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Editorial

Editorial for Special Issue "Clays, Clay Minerals, and Geology"

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1. Introduction

Sedimentary rocks covering most of the Earth's crust are mainly composed of clays, making clay minerals widespread globally. Clay minerals are mainly derived from the interaction of the surface of the Earth's crust with the atmosphere and hydrosphere, without neglecting the contribution of organic matter and bio-agents mainly characterizing the soil. Since the beginning of the last century, with the development of the X-ray diffraction technique, a strong interest has arisen in the study of these sediments, particularly clayey minerals. Various specialized journals, many books, and many national and international conferences have been dedicated to these minerals, and national and international associations have been established (e.g., AIPEA–Association Internationale pour l'Étude des Argiles). The main topics covered in journals, books, and conferences concern the determination of crystallo–chemical and chemical–physical characterizations, as well as qualitative and quantitative analyses of the minerals present in clays, genesis, depositional environments, and post-depositional evolution [1].

The mineralogical composition of clayey sediment consists of a non-phyllosilicate component, such as quartz, feldspars, Fe-(hydr)oxides, and components of phyllosilicates, among which clay minerals are represented by smectites, illite, chlorite, and kaolin groups, wherein mixed layers of illite/smectite and chlorite/smectite are the most frequent minerals. Phyllosilicates have a small grain-size, while the others are concentrated in the silt and sand grain-size. Clay minerals are characterized by tetrahedral sheets occupied by Si and subordinately Al and Fe^{3+}. These sheets join together along the surfaces with different combinations, giving rise to different layers, which in turn join to form different clay minerals. In the various clay minerals, the layers have different layer charges as a function of the substitution of higher charge cations with cations with lower charges (e.g., replacement of Si^{4+} with Al^{3+} in tetrahedral sheets). Cations such as K, Ca, and Na can be linked to the layers more or less strongly depending on the layer charge (e.g., smectite < illite < muscovite). In the smectites, the cations can be easily exchanged and this group of minerals also has the ability to exchange organic molecules. Minerals such as kaolinite, pyrophyllite, and chlorite have no interlayer cations.

Due to their structure and small grain-size, clays and clay minerals are characterized by specific properties, such as cation-exchange capacity (CEC), sorption of water and organic substance, thixotropy, swelling, impermeability, and plasticity, making them very versatile and therefore useful in various technological fields and industrial productions. The above properties control the geotechnical parameters; therefore, mineralogical knowledge of clayey materials is important for landslide/mass movement and natural hazard assessment [2,3]. In addition, based on these properties, clay minerals respond differently to thermo–chemical treatments, which are useful for their identification through X-ray diffraction [4].

The characteristics of the clayey sediments depend on geological history, such as the nature of the parent rocks, from which they derive through alteration, tectonic activity and climate of the source area, transportation, depositional environments, and the subsequent diagenetic processes or very low metamorphic degree (Reference [5] and reference therein).

Based on the above and as already mentioned, clay minerals are useful proxies for the reconstruction of the dynamics of previous geological processes affecting the Earth.

2. The Main Geological Environments for the Genesis of Clay Minerals

Clays minerals occur in many different geological environments and are the result of many geological processes occurring on the Earth's crust. One of the most relevant processes is represented by the weathering of parent rocks present on the Earth's surface, as well as by the erosion of the soils.

In analyzing the distribution of clayey minerals in soils and current marine sediments, it is possible to determine an evident concentration of different types of these minerals along the climatic bands [6].

In particular, the equatorial belt is characterized by a warm humid climate and therefore by aggressive chemical weathering responsible for the removal of alkaline and alkaline-earth cations (Na, K, Mg, and Ca). This process occurs in soils and can be detected in marine sediments with high concentrations of kaolinite, which has a very simple crystallochemistry [$Al_2Si_2O_5$ $(OH)_4$]. Close to the tropical belts or where there are temperate or sub-arid climate conditions and in the more distal oceanic areas, high concentrations of smectites are found, which represent an intermediate alteration product. These minerals are characterized by a more complex crystallochemistry than kaolinite. The greater concentration of smectite in the more distal area can be explained by the small size of the flakes and by the dispersed aggregate both remaining in the water column and subsequently accumulating in the more distal floor basin, or deriving from the alteration of volcanic ash due to seawater action [5]. Finally, minerals such as illite and chlorite are concentrated at high latitudes at which the chemical alteration is less aggressive. However, these minerals can also be inherited from the parent rocks (Reference [6] and reference therein).

The overview of the distribution of clay minerals in current sediments suggests that clay minerals can be useful proxies for paleoclimatic reconstructions, as reported by the extensive literature data (e.g., Reference [7] and reference therein). One of the most studied climatic changes of the past is the Paleocene–Eocene Thermal Maximum (PETM), which lasted about 200,000 years and led to an increase in temperature of about 5–8 °C due to the greenhouse effect caused by the increase in CO_2 [7]. In this period, the sedimentary sequences formed in areas also characterized by intense rainfall and therefore by a high water/rock ratio, and recorded an evident increase in kaolinite (Reference [7] and reference therein). In sedimentary basins dominated by a hot–dry climate, including lakes and lagoons, instead, kaolinite is scarce or absent and Mg-smectites, paligorskyte, and sepiolite are present (References [7,8] and reference therein). These data confirm the importance of studying the PETM and how it is very relevant for both the present and future, as it shares several similarities with present greenhouse behaviors.

In addition to the chemical weathering mainly influenced by climatic conditions, we must not overlook the effect of tectonic activity on clay mineral formation. Tectonic activity involving a source area leads to rejuvenation of the reliefs, accentuation of the slope, thus favoring the drainage of water, as well as the acceleration of transport speed and therefore of mechanical weathering, with consequent shortening of the time available for the chemical weathering of primary minerals. The resulting clayey minerals are produced by a weak alteration process or are inherited as they are from the source areas. This type of mineralogical association is typical of thrust-sheet-top and foredeep basins, which are present in areas at the front of mountain belt. The erosion and transportation occur, in particular, by means of water, but we must not neglect the effects of wind and glacier erosion mainly in desertic and glacier environments, respectively [6].

Erosion and transport occur in a short time compared to mineralogical changes; thus, they are irrelevant [5]. Based on the above, it is possible to conclude that the analysis of clay minerals provides information on climate conditions, weathering, tectonic activity, and, in general, the environmental conditions of sources areas [9–13].

Clay minerals can also be formed during the placement of volcanic deposits as a result of rock alteration produced by hot fluids due to intrusion magna in the crust or by the action of hydrothermal fluids ([14] and reference therein). In this context, the clay minerals represent a fundamental tool for the identification and characterization of the active and fossil hydrothermal systems [14]. The occurrence and composition of hydrothermal alteration facies as well as the crystal–chemical features of clay minerals are fundamental to define important parameters that strongly influence the development of water/rock interaction processes, such as the temperature and pH of the hydrothermal environment.

After deposition in sedimentary basins, the clay minerals formed in the subaerial environment are transformed into other, with more stable minerals in the new pressure and temperature conditions acquired during diagenetic or low metamorphic conditions according to the lithostatic and/or tectonic load. The characterization of newly formed minerals by determining specific parameters, such as the percentage of terminal elements of the mixed layers (illite/smectite and chlorite/smectite), the staking order (Reichweite; R), the Kübler and Arkai index, the politipe types, and b_0 of illite-muscovite, is a useful indication of the PT conditions occurring from the upper part of the lower diagenesis, from about 50 °C to 350 °C, and with pressures as high as 12 Kbar (Reference [15] and reference therein).

This kind of study is a valuable tool for the basin analysis and the setting-up of the tectonic unit is useful for the geodynamic reconstruction of the orogenic belt.

3. Main Techniques for Clay Mineral Characterization

As mentioned above, the study of clay minerals represents a useful tool to determine many geological surface processes and geodynamic reconstructions. All this cannot be separated from an accurate qualitative and quantitative characterization of these minerals using a multidisciplinary approach based on the application of different techniques, and the researcher's experience cannot be neglected, either.

Although the most frequently used technique is X-ray diffraction (XRD), other methods such as High-Resolution Transmission Electronic Microscopy (HRTEM), Field Emission Gun Scanning Electron Microscopy (FEG-SEM), Thermogravimetry and Differential Thermal Analyzer (TG-DTA), and Fourier Transform InfraRed (FTIR) spectroscopy are also very useful. These techniques provide both peculiar and complementary information, sometimes in a more expeditious way (e.g., [16]). For a more holistic characterization of sediments, the characterization of the bulk sample's chemical composition by techniques such as X-ray florescent (XRF), Inductively Coupled Plasma–Optical Emission Spectrometry (ICP-OES), and Inductively coupled plasma–mass spectrometry (ICP-MS) could be accomplished. However, quite often, it is not possible to analyze specimens in the laboratory and to obtain chemical and/or mineralogical information, it is necessary to perform in situ analyses. In recent years, the portable XRF spectrometer has been widely used to execute field geochemical analyses related to mining and environmental studies. It has been also used in the oil industry, although there are still very few case studies (Reference [17] and reference therein). Kowalska et al. [17] showed that, after appropriate calibration, the portable XRF could be a useful tool allowing for the rapid identification of the accurate mineral composition of perforated rocks and for the reconstruction of the lithological profile, even in the case of rock formations containing clay minerals. The main advantage of this approach is represented by the possibility of applying it directly to wells without the need for coring.

4. Conclusions

Based on the above, it is possible to conclude that clay minerals represent a useful proxy for many geological processes occurring on the Earth's surface or at few kilometers deep. Additionally, in-depth geological knowledge of a specific environment can be useful to understand the genesis of these minerals. At an increasing frequency, mainly in recent years, these studies are characterized by multidisciplinary approaches, thus permitting a more holistic view of both geological processes and clay mineral genesis. Additionally, the refinement of existing techniques and the development of new ones contribute to the aforementioned purposes. As highlighted, the information derived from clay mineral characterization contributes to solving unanswered questions in many fields of geological sciences. With a view of future prospects, clay minerals can assume a determining role in the framework of paleoclimate studies. In this context, it could be very useful to deepen the study of stratigraphic sequences, such as those corresponding to the PETM showing several similarities to the present greenhouse effect. In the same way, it could be interesting to analyze the Quaternary sedimentary sequences that record climate changes of the glacial and interglacial periods (e.g., [18]). These studies, which enable a high-time resolution of environmental responses to climate changes, are important and can benefit from the mineralogical tool represented by clay minerals.

A further development of clay mineral study of environmental reconstructions is represented by the projection of the conceptual model of clay mineral formations and distributions on Mars. Due to the capabilities of satellite remote sensing, a clay mineral signature was recognized in the Martian stratigraphic record and on the surface [19]. Both climatic and volcanic/hydrothermal processes are involved in the Martian environment and the development of new spatial techniques for clay mineral study could possibly be applied to study the Earth.

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