Lead Isotopes as Age-sensitive Genetic Markers in Hydrocarbons. 3. Leaded Gasoline, 1923–1990 (ALAS Model)

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ABSTRACT ●

The anthropogenic lead archaeostratigraphy (ALAS) model) uses measured lead isotope ratios of documented gasoline releases as preserved in a variety of matrices (product, soils, water) to accurately estimate the year of the release. ALAS is unique in that it is the only model for which historical data (i.e., U.S. lead production figures) are available that allow the nature of the calibration curve to be modeled and calculated for time intervals where calibration samples are scarce (pre-1960). Independent modeling of the data also allows one to evaluate the assumption that lead isotope ratios (e.g., $^{206}Pb/^{207}Pb$) of gasoline additives, such as tetraethyllead, closely followed those of average annual U.S. industrial lead. By integrating U.S. lead production figures with lead isotope ratios of domestic, foreign, and recycled sources, $^{206}Pb/^{207}Pb$ ratios of average annual U.S. industrial have been calculated from the year lead additives were first introduced, 1923, through 1990, which for practical purposes marks the end of the leaded gasoline era. The calculated $^{206}Pb/^{207}Pb$ ratios are in excellent agreement with those of ALAS model calibration samples between 1923 and 1990 ($R^2 = 0.945$). The results indicate that the production of alkylleads by firms such as Ethyl and DuPont relied on lead purchased from that available on the U.S. market rather than sources that were nonrepresentative of that market. In addition to the ALAS model's utility in estimating the year of gasoline releases, temporal fluctuations and trends observed in the model between 1923 and 1990 provide a series of chronostratigraphic markers, which can be related to variations in U.S. industrial lead sources and, in some instances, historic events during the 20th century.

Key Words: gasoline, age-dating, lead, isotopes, chronostratigraphy

INTRODUCTION ●

Although the combustion and accidental release of gasoline containing alkylleads (e.g., tetraethyllead [TEL]) have resulted in lead pollution on both continental and local scales, gasoline-derived lead preserved in the environment has potential to be used as both a chronometer and strati-

graphic marker of the 20th century during the years when leaded gasolines were prevalent (1923 to ~1990). Previous work by Hurst (2000) demonstrated that systematic increases in the lead isotopic composition (e.g., $^{206}Pb/^{207}Pb$) of gasoline after 1965 could be calibrated and the resultant calibration curve, termed the ALAS model (anthropogenic lead archaeostratigraphy), used to estimate the age of episodic and multiple gasoline releases.

Before the ALAS model, methods used to estimate the age of a gasoline release relied on degradation rates of alkylbenzenes (Odermatt, 1994; Kaplan et al., 1997) and/or using knowledge of time intervals when certain additive formulations were blended with gasoline (Gibbs, 1990, 1993; Bruce and Schmidt, 1994; Stout et al. 1998). Although these methods were convenient, because the gasoline constituents used to estimate the age of a release were routinely analyzed in the course of environmental remediation, critical reviews of these methodologies indicate the accuracy and age resolution is often insufficient (Morrison, 2000a, 2000b). By comparison, age resolution of the ALAS model ranges from ±1 to 2.5 years for releases that occurred between 1965 and 1990 (Hurst, 1996, 2000).

The objective of this article is the extension of the ALAS model to 1923, the year alkylleads were first introduced as antiknock compounds to motor fuel (Robert, 1984). Ideally, this would be accomplished in the same manner the ALAS model was developed, by analyzing samples of well-dated gasoline releases or actual gasoline samples produced between 1923 and 1965. Although acquisition of such samples is difficult, five have been identified and analyzed for this purpose.

To fill in the gaps where calibration samples are not available, a second approach was used involving the calculation of $^{206}Pb/^{207}Pb$ ratios of the ALAS model by assuming gasoline lead isotope ratios follow those of the annual average U.S. industrial lead isotopic signature. The $^{206}Pb/^{207}Pb$ ratios of the latter can be modeled by integrating published lead production data (U.S. Bureau of Mines, 1920–1992) with lead isotope ratios of ore sources published in the literature (Doe, 1970; Doe and Deleveaux, 1972; Stacey and Kramers, 1975; Faure, 1986). If $^{206}Pb/^{207}Pb$ ratios of calcu-

lated U.S. industrial lead are in accord with those observed in ALAS model calibration samples (i.e., leaded gasoline), it implies that major producers of TEL purchased lead from the average annual U.S. market and that the calculated values are representative of the ALAS model, allowing the calibration to be accurately extended back in time.

Statistically, there are ∼125 data points defining the ALAS model calibration curve, which for the sake of brevity and due to their restricted $^{206}Pb/^{207}Pb$ ratios are averaged for each year data exist and compared with the calculated value for that year. The maximum age resolution of the ALAS model is 1 year; hence, attempts to evaluate shorter term fluctuations would not be meaningful. The ALAS model is unique, being the only method of estimating the age of a gasoline release for which published historical data exist from which the nature of the calibration curve can be modeled.

LEAD ISOTOPIC EVOLUTION OF ORES

There are four naturally occurring stable isotopes of lead (Pb), three of which are radiogenic, that is, their abundances increase over time due to the radioactive decay of either uranium (U) or thorium (Th) isotopes. The three radiogenic Pb isotopes, their radioactive parent nuclides, and half-lives ($t_{1/2}$) given in billions of years (Ga) are as follows: ^{208}Pb-^{232}Th ($t_{1/2}$ = 14.01 Ga), ^{207}Pb-^{235}U ($t_{1/2}$ = 0.7038 Ga), and ^{206}Pb-^{238}U ($t_{1/2}$ = 4.468 Ga) (Faure, 1986). The fourth isotope of lead, ^{204}Pb, is nonradiogenic, having no radioactive parent nuclide. Although either ^{204}Pb or ^{206}Pb can be used as a reference isotope (i.e., analytical results reported as $^{206}Pb/^{204}Pb$ and/or $^{206}Pb/^{207}Pb$ ratios), most environmental studies use the latter ratio for comparisons. Despite the long half-lives of U and Th isotopes, high crustal U/Pb and Th/Pb ratios have resulted in increases of ∼30% in $^{206}Pb/^{207}Pb$ over 4.6 Ga of Earth history (Stacey and Kramers, 1975).

The common ore of lead used in the production of alkyllead is galena (PbS), which contains trace quantities of uranium and thorium relative to ∼865,000 ppm Pb. As a result, once galena is formed during a mineralization event in the crust, its lead isotopic evolution ceases because U and Th concentrations are virtually zero. Hence, galenas that are geologically older generally have lower less radiogenic lead isotope ratios. One exception, however, are ores derived from crustal sources enriched in U and Th, such as the Mississippi Valley type (MVT) ores discussed below.

Major sources of lead used in the production of alkyl-leads, such as TEL, include ores from Australia, Canada, South Africa, Peru, Chile, Mexico, and the former Yugoslavia; domestic sources include lead deposits found in Idaho, Colorado, Utah, Arizona, California, and the Mississippi Valley (U.S. Bureau of Mines Mineral Yearbooks, 1920–1992). Geologic ages of these ore deposits are diverse, ranging from the early Precambrian Era (∼2.5–3.5 Ga) to the

early Tertiary Period of the Cenozoic Era (30–65 million years) (Doe, 1970; Faure, 1986). The $^{206}Pb/^{207}Pb$ ratios of the early Precambrian-age galenas from Australia, Canada, South Africa, and Idaho range from 1.00 to 1.15, whereas those of Tertiary-age galenas from Peru, Chile, Mexico, and Yugoslavia average ∼1.20 (Doe, 1970; Chow et al., 1975).

The MVT lead deposits are hosted in Paleozoic (245–570 million years) carbonate rocks and are referred to as "anomalous leads" (Doe, 1970; Doe and Deleveaux, 1972). Lead isotope ratios of these ores are extremely radiogenic given their geologic age, with $^{206}Pb/^{207}Pb$ ratios of some ores exceeding 1.30 (average ≈ 1.28). The systematic increased reliance of the U.S. lead industry on lead from MVT sources was proposed as the reason for the observed increases in gasoline lead isotope ratios beginning circa 1968 as first observed in southern California marine sediments (Ng and Patterson, 1982) and corroborated by the ALAS model (Hurst, 1996, 2000).

ANTHROPOGENIC LEAD ISOTOPIC RATIOS AND THE ALAS MODEL

Temporal variations in anthropogenic lead isotope ratios are controlled by changes in the sources of lead emitted into the environment. Documented regional variations have been correlated to coal burning (Chow and Earl, 1972) and urbanization of the Great Lakes region, beginning with deforestation and coal combustion circa 1860, ore smelting in 1930, and finally gasoline combustion between 1930 and 1980 (Ritson et al., 1994; Graney et al., 1995). Lead isotopic fluctuations in the anthropogenic component of soils (Erel and Patterson, 1994; Monna et al., 1997), aerosols (U.S.–Canada, Sturges and Barrie, 1987), and polar ice (Boutron et al., 1991, 1994; Rosman et al., 1994) have been attributed to temporal changes in lead input derived from different industrial sources, each source being identified by their unique lead isotopic fingerprint.

Principles of the ALAS Model

Shirahata et al. (1980) and Ng and Patterson (1982) reported rapid temporal increases in $^{206}Pb/^{207}Pb$ ratios of the anthropogenic lead component of terrigenous and marine sediment in southern California, which they believed were related to increasing proportions of MVT lead used in gasoline through the 1970s. Their work, however, focused on global lead pollution and refinements in analytical methods required to deal with sub-ppb levels of lead in samples (Patterson and Settle, 1976, 1987) rather than the development of a chronometer to estimate ages of gasoline releases. In conjunction with work by Chow et al. (1975), these investigations identified gasoline combustion as the major source of lead pollution and demonstrated that lead isotope ratios in sediment were conservative, remaining unaltered by biogeochemical processes in soils.
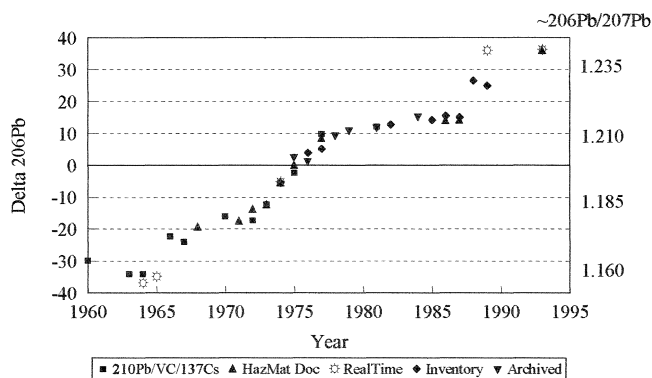
FIGURE 1: (FT)ALAS model calibration curve. (COP Richard W. Hurst, 1997; Hurst, 2000.)
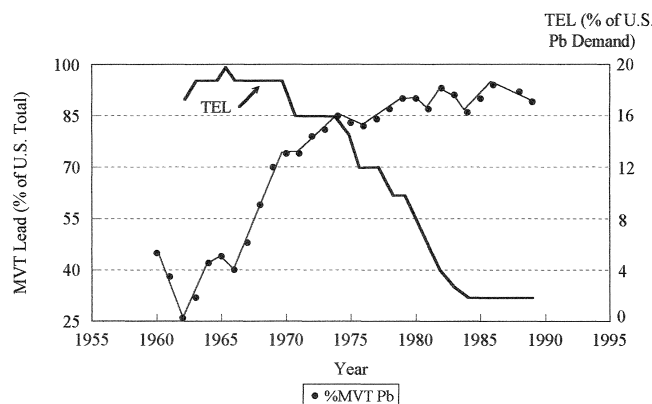

FIGURE 2: (FT)U.S. domestic lead since 1960. Percentage derived from Mississippi Valley type (MVT) sources; tetraethyllead (TEL) production percentage of U.S. lead.

The development of the ALAS model built on these previous investigations by acquiring reliable calibration samples and analyzing them using high precision lead isotopic methods. Sources of samples used to calibrate the ALAS model include university archives (California Institute of Technology, Oregon State University), petroleum industry research lab collections, operating service stations, and sites of documented gasoline releases in the United States (Hurst, 2000). An early version of the ALAS model is shown in Figure 1. Only 41 of ∼125 calibration points can be resolved at the scale of the diagram. The data are presented using a "delta" notation similar to that used in light stable isotope analyses (e.g., C, H, O, N, S; Faure, 1986):

$$\delta^{206}Pb_{ALAS} = 1000$$

$$\frac{[^{206}Pb/^{207}Pb_{SAMPLE} - {}^{206}Pb/^{207}Pb_{STANDARD}]}{^{206}Pb/^{207}Pb_{SAMPLE}}$$

Approximate $^{206}Pb/^{207}Pb$ ratios are presented in Figure 1 for reference.

The morphology of the post-1960 ALAS model curve is controlled by the systematic increase in the use of radiogenic ores from MVT sources, which account for ∼40–45% of domestic lead production pre-1960 but increase to ∼90% by the late 1980s (Figure 2; U.S. Bureau of Mines 1920–1992). The introduction of these highly radiogenic ores to alkyllead production is the controlling factor driving the $\delta^{206}Pb_{ALAS}$ value up from −24 in the late 1960s to values of +12 by 1980. The influence of MVT lead is evident when one compares the morphology of the ALAS calibration curve in Figure 1 with changes in the percentage of MVT ores as a percentage of U.S. lead between 1960 and 1990 (Figure 2). The similarity is striking, with each curve exhibiting steep slopes between ∼1965 and 1980, followed by more moderate slopes through the 1980s.

The lack of scatter in $^{206}Pb/^{207}Pb$ ratios, apparent in the

ALAS model (Figure 1), and applicability throughout the United States are attributed to two factors: a relatively well-mixed domestic lead supply (Ng and Patterson, 1982; Hurst, 2000) and nationwide TEL distribution. Lead on the U.S. market during the 20th century relied heavily on MVT and recycled sources (Figures 2 and 3). Collectively, these two sources have accounted for ∼60–85% of total U.S. industrial lead from 1923 to 1990. As a result, the average lead isotopic composition of lead on the U.S. market has been constrained by the well-mixed, rapidly used, recycled pool (Smith, 1998) and MVT lead whose isotopic range is restricted ($^{206}Pb/^{207}Pb$ ∼1.30 ± 0.02) (Doe, 1970; Faure, 1986).

The distribution of TEL plays a significant role in the geographic applicability of the ALAS model. Major alkyllead manufacturers, Ethyl and DuPont, often collaborated rather than competed on the production and distribution of alkylleads (Robert, 1984), purchasing lead from a U.S. market controlled by the recycled pool and MVT sources. For more than 50 years, through ∼1980, TEL not only accounts for ∼10–25% of lead consumption annually in the United
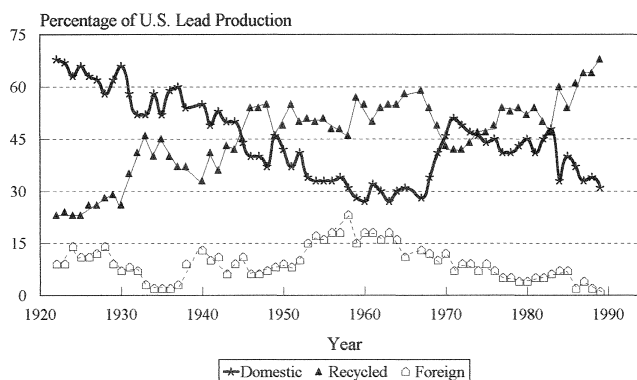

FIGURE 3: (FT)Variation in contributions from domestic, recycled, and foreign sources to U.S. lead production since 1923.

States (Figure 2; U.S. Bureau of Mines 1920–1992), but also is rapidly distributed nationwide, explaining the applicability of the ALAS model throughout the United States (Hurst, 2000).

CALCULATED VERSUS CALIBRATED δ^{206}Pb OF THE ALAS MODEL

By integrating published U.S. Bureau of Mines lead production figures with lead isotopic ratios of ore deposits, the annual average ^{206}Pb/^{207}Pb ratio of U.S. industrial lead, hereafter R_C, can be calculated using the following relationship:

$$R_C = \Sigma\{[X_D\Sigma(A_iR_{Di})] + [X_F\Sigma(B_iR_{Fi})] + [X_RR_R]$$

As discussed next, variables in the calculation of R_C include the weight fractions of U.S. lead derived from domestic, foreign, and recycled lead (X_D, XF, and X_R, respectively) and weight fractions of lead produced by individual states or foreign nations (A_i and B_i, respectively). Average lead isotope ratios of ore deposits, as published in the literature mentioned above, have been used. Once R_C is determined, δ^{206}Pb$_{ALAS}$ (hereafter δ^{206}Pb) is calculated as discussed earlier.

Model Parameters

Weight Fractions of Domestic, Foreign, and Recycled Lead

Yearly production figures are first used to determine the weight fractions of domestic, foreign, and recycled lead (X_D, X_F, and X_R) that contribute to annual U.S. lead production. Note that recycled lead is classified as "old scrap" in government publications. Variations in these three model parameters are presented in Figure 3. Note that foreign lead, derived primarily from Canada, Mexico, and South America, rarely exceeds 15% of U.S. lead production; domestic and recycled lead production figures mirror each other, that is, when domestic ore production drops, it is replaced with recycled lead, and consistently total ~90% of the U.S. lead pool since 1923 when TEL was introduced.

Domestic and foreign contributions can be apportioned further using lead production data from individual states and nations; these weight fractions are referred to as A_i and B_i, respectively. States or foreign nations whose lead accounted for more than 1% of U.S. lead production in any given year have been included in the calculation.

Ore Lead Isotope Ratios

As discussed earlier, ^{206}Pb/^{207}Pb ratios of each domestic and foreign lead ore source (R_{Di} and R_{Fi}, respectively) have been published, allowing the contribution of each of these components to the average lead isotopic ratio of U.S. industrial lead, including TEL, to be modeled. The lead isotopic composition of the recycled lead component (R_R) requires a

knowledge of the time lag of lead recycling and the lead isotopic ratio of the recycled lead.

Time lags associated with recycling of lead have been estimated to range from ~5 to 10 years, being a function of the time scale of lead production and the useful lifetime of products (~3–10 years), such as batteries, which consume lead (Graney, 1994; Graney et al., 1995; International Lead and Zinc Study Group, 1995; Smith, 1998). The efficiency of lead recycling, more than 90%, and the expediency with which old scrap lead is recycled subsequent to the end of a product's useful lifetime, ~1 year, is dramatic (Smith, 1998). Hence, the 5- to 10-year lag times assumed in the calculation of R_R discussed next are a reasonable average range for this model parameter.

To assess the effect on R_C by 5- to 10-year lag times, two calculations were performed using the calculated ^{206}Pb/^{207}Pb of U.S. industrial lead 5 and 10 years before the year R_C was calculated; that is, when calculating the R_C of U.S. industrial lead in 1975, R_R is assigned the calculated value for ^{206}Pb/^{207}Pb of U.S. industrial lead as determined for 1970, then for 1965, producing two results for R_C, which take into account lag times of recycling of 5 and 10 years, respectively. As will be observed, calculated values of R_C using a 5- versus a 10-year lag time are not significantly different except for the time period between 1980 and 1986.

Uncertainty in R_C and δ^{206}Pb

Variations in average ^{206}Pb/^{207}Pb ratios of ore deposits produce average uncertainties in R_C ranging from ±0.003 (1946 to 1990) to ±0.005 (1923 to 1945); resulting uncertainties in δ^{206}Pb are ±3 to ±4, respectively. The subsequent discussions of temporal variations in δ^{206}Pb are predicated on observed fluctuations in δ^{206}Pb that exceed those of the uncertainties.

U.S. INDUSTRIAL LEAD AND THE ALAS MODEL

Results of the calculations to model the evolution of U.S. industrial lead between 1923 and 1990 are plotted in Figure 4. Relationships between δ^{206}Pb and ^{206}Pb/^{207}Pb ratios are identical to those presented in Figure 1.

Pre-1960 U.S. Industrial versus ALAS Model δ^{206}Pb

Before 1960 the δ^{206}Pb of U.S. industrial lead ranged from ~-20 to -36, with observed fluctuations dependent on the annual input of radiogenic MVT lead, which averages ~43% of annual domestic U.S. lead production before 1960. The recycled lead component, which increases over this same interval, contributes less radiogenic old scrap to annual production. Both factors work to maintain less radio-
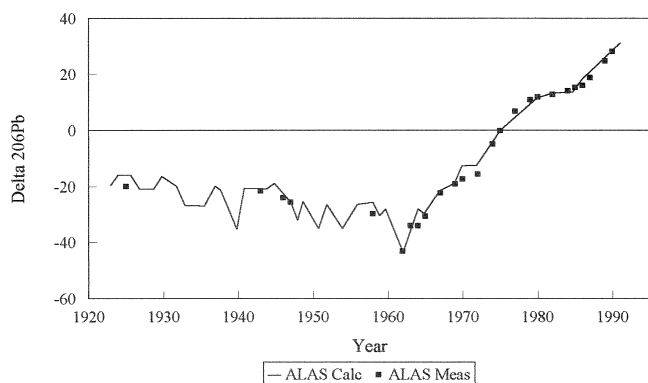
FIGURE 4: (FT)Comparison between measured lead isotopic compositions ($\delta^{206}Pb$) of ALAS calibration samples and those calculated using U.S. Bureau of Mines annual lead production data. For clarity, annual average $\delta^{206}Pb$ values are plotted for calibration samples.

genic $^{206}Pb/^{207}Pb$ ratios and lower values of $\delta^{206}Pb$ for U.S. industrial lead from 1923 to 1960.

It is possible to subdivide 1923 to 1960 into five time intervals, each defined by statistically distinct mean values for $\delta^{206}Pb$. The subdivisions are as follows (errors are 95% confidence levels; note that mean $\delta^{206}Pb$ for 1937–1939 and 1941–1946 are identical):

1923–1933 -18 ± 1.5
1934–1936 -26 ± 0.8
1937–1939 -21 ± 0.8
1940 -36 ± 0.8
1941–1946 -21 ± 0.8
1947–1960 -30 ± 1.5

The post-1933 period is significant because nationwide distribution and market expansion of TEL commences at this time (Robert, 1984).

Five calibration samples identified to date define the ALAS model curve before 1960. Three archived California marine sediments impacted by gasoline lead have ^{210}Pb ages of 1925 ± 3, 1947 ± 2, and 1959 ± 1 (Ng and Patterson, 1982); measured $\delta^{206}Pb$ values for these samples are -19.8, -23.9, and -29.7, respectively. The fourth sample, a leaded gasoline, was recovered from an underground storage tank at a service station that operated from 1941 to 1945 (1943 ± 2) (Oregon Department of Environmental Protection; R. Miller, personal communication); $\delta^{206}Pb$ for this product was determined to be -21.4. The fifth datum point was acquired through Professor Emeritus T.J. Chow (1998, personal communication) and is a recalculation of lead isotope results of 1947 TEL published by Chow et al. (1975). Their analysis, as was common in the early 1970s, did not include corrections for instrumental variations and normalization to isotopic standards. Following current protocols, the analysis of the 1947 TEL was corrected, yielding a value for $\delta^{206}Pb$ of -25.5. The measured $\delta^{206}Pb$ values for these

five calibration sample are in excellent agreement with those calculated for U.S. industrial lead (Figure 4).

The War Years

The time interval from 1937 to 1954, encompassing U.S. involvement in World War II and the Korean War, reflects changes in the utilization of lead for national defense. During 1940, contributions by less radiogenic ore, both foreign and domestic, increase by 25–50%, whereas MVT sources declined (U.S. Bureau of Mines, 1920–1992). The result is an anomalously low value of $\delta^{206}Pb$ in 1940 (~-35) relative to other years where lead ore production is more representative of the times (Figure 4). A portion of lead production records remained confidential in 1940 for national security reasons, leading to the possibility that MVT ores were used by labs developing U.S. thermonuclear capabilities (e.g., Oak Ridge, Tennessee; Los Alamos, New Mexico) and other defense-related products. Similar low values of $\delta^{206}Pb$ during the early 1950s (1951–1955), the Korean War years, reflect a drop in domestic production and increased reliance on less radiogenic recycled lead (Figures 2 and 4).

Post-1960 U.S. Industrial versus ALAS Model $\delta^{206}Pb$

The post-1960 interval is initially marked by a decrease in $\delta^{206}Pb$ to ~-40, which is followed by the steady rapid increase in $\delta^{206}Pb$ to values of $\sim+30$ by 1990. The increased reliance on MVT lead, recycling of old scrap lead that becomes more radiogenic as stockpiles accrue higher proportions of MVT lead, and a gradual decline in contributions from foreign sources of lead contribute to the dramatic increase in $\delta^{206}Pb$ of U.S. industrial lead during this time interval (Figures 2 and 3).

The number of calibration points defining the post-1960 portion of the ALAS model exceeds 100; hence, for brevity comparisons with calculated values of $\delta^{206}Pb$ use average annual values from the ALAS model. The correlation between $\delta^{206}Pb$ values of calculated U.S. industrial lead versus those of the ALAS model from 1960 to 1990 is significant ($R^2 = 0.936$; Figure 4). If the five pre-1960 comparisons are added, the impact on the regression analysis is not statistically different ($R^2 = 0.945$), but their inclusion further supports the conclusion that $\delta^{206}Pb$ values of the ALAS model, and therefore leaded gasoline, followed those of average annual U.S. industrial lead (Hurst, 2000). Average annual $^{206}Pb/^{207}Pb$ ratios of the ALAS model versus R_C agree to better than 0.25%, indicating that alkylleads were manufactured from stores of lead that were representative of the average annual U.S. market rather than from nonrepresentative sources as implied by critics of the model (see Morrison, 2000a, 2000b).

The $^{206}Pb/^{207}Pb$ ratio (R_R) of the recycled lead component and choice of 5- versus 10-year lag times influence calculated values of R_C between 1980 and 1986 due to rapidly increasing $^{206}Pb/^{207}Pb$ ratios of U.S. industrial lead after 1970. Before 1970, and excluding the observed low values of $\delta^{206}Pb$ (1940, 1951–1955, 1962), the $\delta^{206}Pb$ of U.S. industrial lead is relatively uniform, averaging -23 ± 2; hence, the choice of a 5- versus a 10-year lag time in recycling has a negligible impact on R_C because R_R is almost constant.

Between 1980 and 1990 the sharp increase in MVT lead use prevalent through the 1970s leveled off, but MVT ores accounted for more than 85% of the total domestic U.S. lead (Figure 2). From 1980 to 1986 the lag time for recycled lead impacted the value of R_C because lead recycled from the late 1970s was more radiogenic than lead in the early 1970s (5- versus 10-year lag times, respectively). As a result, each R_C calculated using a 5-year lag time exceeded that based on a 10-year lag time by 0.5% to 0.8%. However, the different lag times do not degrade the agreement between calculated values of R_C relative to those of the ALAS model, which average less than 0.3% for the 5-year and less than 0.6% for the 10-year lag times. Overall, the average $\delta^{206}Pb$ for U.S. industrial lead between 1980 and 1986 calculated using 5- and 10-year lag times is $+12.2$, in excellent agreement with the average $\delta^{206}Pb$ of ALAS model calibration samples ($+12.3$; Figure 4).

Between 1986 and 1990, as the era of leaded gasoline approached its end, annual $\delta^{206}Pb$ values of calculated U.S. industrial lead and those of the ALAS model were virtually identical and increased (Figure 4). As was the case for the pre-1970 recycled lead component, $\delta^{206}Pb$ was relatively uniform in the early 1980s ($+13 \pm 2$); hence, the influence of 5- versus 10-year lag times on R_C between 1986 and 1990 is negligible. The large inputs of radiogenic lead from both the recycled pool and MVT sources cause $\delta^{206}Pb$ to increase, approaching $\sim +30$ by 1990.

$\delta^{206}Pb$ Minima

In addition to the observed minima in $\delta^{206}Pb$ during the war years, 1940 and 1951–1955, another occurred in 1962 ($\delta^{206}Pb \sim -40$). This minimum is documented not only in calculated values of $\delta^{206}Pb$, but also by ALAS model calibration samples (Figure 4).

This minimum in 1962 can be linked directly to a worker's strike at the largest lead mine in Missouri. Although production of MVT ores ceases for months, production of less radiogenic lead from Idaho increases dramatically to fill market needs (U.S. Bureau of Mines, 1920–1992). As is evident in Figure 4, the decrease in $\delta^{206}Pb$ due to the influx of less radiogenic lead was immediately apparent. The response of the U.S. lead market to the drop in radiogenic MVT ore production in 1962 was rapid, as evidenced by the precipitous decrease in $\delta^{206}Pb$. This rapid

response plus observed concordance between $\delta^{206}Pb$ of calculated U.S. industrial lead and ALAS model calibration samples between 1961 and 1963 countermands concerns that alkylleads were occasionally manufactured using large quantities of lead that were nonrepresentative of that available on the U.S. market, thereby increasing the uncertainty and compromising the accuracy of the ALAS model. Rather, the data support earlier conclusions by Hurst (1996, 2000), that the occasional use of large quantities of lead from sources that were nonrepresentative of the average U.S. market did not occur because they would have either been recorded as major fluctuations in $\delta^{206}Pb$ as observed in 1962 or led to far more scatter than is observed.

The years in which $\delta^{206}Pb$ exhibit minima, 1940, 1951–1955, and 1961–1963, coincide with those associated with the development and atmospheric testing of thermonuclear devices; perhaps coincidentally, during the latter two periods dramatic increases in atmospheric concentrations of radioactive fallout products also occurred (e.g., ^3H, tritium, and ^{137}Cs) (Faure, 1986; Geyh and Schleicher, 1990). Although the relationship between lead and thermonuclear devices may be more than coincidental given military applications of lead, temporal variations observed in $\delta^{206}Pb$ from 1923 to 1990 provided a series of chronostratigraphic markers with each minimum or trend directly relatable to variations in U.S. industrial lead sources, which in turn may be tied to historic events of the 20th century. Where detailed data permit, the ALAS model should and is being compared with other anthropogenic signals to evaluate the possible existence of international or global archaeostratigraphic markers.

CONCLUSIONS ●

Annual $^{206}Pb/^{207}Pb$ ratios and resultant $\delta^{206}Pb$ values, calculated from U.S. lead production figures and lead isotope ratios of ores, are in excellent agreement and exhibit significant correlations with those of ALAS model calibration samples between 1923 and 1990. Thus, on the time scale of 1 year, the maximum resolution of the ALAS model, and time frame of the comparisons discussed herein, the results indicate that the production of alkylleads by firms such as Ethyl and DuPont relied on lead acquired from the average U.S. market rather than from sources that were nonrepresentative of that market, as has been suggested in critical reviews of the ALAS model. Despite the gradual phasing out of lead additives in gasoline in the mid-1970s (Gibbs, 1990, 1993), a significant fraction of lead production in the U.S. went into the manufacturing of TEL until ~ 1980 (U.S. Bureau of Mines Yearbooks, 1920–1992).

Before ~ 1960, $\delta^{206}Pb$ values of five ALAS model calibration samples are concordant with those calculated form U.S. lead production figures, both being low and relatively uniform, averaging ~ -23. Major decreases are observed

in δ^{206}Pb circa 1940 and 1951–1955, responding primarily to declining inputs from radiogenic MVT ores to the U.S. lead market, which may in turn be related to the use of lead in military applications.

Subsequent to ~1965, δ^{206}Pb values of the ALAS model began a steady increase from ~−40 observed circa 1962 to ~+30 by 1990 as the era of leaded gasoline approaches its end. During this time interval, δ^{206}Pb values of ALAS model calibration samples and those calculated from U.S. industrial lead production are significantly correlated ($R^2 = 0.936$) and in excellent agreement; both values increased due to the systematic increased reliance upon MVT ores by the U.S. lead industry. Both calculated and ALAS model calibration sample values of δ^{206}Pb exhibit a prominent decline in 1962, rapidly reflecting the removal of radiogenic lead from the U.S. market due to a worker's strike at the largest lead mine in Missouri that same year.

The results of this work countermand suggestions that alkyllead manufacturers used lead that was nonrepresentative of that available on the U.S. market, which, if correct, could compromise the accuracy of the ALAS model. The modeling supports conclusions that the routine use of nonrepresentative lead by Ethyl and DuPont would have resulted in significant lead isotopic variability and scatter in the model, neither of which is observed (Hurst, 1996, 2000).

Fluctuations and trends observed in δ^{206}Pb from 1920 to 1990 provide a series of chronostratigraphic markers, which can be related to variations in U.S. industrial lead sources and, in some instances, historic events during the 20th century. The ALAS model is being compared with other anthropogenic signals to evaluate the possible existence of international or global archaeostratigraphic markers.

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