COMPARISON OF LASER ABLATION OF BIRD FEATHERS USING 266nm AND 213nm LASERS

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ABSTRACT

Trace element concentrations incorporated in metabolically inert tissues such as bird feathers reflect the signature of the local environment in which the feather was grown and help to identify geographical origins of birds. We have used Laser Ablation –Inductively Coupled Plasma –Mass Spectrometry (LA-ICP-MS) to study trace metal concentrations in bird feathers. LA-ICP-MS is preferred to microwave digestion and ICP-OES due to reduced interferences that could affect signal intensities negatively. Studies have shown better ablation pits and improved spatial resolution at lower wavelengths confirming that the interaction of the laser with the sample is wavelength dependant. Certain biological materials such as otoliths and shells ablate better by the 213nm as opposed to 266 nm. However, little is known whether bird feathers ablate better by the shorter wavelength. The ablation characteristics of a 266nm Nd:YAG laser and a 213nm laser on bird feathers were compared by experiments using different spot sizes for ablation and measuring signal intensities using ICP-MS. Our 213 nm laser ablation results indicate signal intensities which exhibit a much higher degree of temporal stability when compared to those generated using the 266 nm laser.

INTRODUCTION

➢Nd:YAG lasers are the most widely used laser source for LA-ICP-MS.
➢Generating the Nd:YAG fourth harmonic requires two harmonic generators; the first that doubles the frequency and converts the fundamental to a wavelength of 532nm and the second which doubles the 532nm beam to a wavelength of 266nm. The 5th harmonic is generated by sum frequency mixing the 1st and 4th harmonic (or the 2nd and 3rd) using a BBO 5th harmonic generator (Jackson 2001).
➢Better ablation pits and hence improved spatial resolution observed at lower wavelengths indicate that interaction of the laser with the sample is wavelength dependant for some matrices (Durrant & Ward 2005, Guillong, Horn & Günther 2001).
➢ Poor absorption by transparent materials is overcome with the use of shorter wavelength which deliver higher energy photons and increase absorption; shorter the wavelength, greater the energy absorbed.
➢For analysis of difficult matrices such as feathers (for which an appropriate matrix matched standard is not available), good absorption efficiency and long, stable signal durations are essential for multi-elemental measurements.
➢Certain biological materials such as otoliths and shells ablate better by the 213nm as opposed to 266 nm.
➢Two previous known studies concerning LA-ICP-MS analysis of bird feathers by Jensen et al. 2002 and Ek et al. 2004 have used the 266nm laser ablation system.
➢Studies are needed to determine whether feathers ablate better by the 213nm or the 266nm.

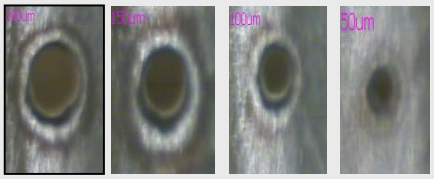
METHODS

➢Feathers were cut to lengths of 3-4cm and fixed on the sample chamber using sticky tape in the sample holder of the Laser Ablation system. Special care was taken to ensure a level surface for ablation during the adhesion process.
➢266nm and 213nm CETAC Technologies laser ablation systems were coupled to the PerkinElmer DRCII ICP-MS for the analysis of trace metals in feathers. Instrument settings for ablation systems using 266nm and 213nm lasers are shown below.
➢We ablated feathers using the following spot sizes- 50 µm, 100 µm, 150 µm, 200 µm and signal intensities. We avoided spot sizes below 50 µm because it yields poor signal intensity.

LASER OPERATING CONDITIONS

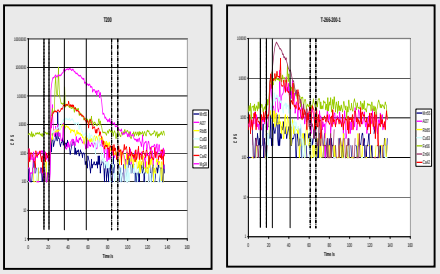
Energy	100%
Pulse Rep Rate	10 µm/sec
Spot Size	50 µm, 100 µm, 150 µm, 200 µm
Bursts	500 shots
Calibration standard	NIST612
Internal Standard	^{42}Ca
Carrier gas (266 nm)	Ar (0.75 to 1.04 L/min)
Carrier gas (213 nm)	Ar (0.75 to 1.04 L/min) + He (500 ml/ min)

RESULTS

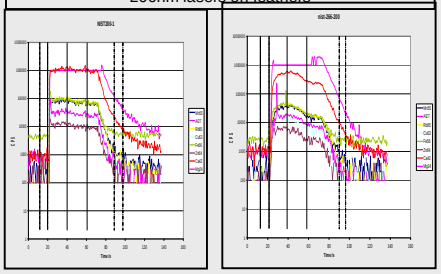


Ablation craters using 213nm laser. Spot sizes 200µm, 150µm, 100µm and 50µm

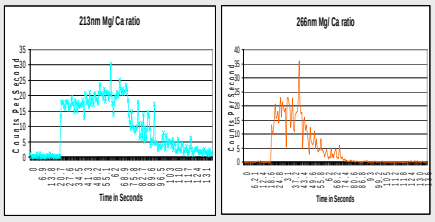
Ablation craters using 266nm laser. Spot sizes 200µm, 150µm, 100µm and 50µm



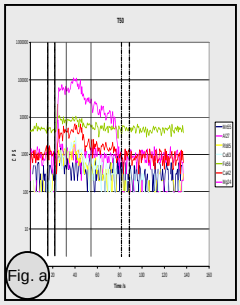
Signal intensities for 200µm spot size using 213nm and 266nm lasers on feathers

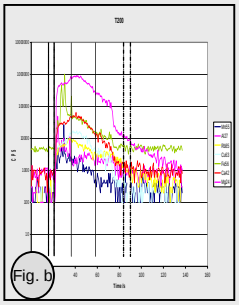


Signal intensities for 200µm spot size using 213nm and 266nm lasers on NIST612



Mg/Ca ratio for 200µm spot size using 213nm and 266nm lasers on feathers





Signal stability and intensity was poorer at 50µm (Fig. a) than at 200µm (Fig. b) despite the type of laser used. Poor signal stability can be partially attributed to the non-uniform distribution of elements in the sample.

DISCUSSION

➢Long and stable signal using 213nm laser. Order of magnitude drop in sensitivity using 266nm laser.
➢Based on signal stability and intensity, better crater profiles, improved depth resolution, and precise depth profiles are obtained with the 213nm versus 266nm wavelengths.
➢Feathers absorb better at 213nm wavelength as seen by the longer, more intense and stable signals.
➢For bulk analysis of homogenous materials larger spot sizes are preferable. At higher spot sizes signal intensities were better resolved above background noise.
➢Guillong (2004) found that ablation rates significantly differ between matrix types which may be absorption controlled and is not dependant on the ablation medium (Ar or He).
➢Metabolically inert tissues such as feathers are a record of trace element concentrations in bird feathers which enable the identification of geographical origins and assist in differentiating populations of migrating animals (Szèp et al. 2003, Donovan et al. 2006).

LIMITATIONS

➢Lack of reference material for feathers.
➢Feather shaft is curved and is not evenly thick which affects ablation characteristics.
➢Feathers from different species ablate differently due to differences in absorption coefficients.
➢Difficult to shoot the same part of the feather among different samples.
➢Differences in transport efficiencies may be based on different proportions of carrier gases. Helium was only used with the 213 nm laser. Helium has been shown to be a more efficient carrier gas for sample transport.
➢Differences in absorption coefficients of feathers using 213nm and 266nm affects signal intensity.

FUTURE WORK

➢Develop standard using keratin powder which may serve as matrix matched laboratory standard LA-ICP-MS of bird feathers.

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