

Geochemical and sedimentological indicators of anoxia in a polar Cretaceous lake with exceptional fossil preservation

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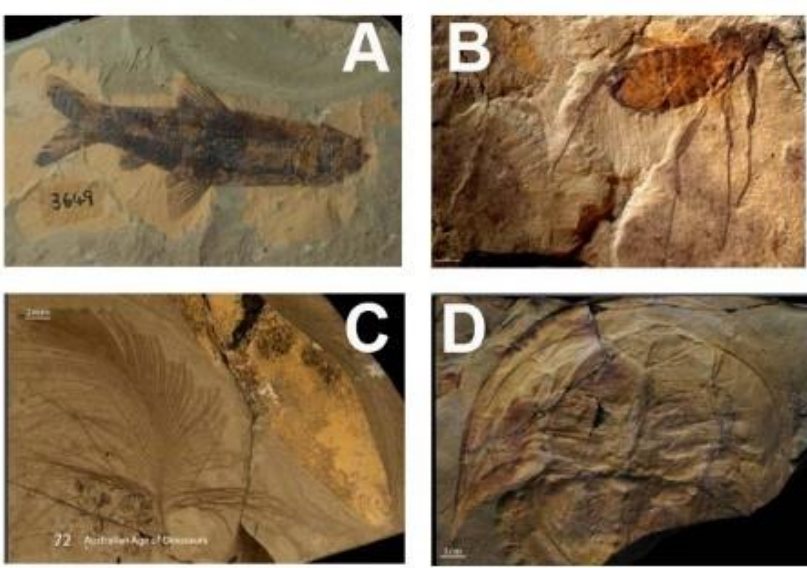
The polar latitude and remarkable level of fossil preservation in the Cretaceous Koonwarra fossil beds of Australia make this lacustrine deposit a unique lagerstätte, and recent coring of the discovery site allows for time-series paleoenvironmental reconstructions. Fine-grained silts and shales accumulated in this rift valley lake associated with the breakup of Australia and Antarctica during the Barremian to Aptian stages of the Cretaceous Period (ca. 125 to 113 million years ago). The exceptional preservation of fossil fish, insects, and feathers coupled with the presence of undisturbed varves are suggestive of anoxic bottom waters. To test this hypothesis, the mineralogical, elemental, and isotopic compositions of ~100 closely-spaced stratigraphic samples were determined to better understand whether a change in the degree of bottom water anoxia was the cause of exceptional fossil preservation. There are notable down core increases in the abundance of organic carbon, total nitrogen and pyrite sulfur starting around the 16 m depth. While the $\delta^{13}\text{C}$ composition of organic matter shows no apparent change – suggesting balanced terrestrial and algal inputs to these lacustrine sediments – ^{15}N abundances increase in the lower half of the core, while the $\delta^{34}\text{S}$ trend reveals three marked oscillations (ranging between -8 and -2‰) through the same interval. These observations, coupled with the fossil distributions, suggest bottom water anoxia during deposition of the lower Koonwarra lake sediments. Microbial denitrification would likely have been the primary driver of organic carbon remineralization, which would result in the loss of ^{14}N as N_2 to the atmosphere and production of authigenic carbonate. The strong sulfur isotope variations are understood in terms of variable sulfate content of the lake, which affects the magnitude of fractionation by microbial sulfate based on either a reservoir effect or environmental conditions that control the rate of sulfate reduction or both. Episodic sulfate enrichment in the lacustrine environment may be controlled by marine incursions, weathering of source terrains, or volcanic episodes. Given that the time scale of sediment accumulation in the lower half of the core (as estimated by varve counts) is ~2500 years, marine incursion and changes in weathering are unlikely, but episodic volcanism in the rift setting where the lake was situated seems the plausible cause of changes in Koonwarra lake sulfate concentrations.

Introduction & Background

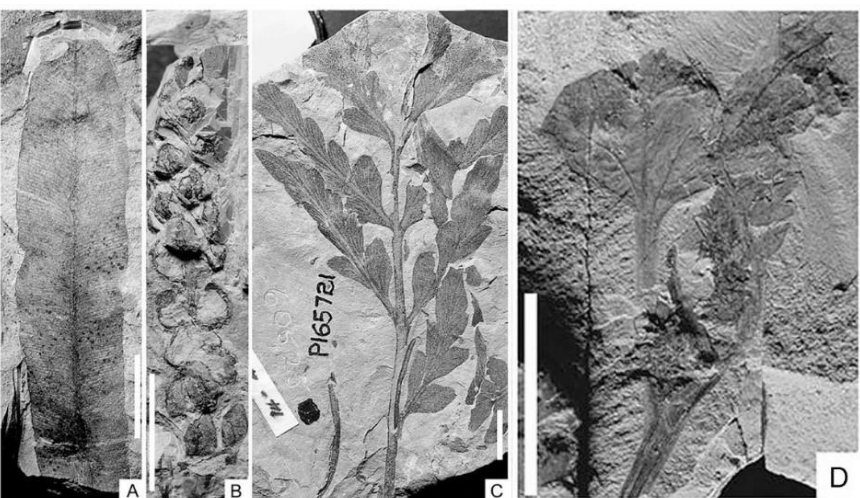
Koonwarra was discovered in Victoria, Australia in 1960 and has been visited by geologists for years due to the exceptional degree of fossil preservation. It is a lake deposit from the Aptian stage of the Cretaceous Period. During deposition the lake was at a high polar latitude; despite the overall warmth of the Cretaceous the Aptian actually was a time of cooling.



Geologists working in the field at Koonwarra. Photo by Andrew Drinnan.



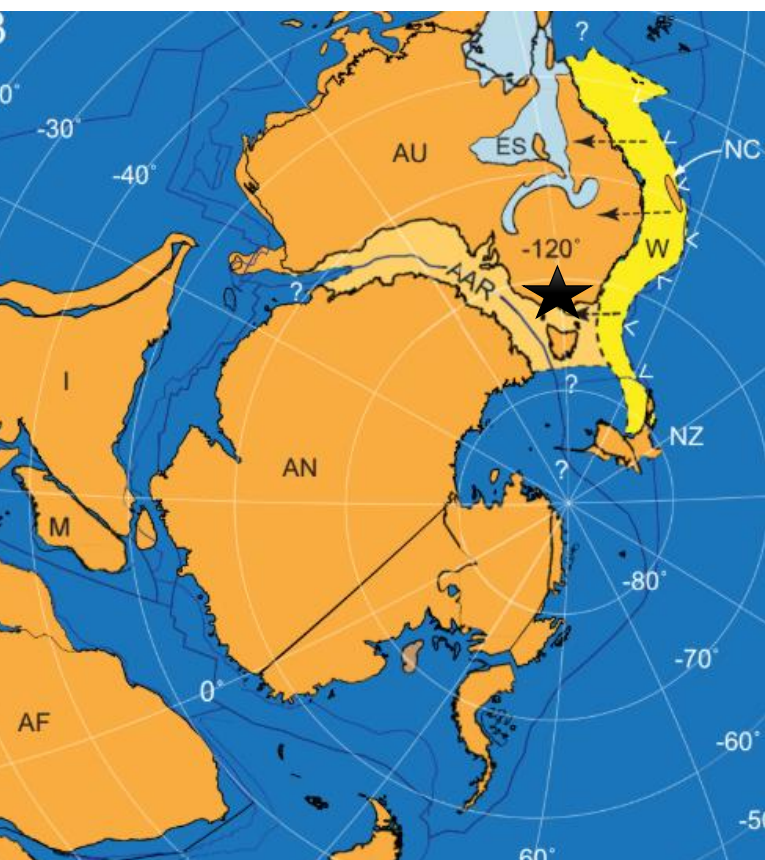
Fish(A), Flea(B), Feather(C), and Horseshoe Crab(D) fossils found at the Koonwarra site. Photos from Stephen Poropat (A,C), John Broomfield (B), and Frank Holmes (D).



The Koonwarra area is also the location of one of the oldest angiosperms. Seed ferns and conifers were common. Photos after Poropat et al. (2018) with scale bars = 10 mm.

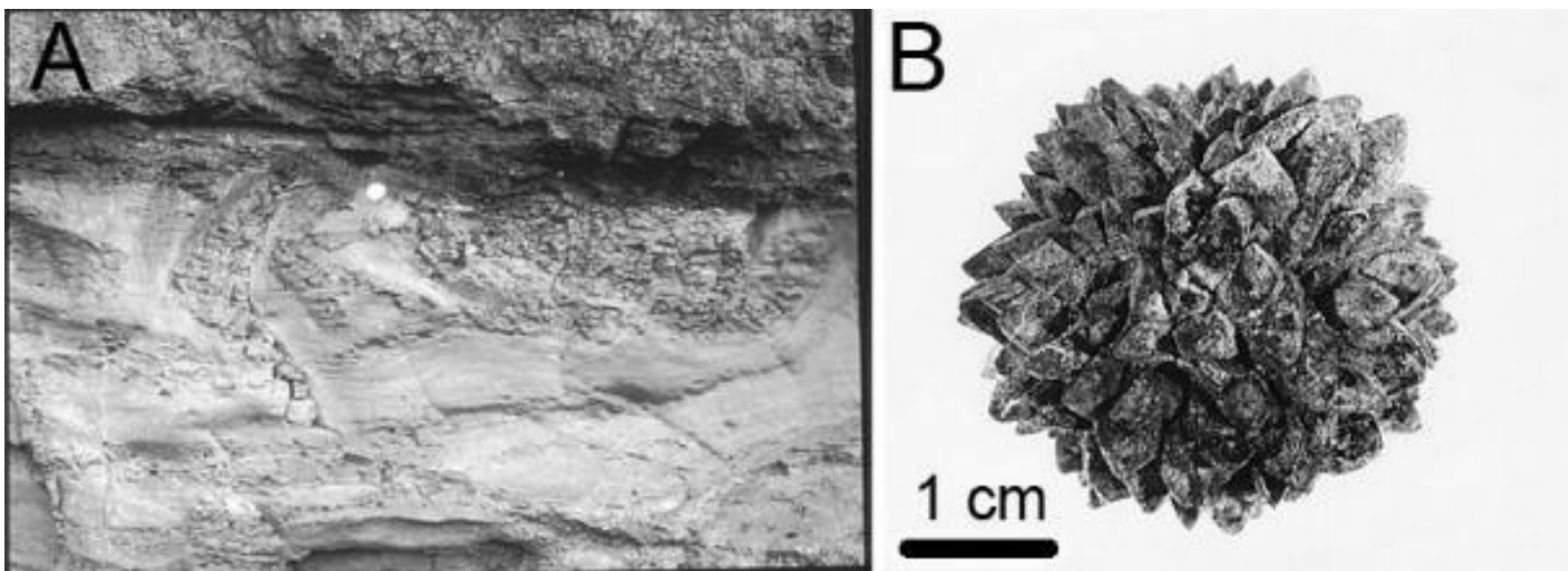
Hypothesis

If the Koonwarra core samples have a high abundance of ^{15}N as well as high abundances of total organic carbon (relative to modern polar lakes), then the ancient lake likely experienced periodic anoxic conditions in the water column and in the sediments consistent with the denitrification processes. If there is no enrichment in ^{15}N or of organic matter in the Koonwarra lake sediments (relative to modern polar lakes), then the water column was likely to be constantly oxygenated.

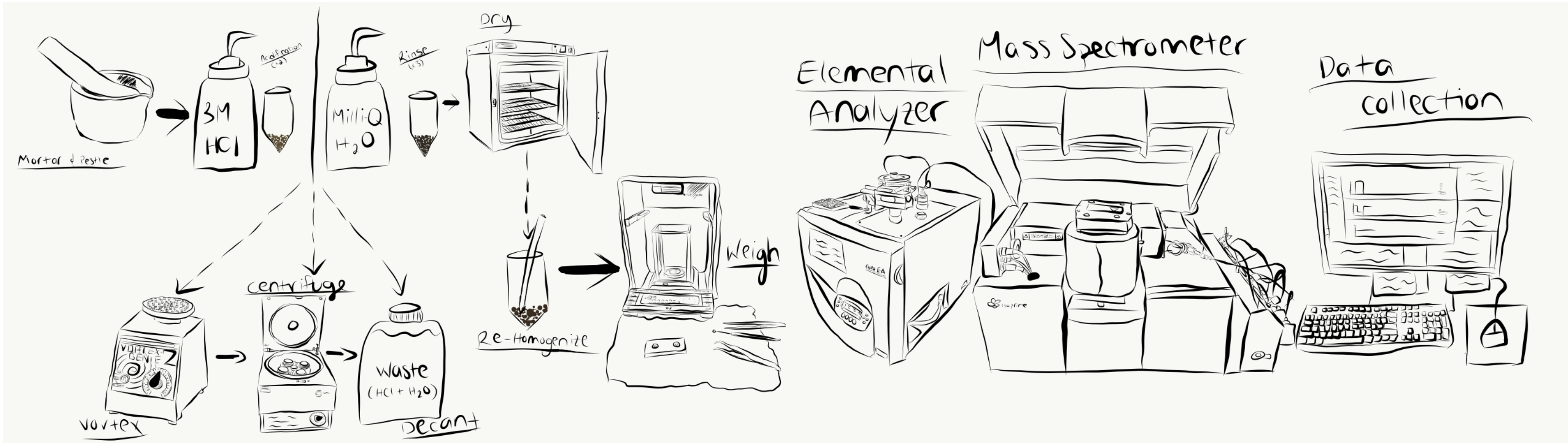


A paleogeographic reconstruction of Australia during the Cretaceous modified from Herne et al. (2019). The black star represents the position of Koonwarra, which was at a polar latitude (~70°S) and situated along the Antarctica-Australia rift basin (AAR). Rifting was likely associated with episodic volcanic eruptions and potential seawater incursion.

Cryoturbation structure (A) (Constantine et al., 1988) and Glendonite (B) (Delurio and Frakes, 1999) found in the Koonwarra region. Both are evidence of nearby glaciation. There have also been dropstones and glacial tillite found in formations across Southern Australia.

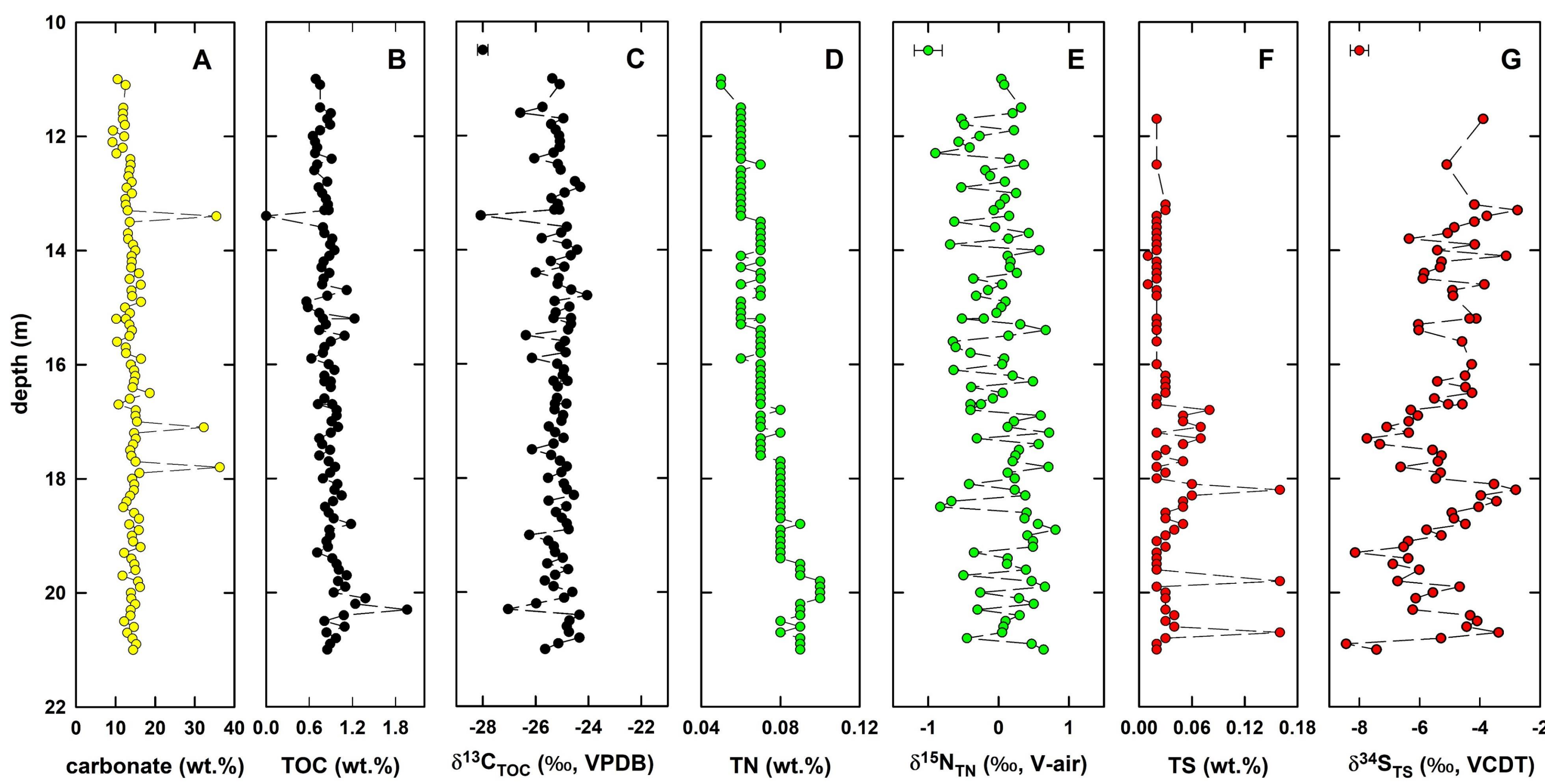


Methods



$$\delta = (((aX/bX)_{\text{sample}} / ((aX/bX)_{\text{standard}}) - 1) \times 1000$$

Results



Carbonate

Carbonate values have the largest range of values as well as the largest standard deviation, since they varied so much. They have a trend of increasing with depth.

Organic Carbon

The $\delta^{13}\text{C}$ values do not have any significant trend in terms of increasing or decreasing with depth. TOC values do significantly increase with depth.

Nitrogen

Total Nitrogen (TN) and $\delta^{15}\text{N}$ show an increasing trend with depth. The $\delta^{15}\text{N}$ values show many oscillations. There is also a distinct shift around 16 m where TN values increase and move more to the right.

Sulfur

Total Sulfur (TS) values remain fairly constant with a slight increasing trend with depth. There are also three points of higher TS abundance than throughout the rest of the core. These three points appear to coincide with the inflection points of the $\delta^{34}\text{S}$ values. The $\delta^{34}\text{S}$ values show a trend below 16 m of distinct cyclicity and have an overall decreasing trend.

Discussion

Carbonate

The processes of denitrification and sulfate reduction create alkalinity so authigenic carbonate would seem to be the most likely input. There is also a lack of fossilized carbonate shells in the lake. This could mean that the lake may have been anoxic and had a lower pH.

Organic Carbon

Since $\delta^{13}\text{C}$ did not change significantly with depth the carbon input was not changing much throughout deposition. Organic geochemical studies suggest that the carbon in the lake was dominantly coming from terrestrial sources, as opposed to algal sources. The TOC has an increasing trend with depth which would be due to the slowing of respiratory processes in anoxic environments.

Nitrogen

The increase in TN and the more positive values below 16 m could be a sign of more anoxic water although it is likely not a sharp contact between oxic and anoxic water. The increase in $\delta^{15}\text{N}$ values is what is expected in a denitrifying environment, since the ^{15}N isotope is left behind in the sediments during the process.

Sulfur

The major shifts in the sulfur isotope may be supportive of an anoxic environment because sulfate reduction and formation of pyrite requires ferrous iron, which is only soluble in anoxic waters. One way to create shifts in $\delta^{34}\text{S}$ is by a differential source terrain or intensity of weathering products. An increase in sulfate composition could also be due to marine incursions. The most plausible source of sulfate would be from the volcanic activity in the region due to the rifting. This type of explosive event could also be a kill mechanism for the fish. These events would be episodic and make more sense than marine incursions and weathering changes, with a ~2500 year time scale.

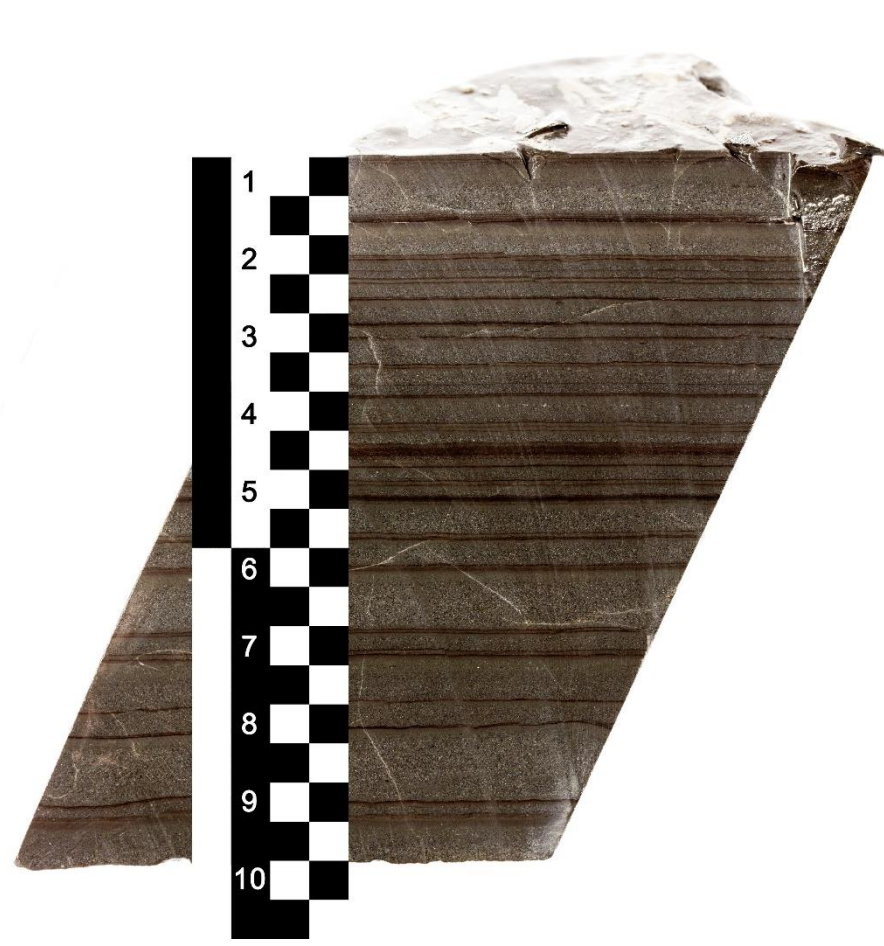
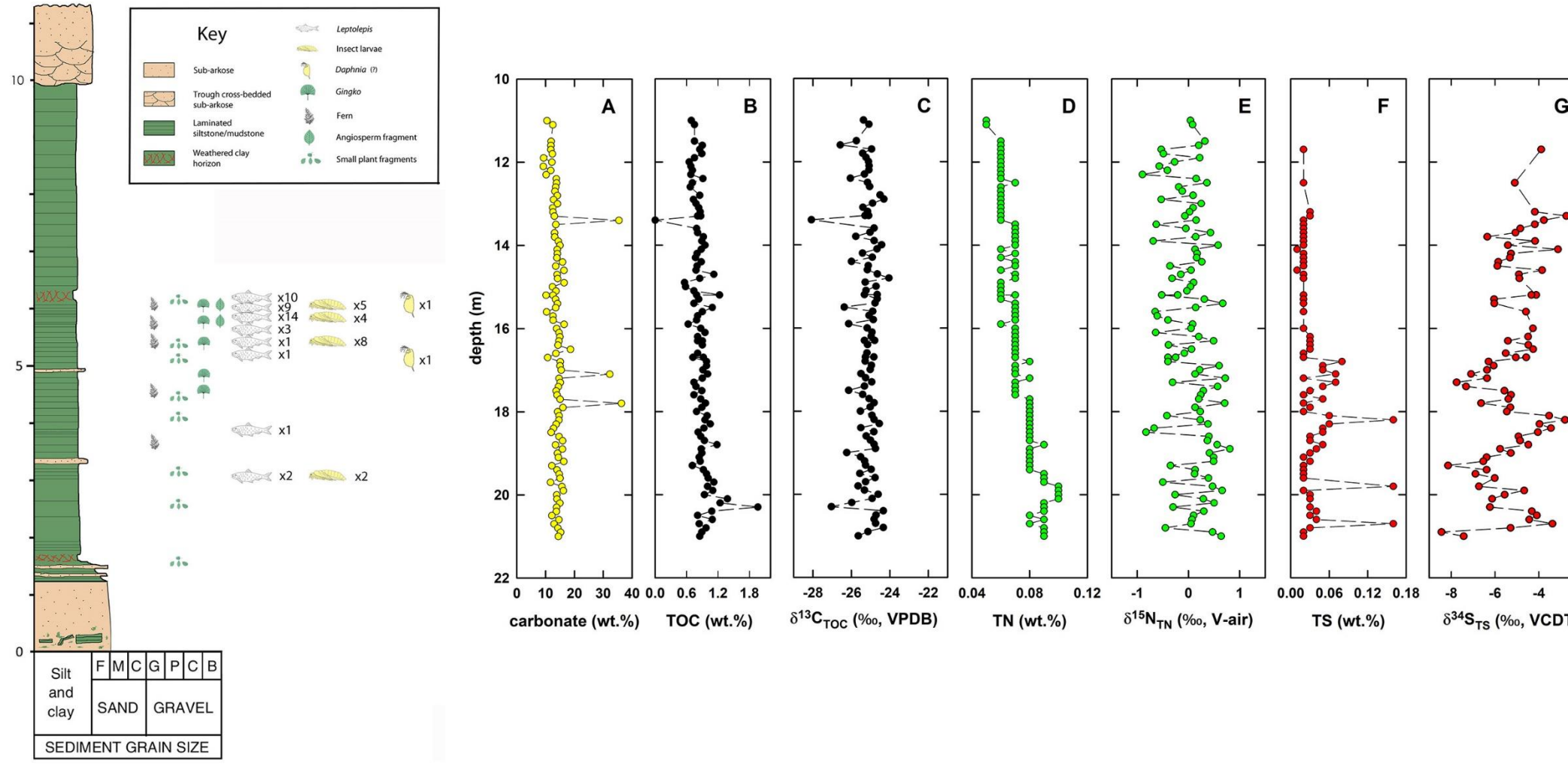


Image from Tom Rich of varves from a 10 cm interval at 17.80 meters in the Koonwarra Fossil Beds core. This was used to determine the time scale of the core.



Most of the geochemical markers that were measured showed distinct shifts at 16 m depth. 16 m is also where the fossils appear in the strata. This could be a point of greater anoxia or a point where water became completely anoxic.

References & Acknowledgments

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