Lead Isotopes as Age-Sensitive, Genetic Markers in Hydrocarbons: 2. Kerogens, Crude Oils, and Unleaded Gasoline

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ABSTRACT ●

The ability to use lead isotopes as a means of dating sedimentary, stratiform ore deposits suggests that lead isotope analyses of sedimentary kerogen and crude oil may also provide age-sensitive, genetic information that is pertinent to petroleum generation. In order to evaluate this premise further, lead isotopic analyses were performed on suites of kerogens, crude oils, and unleaded gasolines to assess lead isotopic relationships during catagenesis of kerogen and refining of crude oil.

Alaskan North Slope kerogen–crude oil samples from Cretaceous source rocks, as well as unleaded gasoline refined from North Slope crude oil feedstock, exhibit overlapping or concordant $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{204}Pb$ ratios (1.215–1.225 and 18.9–19.2, respectively). This indicates that lead isotopic ratios are conservative, being passed on from kerogen to crude oil during catagenesis and from crude oil to gasoline during refining. Lead isotope ratios of North Slope hydrocarbons are consistent with those expected of Cretaceous crustal rocks in the region, indicating that lead isotope ratios of kerogens and crude oils serve as age-sensitive genetic markers during petroleum generation.

A second suite of crude oils, with known source rock ages (Devonian to Tertiary), was also analyzed. Lead isotopic ratios of crude oils of different geologic age vary systematically, increasing with decreasing geologic age, being consistent with average crustal lead growth models. Results indicate that crude oil lead isotopic evolution follows the same systematics as crustal rocks, increasing through the Phanerozoic because of production of radiogenic lead via radioactive decay of uranium isotopes. As observed with model lead ages of stratiform ore minerals, model lead ages based on crude oil lead isotopic ratios are in good agreement with known source rock ages, with age resolution potentially approaching that of individual geologic periods.

The observed lead isotopic variations of crude oils explain why lead isotopic ratios of unleaded gasolines produced by different manufacturers differ. Unleaded gasoline $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{204}Pb$ ratios range from approximately 1.19 and 18.40 to approximately 1.24 and 19.5, respectively, and are consistent with lead isotopic ranges of Cretaceous-/Tertiary-age crude oils, which are blended in variable proportions with North Slope crude oil to produce most U.S. unleaded gasolines. However, each of the six manufacturer's unleaded gasoline lead isotope ratios are distinct, indicating that lead isotopes can be used to discriminate among sources of unleaded gasoline accidentally released into the environment.

Key Words: lead, isotopes, gasoline, hydrocarbons, crude oil.

INTRODUCTION ●

The radioactive decay of uranium isotopes ^{238}U and ^{235}U to stable isotopes of lead ^{206}Pb and ^{207}Pb, respectively, has provided a mechanism by which the lead isotopic evolution of the earth's crust has been modeled (Cumming and Richards, 1975; Stacey and Kramers, 1975). Specifically, these models allow ages of sedimentary, stratiform ore deposits to be determined quite accurately by using measured $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{204}Pb$ ratios of ore minerals (Faure, 1986; Geyh and Schleicher, 1990). Given that sedimentary organic matter, kerogen, and the crude oil produced by the catagenesis of kerogen are part of the earth's crustal system and, therefore, are expected to follow similar lead isotopic evolutionary pathways as the crustal rocks in which they reside, it is conceivable that lead isotopic analyses of these hydrocarbons may provide genetic and age-sensitive information, with potential applications in petroleum exploration and the environmental arena. The focus of this article concerns the measurement of lead isotopic ratios in kerogen, crude oil, and unleaded gasoline produced from crude oil in order to assess the genetic and age significance of lead isotope ratios in these hydrocarbons.

Concentrations of lead in hydrocarbons, exclusive of leaded gasoline, are typically in the parts per billion (pbb) range; however, these levels are sufficient for the determination of precise lead isotopic ratios (Hurst, 1998, 2000; Hurst et al., 1996). In contrast to preconceived notions concerning lead in hydrocarbons, in which lead is often presumed to be present either as included mineral phases in crude oil or particulate lead derived from metal storage tanks in the case of gasoline, lead does occur as organic species in hydrocarbons, bonded to alkyl groups, and/or as a coordinating metal ion (Berkowitz, 1997; Dougherty, 1996;

Lewan and Maynard, 1982; Ma and Dougherty, 1997; Pedley et al., 1986).

In this article, the results of lead isotopic analyses of 27 crude oils, 12 kerogens, and 38 unleaded gasolines from six different producers are presented. Attempts were made to avoid selecting samples from areas with complex geologic histories (e.g., metamorphism and degradation) at this stage of the investigation. Kerogen–crude oil lead isotopic relationships are investigated in a suite of samples from the North Slope of Alaska. This suite was selected for the following reasons: (1) Organic geochemical data indicate the kerogens and crude oils are genetically related, with the crude oil being derived from kerogen in Cretaceous source rocks (Kvenvolden et al., 1993; Magoon and Claypool, 1985), and (2) Jurassic–Tertiary crustal lead evolution is well established in the area, allowing age-sensitive relationships to be evaluated (Alldrick et al., 1993). Lead isotope ratios were also analyzed in domestic and foreign crude oils in which the source rock's geologic age is known; ages ranged from the Devonian to the Miocene. These analyses allowed lead isotopic model ages derived from the crude oil analyses to be compared with those of the source rock, to evaluate the age significance of lead isotope ratios in crude oils.

In the case of the North Slope and California crude oils, comparisons can be made to lead isotopic ratios of unleaded gasolines produced exclusively from each of these crude oil feedstocks. The results bear on the use of lead isotopes as a means of differentiating among accidental releases of unleaded gasoline into the environment and the relationship between lead isotope ratios of refined products with those of their crude oil source(s).

ANALYTICAL METHODS

An overview of the lead isotopic analyses and the sample preparation is presented. Details of the procedures are available in other publications (Hurst, 2000; Odermatt, 1986).

Sample Preparation and Thermal Ionization Mass Spectrometry

All sample preparation procedures use ultraclean conditions (total Pb blank <1 picogram) and include centrifuging, filtering, and/or chemical extractions to remove inorganic particulates. Lead isotopic analyses of organic phases require approximately 1 to 50 mL of liquid or approximately 0.1 to 0.5 g of kerogen, depending on the lead content. Refractory organics, such as kerogen or crude oil, are sequentially hot acid extracted using aqua regia. In crude oils, the intent is to focus on the more refractory, relatively metal-rich asphaltene fraction. Although carbon disulfide, CS_2, is normally used to precipitate the asphaltene fraction from crude oils, ultrapure CS_2 is not available; hence, lengthy acid extractions are preferable to remove included mineral phases, if present, and avoid contamination.

Lead is separated from other elements using ion exchange chromatography in order to eliminate potential interferences in lead isotope analyses that may arise from instabilities in the thermal ionization mass spectrometry ion current (chemically induced interference) and/or isobaric mass overlaps. Individual sample analyses for lead isotopic composition involve 100 to 200 scans of the four naturally occurring lead isotopes. Isotope ratios are corrected for machine fractionation, approximately 0.1% per amu, using NIST SRM 981. Overall accuracy (95% confidence level) in lead isotopic ratios after fractionation corrections is typically $\leq \pm 0.05\%$ for $^{206}Pb/^{207}Pb$ and $< \pm 0.1\%$ for $^{206}Pb/^{204}Pb$.

RESULTS ●

Crude Oils and Kerogens

Biomarkers, geologically persistent molecular fossils, and stable isotopes have been used extensively to investigate petroleum genesis and to constrain the geologic age of crude oils (Holba et al., 1998; Moldowan et al., 1994; Peters and Moldowan, 1993; Sofer, 1984). However, even the most recalcitrant biomarkers may eventually degrade, obscuring genetic and age relationships of crude oils (Wells et al., 1995). Lead and its isotopes neither degrade nor fractionate (Faure, 1986; Geyh and Schleicher, 1990); furthermore, it is well known that lead isotope ratios in the earth's crust evolve over geologic time because of U/Th decay, allowing ages of sedimentary ore deposits to be determined because of the lead isotopic equilibrium achieved between ores and their host sediment during ore genesis (Cumming and Richards, 1975; Stacey and Kramers, 1975). As stated earlier, isotopic equilibrium should also occur between petroleum source rocks, included organic matter (i.e., kerogen), and crude oil during catagenesis, imparting age diagnostic and genetic information to the resultant crude oil.

Kerogen–Crude Oil Isotopic Equilibrium

In order to evaluate whether equilibrium during catagenesis is achieved, samples of Alaska North Slope kerogens and crude oils were analyzed for their $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{204}Pb$ ratios. Details pertinent to the selection of these samples include a knowledge of the (1) genetic relationships between crude oils and source rocks (kerogen in the early Cretaceous pebble shale), which are nonproprietary (Magoon and Claypool, 1985), and (2) crustal lead isotopic evolution for the region during the geologic times periods of interest (Jurassic, Cretaceous, and Tertiary) has been developed through studies of ore mineralization (Alldrick et al., 1993). Results and the geologic evolution of $^{206}Pb/^{207}Pb$ versus $^{206}Pb/^{204}Pb$ in Alaska from the late Jurassic through the Tertiary period are presented in Figure 1.

Using $^{206}Pb/^{207}Pb$ for discussion purposes, the kerogen and crude oil data define two predominant clusters, where

^{206}Pb/^{207}Pb is approximately 1.215 and 1.225. The fact that the comparative average lead isotopic ratios of kerogens versus crude oils within each cluster are statistically identical ($2\sigma < 0.02\%$) indicates that lead isotopic equilibrium is established between kerogens and crude oils during catagenesis; that is, lead isotope ratios are transferred conservatively from the kerogen to crude oil. This conclusion is also supported by the concordancy observed between the ^{206}Pb/^{207}Pb–^{206}Pb/^{204}Pb ratios of the Cretaceous-age Alaskan North Slope crude oil–kerogen group and those for the Cretaceous period, as defined by the crustal lead isotopic evolution of the region (region K in Fig. 1; Alldrick et al., 1993). Such concordancy would not be expected if either lead isotopic equilibrium was not established between source rocks, kerogen, and crude oil during catagenesis or if lead in the organic phases was present as allogenic mineral inclusions rather than organolead.

Variations in the lead isotopic ratios in the kerogens and therefore in the resultant crude oils are related to differences in the kerogen uranium content (approximately 1 to 21 ppm); higher uranium concentrations result in higher, more radiogenic lead isotope ratios over time. Kerogen uranium concentrations increase from 1–3 ppm in the least radiogenic group (^{206}Pb/^{207}Pb, approximately 1.215), to 5–9 ppm in the more radiogenic group (^{206}Pb/^{207}Pb, approximately 1.225); the most radiogenic kerogen datum point, which lies in the Tertiary segment of the lead isotopic evolution line (region T; Fig. 1), contains the most uranium (21 ppm).

The statistically significant correlation ($R^2 = 0.987$) between uranium concentrations and ^{206}Pb/^{207}Pb ratios in kerogens indicates the lead is radiogenic in origin and inherent in the kerogen structure (Fisher and Hurst, 1996). These results strongly suggest that crude oils derived from source rocks of different geologic age have different, age-sensitive, lead isotopic ratios, which can be used to correlate crude oils to their source rock and determine their geologic age using established crustal lead evolution models. This point is addressed further in the subsequent section.

Note that the lead isotopic ratios of unleaded gasoline refined exclusively from Alaskan North Slope crude oil feedstock lie within the same lead isotopic range of the North Slope crude oils (Fig. 1). An identical result is obtained for a suite of unleaded gasolines sampled from a gasoline manufacturer in California that relied exclusively on California crude oil feedstock for their gasoline (Fig. 2). In both cases, the data indicate that lead isotopic ratios of crude oils are passed on to unleaded gasoline during the refining process. Furthermore, as discussed later in the section dealing with unleaded gasolines, high-precision lead isotope analyses of unleaded gasoline produced from different crude oil feedstocks or blends thereof should exhibit variations in lead isotopic ratios, potentially providing a method by which sources of unleaded gasoline released into the environment may be differentiated.

Age Dating Crude Oil

The concordance between the measured lead isotopic ratios of North Slope crude oils originating in Cretaceous-age source rocks with those expected for Cretaceous-age crustal rocks indicates that age-diagnostic information is retained by crude oils following catagenesis. The apparent age resolution, that is, a geologic period, using lead isotopes, exceeds those that have been achieved using biomarkers, which constrain ages to within three to five geologic periods

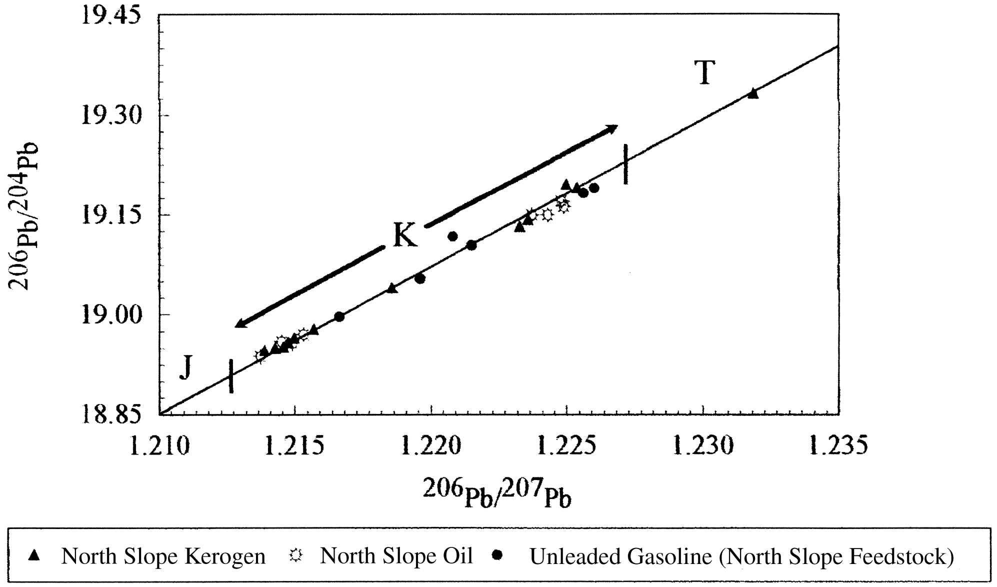

FIGURE 1: Lead isotopic discrimination diagram for kerogens and crude oils from Alaska's North Slope; note the similar lead isotopic range for not only kerogens and crude oils, but also for unleaded gasoline refined from North Slope feedstock. Lead isotopic ratios of kerogens and crude oils are consistent with the known Cretaceous age of the North Slope crude oil source rocks, as determined from lead model ages based on lead isotopic evolution in the region from the Jurassic to Cretaceous through the Tertiary periods (regions J, K, and T, respectively).

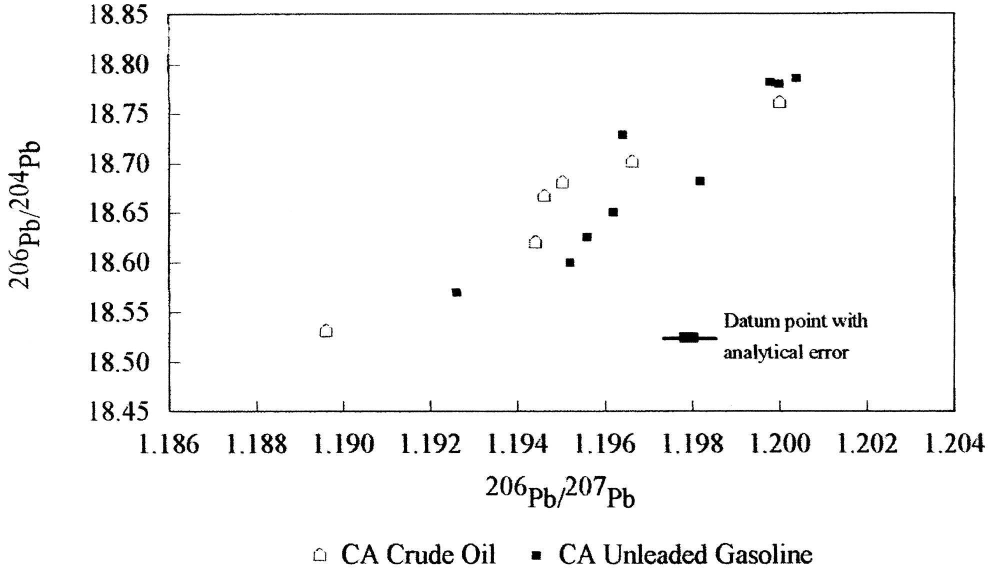

FIGURE 2: Lead isotopic discrimination diagram for California crude oils and unleaded gasoline produced exclusively from California crude oil feedstock.

(Holba et al., 1998; Moldowan et al., 1994; Peters and Moldowan, 1993).

In order to evaluate further the potential of lead isotopes to model ages of crude oils, 20 additional crude oil samples were analyzed. The geologic age of each crude oil's source rock was known. General locations and ages of the crude oils, from geologically oldest to youngest, are as follows (numerical ages from Palmer, 1983): Oklahoma/Devonian (408–360 Ma), Texas and Wyoming/Permian (286–245 Ma), Florida/Lower Cretaceous (144–97 Ma), Venezuela/Upper Cretaceous (97–66 Ma), and California/Tertiary (66–1.6 Ma). Lead isotopic results and model ages (determined using the crustal lead evolution model of Stacey and Kramers, 1975) for each suite of crude oils are shown in Figure 3. Average crustal lead growth in ^{206}Pb/^{207}Pb and ^{206}Pb/^{204}Pb is also depicted in Figure 3 for the Phanerozoic (545 Ma to the present; average crustal Pb growth line; Stacey and Kramers, 1975). For reference, analytical errors in the lead isotopic ratios of approximately $\pm 0.1\%$ at the 95% confidence level yield errors in the model ages (discussed later here) of approximately ± 20 Ma.

The observed increase in the crude oil's lead isotopic ratios as the geologic age of the crude oil source rock decreases, and clustering of the data around the average crustal Pb growth line is consistent with the generation of radiogenic lead by uranium decay in crustal reservoirs. Crude oil lead model ages or ranges of ages are in excellent agreement with the known age of each crude oil's source rock ($R^2 = 0.994$). Lead isotopic model ages for each crude oil are constrained to a geologic period, a potential improvement over techniques based on biomarkers (Holba et al., 1998; Moldowan et al., 1994; Peters and Moldowan, 1993). There are some observations and discrepancies inherent in the results shown in Figure 3 that need to be addressed.

The Tertiary-aged crude oils from California (Tca) yield model ages that are, with one exception, in agreement with the age of their source rock, the Miocene Monterey Formation. The model ages range from 5 to 26 Ma, initially suggesting that an age resolution approaching that of an epoch rather than period (e.g., Miocene vs. Tertiary) may sometimes be possible. However, when one factors in the ± 20 Ma error associated with each lead isotopic model age, constraining each age estimate to that of a specific geologic period is a more conservative, realistic approach. One Tca crude oil, in which the ^{206}Pb/^{207}Pb and ^{206}Pb/^{204}Pb ratios are 1.1895 and 18.530, respectively, yields an anomalous Cretaceous age of 88 Ma. Organic geochemical data for this crude oil from the San Joaquin Valley indicate that the lighter, more water-soluble alkanes have been removed via interactions with groundwater being recharged in the Cretaceous-age Sierra Nevada foothills. The anomalously old age most likely results from the incorporation of lead by the crude oil during degradation by groundwater whose source of lead is the Cretaceous Sierra Nevada Batholith.

The Cretaceous-age crude oils from both Florida and Venezuela (LKfl and Ukvnz, respectively, in Fig. 3) yield lead model ages ranging from 91 to 124 Ma, which are consistent with those of the Cretaceous, 65 to 144 Ma (Palmer, 1983). Similarly, the Permian crude oils from Texas (Ptx, 284–292 Ma) and Wyoming (Pwy, 257–274 Ma) yield ages consistent with those of the Permian, which range 245–286 Ma. Note that the lead isotope ratios and resultant lead model ages of crude oils originating from source rocks of the same geologic age can be similar (Fig. 3), even though

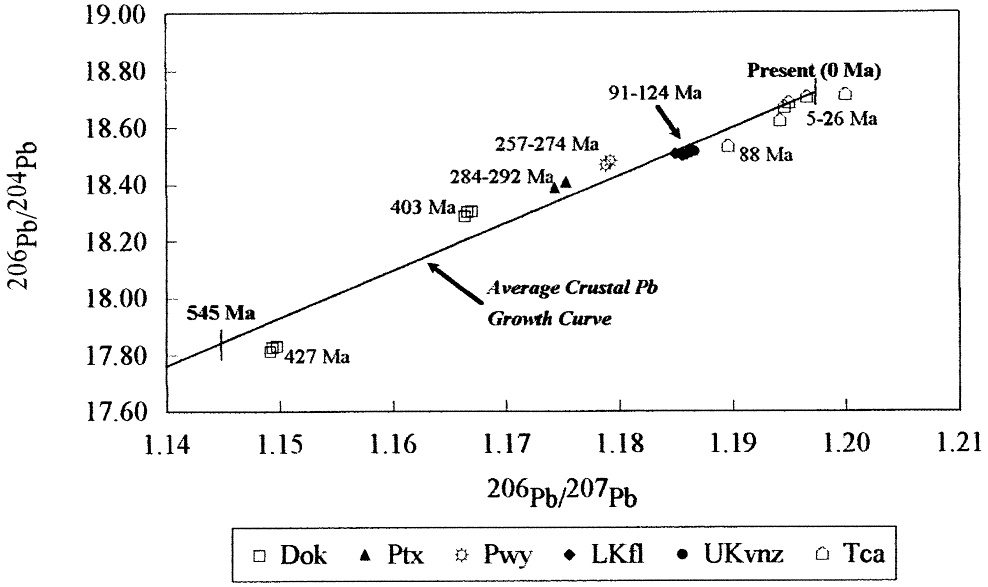

FIGURE 3: Lead isotopic discrimination diagram and resultant lead model ages in millions of years (Ma) for crude oils of known geologic age from various geographic locations: Devonian/OK (Dok); Permian/Texas (Ptx); Permian/Wyoming (Pwy); Lower Cretaceous/Florida (LKfl); Upper Cretaceous/Venezuela (Ukvnz); Tertiary/California (Tca). The average crustal Pb growth line is based on the crustal lead growth model proposed by Stacey and Kramers (1975).

they are located in oil fields that are geographically separated. This occurs when crude oils of the same geologic age evolve lead isotopes in crustal reservoirs with similar geochemical characteristics (e.g., similar uranium concentrations and U/Pb ratios).

The Devonian crude oils from Oklahoma (Dok), sampled from different oil fields, exemplify the influence that different U/Pb ratios can have on lead isotopic evolution. The lead isotopic data define two clusters ($^{206}Pb/^{207}Pb$, approximately 1.15 and 1.166, respectively; Fig. 3). When errors are considered, the lead model ages of 427 Ma and 403 Ma are similar and consistent with the Devonian age (360–408 Ma; Palmer, 1983) of the source rocks. However, the variation in lead isotopic ratios between these two groups of crude oils arises from differences in the U/Pb or, more specifically, the $^{238}U/^{204}Pb$ ratios of their crustal reservoirs, which range from approximately 9.2 to approximately 10.1 in the older and younger lead model age groups, respectively.

LEAD ISOTOPIC RATIOS OF UNLEADED GASOLINE

Given that the lead isotopic results indicate that crude oils of different geologic age bear distinctive lead isotopic signatures and that the lead isotopic signature of crude oil feedstocks are transferred conservatively to refined products, such as unleaded gasoline, then unleaded gasolines produced from different crude oils or blends of crude oils should also be isotopically distinct. Although this possibility was proposed earlier (Hurst, 2000), lead isotopic analyses of crude oils had not been performed at that time.

In order to expand on the previous work, additional samples of unleaded gasolines were collected between 1997 and 1999 from each of six different manufacturer's service stations; with the exception of MFG #6, each had been sampled between 1993 and 1995 (Fig. 4; MFG #1 to MFG #6). Most samples were collected in southern California, within approximately 100 miles of Los Angeles; unleaded gasoline from MFG #3 and MFG #5 were also sampled in New Jersey and Massachusetts, respectively. Sampling was designed to evaluate random temporal variations among different manufacturer's unleaded gasoline lead isotopic ratios and, when the opportunity presented itself, to compare and contrast the same manufacturer's product in different states.

As observed in Figure 4, although there are lead isotopic similarities among some unleaded gasolines when only one of the lead isotopic ratios is used as a discriminator, significant statistical variations exist among products when both lead isotopic ratios are employed. Although the unleaded gasolines from MFG #2 and MFG #4 exhibit similar ranges in $^{206}Pb/^{204}Pb$ ratios (approximately 18.9–19.2), their $^{206}Pb/^{207}Pb$ ratios do not overlap, differing significantly at their closest values (1.2162 vs. 1.2115, respectively). A similar situation arises between the California unleaded gasolines of MFG #1 and MFG #3, in which the $^{206}Pb/^{207}Pb$ ratios overlap slightly but in which the $^{206}Pb/^{204}Pb$ ratios, for a given $^{206}Pb/^{207}Pb$ ratio, exhibit differences of approximately 0.1. In each case, the differences exceed the 95% confidence level error in $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{204}Pb$ ratios by an order of magnitude (±0.0004 and 0.008, respectively).

The similarity in the lead isotopic ratios of each manufacturer's unleaded gasoline over time and in two cases (e.g.,

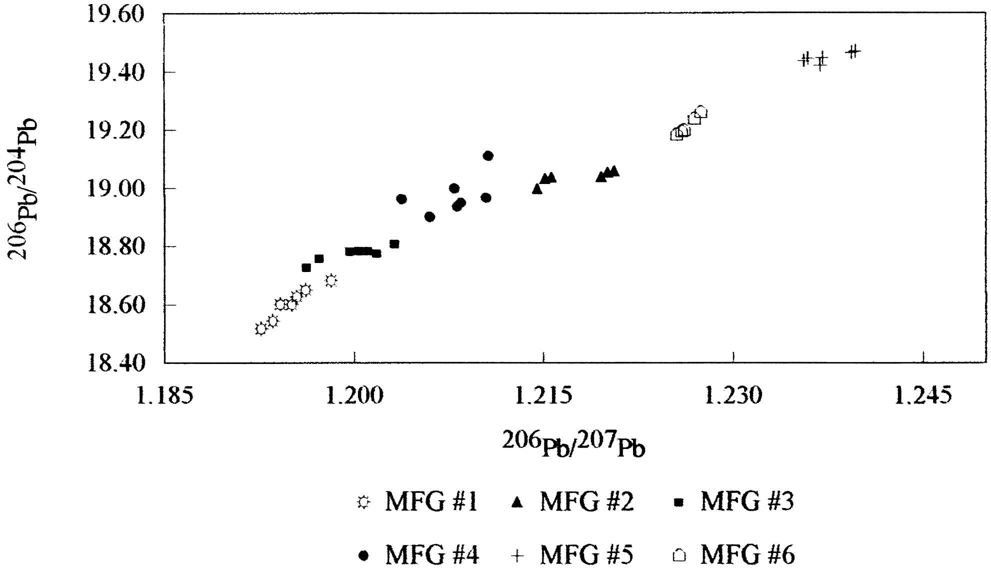

FIGURE 4: Lead isotopic discrimination diagram for unleaded gasolines.

MFG #3 and #5) in different states suggests that domestic refineries have longer term commitments to particular crude oil stocks and refining techniques in the production of unleaded gasolines. If this were not the case, the lead isotopic ratios of a specific manufacturer's unleaded gasoline would not be expected to define the relatively tight clusters observed in Figure 4. The observed lead isotopic range of unleaded gasolines is consistent with the known production of unleaded gasoline from crude oil feedstocks derived by refining Cretaceous–Tertiary age crude oils ($^{206}Pb/^{207}Pb$, approximately 1.185 to 1.195) and blending the product, in varying degrees, with more radiogenic North Slope crudes ($^{206}Pb/^{207}Pb > 1.215$).

The results indicate that statistically significant lead isotopic variations exist among different manufacturer's unleaded gasolines. Hence, on a site- and time-specific basis, these variations afford the opportunity to discriminate among sources of accidental releases of unleaded gasoline into the environment.

CONCLUSIONS ●

High-precision lead isotope ratio analyses are possible on a wide variety of hydrocarbons typically considered to be devoid of lead. However, although processing of these samples, particularly kerogens and crude oils, can be complex and time consuming, lead isotopic analyses of these hydrocarbons can provide age-sensitive, genetic data pertinent to petroleum production, such as identifying the possible age of the source rock from which the petroleum was derived. The results also indicate that lead isotopic ratios of kerogen are carried conservatively to crude oils during catagenesis and from crude oils to unleaded gasolines during refining.

The systematic increase in crude oil lead isotopic ratios over geologic time is the result of the radioactive decay of uranium isotopes. As a result, lead isotope analyses of crude oils can be used, at least in cases in which geologic histories of the crude oil are straightforward, like those of stratiform ore minerals to produce lead model ages to estimate the age of the crude oil source rock. The variations in lead isotopic ratios of crude oils are passed on conservatively during refining to unleaded gasolines, producing significant differences in lead isotopic ratios among manufacturer's refined products, providing a method of evaluating potential sources of unleaded gasoline released accidentally into the environment.

The potential application of lead isotopes to more geologically complex situations involving petroleum generation should be addressed. Furthermore, the results suggest that lead isotopic analyses of crude oils, if developed, may allow cogenetic crude oils to be dated in a manner similar to that possible for rocks of the earth's crust and mantle, at precisions exceeding those currently possible.

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