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PETROGRAPHY AND GEOCHEMISTRY OF A LOWER CARBONIFEROUS, LACUSTRINE, HOT-SPRING DEPOSIT, EAST KIRKTON, BATHGATE, SCOTLAND

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ABSTRACT.

The East Kirkton, Brigantian "limestone" was thought by Hibbcrt, (1836) to be of hot-spring origin due to the occurrence of numerous, small, spherulitic growths. This view was supportcd by Cadell, (1925) following his observations of active hot-springs in Yellowstone National Park and in New Zealand. The aim of the continuing research is to constrain this geological setting by examination of textural evidence and detailed geochemical analyses.

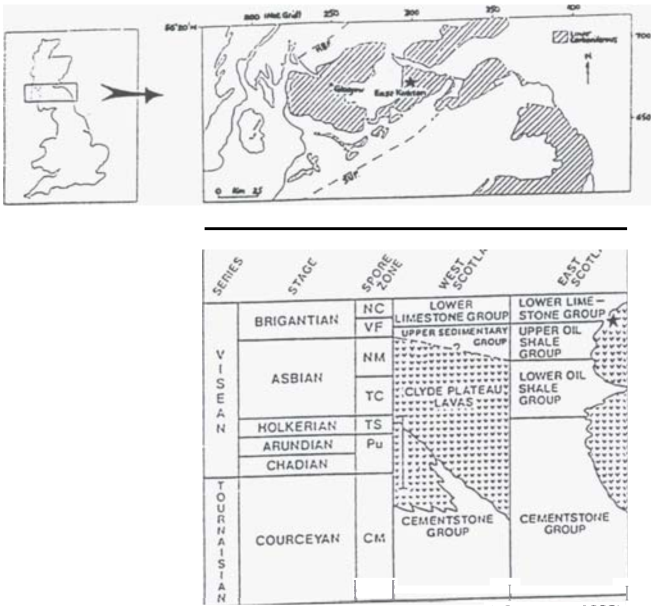
The spherules occur in most horizons of this finely laminated sequence, which includes: bituminous shales; carbonate rich and silica rich sediments; and occasional limestone bands and lenses. The regular laminae are typical of lake deposits, reflecting a low energy, environment of restricted circulation, with freshwater organisms preserved in many horizons. This study has focussed on tne silicic sediments, unusual in a fresh water lake. At East Kirkton many chert textures suggest an origin as gel-like precipitates. Synsedimentary slumping without brittle fracturing indicates a silica precipitate capable of ductile movement. Cracks have formed perpendicular to bedding, confined within the silica laminae. These may be the shrinkage cracks of silica gel. Both silica and carbonate form primary precipitates, though both also form several replaave phases. Cathodoluminescence (CL), UV fluorescence and SEM identify the presence of both carbonate and silica spherules, and also differentiate a variety of carbonate phases, principally calcite and dolomite.

Isotopic analysis of $\delta^{18}O$ and δD are presented constraining the origins of the siliceous fluids. The analyses ($\delta^{18}O$ = 21.3 to 26.9960, n=18; δD = -52.2 to -90.7‰, n=13) fall close to the "agate line" of Fallick et al (1986) and are consistent with equilibration of the cherts with L. Carboniferous meteoric water of $\delta^{18}O$ = -4‰ and δD = -20% at 40 to 90°C. Fluids in equilibrium with this silica "gel" may have been trapped only as the "gel" cooled and hardened, upon mixing with the lake waters, to results in fine, laminae of chert.

INTRODUCTION.

The East Kirkton "limestone" quarry is situated in an area of poor exposure in the Bathgate Hills, towards the eastern side of the Midland Valley of Scotland (Figure 1). The limestone is located stratigraphically at the top of the Upper Oil Shale Group, Brigantian (Stephenson and Monro, 1986). The East Kirkton sequence is 12m at its thickest, and is an alternation of finely laminated, lacustrine sediments, and ash horizons which are only poorly bedded and show little lateral continuity. Lake sediments preserve freshwater bivalves and evidence of considerable biological activity. The aim of the petrographic study and geochemical analyses is to constrain the geological setting of this deposit to reconcile evidence of low temperature environment indicated by the biological activity and high temperature input as indicated by the silica gel isotope analyses. Future research will include a soil geochemical survey to explore for zssociated mineralisation.

This small, disused quarry has become famous for its unusual fossil biota, including several unique, species of plant and animal. The fossil of the earliest reptile, nicknamed "Lizzie", is particulary well known since it has been featured in papers by Wood et al, (1985) and Gee, (1988), on television, and was even discussed by the British Parliament when it was to be sold abroad. The sale of this fossil eventually realised €200,000 and it is now exhibited in the National Museum of Scotland (NMS) in Edinburgh. It is hoped that by study of the flora



(after Scott. 1990).

Figure 1. Location map and extract from the Lower Carboniferous stratigraphic column indicating the position of the East Kirkton limestone.

and fauna of this quarry, much may be learned about the evolution of early terrestrial life. The research reported here forms part of the East Kirkton Project co-ordinated by W.D.I. Rolfe, (NMS). A review of studies under-taken up to 1989 has been published by Rolfe et al, (1990).

PALAEOENVIRONMENT.

Current interpretations suggest that the finely laminated sediments of which the succession is largely comprised, indicate a low energy, lacustrine environment which is disrupted by periodic volcanic eruptions depositing ash horizons of varying thickness (1m to 5cm). Tlie volcanic centre identified by Cadell, (1925) was situated 8 km to the north of the quarry. There has been slumping within tlie sequence triggered either by the volcanic activity or by syn-sedimentary faults.

The preserved fossil plants and animals have been washed into the lake from their terrestrial habitat. Some of the plant remains are preserved as fusain and may have been burnt by forest fires sparked by volcanic activity. Other sediments, including the carbonate splierules and slumped chert horizons appear to have been derived from a hot-spring. There were also laminae comprised of pellets that could have been the faecal pellets of some animal living in or beside the lake. Delicate plant spores are often preserved in these laminae and this combined with small cubes of pyrite indicate a reducing environment. Tlie therma' energy for the hydrothermal system could wcll have been high level intrusives such as alkali dolerites (teschenites) (Frances, 1983) associated with Lower Carboniferous volcanism in the Midland Valley of Scotland. The siliceous fluids are a possible product when meteoric water reacts with hot, alkaline basalt to produce hydrated alumino silicates such as prehnite and zeolites (Hall et al, 1989) and may thus have been derived from associated lavas and ashes.

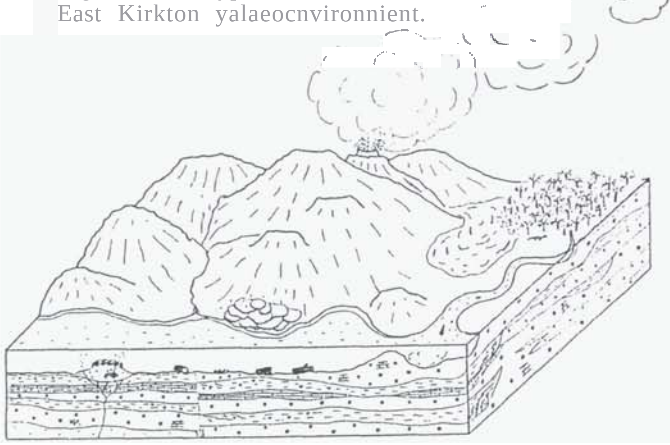
Within tlie quarry are two well defined massive lenses of carbonate. The lower of these was thought by Rolfe et al, (1990) to represent a carbonated sinter deposit. Present work suggests that it may have been a low mound grown around an active fluid conduit with both major carbonate and minor silica as chemical precipitates caused by tlie fluids expelled from the vent or by algal growth. The carbonate commonly forms in a stromatiform habit and distinct stromatolites are observed above tlie level of tlie sediments blanketing the lower parts of the lens; silica in the stromatolites may be a replacement of the carbonate or could have been fixed by tlie algae from a supersaturated silica solution. The second higlier lens is possibly a channel deposit, since some of the bedding is truncated against the lens aiid tlie overall shape of the lens was convex downwards with a flatter top. No evidence of layering was found in either of tlie lenses. Similar, smaller features were observed elsewhere in tlie quarry, formed from the stromatiform carbonate, these znay be fragments broken from a larger lens or they may be discrete growths.

PETROGRAPHY.

General Features.

The most striking feature of tlie succession is the occurrence within limited intervals of regular, fine laminae (Muir and Walton, 1957). These laminae are mainly carbonate rich and vary in colour, dark layers containing compressed organic debris. Many layers consist of a combination of carbonate spherules and organic debris, but some laminae are formed of silica. In hand specimen isolated lamina of dark brown chert can be seen within groups of carbonate laminae which vary in their colour, organic and clay content and frequency of spherule occurrence. Although the chert is less common than the carbonate, its occurrence throughout the succession suggests

Figure 2. A liypothetical reconstruction of the East Kirkton yalaeocnvironnient.



KEY

Carbonate – massive carbonate, quite coarsely crystalline and buff in colour except for darker more organic rich patches within it.
– carbonate rich patches within other lithologies, usually ash. - both maybe replacive but within the shales, individual laminae are often primary carbonate.
– buff coloured carbonate which appears stromatiform, fragments are often found in other horizons especially in the tuff.

Shale – well laminated material, with chert and bituminous horizons, often containing carbonate spherules.

Silica / chert – forming individual laminae as a primary deposit, but also replacing the organic rich and carbonate rich horizons

Tuff / ash – containing fragments of carbonate, plant material, silica and lithic volcanic clasts both vesicular and holocrystaline layers pinch and swell with little lateral continuity

Basalt – generally fine grained with vesicular flow tops

that understanding its origin and formation will contribute significantly towards interpretation of the palaeoenvironment. XRD analyses indicate that typical laminated limestone contains major calcite aiid quartz with minor kaolin and dolomite (probably ferroan). Tuffaceous layers are mainly calcite with minor kaolin, quartz aiid chlorite. Chert layers consist of quartz with minor calcite and trace dolomite.

A suite of thin sections was prepared by the NMS with material from a stratigraphic sequence logged through the quarry succession. By studying the textures of the whole sequence an initial ovcrvicw of the lithologies was gained before selecting the silica rich horizons to be studied in more detail. Thin sections were then prepared for all these silica laminae and various other types of silica from samples collected *in situ* and loose in tlie quarry.

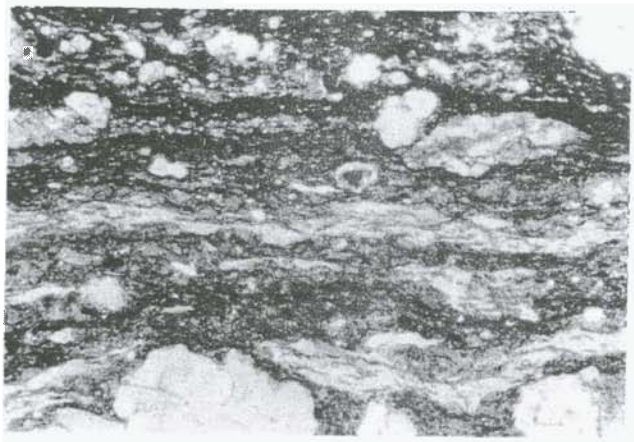


Plate 1. Attenuated lenses of clicrt formed due to compaction of the sediments (PPL). Field of view is 2mm.

Silica Textures.

There are several textural reasons why many chert laminae are considered to be primary. The chert layers (1mm to 3cm thick) are often slumped, like the carbonate and ash horizons around them. This is due to syn-sedimentary deformation (first recognised by Walton and Muir, 1957) where both carbonate and chert horizons have behaved plastically. For the chert a gel-like stage is envisaged for the unlithified layers. This is suggested by the pinching of some chert laminae around carbonate spherules. In other horizons there are small silica lenses, flattened and stretched by early compaction (plate 1). Similar textures are found in the carbonate, but they are usually of medium grained, granular calcite whereas the silica laminae and lenses are very fine grained.

There is no sharply defined contact between carbonate-silica laminae and in many cases the carbonate appears to grade into the silica, with isolated, often euhedral, carbonate crystals growing as though suspended within the chert (plate 2). These crystals may have formed from carbonate

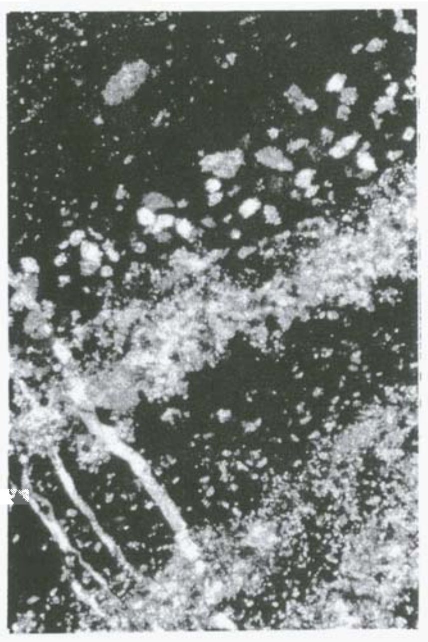


Plate 2. Typical alternation between carbonate and chert laminae, with rhombs of carbonate growing in the almost isotropic chert (XPL). Field of view is 2mm.

rich fluids trapped in the chert before it was fully hardened, thus allowing the crystals to grow euhedrally. However, they may have grown by replacement of the chert during early diagenesis.

Within some chert laminae a disordered pelloidal texture (plate 3) was observed using Ultra-Violet Fluorescence. Patches of many of the primary chert layers appear to be replaced organic material. From the lack of compaction of the organic pellets it can be concluded that replacement was an early feature of the primary lacustrine fluids. Similar pellets are found cemented by carbonate.

Many silica laminae have chert-filled and calcite-filled cracks cutting perpendicular to layering. It is thought that these may either be shrinkage cracks of the hardening silica gel or represent differential compaction of the layers, since they do not continue into adjacent carbonate laminae (plate 4).

Other occurrences of silica include isolated dark chert lenses within carbonated ash horizons and silica cement in stromatiform and pisolithic carbonate in the lower carbonate lens. The cementing silica is often a bluish white banded chalcedony but can also be amorphous white silica coating the walls of vugs and cavities. The centres of chalcedony coated vugs are often filled with equant megaquartz (Milliken, 1979) but are occasionally filled with single coarse calcite crystals, some of which contain small droplets of bitumen. In some vugs the chalcedony is zebraic (photograph 5) and takes an almost spherular form.

Plate 3. Pelloidal sediment suspended within a laminae of chert (UV Fluorescence). Field of view is 1mm.

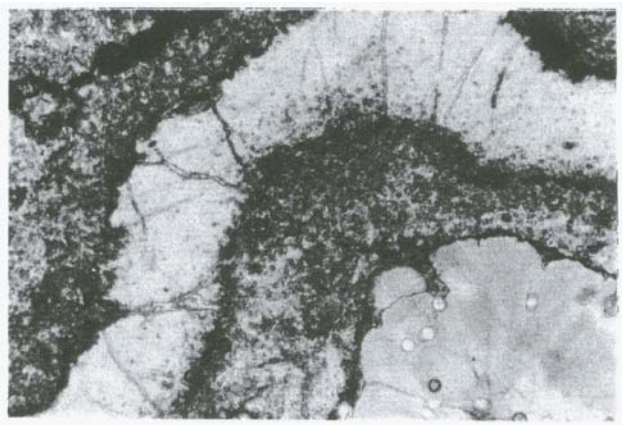


Plate 4. Laminae of chert and carbonate deposited above a carbonate spherule which has holes bored through it by some organism. The chert layer shows shrinkage cracks which do not continue into the carbonate horizons (PPL). Field of view is 2mm.

Spherulites.

Carbonate spherules are a common feature of the East Kirkton sediments and there may have been a feature of this environment that prompted both silica and carbonate phases to take spherular habits. There is a diversity of spherule types, the commonest being of radiating carbonate with no apparent nucleus. Others, buff-coloured in hand specimen and irregularly shaped, are of carbonate which forms a coating around plant fragments.

A few spherules have concentric rings and appear isotropic in thin section. These may consist

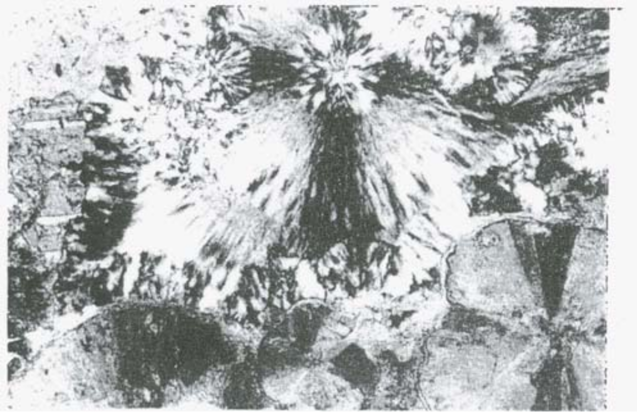


Plate 5. Vugs in the sediment of carbonate spherules filled by radiating zebraic chalcedony which also appears to form spherules (PPL). Field of view is 1mm.

of microcrystalline silica. Concentric banding of carbonate spherules was only observed when cathodoluminescence (CL) was used. CL is sensitive to changes in the ionisation state of Fe and Mn ions inherited from the solutions that formed the spherules. Thus the banding indicates that the Eh and the pH of the fluids changed several times during the formation of each spherule. Tlie more complex shape of some spherules can be explained by banded overgrowtiis around an original core (plate 6).

CL shows where neomorphism has occurred within a spherule, usually as a brighter patch of luminescing carbonate that cuts across the growth banding. The overgrowth stages are often preceded by erosion of the original core, although spherules that have been bored can have both the

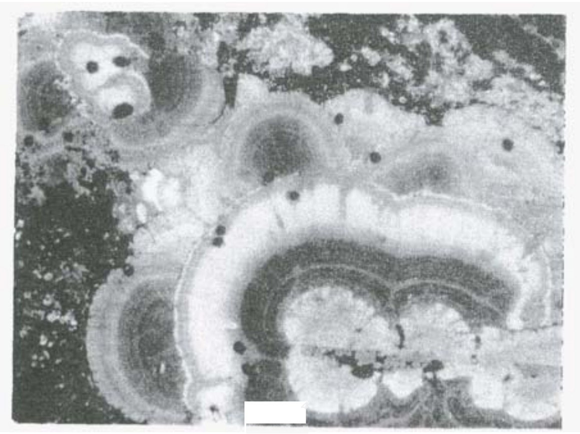


Plate 6. A carbonate spherule showing four stages of overgrowth around the original core. In this spherule both the core and the overgrowths have been bored and some of the brighter patches of the spherule appear to have been neomorphosed, due to tlie irregularity of their boundaries (CL). Field of view is 3mm.

central sphere of carbonate and tlie later overgrowths similarly bored (plate 6). Tliese borings may act as the passage-way along which neomorphosing fluids pass, but alteration around them is seldom observed. It is not clear why tlie organisms should choose to bore through these spherules but it can be concluded that they formed a loose aggregate for a period of time long enough for tlie boring to occur.

In some horizons many spherules are broken and this is another indicator of the transport of tlie spherulitic sediment. Many of the spherules wliicli appear whole in plane polarised and cross polarised light were observed in CL to have sections of their outermost growth rings broken off. This indicates that the ares of accumulationwere not the areas of generation.

Some of tlie primary carbonate was replaced by later carbonate as in the neomorpliisni in the spherules, but tlie carbonate is also replaced by silica. This is especially common in the stromatiform carbonate where only a skeletal remnant of carbonate remains. Often the process of replacement appears to highlight tlie growth banding of the spherule.

STABLE ISOTOPE ANALYSES.

Oxygen isotope analyses of the silica and hydrogen isotope analyses of the bound water (thought to be present as a silanole group, Si-Oil) have been obtained for some fifteen samples of variable silica forms, and data will be reported elsewhere (McGill et al 1990, in preparation). Here we are concerned with the implications of the data.

Earlier analyses measured $\delta^{18}O$ of only six silica samples (Rolfe et al, 1990). The results that have now been obtained extend the range of oxygen values, while confirming the earlier results, and including hydrogen isotope analyses. Eighteen silica samples give a range of $\delta^{18}O$ = 21.3 to 26.9‰.

Thirteen samples were analysed for hydrogen isotopes. The range of values obtained is δD = -52.2 to -90.7‰. Tlie water contents of the samples were measured during analysis and the range is 0.28 to 0.52 wt% H_2O. There was no correlation between the water contents of the silica samples and δD showing that the isotope results were riot influenced by yield.

INTERPRETATION OF ISOTOPE RESULTS.

The East Kirkton isotopic analyses plot relatively close together (Figure 3) suggesting that the different silica samples were formed by similar fluids, or by a fluid with a small variation in isotopic composition, and within a narrow range of temperatures (see line to represent 10°C variation, Figure 5). They plot quite close to the "agate line" indicating similar fractionation and formation processes. The "agate line" is the best fit line through data from Scottish Tertiary and Devonian agates (Fallick et al, 1986). This line has an equation similar to tlie present day Global Meteoric Water Line (MWL), $\delta D = 7.9\delta^{18}O - 260$ and it was concluded (ibid.) that the East Kirkton silica had formed from slightly heavier meteoric water than Devonian agates. These values are consistent with formation from L. Carboniferous meteoric water which would have approached the zero seawater value as Scotland approached equatorial latitudes. Formation fluids of a magmatic origin are ruled out.

Assuming a Scottish L. Carboniferous meteoric

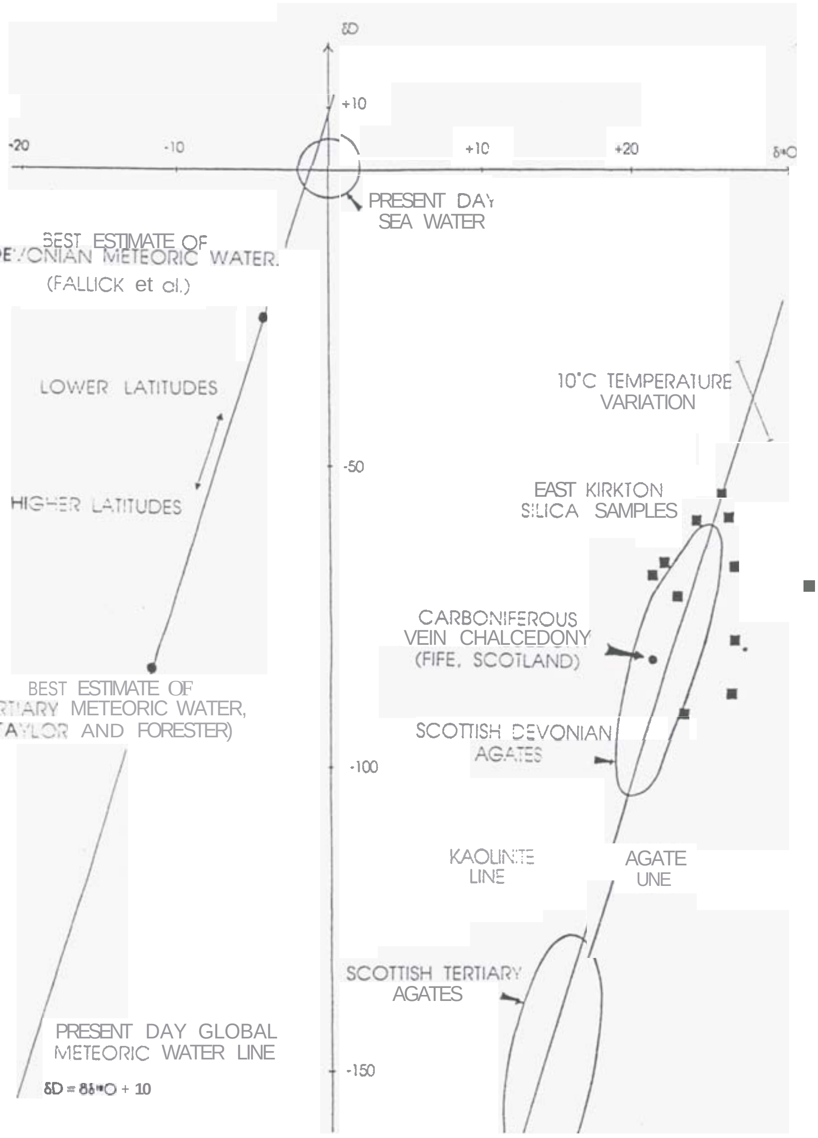


Figure **3.** $\delta^{18}O$ v δD plot of East Kirkton chert (■). Also shown are agate data from Fallick et al., (1986) and the best estimates of Devonian (ibid.) and Tertiary (Taylor and Forester, 1971) Scottish meteoric water. The probable position of L.Carboniferous meteoric water will be heavier than Devonian (-5‰, -20‰) and may be modified hydrothermal system (this would result in even heavier $\delta^{18}O$ of closer to 0). A 10°C temperature variation about the agate line is indicated (Fallick et al., 1986).

$\delta^{18}O_{H_2O}$ value of -4‰, the equation of Matsuhisa et al (1979) can be used to obtain temperature estimates:

$$\delta^{18}O_{qtz} - \delta^{18}O_{H_2O} = \frac{3.34 \times 10^6}{T^2(°K)} - 3.31$$

These calculations yield a temperature range of 40-90°C corresponding to the equilibrium temperatures of the cooled silica gel and associated fluid. The results are consistent with periodic input of high temperature (near to or above boiling) siliceous solutions into the cool lake water, where mixing of the fluids resulted in the precipitation of silica.

While much of the variation in isotopic composition may he due to temperature differences, it is also probable that the isotopic signature of the meteoric water was modified within the hydrothermal system as the water tended towards re-equilibration with hot basalt. The modified oxygen isotope value would approach +8‰ and this would lead to higher calculated equilibrium temperatures (+80°C approx.) due to the correspondingly smaller fractionation. Organic matter is abundant in the samples and this is known to possibly absorb deuterium giving anomalously light δD measurements. Future analyses will be undertaken on organic-free samples.

CONCLUSIONS

1. Regular laminated horizons indicate a quiet, lacustrine environment with minor, fine sediment enriched in organic material and disturbed by influxes of silica gel, carbonate spherules, and poorly graded basaltic ash.

2. The lake water may have been stratified due to influxes of fluids at different temperatures. Pyrite is also common in some laminated horizons and indicates anoxic conditions, associated with abundant organic material, in deeper parts of the lake.

3. Primary silica originated as a gel. This is shown by syn-sedimentary slumping in some laminae, the possible shrinkage cracks, carbonate rhombs which grow in suspension in the chert, and the occasional grading of carbonate laminae into chert.

4. The prescence of both silica and carbonate splierules suggests that the precipitation of silica and carbonate may have been controlled in a similar way to promote spherular growth.

5. The silica probably originated from a hydrothermal remobilisation of silica in the mildly alkaline associated volcanics, with circulation triggered by the intrusion of the later, high-level, alkali dolerite dykes and sills.

6. Carbonate spherule zones seen with cathodoluminescence indicate frequent changes in Eh and pH of formation waters.

7. High organic content in silica and carbonate laminae and bituminous shales suggest high biological productivity and preservation potential.

8. A dominantly low temperature environment is suggested by: (i) the temperature range from $\delta^{18}O$ results (ie 40-90°C), (ii) organic matter eg. spores are well preserved, and (iii) organisms must have lived in the water, since some excreted pellets and others bored into spherules. The above give a picture of mixing fluids, some warmer and some cooler allowing organisms to live close to a hostile hot-spring environment.

9. The isotopic signature is that of water in equilibrium with the silica gel until a certain temperature at which it hardened and no further isotopic exchange occurred.

10. Meteoric water is the major component of the silica formation fluids.

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