Geochemistry of Trace Elements and the Fingerprints of Environmental Change in Core Sediments of the Tagus River

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INTRODUCTION.

Episodes of major environmental and climatic changes in the geological past leave a mark in the geological record. Depending on the type of record, these marks may be more or less discernible and interpretable as a consequence of such changes. Stable isotopes are a powerful tool to unravel such geological episodes because isotope fractionation relies on mechanisms that can be attributable to the predominance of specific processes. Geochemical distributions are rarely the outcome of a unique process unless it is focused on a specific trace element. The repeated reworking of the crust tends to smooth heterogeneous geochemical distributions, but the question is if it is still possible to recover any vestiges of such heterogeneity and how. In this work we present numerical techniques to outline anomalous concentrations of trace metals in core sediments of the Middle Tagus alluvial plain, 60 km upstream Lisbon (SEV core; Azevêdo & Gonçalves, 2009). The results obtained were striking because they showed consistent anomalous zones, the most important one affecting all analysed elements in a specific core segment with ages between 6000-10000 cal. years BP. A more detailed analysis together with information from other sources makes this a case where it is possible to use such techniques to relate major events either due to environmental or human impacts to the distribution of specific trace elements in several segments of the core sediments.

NUMERICAL TECHNIQUES.

A central step towards the aim just introduced is to use adequate methods to define background values for the different elements analysed. These become the reference values against which all others can be relatively compared. Determining background values poses some major problems, starting by the significance of the methods used for their estimation. Acknowledging that the notion of background is often imprecise, this term is used here in the context of exploration geochemistry, which is closely related to the notion of anomaly and threshold value. Threshold values thus separate background values from anomalous ones. The question is then, how do we compute a threshold value? A way is to use statistical methods, normally assuming that the distribution of natural elements is usually normal or log-normal. However, an overprinting of n processes results in the overlap of n normally distributed data sets. Thus, small fingerprints disturbing the normal distribution of the data may be detected, and empirical statistical methods can be applied, such as the method of relative cumulative frequency curves. Also, the concentration-area method for anomaly separation proposed by Cheng et al. (1994) has been tested in several situations and proved reliable for the definition of anomalous areas related to different geological processes. Gonçalves et al. (2001) used an adaptation of the method for profiles, termed "concentration-length" which has been the one used.

RESULTS AND DISCUSSION.

The geochemistry of the SEV core is shown in Fig. 1, with a set of selected elements along with ^{14}C ages (Ramos-Pereira et al., 2009). Some considerations may be put forward by the analysis of the profile: *i*) the mud content separates the three major sedimentological units (I, II, and III from base to top; Ramos-Pereira et al., 2009); *ii*) between 100 and 300 cm, there is a general decrease in mud content accompanied by a decrease in most elements; *iii*) elements such as Au, As, and Zn show an irregular behaviour, while the remaining ones have a more or less constant pattern along the core; *iv*) Cu is the only element which is

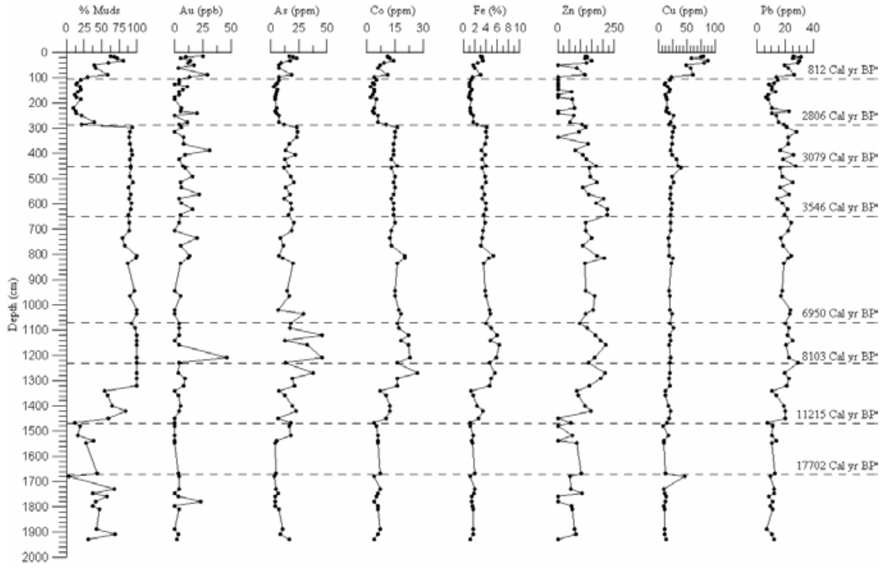

fig 1. Geochemistry of the SEV core for selected elements, and the corresponding ^{14}C ages.

palabras clave: Cambio Ambiental, Anomalía geoquímica, Método área/concentración.	*key words:* Environmental Change, Geochemical anomaly, Concentration/area method.

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clearly enriched in the upper layers of the core, a behaviour that is slightly followed by Pb as well. The computed background values (Azevêdo & Gonçalves, 2009) were used as an indicator threshold to suppress all data points whose chemical concentration in an element is below the computed background. The result is qualitatively shown in Fig. 2. It is possible to recognize five segments in the core: *i*) upper 100 cm with anomalous values of Au, Cu, and Pb; *ii*) 423-490 cm, where Cu and Pb are above background; *iii*) 577-674 cm with Zn and Au; *iv*) 764-834 cm where Zn, Fe, Co, and Au have values above background; and *v*) 1034-1339 cm where almost all elements have higher than background values, Au (7%), As (83%), Co (67%), Cr (67%), Fe (80%), U (100%), Zn (50%), and Pb (14%); percentage of higher than background samples relative to the total number of samples is indicated.

The SEV core spans more than 17,000 years record of sedimentation in a particular site of the Tagus basin, ever since the termination of the Last Glacial Maximum. Shortly after this period, the geological record shows the initiation of the so-called Early Holocene Warm Period, between 9,000-6,000 cal. yr. BP. Palynological studies are able to identify environmental changes of the landscape from the end of the Younger Dryas Period to around 5,500-5,000 cal. yr. BP. Upstream this area, climatic conditions were becoming wetter but

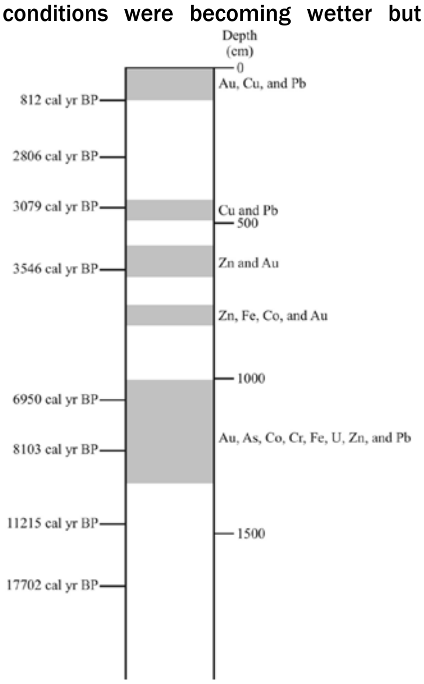

***fig 2**. Segments of the SEV core with higher than background concentrations for the indicated elements.*

cooler between 8,700-5,670 cal. yr. BP, while in the northern Iberian Cordillera this also lead to the expansion of the arboreal elements, later replaced by Mediterranean forest under dryer conditions circa 5,060 cal. yr. BP (van der Knaap and van Leeuwen, 1995; García et al., 2002). These alterations resulted in modifications of the weathering rates and hydrologic conditions. Although somewhat counter-intuitive, glacial areas have relatively high weathering rates comparable to temperate catchments regions, due to glaciation/deglaciation cycles (Tranter, 2003). The base of the SEV core, as in other cores in this alluvial plain, show the same Unit I with low mud content, interpreted as the accumulation of coarse-grained sediments from deglaciation processes. Nevertheless, the most interesting geochemical feature occurs in the base of Unit II (1034-1339 cm), where most trace elements have consistently higher than background values. The ^{14}C dates constrain the event to have occurred by 10,000-6,500 cal. yr. BP, lasting no less than 1,500 years. This feature cannot be overlooked because this pattern is common to 8 of the analysed chemical elements, suggesting some sort of major modification in the environment. This event coincides with the Early Holocene Warm Period, and an area with retreating glaciers has substantial amounts of high surface area ground rock debris prone to be easily weathered. With evidences of wet conditions, chemical weathering rates likely increased accordingly. The sequences between 764-834 cm and 577-674 cm outlined by Zn, Au, Co, and Fe, reflect mostly the local mineralogy. This sequence shows both sulphides (pyrite-rich sediments) and sulphates (gypsum and jarosite) and may reflect redox transition zones typical of coastal, deltaic, or estuarine environments. This is consistent with the continuous sea level rise in the Portuguese coast ever since 10,000 cal. yr. BP to about its present level reached by 3,000 cal. yr. BP. Between 423-490 cm lay the first sediments where Cu values are above background. This segment has pedorelicts, finely comminuted charcoal, and charred organic matter. Natural fires are an explanation, but practices of deforestation and heathland expansion are known to have begun in the region in the Bronze Age. Should the Cu grades, by its relative magnitude, be an evidence of a contamination signal from metallurgical processes akin to the Bronze Age practices is, however, still a matter of pure speculation. Since Cu has a great affinity for organic compounds and surfaces, these grades might just reflect this behaviour. The upper sequence shows an anomalous pattern for Cu, Pb, and Au. Here are the last 812 years of sedimentation until the present. Mining activities are known all over the Iberian Peninsula and the Roman presence did contribute for a substantial increase in mining activity in Paleozoic terrains upstream the Tagus basin. Since 5 out of 9 samples show Au grades above background, which is quite significant compared with the remaining segments of the core, a likely hypothesis are the more easily weathered remobilized sizeable rock masses from mining activities, which become an important source of metals, including Pb. This kind of anomaly is well documented in several other regions of Portugal. As to Cu, it is most probably due to sulphatation in vineyards, an agricultural practice known from antique times, being the most important contaminant in the upper layers of all core sediments in the Tagus basin.

REFERENCES.

Azevêdo, T.M. & Gonçalves, M.A. (2009): Geochemistry of core sediments from the Middle Tagus alluvial plain (Portugal) since the Last Glacial: using background determination methods to outline environmental changes. Environ. Earth Sci., ***59****, 191-204*

Cheng, Q., Agterberg, F.P., Ballantyne, S.B., (1994): The separation of geochemical anomalies from background by fractal methods. J. Geochem. Explor., ***51****, 109-130.*

García, M.J.G., Valiño, M.D., Rodríguez, A.V., Zapata, M.B.R. (2002): Late-glacial and Holocene palaeoclimatic record from Sierra de Cebollera (northern Iberian Range, Spain). Quat. Internl., ***93****, 13-18.*

Gonçalves, M.A., Mateus, A., Oliveira, V. (2001): Geochemical anomaly separation by multifractal modelling. J. Geochem. Explor., ***72****, 91-114.*

Ramos-Pereira, A., Ramos, C., Azevêdo, T. M., Nunes, E. (2009): Middle Tagus alluvial plain evolution since tha last glacial (Portugal). Geomorphology, submitted.

Tranter, M. (2003): Geochemical weathering in glacial and proglacial environments. In "Treatise on Geochemistry: Surface and Ground Water, Weathering, and Soils", J.I. Drever, ed. Elsevier, 189-205.

van der Knaap, W.O. & van Leeuwen, J.F.N. (1995): Holocene vegetation succession and degradation as responses to climatic change and human activity in the Serra de Estrela, Portugal. Rev. Palaeobot. Palynol, 153-211.