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# Validation of a database of mean uranium, thorium and potassium concentrations in rock samples of Portuguese geological units, generated of literature data

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# Highlights

- A database of U, Th and K concentrations in rocks of Portugal established;
- Mean U, Th and K concentrations in rock per geological unit calculated;
- Validation by comparison of calculated to measured mean terrestrial dose rate;
- Investigation of variance components traceable to the geochemical analysis;
- Use of scattered local geochemical data to establish large scale maps enabled.

#### 1 Abstract

The European Atlas of Natural Radiation has been under development for the past 2 3 15 years. Among the lacunae of the Atlas are maps of U, Th and K concentrations in rocks due to lack of European-wide geochemical surveys of bedrock units. The objective 4 of this paper is to investigate the usability of scattered geochemical data of rock samples 5 for large-scale mapping of U, Th and K concentrations in geological units. For this 6 7 purpose, geochemical data were compiled from grey literature sources to produce a geochemical database (LIT database) that includes 2817 results of U, Th and K 8 9 concentrations measured in rock samples.

10 Given the methodical heterogeneity within LIT database, the influence of the 11 geochemical analysis techniques was assessed through a three-way analysis of 12 variance (ANOVA) using geological units, geochemical analysis techniques and loss on 13 ignition (LOI) as categorical variables. The percentage of variation explained by geological factors was 53 % for U, 38 % for Th, 50% for K and 51 % for the terrestrial 14 gamma dose rate (TGDR), while the percentage of variation explained by the 15 geochemical analysis techniques and LOI was generally lower than 5 %. The geological 16 17 factors were thereby the main source of variability in the data, followed by the error component which can be assumed to represent true spatial variability of geochemical 18 concentrations, hence, variability within the geological units. The reliability of LIT 19 database between the different geochemical analysis techniques was investigated 20 through pairwise comparison of the least square (LS) means computed through the 21 three-way ANOVA for each geochemical analysis technique. The results show an 22 agreement of the LS means between the different geochemical analysis techniques, 23 24 which indicates that LIT database can be considered consistent within itself, thus, reliable. 25

In order to validate the usability of literature data, the TGDR calculated from literature
 data (TGDR<sub>calc</sub>) was compared to the measured TGDR (TGDR<sub>obs</sub>) displayed in the

Radiometric Map of Portugal (RMP) using geological units as reference units. The 28 29 correlation between TGDR<sub>calc</sub> and TGDR<sub>obs</sub> was highly significant (p < 0.001) and the 30 results of a paired sample t-test and Wilcoxon median tests indicate that the differences between the arithmetic means of TGDR<sub>calc</sub> and TGDR<sub>obs</sub> were not statistically significant 31 (p = 0.126 and p = 0.14, respectively). Distributions of TGDR<sub>calc</sub> and TGDR<sub>obs</sub> are 32 seemingly equal according to the Kolmogorov-Smirnov and Anderson-Darling tests. The 33 34 pooled standard deviation (SD) of the RMP dataset was set as criterion to assess the discrepancy between the arithmetic means of the RMP and LIT databases. About 14 out 35 of 26 geological units are located within one pooled SD around TGDR<sub>obs</sub> and only 1 out 36 of 26 units is located outside 2 pooled SDs. Systematic discrepancies were observed for 37 38 sedimentary rocks possibly due to the lack of representativeness of the data. 39 Nonetheless, the compatibility of the RMP and LIT databases can be considered acceptable, which implies that the estimation of the contents of terrestrial radionuclides 40 using literature data for large-scale mapping of U, Th and K contents in geological units 41 42 is reasonable.

43 Keywords: Data compilation; Geochemical analysis techniques; Terrestrial
44 radionuclides; Terrestrial gamma dose rate; Geological units.

45 **1. Introduction** 

#### 46 **1.1 Motivation**

47 A long-term European project, under way for about 15 years, is the European Atlas of Natural Radiation, of which web and printed versions exist (Cinelli et al., 2019; EC, 48 2019). The Atlas is however incomplete, as certain compartments and environmental 49 50 media are missing or fragmentary due to lack of data. Among these lacunae are maps of concentrations of naturally occurring radionuclides, namely isotopes of U, Th and K, 51 in rock. While Europe-wide geochemical surveys of agricultural and pasture soil including 52 these radionuclides exist (FOREGS and GEMAS, maps and references in the Atlas), 53 54 literature data of U, Th and K in rock are scattered and methodically highly

heterogeneous. Therefore, creating Europe-wide maps from such data appeared 55 questionable. The alternative, on the other hand, namely creating a methodically 56 57 homogeneous geochemical database of European rocks from scratch, would pose a tremendous task which is beyond realistic feasibility. Therefore, it has been concluded 58 59 by the board of experts of the Atlas (to which the authors of this paper belong) to explore 60 the feasibility of maps of U, Th and K concentrations in rocks, derived from literature 61 data. This requires, as very first step, to investigate whether literature data can be used to this end, observing standards of accuracy and precision, given methodical 62 heterogeneity. The objective of this paper is thus, investigating the usability of scattered 63 geochemical literature data for large-scale (in perspective, European scale) mapping. As 64 test region for this study we use the territory of Portugal and as geochemical data 65 66 sources, local studies on rock geochemistry performed in Portugal.

67

#### 1.2 Geochemical surveys

Local surveys of geochemistry are profusely available in scientific literature. Large scale surveys are, however, scarce because the generation of a truly representative sample of the media is difficult with limited resources, and sampling of the entire population of landscape units is impractical and costly.

UNESCO initiated the first attempt to create a geochemical map of the world in 1988 72 73 through the International Geochemical Mapping Project (IGCP 259) (Xuejing and 74 Hangxin, 2001). The main goal of the project was to estimate the concentration of several 75 elements at a global scale with particular focus on ore pathfinders and radioelements 76 (Darnley 1995, Darnley et al. 1995, Xuejing and Hangxin, 2001). The project intended to 77 overcome the lack of numerical equivalence between compiled datasets that are subject 78 to different sampling and analytical techniques as well as different levels of quality control 79 (Darnley et al. 1995). However, the compilation and normalization of existing datasets 80 required that data at multiple spatial scales be interlinked (Darnley 1995, Darnley et al. 81 1995).

A compilation of geochemical data hardly fulfills the assumptions of statistical inference (ex. the sampling must be random, unbiased and designed to adequately represent the population, Crumbling, 2001; Ramsey and Hewitt, 2005) as the data have been acquired for different purposes, at different scales and with different methods. However, every geochemical survey must rely on a suitable knowledge of the geology of the surveyed area (e.g. Rollinson, 1993). Thus, geochemical surveys can be presumed to be representative of the geological units sampled.

The estimation of the contents of terrestrial radionuclides, radon, gamma dose rate and air-absorbed dose rate using geochemical data has been attempted at both a local (e.g. lelsch et al. 2010; Ye and Gan, 2013) and regional scale (e.g. Appleton et al. 2008; Beamish 2014; lelsch et al. 2017; Marsac et al. 2016). However, the authors often resort to geochemical data available in national databases that have been acquired with consistent analytical techniques and quality control procedures.

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#### 1.3 Heterogeneity of literature data

96 Heterogeneity of literature data occurs on several levels. (1) The data come from 97 regional or local studies of certain rock formations or types with certain geochemical 98 objectives, such as mineral exploration, hydrological investigations etc. While 99 representativeness for the study area can be assumed, it is unclear to which extent this 100 applies to an entire lithological class.

(2) Sampling and sample geo-referencing methods are heterogeneous. For example,
 many literature sources do not quote locations of individual samples, but only regions of
 origin. Sometimes, no individual but only aggregated results are given, e.g. arithmetic
 mean concentrations and standard deviations. This circumstance inhibits the use of
 geostatistical tools.

(3) Finally, geochemical analytic methodology is heterogeneous. Comparability of
 results between different studies is therefore not given a priori. Both radiological and
 geochemical data can be used to evaluate U, Th and K concentrations and distributions

(IAEA, 2010). Radiological data refers to radionuclide concentrations determined
through alpha- or gamma-spectrometry while geochemical data may be acquired
through various geochemical analysis techniques (hereafter referred to as analytical
techniques), such as X-Ray Fluorescence (XRF), Induced Coupled Plasma
Spectrometry (ICP) or Instrumental Neutron Activation Analysis (INAA), among others.

114 It should be stressed again that heterogeneity between studies does not mean to 115 invalidate the individual studies, but it is an obstacle to using them as input for maps 116 beyond the scale of the individual ones. Investigating whether it is still possible, is the 117 subject of this paper.

#### **118 1.4 Variability of true and measured geochemical concentrations**

The idea underlying the analysis performed in this study is that there are essentiallythree components of variability:

121 (A) Variability between geological units, leading to variance between geochemical 122 concentrations of samples (or studies, representing aggregated samples) located in 123 different geological units, as this factor is assumed to control geochemical concentration; 124 this component represents *true spatial variability* of the investigated variable 125 (geochemical concentration).

(B) Variance due to different analytical techniques, as it is known that different techniques applied to the same sample, i.e. same true concentration, can lead to systematically different results (e.g. Rollinson, 1993). This component refers to the *observation process* of the variable, not to its true variability over a geological unit.

130 (C) Variance due to lack of spatial representativeness: assume two studies using 131 same analytical technique, performed in different parts of the same geological unit. Due 132 to true spatial variability within geological units, the results will still be different, in general, 133 in spite of variance sources (1) and (2) excluded. This effect can only be avoided 134 (asymptotically with sample size) if the sample covers the domain (geological unit) 135 representatively. (Representativeness means that the statistical distribution of the 136 sample is asymptotically the same as the true distribution of the investigated variable,

here geochemical concentration.) This component refers to availability of data within a
geological unit and their aggregation within and can be understood as sampling effect
induced by true variability, component (1). Getting hold of this component is particularly
difficult.

#### 141

#### 1.5 Validation of usability of literature data

The tool to validate the usability of geochemical literature data is comparison of 142 terrestrial gamma dose rate (TGDR) calculated from geochemical concentrations with 143 144 measured ones. Coincidence within tolerable deviation is a necessary condition of the 145 validity of regional estimates from scattered literature data. The strategy is therefore, 1) estimate mean U, Th, K concentrations of geological units from literature data; 2) 146 147 calculate the mean TGDR per unit and 3) compare these calculated with measured mean 148 TGDR of the same units. This is possible for Portugal as test region, as a fine-grained TGDR map of Portugal is available. If it is proven that creating maps of rock geochemistry 149 from scattered literature data is possible in Portugal, it can plausibly be assumed that 150 this is possible also in other regions. 151

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#### 2 **1.6 Organization of this paper**

In the methods section (2), we first establish the geological classification scheme which leads to the set of geological units in which geochemical literature data are aggregated and mean dose rates are calculated. This is followed by a presentation of the compiled geochemical database (section 2.2) and the TGDR map of Portugal (2.3). In section 2.4, the conversion of geochemical concentration into TGDR is reviewed and in 2.5, we explain statistical techniques.

The results section (3) is firstly devoted to analyzing the sources of variance A and B (geology and analytical techniques) in section 3.1. Then an attempt is made to remove source B, to assess the effect of lack of representativeness at least qualitatively (section 3.2). The validation analysis through terrestrial dose rate is shown in section 3.3.

163 **2. Materials and Methods** 

#### 164 **2.1. Geological classification scheme**

OneGeology-Europe (OGE) data were chosen as the geological map to be used as 165 166 reference because they are available at the European level (at http://www.onegeologyeurope.org/), providing access to geological maps at the scale of 1:1.000,000 (Baker and 167 Jackson, 2010). The OGE map for Portugal was developed through collaboration with 168 the Portuguese National Laboratory of Energy and Geology (LNEG), and comprises 169 three distinct layers, namely lithology, age and geological structures. The code 170 classification scheme of the OGE map is equivalent to the code classification scheme of 171 the Portuguese Geological Map (PGM) at the scale of 1:1,000,000 published in 2010 by 172 173 LNEG, and available at http://geoportal.lneg.pt/geoportal/mapas/index.html. The OGE classification comprises 76 geological units in mainland Portugal and 11 units in the 174 Madeira and Azores archipelagos. A summary description of the geological units studied 175 176 in the present work is presented in Table 1 according to Baker and Jackson (2010). A 177 simplified geological map is presented in Figure 1a.

178

#### 2.2. The Radiometric Map of Portugal

179 The Radiometric Map of Portugal (RMP, Figure 1b, Batista et al. 2013) displays the terrestrial gamma dose rate in mainland Portugal and is further denoted as TGDRobs. A 180 raster layer is available freely at http://geoportal.lneg.pt/geoportal/mapas/index.html. The 181 182 data were acquired with hand-carried, vehicle-borne and air-borne equipment from 1955 onwards (Batista et al. 2012). The equipment used were calibrated either using sources 183 of terrestrial radionuclides with known concentrations of U, Th and K or by measuring 184 the same sites with different equipment (Batista et al. 2012; Grasty et al. 1993). The first 185 186 radiometric maps of Portugal were produced based on 733,201 measurement points by linear interpolation with the minimum curvature method. The estimation grid consists of 187  $250 \text{ m} \times 250 \text{ m}$  cells. A minimum of 10 measurement points was defined necessary for 188 189 estimation on each grid point, to assure reasonable statistical reliability. This required a 190 search radius of 10 km around every grid point to make sure that the required minimum

number of observations could be achieved (Torres et al. 1997; Saraiva et al. 1998). The
updated RMP was produced based on 841,440 measurement points following the
acquisition of new data to fill the gaps in the previously developed maps (Batista et al.
2012; Batista et al. 2013).

The cell size of the RMP constitutes an important limitation for geological units that 195 have a large perimeter to area ratio, such as vein-type rocks (perimeter to area ratio 196 generally higher than 5). The width of the f1 and f2 (basic vein-type rocks) and gz (guartz 197 veins) units is generally lower than 500 m. Given the RMP cell size of 250 m and the 198 search radius of 10 km used to reach a minimum of 10 measurement points for 199 200 interpolation, the TGDR<sub>obs</sub> for these units is highly influenced by the TGDR<sub>obs</sub> of neighboring geological units. Therefore, the TGDR<sub>obs</sub> of vein-type rocks displayed in the 201 RMP is unreliable. For this reason, vein-type geological units were excluded from the 202 203 analysis. This is unfortunate because these units often contain concentrations of 204 radioactive elements strongly different from their surroundings and should therefore be 205 given particular attention for radioprotection reasons. The methodical alternative would 206 have been a different interpolation scheme for such units, but the original raw TGDR 207 data which would be necessary for this, are not available to us.

208 The lack of access to the original raw TGDR data inhibits the assessment of the influence of the presence of unconsolidated overburden and soil units in the measured 209 210 TGDR. However, the RMP was primarily developed for the purpose of mineral exploration (Batista et al. 2012; Grasty et al. 1993, Saraiva et al. 1998; Tauchid and 211 Grasty, 2002; Torres and Grasty, 1993). Sampling was focused on the main geological 212 units, as surveys were carried preferentially over crystalline areas, followed by the 213 214 Mesozoic and Cenozoic sedimentary basins (Torres and Grasty, 1993). Data from car, foot and air-borne surveys were calibrated through measurement of selected areas of 215 exposed bedrock of the main geological units (Torres and Grasty, 1993). The RMP thus 216 reflects the geological character of Portugal (Batista et al. 2012; Grasty et al. 1993, 217

- Saraiva et al. 1998; Tauchid and Grasty, 2002; Torres and Grasty, 1993). Thus, the RMP
- 219 data can be presumed to be representative of the geological units.

# **Table 1.** Summary description of the geological units studied according to OGE data

# (Baker and Johnson, 2010).

Group	OGE unit	Perimeter/Area ratio	Lower age	Upper age	Predominant Lithology	Subordinate lithology
	N2	0.9	Pliocene	Pliocene	Sandstone	Conglomerate, Siltstone
	N1c	1.2	Miocene	Miocene	Sandstone	Conglomerate, Siltstone
	K1-2	1.4	Cretaceous	Cretaceous	Limestone	Sandstone, Impure carbonate sedimentary rock, Dolomite
rocks	К1	1.8	Early/Lower Cretaceous	Early/Lower Cretaceous	Sandstone	Limestone, Impure carbonate sedimentary rock, Dolomite
	TJ1	2.2	Late/Upper Triassic	Middle Jurassic	Sandstone	Claystone, Evaporite, Limestone
	C2	3.6	Pennsylvanian	Pennsylvanian	Conglomerate	Sandstone, Claystone, Coal
	C1-2	0.3	Carboniferous	Carboniferous	Phyllite	-
Metamorphic rocks	D2-3	1.9	Middle Devonian	Late/Upper Devonian	Phyllite	Quartzite
	SDof	1.2	Silurian	Silurian Devonian Amphibolite		Schist, Fine grained igneous rock
	SD	0.4	Silurian	Silurian Early/Lower Phyllite		-
	SDP	0.7	Ordovician	Devonian	Phyllite	-
	ODP	0.8	Ordovician	Devonian	Quartzite	-
	O_a	1.6	Ordovician	Ordovician	Quartzite	Phyllite
	gz	1.1	Furongian Middle Orthogneiss		Granite, Diorite	
	Npep	0.6	Ediacarian Cambrian Phyllite		-	
	NP2	1.4	Neoproterozoic	Neoproterozoic Phyllite		-
	NP1	1.6	Neoproterozoic	Neoproterozoic	Schist	Gneiss, Migmatite
	GAMA2	3.8	Late/Upper Cretaceous	Late/Upper Cretaceous	Diorite	Gabbro
	CVL	2.2	Late/Upper Cretaceous	Late/Upper Cretaceous	Basalt	Pyroclastic material, Gabbro,
	g1_b	1.1	Pennsylvanian	Cisuralian	Granite	-
	g2_b	0.3	Pennsylvanian	Cisuralian	Granite	-
laneous rocks	g3	0.7	Pennsylvanian	Cisuralian	Granite	-
Igricous rooks	g1_a	0.7	Mississippian	Pennsylvanian	Granite	-
	g2_a	0.7	Mississippian	Pennsylvanian	Granite	-
	g1a	0.8	Late/Upper Devonian	Pennsylvanian	Tonalite	Granodiorite,
	GAMA	1.3	Late/Upper Devonian	Pennsylvanian	Gabbro	Anorthositic rock, Diorite
	D3C1	1.4	Late/Upper Devonian	Pennsylvanian	Fine grained igneous rock	Phyllite
*The perimeter t the geological u	to area ratio nit.	was computed as th	ne ratio between the	sum of the perimeter	to the sum of the a	rea of all polygons of



Figure 1. a) Geological units studied. Adapted from the Geological Map of Portugal at
the scale of 1:1,000,000 (LNEG, 2010). b) Radiometric Map of Portugal (Batista et al.
2013). Bathymetry was retrieved from http://portal.emodnet-bathymetry.eu/mean-depthfull-coverage (last accessed in February 2017).

#### 227 **2.3. The geochemical database**

A compilation of geochemical surveys available in mainland Portugal was carried out 228 229 in order to produce a new geochemical database, called LIT to denote that is consists of literature data. The LIT database includes 2817 observations of U. Th and/or K 230 concentrations measured in rock samples presumed to be representative of the 231 geological units studied. The data included in LIT database were retrieved from the 232 references listed in table A1 (Supplementary material). All samples included in LIT 233 database were collected in areas of bedrock exposed on the earth surface excluding 234 data retrieved from Cerejo (2013), Pinto (2014), Oliveira (2015) and Dinis et al. (2011) 235 236 whom also studied rock samples retrieved from boreholes and/or underground galleries. 237 Due to the inherent modifications caused by in-situ chemical and physical weathering, erosion and transport, among others, soil samples and unconsolidated materials are not 238 239 considered representative of geological units, hence, were excluded from the analysis. 240 Data for the Azores and Madeira archipelagos were not included in the database as the 241 RMP only covers mainland Portugal (Batista et al. 2013).

Three types of samples were considered as observations: (1) individual analyses of 242 243 rock samples; (2) analyses of composite samples (mixtures of several individual samples taken within an area, analyzed as one sample; the purpose is to reduce variability) and 244 (3) averages of individual samples' analyses. Statistically, sample averages were treated 245 246 as individual samples; (3) can be thought as mathematical mixing in analogy to physical mixing in (2). The accurate location of the sampling sites of the observations are mostly 247 unknown inhibiting the use of geostatistical tools. This is because in earlier surveys, geo-248 referencing was not considered necessary. Due to this limitation, the regionalization of 249 250 the available data was carried out using geological information.

Each observation of the LIT database was classified with a code of the geological classification scheme described in section 2.1. according to the location of the observations or the study area (when provided by the authors), or, in alternative, through

the lithologic, petrographic or paleontological features of the samples. A summary of the
data available by geological unit (Table A1) and by analytical techniques (Table A2) are
given as supplementary material.

257 For each observation of U. Th and/or K, the element concentration and analytical techniques were registered as provided by the authors. No corrections to U, Th and/or K 258 concentrations were applied for loss on ignition (LOI) or the volatile content. A binary 259 categorical variable for the computation of the effects of LOI in an Analysis of Variance 260 (ANOVA) was defined. Each observation was classified as "TRUE" if the authors 261 estimated LOI (and/or the volatile content) but did not correct the data for LOI and 262 263 "FALSE" if the authors estimated and corrected the concentration of terrestrial 264 radionuclides using LOI data.

Values reported as below the lower limit of detection (LLD) as well as zeroes were set to 0.65LLD or to an arbitrary small value in case the LLD was not provided by the authors. The overall percentage of values below the LLD was 6% for U, 4% for Th and less than 1% for K.

#### 269 **2.4 Calculation of terrestrial gamma dose rate TGDR**

U, Th and K concentration were converted into activity concentration using appropriate conversion factors (Table 2). The TGDR, further denoted as TGDR<sub>calc</sub>, was computed from U, Th and K activity concentration (in Bq/kg) according to the following equation:

274 
$$TGDR_{calc} = 0.0417 \times {}^{40}K + 0.462 \times {}^{238}U + 0.604 \times {}^{232}Th$$
(1)

The dose conversion factors (in Bq/kg) of 0.0417, 0.462 and 0.604 were from UNSCEAR (2010). All observations were considered valid, regardless of the analytical technique used in the analysis, and representative of the geological unit sampled by the authors. The database of U, Th and K contents in activity concentration is presented as Supplementary material (Table B1).

 Table 2. Conversion factors.

From	То	Conversion
U (mg/kg)	<sup>238</sup> U (Bq/kg)	<sup>238</sup> U (Bq/kg) = U (mg/kg) x 12.35
U (mg/kg)	<sup>226</sup> Ra (Bq/kg)	<sup>226</sup> Ra (Bq/kg) = U (mg/kg) x 12.35
Th (mg/kg)	<sup>208</sup> TI (Bq/kg)	<sup>208</sup> Tl (Bq/kg) = Th (mg/kg) x 4.063
K (%)	<sup>40</sup> K (Bq/kg)	<sup>40</sup> K (Bq/kg) = K (%) x 312.5

281

#### 282 **2.5. Data analysis**

a) Influence of analytical techniques

284 The influence of the analytical techniques in the LIT database was assessed through 285 a three-way Analysis of Variance (ANOVA) using the OGE classification scheme, the analytical techniques and LOI as categorical variables. The ANOVA design was 286 287 unbalanced due to the unequal number of observations resulting from the level 288 combinations of each factor (OGE, LOI and analytical techniques). Given an unbalanced 289 design, the differences between the geochemical analysis techniques were assessed by 290 pairwise comparisons of the Least square (LS) means calculated with the three-way 291 ANOVA (the LS mean is an estimate of the population mean, gained from grouped data 292 by adjusting for the influence of grouping, thereby adjusted for the imbalance of the 293 ANOVA design). If the results of the pairwise comparison of the LS means show an 294 agreement of the LS means between the different geochemical analysis techniques, the 295 compiled database can be considered consistent within itself, thus, reliable. Data 296 showing strong deviations from normality were transformed through the Box-Cox transformation (Zar, 2010). 297

298

#### b) Accuracy of the LIT database

One objective of the study is to evaluate whether the LIT database is accurate in the sense that mean geochemical concentrations per geological unit are representative for the units. Representativeness means that the frequency distribution of concentrations in samples is equal the true, but unknown one; in particular, the sample mean must be equal to the true mean. Deviation is called bias or inaccuracy. Since the true distributions

are not known, accuracy of samples cannot be validated by comparing sample and true distributions. However, a necessary – though not sufficient – condition for accuracy is that for each geological unit mean  $TGDR_{calc}$  is equal (up to permitted tolerance) to mean  $TGDR_{obs}$  in the same unit, taken from the RMP.

As a first step, the arithmetic mean of the TGDR<sub>obs</sub> for each geological unit studied 308 of the OGE classification scheme (Table 1 and Figure 1) was estimated. The zonal 309 statistics tool in ArcGis 10.5.1 (ESRI, Redland CA, USA, 2017) was used for this 310 311 purpose. Given that the RMP data corresponds to data modelled by linear interpolation, 312 due to the absence of outliers, the arithmetic mean is a robust measure of central 313 tendency. Since the TGDR per pixel of the RMP are given as class values, i.e. belonging 314 to a class "i", TGDR  $\in$  (x<sub>i</sub>, x<sub>i+1</sub>), the AM cannot be simply calculated from pixel values. 315 This would be the straight-forward way, but the means per pixel are not available. An 316 approximation is the weighted mean of class means,  $(x_{i-1}+x_i)/2$ , with weight the number 317 of pixels N(i-1, i) in this class divided by the total number of pixels, N. x<sub>0</sub> is set equal zero, which is the physically possible lower bound of a geochemical concentration. The 318 question is how to deal with the highest class, labeled "> $x_n$ ", as no class mean can be 319 calculated, since its upper bound is not known. This can be done approximately by 320 assuming a tentative analytical model of the upper tail of the TGDR distribution and 321 322 calculate its contribution to the AM analytically. The maximum TGDR<sub>obs</sub> was estimated 323 by polynomial regression of the TGDR values displayed in the legend of the RMP (Batista 324 et al. 2013). Polynomials of degree 6 and 7 were applied to maximize the multiple Rsquared and minimize the residual standard error. A maximum TGDR<sub>obs</sub> of 236.911 325 326 nGy/h and 238.358 nGy/h were predicted from the 6-degree and 7-degree polynomial regression model fittings, respectively. The mean value of 237.6 nGy/h was set as the 327 maximum TGDR<sub>obs</sub> in order to estimate the arithmetic means of TGDR<sub>obs</sub> for each 328 329 geological unit. We tried two additional tail models, but the results are very similar and 330 these models are not further discussed here.

As second step, the comparison of the arithmetic means between the LIT database and the RMP for each geological unit was carried out using the Student's paired sample t-test, the Wilcoxon median test and Pearson's correlation coefficient. The distributions of TGDR<sub>calc</sub> and TGDR<sub>obs</sub> were compared with the Anderson-Darling and Kolmogorov-Smirnov tests. Statistical analyses were performed with Statistica 7.0 (StatSoft Inc., USA) and R (Lenth, 2016; R Core Team, 2017).

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### 3. Results and discussion

#### 338 **3.1.** Analysis of the influence of the analytical techniques on LIT database

#### 339 a) Effect size

The results of a three-away ANOVA performed on Box-Cox transformed data using the OGE classification scheme, LOI and the analytical techniques as categorical variables are shown in Table 3. The differences between the mean values of the analytical techniques and geological factors were significant at a 0.001 level of significance for U, Th, K and TGDR<sub>calc</sub>. The effects of LOI were not significant at a 0.01 level of significance for U, Th, K and TGDR<sub>calc</sub>.

The percentage of variation explained by the analytical techniques and LOI given by 346 347 the partial eta-squared was close to or lower than 2 %, being lower than the variance explained by geological factors. According to Cohen's (1977) rule of thumb, the size of 348 the effects of the analytical techniques and particularly LOI can be considered small (< 349 2 %) while the size of the effects of the geological factors was large (> 14 %). The 350 variance explained by the LOI effects was generally lower than the variance explained 351 by the analytical techniques (Table 3). The size of the effects of the analytical techniques 352 was higher for the TGDR<sub>calc</sub> compared to the individual radioelements which is likely due 353 354 to the combination of analytical techniques that results in a higher number of categories, hence, in a higher variability of geochemical analysis techniques used (Table 3). 355

The percentage of variation explained by geological factors was on average 53 % for U, 38 % for Th, 50% for K and 51 % for the TGDR<sub>calc</sub>. The variance explained by 358 geological factors was much higher than the variance explained by the analytical 359 techniques and LOI (Table 3). The geological factors are thereby the main source of 360 variability in the data, followed by the error component. The latter can be assumed to 361 mainly represent true spatial variability of geochemical concentrations – and in 362 consequence the calculated dose rate TGDR<sub>calc</sub> – within geological units.

Table 3. Summary table of a three-way ANOVA performed on U, Th, K and TGDR<sub>calc</sub>
 Box-Cox transformed data using the OGE classification, LOI and the analytical
 techniques as categorical variables.

		SS	df	MS	F	р	Partial eta- squared (%)
	OGE	2009.7	25	80.4	95.7	< 0.001	52.7
	LOI	5.4	1	5.4	6.5	0.011	0.3
0	techniques	33.0	2	16.5	19.7	<0.001	1.8
	Error	1801.1	2144	0.8			
	OGE	3457.9	26	133.0	58.70	<0.001	37.6
-	LOI Analytical techniques Error	0.9	1	0.9	0.38	0.536	<0.1
Th		37.9	2	18.9	8.35	<0.001	0.7
		5741.2	2534	2.3			
	OGE	1909.4	26	73.4	106.8	<0.001	50.4
	LOI Analytical techniques	0.7	1	0.7	1.0	0.306	<0.1
К		21.9	5	4.4	6.4	<0.001	1.2
	Error	1880.5	2735	0.7			
TGDR <sub>calc</sub>	OGE	37380	25	1495	83.1	<0.001	50.7
	LOI	40	1	40	2.2	0.137	0.1
	Analytical techniques <sup>a</sup>	1882	9 <sup>a</sup>	209	11.6	<0.001	4.9
	Error	36311	2018	18			

SS – Sum of squares; df – degrees of freedom; MS – Mean square; F – F-test; p – p-value. <sup>a</sup>The effects of the group where U and Th were determined by NAA and K by AAS are not estimable for the TGDR<sub>calc</sub>, thus were excluded from the analysis.

#### 366 b) Component effects

The differences between the LS means of the analytical techniques were investigated in Figure 2. The results of the pairwise comparison of the LS means are presented as supplementary material for U, Th and K (Table A3) and TGDR<sub>calc</sub> (Table A4). The ICP-MS LS mean was lower than the NAA and XRF means for both U and Th (Figure 2). For U, the LS means for NAA and XRF were 35 % higher, on average, than the ICP-MS mean. For Th, the XRF LS mean was 8 % higher while the NAA LS mean was 20 % higher than the ICP-MS mean. The pairwise comparison of the LS means showed a
systematic statistically significant differences between the ICP-MS data compared to
other datasets (NAA and XRF) for U (Table A3). For Th, a statistically significant
difference was observed between NAA and ICP-MS datasets, however, the differences
between XRF and NAA, and XRF and ICP-MS were not significant (Table A3).

The analytical technique used to determine U was identical to the analytical technique 378 used to determine Th (ICP-MS, NAA or XRF in 2084 out of the 2173 observations 379 available for U (96% of the available data). As the ICP-MS LS means were generally 380 381 lower for both elements, a significant bias of this analytical technique is suggested. The bias could be due to (1) a preference of the authors for analyzing rock samples with lower 382 383 U and Th concentrations with the ICP-MS technique; (2) lower detection limits achieved 384 by ICP-MS compared to other analytical techniques (e.g. Gill, 1997) or (3) by the technique limitations such as an inefficient digestion of typically resistant U- and Th-385 bearing minerals (e.g. zircon) or selective coprecipitation of these elements with fluorides 386 when hydrofluoric acid is used in the digestion process (Preusser and Kasper, 2001). 387

388 For K, the pairwise comparison of the LS means indicated a general agreement between datasets apart from the observed statistically significant differences of the LS 389 means where K was determined by the ICP technique (Table A3). These results are 390 congruent with the observed LS mean of the ICP analysis technique which was 30 % 391 392 higher than the reference mean chosen (XRF, see Figure 2). Given that only 8 out of 393 2768 observations present a K concentration below the LLD, it is unlikely that the observed difference could be caused by LLD values. Given that the ICP results were 394 395 retrieved from older literature sources (ex. Mitjavila et al. 1997; Ribeiro 1998; Table A1) 396 and that the ICP LS mean was higher than the reference mean chosen, the observed 397 difference could be due to lack of reporting of values below the LLD by the authors. Apart 398 from ICP and ICP-AES, deviations of the LS means from the reference mean chosen 399 were generally lower than 10 %.

The results of the pairwise comparison of the LS means for TGDR<sub>calc</sub> showed a 400 general agreement of the LS means between different geochemical analysis techniques 401 402 (Table A4). Statistically significant differences between the LS means were only observed in 6 out of the 45 pairwise comparisons performed (Table A4). The compiled 403 404 database can thus be considered consistent within itself, hence reliable. Apart from the dataset where K was determined by ICP-AES and ICP-MS, deviations of the LS means 405 406 from the reference mean chosen are equal to or lower than 10 %. The LS means where 407 U and Th data were acquired with ICP-MS are systematically lower than the LS means 408 where U and Th data were acquired with NAA and XRF, which is consistent with the 409 results observed for U and Th individually and can thus be caused by error propagation. 410 The LS means for the OGE units and LOI are presented as supplementary material 411 (Figures A1 and A2). The LS means display large differences between the various OGE units for U, Th, K and TGDR<sub>calc</sub> (Figure A1), which are in accordance with the high 412 percentage of variation explained by the OGE classification system (Table 3). With 413 respect to LOI, higher LS means were expected in data corrected for the LOI and/or 414 415 volatile content (corresponding to effect named "FALSE"), as are observed for K and the TGDR<sub>calc</sub> (Figure A2). However, lower LS means in LOI corrected data compared to 416 uncorrected data are observed for U and Th (Figure A2 in Supplementary material). 417 418 These results support the lack of a systematic influence of LOI. Given that the effects of 419 LOI are not significant for U, Th and K (Table 3), it can be concluded that the correction 420 of U, Th and K data for LOI or lack thereof does not affect significantly the results.



Figure 2. Plots of the least squares (LS) means of the analytical techniques effect for U,
Th, K and TGDR<sub>calc</sub> Box-Cox transformed data. The bars indicate the 95% confidence
interval of the LS mean. A LS mean was chosen as reference for comparison according
to higher sample size and number of geological units sampled (see Tables A1 and A2,
supplementary material). The proportion of the LS means were calculated assuming the
ICP-MS mean as reference for U and Th; the XRF mean for K and the dataset where U,
Th and K were determined by XRF for the TGDR<sub>calc</sub>.

#### 429 **3.2.** Variance component originating from spatial variability

In the previous analysis, variance has been attributed entirely to geology (component A, see section 1.4) and analytical techniques (B), while component C was ignored, i.e. possible lack of representativeness of data for a geological unit. A possible procedure for resolving this would be performing an even higher stage ANOVA including individual data sources (each consisting of a number of data) as additional classification variable, or as simplification, simple ANOVA for data sources within individual geological units and for same analytical technique. However, data are not sufficient for this.

The sources of the error terms in Table 3 are measurement uncertainty and probably dominantly, spatial variability within units. Its contribution to the SS (sum of squares) is in the same order of magnitude as the one due to OGE. Given the data situation, it is however difficult to say to which degree possibly unrepresentative samples from the variable population contribute to bias of the mean. The question deserves further investigation in the future.

#### 443 **3.3. Comparison of the LIT and RMP datasets**

444 The arithmetic means of the TGDR<sub>calc</sub> from U, Th and K compiled data were 445 compared to the TGDR<sub>obs</sub> for each geological unit in Figure 3 and Table 4. The correlation between TGDR<sub>calc</sub> and TGDR<sub>obs</sub> was highly significant (p < 0.001). The results 446 447 of a paired sample t-test and Wilcoxon median tests indicate that the differences between 448 the arithmetic means of TGDR<sub>calc</sub> and TGDR<sub>obs</sub> were not statistically significant (p = 0.126and p = 0.14, respectively). Distributions of TGDR<sub>calc</sub> and TGDR<sub>obs</sub> were about equal 449 450 according to Kolmogorov-Smirnov and Anderson-Darling tests. If deviation from TGDRobs 451 by pooled standard deviation (SD) is taken as criterion, 14 out of 26 OGE units are located within one pooled SD around TGDR<sub>obs</sub> (dashed lines in Figure 3), only 1 out of 452 26 is located outside 2 pooled SDs. 453

454 (The pooled SD is defined as

455 
$$s_{pooled} = \sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2 + \dots + (n_k - 1)s_k^2}{n_1 + n_2 + \dots + n_k - k}}$$
(2)

456 with  $s_i$  the individual SDs and  $n_i$  the number of data in OGE unit (i). Its value is 29 457 nGy/h.)

458 A systematic overestimation of the TGDR<sub>calc</sub> compared to TGDR<sub>obs</sub> was observed for 459 the sedimentary rocks (N2, N1c, K1-2, K1, TJ1 and the C2 units) coupled with absolute 460 differences of the TGDR<sub>calc</sub> generally higher than 29 nGy/h (the pooled SD of the RMP dataset; Table 4, Figure 3). This effect may be caused, by (1) the lack of spatial 461 representativeness of the data (as sampling of stratigraphic sequences is commonly 462 463 carried out along vertical profiles instead of spatial grids) or (2) the lack of data from 464 carbonate rocks. Carbonate rocks are a common subordinate lithology of the abovementioned geological units (see Table 1), presenting average radionuclides 465 concentrations generally lower than siliciclastic rocks (e.g. Sêco et al. 2016). 466

467 **Table 4.** Comparison of the arithmetic means (± standard deviation) of the TGDR
468 between LIT (TGDR<sub>calc</sub>) and the RMP datasets (TGDR<sub>obs</sub>).

Group	OGE unit	TGDR <sub>calc</sub> [1]	TGDR <sub>obs</sub> [2]	Difference [2] – [1]
	N2	78 ± 26	32 ± 19	-46
	N1c	70 ± 23	36 ± 22	-34
Codimontory rooks	K1-2	106 ± 21	42 ± 28	-63
Sedimentary rocks	К1	73 ± 21 <sup>b</sup>	46 ± 21	-27
	TJ1	85 ± 29	44 ± 20	-41
	C2	94 ± 15	59 ± 34	-35
	C1-2	78 ± 27 <sup>b</sup>	65 ± 14	-13
	SDof	71 ± 18	19 ± 13	-52
	SD	39 ± 41	90 ± 22	51
	SDP	107 ± 37 <sup>b</sup>	91 ± 21	-16
Matamarahia raaka	ODP	81 ± 58 <sup>b</sup>	104 ± 34	23
Metamorphic rocks	O_a	69 ± 38 <sup>b</sup>	88 ± 27	18
	gz	77 ± 25 <sup>b</sup>	87 ± 28	10
	Npep	82 ± 23 <sup>b</sup>	80 ± 29	-2
	NP2	46 ± 30 <sup>b</sup>	60 ± 21	14
	NP1	31 ± 31 <sup>b</sup>	56 ± 29	25
	gama2	68 ± 35 <sup>b</sup>	63 ± 16	-4
Igneous rocks	CVL	52 ± 23	14 ± 10	-38
	g1_b	194 ± 101 <sup>b</sup>	157 ± 39	-37
	g2_b	137 ± 59 <sup>b</sup>	172 ± 40	35

	g3	157 ± 52 <sup>b</sup>	142 ± 46	-15			
	g1_a	157 ± 88 <sup>b</sup>	136 ± 32	-21			
	g2_a	150 ± 49 <sup>b</sup>	121 ± 24	-29			
	g1a	61 ± 34 <sup>b</sup>	62 ± 23	1			
	gama	9 ± 10	51 ± 19	43			
	D3C1	$50 \pm 40^{b}$	75 ± 26	25			
<sup>a</sup> TGDR <sub>obs</sub> was calculated assuming an arbitrary maximum TGDR <sub>obs</sub> of 237.6 nGy/h.							
<sup>b</sup> The TGDR <sub>ade</sub> is located w	ithin one pooled SD of	the TGDR <sub>aba</sub>					

The arithmetic means of the TGDR<sub>calc</sub> of granitic rocks are also generally 469 470 overestimated in LIT database (g1\_b, g3, g1\_a and g2\_a). In this case, the limitations of the RMP data must be taken into account, namely the fact that the maximum TGDRobs 471 472 in mainland Portugal is unknown. A value of 237.6 nGy/h was set as the maximum TGDR<sub>obs</sub> in order to compute the mean TGDR<sub>obs</sub> by geological unit. This issue only 473 474 affects the geological units which display a TGDRobs higher than 216.2 nGy/h, which are 475 listed in Table 5 and include the abovementioned granitic rocks (g1 b, g2 b, g3, and 476 g1 a). These units present a high percentage of their area (> 3 %) characterized by a 477 TGDR<sub>obs</sub> above 216.2 nGy/h. The underestimation of TGDR<sub>obs</sub> of these units may be 478 caused by the underestimation of the maximum TGDR<sub>obs</sub> chosen (of 237.6 nGy/h), 479 biasing the estimation mean TGDR<sub>obs</sub> by geological unit.

	an 216.2 nGy/h.	a TGDR <sub>obs</sub> higher than	e area characterized by	able 5. Percentage of the	480
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	OGE units	% of Area
	N2	0.01
Sedimentary	N1c	0.05
TOCKS	K1_2	0.68
	ODP	1.20
Metamorphic	O_a	0.16
rocks	gz	0.06
	NPep	0.47
	g1_b	5.36
	g2_b	15.15
Igneous	g3	9.54
10013	g1_a	3.04
	g2_a	0.37

From a health perspective, the overestimation of the TGDR<sub>calc</sub> is not as concerning as its underestimation, which was observed systematically in the SD, g2\_b and the gama units. In the case of the g2\_b unit, the difference observed between the TGDR<sub>calc</sub> for

Model 1 is, however allocated within one SD of the TGDRobs. The underestimation of the 484 TGDR<sub>calc</sub> of the g2 b may be due to the underrepresentation of quantitative data from 485 486 metallogenic deposits of uranium and/or radium that are common in the g2 b unit (ex. Margues et al. 2010; Neiva et al. 1987; Trindade et al. 2013). Because the g2 b dataset 487 488 corresponds to one of the largest datasets available (Table A1, Supplementary material), 489 this enforces the hypothesis that the major source of error within the compiled database 490 was the insufficient representativeness of the data, which leads to a biased estimate of 491 the mean, rather than the amount of data or the analytical techniques. Apart from the SD 492 and SDof units, the absolute deviations between the arithmetic means of TGDR<sub>calc</sub> and TGDR<sub>obs</sub> were generally lower than 29 nGy/h for the metamorphic rocks (Table 4). For 493 494 the SD unit, the only dataset available was retrieved from Dahn et al. (2014) and refers 495 to mafic rocks outcropping in the SD unit. Thus, the underestimation of the TGDR<sub>calc</sub> reflects the lack of data from other types of rocks within the unit, particularly of the 496 predominant lithology of the unit namely phyllites (Table 1). The underestimation of the 497 TGDR<sub>calc</sub> of the gama unit may be due to the lack of data from differentiated rocks, such 498 499 as anorthositic rocks and diorites (the subordinate lithologies of the gama unit, Table 1) 500 that may present higher contents of terrestrial radionuclides than gabbros as U, Th and 501 K become enriched with magmatic differentiation (Heier and Rogers, 1963).



502

Figure 3. Scatterplot of the arithmetic means of the TGDR (in nGy/h) of each geological
unit. The dashed lines indicate deviations of 29 nGy/h (the pooled SD) from the identity
line.

The pooled SD of the RMP dataset was set as criterion to appraise the discrepancy between the arithmetic means of the RMP and LIT databases. Given the statistical parameters of the differences between  $TGDR_{calc}$  and  $TGDR_{obs}$  and their distributions, the compatibility of the RMP and LIT databases can be considered acceptable, but not perfect. For some geological units, the exact reason for discrepancy remains to investigated, in order to improve further attempts of the kind.

512 As the TGDR<sub>calc</sub> was calculated from U, Th and K data compiled from scientific 513 literature, the compatibility of the TGDR between the LIT and the RMP datasets (namely, 514 TGDR<sub>calc</sub> and TGDR<sub>obs</sub>) implies that the estimation of the contents of the terrestrial 515 radionuclides in bedrock from compiled datasets is also reasonable. Putting it more 516 precisely, since the approximate equality of TGDR<sub>calc</sub> and TGDR<sub>obs</sub> is only a necessary 517 condition for the hypothesis to be true that the LIT database represents U, Th and K 518 concentration in rocks reasonably well, the result of this investigation does not reject the 519 hypothesis.

Vein-type rocks were excluded from the comparison exercise of LIT and RMP 520 databases due to their large perimeter to area ratio. Given the compatibility of the RMP 521 and LIT datasets, the TGDR<sub>calc</sub> of vein-type rocks was estimated resorting to data 522 compiled from local geochemical surveys. The mean TGDR<sub>calc</sub> for the f1 and f2 (basic 523 524 veins) and gz (quartz veins) units are presented in Table 6. The TGDR<sub>calc</sub> of basic veintype rocks (f1 and f2) is similar to other mafic rocks units (ex. CVL, gama, and SDof units, 525 526 Tables 1 and 4) as expected. Quartz veins present a similar TGDR<sub>calc</sub> to sedimentary 527 and metamorphic rocks, being lower than the average TGDR<sub>calc</sub> of granitic rocks (Tables 1 and 4). 528

529 **Table 6.** Estimation of the TGDR of vein-type units using LIT data.

		Number of	TGDR <sub>calc</sub> (nGy/h)			
	OGE units	samples	Mean Standard deviation		References	
Vein-	f1	26	14	5	Cebriá et al. (2003); Martins (1999); Martins et al. (2009); Youbi et al. (2003);	
rocks	f2	17	34	14	Trindade et al. (2013); Alves (2010);	
	qz	16	83	20	Lima (2000)	

#### 530 **4. Conclusions**

531 Two databases were compared with the aim of validating the compilation of literature data to estimate the mean concentrations of terrestrial radionuclides in bedrock using 532 geological units as reference units. The results show that the compatibility of the 533 534 databases was essentially reasonable. The differences between the arithmetic means 535 were generally lower than the maximum allowable discrepancy set and the differences 536 between the two databases were not statistically significant. A systematic overestimation 537 of the contents of radionuclides calculated from the compiled data and observed in 538 sedimentary rocks probably reflects the lack of representativeness of the data compiled 539 for these units, while the differences observed for some granitic rocks may reflect the limitations of the TGDR<sub>obs</sub>. Despite the significance of the effects of the analytical 540 techniques, the variance explained by them, ranging from less than 1% to 5%, is 541 542 sufficiently low, thereby lacking a significant impact on the comparability of the results 543 acquired with different analytical techniques. The major sources of variability in the data 544 are geological factors as demonstrated by the high percentage of variation explained by 545 this factor in the ANOVA computed, as well as the true spatial variability of geochemical 546 concentrations within geological units.

547 Geochemical characterization of geological units based on scattered literature data, 548 as attempted in this study, allows the development of maps of terrestrial radionuclides 549 contents in bedrock without large-scale sampling efforts, since a large amount of data is 550 already available. Where extensive TGDR surveys are available, validation may be 551 repeated e.g. along the lines presented here.

While the estimates computed for some units may be unreliable, they also set the groundwork needed to support further research. Certainly, a key problem is representativeness of the data, on which depends the reliability of the estimates of the mean contents of U, Th and K per geological units. It can be improved when more data with better coverage of geological units are available. Nonetheless, we think that generation of maps of U, Th and K concentrations in rock based on geological units is feasible.

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# 1029 Supplementary material

**Table A1.** Summary of the data available in LIT database for the OGE units sampled by
geological unit. 2173 observations were compiled for U, 2564 for thorium and 2768 for K
acquired with 7 different analytical techniques.

OGE unit	Analytical Technique <sup>a</sup>	N (U)	N (Th)	N (K)	References
	ICP-MS	74	74	0	_
C1-2	ICP-OES	0	0	74	Jorge et al. (2013);
0.2	NAA	7	7	0	Trindade (2007)
	XRF	0	0	7	
C2	ICP-MS	18	20	18	Dinis et al. (2011); Ribeiro
	XRF	0	0	2	et al. (2010)
CVL	ICP-MS	62	62	62	al. (2009)
D2-3	XRF	0	30	32	Boulter et al. (2004)
	ICP	0	0	59	Boulter et al. (2004);
D3C1	NAA	59	129	0	Miljavila et al. (1997); Rosa
	XRF	28	27	135	Schützet al. (1987)
	AAS	0	0	17	Coelho et al. (2007); Costa
	ICP	0	0	32	et al. (2014); Ferreira
		0	0	7	(1986, 1991): Comes
				1	(1989): Gomes and Neiva
	ICP-MS	11	11	0	(2002, 2005); Gomes et al.
g1_a	NAA	4	13	0	(2011, 2013); Neiva and
	XRF	150	205	230	Gomes, (1991); Neiva et al. (2008, 2009); Neves et al. (1999); Silva (2000, 2014a); Teixeira (2008); Teixeira et al. (2012)
	ICP-AES	0	0	15	Costa (2011): Costa et al
a1 h	ICP-MS	15	15	0	(2014): Gomes and Neiva
91_0	NAA	6	6	0	(2005):
		0	0	6	
	ICP-AES	0	0	22	Antunes et al. (2010); Lima
gia	ICP-MS	57	79	57	al. (2009)
	ICP-AES	0	0	12	Cereio (2013) <sup>.</sup> Neves et al
α2 a	ICP-MS	12	12	0	(2007): Silva and Neiva
3	NAA	10	10	0	(1990)
	XRF	8	8	18	, , ,
	AAS	0	0	43	Antunes (2006); Antunes et al. (2008, 2013); Carvalho et al. (2012): Costa (2006
	ICP-AES	0	0	134	2011); Godinho et al. (1991); Lima et al. (2013,
	ICP-MS	165	164	24	2014); Marques et al. (2010); Martins et al.
g2_b	NAA	23	13	0	(2013); Neiva et al. (1987, 2009, 2011a, 2011b);
	XRF	185	259	281	(2000); Silva (2014b); Silva et al. (2000); Trindade et al. (2013); van der Weijden and van der Weijden (1995)
c.)	ICP-AES	0	0	64	Costa (2006, 2011);
g3	ICP-MS	56	56	6	Gomes (2008); Jaques et

OGE unit	Analytical Technique <sup>a</sup>	N (U)	N (Th)	N (K)	References
	NAA	0	3	0	al. (2016); Martins et al.
	XRF	14	14	32	(2009); Neiva (1993); Neves and Pereira, (2007); Ramírez and Menéndez (1999)
	ICP	0	0	60	Caldeira et al. (2007);
CAMA	ICP-MS	92	97	138	Jesus et al. (2014, 2016);
GAMA	NAA	32	32	0	Pedro (2004); Quesada et
	XRF	0	0	15	al. (1994)
GAMA2	ICP-MS	16	16	16	Grange et al. (2010); Miranda (2010)
	ICP-MS	8	8	4	Antunes (2006); Antunes et al. (2009); Cruz (2007);
gz	XRF	25	57	62	Godinno et al. (1986); Neves et al. (1998); Pereira et al. (2006, 2011); Sánchez-García et al. (2010, 2013)
<b>K</b> 1	NAA	52	52	0	Trindade (2007); Trindade
NI NI	XRF	0	0	52	et al. (2010)
K4 0	ICP-MS	45	45	0	Disis at al. (2010)
K1-2	XRF	0	0	45	Diffis et al. (2016)
	ICP	0	0	32	Arribas et al. (2014);
	ICP-AES	0	0	5	Bustillo et al. (2012);
N1c	ICP-MS	48	48	0	Lisboa et al. (2015);
	NAA	16	16	0	Marques et al. (2010); Reis
	XRF	0	0	16	et al. (2012)
	ICP-MS	45	72	5	Dinis and Oliveira (2016);
N2	NAA	6	6	0	Dinis et al. (2011); Pereira
	XRF	0	0	88	et al. (2006); Trindade (2007)
	ICP-AES	0	0	69	Gómez-Pugnaire et al.
NP1	ICP-MS	90	90	0	(2013); Henriques et al.
	XRF	0	0	21	(2017); Silva (2007)
	ICP	0	0	14	Dinis et al. (2011);
NP2	ICP-AES	0	0	5	Henriques et al. (2006,
	ICP-MS	16	63	42	2016); Lorda et al. (2013);
	XRF	1	1	3	Pereira et al. (2006, 2011)
	AAS	0	0	16	Aires et al. (2011); Candeias et al. (2015);
	ICP	0	0	35	Cerejo (2013); Coelho et
	ICP-AES	0	0	176	al. (2007); Dinis et al.
		210	244	96	(2011); Fuenlabrada et al.
		310	341	00	(2016); Godinho et al.
	ICP-OES	0	0	24	(1991); Marques et al. (2010): Novos et al. (1990):
Npep	NAA	9	9	0	Noronha et al. (2012);
прор	XRF	22	22	30	Oliveira (2015); Pinto (2014); Ribeiro (1998); Silva (2014a); Trindade et al. (2013); Ugidos et al. (1997a, 1997b, 2003a, 2003b, 2010); Valladares et al. (2000, 2002); Villaseca et al. (2014)
	ICP	0	0	1	Oliveira (2015): Pereira et
Оa	ICP-MS	2	2	1	al. (2011); Ribeiro et al.
	XRF	15	15	15	(2010); Silva (2014a)
	ICP	0	0	52	
	ICP-MS	41	41	0	Dias (2011); Noronha et al.
	NAA	46	46	0	(2012); Ribeiro (1998)
	XRF	6	6	47	
SD	XRF	33	33	33	Dahn et al. (2014)

OGE unit	Analytical Technique <sup>a</sup>	N (U)	N (Th)	N (K)	References
	AAS	0	0	5	Fuenlabrada et al. (2010,
SDof	ICP-MS	48	43	0	2012); Teixeira et al.
	ICP-OES	0	0	43	(2010)
	ICP	> 0	0	60	Neranha at al. (2012):
SDP	NAA	54	55	0	$\begin{array}{c} \text{Noronna et al. (2012),} \\ \text{Diboiro (1008)} \end{array}$
	XRF	3	3	3	Ribello (1990)
T 14	NAA	62	62	0	Trindade (2007);
I J1	XRF	0	0	60	Trindade et al. (2010)

#### N – number of observations.

aICP-MS – Inductively Coupled Plasma Mass Spectrometry; ICP-OES – Inductively Coupled Plasma Optical Emission Spectrometry; NAA – Neutron Activation Analysis; XRF – X-Ray Fluorescence; ICP -Inductively Coupled Plasma; ICP-AES – Inductively Coupled Plasma Atomic Emission Spectrometry; AAS – Atomic Absorption Spectrometry.

	Ana	lytical tech	nique	Number of		Number of	
	U	Th	к	samples (N)	% N	OGEs sampled	%OGE
	NAA			386	17.8	14	51.9
U	XRF			490	22.5	12	44.4
	ICP-MS			1297	59.7	21	77.8
		NAA		459	17.9	15	55.6
Th		XRF		680	26.5	13	48.1
		ICP-MS		1425	55.6	21	77.8
			AAS	81	2.9	4	14.8
			ICP-OES	141	5.1	3	11.1
K			ICP-MS	459	16.6	12	44.4
ĸ			ICP	345	12.5	9	33.3
			ICP-AES	509	18.4	10	37.0
			XRF	1233	44.5	23	85.2
	ICP-MS	ICP-MS	ICP-MS	330	16.1	12	44.4
	ICP-MS	ICP-MS	ICP-OES	141	6.9	3	11.1
	ICP-MS	ICP-MS	ICP	143	7.0	5	18.5
	NAA	NAA	ICP	176	8.6	5	18.5
	NAA	NAA	XRF	160	7.8	8	29.6
	XRF	XRF	XRF	421	20.5	11	40.7
	ICP-MS	ICP-MS	XRF	217	10.6	10	37.0
	ICP-MS	ICP-MS	ICP-AES	380	18.5	8	29.6
	ICP-MS	ICP-MS	AAS	76	3.7	3	11.1
	NAA	XRF	XRF	10	0.5	1	3.7

# **Table A2.** Summary of the data available by analytical technique.

<sup>a</sup>The analytical techniques listed for the TGDR<sub>calc</sub> refer to the compilation of the analytical techniques used to analyse U, Th and K.

**Table A3.** Pairwise comparison of the LS means of the analytical techniques for U, Th and K. P-values were adjusted with the false discovery rate (FDR) method (Lenth, 2016).

	Analytical techniques under comparison	Difference between the LS means	SE	t	p
U	NAA x ICP-MS	-0.399	0.085	-4.691	<0.001(*)
(df =	NAA x XRF	-0.022	0.091	-0.240	0.9688
2144)	ICP-MS x XRF	-0.421	0.075	-5.589	<0.001(*)
Th	NAA x ICP-MS	-0.532	0.132	-4.033	<0.001(*)
(df =	NAA x XRF	0.316	0.145	2.171	0.076
2534)	ICP-MS x XRF	-0.217	0.115	-1.890	0.142
· · · · ·	AAS x ICP	-0.394	0.116	-3.411	0.009(*)
	AAS x ICP-AES	-0.276	0.112	-2.469	0.134
	AAS x ICP-MS	-0.076	0.114	-0.667	0.986
	AAS x ICP-OES	-0.119	0.169	-0.708	0.981
K (df = 2735)	AAS x XRF	-0.081	0.099	-0.822	0.964
	ICP x ICP-AES	0.119	0.076	1.562	0.624
	ICP x ICP-MS	0.319	0.077	4.163	0.001(*)
	ICP x ICP-OES	0.275	0.155	1.770	0.485
	ICP x XRF	0.313	0.067	4.664	<0.001(*)
	ICP-AES x ICP-MS	0.200	0.075	2.674	0.081
	ICP-AES x ICP-OES	0.156	0.148	1.055	0.899
	ICP-AES x XRF	0.194	0.066	2.923	0.041
	ICP-MS x ICP-OES	-0.044	0.154	-0.282	1.000
	ICP-MS x XRF	-0.006	0.071	-0.078	1.000
	ICP-OES x XRF	0.038	0.151	0.253	1.000

SE – standard error; t, p – t-test and respective p-value. Significant values at  $\alpha$  = 0.01 are indicated with (\*).

# 1039 Table A4. Pairwise comparison of the LS means of the analytical techniques for TGDR<sub>calc</sub>

1040 (df = 2018). P-values were adjusted with the false discovery rate (FDR) method (Lenth,

1041 2016).

	Ana	lytical tecl	hniqu	Difference between the LS	SE	t	p			
U	Th	к		U	Th	к	means			
				ICP-MS	ICP-MS	ICP	0.162	0.780	0.208	1.000
				ICP-MS	ICP-MS	ICP-AES	-3.082	0.761	-4.052	0.002(*)
				ICP-MS	ICP-MS	ICP-MS	1.005	0.653	1.538	0.877
				ICP-MS	ICP-MS	ICP-OFS	-0.275	1.058	-0.260	1.000
ICP-MS	ICP-MS	AAS	х	ICP-MS	ICP-MS	XRF	-0.118	0.712	-0.166	1.000
				NAA	NAA	ICP	-2.611	0.900	-2.902	0.106
				NAA	NAA	XRF	-1.168	0.888	-1.316	0.950
				NAA	XRF	XRF	-2.175	1.434	-1.517	0.886
				XRF	XRF	XRF	-1.038	0.544	-1.907	0.664
				ICP-MS	ICP-MS	ICP-AES	-3.245	0.516	-6.289	<0.001(*)
				ICP-MS	ICP-MS	ICP-MS	0.842	0.561	1.501	0.892
				ICP-MS	ICP-MS	ICP-OES	-0.437	0.901	-0.485	1.000
				ICP-MS	ICP-MS	XRF	-0.280	0.587	-0.478	1.000
ICP-MS	ICP-MS	ICP	х	NAA	NAA	ICP	-2.774	0.786	-3.530	0.015
				NAA	NAA	XRF	-1.330	0.798	-1.668	0.814
				NAA	XRF	XRF	-2.338	1.498	-1.560	0.867
				XRF	XRF	XRF	-1.200	0.630	-1.906	0.665
				ICP-MS	ICP-MS	ICP-MS	4.087	0.527	7.749	<0.001(*)
				ICP-MS	ICP-MS	ICP-OES	2.807	0.828	3.392	0.025
				ICP-MS	ICP-MS	XRF	2.964	0.545	5.439	<0.001(*)
ICP-MS	ICP-MS		х	NAA	NAA	ICP	0.471	0.778	0.606	1.000
		ALO		NAA	NAA	XRF	1.914	0.782	2.448	0.298
				NAA	XRF	XRF	0.907	1.482	0.612	1.000
				XRF	XRF	XRF	2.045	0.616	3.318	0.031
				ICP-MS	ICP-MS	ICP-OES	-1.280	0.895	-1.429	0.918
				ICP-MS	ICP-MS	XRF	-1.123	0.555	-2.024	0.582
ICP-MS	ICP-MS	ICP-MS		NAA	NAA	ICP	-3.616	0.760	-4.759	<0.001(*)
				NAA	NAA	XRF	-2.173	0.751	-2.894	0.108
				NAA	XRF	XRF	-3.180	1.429	-2.225	0.440
			ļ	XRF	XRF	XRF	-2.042	0.492	-4.155	0.001(*)
				ICP-MS	ICP-MS	XRF	0.157	0.932	0.168	1.000
		ICP-		NAA	NAA	ICP	-2.336	1.074	-2.176	0.474
ICP-MS	ICP-MS	OES	х	NAA	NAA	XRF	-0.893	0.988	-0.903	0.996
				NAA	XRF	XRF	-1.900	1.661	-1.144	0.980
				XRF	XRF	XRF	-0.763	0.963	-0.792	0.999
				NAA	NAA	ICP	-2.493	0.695	-3.586	0.013
ICP-MS	ICP-MS	XRF	х	NAA	NAA	XRF	-1.050	0.782	-1.343	0.944
				NAA	XRF	XRF	-2.057	1.456	-1.413	0.924
				XRF	XRF	XRF	-0.920	0.542	-1.696	0.798
		105		NAA	NAA	XRF	1.443	0.944	1.528	0.881
NAA	NAA	ICP	х	NAA		XRF	0.436	1.558	0.280	1.000
			l	XKF	XKF	XKF	1.574	0.769	2.047	0.566
		VDF	,	NAA	XRF	XRF	-1.007	1.552	-0.649	1.000
INAA	INAA	<b>VKL</b>	х	XRF	XRF	XRF	0.130	0.764	0.170	1.000
NAA	XRF	XRF	х	XRF	XRF	XRF	1.137	1.375	0.827	0.998

SE – standard error; t, p – t-test and respective p-value. Significant values at  $\alpha$  = 0.01 are indicated with (\*). <sup>a</sup>The analytical techniques listed for the TGDR<sub>calc</sub> refer to the compilation of the analytical techniques used to analyse U, Th and K.

**Table B1.** Compiled geochemical database.

a) BC_U (ppm)			b) BC_Th (ppm)			c) BC_K (%)			d) BC_TGDR (nGy/h)				
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	C1-2		0									Ю	
	D3C1	0			1 0 1				н				
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logical unit	gama ]										0		
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Figure A1. Plots of the least squares (LS) means of the OGE effect for U, Th, K and
 TGDR<sub>calc</sub> Box-Cox (BC) transformed data by geological unit. The bars indicate the 95%

1047 confidence interval of the LS mean.



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**Figure A2.** Plots of the least squares (LS) means of the LOI effect for U, Th, K and TGDR<sub>calc</sub> Box-Cox (BC) transformed data. The bars indicate the 95% confidence interval of the LS mean. Each observation of U, Th, K and TGDR<sub>calc</sub> is classified as "true" if the authors estimated but did not corrected the data for LOI (or the volatile content) and "false" otherwise.