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Provenance Determination of Freshwater Cultured Pearls by Laser Ablation ICP-MS

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It is increasingly difficult to differentiate between freshwater cultured pearls from Lake Kasimigaura in Japan and those coming from China. We are developing a new objective method of provenance determination using the trace element composition of pearl. Measurements are carried out in situ by Laser Ablation ICP-MS and create small(100μm maximum) laser craters in the samples close to the borehole or other natural irregularities in the pearl. Since the laser craters are hardly visible by eye, this method is quasi-non-destructive and requires minimal sample preparation. Material extracted form the minute laser drill hole at the pearl's surface is transported by a stream of Ar gas into an ICP-MS, where its trace element composition is determined. In this way it is possible to measure up to 30 trace elements simultaneously at high accuracy and precision. Standardisation is carried out both by an internal standard and external, international certified reference material. Detection limits are typically in the ppb area and measured element concentrations are at least a factor of ten more abundant in the samples. While Chinese and Japanese FWCP overlap in most measured element concentrations(Li, Li, B, Mg, Mn, Co, Ni, Cu, Zn, Ga, Sr, Ba), Ba/Sr- and Ga/Sr-ratios clearly distinguish Japanese Kasimigaura pearls from Chinese FWCP. Japanese FWCP show relatively uniform ratios, whereas Chinese samples have much higher and more variable ratios. We propose that the differences in Ga/Sr and Ba/Sr ratios between the two provenances reflect regional differences in water chemistry that, in turn, mirrors anthropogenic input, differences in geology and weathering environment between the pearl culturing areas in Japan and China. However, it should be noted that the correspondence between pearl composition and water chemistry may not be one-to-one, because metabolic enrichment processes still need to be assessed. The higher variability in the Chinese samples is most likely a reflection of the local culturing technique which involves repeated transfer of the pearl mussels between different pearl farms in the country. In contrast, Japanese FWCP from Lake Kasimigaura are cultured stationary only. We are currently testing if Japanese FWCP from Lake Kasumigaura and Lake Biwa can further be differentiated this method, or if the geological environment is too similar for these two localities to allow for this. Further preliminary data shows that LA-ICP-MS can also be used to identify silver-treated FWCP from China.