Reconstructing anthropogenic, atmospheric emissions of trace metals using environmental archives: comparison of polar snow and ice, ombrotrophic peat bogs, *Sphagnum* moss from herbaria, and lake sediments

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Given the long history of mining and metallurgy, many trace elements of contemporary environmental interest have been released to the environment since Antiquity. Reconstructing anthropogenic emissions requires suitable archives to provide records extending sufficiently far back in time to allow the natural fluxes and sources to be determined, for comparison with modern values. A number of archives have been employed to reconstruct historical records of atmospheric trace elements, each with its inherent advantages and disadvantages.

Ice cores from the Arctic and peat cores from ombrotrophic bogs both receive inputs of Pb exclusively from the atmosphere. Using examples from Devon Island, Nunavut, Canada and Etang de la Gruére, Jura Mountains, Switzerland, it was found that

1) the natural ratio of Pb to Sc was effectively constant for thousands of years and comparable values were found in both archives; this supports the hypothesis that natural atmospheric Pb was effectively dominated by soil dust particles supplied by weathering of crustal rocks.

2) anthropogenic Pb inputs to the Arctic are clearly seen in ice layers ca. 3,000 years old, with pronounced Pb enrichments and declines in $^{206}Pb/^{207}Pb$ ratios in samples from the Roman and Medieval periods, supporting the hypothesis that human activities have dominated atmospheric Pb inputs for three millenia.

3) although Pb enrichments have declined during recent decades, even in the most recent snow samples, the Pb/Sc and Pb isotope data show that 90 to 95% of the Pb is still anthropogenic.

Although *Sphagnum* moss from herbaria do not extend back in time further than ca. 200 years, they received trace metals exclusively from the atmosphere, the date of sample collection is known exactly, and they are not affected by chemical diagenesis in acidic, anoxic bog waters. The isotopic composition of atmospheric Pb obtained using peat cores from Europe (dated for the past ca. 150 years using ^{210}Pb) are in excellent agreement with the records for the same interval preserved in *Sphagnum* moss from herbaria.

Comparing the isotopic composition of Pb in recent layers of lake sediments from the Kawagama Lake watershed in central Ontario with a peat core from a local bog shows that the sediments are a much less sensitive indicator of atmospheric change, largely failing to record the declines in $^{206}Pb/^{207}Pb$ ratios since the elimination of leaded gasoline, and the growing relative importance of Pb from smelters in northern Ontario and Quebec.

The *in situ* occurrence of bacteria on gold grain surfaces: Implications for bacterial contributions to gold nugget structure and chemistry

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16a. Microbe-mineral interactions in time and space

Natural gold grains often possess secondary gold as colloidal particles, crystalline gold and bacteriomorphic structures. The latter form known as 'biogenic' gold that was first reported as structures resembling gold-encrusted microfossils on placer gold specimens [1]. Recent research suggest that Bacteria and Archaea are involved in the biogeochemical cycling of gold [2, 3, 4]. In this study gold grains from sediment sampled from Rio Saldana, Colombia were analyzed for the purpose of better understanding the formation of secondary gold in a tropical placer environment. Morphological analysis, using scanning electron microscopy, demonstrated that gold grains appeared as elongated disk shapes with articulated surfaces occurring predominantly on the perimeter. Bacteria were directly and indirectly attached as biofilms on the articulated surfaces of all gold grains. Iron oxide occurred on some grains as globular and patina coatings possessing casts of bacteria. The grains also possessed micron size secondary gold textures occuring on the outer periphery of the grains. Compositional analysis, inferred from energy dispersive spectroscopy and x-ray absorption fine structure, indicated that trace silver, mercury and copper was associated with gold. Unlike silver, mercury and copper appeared to have localized regions of heterogenous distributions throughout the gold grain. A pure bacterial culture, isolated from a single gold grain, was identified as *Nitrobacter* sp. 263 based on 16S sequencing. This *Nitrobacter* sp. removed gold from a gold (III) chloride solution within an hour. Transmission electron microscopy and scanning electron microscopy demonstrated that gold immobilization occurred as abundanct colloids and octahedral platelets less than 100 nm in diameter concentrated within the cell envelope. The occurrence of secondary gold on the surface of these grains and the ability of *Nitrobacter* to form crystalline gold suggests that this organism may contribute to the growth of gold grains in this placer environment. Gold biomineralization would be continuous if concentrations of aqueous gold input are low and bacterial metabolic growth is maintained by reproducing biomass lost to biomineralization.

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