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Contemporary ^{14}C radiocarbon levels of oxygenated polybrominated diphenyl ethers (O-PBDEs) isolated in Sponge-Cyanobacteria associations

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Considerable debate surrounds the sources of oxygenated polybrominated diphenyl ethers (O-PBDEs) in wildlife as to whether they are naturally produced or result from anthropogenic industrial activities. Natural radiocarbon (^{14}C) abundance has proven to be a powerful tool to address this problem as recently biosynthesized compounds contain contemporary (i.e. modern) amounts of atmospheric radiocarbon; whereas industrial chemicals, mostly produced from fossil fuels, contain no detectable ^{14}C . However, few compounds isolated from organisms have been analyzed for their radiocarbon content. To provide a baseline, we analyzed the ^{14}C content of four O-PBDEs. These compounds, 6-OH-BDE47, 2'-OH-BDE68, 2',6-diOH-BDE159, and a recently identified compound, 2'-MeO-6-OH-BDE120, were isolated from the tropical marine sponges *Dysidea granulosa* and *Lendenfeldia dendyi*. The modern radiocarbon content of their chemical structures (i.e. diphenyl ethers, $\text{C}_{12}\text{H}_{22}\text{O}$) indicates that they are naturally produced. The existence of potentially different sources of O-PBDEs in the environment (i.e. synthetic, natural and transformed), challenges the issue of the source and the potential risks to exposed wildlife. Therefore, elucidation of sources is a key to understanding the environmental occurrence, transformation processes, transport processes and bioaccumulation of O-PBDEs. The molecular level radiocarbon technique (by Accelerator Mass Spectrometry, AMS) allows discriminating between these origins. The baseline data presented in this study provides evidence of natural production in marine sponge–bacteria associations.

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Compound-specific chlorine isotope analysis in contaminant hydrogeology

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Organic compounds are among the most commonly detected groundwater contaminants. Compound-specific isotope analysis (CSIA) can provide unique insight into their origin and fate in the subsurface. Recent advances in analytical methods have opened new possibilities for the application of CSIA to chlorinated contaminants, which are of particular concern due to their high toxicity and persistence in the environment. This presentation provides an overview of the current understanding of the chlorine isotope behaviour during physical and reactive processes, and illustrates the application of chlorine isotope methods in contaminant hydrogeology.

A characteristic feature of chlorine isotopes is the high abundance of the heavy isotope (³⁷Cl). While this has made it possible to use conventional GC-quadrupole-MS for high precision isotope analysis ¹, it complicates data interpretation as multiple isotopologues need to be taken into account. However, it can be shown that during many physical and reactive processes, pairs of isotopologues with different numbers of heavy chlorine isotopes fractionate proportionally in good approximation. This makes it possible to relate isotopologue ratios to isotope ratios using simple expressions and simplifies analytical procedures.

In addition, a novel application of isotope analysis to differentiate between natural and anthropogenic chloroform in groundwater will be presented. Due to its origin from natural organic matter, natural chloroform has a distinctly different carbon isotope signature (−20 to −30‰) compared to anthropogenic chloroform (−40 to −60‰), which is based on methane ². However, during its migration through the subsurface, the isotopic signature can be altered significantly due to the strong isotope fractionation associated with reductive dechlorination of chloroform. However, a dual carbon-chlorine isotope approach makes it possible to differentiate between natural and anthropogenic chloroform even if biodegradation occurs.

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Lead isotope signature of Mesozoic and Cenozoic ore deposits in Northern Tunisia

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In Northern Tunisia, sediment-hosted Pb-Zn deposits are found mainly in the following four structural zones from the northwest to the southeast of the fold belt: the Nappes zone, the Diapirs zone (or Triassic Domes zone), the Trough zone and the Jurassic Mountains zone (Fig. 1). The majority of ore deposits and occurrences are: (i) Pb-Zn mineralization with arsenic and antimony hosted in the continental Neogene volcanics or situated immediately below them (Jebel Hallouf-Sidi Bou Aouane, Jalta, Bechateur); (ii) Pb-Zn mineralization with arsenic and mercury in fractures with local intrusions related to the Neogene volcanics (Fej Hassene, Oued Maden); (iii) stratabound lenticular orebodies in the contact zone (or transition zone) between Triassic and Cretaceous strata (Bou Grine, Guern Halfaya); (iv) stratabound orebodies associated to Cenomanian-Turonian strata (Bou Grine, Guern Halfaya); (v) veins, stockworks and open-space fillings developed in the peridiapiric cover (Bou Grine, Fedj-el-Adoum); (vi) stratabound or stratiform bodies, either within or immediately above the Jurassic reef limestones of Kimmeridgian-Tithonian-Berriasian age (Hammam Zriba, Jebel Rexas, Jebel Mecella), along unconformity surfaces highlighted by shoals, condensed layers, stratigraphic gaps, karstification and pedogenesis, that separate Rexas Formation from overlying units. Pb-isotopic composition of galena display an homogeneous lead isotope signature ($^{206}\text{Pb}/^{204}\text{Pb}$: 18.723–19.002 and $^{207}\text{Pb}/^{204}\text{Pb}$: 15.663–15.700; Fig. 2) suggesting a single lead reservoir for deposits of the Domes and Jurassic Mountain zone, and a mixing lead reservoir for the Nappes zone. Pb isotope values of deposits of Jurassic Mountains zone are slightly more radiogenic than lead from the other deposits, possibly reflecting the influence of a more evolved upper crustal source. The homogeneous lead and the lack of extensive wall-rock alteration suggests that the lead was not leached from the country rocks. Underlying Paleozoic sediments are proposed as lead source for mineralization in all ore deposits. Model-lead ages are about 12,5–13 Ma and 86 Ma for the Nappes zone and Diapirs zone, respectively, whereas in the Jurassic Mountain zone, the age is not in accordance with the geological settings.

Fig. 1
The Triassic exposures and Pb–Zn deposits in Northern Tunisia

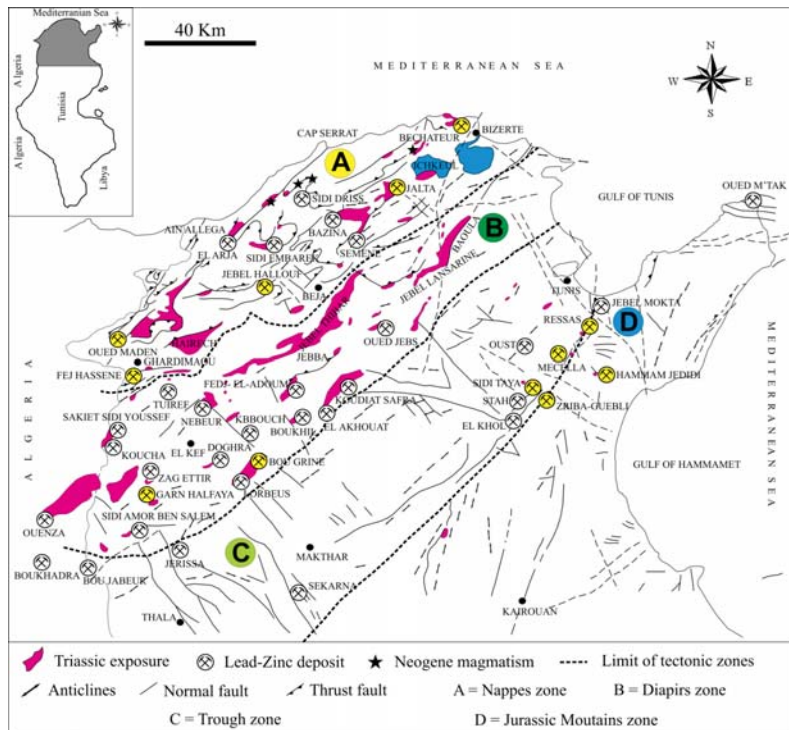
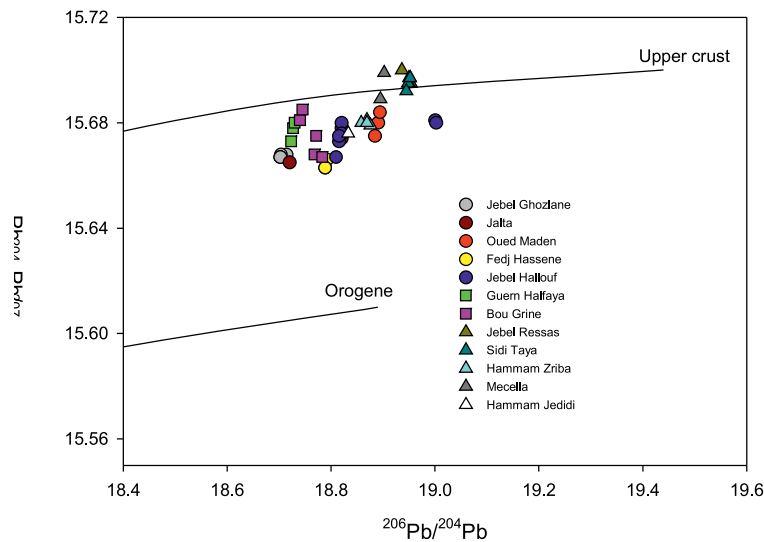


Fig. 2
Plots of $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ for the Pb–Zn deposits in Northern Tunisia. Curves of growth trends for Pb isotope ratios are from the plumbotectonic model of Zartman and Doe (1981).



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Role of mantle/magmatic derived auriferous fluid for Archean Orogenic Gold deposits from Sangli mine area, Gadag Schist Belt, South India – Evidence from C-O stable isotope and fluid inclusion study

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Carbon ($\delta^{13}\text{C}_{\text{pdb}}$) and Oxygen ($\delta^{18}\text{O}_{\text{smow}}$) isotopic compositions of auriferous quartz carbonate veins (QCVs) of orogenic gold deposits from Sangli mine area, Gadag gold deposit of the Archaean Gadag Schist Belt, Dharwar Craton, Karnataka have been examined for the first time in this deposit to understand the origin of the mineralizing fluids. The average $\delta^{13}\text{C}_{\text{pdb}}$ and $\delta^{18}\text{O}_{\text{smow}}$ isotope compositions of auriferous QCVs are -4.5‰ ($\pm 2.5\text{‰}$), 24.26‰ (± 5.2) respectively. However, $\delta^{13}\text{C}$ data of only 5 samples out of 36 number of samples analysed, range within those of metasedimentary carbonates reported from Chitradurga Schist belt (i.e. 0 to -2‰ , Das Sharma et al. 1994). Most of the $\delta^{13}\text{C}$ values of carbonates of QCVs are well within the $\delta^{13}\text{C}$ range of carbonates or CO_2 derived from magma ($-5 + 3\text{‰}$; Burrows et al. 1986) or mantle ($6 + 2\text{‰}$; Ohmoto, 1986). Hence, it is proposed that the fluids responsible for gold mineralisation in the area under study could have been derived from multiple sources. The major source could be from mantle and/or magma and a very minor component might have been derived from metamorphic devolatilisation of pre-existing sedimentary rocks.

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