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Zinc Isotopes in Miocene Plant Fossils at Andance, France: Implications for Biogenicity Criteria

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The identification of potential fossilized remains from the Precambrian has highlighted the limitations of morphological criteria and the increasing necessity for geochemical biomarkers to differentiate biological from sedimentary origins. To explore new biogenicity criteria applicable to fossilized remains, we investigated the zinc abundances and isotopic compositions of Miocene plant fossils (leaves and wood fragments) and their associated host rock (diatomite) from the Andance volcano crater lake in France. Zinc is a particularly promising geochemical biomarker due to its essential role as a metal cofactor in eukaryotic proteins and its relatively low susceptibility to post-depositional diagenetic alteration.

The Andance diatomite and fossilized plants provide an ideal natural setting for geochemical investigations, as they have experienced minimal diagenesis and no metamorphic overprint, preserving original chemical signatures. Using multi-elemental quadrupole and multi-collector inductively coupled plasma mass spectrometry, we analyzed the major and trace element concentrations, including Zn, and Zn isotopic compositions of the fossils and their host diatomite. The results showed no significant variations in either Zn concentration or isotopic composition between the fossils ($\delta^{66}Zn = +0.33 \pm 0.18$ ‰) and the diatomite host rock ($\delta^{66}Zn = +0.41 \pm 0.14$ ‰), with values consistent with the Zn isotopic range of magmatic rocks. This suggests a detrital contribution of Zn from volcanic sediments rather than a biological isotopic signature.

Although we did not observe distinct biogenic Zn isotope fractionation in this study due to magmatic overprint, we demonstrated that Zn isotopic compositions can be successfully analyzed in samples with high silica and organic matter content. The analytical protocol we developed by modifying the standard acid digestion procedure, can be applied to other organic-rich samples. This work hence contributes to the development of establishing geochemical biogenicity criteria and paving the way for future applications in paleobiological and astrobiological studies.