Manchester Geographical Society

Funding Report

Impact of analytical approaches on geochemical composition: Implication for palaeoenvironmental studies of loess

Kaja Fenn[1], **Jacek Skurzyński**[2]
[1]University of Liverpool, Department of Geography and Planning, Liverpool L69 7ZT, UK
[2]University of Wroclaw, Institute of Geography and Regional Development, 50-137, Wroclaw, Poland.

1. Introduction

Loess deposits represent a key terrestrial climate archive (Marković *et al.*, 2015) and provide an unparalleled opportunity to investigate the past dust cycle, a major component of the past climate system. These deposits also preserve evidence of its origins, critical to deciphering climatic signals in proxies, sediment transport, and dynamics, as well as factors controlling dust emission (Shao *et al.*, 2011).

Studies using geochemical proxies in loess have increased exponentially in recent years given the potential wealth of environmental information they can offer including weathering (Buggle *et al.*, 2011; Hošek *et al.*, 2015; Krauß *et al.*, 2016), provenance and sediment transport (Hao *et al.*, 2010; Muhs *et al.*, 2018; Skurzyński *et al.*, 2020; Sun, 2002; Sun *et al.*, 2007), palaeoclimate (Gocke *et al.*, 2014; Guo *et al.*, 2021; Schatz *et al.*, 2015b), and even properties of luminescence dating (Fenn *et al.*, 2020b). In particular, multi-site comparison studies have become very popular. There are however several methodological approaches available for obtaining the elemental composition of samples, and there is practically no data on cross-verification of the same research sites or samples using different methods. Therefore, any studies using published datasets assume the results from various methods are comparable.

To test the impact of methodological approaches on geochemical results and their effect on environmental interpretation, 10 loess samples were analysed using three research methods: two Inductively Coupled Plasma (ICP) analyses with different preparation methods, and X-ray fluorescence (XRF).

2. Methodology

To ensure a wide range of geochemical compositions driven by weathering pathways and/or varied sources, samples were selected from six loess-palaeosol sites across Europe; two from Biały Kościoł, Poland (Moska *et al.*, 2019), two from Tyszowce, Poland (Skurzyński *et al.*, 2019), one from Złota, Poland (Skurzyński *et al.*, 2020), one from Erdut, Croatia (Fenn *et al.*, 2020a), one from Surduk 2, Serbia (Fenn *et al.*, 2020b), and three from Slivata, Bulgaria (Fenn *et al.*, 2021). All samples were dried and crushed in an agate mortar.

"HF protocol": ICP-MS analysis was conducted at the British Geological Survey, Keyworth. Samples were digested with a mixture of acids that included hydrofluoric acid (HF). Alongside all samples a series of blanks, duplicates and 3 reference materials were also digested which were measured to assess repeatability and to monitor drift. Following digestion, samples were analysed using an Agilent Technologies 8900 ICP-MS Triple Quadrupole.

"LiB protocol": ICP-MS and ICP-OES following lithium borate fusion was performed at the Bureau Veritas (formerly ACME) laboratory, Canada. Samples were first subject to loss-on-ignition to remove organics, following which fusion with lithium metaborate/tetraborate and digestion with HNO was carried out (analytical package LF202). Analytical precision RSD (relative standard deviation), as estimated from 5 measurements of reference sample STD SO-19, is less than ± 5% for most of the elements (only for Cs and W RSD is less than ± 10%).

XRF analyses were conducted at the University of Liverpool and carried out using a Bruker S2 Ranger energy-dispersive X-ray fluorescence analyser with a PdX-ray tube and Peltier-cooled silicon drift detector. The analysis was conducted under helium and 20, 40 and 50 keV tube excitement conditions. Powder cups were filled with approximately 7g of sediment of each granulometric fraction, sealed with spectroscopic grade 6µm

---

Editor's Note: This report provides initial results for a research proposal funded by the Manchester Geographical Society on: "Identifying provenance changes in silt and sand size sediment using bulk sample geochemistry: the influence of methodological approaches on chemical signatures".

polypro-pylenefilm (Chemplex 295 Cat. No. 425) and the sediment was hand pressed. Calibration used a set of up to 18 certified reference materials.

3. Results and discussion

The UCC (Upper Continental Crust) normalised elemental composition of samples analysed using three methods for bulk sediment (Figure 1) shows significant differences in chemical composition between all methods. For example, XRF and “LiB protocol” show Zr (zirconium) and Hf (Hafnium) enrichment in relation to the UCC, whilst “HF protocol” analysis shows significant depletion in both elements. The concurrent shift in both elements is indicative of proportion of zircons in the material, with Zr and Hf enrichment indicating increased content. As loess is generally enriched in zircons, patterns demonstrated by “LiB protocol” and XRF are expected. The lower values obtained by “HF protocol” demonstrate the inability of hydrofluoric acid to fully digest resistant mineral phases. If enrichment/depletion in both elements was observed during a routine investigation, it likely would be interpreted as a change in source and result in an erroneous interpretation. The other area where an offset between elements is noted is TiO_2 which appears to be lightly enriched where XRF and “LiB protocol” are used but depleted for “HF protocol”. This would have a significant impact on the commonly used Al_2O_3/TiO2 and Fe_2O_3/TiO_2 ratios. Again, the distortion suggests that HF treatment is unable to dissolve Ti rich mineral phases. Encouragingly almost all the major elements patterns are similar across the methods though the specific values vary (e.g. CaO, Fe_2O_3). Therefore, whilst the values are off, the interpretation is likely to be similar.

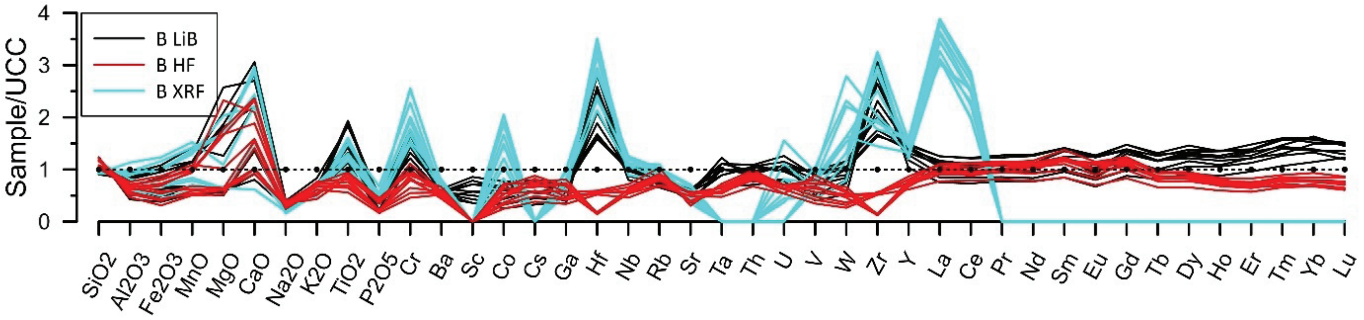

Figure 1: UCC-normalized multi-elemental spidergrams for all samples and methodologies.

In the realms of the Rare Earth Elements (REE) the “HF protocol” and “Lib protocol” show overlapping results for the light REE but divergence for heavy REE. This again suggests that HF is unable to digest and dissolve resistant mineral phases. Overall, this work shows that the results between methods are unlikely to be comparable especially for trace and REE. Therefore, studies focused on comparison of sites should ensure that methods are comparable as otherwise this could result in erroneous provenance or weathering interpretations. It also follows that greater care should be taken with how geochemical data is reported, even when samples are sent off to commercial labs for analysis.

4. Conclusions

In conclusion, this research demonstrates that open-vessel HF treatment (“HF protocol”) prior to ICP analysis is not able to dissolve more resistant minerals, such as zircons. Consequently, the underestimation of e.g. Ti, Hf, Zr, and REE in comparison to the lithium borate fusion approach (“LiB protocol”), can result in differences in the interpretation of provenance changes. Moreover, this study demonstrates that cross method validation (even just for a couple of samples) would greatly improve confidence in the final results.

References

Buggle, B., Glaser, B., Hambach, U., Gerasimenko, N.P., Marković, S.B., 2011. An evaluation of geochemical weathering indices in loess-paleosol studies. Quat. Int. 240, 12–21. https://doi.org/10.1016/j.quaint.2010.07.019

Fenn, K., Durcan, J.A., Thomas, D.S.G., Banak, A., 2020a. A 180ka record of environmental change at Erdut (Croatia): a new chronology for the loess–palaeosol sequence and its implications for environmental interpretation. J. Quat. Sci. 35, 582–593. https://doi.org/10.1002/jqs.3201

Fenn, K., Durcan, J.A., Thomas, D.S.G., Millar, I.L., Marković, S.B., 2020b. Re-analysis of late Quaternary dust mass accumulation rates in Serbia using new luminescence chronology for loess–palaeosol sequence at Surduk. Boreas 49, 634–652. https://doi.org/10.1111/bor.12445

Fenn, K., Thomas, D.S.G., Durcan, J.A., Millar, I.L., Veres, D., Piermattei, A., Lane, C.S., 2021. A tale of two signals: Global and local influences on the Late Pleistocene loess sequences in Bulgarian Lower Danube. Quat. Sci. Rev. 274, 107264. https://doi.org/10.1016/j.quascirev.2021.107264

Gocke, M., Hambach, U., Eckmeier, E., Schwark, L., Zöller, L., Fuchs, M., Löscher, M., Wiesenberg, G.L.B., 2014. Introducing an improved multi-proxy approach for paleoenvironmental reconstruction of loess-paleosol archives applied on the Late Pleistocene Nussloch sequence (SW Germany). Palaeogeogr. Palaeoclimatol. Palaeoecol. 410, 300–315. https://doi.org/10.1016/j.palaeo.2014.06.006

Guo, F., Clemens, S.C., Wang, T., Wang, Y., Liu, Y., Wu, F., Liu, X., Jin, Z., Sun, Y., 2021. Monsoon variations inferred from high-resolution geochemical records of the Linxia loess/paleosol sequence, western Chinese Loess Plateau. Catena 198, 105019. https://doi.org/10.1016/j.catena.2020.105019

Hao, Q., Guo, Z., Qiao, Y., Xu, B., Oldfield, F., 2010. Geochemical evidence for the provenance of middle Pleistocene loess deposits in southern China. Quat. Sci. Rev. 29, 3317–3326. https://doi.org/10.1016/j.quascirev.2010.08.004

Hošek, J., Hambach, U., Lisá, L., Grygar, T.M., Horáček, I., Meszner, S., Knésl, I., 2015. An integrated rock-magnetic and geochemical approach to loess/paleosol sequences from Bohemia and Moravia (Czech Republic): Implications for the Upper Pleistocene paleoenvironment in central Europe. Palaeogeogr. Palaeoclimatol. Palaeoecol. 418, 344–358. https://doi.org/10.1016/j.palaeo.2014.11.024

Krauß, L., Zens, J., Zeeden, C., Schulte, P., Eckmeier, E., Lehmkuhl, F., 2016. A Multi-Proxy Analysis of two Loess-Paleosol Sequences in the Northern Harz Foreland, Germany. Palaeogeogr. Palaeoclimatol. Palaeoecol. 461, 401–417. https://doi.org/10.1016/j.palaeo.2016.09.001

Marković, S. B. and 20 others, 2015. Danube loess stratigraphy - Towards a pan-European loess stratigraphic model. Earth-Science Rev. 148, 228–258. https://doi-org.mmu.idm.oclc.org/10.1016/j.earscirev.2015.06.005

Muhs, D.R., Bettis, E.A., Skipp, G.L., 2018. Geochemistry and mineralogy of late Quaternary loess in the upper Mississippi River valley, USA: Provenance and correlation with Laurentide Ice Sheet history. Quat. Sci. Rev. 187, 235–269. https://doi.org/10.1016/j.quascirev.2018.03.024

Schatz, A.-K., Scholten, T., Kühn, P., 2015b. Paleoclimate and weathering of the Tokaj (Hungary) loess-paleosol sequence. Palaeogeogr. Palaeoclimatol. Palaeoecol. 426, 170–182. https://doi.org/10.1016/j.palaeo.2015.03.016

Shao, Y. and 9 others, 2011. Dust cycle: An emerging core theme in Earth system science. Aeolian Res. 2, 181–204. https://doi-org.mmu.idm.oclc.org/10.1016/j.aeolia.2011.02.001

Skurzyńki, J., Jary, Z., Kenis, P., Kubik, R., Moska, P., Raczyk, J., Seul, C., 2020. Geochemistry and mineralogy of the Late Pleistocene loess-palaeosol sequence in Złota (near Sandomierz, Poland): Implications for weathering, sedimentary recycling and provenance. Geoderma 375, 114459. https://doi.org/10.1016/j.geoderma.2020.114459

Skurzyński, J., Jary, Z., Raczyk, J., Moska, P., Korabiewski, B., Ryzner, K., Krawczyk, M., 2019. Geochemical characterization of the Late Pleistocene loess-palaeosol sequence in Tyszowce (Sokal Plateau-Ridge, SE Poland). Quat. Int. 502, 108–118. https://doi.org/10.1016/j.quaint.2018.04.023

Sun, J., 2002. Provenance of loess material and formation of loess deposits on the Chinese Loess Plateau. Earth Planet. Sci. Lett. 203, 845–859. https://doi.org/10.1016/S0012-821X(02)00921-4

Sun, J., Li, S.H., Muhs, D.R., Li, B., 2007. Loess sedimentation in Tibet: provenance, processes, and link with Quaternary glaciations. Quat. Sci. Rev. 26, 2265–2280. https://doi.org/10.1016/j.quascirev.2007.05.003