226Ra/238U DISEQUILIBRIUM AS A WEATHERING INDEX IN HEAVY MINERALS ENRICHED BEACH SAND SEDIMENTS FROM SITONIA AND KAVALA

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ABSTRACT

Weathering indices can be used to quantify weathering of sediments at various stages of weathering and provide a better understanding of element mobility during weathering. For these purposes, various weathering indices are proposed in the literature. 11 heavy mineral-enriched samples from Kavala (N. Greece) and 3 from Sithonia (Chalkidiki Peninsula, N. Greece) beach sands, all of them being the weathering products of the local granitic plutons are studied for their secular disequilibrium in 238U-series (226Ra/238U ratios) and the results are compared to those of the weathering indices already in use worldwide. The parental rocks of the beach sand sediments were in radioactive secular equilibrium concerning 226Ra/238U. The results of 226Ra/238U radioactive disequilibrium are quite similar to those given by Weathering Index of Parker (WIP) and Product of Weathering Index (PWI). Therefore it could be used as a relatively sensitive weathering index in sediments, considering, however, the mineralogical composition and sediment sorting.

ΠΕΡΙΛΗΨΗ

Οι δείκτες αποσάθρωσης χρησιμοποιούνται για την ποσοστοποίηση της αποσάθρωσης των ιζήματων στα διάφορα στάδια και επιπέδων την καλύτερη κατανόηση της κινητικότητας των στοιχείων. Για το σκοπό αυτό, προτείνονται διάφοροι δείκτες αποσάθρωσης στη βιβλιογραφία. 11 δείγματα παράκτιων άμμων από την Καβάλα και 3 από τη Σιθωνία (Β. Ελλάδα), που αποτελούν προϊόντα αποσάθρωσης των γειτονικών πλουτωνιτών και είναι εμπλουτισμένα σε βαρέα ορυκτά εξετάστηκαν για τη ραδιενεργό ανισορροπία στη σειρά του 226Ra/238U. Τα αποτελέσματα του λόγου 226Ra/238U είναι αρκετά παρόμοια με αυτά του Δείκτη Αποσάθρωσης Parker (WIP) καθώς και του Ποσοστού του Δείκτη Αποσάθρωσης (PWI). Ως εκ τούτου, ο λόγος 226Ra/238U θα μπορούσε να χρησιμοποιηθεί ως ένα σχετικά ευαίσθητο δείκτης αποσάθρωσης στα ιζήματα, λαμβάνοντας όμως υπόψη την ορυκτολογική σύσταση και την διαβάθμιση των ιζήματων.

1 INTRODUCTION

The use of uranium series disequilibrium in the geological sciences includes applications such as age determination of deposits younger than 1 Ma (Schwarz and Gascoyne 1984), mantle evolution (Condonimes et al. 1988), hydrological tracing (Guttmann and Kronfeld 1982), determination of mineral weathering rates (Rihs et al. 2013) and nuclear waste disposal (Schwarz et al. 1982, Smellie 1982). In the latter application, the 238U series technique examines the state of radioactive equilibrium, existing between the radionuclides of the 238U decay series (Schwarz et al. 1982; Smellie et al. 1986, Gascoyne and...
When an isotopic system is undisturbed, it can be considered as closed. In this case the activity of the parent radionuclide is similar to that of its intermediate or final decay product, suggesting that the decay rate of the radionuclides of a particular isotopic series is nearly the same. This state of a radioactive series is defined as radioactive secular equilibrium. U-series equilibrium is reached after a short or long time of system closure depending on the half-lives of the radionuclides.

The radioactive secular equilibrium can be disturbed when the parent radionuclide or its decay products enter or depart from the isotopic system, during a period comparable to the half-life period of the daughter radionuclide and at distance comparable to the size of the system. This could be caused by mechanisms such as dissolution and precipitation of more geochemically soluble radionuclides of a radioactive series, diffusion of nuclides of radon and the effects of alpha particle recoil (Gascoyne, 1992; Ivanovich and Harmon, 1982, 1992; Osmond and Cowart, 1976, 1982).

The state of radioactive secular disequilibrium is a non-steady state and the time needed for the radioactive equilibrium to be restored depends on the decay rate of the radionuclides. If the isotopic system becomes closed again, it is generally known that the equilibrium between the parent–daughter radionuclide will be restored at a period equal to 5 or 6 times the half-life period of the daughter radionuclide (Spiegelman and Elliot, 1993; Dosseto et al., 2008), otherwise the equilibrium will not be restored. In order to investigate the presence of radioactive secular equilibrium in an isotopic system, the activity of the long half-life period parent radionuclide is correlated to one of its decay products having significantly shorter half-life period (Osmond et al., 1983).

Weathering indices are useful in pedogenesis and other applications. Some of them are: 1. Ruxton Ratio (R): This simple weathering index, proposed by Ruxton (1968), and termed Ruxton Ratio by Chittleborough (1991) is best suited for the weathering profiles with acid to intermediate bedrocks. The Ruxton Ratio relates silica loss to total element loss and considers alumina to be immobile during weathering. 2. Weathering Index of Parker (WIP). This index introduced by Parker (1970) for silicate rocks is based on the proportions of alkaline and alkaline-earth metals (sodium, potassium; magnesium and calcium) present which are the most mobile major elements during weathering. The WIP also takes into account the individual mobility of sodium, potassium, magnesium and calcium, based on their bond strengths with oxygen (Parker 1970). WIP was initially applied to acid, intermediate and basic igneous rocks. 3. Product of Weathering Index (PWI): This index was introduced by Souri et al. (2006) to study soil weathering from different regions in Japan. 4. Vogt's Residual Index (V): Vogt in 1927 proposed a geochemical method for assessing the maturity of residual sediments; the Vogt's Residual Index. Roaldset (1972) used this index to determine the weathering status of clays in Quaternary deposits of the Numedal Area in Norway. The index was used to compare the bulk chemistry of moraine and marine clay deposits. 5. Chemical Index of Alteration (CIA): This index was developed by Nesbitt and Young (1982) in reconstructing the paleoclimate from Early Proterozoic sediments of the Huronian Supergroup, north of Huron Lake. CIA is interpreted as a measure of the extent of feldspars conversion to clays such as kaolinite (Fedo et al. 1995, Maynard et al. 1995, Nesbitt and Young 1984, Nesbitt and Young 1989). 6. Chemical Index of Weathering (CIW): The CIW index was proposed by Harnois and Moore (1988). This index is identical to the CIA, except that it eliminates K2O from the equation. Because the CIW does not account for the aluminium associated with K-feldspar, it may yield very high values for K-feldspar-rich rocks, whether they are chemically weathered or not (Fedo et al. 1995). Like the CIA, the CIW is also essentially a measure of the extent of feldspars conversion to clay minerals (Fedo et al. 1995, Maynard et al. 1995, Nesbitt and Young 1984, Nesbitt and Young 1989). 7. Plagioclase Index of Alteration (PIA): This index was proposed by Fedo et al. (1995) as an alternative to the CIW. Because plagioclase is abundant in silicate rocks and dissolves relatively rapidly, the PIA may be used when plagioclase weathering needs to be monitored (Fedo et al. 1995).

The granitic rocks from Kavala and Sithonia plutons can be assumed as closed isotopic systems presenting $^{230}$Ra-$^{238}$U secular equilibrium (Papadopoulos et al. 2013). These granitic rocks are the parental rocks of the adjacent beach sands (Papadopoulos et al. 2015 and yet unpublished data of the authors). Since their parental rocks are in secular equilibrium (Papadopoulos et al. 2013), any distortion in the $^{226}$Ra-$^{238}$U system of the beach sands has occurred during their weathering and transport. This work aims to compare the results of weathering indices in use, with the results of radioactive secular disequilibrium between $^{226}$Ra and $^{238}$U in the beach sands from Kavala and Sithonia in order to understand if they are driven by the same weathering processes and suggest the application of U-series isotope ratios as a new weathering index.

2. GEOLOGICAL SETTING

2.1 Kavala pluton

Kavala pluton intrudes the metamorphic rocks of the Lower Tectonic Unit of the Rhodope Massif following a SW-NE direction. It is composed by I-type calcalkaline granitic rocks (Neiva et al. 1996) (Fig. 1A). The main rock-type present is a medium to coarse-grained hornblende-biotite granodiorite, with numerous enclaves of dioritic to tonalitic composition. Aplitic veins are also present. Coarse-grained granodiorite is present only at the NE part of the pluton. Small occurrences of biotite-hornblende tonalite and biotite monzogranite are also present (Kokkinakis 1977, Neiva et al. 1996, Papadopoulos 2011). Granodiorite is light to dark colored and is characterized by gneissic texture due to magmatic and post magmatic tectonic
activity. The mineral constituents of the rock-types of Kavala pluton are quartz, feldspars, biotite, hornblende, titanite, zircon, monazite and apatite (Neiva et al. 1996, Papadopoulos 2011). Rb-Sr whole-rock age of 18 Ma was interpreted as the mylonitization age (Kyriakopoulos et al. 1989), but according to Dinter et al. (1995) the emplacement and mylonitization age of the Kavala pluton took place at about 21-22 Ma ago (U-Pb and Ar-Ar dating on titanite and mylonitic hornblende respectively). K-Ar biotite ages of 15.5 ±0.5 and 17.8 ±0.8 Ma (Dinter et al. 1995) and Rb-Sr biotite ages of 14-16 Ma (Kyriakopoulos et al. 1989) have been interpreted as reset metamorphic ages. Dinter and Royden (1993) considered them as cooling ages related to the emer- gence of the Rhodope metamorphic core complex in the footwall of the Strymon Valley detachment which is corroborated by the Strymon Valley detachment is a result of Middle-Jurassic tectonic activity. The intrusion itself has been affected by younger tectonic activity that took place most probably in the Late Eocene–Oligocene and induced minor shear effects marked by mica orientation (Sakellariou 1989). The major rock-types present in the SPC are, from north to south, Two-Mica Granites to Granodiorites (TMG), Leucogranites (LG), Biotite Granodiorites (BGd) and Hornblende-Biotite Granodiorites (HBGd). Small occurrences of Hornblende-Biotite Tonalites (HBton) are also present. Enclaves of quartz-dioritic composition are quite common within the granodiorites and tonalites (Sapountzis et al. 1976, 1979; Christofides et al. 1990; Christofides et al. 1998; D’Amico et al. 1990; Christofides et al. 2007). Aplites and pegmatites occur throughout the SPC, intruding the pluton as well as the country rocks. The mineral constituents of the rock-types of Sithonia pluton are quartz, feldspars, biotite, muscovite, hornblende, titanite, chlorite, allanite, zircon, magnetite, ilmenite and apatite (Christofides et al. 1998, Papadopoulos 2011). Field relationships indicate that the TMG intruded metasediments, and is cut by the LG with sharp contacts. The LG penetrated the HBGd, as indicated by the occurrence of LG dykes in the latter. In addition there are also deformed masses of HBGd, often displaying crenulated contacts, in the LG. All the granitoid masses, as well as the country rocks, were intruded by pegmatitic and aplitic dykes and veins, being more abundant in the LG and the TMG than in the other rock types. The rock-types of the SPC are calc-alkaline. The rocks show characteristics of pre-plate-collisional setting, indicating subduction-related magma genesis (Christofides et al. 2007).

2.2 Sithonia Plutonic Complex (SPC)

The greatest part of the Sithonia Peninsula (northern Greece) belongs to the Circum Rhodope Belt which is mainly composed of Mesozoic sedimentary and metamorphic rocks, and only a small part lies within the Serbomacedonian Massif, mainly composed of amphibolites and gneisses (Vergely 1984). The SPC is a NW–SE trending granitic body of about 350 km² (Fig. 1B). It intrudes mainly the Circum Rhodope Belt and partially the Serbomacedonian Massif. An Eocene age (~50 Ma) has been determined for the pluton emplacement (Christofides et al. 1990). The intrusion of the SPC affected the regional NW–SE strike of the schistosity and fold axes of the country rocks, considered as a result of Middle-Jurassic tectonic activity. The intrusion itself has been affected by younger tectonic activity that took place most probably in the Late Eocene–Oligocene and induced minor shear effects marked by mica orientation (Sakellariou 1989). The major rock-types present in the SPC are, from north to south, Two-Mica Granites to Granodiorites (TMG), Leucogranites (LG), Biotite Granodiorites (BGd) and Hornblende-Biotite Granodiorites (HBGd). Small occurrences of Hornblende-Biotite Tonalites (HBton) are also present. Enclaves of quartz-dioritic composition are quite common within the granodiorites and tonalites (Sapountzis et al. 1976, 1979; Christofides et al. 1990; Christofides et al. 1998; D’Amico et al. 1990; Christofides et al. 2007). Aplites and pegmatites occur throughout the SPC, intruding the pluton as well as the country rocks. The mineral constituents of the rock-types of Sithonia pluton are quartz, feldspars, biotite, muscovite, hornblende, titanite, chlorite, allanite, zircon, magnetite, ilmenite and apatite (Christofides et al. 1998, Papadopoulos 2011). Field relationships indicate that the TMG intruded metasediments, and is cut by the LG with sharp contacts. The LG penetrated the HBGd, as indicated by the occurrence of LG dykes in the latter. In addition there are also deformed masses of HBGd, often displaying crenulated contacts, in the LG. All the granitoid masses, as well as the country rocks, were intruded by pegmatitic and aplitic dykes and veins, being more abundant in the LG and the TMG than in the other rock types. The rock-types of the SPC are calc-alkaline. The rocks show characteristics of pre-plate-collisional setting, indicating subduction-related magma genesis (Christofides et al. 2007).

3 MATERIALS AND METHODS

3.1 Sampling

Representative sand samples obtained from spots separated each other by around 500m were collected
from beaches, close to the rocks of Kavala and Sithonia plutons respectively (Fig. 1), using sampling intervals relative to the length of each beach. Among the Kavala samples, 11 were collected from specific horizons of black color with a thickness of 1-4 cm, enriched in heavy minerals, whereas 3 samples from Sithonia were collected from a specific horizon of dark green color (due to high epidote concentration). For each sand sample analyzed, three sub-samples of equal mass (=500g) were obtained from a depth of 20 cm. The sub-samples, corresponded to 3 different points, forming an equilateral triangle (with dimensions of ≈1.4 m) representing an area of approximately 1 m². The three sub-samples were homogenized by mixing in situ and this sand mixture, weighing approximately 1.5 kg, was considered as representative. All the heavy mineral-enriched samples were well or very well sorted.

3.2 Major element chemical analyses

The major element analyses were performed on bulk sand samples by ICP-MS at Activation Laboratories (ACTLABS, Ontario, Canada) following lithium metaborate/tetraborate fusion. The grinding of the samples was made on agate mortar. The detection limits for the major elements are 0.01% except for TiO₂ and MnO which are 0.001%. The analyses have been used to calculate the weathering indices (Table 1).

Table 1. Weathering indices of the samples.

<table>
<thead>
<tr>
<th></th>
<th>R</th>
<th>CIA</th>
<th>WIP</th>
<th>PWH</th>
<th>V</th>
<th>CIW</th>
<th>PIAB</th>
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<td>36.0</td>
<td>3932</td>
<td>86.4</td>
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<td>51.2</td>
<td>4218</td>
<td>78.9</td>
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<td>59.3</td>
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<td>6.61</td>
<td>45.9</td>
<td>3923</td>
<td>69.9</td>
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<td>51.5</td>
<td>44.8</td>
</tr>
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<td>KB2D</td>
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<td>416</td>
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<td>52.7</td>
<td>4299</td>
<td>71.6</td>
<td>1.53</td>
<td>57.6</td>
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<td>58.3</td>
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<td>2.42</td>
<td>67.2</td>
<td>61.3</td>
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<td>56.1</td>
<td>4550</td>
<td>79.4</td>
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<td>KB20B</td>
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</tr>
<tr>
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<td>55.9</td>
<td>4021</td>
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<td>64.1</td>
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<td>0.95</td>
<td>50.5</td>
<td>48.8</td>
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</table>

3.3 Gamma spectrometry

For the gamma-ray spectroscopy, the bulk sand samples were crushed into grains less than 400 μm in diameter, oven-dried at 60°C to constant weight, well-blended and measured using two high-resolution gamma ray spectrometry systems. The first one consisted of an HPGe coaxial detector with 42% efficiency and 2.0 keV resolution at 1.33 MeV photons, shielded by 4" Pb, 1mm Cd and 1mm Cu and the second one consisted of a LEGe planar detector with 0.7 keV resolution at 122 keV photons, shielded by 3.3" Fe-Pb, 1mm Cd and 1mm Cu. The first spectrometry system with the High Purity Ge detector was used to measure the majority of the natural radionuclides examined in this work, except for ²³⁵U. The second one with the Low Energy planar Ge detector, was used only for the determination of the specific activities of ²³⁴U by considering the low γ-ray of 63 keV emitted by its daughter ²³⁴Th. The measurement of ²²⁶Ra from its own γ-ray at 186.25 keV introduces some problems because of the adjacent photo peak of ²³⁸U at 185.75 keV, so that the isotopic ratio between ²³⁴U and ²²⁶Ra was considered being the natural one, i.e. 0.0072 and secular equilibrium between ²³⁸U and ²²⁶Ra had to be assumed. The determination of ²²⁶Ra content was based on measurement of ²²⁶Ra decay products being in equilibrium. Accuracy in the measurements of ²²⁶Ra concentrations by ²²⁶Ra decay products depended on the integral trapping of radon gas in the sample volume, so a small addition (~2%) of charcoal in powder form (less than 400 μm in size) was mixed with the sample before sealing it hermetically and storing it in a freezer during ²²⁶Ra in-growth period (Manolopoulou et al. 2003).

The efficiency calibration of the gamma spectrometry systems was performed with the radionuclide specific efficiency method in order to avoid any uncertainty in gamma ray intensities as well as the influence of coincidence summation and self-absorption effects of the emitting gamma photons. A set of high quality certified reference materials (RGU-1, RGTb-1, RGG-1) (I.A.E.A. 1987) was used, with densities similar to the building materials (bricks, tiles etc.) measured after pulverization. Cylindrical geometry was used assuming that the radioactivity is homogeneously distributed in the measuring samples. The samples were measured up to 200,000 s in order to achieve a Minimum Detectable Activity of 2 Bq kg⁻¹ for ²²⁶Ra and 21 Bq kg⁻¹ for ²³⁸U, with 33% uncertainty. The total uncertainty of the radioactivity levels was calculated by propagation of the systematic and random errors of measurements. The systematic errors in the efficiency calibration ranges from 0.5–2% and the random errors of the radioactivity measurements extend up to 5%, except in the ²³⁸U measurement, where the error extends up to 12%.

4 RESULTS AND DISCUSSION

The specific activities of ²³⁵U, ²²⁶Ra (Bq/kg), along with the ²²⁶Ra/²³⁵U isotopic ratios and the respective standard errors are presented in Table 2. The absolute values of the differences between the isotopic ratios and 1 as a measure of the disequilibrium in the U-series radionuclides, are also given. The isotopic systems of the samples that show ²²⁶Ra/²³⁵U ratios close to 1 appear to have remained closed in time comparable to the half-lives of ²³⁴U (T1/2=245 ka) and ²³⁰Th (T1/2=75.4 ka), which are the intermediate radionuclides between ²³⁶U and ²³⁸U in the ²³⁸U radioactive series. Papadopoulos et al. (2013) report that the granitic rocks of Sithonia and Kavala are in ²²⁶Ra/²³⁸U secular equilibrium. Since the age of all the granitic rocks being the parental rocks of the beach sands studied is a lot higher than 1 Ma, for the samples that exhibit ²²⁶Ra/²³⁸U isotopic ratios significantly different than 1, their ²³⁸U isotopic system can be considered as open.
due to secondary processes (rock–water interactions) in a period between 1 Ma up to now. On the other hand, the samples exhibiting 226Ra/238U=1 are considered really unaltered during the above mentioned periods (Gascoyne and Miller, 2001).

As long as the distortion of the secular equilibrium in the above samples is quite recent in geological time, the reasons of the disequilibrium should be found at the low temperature geochemistry of U and Ra. Intensive leaching and transportation of U as U(VI) (UO₂⁺ in surface waters) in low temperatures can occur in the presence of various anions such as F⁻, Cl⁻, CO₃²⁻, SO₄²⁻ and PO₄³⁻, depending on the oxidation potential of the fluid (Kyser and Cuney, 2008 and references therein). U is more soluble in oxidising, alkaline and carbonate-rich waters than in acidic waters (Kyser and Cuney, 2008 and references therein). Consequently, such conditions could be the reason of secular disequilibrium in the samples exhibiting 226Ra/238U=1.

In the samples that are out of radioactive secular equilibrium, displaying 226Ra/238U≠1, 238U and 226Ra have either leached, or have been deposited.

For samples displaying 226Ra/238U=1, there is an indication of either selective deposition of 230Th or 226Ra, or/and depletion and removal of 238U. The deposition and enrichment in 226Ra can occur locally and can be caused by the mixing of sea and superficial water (Gascoyne and Schwarz, 1986). Between 230Th and 226Ra, 230Th is less soluble in water than U. 226Ra could be more soluble than U depending on the pH, Eh and anion content of the water (Latham and Schwarz, 1987; Ibraheim, 2003). 226Ra/238U<1 ratios suggest that the enrichment in 238U is probably due to its transportation in the rock and to subsequent deposition. Another explanation could be the 226Ra removal, supposing that the geochemical conditions favors a greater mobility of Ra compared to U.

In figure 2 the measure of U-series disequilibrium (as expressed by the absolute difference of both 226Ra/238U ratios from 1) is correlated with the values of the weathering indices for all the heavy mineral-enriched beach sand samples from Kavala and Sithonia.

Among the weathering indices used for comparison, WIP and PWI are the most sensitive, as their results are similar especially to those of U-series disequilibrium. The sensitivity of WIP is a result of the fact that it considers alkaline and alkaline-earth metals, being the most mobile major elements. WIP is also applied to detect chemical weathering in acid, intermediate and basic igneous rocks, which are the parental rocks of the beach sands studied. PWI seems to be in well agreement especially with the U-series disequilibrium exhibited from the samples of Kavala as it considers Fe₂O₃, which is very abundant in the hematite and magnetite rich heavy mineral-samples from Kavala.

The other weathering indices used for comparison are less sensitive than WIP and PWI as they involve mainly the conversion of feldspars to clay minerals and therefore cannot be applied in heavy mineral-enriched sands. These weathering indices are well suited for soils and weathering profiles studies where the unweathered bedrock and the weathering reactions are clearly known, so that the intensity of weathering can be measured. However, the geochemistry of the beach sands is mostly driven by erosion, mixing and sorting of primary minerals with very small amounts of clays and calculated weathering index are not very representative of chemical weathering. On the other hand, U-series disequilibria are clearly mostly driven by chemical weathering if we assume that the bedrock is at secular equilibrium. Sorting of sediments is indicative of the processing time of the weathered material. Time should be important as several ka would be enough to keep the U-series system open. On the other hand, very short time period would not give significant disequilibrium in the U-series. Therefore, the samples being well or very well sorted (this is the case for all the heavy mineral-enriched samples) from both investigated areas, show correlation coefficients (R²=0.90) for WIP and (R²=0.93) for PWI with U-series disequilibrium (Fig. 2).

### Table 2. Activities of 238U, 226Ra, 228Ra, 228Th (Bq/kg) as well as 238U and 232Th-series disequilibrium as expressed by 226Ra/238U, 228Ra/230Th, 226Ra/238U ratios and their absolute differences from 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>238U Bq kg⁻¹</th>
<th>±σ</th>
<th>226Ra Bq kg⁻¹</th>
<th>±σ</th>
<th>238U-series disequilibrium 226Ra/238U</th>
<th>±σ</th>
<th>1−226Ra/238U</th>
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<tr>
<td>KB1B</td>
<td>83</td>
<td>7</td>
<td>64</td>
<td>1</td>
<td>0.77</td>
<td>0.07</td>
<td>0.23</td>
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<tr>
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<td>187</td>
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<td>191</td>
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<td>0.93</td>
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CONCLUSIONS

The mineralogical composition and the time of processing of sediment are two factors that affect the extent of weathering. U-series disequilibrium is very good correlated with WIP and PWI for the heavy mineral–enriched and well or very well sorted samples studied. U-series disequilibrium can therefore be used as a relatively sensitive weathering index in sediments. However, the mineralogical composition and sediment sorting must be considered.

Figure 2. Correlations between the weathering indices and the values of the absolute differences from 1 of the $^{226}$Ra/$^{238}$U (U-series disequilibrium) for all the heavy mineral-enriched samples from Kavala and Sithonia being very well sorted.

5 CONCLUSIONS
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REFERENCES


Nesbitt H. W., Young G. M., 1989. Formation and Diagenesis of Weathering Profiles, J. Geol. 97, 129–147

Ruxton B. P., 1968. Measures of the Degree of Chemical Weathering of Rocks, J. Geol. 76, 518–527