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

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#### **Abstract**

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. On average, the fine grained siliciclastic specimens contain between 10 and 15% calcite throughout the core, but 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  $\delta^{13}$ C composition of organic matter shows no apparent change – suggesting balanced terrestrial and algal inputs to these lacustrine sediments - <sup>15</sup>N abundances increase in the lower half of the core, while the  $\delta^{34}$ 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 (an anaerobic process) 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, with the subsequent buildup of <sup>15</sup>N in sedimentary organic matter, 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 reduction (another anaerobic process, which similarly results in carbonate formation) 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. Whether occasional volcanic inputs were also responsible for exceptional fossil preservation remains unknown. This time-series study provides a new geochemical window in which to observe environmental changes in a polar Cretaceous lake during a time that global climates were warmer and dinosaurs roamed highlatitude land masses.

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#### **Introduction**

The Koonwarra fossil beds in Victoria, Australia were discovered in 1961 while road workers were straightening a portion of the South Gippsland Highway (Waldman, 1973). One of these workers found a fish fossil on the surface of the exposed sediments, which subsequently attracted local geologists. Because of the numbers of specimens and the exceptional level of fossil preservation in some horizons, the deposits are considered to be a lagerstätte. Since its discovery, researchers have found numerous insect, and fish species, as well as some of the oldest known feathers (Talent et al., 1966; Waldman, 1970), and a horseshoe crab (Fig. 1). Plants, which include ginkos and the earliest potential angiosperm flower (Taylor & Hickey, 1990) (Fig. 2), are also abundant in the Koonwarra deposit. The high quality of preservation and the presence of feathers (as well as a typically marine crustacean) make this an especially intriguing lacustrine paleontological site, but even more so due to its polar latitude at the time of deposition (Torsvik et al., 2012; Van Hinsbergen et al., 2015). At 70°S latitude, Lake Koonwarra would have experienced prolonged periods of darkness each year with virtually no daylight for nearly two months (see: <a href="https://aa.usno.navy.mil/data/docs/Dur\_OneYear.php">https://aa.usno.navy.mil/data/docs/Dur\_OneYear.php</a>).

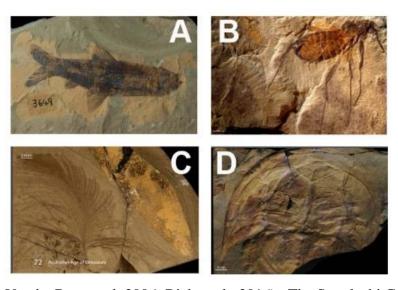


Figure 1: (A) fish [Waldmanichthys koonwarri (Waldman 1971a) Sferco, López-Arbarello & Báez 2015a], (B) flea [Tarwinia australis Jell & Duncan 1986], (C) feather, and (D) horseshoe crab [Victalimulus mcqueeni Riek & Gill 1971] from the Koonwarra site in Victoria, Australia (images from Poropat et al., 2018).

The Koonwarra Fossil Beds occur in the upper Strzelecki Group (Holdgate et al., 2015;

VandenBerg et al. 2006; Rich et al., 2016). The Strzelecki Group was much earlier considered to be Jurassic in age, but the discovery of dicotyledonous leaves (Kenley, 1954: Medwell, 1954) and palynological research on various deposits throughout Victoria (Cookson & Dettmann 1958, Dettmann, 1963) more recently indicated an Early Cretaceous age for the deposit. Fission track dating of Koonwarra samples yield an age of  $118 \pm 5$  Ma and  $115 \pm 6$  Ma indicating a middle to late Aptian age (Gleadow & Duddy, 1980; Lindsay, 1982).

The Cretaceous is known as a time with a warmer climate, higher sea levels resulting in flooding of the emergent continents and creation of shallow inland seas, and dinosaur domination. The Aptian, however, likely experienced a relative cool spell during the Cretaceous (Nunn and Price, 2010). Glaciation was possible at high latitudes during the Aptian, especially with over two months of darkness, and with direct evidence of glacial deposition throughout Australia, including the Koonwarra region (Frakes et al., 1995; Constantine et al., 1998; DeLurio et al., 1999; Alley & Frakes, 2003).

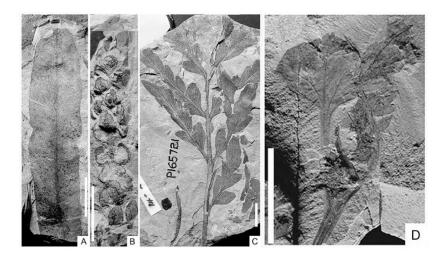


Figure 2: Typical seed ferns found at Koonwarra: (A) *Taeniopteris daintreei* McCoy 1874, (B) *Palissya elegans* Parris, Drinnan & Cantrill 1995, and (C) *Komlopteris indica* Barbacka 1994; and (D) the oldest (Aptian) angiosperm flower with stem and leaves known from Australia. Images after Poropat et al. (2018) with scale bars = 10 mm.

The mean annual temperature in Victoria, Australia in the Aptian has been estimated to be between -2 and 3°C (Constantine et al., 1998). Other estimates were mentioned, however this range was deemed the most consistent and encompassing by the authors (Poropat et al., 2018). At this high latitude site there is abundant evidence for annual freezing cycles as recorded in the Koonwarra varves, as well as cryoturbation (Constantine et al., 1988)(Fig. 3A), dropstones (Frakes & Krassay, 1992), glendonite (Fig. 3B)(Delurio & Frakes, 1999), and glacial tillite (Alley & Frakes, 2003) in other Aptian formations across southern Australia.

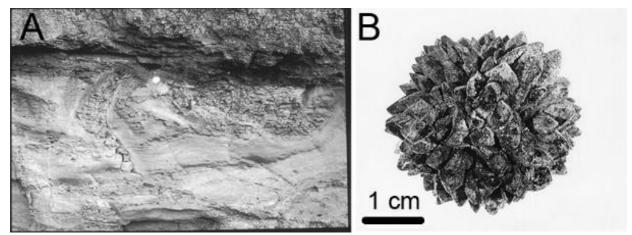
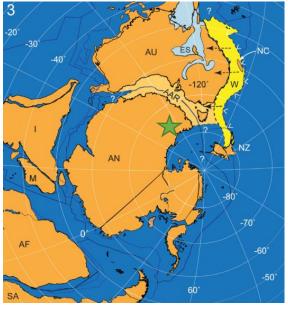


Figure 3: (A) cryoturbation structure in the Wonthaggi Formation near to Koonwarra (Constantine et al., 1988) [width of photo approximately 1 meter] and (B) glendonite, a pseudomorph after ikaite from the Bulldog Formation of the Aptian Eromanga Basin that forms in a marine environment with near freezing temperatures (not higher than  $4^{\circ}$ C), high alkalinity, orthophosphate and pCO<sub>2</sub> (Delurio and Frakes, 1999).

The Koonwarra Fossil Beds were situated within the Australia-Antarctica rift zone during the Early Cretaceous (Fig. 4). The rifting of this area began in the Jurassic (Willcox & Stagg, 1990, Totterdell et al., 2000) and the plates were fully separated by the Campanian Stage (Norvick & Smith 2001, Seton et al., 2012). Rifting took place in three stages, during the Tithonian,

Hauterivian-Barremeian, and the Aptian-Albian (Norvick & Smith, 2001, Hill & Exon, 2004). Since Koonwarra has been dated as being late Aptian in age, sediment accumulation in the lake would have been associated with the ultimate phase of rifting. The basin was dominantly filled with volcanogenic sediments from the east (Edwards & Baker 1943, Edwards et al., 1996), providing indirect evidence for volcanic activity during Koonwarra deposition.

Figure 4: A paleogeographic reconstruction of the southern polar region during the Early Cretaceous Period. Koonwarra is situated beneath the green star. AAR (Australia-Antarctic Rift), AU (Australia), AN (Antarctica), as modified from Herne et al. (2019). Rifting was likely associated with episodic volcanic eruptions and potential seawater incursion to the Koonwarra region.



Because the Cretaceous is known as the age of dinosaurs, it is no wonder that the discovery of a dinosaur feather at the Koonwarra site drew heads. Polar dinosaurs of Barremian to Aptian age have been discovered at various localities near Victoria, including the Dinosaur Cove (Molan, 2008), Flat Rocks (Seegets-Villiers, 2012, Kool, 2015), and Eric the Red West sites (Rich et al., 2009). Polar dinosaurs would have been well adapted to the cooler climate and the months of darkness that accompanied it (Fig. 5), especially if they were warm blooded and had a thick armor of plumage. Koonwarra is one of the leading sites for finding more information about what kind of dinosaurs were living in high latitude conditions (Constantine, 1998).



Figure 5: Reconstruction by Peter Trusler of the floral and faunal polar winter environment near Lake Koonwarra, with dinosaurs represented by *Leaellynasura amicagraphica*.

The lake was most likely freshwater since most of the fossils found at Koonwarra are freshwater animals. Its size and depth are not well constrained, but it must have been deep enough for varves to form. It could have been an isolated large lake or a small lake off of a larger lake that may have been

constantly or occasionally connected to it (Poropat et al., 2018). Koonwarra has been described as a moist, mainly lacustrine or fluviatile environment with relatively continuous sedimentation (Lowry 1988, Felton 1997, Edwards & Baker 1943). Conifers and ferns were some of the abundant plant life in the area (Edwards & Baker 1943), although these plants (and the animals) had to contend with long dark months and frigid temperatures.

The core being studied has visible varves throughout. Varves are a common indicator of seasonal changes, particularly freezing, in freshwater lakes. There must have been environmental cyclicity to change the focus of deposition in the lake from clay-sized to silt-sized particles. There is also suggestive evidence that the sediments were always anoxic, insofar as there is no bioturbation recognized in any part of the core. However, water column chemistry is rarely determined by the sediments, and given the profundity of life in the lake, the surface waters were likely to be oxic for most of the year (Talbot & Baird, 1985). It is only during summer eutrophication or winter freeze over that the oxygen contents of the water column may have fallen significantly. The isotopic composition of the sediments may provide constraints on the redox conditions of the bottom waters, which, if anoxic, would have been a major contributor to the pristine preservation of fossils. Another paleontological factor of note is the discovery of a horseshoe crab (Fig. 1D) in the deposit. Insofar as all known horseshoe crabs are marine in origin, its preservation at Koonwarra might suggest that the lake experienced punctuated (or perhaps a constant) influx of seawater. While contrary to the prevailing view, it seems plausible given the rift environment and overall warmth of the Cretaceous Period.

One of my objectives of this study is to understand how these fish and insects were preserved so well and intact. The geochemistry of the lake can give clues as to what might have been happening to aid in the preservation of these fossils. There are a variety of ideas throughout the literature including, seasonality (including annual freeze thaw cycles) causing changes in the degree of water column anoxia, higher volcanic activity raising CO<sub>2</sub> levels and both creating anoxic conditions and killing fish, and constantly anoxic bottom waters that allow the fish to be preserved as they die from natural causes. Given that bottom water or sediment pore water anoxia has geochemical consequences, a second objective of this study is to determine if the anaerobic processes of remineralization are evident in the mineralogical, elemental, and isotopic compositions of core samples through Lake Koonwarra.

#### **Hypothesis**

If the Koonwarra core samples have a high abundance of <sup>15</sup>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 <sup>15</sup>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.

The background chemistry for this senior thesis includes redox and combustion reactions. Redox reactions involve an exchange of electrons, often associated with anaerobic microbial metabolism, and combustion reactions that involve the burning of hydrocarbons in the presence of oxygen to produce gases for mass spectrometry. I am hypothesizing that this lake went periodically anoxic and two isotope systems that may be particularly useful in determining the conditions of this ancient lake system are those of nitrogen and sulfur. For example, one sure

sign of anoxia is evidence for denitrification insofar as denitrifying microbes are obligate anaerobes. As nitrate is utilized by these microbes, they produce nitrogen gas that is enriched in  $^{14}N$  and released to the atmosphere. This leaves behind a higher abundance of the  $^{15}N$  in the water column, which ends up in sedimentary organic matter. This process can be expressed using this redox reaction 2 NO<sub>3</sub> $^-$  + 10 e $^-$  + 12 H $^+$   $\rightarrow$  N<sub>2</sub> + 6 H<sub>2</sub>O.

There are a few reasons why I believe this to be a valid hypothesis. Based on the high-resolution core photos (Fig. 6) and the borehole log (see Appendix) there is visible grading in the beds on a sub-centimeter scale from coarser to finer grained sediments. The alternation of grain sizes and their grading indicates periodicity in the energy of the environment. There is also evidence based on the fish and insect fossils, which have been found as articulated skeletons in multiple horizons indicating that these species were killed and survived scavenging by animals. Furthermore, the multiplicity of fossil horizons suggests that mass die offs happened episodically (Bean, 2017).



Figure 6: The Vic Roads core (B18-68600) drilled in February 2018 from which 100 samples were collected in the interval between 11 and 21 m depth.

In my view, the anoxia could be due to seasonal changes between the summer and long dark high latitude winter when photosynthetic rates diminished, and the lake apparently froze over. Paleogeographic reconstructions place southern Australia in the Antarctic Circle during this time and arctic lakes today can stay ice covered for greater than 8 months out of the year (Cadieux et al., 2017). Thus, seasonality could explain the periodicity of the grain size deposition as well as the episodic fish kills. The water column was most definitely oxic for at least periods, because the fossils were once living fish in the lake. This suggests a strong oxygen gradient in

the lake with oxic surface waters and anoxic bottom waters (Waldman, 1971). Due to the lack of bioturbation, there is no evidence of organisms (animals or insects) living on the lake bottom even during the short summer months, so it is likely that the sediments always remained anoxic. On the other hand, the water column could have also cycled between oxic and anoxic conditions.

#### Methods

The Vic Roads core through the Koonwarra Fossil Beds is 21 meters in length; however, samples were not taken from the upper most 11 meters given that this interval is highly oxidized



and sandy (Fig. 6). The remaining ten meters were collected at 10 cm intervals by Dr. Kaufman and his colleagues at Vic Roads and the Melbourne Museum in late May 2018. Each sample contains varying cycles of seasonality represented by the spacing of the varves. The number of varves in each specimen was difficult to quantify given that archived samples were dry, fractured, and largely disaggregated. Thus in order to estimate the number of varves in the sampled interval, a high-resolution photo of one 10 cm section of the core was used to quantify (Fig. 7) and then that value was extrapolated to the entire 10 meter sampled interval. Based on this method, there is an estimated total of ~5000 varves, which would equate to an average of 50 varves per 10 cm and a period of deposition of around 5000 years.

Figure 7: Image of varves from a 10 cm interval at 17.80 meters in the Koonwarra Fossil Beds core.

Approximately one gram of each of the 100 samples was homogenized with a ceramic mortar and pestle, which were cleaned between samples with annealed quartz sand and 100% ethanol. Each weighed powder was then reacted with 10 mL of 3M HCl for 24 hours in 50 ml plastic centrifuge tubes before centrifugation and decanting of the supernatant into a waste container. This process was repeated to assure quantitative removal of all carbonate from the samples. After acidification each sample was washed with 10 mL of Milli-Q (18 M $\Omega$ ) water, vortexed, centrifuged, and decanted. This process was repeated three times to remove residual acid and approach neutral pH. Then each sample was placed in a low temperature oven (80°C) for 48 hours to dry. The centrifugation process notably stratified the clay and silt fractions of the samples in the tubes. After drying, each residue was reweighed in order to calculate the percent carbonate, and then homogenized with a glass probe that was cleaned between samples with 100% ethanol.

To make sure that the acidification process was reproducible, multiple acidification tests were conducted on two samples: one with a high percent of carbonate and one with a low

percent. Table 1 shows the data from these tests, which confirms that this process does give significant, reproducible results for percent carbonate.

Sample	Tube (g)	Tube+Sample	Sample	Tube+Sample	Residue	%
Number		( <b>g</b> )	(g)	After Drying	(g)	Carbonate
				<b>(g)</b>		
12.10 a	14.31	15.33	1.01	15.21	0.90	11.62
12.10 b	14.34	15.23	0.89	15.13	0.79	11.43
12.10 c	14.36	15.31	0.95	15.20	0.85	10.80
12.10 d	14.38	14.83	0.46	14.78	0.40	11.79
12.10 e	14.29	14.84	0.55	14.78	0.48	11.96
					Average	11.52
					St. Dev.	0.45
17.10 a	14.42	15.29	0.87	15.01	0.59	32.71
17.10 b	14.31	15.27	0.96	14.96	0.65	32.42
17.10 c	14.27	14.79	0.53	14.61	0.34	34.55
17.10 d	14.30	14.78	0.48	14.62	0.32	33.03
					Average	33.18
					St. Dev.	0.95

Table 1: Percent carbonate reproducibility tests. This table shows two samples weighed out four or five times, and the reproducibility is generally good. Small variations between aliquots are likely the result of losses during decanting, or of weighing errors.

The instrumentation required includes a Eurovector elemental analyzer (EA) and an Elementar Isoprime isotope ratio mass spectrometer. This instrument system both creates gases from solids and measures their abundances and isotope ratios. Small aliquots of the acidified residues were weighed out from each sample and folded into tin cups. For the C/N analyses, the cups were sequentially dropped into a combustion furnace (containing chromium oxides and silvered cobaltous/ic oxide) at  $1040^{\circ}$ C with a pulse of  $O_2$  and a carrier gas of ultra-high purity (UHP) He to produce  $CO_2$  and  $NO_x$  gases. The nitrous oxides were subsequently reduced to  $N_2$  in a flow through reduction column packed with elemental Cu at  $650^{\circ}$ C. The gases then pass through a magnesium perchlorate water trap and a GC column at  $60^{\circ}$ C where the  $N_2$  is separated from the  $CO_2$ , which then flow to the source of the mass spectrometer. For the S analyses, aliquots are weighed out and folded into tin cups with an addition of  $\sim 0.3$  mg of  $V_2O_5$  as an extra oxidant to produce  $SO_2$  and SO gases. The EA is configured for the S analyses with a combustion column packed with elemental Cu and heated to  $1030^{\circ}$ C, a different GC column (set to  $90^{\circ}$ C), and no reduction column.

Carried in a stream of UHP He, these gases reach the source of the isotope ratio mass spectrometer where they were impacted with a spray of electrons from a heated W filament in order to create charged ions (Fig. 8). These positive ions are then accelerated through an electron field where they are focused, and then separated by a magnetic field that deflects each ion differently based on its mass. For  $CO_2$  ions this includes m/z (mass/charge) of 44, 45, and 46 while for  $N_2$  this includes m/z 28, 29, and 30; SO and  $SO_2$  isotopes are measured at m/z 48, 49

and 50, and 64 and 66, respectively. The lightest ions are deflected the most by the magnetic field set for each analyte. Cups at the end of the mass spectrometer flight tube collect and quantify ion counts, which are then converted to delta values with the Isoprime computer. The  $\delta$  equation for carbon is  $\delta = (((^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{standard})-1)x1000$ . The equation is used for all of the isotope  $\delta$  values with each appropriate element because it allows for easier comparison to a reference and to mathematically see fractionation more clearly.

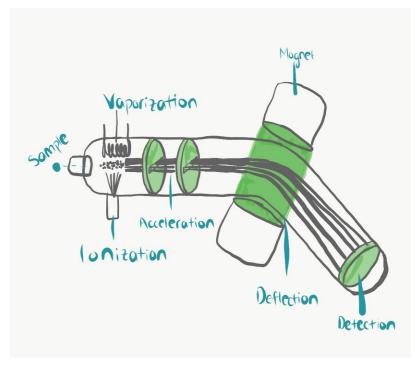


Figure 8: A schematic of the critical parts of a gas source isotope ratio mass spectrometer similar to the Elementar Isoprime used in this study.

Many different sample weights were tested with the mass spectrometer, and it was concluded that to get reproducible nitrogen data a larger mass was needed than for carbon due to the high C/N of the residual sediments. Hence, three aliquots of each sample were prepared: one with ~20 mg for the N measurement, ~20 mg for the S measurements, and one with ~2 mg for the C

#### measurements.

To test for reproducibility of the EA-IRMS method, a series of standard urea samples were run for carbon and nitrogen abundance and isotope composition (Table 2). Urea contains 20% carbon with a  $\delta^{13}$ C of -29.39‰, and 46.64% nitrogen with a  $\delta^{15}$ N of +1.18‰. Urea is run at the beginning of each analytical session to demonstrate reproducibility, and throughout the run to evaluate drift in the system. Urea was used as the standard in the carbon and nitrogen measurements because it is the best available substance with consistent, known nitrogen and carbon values. There is no sedimentary standard available to use in its place, although the laboratory is currently working on an in-house standard with C/N closer to natural sediments and soils that will be calibrated against international standards.

<b>Sample</b>	Weight (mg)	C Peak (nA)	<u>δ 13C</u>	<u>%C</u>	N Peak (nA)	$\delta^{15}N$	<u>%N</u>
Urea 1	0.11	2.30	-18.79	19.78	7.76	1.39	46.05
Urea 2	0.12	2.50	-19.94	20.44	8.56	1.52	48.20
Urea 3	0.12	2.57	-19.97	20.69	8.68	1.35	47.90
Urea 4	0.12	2.44	-19.80	19.59	8.30	1.29	45.85
Urea 5	0.11	2.26	-20.20	19.29	7.64	1.46	44.93
Urea 6	0.12	2.55	-18.59	20.43	8.66	1.39	47.72
Average			-19.55	20.04	8.27	1.40	40.78

St. Dev.		0.68	0.56	0.46	0.08	1.34

Table 2: Urea Standard Reproducibility. The average values determined daily are corrected to the true value (see above). The weight percent has a typically greater uncertainty than the isotope measurements due to weighing errors. This is an example of a suitability test run at the beginning of each analytical session before running any samples for carbon or nitrogen.

Sample	Weight (mg)	S Peak (nA)	$\delta^{34}S$	<u>%S</u>
NBS127 1	0.21	7.34	12.90	14.11
NBS127 2	0.18	6.52	12.97	14.69
NBS127 3	0.23	8.19	12.74	14.88
NBS127 4	0.24	8.59	12.80	14.87
NBS127 5	0.20	6.91	12.67	14.41
NBS127 6	0.23	7.80	12.72	14.07
Average			12.80	14.51
St. Dev.			0.11	0.36

Table 3: NBS127 (Barium Sulfate) Standard Reproducibility. The weight percent, once again, has a typically greater uncertainty than the isotope measurements due to weighing errors. This is an example of a suitability test run at the beginning of each analytical session before running any samples for sulfur.

#### **Results**

Results of the mineralogical, elemental, and isotopic analyses on 100 samples from the Vic Roads Koonwarra core are found in Tables 4 and 5, and S1 (see Appendix) and shown graphically in Figure 9. Table 3 shows the ranges as well as the average and standard deviation (1s) for each of the mineralogical, elemental, and isotopic results of this time-series study. Because there is an apparent change in most of these measurements at around 16 meter depth in the core, averages and standard deviations were calculated for the populations above and below this divide.

	% Carbonate	$\delta^{13}$ C	TOC	$\delta^{15}$ N	TN	$\delta^{34}S$	TS
Min	9.23	-28.08	0.00	-0.56	0.05	-6.35	0.00
Max	35.45	-24.05	1.23	1.01	0.07	5.52	0.03
Average	13.56	-25.21	0.79	0.06	0.06	-2.00	0.01
St. Dev.	3.62	0.67	0.17	0.27	0.01	3.70	0.01

Table 4: Ranges, averages, and standard deviations for all of the measured geochemical markers from meters 11-16 of the core.

	% Carbonate	$\delta^{13}$ C	TOC	$\delta^{15}N$	TN	$\delta$ <sup>34</sup> S	TS
Min	10.75	-27.04	0.71	-0.49	0.07	-8.44	0.01
Max	36.31	-24.34	1.96	0.81	0.10	-2.81	0.16
Average	15.16	-25.18	0.95	0.26	0.08	-5.53	0.04
St. Dev.	4.13	0.48	0.19	0.29	0.01	1.29	0.03

Table 5: Ranges, averages, and standard deviations for all of the measured geochemical markers from meters 16-21 of the core. Notably carbonate, TOC,  $\delta^{15}N$ , TN, and TS have all quantitatively increased down core.  $\delta^{34}S$  has become more negative and  $\delta^{13}C$  has stayed consistent.

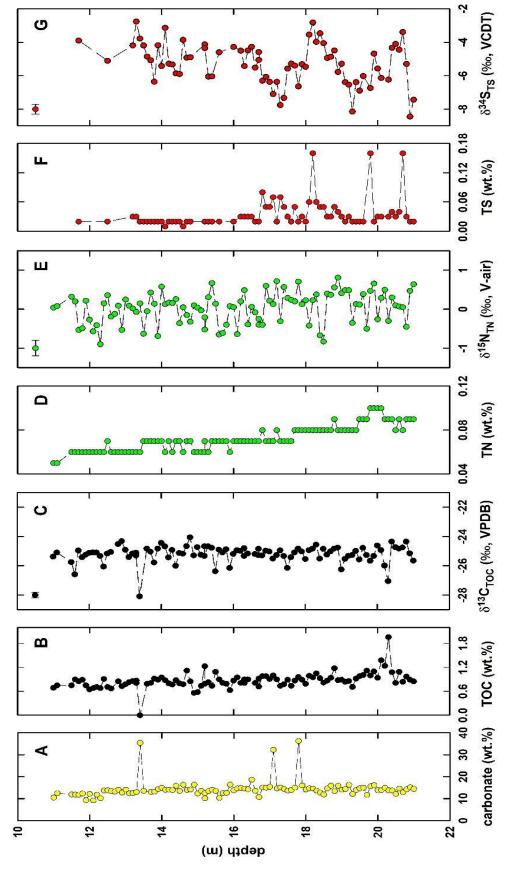


Figure 9: Time series results of the geochemical study. Y-axis depth in meters, x-axis isotope and elemental values.

#### Carbonate

Carbonate values reached higher than expected for a freshwater lake. It has 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.

#### Carbon

The  $\delta^{13}C$  values do not have any significant trend in terms of increasing or decreasing with depth. TOC values do significantly increase with depth. The lake sediments also have a high C/N ratio and a higher abundance of long chained alkanes to short chained alkanes, as well as a low sterane/hopane ratio (Fig. 10).

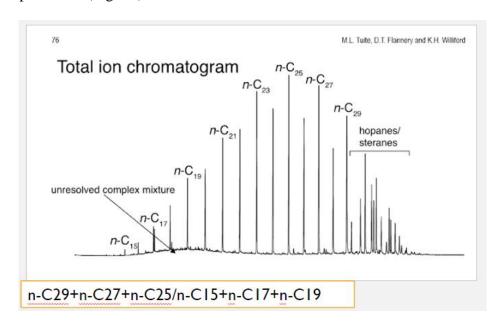


Figure 10: Carbon isotopes from the Koonwarra core measured by Tuite and Flannery and Williford showing hopane/sterane ratios and a higher abundance of long chained alkanes to short chained alkanes.

#### Nitrogen

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

#### Sulfur

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 could coincide with the inflection points of the  $\delta^{34}S$  values. The  $\delta^{34}S$  values show a trend below 16 m of distinct cyclicity and have an overall decreasing trend.

#### **Discussion**

Looking at all the trends, it appears there is a change in most of the geochemical markers around 16 meters depth, which is likely associated with deepening and an increase in bottom water anoxia. Interpretations are in part based on the varve time scale for accumulation of these sediments, being about 5000 years.

#### Carbonate

The high carbonate values could have formed because of plankton or algae biomineralizing in the upper water column and points to potentially more alkaline water. The carbonate may reflect detrital inputs, primary inputs, or authigenic inputs. 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 and it is unusual to not have many carbonate shells in a lake like this. Only one ostracod has been found in the region. This could mean that the lake was just too acidic to preserve these shells. Anaerobic processes create acidity and these are the processes happening in an anoxic lake. Therefore, the anoxia of this lake may have been coupled with a lower pH.

#### Organic Carbon

Since  $\delta^{13}$ C did not change significantly with depth this suggests a balanced carbon input. This means that the carbon input was not changing much throughout deposition. The high C/N ratio, higher abundance of long chained alkanes to short chained alkanes, as well as a low sterane/hopane ratio all point to the carbon in the lake 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. When respiratory processes slow down due to lack of oxygen, less organic carbon can be remineralized and so more would be left in the sediments.

#### **Nitrogen**

The increase in TN and the more positive values below 16 m also attests to an anoxic environment. It is likely not a sharp contact between oxic and anoxic water, but this could be a point of stronger anoxia in the lake. The increase in  $\delta^{15}N$  values is what is expected in a denitrifying environment as well, since the  $^{15}N$  isotope is left behind in the sediments during the process. Since denitrification is an anaerobic process, this lake would have had anaerobes living on its bottom and must have been anoxic to support their activity. The small oscillations in  $\delta^{15}N$  could be due to the seasonal changes or be insignificant noise; whichever it is the increase is significant.

#### Sulfur

The cyclicity in the  $\delta^{34}S$  values could be due to multiple environmental factors that likely relate to the size of the sulfate reservoir or to the pace of microbial sulfate reduction (an anaerobic process). 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 because otherwise it would precipitate as an oxide.

One way to create shifts in  $\delta^{34}S$  is by a differential source terrain or intensity of weathering products. However, this is not conducive to the time scale and degree of oscillations.

An increase in sulfate composition could also be due to marine incursions. This is supported by the finding of a horseshoe crab fossil at the site. Cretaceous seawater  $\delta^{34}S$  is estimated at +19‰ (Payton et al., 2004), so that a small volume of seawater could cause the positive sulfur isotope excursions. However, if seawater had interacted with this lake the degree of change in  $\delta^{34}S$  values would be much higher; coming close to the +19‰ value, as seen in the Songliao Basin (Cao et al., 2016). It would have likely also had an effect on the other measurements, which is not seen. The shifts seen in the time series also happen on a quicker time scale than most transgression and regression sequences. Lakes tend to be stable for 10s to 100s of thousands of years.

There was volcanic activity in the region during this stage due to rifting, which also serves as a viable S input mechanism. Volcanics have a mantle like composition and through volcanic rock and ash debris the sulfate composition of the lake could increase. The  $\delta^{34}$ S of this input would likely be near 0‰, but the greater effect on the sulfur isotope composition of pyrite formed through microbial sulfate reduction (MSR) would be to increase the abundance of sulfate that could be reduced. If sulfate concentrations were higher, the fractionation between reactant sulfate and product sulfide would be larger, whereas if sulfate were low most of it would be reduced and the fractionation would be minimal (Gomes & Hurtgen, 2015). 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 with a ~2500 year time scale.

Most of the geochemical markers that were measured showed distinct shifts at 16 m depth. When the time series is correlated to the core (Fig. 11) 16 m is also where the fossils begin to appear in the strata. As mentioned previously this could be a point of greater anoxia or a point where water became completely anoxic. It also offers support for the idea that the data collected is relevant to the fossil preservation and agrees with an anoxic environment.

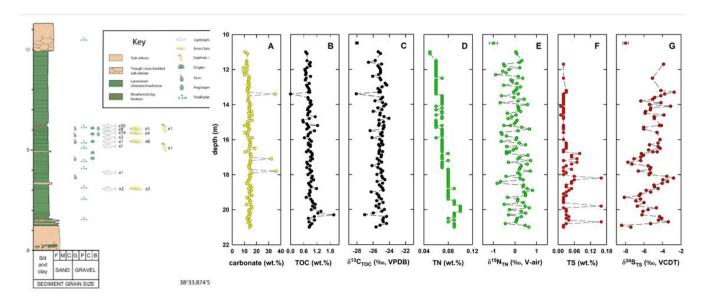


Figure 11: Correlation between time series plot and beds of fossils. Fossils begin to be found around 16 m depth

#### Modern Polar Lakes

To compare the results from Koonwarra, a Cretaceous polar lake, I investigated a series of modern polar lakes (Holland, 2010; Kling & Luecke, 2007; Thompson et al., 2018; Young et al., 2018; Cadieux et al., 2017; Engstrom et al., 2000; Lawson et al., 2004; Syvaranta et al., 2006). This directly relates to my stated hypothesis, which suggests higher TOC and  $d^{15}N$  in the Cretaceous example. However after searching the literature for modern polar lake  $\delta^{15}N$  and TOC values the hypothesis originally proposed has been falsified. While there were no distinct trends in isotopic data between today's polar lacustrine sites, all of the lakes that were read about had mostly values higher than the Koonwarra samples, which directly contradicts the hypothesis. Many of these studies were doing data collection and so did not have significant analyses of what the values may say about the current environment. Despite this finding there is still quite a bit of support for freezing and anoxia at Koonwarra. The sediment and fossil evidence for anoxia is strong because of the exceptional preservation, lack of bioturbation, varving, polar latitude and many more reasons listed throughout this paper.

So why might the hypothesis have been falsified? To begin it may not have been realistic to compare lakes during such different climates and tectonic settings. Polar lakes today are mostly not situated along above water rift basins and surrounded by volcanic activity. They also do not have temperate qualities and lush forests surrounding them. Polar lakes today also have lower C/N values indicating a more algal input which is different from the terrestrial domination at Koonwarra. It could also be that because Koonwarra is so old, the organic matter has been eaten away over time placing the values lower than they may have been originally.

#### **Conclusion**

Overall, even though the hypothesis has been falsified, it is possible to make conclusions about the state of Koonwarra from the data alone and many of the trends and previous work support a periodic freezing and anoxic bottom water lake. The trends that were uncovered during this thesis were significant in helping to better understand this lake environment and could be the beginning of uncovering more about this site and this time period in general.

This research can give a greater insight into this Cretaceous lacustrine site, which is unlike any other in the world due to its polar aspect (Rich, 2018). The history of ancient lakes is useful in comparing possible conditions in modern lakes. The data can also be related back to climatic reconstructions of the lower Cretaceous, where the sort of climate that produced these results can be compared to our modern climate. If the work is taken further, a greater understanding of what environmental conditions lead to such high quality preservation is possible. The sulfur cyclicity is also of great interest since it could help us better understand the tectonics of the time if the cause can be pinpointed as being volcanic eruptions or marine incursions.

There is also a push for a large scale excavation effort at Koonwarra due to its similarities to the Jehol site in China. Dinosaur and mammal fossils were found at that site after a large fossil rush drastically increased the man power working on it (Rich, & Xiao-Bo, 2012). This research can give a greater understanding of what sorts of species might have lived around this lake and any more research on the site can give some basis on the decision of whether or not such an excavation is warranted.

There is plenty more work that could be done on these samples, and that is being done by colleagues that also have access to this core. In the future, samples from this area could also be analyzed using optical petrography to see whether or not there are igneous minerals in the rocks and a better varve count could be produced. Given more time I also would have done a grain size analysis, and a XRD plus a carbon and oxygen isotope analysis on the carbonate to determine its mineralogy and its input mechanism.

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#### **Student Honor Code**

I pledge on my honor that I have not given or received any unauthorized assistance on this assignment/examination.

## **Appendix**

depth							
(m)	% Carbonate	13-C	тос	15-N	TN	34-S	TS
21	14.44294091	-25.64	0.85	0.64	0.09	-7.43	0.02
20.9	15.22319488	-25.14	0.89	0.47	0.09	-8.44	0.02
20.8	14.28163382	-24.34	0.97	-0.11	0.09	-5.29	0.03
20.7	12.96279695	-24.74	0.84	0.39	0.08	-3.38	0.16
20.6	14.63849081	-24.82	1.09	0.07	0.09	-4.44	0.04
20.5	12.16957606	-24.72	0.81	0.10	0.08	-4.09	0.03
20.4	13.77718449	-24.34	1.08	0.30	0.09	-4.32	0.04
20.3	13.83026831	-27.04	1.96	0.04	0.09	-6.23	0.03
20.2	14.96251562	-25.98	1.24	0.50	0.09		
20.1	13.96360759	-24.92	1.38	0.29	0.10	-6.13	0.03
20	13.87548065	-24.61	0.94	0.08	0.10	-5.56	0.03
19.9	16.18562111	-25.32	1.10	0.66	0.10	-4.67	0.02
19.8	15.67434449	-25.65	1.00	0.47	0.10	-6.73	0.16
19.7	11.75072168	-25.26	1.12	-0.16	0.09		
19.6	15.02160881	-24.77	1.01	0.39	0.09	-6.01	0.02
19.5	14.73601261	-25.56	0.98	0.46	0.09	-6.89	0.02
19.4	13.98564677	-24.97	0.92	0.13	0.08	-6.38	0.02
19.3	12.17100372	-25.26	0.71	-0.01	0.08	-8.14	0.02
19.2	16.31510174	-25.31	0.86	0.49	0.08	-6.53	0.03
19.1	14.44800971	-25.52	0.84	0.49	0.08	-6.38	0.02
19	14.12352041	-26.24	0.89	0.41	0.08	-5.28	0.03
18.9	15.87119034	-24.75	0.88	0.81	0.08	-5.77	0.04
18.8	13.46138261	-24.82	1.18	0.56	0.09	-4.48	0.05
18.7	15.91549296	-25.01	0.94	0.37	0.08	-4.86	0.03
18.6	14.69908477	-25.23	0.87	0.40	0.08	-4.93	0.03
18.5	11.943684	-24.83	0.82	-0.49	0.08	-4.04	0.05
18.4	12.78783618	-25.51	0.93	-0.33	0.08	-3.45	0.05
18.3	13.69125234	-24.55	1.05	0.38	0.08	-3.97	0.06
18.2	14.62264151	-24.82	0.95	0.23	0.08	-2.81	0.16
18.1	14.71457162	-24.93	0.99	-0.08	0.08	-3.53	0.06
18	14.20104315	-25.53	0.79	0.23	0.08	-5.46	0.02
17.9	16.03072349	-25.02	0.89	0.13	0.08	-5.30	0.03
17.8	36.30704063	-24.82	0.96	0.71	0.08	-6.63	0.02
17.7	15.04732739	-25.08	0.87	0.20	0.08	-5.39	0.05
17.6	13.99425287	-25.41	0.74	0.24	0.07	-5.27	0.02
17.5	13.69365362	-26.14	0.89	0.29	0.07	-5.57	0.03
17.4		-25.32	0.78	0.57	0.07	-7.32	0.05
17.3	15.10940272	-24.94	0.74	0.03	0.07	-7.75	0.07

17.2       14.69439728       -25.26       0.90       0.72       0.08       -6.36         17.1       32.28210488       -25.50       1.00       0.13       0.07       -7.09         17       15.41437414       -25.02       0.91       0.56       0.07       -6.36         16.9       15.03386435       -24.96       0.98       0.60       0.07       -6.06         16.8       15.11434329       -25.28       0.98       -0.06       0.08       -6.29         16.7       10.7547781       -25.27       0.92       -0.06       0.07       -4.58         16.6       13.60866079       -25.19       0.81       0.26       0.07       -5.51         16.5       18.65463793       0.06       0.07       -4.26         16.4       14.3053106       -25.16       0.90       -0.05       0.07       -4.48         16.3       14.64174455       -25.32       0.90       0.49       0.07       -5.41         16.2       14.97835972       -24.97       0.81       0.20       0.07       -4.49         16.1       14.69689661       -24.93       0.95       -0.30       0.07       -8.4         Max       36.30704063	0.16 0.041508
17         15.41437414         -25.02         0.91         0.56         0.07         -6.36           16.9         15.03386435         -24.96         0.98         0.60         0.07         -6.06           16.8         15.11434329         -25.28         0.98         -0.06         0.08         -6.29           16.7         10.7547781         -25.27         0.92         -0.06         0.07         -4.58           16.6         13.60866079         -25.19         0.81         0.26         0.07         -5.51           16.5         18.65463793         0.06         0.07         -4.26           16.4         14.3053106         -25.16         0.90         -0.05         0.07         -4.48           16.3         14.64174455         -25.32         0.90         0.49         0.07         -5.41           16.2         14.97835972         -24.97         0.81         0.20         0.07         -4.49           16.1         14.69689661         -24.93         0.95         -0.30         0.07         -4.27           Min         10.7547781         -27.04         0.7056         -0.49         0.07         -8.4           Mex         36.30704063         -24.34	0.05 0.08 0.02 0.02 0.03 0.03 0.03 0.01 0.02 4 0.0101 1 0.16 1 0.041508 5 0.033846
16.9         15.03386435         -24.96         0.98         0.60         0.07         -6.06           16.8         15.11434329         -25.28         0.98         -0.06         0.08         -6.29           16.7         10.7547781         -25.27         0.92         -0.06         0.07         -4.58           16.6         13.60866079         -25.19         0.81         0.26         0.07         -5.51           16.5         18.65463793         0.06         0.07         -4.26           16.4         14.3053106         -25.16         0.90         -0.05         0.07         -4.48           16.3         14.64174455         -25.32         0.90         0.49         0.07         -5.41           16.2         14.97835972         -24.97         0.81         0.20         0.07         -4.49           16.1         14.69689661         -24.93         0.95         -0.30         0.07         -4.27           Min         10.7547781         -27.04         0.7056         -0.49         0.07         -8.4           Average         15.15882909         -25.178         0.953768         0.260588         0.080784         -5.5253           St. Dev.         4.13437192	0.05 0.08 0.02 0.02 0.03 0.03 0.03 0.01 0.02 4 0.0101 1 0.16 1 0.041508 5 0.033846
16.8         15.11434329         -25.28         0.98         -0.06         0.08         -6.29           16.7         10.7547781         -25.27         0.92         -0.06         0.07         -4.58           16.6         13.60866079         -25.19         0.81         0.26         0.07         -5.51           16.5         18.65463793         0.06         0.07         -4.26           16.4         14.3053106         -25.16         0.90         -0.05         0.07         -4.48           16.3         14.64174455         -25.32         0.90         0.49         0.07         -5.41           16.2         14.97835972         -24.97         0.81         0.20         0.07         -4.49           16.1         14.69689661         -24.93         0.95         -0.30         0.07         -4.27           Min         10.7547781         -27.04         0.7056         -0.49         0.07         -8.4           Average         15.15882909         -25.178         0.953768         0.260588         0.080784         -5.5253           St. Dev.         4.134371929         0.481291         0.19249         0.289906         0.009131         1.29229           15.9	0.08 0.02 0.03 0.03 0.03 0.03 0.01 0.02 4 0.0101 1 0.16 1 0.041508 5 0.033846
16.7       10.7547781       -25.27       0.92       -0.06       0.07       -4.58         16.6       13.60866079       -25.19       0.81       0.26       0.07       -5.51         16.5       18.65463793       0.06       0.07       -4.26         16.4       14.3053106       -25.16       0.90       -0.05       0.07       -4.48         16.3       14.64174455       -25.32       0.90       0.49       0.07       -5.41         16.2       14.97835972       -24.97       0.81       0.20       0.07       -4.49         16.1       14.69689661       -24.93       0.95       -0.30       0.07       -6.73         16       13.85779123       -25.18       0.87       0.39       0.07       -8.4         Max       36.30704063       -24.34       1.96       0.81       0.1       -2.8         Average       15.15882909       -25.178       0.953768       0.260588       0.080784       -5.5253         St. Dev.       4.134371929       0.481291       0.19249       0.289906       0.009131       1.29229         15.9       16.42756681       -26.14       0.63       0.08       0.06       5.46 <t< th=""><th>0.02 0.03 0.03 0.03 0.03 0.01 0.02 4 0.0101 1 0.16 1 0.041508 5 0.033846</th></t<>	0.02 0.03 0.03 0.03 0.03 0.01 0.02 4 0.0101 1 0.16 1 0.041508 5 0.033846
16.6       13.60866079       -25.19       0.81       0.26       0.07       -5.51         16.5       18.65463793       0.06       0.07       -4.26         16.4       14.3053106       -25.16       0.90       -0.05       0.07       -4.48         16.3       14.64174455       -25.32       0.90       0.49       0.07       -5.41         16.2       14.97835972       -24.97       0.81       0.20       0.07       -4.49         16.1       14.69689661       -24.93       0.95       -0.30       0.07       -6.73         16       13.85779123       -25.18       0.87       0.39       0.07       -4.27         Min       10.7547781       -27.04       0.7056       -0.49       0.07       -8.4         Max       36.30704063       -24.34       1.96       0.81       0.1       -2.8         Average       15.15882909       -25.178       0.953768       0.260588       0.080784       -5.5253         St. Dev.       4.134371929       0.481291       0.19249       0.289906       0.009131       1.29229         15.9       16.42756681       -26.14       0.63       0.08       0.06       5.46         <	0.02 0.03 0.03 0.03 0.01 0.02 4 0.0101 1 0.16 1 0.041508 5 0.033846
16.5       18.65463793       0.06       0.07       -4.26         16.4       14.3053106       -25.16       0.90       -0.05       0.07       -4.48         16.3       14.64174455       -25.32       0.90       0.49       0.07       -5.41         16.2       14.97835972       -24.97       0.81       0.20       0.07       -4.49         16.1       14.69689661       -24.93       0.95       -0.30       0.07       -6.73         16       13.85779123       -25.18       0.87       0.39       0.07       -4.27         Min       10.7547781       -27.04       0.7056       -0.49       0.07       -8.4         Max       36.30704063       -24.34       1.96       0.81       0.1       -2.8         Average       15.15882909       -25.178       0.953768       0.260588       0.080784       -5.5253         St. Dev.       4.134371929       0.481291       0.19249       0.289906       0.009131       1.29229         15.9       16.42756681       -26.14       0.63       0.08       0.06       5.46         15.8       12.63918896       -24.86       0.79       -0.06       0.07       1.72         <	0.03 0.03 0.03 0.01 0.02 4 0.0101 1 0.16 1 0.041508 5 0.033846
16.4       14.3053106       -25.16       0.90       -0.05       0.07       -4.48         16.3       14.64174455       -25.32       0.90       0.49       0.07       -5.41         16.2       14.97835972       -24.97       0.81       0.20       0.07       -4.49         16.1       14.69689661       -24.93       0.95       -0.30       0.07       -6.73         16       13.85779123       -25.18       0.87       0.39       0.07       -4.27         Min       10.7547781       -27.04       0.7056       -0.49       0.07       -8.4         Max       36.30704063       -24.34       1.96       0.81       0.1       -2.8         Average       15.15882909       -25.178       0.953768       0.260588       0.080784       -5.5253         St. Dev.       4.134371929       0.481291       0.19249       0.289906       0.009131       1.29229         15.9       16.42756681       -26.14       0.63       0.08       0.06       5.46         15.8       12.63918896       -24.86       0.79       -0.06       0.07       1.72         15.7       12.5969837       -25.08       0.81       -0.27       0.07	0.03 0.03 0.01 0.02 4 0.0101 1 0.16 1 0.041508 5 0.033846
16.3       14.64174455       -25.32       0.90       0.49       0.07       -5.41         16.2       14.97835972       -24.97       0.81       0.20       0.07       -4.49         16.1       14.69689661       -24.93       0.95       -0.30       0.07       -6.73         16       13.85779123       -25.18       0.87       0.39       0.07       -4.27         Min       10.7547781       -27.04       0.7056       -0.49       0.07       -8.4         Max       36.30704063       -24.34       1.96       0.81       0.1       -2.8         Average       15.15882909       -25.178       0.953768       0.260588       0.080784       -5.5253         St. Dev.       4.134371929       0.481291       0.19249       0.289906       0.009131       1.29229         15.9       16.42756681       -26.14       0.63       0.08       0.06       5.46         15.8       12.63918896       -24.86       0.79       -0.06       0.07       1.72         15.7       12.5969837       -25.08       0.81       -0.27       0.07       -0.56         15.6       10.38932147       -24.89       0.90       -0.31       0.07	0.03 0.03 0.01 0.02 4 0.0101 1 0.16 1 0.041508 5 0.033846
16.2       14.97835972       -24.97       0.81       0.20       0.07       -4.49         16.1       14.69689661       -24.93       0.95       -0.30       0.07       -6.73         16       13.85779123       -25.18       0.87       0.39       0.07       -4.27         Min       10.7547781       -27.04       0.7056       -0.49       0.07       -8.4         Max       36.30704063       -24.34       1.96       0.81       0.1       -2.8         Average       15.15882909       -25.178       0.953768       0.260588       0.080784       -5.5253         St. Dev.       4.134371929       0.481291       0.19249       0.289906       0.009131       1.29229         15.9       16.42756681       -26.14       0.63       0.08       0.06       5.46         15.8       12.63918896       -24.86       0.79       -0.06       0.07       1.72         15.7       12.5969837       -25.08       0.81       -0.27       0.07       -0.56         15.6       10.38932147       -24.89       0.90       -0.31       0.07       -4.59         15.5       13.51508121       -26.37       1.09       0.14       0.07	0.03 0.01 0.02 4 0.0101 1 0.16 1 0.041508 5 0.033846 0.00
16.1       14.69689661       -24.93       0.95       -0.30       0.07       -6.73         16       13.85779123       -25.18       0.87       0.39       0.07       -4.27         Min       10.7547781       -27.04       0.7056       -0.49       0.07       -8.4         Max       36.30704063       -24.34       1.96       0.81       0.1       -2.8         Average       15.15882909       -25.178       0.953768       0.260588       0.080784       -5.5253         St. Dev.       4.134371929       0.481291       0.19249       0.289906       0.009131       1.29229         15.9       16.42756681       -26.14       0.63       0.08       0.06       5.46         15.8       12.63918896       -24.86       0.79       -0.06       0.07       1.72         15.7       12.5969837       -25.08       0.81       -0.27       0.07       -0.56         15.6       10.38932147       -24.89       0.90       -0.31       0.07       -4.59         15.5       13.51508121       -26.37       1.09       0.14       0.07       -3.04         15.4       14.14006745       -24.77       0.74       1.01       0.07	0.01 0.02 4 0.0101 1 0.16 1 0.041508 5 0.033846
Min         10.7547781         -27.04         0.7056         -0.49         0.07         -8.4           Max         36.30704063         -24.34         1.96         0.81         0.1         -2.8           Average         15.15882909         -25.178         0.953768         0.260588         0.080784         -5.5253           St. Dev.         4.134371929         0.481291         0.19249         0.289906         0.009131         1.29229           15.9         16.42756681         -26.14         0.63         0.08         0.06         5.46           15.8         12.63918896         -24.86         0.79         -0.06         0.07         1.72           15.7         12.5969837         -25.08         0.81         -0.27         0.07         -0.56           15.6         10.38932147         -24.89         0.90         -0.31         0.07         -3.04           15.4         14.14006745         -24.77         0.74         1.01         0.07         -6.03           15.3         13.47373188         -24.66         0.83         0.31         0.06         -6.04	0.02 4 0.0101 1 0.16 1 0.041508 5 0.033846 0.00
Min         10.7547781         -27.04         0.7056         -0.49         0.07         -8.4           Max         36.30704063         -24.34         1.96         0.81         0.1         -2.8           Average         15.15882909         -25.178         0.953768         0.260588         0.080784         -5.5253           St. Dev.         4.134371929         0.481291         0.19249         0.289906         0.009131         1.29229           15.9         16.42756681         -26.14         0.63         0.08         0.06         5.46           15.8         12.63918896         -24.86         0.79         -0.06         0.07         1.72           15.7         12.5969837         -25.08         0.81         -0.27         0.07         -0.56           15.6         10.38932147         -24.89         0.90         -0.31         0.07         -4.59           15.5         13.51508121         -26.37         1.09         0.14         0.07         -3.04           15.4         14.14006745         -24.77         0.74         1.01         0.07         -6.03           15.3         13.47373188         -24.66         0.83         0.31         0.06         -6.04 <th>4 0.0101 1 0.16 1 0.041508 5 0.033846 0.00</th>	4 0.0101 1 0.16 1 0.041508 5 0.033846 0.00
Max         36.30704063         -24.34         1.96         0.81         0.1         -2.8           Average         15.15882909         -25.178         0.953768         0.260588         0.080784         -5.5253           St. Dev.         4.134371929         0.481291         0.19249         0.289906         0.009131         1.29229           15.9         16.42756681         -26.14         0.63         0.08         0.06         5.46           15.8         12.63918896         -24.86         0.79         -0.06         0.07         1.72           15.7         12.5969837         -25.08         0.81         -0.27         0.07         -0.56           15.6         10.38932147         -24.89         0.90         -0.31         0.07         -4.59           15.5         13.51508121         -26.37         1.09         0.14         0.07         -3.04           15.4         14.14006745         -24.77         0.74         1.01         0.07         -6.03           15.3         13.47373188         -24.66         0.83         0.31         0.06         -6.04	0.16 0.041508 0.033846 0.00
Max         36.30704063         -24.34         1.96         0.81         0.1         -2.8           Average         15.15882909         -25.178         0.953768         0.260588         0.080784         -5.5253           St. Dev.         4.134371929         0.481291         0.19249         0.289906         0.009131         1.29229           15.9         16.42756681         -26.14         0.63         0.08         0.06         5.46           15.8         12.63918896         -24.86         0.79         -0.06         0.07         1.72           15.7         12.5969837         -25.08         0.81         -0.27         0.07         -0.56           15.6         10.38932147         -24.89         0.90         -0.31         0.07         -4.59           15.5         13.51508121         -26.37         1.09         0.14         0.07         -3.04           15.4         14.14006745         -24.77         0.74         1.01         0.07         -6.03           15.3         13.47373188         -24.66         0.83         0.31         0.06         -6.04	0.16 0.041508 0.033846 0.00
Average         15.15882909         -25.178         0.953768         0.260588         0.080784         -5.5253           St. Dev.         4.134371929         0.481291         0.19249         0.289906         0.009131         1.29229           15.9         16.42756681         -26.14         0.63         0.08         0.06         5.46           15.8         12.63918896         -24.86         0.79         -0.06         0.07         1.72           15.7         12.5969837         -25.08         0.81         -0.27         0.07         -0.56           15.6         10.38932147         -24.89         0.90         -0.31         0.07         -4.59           15.5         13.51508121         -26.37         1.09         0.14         0.07         -3.04           15.4         14.14006745         -24.77         0.74         1.01         0.07         -6.03           15.3         13.47373188         -24.66         0.83         0.31         0.06         -6.04	0.041508 0.033846 0.00
St. Dev.         4.134371929         0.481291         0.19249         0.289906         0.009131         1.29229           15.9         16.42756681         -26.14         0.63         0.08         0.06         5.46           15.8         12.63918896         -24.86         0.79         -0.06         0.07         1.72           15.7         12.5969837         -25.08         0.81         -0.27         0.07         -0.56           15.6         10.38932147         -24.89         0.90         -0.31         0.07         -4.59           15.5         13.51508121         -26.37         1.09         0.14         0.07         -3.04           15.4         14.14006745         -24.77         0.74         1.01         0.07         -6.03           15.3         13.47373188         -24.66         0.83         0.31         0.06         -6.04	0.00
15.9       16.42756681       -26.14       0.63       0.08       0.06       5.46         15.8       12.63918896       -24.86       0.79       -0.06       0.07       1.72         15.7       12.5969837       -25.08       0.81       -0.27       0.07       -0.56         15.6       10.38932147       -24.89       0.90       -0.31       0.07       -4.59         15.5       13.51508121       -26.37       1.09       0.14       0.07       -3.04         15.4       14.14006745       -24.77       0.74       1.01       0.07       -6.03         15.3       13.47373188       -24.66       0.83       0.31       0.06       -6.04	0.00
15.8       12.63918896       -24.86       0.79       -0.06       0.07       1.72         15.7       12.5969837       -25.08       0.81       -0.27       0.07       -0.56         15.6       10.38932147       -24.89       0.90       -0.31       0.07       -4.59         15.5       13.51508121       -26.37       1.09       0.14       0.07       -3.04         15.4       14.14006745       -24.77       0.74       1.01       0.07       -6.03         15.3       13.47373188       -24.66       0.83       0.31       0.06       -6.04	
15.8       12.63918896       -24.86       0.79       -0.06       0.07       1.72         15.7       12.5969837       -25.08       0.81       -0.27       0.07       -0.56         15.6       10.38932147       -24.89       0.90       -0.31       0.07       -4.59         15.5       13.51508121       -26.37       1.09       0.14       0.07       -3.04         15.4       14.14006745       -24.77       0.74       1.01       0.07       -6.03         15.3       13.47373188       -24.66       0.83       0.31       0.06       -6.04	
15.7     12.5969837     -25.08     0.81     -0.27     0.07     -0.56       15.6     10.38932147     -24.89     0.90     -0.31     0.07     -4.59       15.5     13.51508121     -26.37     1.09     0.14     0.07     -3.04       15.4     14.14006745     -24.77     0.74     1.01     0.07     -6.03       15.3     13.47373188     -24.66     0.83     0.31     0.06     -6.04	0.01
15.6     10.38932147     -24.89     0.90     -0.31     0.07     -4.59       15.5     13.51508121     -26.37     1.09     0.14     0.07     -3.04       15.4     14.14006745     -24.77     0.74     1.01     0.07     -6.03       15.3     13.47373188     -24.66     0.83     0.31     0.06     -6.04	
15.5     13.51508121     -26.37     1.09     0.14     0.07     -3.04       15.4     14.14006745     -24.77     0.74     1.01     0.07     -6.03       15.3     13.47373188     -24.66     0.83     0.31     0.06     -6.04	0.01
15.4     14.14006745     -24.77     0.74     1.01     0.07     -6.03       15.3     13.47373188     -24.66     0.83     0.31     0.06     -6.04	0.02
<b>15.3</b> 13.47373188 -24.66 0.83 0.31 0.06 -6.04	0.01
	0.02
<b>15.2</b> 12.5955695 -24.66 1.23 -0.18 0.07 -4.34	0.02
	0.02
<b>15.20b</b> 10.19126262 -25.32 0.79 0.13 0.06 -4.12	0.02
<b>15.1</b> 13.62755651 -25.24 0.74 -0.03 0.06 0.93	0.00
<b>15</b> 12.40025105 -24.72 0.58 0.04 0.06 1.40	0.00
<b>14.9</b> 16.43121932 -25.28 0.56 0.10 0.06	
<b>14.8</b> 14.19832339 -24.05 0.85 0.02 0.07 -4.89	0.02
<b>14.7</b> 14.00575731 -24.65 1.12 0.19 0.07 -4.91	0.02
<b>14.6</b> 16.36784553 -25.17 0.78 0.05 0.06 -3.85	0.01
<b>14.5</b> 13.55209061 -25.12 0.80 -0.02 0.07 -5.89	0.02
<b>14.4</b> 15.89416227 -25.99 0.88 0.26 0.07 -5.85	0.02
<b>14.3</b> 13.9224412 -24.91 0.77 0.16 0.06 -5.32	0.02
<b>14.2</b> 14.09486166 -25.42 0.80 0.17 0.07 -5.27	0.02
<b>14.1</b> 14.05152225 -24.67 0.88 0.13 0.06 -3.13	0.01
<b>14</b> 14.99017682 -24.43 0.95 0.58 0.07 -5.41	
<b>13.9</b> 14.41714882 -24.82 0.89 -0.35 0.07 -4.17	0.02

13.8	13.18293596	-25.77	0.92	0.14	0.07	-6.35	0.02
13.7	13.12188168	-25.03	0.81	0.43	0.07	-5.07	0.02
13.6	14.0794837	-24.82	0.79	0.29	0.07	-4.85	0.02
13.5	13.56429292			-0.29	0.07	-4.18	0.02
13.4	35.45334869	-28.08	0.00	0.15	0.06	-3.77	0.02
13.3	13.07518488	-25.10	0.81	0.27	0.06	-2.75	0.03
13.2	12.59931896	-25.16	0.86	0.02	0.06	-4.18	0.03
13.1	12.49249764	-25.40	0.83	0.09	0.06	1.01	0.01
13	14.13151927	-24.90	0.78	0.25	0.06	4.25	0.01
12.9	12.79965753	-24.31	0.73	-0.19	0.06	-2.98	0.01
12.8	14.08004607	-24.51	0.85	0.09	0.06	2.41	0.00
12.7	13.27517706			-0.12	0.06		
12.6	13.52652058	-25.05	0.67	0.15	0.06	-4.50	0.02
12.5	13.81353022	-25.16	0.71	0.36	0.07	-5.10	0.02
12.4	13.7331678	-26.05	0.91	0.15	0.06		
12.3	10.21290752	-25.32	0.68	-0.56	0.06	1.94	0.00
12.2	11.80996753	-25.09	0.71	-0.41	0.06	1.16	0.00
12.1	9.229799968	-25.08	0.68	-0.23	0.06	5.52	0.00
12	12.1935273	-25.11	0.65	-0.27	0.06	2.24	0.00
11.9	9.354143136	-25.24	0.75	0.22	0.06	4.60	0.00
11.8	12.37722808	-25.41	0.89	-0.15	0.06	1.85	0.01
11.7	11.82258775	-24.95	0.85	-0.19	0.06	-3.89	0.02
11.6	11.86646962	-26.58	0.90	0.20	0.06	-4.12	0.01
11.5	11.95029341	-25.74	0.75	0.32	0.06		
11.1	12.53194465	-25.09	0.75	0.08	0.05	2.53	0.00
11	10.53051911	-25.37	0.69	0.04	0.05	4.06	0.00
Min	9.229799968	-28.08	0	-0.56	0.05	-6.35	0
Max	35.45334869	-24.05	1.225	1.01	0.07	5.52	0.0294
Average	13.55687669	-25.2074	0.790804	0.062292	0.063333	-2.00159	0.013123
St. Dev.	3.619987911	0.670775	0.174474	0.271515	0.005586	3.702133	0.009049

 $\underline{\mathbf{S1:}}$  Complete data set from meters 11-21 of the Koonwarra Core.



## **BOREHOLE LOG**

| Page No 1 of 3 | | Borehole No: | B18-68600 | | File No: | GE101-35 |

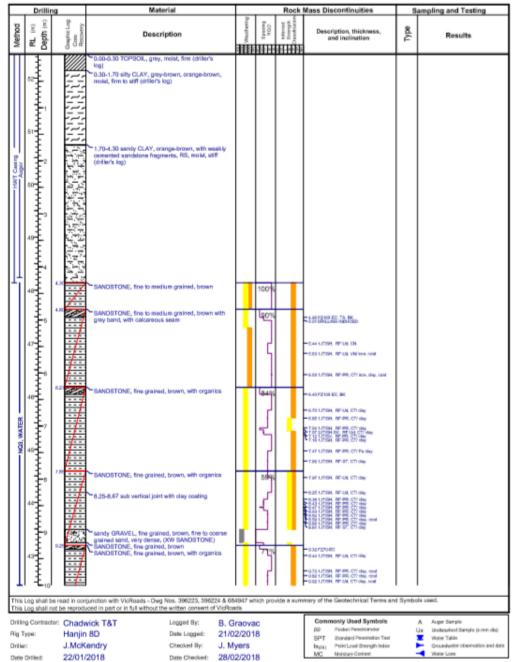
Client: South Eastern Projects

 Road:
 SGH
 Easting:
 409613.6

 Section:
 Koonwarra
 Northing:
 5731012.87

 Section:
 Koonwarra
 Northing:
 5731012.87
 Bearing:

 Location:
 Fish Beds - Private Property
 R.L. (m):
 52.44
 Angle:
 90\*





## **BOREHOLE LOG**

Page No 2 of 3

Borehole No: B18-68600

File No: GE101-35

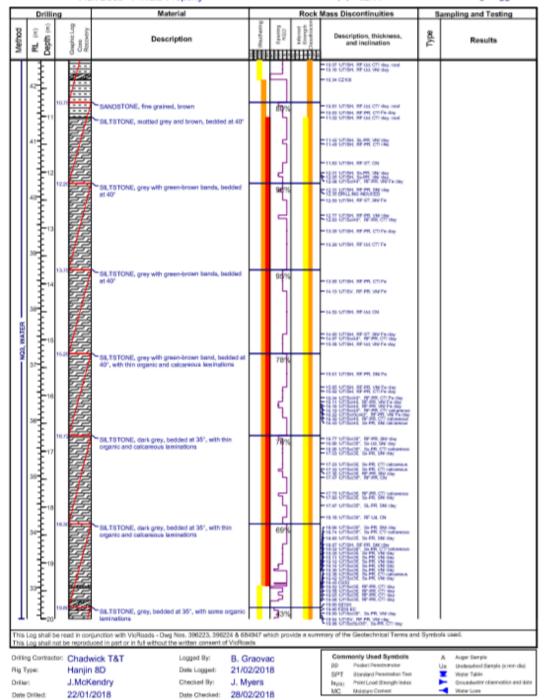
Client: South Eastern Projects

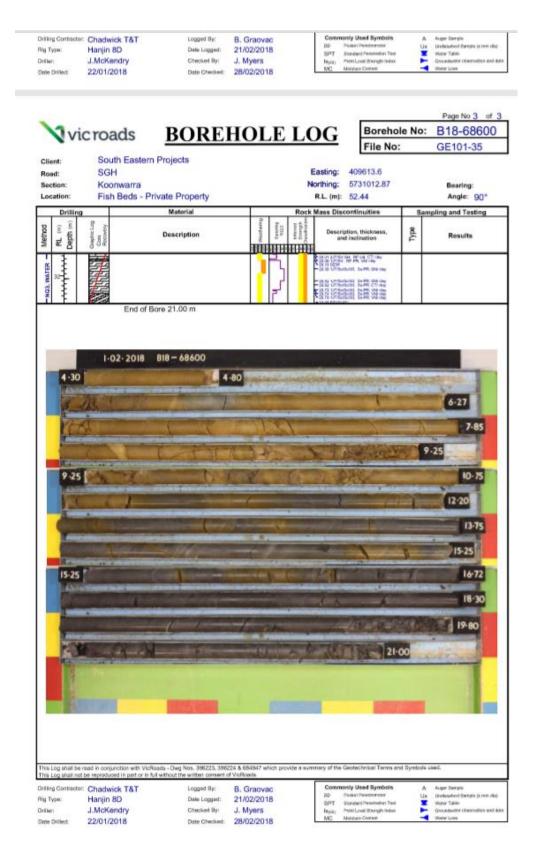
 Road:
 SGH
 Easting:
 409613.6

 Section:
 Koonwarra
 Northing:
 5731012.87

 Section:
 Koonwarra
 Northing:
 5731012.87
 Bearing:

 Location:
 Fish Beds - Private Property
 R.L. (m):
 52.44
 Angle:
 90°





**S2:** Complete borehole log of the Koonwarra core.