

Editorial

Editorial for Special Issue “Clay Minerals: From Paleoclimatic and Paleoenvironmental Indicators to Industrial Raw Materials”

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Clays and clay minerals constitute important mineral resources from both scientific and industrial perspectives. The genesis of clay minerals takes place when low-temperature aqueous solutions interact with rocks on the Earth's surface. Certain factors, such as the environment, temperature, amount of water available, and the type of weathered rock, determine the clay minerals formed. Therefore, clay minerals can provide information about the paleoclimate or paleoenvironment under which they were formed. Additionally, clays are also materials of great industrial and economic interest. Currently, clays are used in many types of industries since they constitute important components used in the manufacturing of many products, such as plastics, paper, cement, absorbent materials, ceramic and refractory materials, among others. The physical and chemical characterization of different clays (e.g., kaolin, smectites, fibrous clays) is of great interest since their industrial applications are closely related to their structure and composition.

This Special Issue, entitled “Clay Minerals: From Paleoclimatic and Paleoenvironmental Indicators to Industrial Raw Materials”, includes ten contributions that investigate the origin, mineralogical characteristics, environmental significance, and technological applications of clay minerals. The studies examine clay deposits formed in different geological settings and highlight their importance both as paleoenvironmental indicators and as valuable industrial resources. Several contributions focus on the genesis of clay minerals in sedimentary environments (contributions 1, 2, 6, 7, 8, 9, and 10). These studies analyze clay assemblages formed in settings such as playa-lake systems, marine evaporitic environments, and ancient sedimentary basins. Through mineralogical and geochemical analyses, the authors explore processes, such as detrital input, authigenic mineral formation, and mineral transformations, related to variations in hydrochemistry and depositional conditions. Some of these papers emphasize the use of clay minerals as paleoenvironmental and paleoclimatic indicators (contributions 1, 2, 7, 9, and 10). Variations in clay mineral assemblages and geochemical characteristics are used to reconstruct past environmental conditions, including weathering intensity, hydrochemical evolution, and climatic regimes affecting sediment deposition. In addition, some contributions also address the mineralogical and physicochemical characterization of clay deposits with potential industrial applications (contributions 3, 4, 5, 8, 9, and 10). Using techniques such as X-ray diffraction, electron microscopy, and spectroscopic analyses, these studies evaluate sepiolite, bentonite, kaolin, and laterites for applications in ceramics, adsorption, and environmental technologies.



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Overall, the papers included in the Special Issue highlight the multidisciplinary significance of clay minerals in both palaeoclimatic and palaeoenvironmental studies and industrial applications.

The paper by Laita et al. (contribution 1) investigates clay-rich and iron-bearing palaeosols developed at the Middle–Upper Jurassic unconformity of the External Prebetic and the Iberian Range (South Iberian Palaeomargin and East Iberian Palaeomargin) in order to reconstruct the palaeoclimatic conditions that affected the exposed carbonate platform during the Callovian–Oxfordian. Their results reveal a mineral assemblage dominated by kaolinite and iron oxides, such as goethite and hematite. The occurrence of kaolinite crystals formed in situ, together with concentric iron-coated grains, indicates the development of plinthitic palaeosols under intense chemical weathering during periods of subaerial exposure. Geochemical proxies also confirm a high degree of alteration consistent with warm and humid climatic conditions during the Callovian–Oxfordian transition. This contribution demonstrates how clay minerals can act as robust indicators of past climatic regimes and weathering intensity. By linking clay mineral genesis with the regional paleoenvironmental evolution in the western Tethys, the study highlights the importance of clay mineral assemblages as key archives for reconstructing ancient climate and surface processes.

The paper by del Buey et al. (contribution 2) investigates the origin and evolution of palygorskite in lacustrine environments, focusing on three recent hyperalkaline playalakes in Central Spain and their relationship with nearby Miocene lacustrine deposits. The authors address this issue through an integrated mineralogical and microanalytical approach to trace palygorskite from the source (Miocene marlstones and mudstones) to the sink (recent playalakes). The results demonstrate the coexistence of both inherited (detrital) and neoformed (authigenic) palygorskite in the studied lakes. Detrital palygorskite shows degradation, wider fibers, and near-ideal compositions, indicating inheritance from older lacustrine deposits. Authigenic palygorskite forms narrower fibers with compositions controlled by lake hydrochemistry, enriched in Al_2O_3 , MgO , and Fe_2O_3 . Iron-rich varieties occur with saponite, reflecting Mg competition during precipitation, also observed between smectite and palygorskite in Miocene mudstones. These findings highlight how physicochemical differences in closely spaced hyperalkaline lakes can strongly influence the crystallochemistry of authigenic palygorskite and demonstrate the value of palygorskite as a sensitive geochemical proxy for interpreting paleoenvironmental conditions in lacustrine systems.

The paper by Sousa et al. (contribution 3) examines the interaction between expandable clay minerals and glycerin-based drilling fluids, which have been proposed as an alternative to conventional inhibited fluids for drilling highly reactive formations. Despite their potential advantages, operational problems such as drill bit and drill pipe balling, caused by the agglomeration and accretion of cuttings, can still occur. The authors investigate how these interactions affect wellbore stability and the extent to which accretion develops during drilling in clay-rich formations. Bentonite pellets were used as an analog for reactive formations. These pellets are mainly composed of interstratified illite-smectite clay minerals, and they consistently display highly plastic behavior and a strong tendency to expand. Accretion tests using glycerin-based drilling fluids containing different types of expansion inhibitors show that accretion remained significant in all tested fluids, with values exceeding 58%, indicating that neither glycerin nor the tested inhibitors were effective in reducing clay expansion or preventing cuttings aggregation. These findings highlight the critical role of clay mineralogy in drilling performance and demonstrate how detailed mineralogical characterization of clays directly informs their technological performance and industrial applications.

The paper by Bakouan et al. (contribution 4), explores the valorization of two lateritic materials from Bririmian and Precambrian environments in Burkina Faso, focusing on how geological provenance influences their mineralogical and physicochemical properties. The findings reveal that while geological context gives information regarding mineralogical composition of the laterites (quartz, kaolinite, hematite, and goethite), it alone does not determine their suitability as adsorbents. Instead, key physicochemical traits such as specific surface area ($41.15\text{--}58.65\text{ m}^2/\text{g}$), cation exchange capacity ($52.3\text{--}58.7\text{ cmol}(+)/\text{kg}^{-1}$), and anion exchange capacity ($64.6\text{--}86.5\text{ cmol}(-)/\text{kg}^{-1}$) are critical. The results demonstrate high efficacy in removing arsenate and arsenite from aqueous solutions, achieving up to 99.7% removal at optimal conditions, alongside notable removal rates for Pb(II) and Cu(II). These results underscore the potential of the laterites as cost-effective adsorbents for heavy metals and anionic contaminants in groundwater and highlight the role of laterites as versatile industrial raw materials for environmental remediation.

The paper by Ionescu et al. (contribution 5) presents a comprehensive investigation of a Miocene carbonatic clay from Transylvania (Romania), a material historically utilized for over a century in traditional ceramics, bricks, and tiles. The authors explore the mineralogical and microstructural transformations of the clay upon firing between $700\text{ }^{\circ}\text{C}$ and $1200\text{ }^{\circ}\text{C}$. Their results reveal the progressive transformation of primary minerals (illite, muscovite, feldspar, carbonate, Fe oxyhydroxides, and quartz) into high-temperature phases such as gehlenite, clinopyroxene, maghemite, hematite, mullite, and α -cristobalite, alongside a glassy matrix. These firing-induced phases serve as distinctive “ceramic markers,” providing valuable indicators of thermal history. By correlating optical appearance, microstructure, and specific mineral associations, the authors propose a novel “ceramic thermometer” capable of estimating firing temperatures in ancient ceramic artifacts. This approach not only enhances the understanding of thermal behavior in clay-based materials but also bridges geological, archeological, and industrial perspectives. The study exemplifies how detailed mineralogical analyses can inform both heritage studies and modern ceramic production, highlighting the significance of clay as a versatile natural resource.

The paper by Yaremchuk et al. (contribution 6) investigates the mineralogical evolution of clays associated with Lower and Middle Miocene marine evaporite deposits in the Ukrainian Carpathian Foredeep, emphasizing the role of brine concentration in controlling clay mineral transformations. The authors characterize clay mineral assemblages across different evaporite facies (gypsum, halite, and potash) and document systematic variations linked to the geochemical conditions of deposition and diagenesis. In the gypsum facies, assemblages are dominated by smectite and illite, with occasional mixed-layer chlorite-smectite and illite-mectite, as well as chlorite. In halite facies, the composition varies with stratigraphic unit: Eggenburgian rock salt (Vorotyshcha Suite) contains illite, chlorite, and mixed-layer illite-smectite, whereas the Badenian rock salt (Tyras Suite) also includes smectite, corrensite, and mixed-layer chlorite-smectite. Potash facies are characterized primarily by illite and chlorite. These assemblages reflect progressive aggradational transformations of unstable clay minerals such as kaolinite and smectite into the more stable illite and chlorite under increasingly saline evaporitic conditions. The study also highlights the influence of organic matter sorption, which may slow mineral transformation processes. The authors document contrasting mineralogical patterns in the weathering zone of the evaporite deposits, where reduced ionic concentrations promote degradational processes (forming illite-smectite) and neof ormation of kaolinite during desalination. This study demonstrates how clay minerals in evaporitic environments record both palaeoenvironmental conditions and post-depositional alteration.

The paper by Bauluz et al. (contribution 7) provides a comprehensive mineralogical and geochemical characterization of the Monte Castelo kaolin deposits (Burela, NW Spain),

derived from acid igneous rocks undergoing varying degrees of chemical weathering. The authors trace the transformation of primary aluminosilicates (albite, K-feldspar, and K-micas) into kaolinite as weathering intensifies. Their observations reveal that kaolinite preferentially forms booklets and fine-grained matrices, and develops intergrowths along muscovite cleavages, displaying bidimensional crystallographic continuity without detectable intermediate phases. This insight into mica-kaolinite relationships underscores the role of high water-to-rock ratios in controlling weathering processes. The study also addresses analytical challenges in evaluating kaolinite crystallinity, demonstrating that while quartz impurities disrupt Hinckley index calculations, the AGFI index provides a robust alternative, effectively mitigating interference from coexisting minerals. Geochemically, the study documents a general decline in most elemental contents with progressive weathering, except for Al, TiO₂, HREEs, Ta, Hf, Th, U, V, Cr, S, Zr, Mo, and Sn, highlighting selective enrichment processes. By linking nano-scale textures, mineral transformations, and chemical evolution, this study advances our understanding of kaolin genesis under natural weathering conditions.

The paper by García-Rivas et al. (contribution 8) provides a comprehensive mineralogical and crystal-chemical characterization of bentonite deposits from the Benavila outcrop in Portugal, representing the largest known occurrence of bentonite in continental Portugal. The study offers detailed insight into the mineralogical composition, structural characteristics, and geochemical features of these clay-rich materials. The results reveal that smectite is the dominant phase, accompanied by variable proportions of calcite and minor accessory minerals (tectosilicates and other phyllosilicates). Crystal-chemical analyses indicate that the smectites belong to intermediate compositions within the montmorillonite–beidellite series and display mixed cis-vacant and trans-vacant structural configurations, reflecting complex formation and diagenetic processes. In addition, the geochemical data suggests the influence of carbonate-rich fluids in the evolution of the deposit. The combination of all the data shows the possible pathway of alteration that gave rise to the deposit. This study exemplifies how advanced mineralogical and microanalytical techniques can be integrated to unravel the origin, evolution, and structural variability of clay minerals. Additionally, it contributes to a deeper understanding of these bentonites as a basis for further industrial applications.

The paper by Lescano et al. (contribution 9) explores how the geological formation environment influences the physicochemical properties of a lacustrine-derived and a hydrothermal-derived sepiolite from Spanish and Argentinian companies, a critical factor for both palaeoclimatic interpretations and industrial applications. The investigation reveals striking differences between the two sepiolites. The lacustrine-derived sepiolite exhibits a higher SiO₂/MgO ratio and contains amorphous silica impurities, whereas the hydrothermal-derived sepiolite aligns closely with sepiolite's theoretical stoichiometry and displays enhanced crystallinity. Morphologically, the lacustrine-derived sepiolite forms compact, aggregated fibrous structures, while the hydrothermal-derived sepiolite is characterized by disaggregated, needle-like fibers with nanometric diameters and high aspect ratios. Both sepiolites are predominantly hydrophilic, yet the hydrothermal-derived sepiolite shows suspended particles at the interface, hinting at a slightly higher hydrophobicity than the lacustrine-derived sepiolite. These observations underscore the pivotal role of formation environment in determining sepiolite's structural, chemical, and surface features, with direct implications for its dispersibility, adsorption capacity, and interfacial behavior. The study advances our understanding of sepiolite as a paleoenvironmental indicator and informs its optimized use as an industrial raw material.

The paper by Zakusin et al. (contribution 10) provides a comprehensive mineralogical and adsorption properties characterization of smectite-palygorskite clays from the

Dashkovskoye and Borshchevskoye deposits (Lower Carboniferous, Russia), offering critical insights into their formation and environmental history. The study reveals that Al-palygorskite from the Dashkovskoye deposit formed through sedimentation from suspended matter in a shallow-water basin, contrasting with the chemogenic genesis of palygorskites and the clastic/redeposited nature of smectites. In contrast, the Borshchevskoye palygorskites exhibit a more complex terrigenous origin, formed from redeposited chemogenic Al-palygorskites transported from the Dashkovskoye region, with Fe-palygorskites entering via upstream soil redeposition. Notably, the study demonstrates a depth-dependent trend, where deeper basin layers contain increasing smectite proportions and decreasing palygorskite content. Beyond their geological significance, all analyzed clays show substantial adsorption capacities (32–49 mg-eq/100 g), highlighting their potential for industrial applications.

In summary, the contributions published in the Special Issue “Clay Minerals: From Paleoclimatic and Paleoenvironmental Indicators to Industrial Raw Materials” confirm the importance of integrated mineralogical and geochemical approaches in improving our understanding of clay mineral formation and evolution. These studies highlight how the characterization of clay minerals can provide valuable insights into past environmental and climatic conditions, while also clarifying the processes controlling the transformation and stability of clay minerals in different geological settings. The papers included in this Special Issue also emphasize the relevance of clay minerals as industrial raw materials. Through the application of modern analytical techniques, these studies illustrate how the properties of clays are closely linked to their genesis and geological environment, which ultimately determine their technological behavior and potential industrial applications.

As Guest Editors of this Special Issue, we hope that readers will find these contributions both insightful and stimulating, providing new perspectives on the role of clay minerals as indicators of paleoenvironmental and palaeoclimatic conditions and as valuable materials for industrial use. Finally, we would like to express our sincere gratitude to the Minerals editorial staff for their continuous support and guidance, and to all reviewers for their valuable time and constructive comments that helped improve the quality of the published papers.

Conflicts of Interest: The authors declare no conflicts of interest.

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