H60 Characterization of Lead, Transition Metal, and Rare Earth Element Composition of Human Bone by ICP-MS and LA-ICP-MS

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After attending this presentation, attendees will be better informed about the capabilities for compositional and isotopic analysis of trace elements in human bone by traditional ICP-MS techniques. The suitability of lead, strontium, and rare earth element isotopic compositions for geographical sourcing of human bones will be discussed. Lead isotopic analysis will also be used to differentiate between the anthropogenic sources of human lead exposure. Laser ablation ICP-MS will be used to provide spatial resolution of trace element concentrations within various bone tissues (cortical vs. trabecular).

This presentation will have an impact on the forensic science community by demonstrating the utility of trace element systematics, isotopic composition, as well as LA-ICP-MS techniques for the analysis of human bone.

Inductively Couple Plasma Mass Spectrometry has become an accepted method for highly sensitive, rapid, and reliable elemental analysis of human bones and biological tissue. Traditional ICP-MS techniques can provide accurate elemental composition at or below 1 ppb in human bones. In this study the utility of Laser Ablation (LA)-ICP-MS applications which can be used to provide rapid and accurate spatial determination of trace and minor element concentrations is explored. A second application will explore the ability of ICP-MS to determine the isotopic compositions of lead to determine the source of environmental lead in the body for trace elements (i.e., Pb, Sr, and REE).

Laser ablation ICP-MS, will be used in an attempt to provide finite spatial resolution for trace metal concentrations within human femoral heads. Previous research has established that the residence time of trace elements can vary by more than an order of magnitude depending on the type of bone tissue (i.e., Pb: trabecular: 2-3 years vs. cortical ~30 years). LA-ICP-MS analysis has the ability to rapidly determine minor and trace element concen- trations across bone transects. For this reason, it is expected that LA-ICP- MS determination of trace element concentrations (Pb, Cd, Zn, etc.) may be used to quantify and differentiate between long term, time-integrated trace element exposure versus more recent anthropogenic or environmental inputs.

Various geochemical isotopic techniques have been employed in attempts at forensic provenancing (Pb, Sr, O, C, N). The trace element isotopic values of Sr are predominantly a function of soil isotopic values in the areas where food is grown or animals graze or the water consumed. As humans consume food or water from a specific region they inherit the isotopic signature of a specific environment. The application of environ- mental typing techniques has become increasingly difficult as humans have expanded to a 'global' diet obtaining foods at grocers as opposed to farming or local markets etc. The use of two additional isotopic techniques of rare earth elements and Pb isotopes is proposed which may provide specific uses in forensic studies.

In a similar manner to strontium isotopes, rare earth elements (REEs) or lanthanides have distinctive isotopic patterns based upon the geological history of local soils. In many cases geological fractionation can lead to very identifiable REE isotopic patterns in geographical regions. Traditionally REEs have been thought of as having concentrations too low to have a signif- icant use for biological investigations. ICP-MS analysis can provide accurate quantification of REEs at the low ppb level. The fact that REEs also have exceedingly low environmental concentrations with the exceptions of those used in highly specific medical procedures (Gd as a contrast-enhancing agent for magnetic resonance imaging and Sm as radionuclide therapy for painful bone metastases) provides the opportunity to use REEs for specific forensic applications. Unlike Ca or Sr which have fairly substantial concentrations in drinking water, REE concentrations are exceedingly low in drinking water and therefore are almost entirely indicative of food supply or medical procedure. REEs may provide an alternative method of addressing geographical provenance free of external environmental influences. REEs have also proven useful in older fossil analysis as REEs are more resistant to the effects of diagenesis unlike other environmental isotopes.

Unlike Sr, O, C, N, and REEs, the source of Pb to humans is largely environmental. The source and magnitude of trace metal exposure have changed in the last 30 years as environmental regulations have become more stringent (i.e., the removal of Pb from gasoline in the mid 70's and the removal of Pb oxide as a primary pigment in white paint). This study initially looks at Pb isotopic composition in cortical and trabecular bones. The authors expect that as the environmental sources of Pb have changed, we may expect to find isotopic variations between cortical bone and trabecular bone, with residence times of greater than 30 years and 2-3 years respec- tively for Pb retention. As the major sources of Pb contamination have been removed from the environment, cortical bone is expected to have high concentrations and a mixture of soil, gasoline, and lead paint Pb isotopic values. Conversely, trabecular bone formed in the last few years may have lower concentrations with isotopic values indicative of a mixture between modern lead sources (coal combustion, smelters, and a more significant input from natural soil lead). Initial results of Pb isotopic analysis of human bones from our study and others indicate a mixture of Pb from numerous environ- mental sources as well as geographic provenance which will be further explored. Pb isotopes can be useful for provenance in cases where subjects are from distinct geographic regions (i.e., Australia vs. U.S.) with specific Pb isotopic compositions. However, we intend to focus on the use of Pb isotopic compositions of anthropogenic sources as related to environmental exposure. The isotopic patterns of lead ores are distinct yet consistent and therefore can be used for environmental analysis and potentially forensic studies. For example until 1975 Pb was added to gasoline as an anti-knocking agent. As most refineries in the United States are near the Gulf of Mexico, Mississippi Valley lead ore deposits were used as the Pb source. The distinct isotopic composition of this lead ore has been used in various environmental studies to determine the source of lead and may be useful in forensic studies.

Unlike geological applications of Pb isotopes, which rely on accurately determining exceedingly small variations in isotopic composition, environ- mental, and forensic studies can differentiate source by using a three isotope plot (208Pb/206Pb vs. 207Pb/206Pb) of the stable radiogenic Pb isotopes. Utilizing all Pb isotopes allows for easy determination of drastically different isotopic values. Traditional geochemistry employs thermal ionization-MS with 0.05-0.1% analytical error. This method is expensive, which may be limiting to financially deplete departments. The method also requires complete specimen destruction. A comparison of lead isotopic data to tradi- tional TIMS methods will be performed. Lead analysis by ICP-MS can achieve an analytical error ~1% and can easily differentiate between envi- ronmental sources of lead. This study will demonstrate the suitability of ICP-MS and LA-ICP-MS for a quick and reliable method of screening for both provenance and environmental isotopic variations of lead isotopes and trace element patterns.

Lead, Bone Chemistry, LA-ICP-MS/ICP-MS