A method for the selective removal of inorganic ash particles from lake sediments

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Abstract

Inorganic ash particles are formed by the fusing of inorganic material present during the high temperature combustion of fossil fuels. As they accumulate in lake sediments, they record the history of atmospheric contamination produced from such sources. A technique has been developed for concentrating these particles from lake sediments involving the stepwise removal of unwanted components of the sediment, including organic material and biogenic silica.

When applied to a sediment core taken from Loch Tinker, central Scotland, a particle concentration profile, very similar to that of the carbonaceous particle profile (the other component of fossil-fuel combustion ash) is produced. The concentration of the inorganic ash spheres in the sediment is approximately an order of magnitude higher than the carbonaceous particles and there appears to be a continuous pre-industrial background value. This seems to imply a similar source (i.e. coal combustion rather than oil) for both inorganic ash and carbonaceous particles. This method has also been used with success on peat cores.

Introduction

Lake sediments provide a record of atmospheric contamination and have been important in recent studies of lake acidification. Carbonaceous particles derived from fossil-fuel combustion are found in considerable numbers in upper levels of lake sediment cores taken from areas with high acid deposition. At sites in the United Kingdom, there is close correlation between the onset of atmospheric contamination as indicated by fossil fuel derived particles, heavy metals and magnetic particle deposition, and the acidification of lakes as indicated by diatom analysis (Battarbee et al., 1988; Jones et al., 1990).

Inorganic ash spheres, like carbonaceous particles, are produced from the high temperature combustion of coal, oil and peat. They comprise over 80% of the particulates formed from coal combustion (Watt & Thorne, 1965), but much less in peat and only 0.1% in oil (Henry & Knapp, 1980).

To facilitate particle enumeration and determine an origin for these particles by using diagnostic chemical techniques such as energy dispersive X-ray analysis (EDAX), it is first necessary to concentrate the particles by removing unwanted fractions of the sediment.

This paper describes a concentrating technique and uses it to determine particle concentrations in
a sediment core taken from Loch Tinker, central Scotland.

**Inorganic ash spheres in the environment**

Ash spheres, generated in coal fired power stations, nearly all fall within the size range 0.05 \( \mu \text{m} \)– 10 \( \mu \text{m} \) (McElroy et al., 1982) and so will travel long distances in air streams. Industrially derived ash spheres have been found in virtually every environment. Their presence has been recorded in mid-ocean air samples (Folger, 1970; Parkin et al., 1970), marine sediments in both coastal (Puffer et al., 1980) and deep-sea areas (Fredriksson & Martin, 1963), ombrotrophic peat bogs (Oldfield et al., 1978, 1981), high latitude ice deposits, in both Greenland (Hodge et al., 1964b) and the Antarctic (Hodge et al., 1967, Fredriksson & Martin, 1963), as well as estuarine (Allen, 1987) and lake sediments (Puffer et al., 1980, Nriagu & Bowser, 1969).

Natural sources of spherical inorganic particles in this size range include volcanic emissions (Lefèvre et al., 1986) and micrometeorites (Hodge & Wright, 1964a), and so in a sediment profile it might be expected that a record of these particles exists at depths corresponding to pre-industrial times.

**Development of the technique**

Inorganic ash particles formed from coal combustion will be mostly aluminosilicate in composition with different amounts of iron depending on the inorganic inclusions present in the fuel. Thus, they have a similar chemistry to many of the minerals in the sediment and this restricts the range of reagents that can be used in the removal of unwanted fractions.

**Concentration steps**

Organic material can be removed by oxidation using 30% hydrogen peroxide (\( \text{H}_2\text{O}_2 \)), at about 50–60 °C. Basic peroxide (a mixture of 6M KOH and 30% \( \text{H}_2\text{O}_2 \)) and nitric acid (\( \text{HNO}_3 \)) are more effective oxidants than \( \text{H}_2\text{O}_2 \) alone, but these etch the ash particle surfaces.

Biogenic silica, predominantly diatom frustules and chrysophyte cysts, can be removed from other forms of silica, such as mineral silica and non-crystalline or amorphous silica e.g. inorganic ash, by preferential digestion. Wet alkaline extractions are best for this purpose (Krausse et al., 1983), other methods such as fusion and mineral acid attacks are not selective for different forms of silica.

Trials performed on lake sediment, spiked with some coal-fired power station ash (to ascertain the extent of etching on the spheres), compared the effect of different concentrations of sodium carbonate (\( \text{Na}_2\text{CO}_3 \)) and sodium hydroxide (\( \text{NaOH} \)) at 100 °C for various lengths of time. Analyses for dissolved silica (Goltermann, 1970) were performed on sub-samples removed at intervals from the digestion supernate. When the dissolved silicate concentration stops increasing, biogenic silica dissolution has ceased. In most cases, silica dissolved from mineral sources is insignificant compared to the quantity of biogenic silica (Krausse et al., 1983). If this were not the case, the silica concentration in the supernatant liquid would keep increasing with time rather than levelling off as occurs after about 2 hours. No etching of the ash particles occurred until after 6 hours and so 2 to 3 hours was the time selected for the technique.

Various techniques were tried to selectively remove silicate minerals and not the inorganic ash. Hydrofluoric acid (HF) has been used in other extractions to remove silicates as \( \text{SiF}_4 \), but is also very effective at dissolving the silicate ash and even at low concentrations such as a 1% solution, will etch the surface of the particles to reveal the underlying structure, of quartz (\( \text{SiO}_2 \)) and mullite (3\( \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \)) (Hullett & Weinberger, 1980). Fluorosilicic acid (\( \text{H}_2\text{SiF}_6 \)) preferentially removes feldspars from quartz, but this also severely etched the ash spheres.

Pyrosulphate (\( \text{Na}_2\text{S}_2\text{O}_7 \)) fusions (Chapman et al., 1969; Kiely & Jackson, 1965), digested the