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Isotopic Characterization of Various Brands of Corroding Grade Refined Lead Metal

M. B. Rabinowitz

Marine Biological Laboratory, 7 MBL Street, Woods Hole, MA 02543, USA

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Much of contemporary American environmental lead contamination and human exposure is the result of the past manufacturing and use of lead-based paint pigments many decades ago. As part of an effort to isotopically characterize various historical, commercially important brands of lead pigments, we sought first to identify any systematic variations among the brands of refined lead metal (Kaiser 1998). Knowing the manufacturer of a paint pigment would encourage efforts to make the polluter pay for damages and remediation. Lead ores were smelted and refined into metallic lead, the main ingredient for making white lead carbonate, the principle lead pigment (Heckel 1934). Thus, lead ingots could be considered a necessary precursor of lead paint. To this purpose, we sought to analyze as many different brands as possible of refined lead metal or contaminated soils or slag obtained from nearby smelter or refinery sites. From these samples, together with historical records of the sources of lead ores used by the various smelters, a comprehensive picture of the isotopic patterns among the brands would emerge.

Lead was smelted and refined by several different companies, and each applied its own distinctive brand name or hallmark to each ingot indicating its origin and purity (Ingalls 1908). For a given quality grade of lead, the different brands were physically and chemically equivalent. By 1950, for example, 14 different brands of corroding grade lead made by eight different American companies were approved for delivery against Chicago Commodity Exchange contracts (US Bur Mines 1951). Despite this chemical uniformity, brand names, stamped or cast into each ingot, were used for marketing, and preferences were given by certain manufacturers of lead products to their favorite brand of refined lead, even when other brands were available closer (Crane 1927).

Lead metal was made from lead ore, crushed and concentrated at a mill near the mines, and smelted in a blast furnace, also usually nearby, yielding bullion, which required additional refining to make ingots of a marketable grade of lead. The refining took place at either the same factory, as was the practice in Missouri (Isbel 1947) and Idaho (Aiken 1993), or at a separate plant many hundreds of miles away, usually owned by the same company (Neeham and Luff 1948).

Because several different mining districts produced lead ore, and the geological age of that ore body determines the relative abundance of the four stable isotopes of lead, the source ores of the refined lead determine the metal's isotopic composition. Table 1 summarizes the lead 206/204 abundance ratio and annual tonnage of major and minor ore mining districts, using the decade spanning the years of peak production. The tonnage data are from Pehrson and Meyer (1939). The isotopic ratios were derived from Doe and Stacey (1974).

Table 1. Geographic sources of American lead ores and their isotope ratios.

District	Annual Output Kilotons/yr 1925-1935	Range of lead 206/204 ratios
Idaho	123	16.2-17.0
Montana	22	17.3-18.4
Utah	167	17.9-18.6
Colorado	22	17.9-18.2
Kansas/Oklahoma /Missouri	98	20.7-22.7
South East Missouri	208	20.0-21.5
Mexico: Coahuila, Chihuahua, and San Luis Potosi	205	18.5-18.9

Although many regions contributed to domestic lead production, only four (Idaho, Utah, Southeast Missouri and the Southwest Missouri Tri-State) accounted for 89 percent of total domestic production. Nevada and Arizona each produced less than 12 kilotons annually. New Mexico, California, and the Illinois/Iowa/Wisconsin area were less than 4 kilotons each. Mexico, taken as a whole, was also a major source.

The isotopic values fall roughly into four bands: a low, narrow Idaho value below 17; the other Western mountain states with a wider range of 17.3 to 18.6; Mexico with a narrow, higher value; and the much higher and wider range of values from the Mississippi Valley districts. Trail, British Columbia, was also a large lead mining operation, but little of that product entered America. Rather, it went to Europe and the Orient under existing Commonwealth commercial arrangements. Some Peruvian, Argentinian, and Australian ores were also imported, but these were of minor importance. The recovery and refining of scrap lead from batteries and cables was a major part of the lead industry, but this material was processed in separate facilities to make new batteries (Eckel et al. 2001). Scrap lead was not used in making purer grades of refined lead (Parsons 1928).

The eleven major brands of corroding lead sold in the United States from 1925 to 1950 are shown Table 2. Some larger companies assigned a different brand name to each refinery. For example, American Smelting and Refining (ASARCO) sold Selby, Omaha&Grant, Perth Amboy, and Alton brands of corroding grade lead. The number of active primary smelters and refineries in the United States declined from 51 in 1910, to 23 in 1930, to 15 in 1950 and only 3 active in 1989 (Darling 1989).

Table 2. Major brands of corroding grade refined lead metal sold in the United States during the 1940's.

Brand Name and Years Produced	Refinery Location	Company	Major Sources of Ore or Bullion
Alton 1902-1960	Federal IL	ASARCO	Southeast MO
Bunker Hill 1917-1981	Bradley ID	Bunker Hill & Sullivan	ID
CMFyAM 1923-1947	Monterrey and Zimapan MEX	American Metal Cia Min y Fund	Mexico
Doe Run 1902-	Herculaneum MO	St Joseph	Southeast MO
Eagle-Picher 1902-1964	Galena KS Joplin MO	Eagle-Picher	Southwest MO, OK and KS
ILR 1911-1946	East Chicago IN	International (Anaconda)	Tooele UT
Omaha&Grant 1899-1976	Omaha NE	ASARCO	Murray UT, Leadville CO, and Mexico via El Paso TX
Perth Amboy 1910-1964	Perth Amboy NJ	ASARCO	Mexico via Monterrey and El Paso et al.
St Louis 1904-1938	Collinsville IL	National Lead (NL)	Southeast MO
Selby 1898-1970	Selby CA	ASARCO	UT, ID, AZ, CA, NV et al. and foreign
USSElectro 1910-1972	Grasselli IN	US Metal Refining	Midvale UT

In this table only the major sources of ore are listed. Bunker Hill's smelter in Bradley, although situated on the major Idaho deposits, bought some ore from Canada, South America, Australia, and other Western States (Mote and den Hartog 1950). Also, lead from Anaconda's Montana copper refinery was sent to Bunker Hill's lead refinery. The smelter in Selby received ore concentrates from a wide variety of Western and foreign mines, and their relative importance varied over its many decades. So, the Selby brand's isotopic composition could be expected to vary with the sources (Rabinowitz and Wetherill 1972). The Herculaneum smelter was largely dependent on local ores, but it received some ores from Argentina, New York, and elsewhere (Isbell 1947). In other cases, the sources of the ore was more consistent; International's East Chicago refinery got bullion from its Utah smelter (Elton and Sackett 1929), Midvale was US Smelting's Indiana refinery source (Nelson and Whitecotton 1948), and the large Federal and Collinsville refineries used Missouri ores (Ellis 1926). Eagle-Picher relied on local ores (Hallows 1943). Generally, smelters depended on more distant ores only as local ore bodies were depleted, later in the smelter's lifetime.

Three main grades of lead were marketed, each meeting definite chemical standards of purity set by the American Society for Testing Materials, based on the maximum amount of allowed impurities, especially bismuth, copper, zinc, antimony and silver (Pehrson 1932). Smelting of the ores from the Mississippi Valley produced "Soft Lead" with little or no refining, which could be shaped easily by rolling or hammering, and was also alloyed to make bearing alloys, babbitt, and type metal. "Chemical Lead", which was made into sheets and pipes to be used in contact with acids, had traces of copper, making it harder. "Corroding Lead" was double-refined and commanded a premium price, because lead to be converted into white pigments could contain only traces of impurities for the paint to be satisfactory. The major use of this grade was to corrode into white lead carbonate, the paramount lead pigment (Rose 1942). One minor exception was white lead sulfate pigment, which was typically made directly from the smoke of roasting the highest grade ores, rather than corroding metal (Meyer and Mitchell 1938). This study investigated the isotopic composition of various brands of refined lead metal to see if they resembled their presumed source ores.

MATERIALS AND METHODS

We sought to obtain as many appropriate samples as possible. Since the peak of the American lead industry in the late 1920's, its decline in the 1950's, and further shrinkage, the passage of time has made getting every desirable sample impossible. Many old smelter sites have been re-developed. Of the 11 major brands of refined lead used in the 1940's, suitable ingot samples could be located for only 4 brands. Some were purchased from shops in the areas of historical activity and from internet auction sites. Museums held some. For ingot samples, wiping filter paper firmly over the surface provided sufficient material, since only microgram quantities are needed.

For 4 additional brands, soil and slag samples from the smelter or refinery, very high in lead content, were recovered to characterize those brands. Soil samples were taken from the top 2 cm, obtaining typically five 20 gram samples from an area of one square meter using a plastic scoop, choosing spots with minimal vegetation or influence by any nearby structure or road. Slag was recovered with a hammer. These samples were dried, hand crushed, and coarsely sieved with a 18 mesh per inch stainless steel screen. For all sample types, the lead was extracted using ten percent nitric acid at room temperature for 2 days. Aliquots were diluted for atomic absorption flame spectrophotometry with background correction to determine the solutions' lead concentrations. These were further diluted for isotopic analysis with a single collector, sector field mass spectrometer using plasma ionization (SFICPMS, Finnigan MAT model Element I). All three isotope ratios were measured and reported, but often only the 206/204 ratio is shown, because the three ratios all covary so strongly. Quality assurance was addressed using NIST standard 981 was analyzed along with each batch of samples. Ten assays gave a mean value of 16.94 (std dev 0.01), indistinguishable from the certified value. Also, 3 samples were analyzed in duplicate. The analytical uncertainty was much less than the range of vales encountered, 0.01 for 206/204, compared with values ranging from 16 to 21.

RESULTS AND DISCUSSION

Values for the lead concentration and isotope ratios for metal, soil, and slag samples are shown in Table 3. Those marked * are from Rabinowitz and Wetherill (1972). Generally, the Bunker Hill samples are distinct and reflect Idaho ores. Ingots cast 20 years apart (1917 and 1937) are nearly the same, but the more recent ingots have some lead from outside the district, likely Montana. At the other extreme are the Doe Run and Eagle-Picher samples, which appear indistinguishable (Mann-Whitney U test for differences in medians, p value 0.5). The two Doe Run metal samples are very close, although they were collected decades apart and measured in different laboratories. The two Utah brands, USS and ILR are similar and intermediate. The Omaha&Grant, indeed, looks like a mixture of Western and Mexican lead, with Perth Amboy having yet more Mexican lead, consistent with the historical record. It is methodologically reassuring that the soil and slag samples resemble the ingots in two brands where both were available, Doe Run and Eagle-Picher (Mann Whitney p 0.4). Selby metal is indistinct and likely variable. A summary of the predicted and observed values is provided in Table 4.

Unfortunately, samples of Alton from ASARCO's Federal smelter, the world's largest for many years, or the National Lead (NL) nearby Collinsville smelter were not available. They would likely resemble Doe Run samples, because they all originated from Eastern Missouri ore deposits. Similarly, no CMFyAM samples could be found, but those values could be imputed from published values of their Mexican ores. Generally, the observed value was consistent with the value predicted from historical records.

Table 3. Isotope ratios among various brands from samples of ingots, slags and soils.

Brand Name	Sample	206/204	206/207	206/208
Bunker Hill	ingot early 1950's, Wallace pawn shop	17.7	1.14	0.47
	ingot common lead, Wallace Museum	17.1	1.10	0.46
	ingot cast 1937, 99.99+%, Wallace Museum	16.5	1.07	0.46
	ingot cast 1917, 99.93+%, Wallace Museum	16.6	1.07	0.46
Doe Run	80 lb ingot Tri-State Museum	20.8	1.34	0.53
	ingot 99.9995% *	20.7	1.34	0.53
	Herculaneum fan lint 72,000ppm *	20.0	1.31	0.52
	Herculaneum soil 3,600 ppm*	20.2	1.32	0.53
Eagle-Picher	ingot from Dearing KS Country Store	19.2	1.22	0.50
	ingot with Eagle and Bucket	20.3	1.29	0.51
	ingot, Tri-State Museum	21.6	1.36	0.53
	80 lb ingot, Tri-State Museum	18.9	1.21	0.49
	slag Cardin OK >20,000ppm	19.8	1.26	0.51
	slag Galena KS >20,000ppm	21.6	1.35	0.55
	mill chat Cardin OK 5,100ppm	22.1	1.39	0.54
	soil Joplin Porter&B St 1,100 ppm	21.0	1.32	0.52
	soil Joplin Murphy Blvd 16,000ppm	20.8	1.38	0.52
	soil Joplin Inger&Gray St 1,600ppm	20.8	1.33	0.52
	soil Galena KS smelter 6,100ppm	20.4	1.28	0.51
ILR	slag Tooele UT smelter 21,700 ppm	17.9	1.15	0.47
Omaha&Grant	80 lb ingot Galena KS Museum	18.1	1.16	0.47
Perth Amboy	soil refinery 2,850 ppm	18.4	1.18	0.48
	soil refinery 2,900 ppm	18.2	1.17	0.48
Selby	metal *	17.5	1.15	0.47
USS Electro	soil Midvale UT smelter 2,385 ppm	17.9	1.15	0.47

Much has changed in the lead industry. Most operations have ceased. Dutch Boy, once a National Lead brand, is now owned by Sherwin-Williams, Bunker Hill became part of Gulf Resources and then closed in 1981, ASARCO was sold to Grupo Mexico in 1999, and Eagle-Picher ceased all lead mining and smelting activity by 1970 and was acquired by Granaria Holdings, a Dutch concern in 1998. Only Doe Run, under new owners, still operates. Of the many companies that made refined lead, only three converted it to white lead: Eagle Picher, NL, and Anaconda. NL was by far the largest, with many plants nationwide. The other makers of white lead, such as Carter, W.P. Fuller, Glidden, and Sherwin Williams were dependent on outside supplies of refined lead. Lead based paints were typically made simply by thinning white lead carbonate paste with linseed oil and turpentine and adding a drier, often a metallic salt of lead, manganese, or cobalt. Tints might be added, perhaps yellow or orange lead chromate, which might be made from other grade of refined lead (Holman 1925). So, the isotopic signature of a single layer of lead paint might be dominated by the corroded lead, but would also include any lead in these other components.

Table 4. Predicted and observed lead isotope ratios.

Brand Name	206/204 Ratio Predicted from Published Sources of Refinery's Ores	206/204 Ratio Mean of Observed Ratio in Metal Ingot or Slag
Alton	20.0 to 21.5	no sample
Bunker Hill	16.5 to 17.0	17.0
CMF	18.5 to 18.9	no sample
Doe Run	20.0 to 21.5	20.4
Eagle Picher	20.7 to 22.7	20.6
ILR	17.9 to 18.6	17.9
Omaha&Grant	17.9 to 18.9	18.1
Perth Amboy	17.9 to 18.9	18.3
StLouis	20.0 to 21.5	no sample
Selby	variable	17.5
USS	17.9 to 18.6	17.9

From these results, the isotopic composition alone could not distinguish each brand uniquely, but systematic differences do exist among some brands. Thus, for a given unknown sample, some brands might be ruled in or out, especially if the value is not mid-range. Despite the passage of many decades, sufficient samples still exist to demonstrate variations among the brands, reflecting the disparate sources of their ores.

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