolved” stage, according to the glauconite maturity classification of ref. 33). The total Fe contents (defined here as TFe; a sum of Fe₂O₃ and FeO) range from 16 to 26 wt% (Fig. 2e), which shows the glauconites are Fe-rich.

The measured aluminum (Al), magnesium (Mg), and silicon (Si) contents (expressed as oxides) are in the typical range of Mesozoic and Cenozoic glauconites, averaging 7.9 ± 1.0 wt% Al₂O₃, 4.1 ± 0.3 wt% MgO, and 51.8 ± 1.5 wt% SiO₂, respectively. The sodium (Na) (~<0.2 wt% Na₂O) and calcium contents (~<0.2 wt% CaO, but up to 7.9 wt% CaO where hydroxyl-apatite and calcite inclusions are present) are generally low, as expected in mature glauconite.

The calculated structural formula of the glauconites varies in the range of (K₀.₇₅₋₀.₈₂Ca₀.₀₁₋₀.₀₄Na₀.₀₇₋₀.₀₉)(Fe²⁺₀.₁₁₋₁.₀₀Fe³⁺₁.₆₋₁.₀)0.₂₉₋₀.₄₂Mg₀.₄₂₋₀.₄₀Si₀.₆₅₋₁.₃₇Al₀.₂₇₋₁.₃₅O₄₋₀.₇₅(OH)₂ based on averaged chemical data obtained from “pure” glauconite (i.e., inclusion-free glauconite; see Supplementary Table 1).
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 Plänner 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 Plänner Limestones), reflecting the estimated sediment accumulation rate of ~1.3 m Myr⁻¹ and the absolute duration (~1.8 Myr) of the glauconite-bearing Mantelliceras dixoni Zone (henceforth called M. dixoni Zone), which lasted from ~97.9 Myr to ~96.1 Myr. However, this linearized bulk sedimentation rate is much lower compared to the marine mid-shelf sequences of Northern Germany (~70 m Myr⁻¹ at Wunstorf) which is due to the low productivity of the carbonate factory and low clastic sedimentation on the palaeo-shelf at Langenstein. Such transgressive systems tracts and reduced sedimentation rates favor glauconite formation and accumulation. The evolved nature and high abundance of glauconite at the bottom part of the Langenstein profile indicate mega-condensed sedimentation, while the lower abundance of glauconite up-section in the profile suggests low to moderate sedimentation. Similar shallow marine condensed deposits containing glauconite are reported globally from the Cenomanian.

The carbon and oxygen isotopic composition (see Supplementary Table 2) of calcite spar within the sandstones and the conglomerate (−7.5 to −0.8‰ of δ¹³C, VPDB, and −7.5 to −5.4‰ of δ¹⁸O, VPDB), as well as the positive linear correlation between the δ¹³C and δ¹⁸O values (R² = 0.995), suggest a continent-derived carbon source (i.e., low δ¹³C values inherited from soil organic matter) and minor diagenetic overprinting (i.e., low δ¹⁸O 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 progressively more marine sedimentation (~6.0 to 0.4‰ of δ¹³C, VPDB, and −7.3 to −5.0‰ of δ¹⁸O, VPDB), while the carbonate mud within the Glauconitic Plänner Limestones...
exhibits isotopic signatures typical for shallow marine carbonate sedimentation ($1.0$ to $2.1 \, \text{‰}$ of $\delta^{13}C$, VPDB, and $-3.9$ to $-3.4 \, \text{‰}$ of $\delta^{18}O$, 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\textsuperscript{50}. Thus, the palaeo-depositional setting, as well as the composition and the mode of glauconite formation at Langenstein are representative of many modern and palaeo-shelf environments, justifying the use of the Langenstein section for the calculation of rates and fluxes for global shelf settings.

**Rate of elemental uptake by glauconite in marine settings.** Reverse weathering reactions to produce authigenic clay minerals can significantly impact the ratio of element diffusive return fluxes to seawater (i.e., recycling) vs element sequestration in marine sediments. Previous studies have identified "hot spot" areas that favor clay mineral precipitation in marine sediments, such as mangrove forests, deltas, and estuaries\textsuperscript{21,24,26,27,51}, as well as low- to high-temperature hydrothermal sites\textsuperscript{4–7}, and shallow-water settings characterized by reduced sedimentation\textsuperscript{44,46}. In such surroundings, clay retrograde reactions are important controls on marine elemental
output fluxes at or close to the sediment-seawater interface. Here, we constrain glauconite-associated sequestration rates for two classes of major elements, i.e., (i) "conservative elements" (K and Mg), which have high concentrations in seawater (hundreds of ppm) and long residence times (few Myr), and (ii) "scavenged elements" (Al, Si, and Fe), which are depleted in present-day seawater (sub-ppm levels) and have short residence times (few kyr). During glauconite formation, K and Mg are believed to be primarily sourced from seawater or seawater-derived pore fluids, while Al, Si, and Fe are mostly derived from marine sediment sources via dissolution processes of existing mineral phases (e.g., decay of lithogenic particles and biogenic silica, and reductive dissolution of Fe-(hydr)oxides). We do not consider Na and Ca, as they are barely incorporated in glauconite (see Supplementary Table 1).

Assuming a sedimentation rate of 0.13 cm kyr⁻¹ for the basal part of the M. dixoni Zone and of 7.0 cm kyr⁻¹ for the upper part of the M. dixoni Zone (Fig. 3e), as well as a sediment density of 2.7 g cm⁻³ for the glauconitized strata, and considering the composition of the glauconites (see Supplementary Table 1) and the abundance of glauconite across the Langenstein sequence (Fig. 3a, b), element-specific sequestration rates associated with glauconite formation can be calculated (Fig. 3e and Supplementary Table 3). The element sequestration rates range from 0.4 to 8.9 mmol K cm⁻² kyr⁻¹, 0.2 to 4.9 mmol Mg cm⁻² kyr⁻¹, 0.3 to 7.1 mmol Al cm⁻² kyr⁻¹, 1.7 to 40.3 mmol Si cm⁻² kyr⁻¹ and 0.6 to 14.6 mmol Fe cm⁻² kyr⁻¹, reflecting the different sedimentation rates and the extremely low to very high abundances (1 vs 70 wt%) of glauconite in the profile.

Considering an average glauconite content of 5–10 wt% for the Langenstein sequence, which is representative of Phanerozoic glauconite deposits (7 ± 4 wt%)³⁵; the glauconite-associated elemental uptake rate averages ~2.6 ± 1.2 mmol K cm⁻² kyr⁻¹, ~1.5 ± 0.7 mmol Mg cm⁻² kyr⁻¹, ~2.2 ± 1.1 mmol Al cm⁻² kyr⁻¹, ~12.3 ± 5.8 mmol Si cm⁻² kyr⁻¹, and ~4.2 ± 2.0 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 20 μmol K cm⁻² kyr⁻¹, 30 μmol Mg cm⁻² kyr⁻¹, 30 μmol Al cm⁻² kyr⁻¹, 250 μmol Si cm⁻² kyr⁻¹, and 80 μmol Fe cm⁻² kyr⁻¹ (partly recalculated from ref. 28), which is, on average, ~50–130-times lower than the Langenstein sequestration rate. This is because the glauconite content (2.5 wt%, on average), the K concentration (2.9 wt%, on average, reflecting the "nascent" stage, according to the glauconite maturity classification of ref. 33) and the rate of sedimentation (~5-times lower) are substantially lower in deep-water settings than in the shelf regions. The slower rate of glauconite formation in deep-water settings is mainly due to the low temperature (~5 vs ~25 °C) and the reduced supply and sedimentary reflux of Al³⁺ ions and organic matter. The latter controls 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.³⁶

Elemental burial by glauconite in modern marine settings. To the best of our knowledge, elemental output fluxes attributed to widespread glauconite formation taking place at the shallow shelf (defined here as 0–200 m water depth) and in the deep-sea (defined here as >2000 m water depth) of the modern oceans have not been determined yet and are not fully accounted for in earth system models.³⁹,4,14,21,24,25,28,51. We recognize that some of the glauconite deposits of the Quaternary and Holocene are of parautochthonous or detrital origin, representing reworked glauconites of the Neogene or older age.³³ As a first-order approximation to calculate the present-day major element output fluxes attributed to green clay authigenesis, we use published glauconite contents (5.6 wt% vs 2.5 wt%)³⁵,³⁵ and compositions (K: 7 vs 3 wt%, Mg: 3 vs 2 wt%, Al: 4 vs 4 wt%, each ±1 wt%, Si: 24 vs 28 wt%, Fe: 18 vs 18 wt%, each ±2 wt%)²⁸,³⁵ in the shallow and deep marine sediments of the Holocene, the total areas of the modern shelf and deep-sea regions (27.12 × 10¹² m² vs 302.5 × 10¹² m²)¹⁸, an average sediment density of 2.7 g cm⁻³, and estimated global sedimentation rates for shallow-water vs deep-water settings (10–20 cm kyr⁻¹ vs...
0.4–0.8 cm kyr$^{-1}$\textsuperscript{53,54} (Supplementary Table 4). Upscaling predicts global output fluxes associated with glauconite formation of ~0.04–0.09 Tmol K yr$^{-1}$, ~0.02–0.08 Tmol Mg yr$^{-1}$, ~0.03–0.09 Tmol Al yr$^{-1}$, ~0.18–0.43 Tmol Si yr$^{-1}$, and ~0.07–0.16 Tmol Fe yr$^{-1}$ at the shallow shelf, and of ~0.001–0.004 Tmol K yr$^{-1}$, ~0.001–0.005 Tmol Mg yr$^{-1}$, ~0.002–0.008 Tmol Al yr$^{-1}$, 0.02–0.04 Tmol Si yr$^{-1}$, and ~0.01–0.02 Tmol Fe yr$^{-1}$ for the deep-sea glauconites (Fig. 4). The calculated elemental fluxes have relatively high uncertainty but are well within global marine fluxes published in the literature\textsuperscript{4,6,56,58}. However, we consider these fluxes to be conservative estimates, given that they are calculated assuming an overall low to moderate sedimentation rate (i.e., present-day shelf areas display sedimentation rates between 0.1 and 1.0 cm yr$^{-1}$\textsuperscript{55}), which is often associated with glauconite formation in modern shelfal sediments\textsuperscript{33,47,49}.

Deep-water glauconite formation is not significant in the context of marine K budgets, accounting for the removal of merely <0.3 % of the total dissolved riverine K influx (~1.51 Tmol yr$^{-1}$\textsuperscript{58}), and of the K supplied to the ocean by hydrothermal alteration of the modern oceanic crust (~1.51 Tmol yr$^{-1}$\textsuperscript{58}). Shallow-water glauconite formation, by contrast, can play an important role in the global K cycle (Fig. 4), sequestering ~3–6% of the total oceanic K inventory that is sourced from riverine and hydrothermal fluxes or ~2–5% of the K that is removed from the ocean via low-temperature basalt alteration (~1.99 Tmol yr$^{-1}$\textsuperscript{56,60}). Hence, K sequestration by glauconite formation at the shelf is at the same order of magnitude as K burial by authigenic Fe-illite formation taking place in the mangrove forests worldwide (~0.02–0.08 Tmol yr$^{-1}$\textsuperscript{24}, so that changes to K uptake rates by green clay authigenesis have the potential to significantly alter seawater composition over time.

The same conclusions can be drawn for the marine Mg cycle (Fig. 4): Glauconite formation at the shelf consumes <2% of the terrestrial Mg flux (~5.51 Tmol yr$^{-1}$) that is brought to the ocean via continental weathering of Mg-bearing carbonates and silicates and constitutes ~1–3% of the marine Mg sink that is associated with oceanic crust alteration (~2.71 Tmol yr$^{-1}$\textsuperscript{4}). Further, Mg sequestration by glauconite is equivalent to ~1–5% of the estimated Mg sink by enigmatic (yet hidden) dolomite deposits (~1.48–2.88 Tmol yr$^{-1}$\textsuperscript{56}) or ~10–38% of the Mg consumption by authigenic clays forming in the Amazon deltaic sediments (~0.21 Tmol yr$^{-1}$\textsuperscript{56}). Contrary, Mg sequestration associated with deep-water glauconite formation accounts for only <1% of the low-temperature alteration flux (~0.66 Tmol yr$^{-1}$\textsuperscript{56,61}).

As for the Al cycle (Fig. 4), shallow-water glauconite formation is significant, contributing to ~27–82% removal of the dissolved riverine Al influx to the oceans (~0.11 Tmol yr$^{-1}$\textsuperscript{62}), which is consistent with the estimated high loss of dissolved Al to estuarine and shelfal sediments. Deep-water glauconite formation is also critical in the context of marine Al budgets, accounting for ~4–27% loss of the marine Al inventory related to atmospheric dust deposition (~0.03–0.05 Tmol yr$^{-1}$\textsuperscript{56,63}) or almost complete removal of the Al flux injected from hydrothermal vents (~0.006 Tmol yr$^{-1}$\textsuperscript{63}). Thus, we propose that Al uptake via green clay authigenesis could act as an important (yet overlooked) Al sink in deep marine sediments, where active reversible (adsorptive) scavenging of Al in the water column, as well as Al incorporation into diatoms, are currently thought to take key control on the vertical flux and recycling of Al\textsuperscript{62}.

For a long time, reverse weathering reactions at the sediment-seawater interface were thought to constitute only a minor sink of Si in the global ocean (~0.03–0.6 Tmol yr$^{-1}$\textsuperscript{64}). However, extrapolation of cosmogenic $^{32}$Si data obtained from tropical and subtropical deltas suggests that ~4.7 (±2.3) Tmol yr$^{-1}$ of Si is incorporated into authigenic clays on a global scale\textsuperscript{26,51}. The Si flux related to glauconite formation is ~0.18–0.43 Tmol yr$^{-1}$ for the shelfal areas and ~0.02–0.04 Tmol yr$^{-1}$ for the deep-sea, respectively (Fig. 4), which indicates that this process removes
−2−5% of the riverine Si influx to the ocean (~8.1 Tmol yr⁻¹) or 
~1−2% of the hydrothermal Si flux (~1.7 Tmol yr⁻¹), 4−8% of the 
atmospheric Si flux (~0.5 Tmol yr⁻¹), and 5−10% of the glacial Si 
flux (~0.47 Tmol yr⁻¹)53. Nevertheless, we note that global marine 
gross Si bio-productivity, mostly due to silicifying algae such as 
diatoms, is estimated at ~255 (±52) Tmol yr⁻¹, representing the 
first-order control on the modern marine Si cycle51.

Glaucinite acts as an important sink for Fe (Fig. 4), with shallow-
water glauconite formation accounting for up to ~8−33% removal of 
the dissolved and particulate riverine flux of highly reactive Fe to the 
ocean (~0.48−0.86 Tmol yr⁻¹ and ~0.63 Tmol yr⁻¹)1. Although Fe 
uptake by deep-water glauconite formation is less significant (Fig. 4), 
it is still at the same scale as the hydrothermal alteration flux 
(~0.25 Tmol yr⁻¹) or the glacial (~0.20 Tmol yr⁻¹) and atmospheric 
dust fluxes (~0.02 Tmol yr⁻¹)1. Even though oxidation and 
scavenging processes are the first-order controls on the benthic Fe 
fluxes in the ocean51, we argue that glauconite formation in shallow 
and deep marine settings is important, but currently underestimated 
Fe sink.

**Effect of glauconite on global marine palaeo-fluxes.** The source-
sink relations of chemical elements in the modern ocean are 
increasingly well constrained1,2,4,6,14,18,21,24,31,65,66, but the palaeo-fluxes related to authigenic clay formation remain enigmatic. The element uptake rates reported for glauconite forma-
tion at Langenstein (shallow-water; this study) and the Ivory 
Coast (deep-water; recalculated here from data reported in ref. 28) 
may not be directly transferrable to all other marine settings that 
accumulated glauconite through time and space. However, the 
mode of glauconite formation (Fe-smectite-to-glaucinite reaction, 
the micro-environment (focal pellets and foraminifera chambers), the timing (<1 Myr), the composition (Fe-rich), the 
abundance (5−10 wt% vs 2−3 wt%), and the depositional envir-
onment (warm shallow shelf vs cool deep-sea) at the two locations 
are representative of the range expected for many modern and 
past glauconite-forming environments28,33,35,36,40,42−45,47. The 
Langenstein glauconites share similarities with other Mesozoic to 
Cenozoic glauconite deposits, such as a similar abundance (7±4 
w% in the marine rock record from the Triassic to the Holocene; 
Fig. 5a)35 and comparable chemical composition (7±1 wt% K, 
3±1 wt% Mg, 4±1 wt% Al, 24±2 wt% Si, and 18±2 wt% Fe; 
Fig. 5b)35. If we assume a sediment density of 2.7 g cm⁻³ and 
variable sedimentation rates between 0.1 and 100 cm ky⁻¹ 
(Fig. 5c)53,54 are representative of the global shelf through geo-
lithological time, we can compute major element palaeo-sequestra-
tion rates for shallow-water glauconite formation for Mesozoic and 
Cenozoic times (Fig. 5d−h and Supplementary Table 4). With the 
recognition of the aforementioned global elemental fluxes of the 
modern ocean, we propose that the obtained “low” and “high” 
palaeo-sequestration rates are underestimated (i.e., ≤1 cm ky⁻¹; 
functionally zero rates at the yearly time scale are typical for deep 
oceanic basins) and overestimated (i.e., ≥100 cm ky⁻¹; such rates 
are typical for continental margins associated with major rivers, 
deltaic sediments, upwelling zones, and geologically young glacial 
deposits, respectively53,54,57. Thus, the “moderate” sedimenta-
tion rate (~10 cm ky⁻¹; this rate is comparable with authigenic 
illite formation in mangrove forests)54 better represents major 
element uptake related to green clay authigenesis.

It is evident that glauconite formation significantly contributed to 
major element sequestration in shallow marine sediments throughout 
Earth’s history, averaging 3±2 mmol K cm⁻² ky⁻¹, 2±1 mmol Mg 
cm⁻² ky⁻¹, 3±2 mmol Al cm⁻² ky⁻¹, 16±9 mmol Si cm⁻² ky⁻¹, 
and 6±3 mmol Fe cm⁻² ky⁻¹, respectively. We note that major 
element sequestration by glauconite formation also occurred in the 
older sediments of the Archean, Proterozoic, and early Cambrian, but 
this elemental uptake cannot be adequately quantified, given that 
the sedimentary archives of this time are scarce and that most of the old 
glaucinites are at least partly altered to illite or chloride minerals44. 
We are, however, able to make some general inferences. Element 
sequestration by green clay authigenesis was likely of minor 
importance in the Late Ordovician, Early Silurian, and Late 
Devonian, which corresponded to major glacial events, when 
glaucinite formation is inefficient35. Conversely, glauconite forma-
tion and elemental uptake is likely to have been favored at other 
times in the Earth’s past, e.g., during intervals of extensive marine 
anoxia, which featured an elevated seawater Fe pool compared to the 
present, or before the advent and global expansion of marine pelagic 
silicifiers (i.e., sponges, radiolarians, diatoms) decreased the seawater 
Si reservoir from ~550 Myr onward49,60. We, therefore, infer that 
these elements may have been sourced from seawater rather than 
from the dissolution of Fe-(hydr)oxides, biogenic silica, or clastic 
silicates during these times. Returning now to the Mesozoic and 
Cenozoic, we find that high glauconite abundances and related high 
element sequestration rates are evident, for example, in the Neogene 
glaucinite sands from the Flemish Cap (Atlantic Ocean, Northwest 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 glauconites from the Duwi group, Egypt; 
Bakchar glauconite deposit, Western Siberia) (Fig. 5d−h). These 
periods record glauconite deposits of huge economic or geological 
value, with K and Mg being mainly sourced from seawater and Al, Si, 
and Fe being mostly inherited from the marine sediments.

Using average elemental sequestration rates per geological period 
(Fig. 6a) and corresponding occurrences of glauconite on the shelf 
(Fig. 5a), as well as calculated low and high estimates of the shallow 
marine area over time (Fig. 6b)69,70, we can compute major element 
palaeo-fluxes (Tmol yr⁻¹) associated with green clay authigenesis 
that progressed on the world’s shelf area over time (Fig. 6c−g and 
Supplementary Table 5). Based on comparison with global major 
element fluxes of the modern and past ocean, we propose that the 
obtained “high” palaeo-fluxes are overestimated (i.e., the shelf areas 
reported by ref. 69) and that the “low” palaeo-fluxes (i.e., the shelf 
areas reported by ref. 70) better portray the average elemental 
burial related to green clay authigenesis per geological period, which 
averages 0.07±0.09 Tmol K yr⁻¹, 0.05±0.06 Tmol Mg yr⁻¹, 
0.05±0.08 Tmol Al yr⁻¹, 0.32±0.44 Tmol Si yr⁻¹, and 
0.12±0.17 Tmol Fe yr⁻¹ during the Triassic to Holocene.

The ratio of the elemental palaeo-fluxes associated with 
glaucinite formation in the past vs modern ocean (Fig. 6h) 
indicates further that the elemental fluxes were much higher from 
the Jurassic to the Oligocene compared to the modern ocean, 
averaging a factor of 2.1±1.7, which we attribute to the warm and 
sea level highstand “greenhouse” conditions prior to the Eocene-
Oligocene transition. The lower elemental 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 
Southern Hemisphere glaciation (~34 Myr ago) and then North-
ern Hemisphere glaciation (~5 Myr ago), where glauconite 
formation is reduced. Although these estimates have relatively 
high uncertainty and need to be better constrained in future work, 
it is evident that green clay authigenesis greatly affected the 
global marine element cycles throughout Earth’s history.

We conclude that fast retrograde clay mineral reactions, which 
orcur in the ocean floor, are of great significance to the 
marine element cycles and have to be considered in present and past 
earth system models. The major element burial fluxes attributed to 
green clay authigenesis were significantly higher under 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 to estimate how element sequestration through glauconite formation impacts the isotopic composition of the ocean, the pore water reservoir and the marine sediments, and to assess the impact of climate change through time on the elemental burial fluxes attributed to 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-Kα radiation source). The samples were prepared using the top-loading technique. The preparations were examined in the range 4 to 85° 2θ with a step size of 0.008° 2θ and a scan time of 0.01 s/step. The XRD patterns were analyzed using the ICDD PDF-2 database and the Jade 8 software. The peak positions were determined using the d001, d011, and d101 reflections, and the relative intensities were used to calculate the relative crystallinity of the glauconite.

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**Fig. 5** Major element sequestration rates for shallow-water glauconite formation during the Mesozoic and Cenozoic. a Glauconite abundance on the shelf through time. b Average composition (±2 SD) of glauconite over time. c Variation in overall sedimentation rate typical for shelf areas. d–h Elemental sequestration rates associated with shallow-water glauconite formation through time colored curves) and at Langenstein (black stars). Average sequestration rates (±2 SD) are highlighted by the gray shaded intervals. The calculations are based on constant sedimentation rates and a sediment density of 2.7 g cm⁻³ for each geological period.

**Fig. 6** Element palaeofluxes (Tmol yr⁻¹) associated with green clay authigenesis on the shelf during the Mesozoic and Cenozoic. a Average major element burial rates associated with shallow-water glauconite formation through time (see Fig. 5d–h). b Area of the global shallow ocean over time-based on two different paleogeographic reconstructions. The estimate labeled as “low” is the shelf area (average ± 2 SD) that was computed from the respective contours of a series of palaeo-digital elevation models (1° × 1° resolution) developed by ref. 70 using Generic Mapping Tools. The estimate labeled as “high” is the shelf area (average ± 2 SD), which was calculated by ref. 71 based on the palaeogeographic model from ref. 72 that is available as a series of polygons, reconstructed with the plate tectonic model of ref. 73. c–g Element palaeofluxes (average ± 2 SD) associated with shallow-water glauconite formation for the “low” vs “high” paleogeographic reconstructions. h Element palaeoflux ratios (ancient vs modern ocean) for the “low” shallow ocean scenario. The palaeoflux calculations assume a constant occurrence of glauconite (see Fig. 5a) for each geological period.
TEM lattice fringe images were collected parallel to the (001)-plane of the clay emitter, a Gatan imaging
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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 δ18O and δ13C isotopic data and N.M.W. contributed to 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 fieldwork. All authors contributed to the writing.

Competing interests
The authors declare no competing interests.

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