



Routes and progress in age dating fluid residence time in subsurface reservoirs: Issues and E&P Applications.

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Summary

The radiometric dating of geological events was a crucial achievement leading to the establishment of the geological time scale. The dating of the timing of petroleum charge into, and oil residence times in a petroleum trap would also be as significant, eliminating much speculation concerning reservoir charging times and migration routes and providing direct assessment of play concepts in conventional targets and storage phenomena in unconventional reservoirs. The examination of the residence age spatial profiles in a fluid column, coupled to numerical models of fluid flux, might allow estimates of the charge, spillage and leakage fluid fluxes into and out of the trap both for petroleum and CO₂ storage reservoirs. However, current strategies to assess the residence time of fluids in subsurface reservoirs methods fail to provide useful estimates, and arguably the most important constraining information in a petroleum system is currently inaccessible. Based on several years of research, we have defined the geochemical landscape and constraints on fluid radiolysis-based age dating proxies. In theory, the chemical alterations in petroleum reservoir fluids, caused by in-reservoir radioactivity could be used as a chronometer, although there are great analytical challenges associated with such strategy. In this study, we scrutinize the requirements, potential benefits and practical feasibility of such potential technologies, showing preliminary results for a case history data set where residence age is a key determinant of exploration strategy.

Fundamentals

The most robust petroleum fluid residence history assessment methods must involve compositional or concentration variations in petroleum hosted components that do not exchange chemically with reservoir media (minerals, water, and any organic materials), and which are independent of secondary alteration processes such as biodegradation, thermochemical sulfate reduction or evaporative fractionation. Ideal methods must also be able to distinguish reservoir aging impacts from any compositional changes relating to the oil pre-history in the source rock or carrier bed system. Again, ideally, the method would work with gases as well as liquid petroleum components. The impact of radiation from radiogenic nuclides in a reservoir rock on trapped fluid composition seems to potentially be a viable route to an age dating proxy (Larter et al., 2012).

Specific radiolysis products are often hard to measure, as large numbers of low concentration species are produced, from radiolysis of even simple binary compound mixtures (Larter et al., 2012). Frolov et al. (1998) and Curiale and Frolov (1998), described the production of alkenes in crude oils from natural radiation damage (radiolysis), with radiation dose related impacts. This was a crucial observation but, as reported in petroleum mixtures (Frolov et al., 1998), radiation-induced unsaturation has a very complex distribution through essentially all organic fractions, making detection of specific radiation-induced daughter species by classical geochemical approaches, such as GC-MS, very difficult.

Notwithstanding, simply calibrating chemical compositional change to a reservoir radiation dose impact may be insufficient for a chronometric system, as it has been demonstrated that with very radioactive

source rocks such as the Cambrian Alum shale, for example, both kerogen and hosted petroleum is compositionally altered by radiation impacts (Bharati et al., 1995). While more typically, source rocks would not see Alum shale levels of radioactivity, given the higher radionuclide concentrations in shales versus say, sandstones, plus the potentially longer residence times of organic matter in source rocks compared to reservoirs, the radiation dose experienced by pre-, or post-generation organic matter in a source rock, may exceed that experienced by oil in a reservoir. Any effective reservoir fluid residence time chronometer must be able to deal with this phenomenon, so an innovative approach is needed to decouple source and reservoir irradiation effects. We have determined that the local radionuclide distribution will be a definitive source signal for any reservoir fluid based radiation impact and that detection of locally generated radiolysis effect profiles is a potential route to decoupling source versus reservoir radiation impacts. This, in turn, requires that compositional profiles are the route to a chronometer and that mass transport effects and fluid mixing models are key elements that must be included in such data analysis.

Examples

In Larter *et al.* (2017), we have described a series of systematic changes in crude oil composition based on their accumulated radiation dose. Overall, the degree of radiolysis of individual petroleum compounds was found to depend on chemical class, molecular size, initial compound concentration and the nature of the oil matrix, indicating that a proxy system will likely depend on case-specific calibrations. Using the calculated gamma ray radiolysis susceptibility (kGy^{-1}) of different compounds or chemical classes, coupled to oil-specific calibration experiments, one can estimate the accumulated radiation dose (kGy) the fluid has experienced. Reservoir radionuclide profile can be used to estimate the local radiation dose rate (kGy/Ma) experienced by any fluid occupying its pores.

While we are not yet confident that the “dates” we obtain are meaningful and interpretable “process ages”, we have applied this emerging and yet to be validated technology to a set of 24 oils from an active exploration setting, and results are shown in **Fig. 1**, where different colors represent samples from different parts of various reservoirs. Cross plots of geochemically determined radiation dose are related to local reservoir related radiation dose rate, data points with similar fluid residence dates lying along defined lines which is encouraging. Despite the many gaps yet to be filled in terms of further understanding of in-reservoir radiolysis proxy dynamics, the impacts of secondary alterations, and many other factors, the results are encouraging, at at least a relative-date level. Analytical and other uncertainties are still too large to permit real age estimates, but in this play setting, relatively young fluid residence dates (ca <4 Ma) are thought provoking in terms of future exploration target definition.

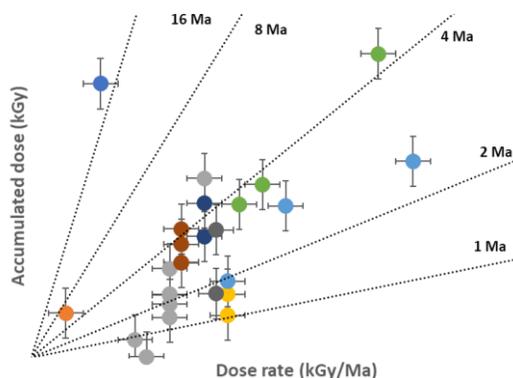


Fig. 1. (A) Crude oil radiolysis dates are estimated from a suite of crude oils from related reservoirs in a play setting. While we do not consider these “dates”, reliable interpretable “ages”, data concordance is encouraging and the young dates raise many exploration related issues for this basin.

Conclusions

Overall, the accumulated dose as measured from geochemical markers can potentially be used as proxies for estimating in-reservoir fluid residence time, albeit with numerous geological and analytical caveats at this stage.

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