# Radiocarbon and Lead for the Petroleum Industry

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### **Petroleum Exploration**

In petroleum exploration, it is vital to be able to interpret and date key occurrences within petroleum systems-including understanding the formation of hydrocarbons from source rock organic compounds to the migration into reservoirs. Prior to extraction, characterizing petroleum deposit processes is required to effectively extract crude oil through isotopic markers. Due to the temperature-dependent water solubility of hydrocarbons, light isotopes (e.g., oxygen) tend to be separated during adiabatic cooling during pumping and extraction of hydrocarbons. Without an abundance of these light isotopes, heavy isotopes are often the most viable option for characterization of oil processes-including lead (Pb), which is not fractionated through the extraction process.

Lead is known to be a very toxic, non-essential element, with origins within the Earth's crust. Lead isotopes come in multiple different forms, four of which are naturally occurring: <sup>204</sup>Pb, <sup>206</sup>Pb, <sup>207</sup>Pb, and <sup>208</sup>Pb. The <sup>206</sup>Pb, <sup>207</sup>Pb, and <sup>208</sup>Pb isotopes are radiogenic as they are the end product of the radioactive decay chain of radioactive elements (<sup>238</sup>U, <sup>235</sup>U, and <sup>232</sup>Th, respectively). The abundance of these isotopes is presented with respect to each other, for example: <sup>206</sup>Pb/<sup>207</sup>Pb. Using isotope ratios, lead sources, migration, and effects can be traced through the atmosphere, biosphere, hydrosphere, and geosphere. The precision of the different lead isotopes is very important in order to distinguish sources and trace its movement through space and time. Measurement through multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) makes such research possible.

Uranium, the upper element within lead's radioactive decay chain, is correlated to the organic contents within carbon-rich sediments and is not impacted by thermodynamics to the same degree as light stable isotopes (e.g., carbon and nitrogen). This makes the isotope systems of Pb and U notably useful in oil generation and migration research including identifying Pb origin in different source rocks and their relative contributions in the generation of crude oil and carbonrich rock. Given the connection between U, Th, and Pb, the combination of these isotopes can be used to compare crude oil and carbon-rich rock with terrestrial values when viewing in threedimensional space (ternary plot). This allows one to compare the sample age with the host rock to see if they're consistent with surrounding geology. If so, migration is limited and the sample has not undergone significant migration. On the other hand, if the sample age is not consistent with the local source rock, then the oil (or oil-bearing matrix) likely originated elsewherepointing to another source of the Pb. For example. through the measurement of U-Th-Pb, Fetter et al. (2019) demonstrated that northern European oil samples combined black shale-dominated Mesozoic sources with a series of other Paleozoic sources and a Proterozoic source.

#### **Identification of Leaded Gasoline**

Leaded gasoline was popular over the past century due to the addition of tetraethyl lead to gasoline, which has been said to improve engine performance. More recently, this has been replaced by ethanol and other alternatives. Even low levels of exposure have led to negative impacts to human health-including lower IQs, more violent crime, and various diseases, as well as disastrous contamination to the environment (Falta et al. 2005; Papanikolaou et al. 2005; Mielke et al. 2021; Huang et al. 2012). Developed countries started to phase out the use of leaded gasoline in the 1970s -typically now only used in aircrafts-but they remained widespread in developing countries for many decades, only recently becoming essentially obsolete (Domonoske 2021). The regulations against leaded gasoline have resulted in declines in Pb pollution (Angrand et al. 2022); however, unleaded gasoline still contains small amounts of toxic Pb and, thus, still contributes to urban aerosol pollution (Yao et al. 2015) and may remain an issue for many years to come due to lingering airborne dust (Resongles et al. 2021). The analyses of various lead isotopes can provide a means of fingerprinting sources of Pb and other pollutants-particularly for fuels, as Pb isotopes do not undergo fractionation during extraction, refining, or emissions (Yao et al. 2015).

#### **Biofuel Verification**

Following the exploration and extraction phase, isotopes can be used to verify the final petroleum product. In cases where modern biomass is utilized in the development of fuels in combination with ancient petroleum sources, the analysis of radiocarbon can be applied to check or verify the accuracy of biofuel blends. Biofuels are transportation fuels developed from partial to fully renewable sources of carbon—such as modern plants and animals.

Carbon of modern age produces a distinct radiocarbon (14C) signature close to that of the current atmosphere, whereas ancient petroleum-derived carbon sources have a radiocarbon content of zero. Without considering radiocarbon, the two carbon sources are chemically indistinguishable. Given this relationship between the age of carbon and biofuel source materials, it is possible to confirm the fuel blend proportions when both sources are used, providing a verification of the quality. A number of initiatives worldwide encourage the use of biofuels and require a measurement of the biogenic fraction of liquid fuels, such as the United States Environmental Protection Agency Renewable Fuel Standard, which stipulates ASTM D6866 testing (see https://www.betalabservices. com/biofuels.html).

#### Conclusions

Stable and radioactive isotopes are powerful tools for the petroleum industry, providing key information from the exploratory and extraction stages through to fuel production and eventually pollution monitoring. Lead and its decay chain of elements allow one to predict the formation of hydrocarbons from source rock to the migration into reservoirs. It can also be used to estimate the relative contribution of different Pb sources in atmospheric pollution. Finally, radiocarbon can be analyzed in biofuels to check the biogenic content and accuracy of blends, as required by clients, suppliers, manufacturers, or distributors.

#### References

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