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Natural radioactivity studies in a paleontology site and paleoclimate interpretation of the last 8 Mya

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ABSTRACT

Fossil bones and sediments from different horizons of the Upper Miocene paleontological site of Platania, Drama-Greece were studied using ^{238}U, ^{235}U, ^{232}Th series and ^{40}K measurements obtained by γ-spectroscopy. Additionally, SEM and XRF analysis was applied to bone and sediment samples while a lithological analysis of the sediments was also carried out. The ^{226}Ra/^{238}U ratios in the fossilization layers are attributed to the ^{238}U depletion from the sediment and its incorporation into the fossils. The ^{226}Ra/^{231}Pa ratio indicates that the absorption of the isotopes started long before 4.2 Ma ago. The ^{232}Th/^{40}K profile demonstrate two distinct geological substrates, the lower corresponding to the Upper Miocene whereas the upper to the Upper Pleistocene–Holocene. Among them mediates a Mn-rich layer associated with the "Zanclean flood" during Pliocene. One layer above the "Glacial maximum event" during the Early Pleistocene was recorded. The natural radioactive sedimentary profile obtained reproduces the paleo-climatic conditions in Southeast Europe, which could be useful for the future.

1. Introduction

Natural occurring radionuclides of the ^{238}U, ^{235}U and ^{232}Th series as well as ^{40}K are a powerful tool for the study of various geological processes including sediment weathering, interaction with surface and ground water, secondary mineral precipitation and ion adsorption by clay minerals. Concentrations of natural radionuclides vary among different sedimentary rocks reflecting the origin of the sediments as well as the geochemistry of the depositional environment. Higher radiation levels are associated with igneous rocks and lower levels with sedimentary rocks. There are exceptions, however, as some shales and phosphate rocks exhibit relatively high radionuclide contents. Concerning sedimentary rocks, high radiation levels are typically associated with fine-grained deposits or clay-rich rock formations such as shale, claystone, and mudstone, whereas low gamma radiation indicates the presence of coarse-grained sandstone and carbonate rock due to their higher water-transmitting capacity (UNSCEAR, 2000).

Certain elements actively participate in various geochemical processes taking place in marine environments and they may become authigenically enriched or depleted in sediments depending on the availability of free oxygen during deposition; as a result, the distribution patterns of such elements are extensively used to understand the variations in paleoredox conditions both in modern marine sediments and in ancient rocks. The high U solubility-mobility, contrary to the Th or K immobility, as well as the U affinity for marine shales and the Th affinity for terrestrial sediments have been demonstrated and thus Th/U ratios can be used as indicators of the relative continental or marine influence on the depositional environment (Koczy, 1956; Adams and Weaver, 1958).

The geochemistry of fine-grained sediments is considered to represent the average composition of the upper continental crust more than any other sedimentary rocks as they preserve the provenance signature and diagenetic history (Hassan and Hossin, 1975; Calvert and Pedersen, 1993; Cullers, 1995). In fact, the geochemical composition of the clastic sediments is a complex function of variables such as the source material, weathering, natural sorting and diagenesis. Therefore, the ratios of natural radioisotopes can be used to interpret sediment composition, provenance and diagenesis (Roser and Korsch, 1988; Chamley, 1989). Th and U and their interrelationships are also useful in deciphering depositional environments. The relative abundance of Th,

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Fig. 1. The Platania-Drama (Macedonia, N. Greece) paleontological site (PLD): (a) view of the site, about 5 m in height, (b) stratigraphic column with the spots of the sediment samples collected, (c) the spot 6 reveals the Late Miocene, blackish-coloured, mammalian remains in the oriented square of the excavation.

K and U also helps to characterize clay mineral type and its abundance in sediments (Rider, 1996; McRoberts et al., 1997). In general, the mineralogy of clays is transformed under the combined effects of temperature and pressure resulting in depth-related changes of the K content (Darnley and Ford, 1987; Ruffell et al., 2002; Canet et al., 2004). The clay mineral composition of sediments can reflect the effects of several paleo-environmental conditions (climate, sea level fluctuations, tectonic activity as well as continental and basin morphology (Madhavaraju and Ramasamy, 2001; Dera et al., 2009; Verma and Armstrong-Altrin, 2013; Deconinck et al., 2014; Herbert et al., 2016; Groeneveld et al., 2017).

In a natural radioactive series the steady-state condition of secular equilibrium, refers to an undisturbed, isolated isotopic system in which the specific activity of the parental nuclide is equal to the daughter nuclide. Disequilibrium refers to any fractionation between radionuclides within a decay chain which results in a non-steady state condition (Broecker, 1963; Kaufman and Broecker, 1965; Merrihue and Turner, 1966). Provided that the system becomes isolated again, the time required to re-establish secular equilibrium of the decay chain equals to approximately six times the half-life of the daughter nuclide. This period is equal to approximately 1.4 My, 300 ky and 40 y for the ^{238}U, ^{235}U and ^{232}Th series, respectively. The ^{232}Th-series disequilibrium does not provide information of geological importance due to the geologically short period required for secular equilibrium. On the contrary, the ^{238}U and ^{235}U series disequilibrium has been extensively applied, also providing the opportunity for accurate radio-chronology studies. ^{40}K in association with its daughter ^{40}Ar is also a useful chronology clock that measures ages up to Gya (Charalambous and Papastefanou, 1977; McDougall et al., 1980; Schwarcz, 1980).

The purpose of the present study is the correlation of significant deviations of the natural radioactivity ratios Th/K and Th/U with paleoclimatic changes recorded in the sediment sequence. Furthermore, the inference of paleoredox conditions in the Platania's cross-section due to precipitation rates received by each layer and the presence of specific elements that alter the redox conditions is also discussed. The ^{238}U, ^{235}U and ^{232}Th series radionuclides as well as the ^{40}K content were measured using γ-spectroscopy of fossil bone and sediment samples obtained from different horizons of the paleontological excavation site in Platania, Drama-Greece, under the direction of Prof. E. Tsoukala. Sediment and fossil bone specimens were additionally characterized by means of Scanning Electron Microscopy (SEM) and X-Ray Fluorescence (XRF) Spectroscopy, while the degree of the bone's histological preservation was evaluated by means of Optical Microscopy. A supplementary lithological analysis was performed on sediment samples. The possible presence of disequilibrium between parent-daughter nuclides of the ^{238}U-series for the different sedimentary layers is also investigated. In the case of fossil bones, the ^{238}U and ^{235}U-series disequilibrium has been studied using the ^{226}Ra/^{238}U, ^{231}Pa/^{235}U and ^{231}Pa/^{226}Ra ratios. Useful remarks have been drawn on the history of sedimentation and the geochronology of the excavation column as well as on the fossilization-redox processes presented in this creative work for the region that compiles natural radioactivity with other experimental methods broadly used for paleontological remains.