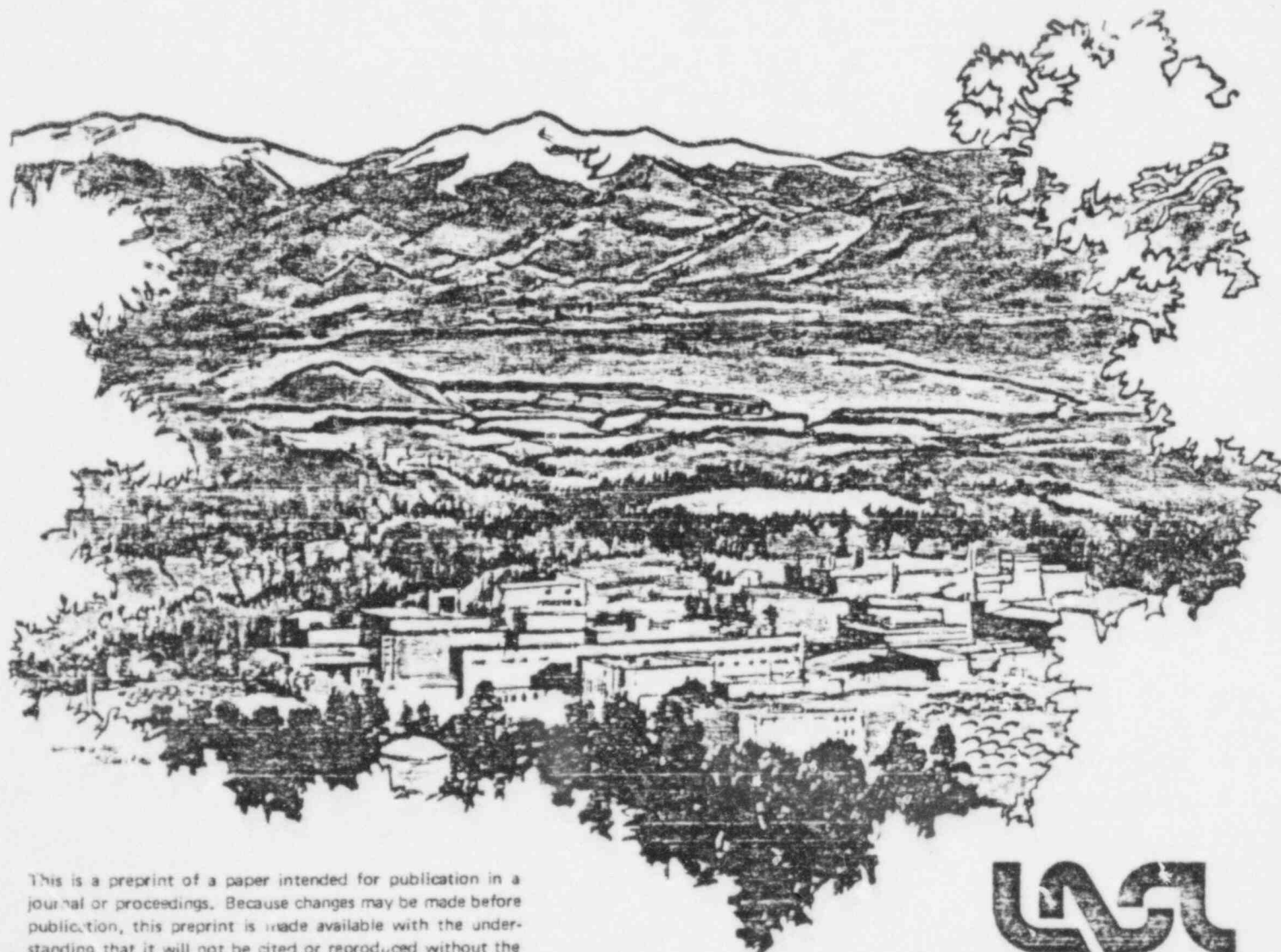


Title: LEAD ISOTOPES AS INDICATORS OF ENVIRONMENTAL CONTAMINATION
FROM THE URANIUM MINING AND MILLING INDUSTRY IN THE GRANTS
MINERAL BELT, NEW MEXICO

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**LEAD ISOTOPES AS INDICATORS OF ENVIRONMENTAL CONTAMINATION
FROM THE URANIUM MINING AND MILLING INDUSTRY
IN THE GRANTS MINERAL BELT, NEW MEXICO**

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The unique isotopic composition of lead from uranium ores can be useful in studying the impact of ore processing effluents on the environment. "Common" lead on the earth's surface is composed of 1.4% ^{204}Pb , 24.1% ^{206}Pb , 22.1% ^{207}Pb , and 52.4% ^{208}Pb . In contrast, lead associated with young uranium ores may contain as much as 95% ^{206}Pb . These extreme differences provide the means to quantitatively evaluate the amount of lead introduced into the environment from the mining and milling of uranium ores by measuring variations of the isotopic composition of lead in environmental samples.

We will discuss the use of Pb isotopes as diagnostic tools in studying the hydrologic transport of materials from U ore dressing plants in the Grants Mineral Belt, New Mexico, USA. Preliminary measurements on effluents intimately associated with processing wastes are consistent with a simple model in which "radiogenic" lead from the ores is mixed with "common" lead from the uncontaminated environments.

**ISOTOPES DE PLOMB EMPLOYES COMME TRACEURS
ENVIRONNEMENTAUX DE L'EXTRACTION DE L'URANIUM ET EFFLUENTS
PROVENANT DE LEUR TRAITEMENT**

La composition isotopique unique du plomb dérivée de minerais d'uranium peut être utile dans l'étude de l'impact des effluents des minerais traités sur l'environnement. Le plomb "commun" à la surface de la terre est composé de 1,4% ^{204}Pb , 24,1% ^{206}Pb , 22,1% ^{207}Pb et 52,4% ^{208}Pb . Par contre, le plomb associé aux minerais jeunes d'uranium peut contenir jusqu'à 95% ^{206}Pb . Ces différences extrêmes produisent les moyens d'évaluer quantitativement le plomb introduit dans l'environnement du à l'extraction et le traitement des minerais d'uranium en mesurant les variations de la composition isotopique du plomb dans des échantillons de l'environnement.

Nous discuterons l'emploi d'isotopes de plomb comme outils diagnostiques dans l'étude du transport hydrologique de matériaux provenant d'usines traitant le minerai d'uranium dans la Zone Minérale de Grants, New Mexico, USA. Des mesures préliminaires sur des effluents intimement associés au traitement de déchets sont consistantes à un modèle simple dans lequel du plomb "radiogénique" provenant des minerais est mélangé au plomb "commun" provenant d'un environnement exempt de contamination.

Work done under the auspices of the U. S. Department of Energy

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INTRODUCTION

Processing of uranium ore presents waste disposal problems not greatly different from other ore dressing procedures except for the unique composition of the materials being handled. Generally the processing involves crushing and grinding the raw materials to an appropriate size, selectively leaching uranium from the main mass, and further processing the pregnant solution to obtain a high grade uranium product. Leaching is usually done with sulfuric acid or sodium carbonate solutions, although other techniques are used in the United States on a small scale. (1) Disposal of solid and liquid wastes constitutes a major problem since these materials contain elevated levels of radioactive nuclides as well as non-radioactive materials. Tailings streams typically contain potential contaminants introduced as part of the ore dressing processes such as sulfuric acid, sulfates, carbonates, chlorides, nitrates, ammonia, lime, magnesia, caustic, potassium permanganate, copper sulfate, manganese dioxide, cyanide, polyacrylamides, several alkylphosphates, tertiary amines, alcohols, kerosene, and fuel oils. (1) In addition, the effluent may contain high concentrations of constituents from the ore such as iron, copper, vanadium, molybdenum, arsenic, lead, fluorine, selenium, and up to 70% of the radioactive materials initially in the uranium deposits. (1) Failure to effectively contain these wastes obviously represents a significant hazard to the environment and the well being of the local population.

Typically, solid tailings containment is accomplished by a retention dam constructed of local mine wastes or previous tailings materials. Piles of these solid wastes can reach appreciable size; some of them in the Grants region are comparable to the prominent natural land forms. Every ton of ore processed produces one to five tons of liquid wastes. Disposal of these liquids is accomplished by evaporation, seepage into the underlying alluvium or release into local rivers and streams. In the Western United States, a typical acid leach plant would require pond areas of several hundred acres to evaporate the liquids generated. (1) There are plants with very large evaporating ponds, although it is estimated that in many cases seepage losses may account for as much as 80% of the liquid loss from waste disposal ponds. It is clear that this seepage of liquid wastes and leaching of solid wastes by invading waters represent a potential source of contamination of local aquifers and water supplies.

This paper will discuss the principles of a technique, based upon lead isotopic systematics, which addresses some aspects of the transport of materials from these waste disposal areas. Because of the unique composition of the ore bodies, the lead isotopes are likely to be diagnostic in studying the movement of material from these waste disposal areas.

LEAD ISOTOPES IN NATURE

The chart of the nuclides indicates that natural lead is composed of 1.4% ^{204}Pb , 24.1% of ^{206}Pb , 22.1% of ^{207}Pb , and 52.4% ^{208}Pb having an atomic weight of 207.2. (2) However, it was demonstrated many years ago that lead from U ores had atomic weights less than this value and those from Th-rich materials were heavier. This perturbation is the result of the radioactive decay of isotopes of uranium and thorium. Uranium-238 decays through a series of radioactive progeny to produce the stable isotope ^{206}Pb , ^{235}U decays to ^{207}Pb and ^{232}Th eventually produces ^{208}Pb . The light isotope ^{204}Pb is not the end product of any known radioactive decay chain, but results from the processes of nucleosynthesis, which produced the elements. It is obvious that "natural" lead can have variable isotopic composition depending upon the relative abundances of U, Th, and Pb and the length of time this melange of elements has been in close association.

"Common" lead, i.e., that with isotopic composition given on the chart of the nuclides is pervasive in the crust of the earth. It reflects the isotopic composition at the time the earth was formed plus the evolution of radiogenic lead in an environment of constant average composition with respect to U, Th, and Pb. Variations from "common" lead occur when these elements are fractionated, as in the formation of ores. Such variations can be quite

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large. For instance, consider the formation of lead in an average uranium ore from the Grants region. Such an ore was deposited $\sim 10^8$ years ago and presently contains 0.65% uranium. (3) Application of the familiar law of radioactive decay indicates that this ore would contain 90 ppm of lead produced *in situ* by the decay of U isotopes. This lead has a ($^{207}\text{Pb}/^{206}\text{Pb}$) ratio of 5×10^{-2} and will hereafter be referred to as radiogenic lead. The average measured concentration in these ores is 80 ppm (3) and the ($^{207}\text{Pb}/^{206}\text{Pb}$) ratio is 8.7×10^{-2} , as opposed to the 8.3×10^{-2} (4) found in "common" lead. The close correspondence between the isotopic composition of pure radiogenic lead and the lead from these ores indicates that the majority of lead was produced *in situ* by the decay of uranium.

Table I presents the average isotopic composition of lead in uranium ores from the Colorado Plateau (3) and the isotopic composition of "common" lead. (4) The differences are significant and provide a means of distinguishing between lead originating in uranium ores or ore residue and lead normally found in the natural environment.

TABLE I
LEAD ISOTOPE RATIOS IN SOME NATURAL MATERIALS

	<u>"Common"</u> ¹	<u>Uranium Ores</u> ²
$^{206}\text{Pb}/^{204}\text{Pb}$	$(5.35 \pm 0.09) \times 10^{-2}$	$(3.9 \pm 3.2) \times 10^{-2}$
$^{207}\text{Pb}/^{206}\text{Pb}$	$(8.34 \pm 0.1) \times 10^{-2}$	$(8.7 \pm 4.6) \times 10^{-2}$
$^{208}\text{Pb}/^{206}\text{Pb}$	2.06 ± 0.04	$(9.0 \pm 12) \times 10^{-2}$

¹Stacey and Kramers (1975)

²Miller and Kulp (1969)

LEAD ISOTOPES AS ENVIRONMENTAL TRACERS

Isotopic labeling involves the introduction of material that is isotopically different but chemically identical to that normally found in the system. Mixing of the isotopically different species provides a means to study the dynamic behavior of that constituent in the system. Isotopic tracers may be radioactive, which can be detected by counting techniques, or they may be non-radioactive, which requires more difficult techniques for detection. Isotopic tracers offer an advantage over chemical ones in that the measured results are normalized relative to chemically identical species, i.e., results may be determined in terms of the specific activity of a radioactive isotope or the isotopic ratio of nonradioactive isotopes. Variations of these quantities directly reflect the mixing of isotopically distinct entities independent of the absolute concentration of the chemical species in the system. Changes in the isotopic composition are dependent upon chemical and physical processes only as they influence the mixing of labeled and unlabeled species.

Stable Isotopes

Consider as an illustration, a uranium mill tailings pile where liquids "percolate" through the tailings and seep into the underlying soil to the surrounding environment. The liquid may be of any origin: leaching agents which eventually become liquid wastes, rainwater, or groundwater which flows into the pile. Initially any such liquid is likely to contain lead that is isotopically normal. Such lead represents the endpoint labeled as "common" in Fig. 1. When this liquid impacts the tailings pile, the lead isotopes in the liquid begin to exchange with isotopes in the wastes and the isotopic composition of lead in the liquid moves down the line toward the "radiogenic" endpoint as shown in Fig. 1. The shift of the isotopic composition toward this endpoint depends upon the relative abundance of lead with the unique isotopic compositions and the efficiency with which they are mixed (either chemically or physically). It does not depend upon a change in the absolute

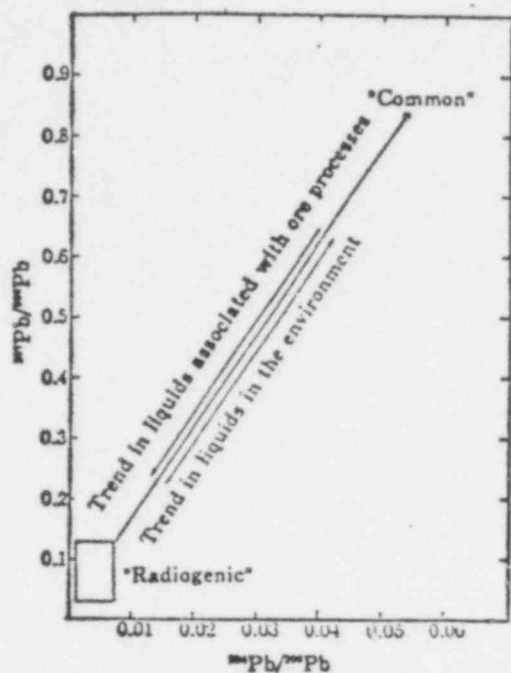


Fig. 1.
Isotopic mixing diagram showing change of isotopic composition resulting from mixing of "radiogenic" lead with "common" lead. Measured isotopic composition in uranium ores from the Colorado Plateau are defined by the box near the "radiogenic" endpoint.

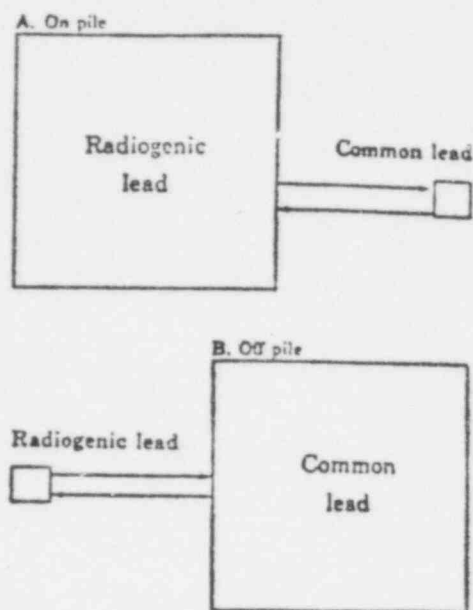


Fig. 2.
A diagram illustrating the differences in the size of the reservoirs of "radiogenic" lead and "common" lead on the wastes from a uranium ore processing plant (A) and in the environment near the waste pile (B).

concentration of lead in any phase. It is likely that the situation on the pile will be like that represented in Fig. 2A. Radiogenic lead is probably an enormous reservoir relative to "common" lead. Further, since the tailings have been ground and leached specifically to promote the exchange of materials, it is possible that exchange of lead between phases is rather facile. Consequently, the isotopic composition of lead in liquids impacting the tailings piles is likely to be strongly shifted toward the "radiogenic" endpoint of the mixing diagram in Fig. 1.

Once the liquid leaves the pile, the situation is reversed as shown in Fig. 2B. Now "common" lead in soils and uncontaminated waters is a large reservoir relative to radiogenic lead leached from the pile. The isotopic composition of lead in the waters will be shifted toward the "common" endpoint as shown in Fig. 1. As before, the extent of the shift will depend upon the relative magnitude of the abundances of the two types of lead and the facility with which they exchange.

The mixing of end members with unique isotopic compositions is a simple isotope dilution problem. A mixing ratio (ρ) can be calculated from measurements of isotopic ratios, assuming the end members are well defined. The equation for calculating this ratio is

$$\rho = \frac{({}^{207}\text{Pb}/{}^{206}\text{Pb})_c - ({}^{207}\text{Pb}/{}^{206}\text{Pb})_m}{({}^{207}\text{Pb}/{}^{206}\text{Pb})_m - ({}^{207}\text{Pb}/{}^{206}\text{Pb})_a}$$

The subscripts C, M, and R refer to common lead, the ratio measured in the sample and radiogenic lead respectively. The mixing ratio is just the quantity of radiogenic ^{206}Pb in the sample relative to ^{206}Pb from lead with "common" isotopic abundances. The fraction of total lead in any sample which originated in the uranium ores (radiogenic lead) may be easily calculated from the mixing ratio.

The previous example is merely an illustration. Such simple models are unlikely to represent the complex interactions that actually exist when the natural environment is impacted by human activities. However, the power of the technique is that it does not rely on any assumptions regarding the chemical and physical behavior of Pb in the system. The only significant assumption in the example involves the isotopic composition of lead in the constituents. Lead from the ore or ore residue from the Grants mineral belt has a unique isotopic composition compared to lead found in the uncontaminated environment. Mass spectrometric techniques that can measure these compositional differences with a precision of a few hundredths of a percent, provide the means to unambiguously identify small proportions of this source of anthropogenic lead in any environmental media. The ability to make such observations provides a tool to study lead contamination from waste associated with the uranium mining and milling industry. It is possible that lead isotope ratios may also have a broader application as general indicators of the encroachment of the anthropogenic wastes on their immediate environment.

MEASUREMENTS OF LEAD ISOTOPIC RATIOS

Because of the interest in lead isotopic ratios as geochronometers, mass spectrometric techniques have been developed to measure highly precise isotopic ratios in as little as a nanogram of lead. The major problem is to chemically separate lead from elements that interfere with the mass spectrometric measurements. Lead introduced by reagents and glassware during separations has the isotopic composition of "common" lead. So the effects of this contaminant will be a shift toward the "common" lead endpoint in Fig. 1. Since lead is a trace element in most natural materials, separations often involve as little as a few nanograms of the element. Extraordinary precautions are necessary to assure that the chemistry is done free of lead contaminants.

The spectrometer separates isotopes of lead and focuses them sequentially on a detector which produces a signal proportional to the abundance of the isotope. No attempt is made to relate the intensity of the output signal to the absolute abundance. Instead, the intensity from each isotope is measured relative to a reference isotope. In our case, all measurements are taken relative to ^{208}Pb and reported as $^{206}\text{Pb}/^{208}\text{Pb}$ ratios. Figure 3 is a strip chart output from the mass spectrometer showing the intensity of lead isotopes in "common" lead. As indicated in Table I, ^{206}Pb is nearly twice as abundant as ^{208}Pb , ^{207}Pb is slightly less abundant than ^{208}Pb , and ^{204}Pb is 20 times less abundant than ^{208}Pb . Figure 4 is the mass spectrometer output of lead isolated from liquid solutions residing on top of solid wastes from a currently active acid leach processing plant. Contrast this with Fig. 3; ^{206}Pb is ~3 times less abundant than ^{208}Pb , ^{207}Pb is ~5 times depleted relative to ^{208}Pb and the minor isotope ^{204}Pb is underabundant by a factor of 100 relative to ^{208}Pb . It is clear from the mass spectrum that this liquid contains a large proportion of radiogenic lead.

APPLICATIONS OF LEAD ISOTOPE TECHNIQUES

As previously indicated, clean separation of lead from matrix material poses the major obstacle to implementing the technique. Most of our efforts have been directed toward the development of such separation procedures. Although this development work is not complete, preliminary results unmistakably identify the presence of radiogenic lead in samples associated with mill tailings piles. Table II presents these preliminary data. Sample 1 is a solution taken from the top of a waste disposal pile at a currently active acid leach processing plant, the mass spectra of lead isotopes from this sample were presented in Fig. 4. Sample 2 represents the lead isotopic composition in a sample of solution taken from a well on

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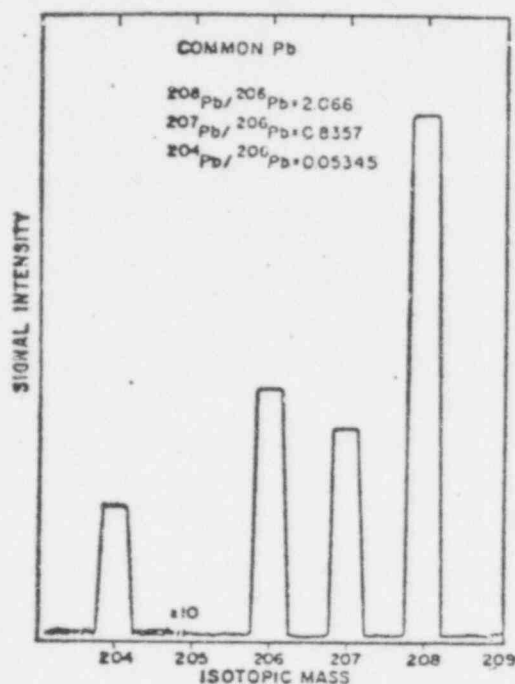


Fig. 3.

The mass spectrum of "common" lead showing the relative abundances of the four isotopes as found in most materials in the earth's crust.

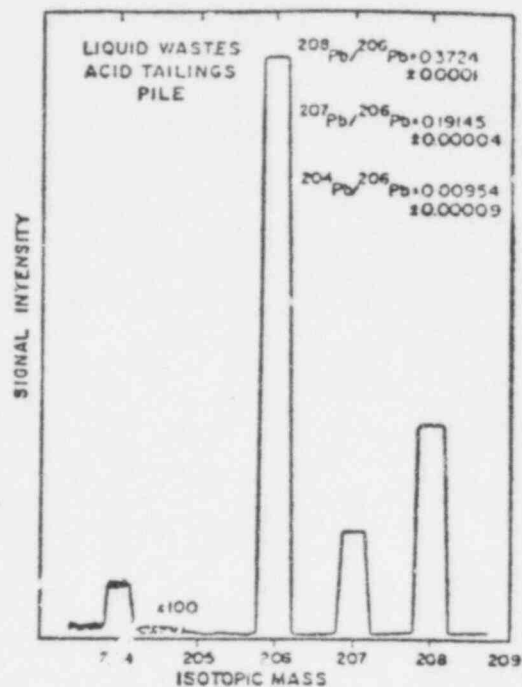


Fig. 4.

The mass spectrum of lead extracted from solutions from the top of the waste disposal pile at a currently active acid leach processing plant. The relative prominence of the signal from ^{208}Pb compared to "common" lead is indicative of a large fraction of radiogenic lead in this sample.

TABLE II

LEAD ISOTOPE RATIOS IN LIQUIDS ASSOCIATED WITH URANIUM ORE WASTES

	Sample 1	Sample 2	Sample 3
$^{208}\text{Pb}/^{206}\text{Pb}$	$(9.54 \pm 0.01) \times 10^{-2}$	$(2.277 \pm 0.009) \times 10^{-2}$	$(5.04 \pm 0.01) \times 10^{-2}$
$^{207}\text{Pb}/^{206}\text{Pb}$	$(1.9145 \pm 0.0004) \times 10^{-1}$	$(3.895 \pm 0.009) \times 10^{-1}$	$(7.900 \pm 0.005) \times 10^{-1}$
$^{204}\text{Pb}/^{206}\text{Pb}$	$(3.724 \pm 0.001) \times 10^{-1}$	$(8.937 \pm 0.01) \times 10^{-1}$	1.9332 ± 0.0007

top of a waste pile associated with a carbonate leach facility. This pile has not been used for 15 yr. Sample 3 is water taken from a well about 5 m from the inactive carbonate waste pile. The well is believed to be hydrologically downgradient from the wastes.

Figure 5 is a plot of the data on a lead isotope mixing diagram exactly like that presented for illustrative purposes as Fig. 1. The close fit to the mixing line indicates that our original assumption was correct. Samples associated with uranium wastes do indeed appear to be simple mixtures of radiogenic lead from the ores and "common" lead. It must be emphasized that this is preliminary data! Quantities of lead introduced into the samples during the separation procedures have not been assessed. Such contamination would shift the points up the mixing line toward the "common" endpoint. As a result, the percent of radiogenic lead given in Fig. 3 must be considered only as a lower limit on the actual

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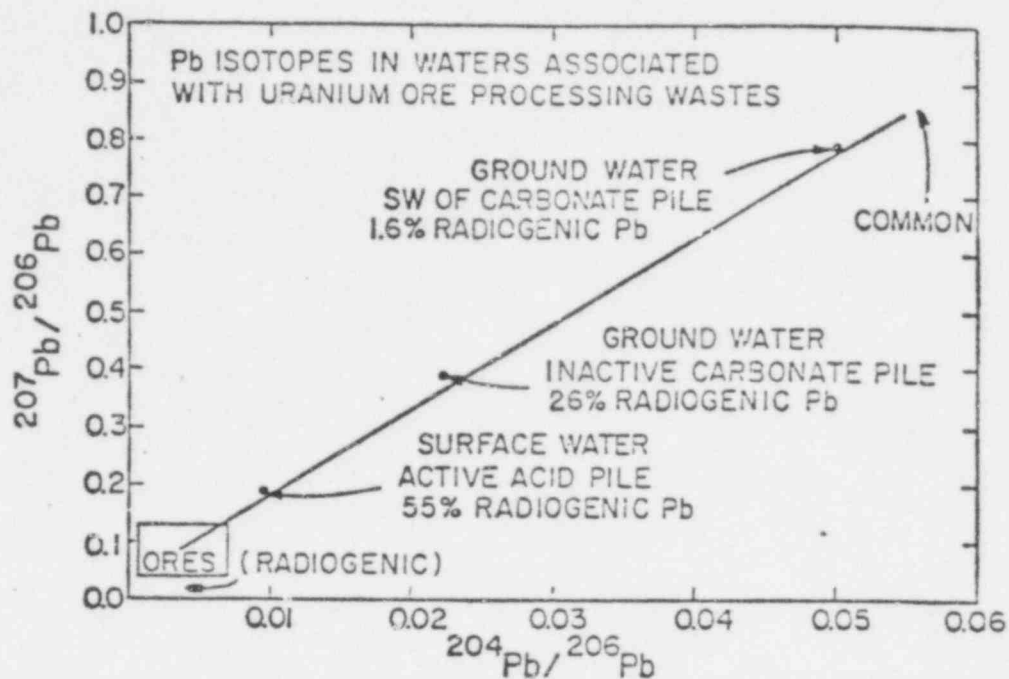


Fig. 5.

Preliminary data showing the measured isotopic composition on or near uranium ore tailings piles. The data is superimposed on an isotopic mixing diagram identical to Fig. 1. The shift away from the "common" endpoint is unambiguous evidence of the presence of radiogenic lead indicating different degrees of contamination of the solutions by lead from the ore residue.

proportion of radiogenic lead in the sample. Nevertheless, these results are extremely important. They demonstrate that the radiogenic lead signature is strongly present in solutions directly associated with the wastes. If these solutions seep from the pile, the lead isotopic ratios are quantitative indicators of the impact. Such seepage is indicated by the data from solutions taken adjacent to the inactive carbonate pile. Lead isotope ratios unmistakably show the presence of radiogenic lead, albeit small, in these liquids.

Preliminary data indicates that lead isotopes are a viable means of studying element migration from wastes associated with the uranium mining and milling industry. They can be used to trace the extent of migration and to study the fundamental physical and chemical processes associated with the movement of materials from anthropogenic sources.

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