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AN EXTRACTION TECHNIQUE FOR MINERAL ASH PARTICLES IN LAKE SEDIMENT

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1.0 INTRODUCTION

Lake sediments provide a record of atmospheric contamination and have been important in recent studies of lake acidification. Carbonaceous and mineral ash 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. Sites in the United Kingdom show close correlation between the onset of atmospheric contamination as indicated by carbonaceous particles, heavy metals and magnetic deposition and the acidification of lakes as indicated by diatom analysis (Battarbee *et al.* 1988). Studies in progress seek to examine the atmospheric record provided by mineral ash spheres in lake sediments.

The particulate emissions from high temperature fossil-fuel combustion can be divided into two groups, carbonaceous particles, which are composed mainly of elemental carbon (Goldberg 1985) and mineral ash spheres, which are formed by the fusing of inorganic minerals within the fuel (Raask 1984). A previous paper, (Rose 1989), showed how carbonaceous particles could be extracted from lake sediments. This paper describes an extraction process for the mineral ash component.

There are three fossil-fuels from which these particles are derived, coal, oil and peat. For coal, the inorganic fraction can be up to 25% of the original fuel and so the mineral ash spheres comprise at least 80% of the final ash (Watt and Thorne 1965). In the case of oil, there is far less inorganic material in the original fuel, usually less than 1% and typically 0.1% (Henry and Knapp 1980). The mineral ash comprises only 0.1% of the final ash, the rest being carbonaceous material.

Although peat does not form spherical carbonaceous particles, it does produce mineral ash spheres upon high temperature combustion. More are formed with sedge peat than with moss peat owing to the silica accumulated in the peat-forming plant. As no electrostatic precipitators are fitted to peat-fired stations, peat emissions of mineral ash spheres may be a significant source of these particles in lake sediments in areas where coal-fired stations are few and oil and peat stations are more abundant, as in the Republic of Ireland.

In order 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 to a much greater extent than that in which they occur in lake sediment. This can be done by using selective techniques to remove unwanted fractions of the sediment, enabling a higher percentage of the material available to be studied.

This paper describes a method for extracting particles from lake sediment and uses it to analyse the particle content of a sediment core from Loch Tinker, central Scotland.

2.0 MINERAL ASH PARTICLES IN THE ENVIRONMENT

The majority of work on mineral ash particles has been done on material taken directly from power stations. This involves the study of the chemical and physical characteristics of the particles as well as uses to which the ash can be applied. A great deal of research has been done by ash marketing and power companies on the pozzolanic properties of power station ash. A pozzolan converts the calcium hydroxide produced during the hydration of Portland cement to calcium aluminates and silicates and so strengthens concrete and makes it more resistant to chemical attack. This property depends solely on the physical and chemical parameters of the ash used (Raask and Street 1978).

Nearly all the fine particles generated in a coal fired power station fall within the size range 0.05 - 20 μm (McElroy *et al.* 1982). Particles with a diameter between 1 and 20 μm have finite settling velocities but these are very low with respect to wind velocities (Wark and Warner 1981). Consequently mineral ash particles, especially those at the smaller end of the size range are able to travel long distances in air streams. Dust particles of 10 μm and less from the Sahara Desert have been recorded as travelling over 3000 miles of open ocean (Parkin *et al.* 1970), thus mineral ash particles may conceivably be found in any environment.

Spherules, most probably of industrial origin (Folger 1970), have been recorded in all samples taken in transects across the North Atlantic, constituting 5% of the total air-borne particulates in mid-ocean samples, but over 60% when near land (Parkin *et al.* 1970).

Opaque spherules (often black and magnetic) have been recorded in marine sediments of both coastal (Puffer *et al.* 1980) and deep-sea locations (Fredriksson and Martin 1963) with highest concentrations occurring in the mid-latitudes of the northern hemisphere where industrial activity is highest. Oldfield *et al.* (1978, 1981) showed that spherules known to be the product of fossil-fuel combustion, contribute significantly to the magnetic record in ombotrophic peat bogs. These relate directly, both spatially and temporally, to industrial activity, pre-industrial levels having values two or three orders of magnitude lower than recent ones.

Spherules have also been found at high latitudes in both Greenland (Hodge *et al.* 1964) and Antarctic ice deposits (Fredriksson and Martin 1963, Hodge *et al.* 1967). It is possible that these may have an industrial origin, although meteorological conditions which allow such particle movement are very rare. Chemical analyses show that most of the spherules in polar ice are very different from those of industrial origin (Hodge *et al.* 1964) so these particles are more likely to be of volcanic or possibly extraterrestrial origin (Hodge and Wright 1964). However, meteoritic dust and mineral ash have been confused in the past (Handy and Davidson 1953). Nickel was used to distinguish the two as it was found to be present in meteoritic material and absent in the ash. Chemical analyses of ash samples have since shown nickel to be present (Davison *et al.* 1974, Gladney *et al.* 1976, Kaakinen *et al.* 1975), therefore an industrial source for some of the particles in polar ice should not be excluded.

Spherical particles composed of magnetite have also been recorded in lake sediments, marsh sediments and beach sands in the New York City area. Spherule concentration decreased both away from the industrial area and down sediment cores, virtually disappearing below 10 cm. It was concluded they were of industrial origin (Puffer *et al.* 1980).

Magnetic particles in the sediments of Lake Mendota, Wisconsin, were similarly identified as industrial through chemical analysis (Nriagu and Bowser 1969). however, these extractions were solely magnetic and as not all mineral ash particles are magnetic, (depending on the iron content of the inorganic inclusion in the original fuel), these are not 'total mineral ash' methods.

Both white aluminosilicate and opaque spheroids have been counted in a profile of Severn Estuary sediments, yielding values of 10^8 grains kg^{-1} in surface (1985) sediments and a background value (down to a depth of 2.5 m) of $2x10^6$ grains kg^{-1} (Allen 1987). No chemical extraction was employed for this profile, a sediment smear of known weight being counted at x128 using a light microscope.

If particles from high temperature fossil-fuel combustion, volcanic and cosmic origins are only differentiable chemically, then counting these spheres using a light microscope, should give a low concentration of particles at all sediment depths. If input from these sources is constant through time, then this pre-industrial background value should also be fairly uniform in these levels, once sediment accumulation rate has been taken into account.

3.0 DEVELOPMENT OF AN EXTRACTION TECHNIQUE FOR MINERAL ASH PARTICLES

Except for the magnetic fraction, no extraction techniques for mineral ash particles appear in the literature, for either soils or sediment. Mineral ash particles are formed from the inorganic component present in the original fuel, so they are mostly aluminosilicate in composition with varying amounts of iron, colouring the spheres from yellow to dark brown and black. This means that they have a similar chemistry to many of the lake sediment minerals from which they are to be extracted thereby restricting the range of reagents that can be used. For example hydrofluoric acid (HF), utilised in other extractions to remove silicates such as SiF_4, is very effective at dissolving the silicate mineral ash and even at low concentrations such as a 1% solution, will etch the surface of the particles to reveal the underlying structure, mostly based on quartz (SiO_2) and mullite ($3Al_2O_3.2SiO_2$) (Hullett and Weinberger 1980).

It is however possible to remove some fractions of the sediment without damaging the mineral ash particles.

3.1 Organic material

This can be removed by using 30% hydrogen peroxide (H_2O_2), at about 50-60°C until the reaction ceases. Basic peroxide (a mixture of 6M KOH and 30% H_2O_2) and nitric acid are more effective oxidants than H_2O_2 alone, but these etch the ash particle surfaces.

3.2 Biogenic silica

Biogenic silica (that which is biologically incorporated in, for example, diatom frustules and chrysophyte cysts) can be removed from other forms of silica, such as mineral silica and non-crystalline or amorphous silica (eg. mineral 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 different concentrations of sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH) at 100°C for various lengths of time. Silicate analyses (Goltermann 1970) were performed on sub-samples removed at intervals from the digestion supernate. When the dissolved silicate concentration stopped increasing, the end of biogenic silica dissolution had been reached. In most cases interference from mineral sources is insignificant compared to the quantity of biogenic silica (Krausse *et al.* 1983), but were this not the case, the silicate concentration in the supernatant liquid would keep increasing with time rather than levelling off (see Figure 1). It can be seen from Figure 1 that for 0.3M NaOH, levelling off occurred after about two hours. No etching of the ash particles occurred until after six hours. Two - three hours was therefore the time selected for the extraction technique.

3.3 Mineral silica

Various techniques were tried to remove silicate mineral species from the mineral ash. Fluorosilicic acid (H_2SiF_6), preferentially removes feldspars and certain other minerals from quartz, but this also severely etched the ash spheres. Pyrosulphate ($Na_2S_2O_7$) fusions (Chapman *et al.* 1969, Kiely and Jackson 1965), digested the ash spheres as well as the minerals leaving only quartz grains, but as a 2M solution there was no effect on either ash spheres or silicate minerals. The same occurred for pyrophosphate ($Na_4P_2O_7$) digestions.

No satisfactory separation was achieved for mineral silicate and the mineral ash particles.

3.4 Magnetic separation

This can be achieved either by repeatedly swirling a covered magnet in a solution of the sediment, until no more magnetic particles are removed (Nriagu and Bowser 1969), or by using a more sophisticated technique, such as an automated self-circulating magnetic separator (Munro and Papamarinopoulos 1978). However, both methods only give a partial extraction, as not all ash particles are magnetic.

3.5 Carbonates

The strongest acid that dissolves carbonates (CO_3^{2-}) and bicarbonates (HCO_3^-), but leaves the ash spheres unaffected, was found to be 3M HCl applied at 80°C for 2 hours.

3.6 Density separations

Mineral ash particles found in lake sediments have a density of >1 g cm^3. Density studies of ash from power stations (Watt and Thorne 1965) show that virtually no particles have a density >2.9 g cm^3 (see Figure 2), thus heavy minerals can be separated by using heavy liquids such as 1,1,2,2 - tetrabromoethane (TBE) [$(CHBr_2)_2$] or sodium polytungstate [$3Na_2WO_4.9WO_3.H_2O$]. When viewed under SEM, the >2.9 g cm^3 fraction removed from lake sediment reveals large angular mineral grains. No spheres were noted at all.

Sodium polytungstate has the advantages over TBE of being non-toxic and non-corrosive. Its density is adjustable up to 3.1 g cm^3. It is neutral in aqueous solution and is stable in the pH range 2-14. It is very easy to handle, but quite viscous at these higher densities and so a centrifuge is required for effective separation.

4.0 LABORATORY PROCEDURE

The digestion is in four steps:

1) Place 0.2 g of dried sediment in a 250 ml beaker and add 50 ml 30% H_2O_2 Once the initial reaction has died down, place in an oven at 55°C and leave overnight. If, after this, a reaction is still occurring, add another 10 ml of H_2O_2 and return to the oven. Once reaction is complete, cool, centrifuge at 2000 rpm for five minutes to settle the residue, and wash in distilled deionised water.

2) Return the residue to the beaker and add 50 ml 0.3M NaOH. Heat at 100°C for 2.5 hours (including heating up time). Cool, centrifuge and wash as before.

3) Density separation.

a) with TBE (density = 2.96 g cm^3)

i) Wash the residue with acetone to remove the water, as water and TBE are immiscible. Remove as much of the supernate as possible.

ii) Add 2 ml of TBE to a glass centrifuge tube. Add the sediment residue and carefully add a further 2 ml TBE.

iii) Gently centrifuge at 500 rpm for two minutes.

iv) Discard the >2.96 g cm^3 fraction.

v) Wash the <2.96 g cm^3 fraction in acetone to remove the TBE and then in water to remove the acetone.

b) with sodium polytungstate (density adjusted to 2.95 g cm^3)

i) Remove as much supernatant water from the residue as possible.

ii) Add 2 ml of polytungstate to a centrifuge tube. Add the residue, then carefully add another 2 ml of polytungstate.

iii) Centrifuge at 500 rpm for two minutes.

iv) Discard the >2.95 g cm^3 fraction.

v) Wash the lighter fraction in distilled deionised water.

NB. Both TBE and polytungstate are recoverable from these methods.

4) Transfer the residue to a 100 ml beaker, add 30 ml 3M HCl and heat for two hours at 80°C. Wash and centrifuge.

4.1 Counting

A known fraction of the final residue is evaporated on to a coverslip, mounted with Naphrax (a diatom mountant) and the particles on the whole coverslip counted at x400 using a light microscope. Polystyrene microspheres (Battarbee and Kneen 1982) were not used as they appear similar to the ash spheres. A known concentration of exotic spores could be added to count in this way, but owing to low concentrations, large errors would be introduced lower down the core.

4.2 Effects of the method on the mineral ash particles

At each stage of the development of the method, samples were checked under the SEM to see the effect of the treatment upon the particles. There is no visible effect on the particles, and using EDAX there appears to be no chemical effect either.

4.3 Repeatability

To ascertain whether separate digestions of a sediment sample would give the same particle concentrations, five digestions from three sediment levels were replicated, followed by triplicate counts from each digestion. This gave 15 particle concentrations for each level from which 95% confidence limits on the statistical counting error were calculated. The results were as follows :

Level	Counts			Mean	S.D.	95% C.L.
4.5-5 cm	267700	282000	294300	257300	21500	250497-262360
	219600	243800	240600			
	238600	248800	273100			
	272400	222100	261600			
	255200	272700	267500			
11-11.5 cm	54240	56280	61170	56700	2760	53462-59345
	56900	55420	53910			
	60310	58510	60180			
	59350	58030	52830			
	53210	55950	54230			
22-23 cm	12230	11670	12740	12530	1250	11322-13784
	11410	11920	9700			
	14080	12780	13450			
	12370	12210	11990			
	12570	14870	13970			

All values in g^{-1} dry weight.

4.4 Recovery rate

A suspension of known mineral ash particle concentration was made up by adding a small amount of coal-fired residue from a power station to water. After homogenisation a known fraction was removed and counted at x400 under a light microscope, to calculate the concentration of the suspension. A known volume of the homogenised suspension was then added to a sediment sample before digestion. The sediment sample was from 100-101 cm depth at Loch Tinker (see Section 5.0), a level which had been previously counted and had only a 'background' value of ash spheres. After the digestion, the particle concentrations were counted as before and the value compared with the number of particles added to give a percentage recovery. These digestions were performed in triplicate and the recovery range was 82% - 102%.

Blank digestions show that no atmospheric or cross contamination from other digestions need occur as long as reasonable precautions are taken. Petri-dishes left in the open laboratory show that atmospheric contamination could cause false results at the lower levels, where only a few particles are present to be counted. Another source of contamination could be core smearing, caused by the action of the core tube entering the sediment and pushing some particles from higher levels down into the lower ones. The presence of low numbers of carbonaceous spheres (not found in volcanic or meteoritic dusts) in sediment levels corresponding to pre-industrial times, shows that smearing does occur, but this can be avoided by core 'trimming', (ie. using sediment from the interior of the core only.

4.5 Detection limit

Owing to the reasons outlined earlier, at the end of the digestion, there is still quite a lot of material present, only a fraction of which is made up of the mineral ash particles. Consequently, the limit of detection for this method is quite high at about 180-200 particles g^{-1} dry weight, although in practice particle numbers never get this low.

5.0 APPLICATION OF THE METHOD TO A SEDIMENT CORE

The technique was applied to a sediment core from Loch Tinker, an upland lake in the Trossachs region of central Scotland. The results are presented in Figure 3.

The basic trend of the profile is similar to that of the carbonaceous particle profile produced for Loch Tinker (Rose 1989) especially in the top 5 cm. The two profiles are compared in Figure 3. The main difference between these profiles is the continuous background value of the mineral ash, whereas the carbonaceous particle record falls to zero at about 24-25 cm depth. Below this, the mineral ash record is low and fairly uniform at between 2000 and 3500 particles g^{-1} dry weight. If this record is attributable to a constant background flux from non-industrial sources through time, the start of the 'industrial' mineral ash record can be identified and occurs here at approximately the same depth/date as the carbonaceous particle record.

Marked changes in the pre-industrial background concentration of particles may be related to significant changes in sediment accumulation (causing dilution), or to changes in atmospheric flux (eg. following a volcanic eruption). The identification of such events using this technique may be of additional palaeoecological or chronological value.

6.0 CONCLUSIONS

Although the method described does not remove all extraneous material it concentrates the particles sufficiently to make particle counting quick and accurate. The remaining residue is similar to mineral ash both chemically and in some physical aspects and it is difficult to carry out further extractions and, at the same time, retain all the mineral ash spheres.

The close similarity between mineral ash and carbonaceous particle profiles shows that their origins may well be closely linked, and as the mineral ash is derived mainly from coal-fired power stations, it seems reasonable to suggest that the majority of the carbonaceous particles are too. The origin of both types of particle should be made clearer by chemical characterisation.

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Figure 1. Biogenic Silica Digestion
0.3m NaOH at 100^{0}C

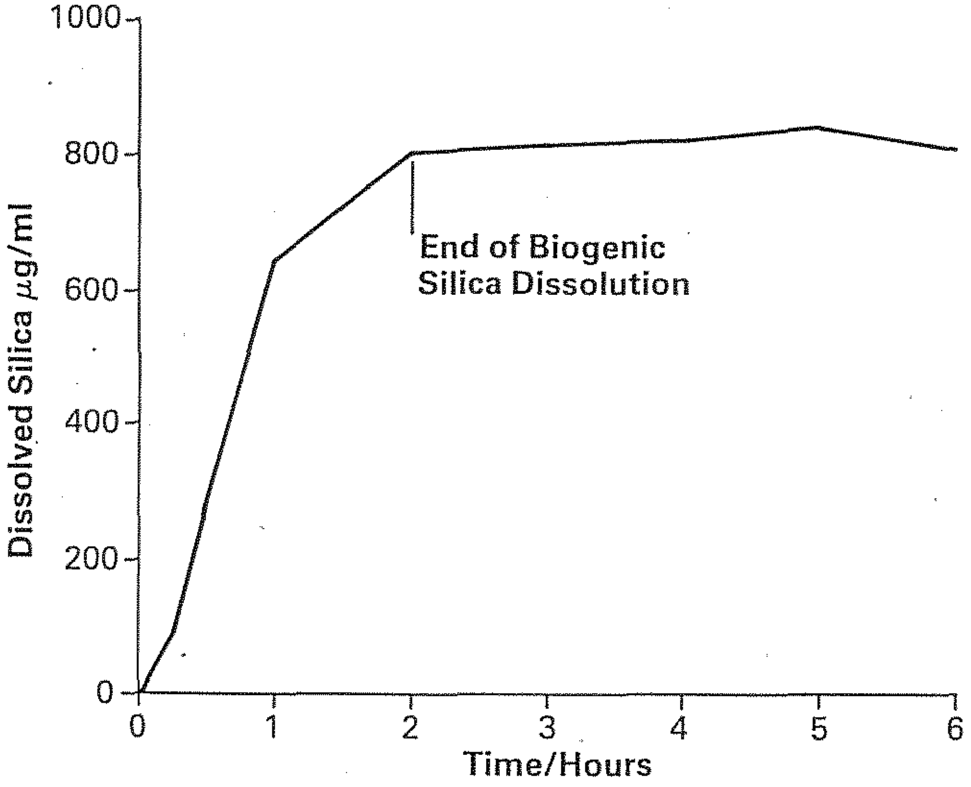
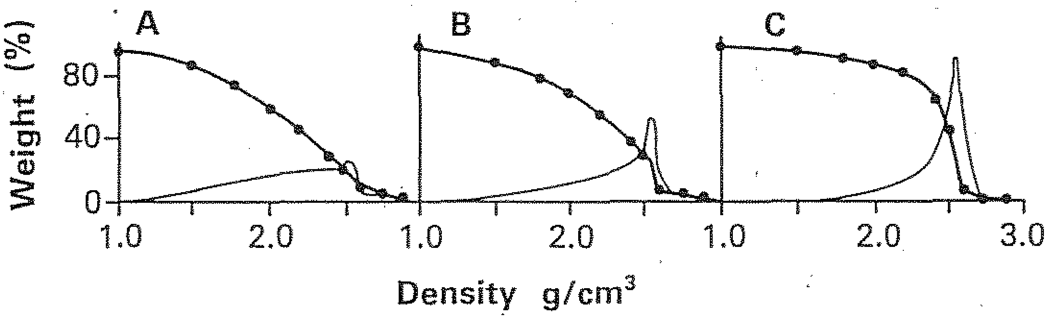
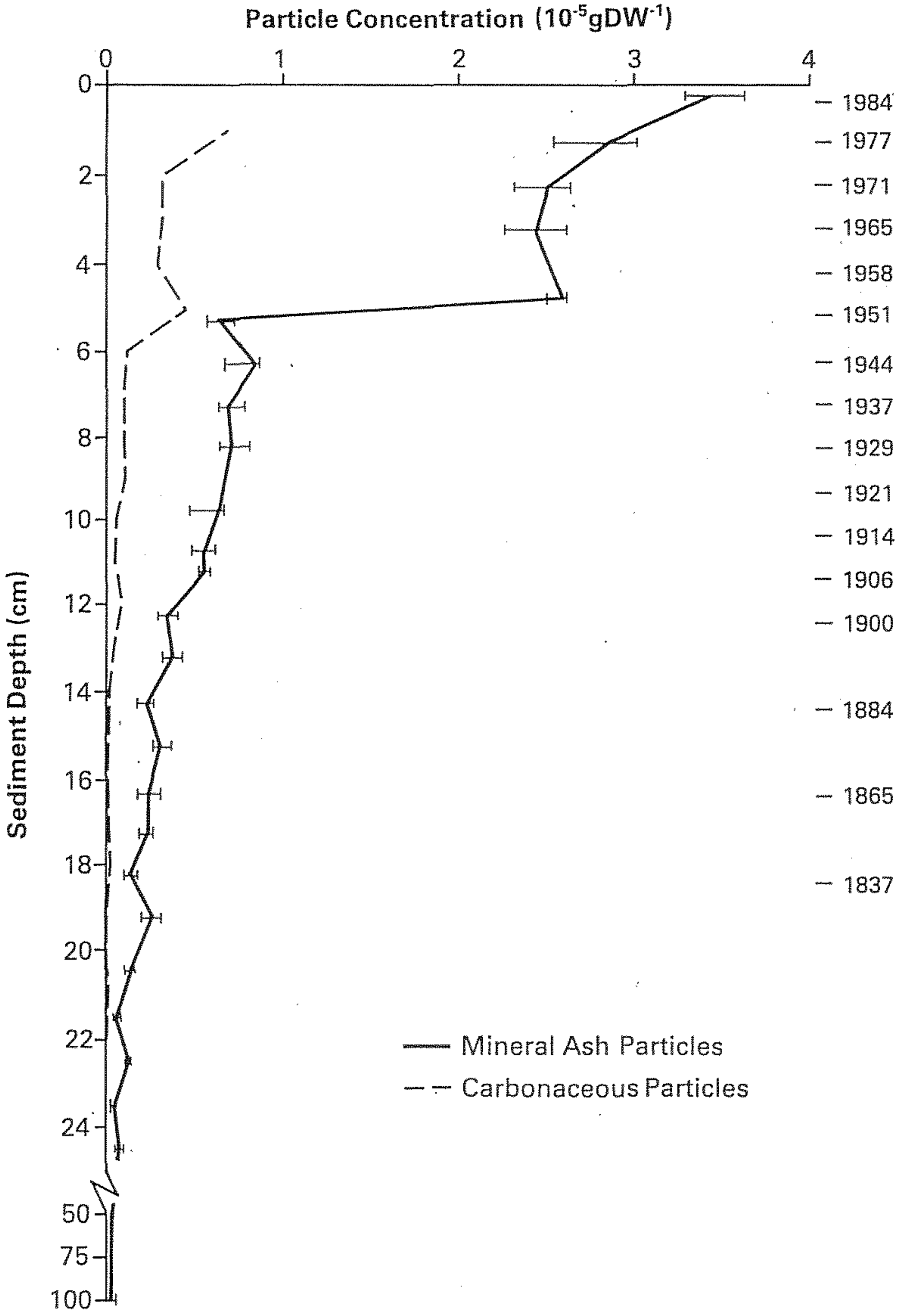


Figure 2. Density Distribution of Three Mineral Ashes



A) Carmarthen Bay
B) Castle Donington
C) Hams Hall
Curves without points are the Differential Points
(After Watt & Thorne, 1965)

Figure 3. Carbonaceous & Mineral-Ash Particle Concentration Profiles for Loch Tinker with 95% Confidence Limits



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