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A comparison of lignin phenols and branched/isoprenoid tetraethers (BIT index) as indices of terrestrial organic matter in Doubtful Sound Fiordland, New Zealand

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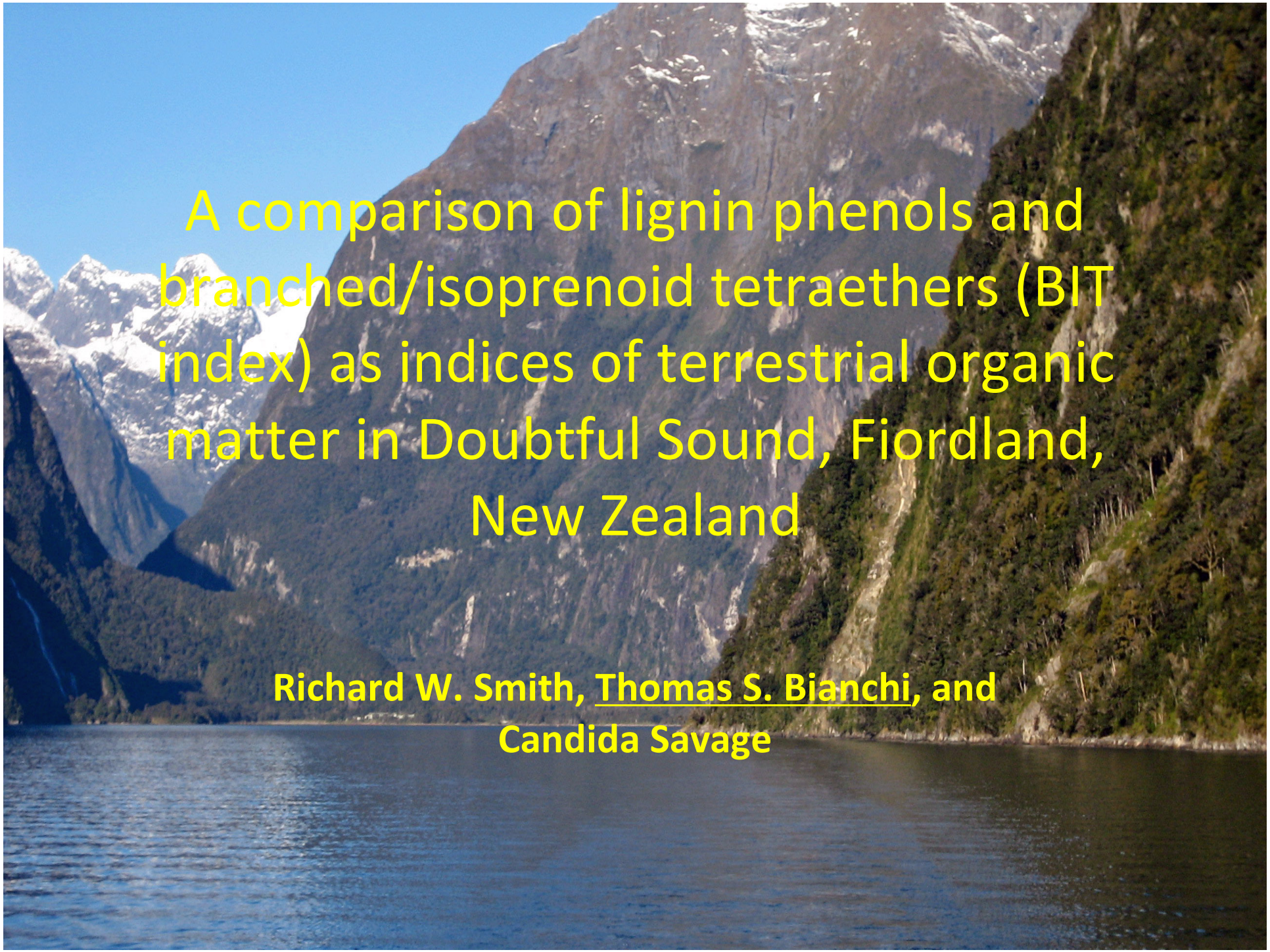


A comparison of lignin phenols and branched/isoprenoid tetraethers (BIT index) as indices of terrestrial organic matter in Doubtful Sound, Fiordland, New Zealand

Richard W. Smith, Thomas S. Bianchi, and Candida Savage

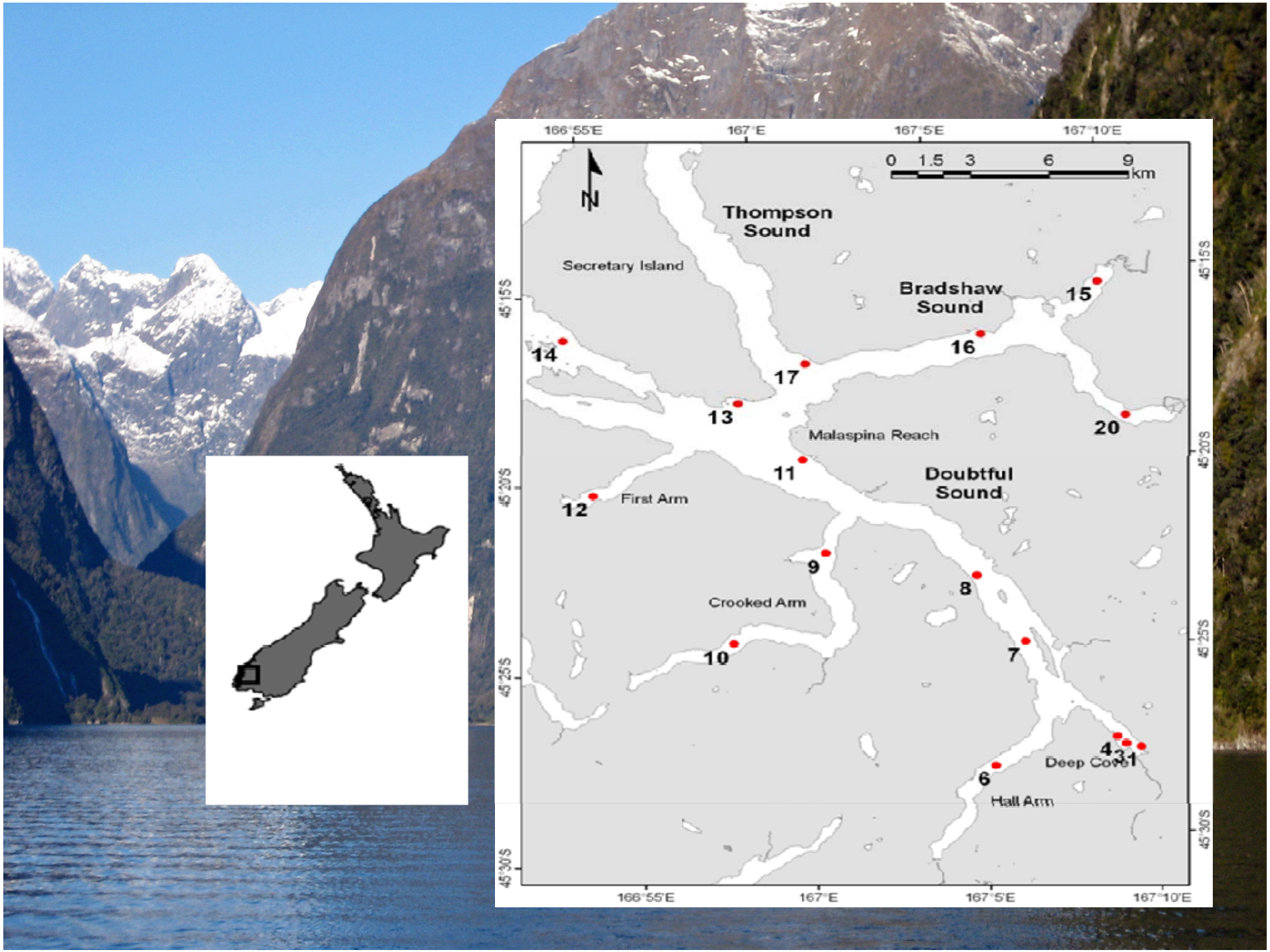
Objectives

- 1. To compare the branched/isoprenoid tetraether (BIT) index with lignin oxidation products (LOP) and bulk organic matter proxies (d13C, C/N) as indices of terrestrial organic matter in fjord sediments

- 2. To examine the spatial and depths variations in proxies, as they may relate to source inputs and hydrodynamic sorting.

- 3. To use this data to make inferences on the varying sources of the biomarkers, and their applicability in different marine environments.

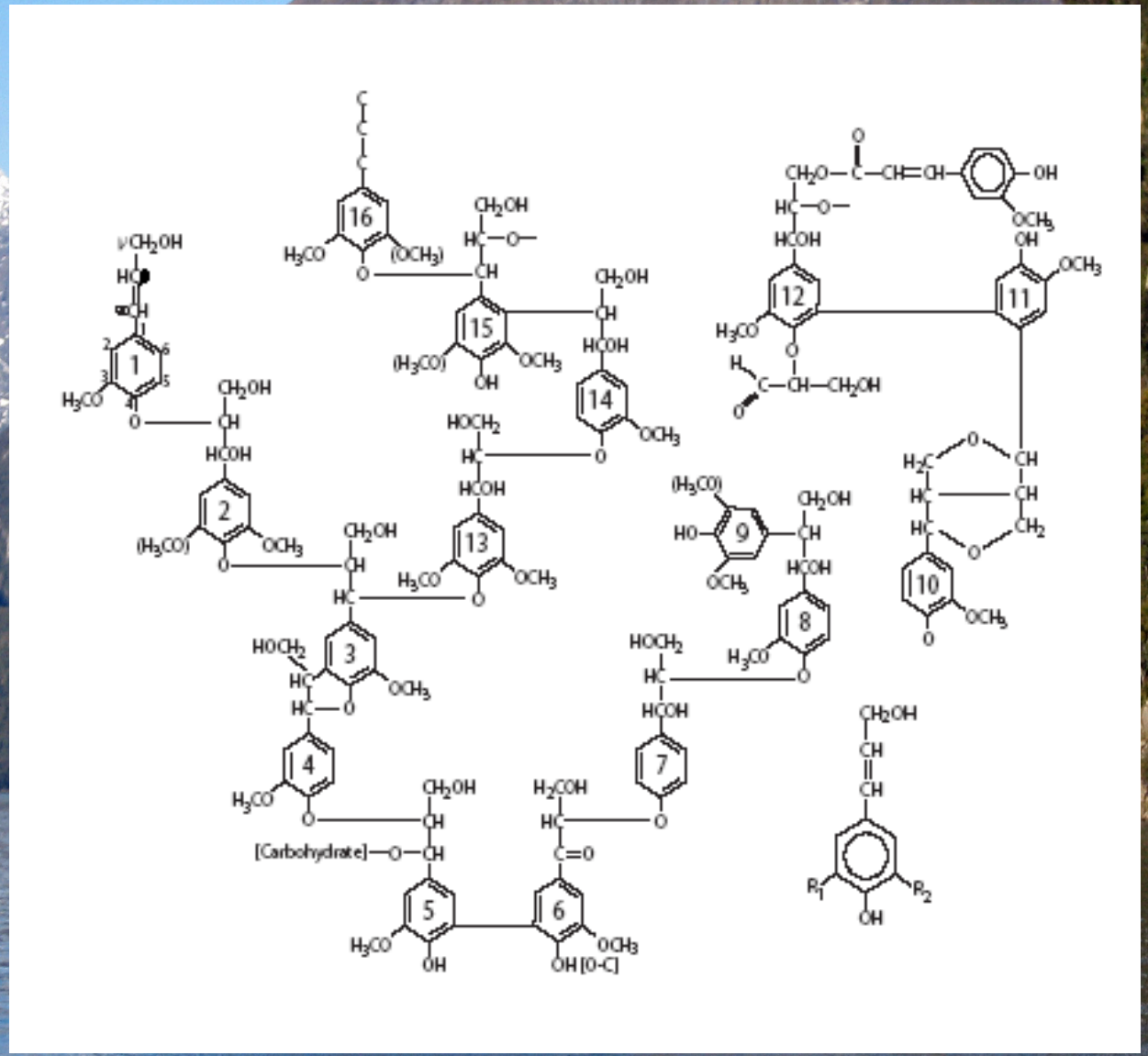
- 4. To provide preliminary data on Doubtful Sound lignin source and degradation state


166°55'E
167°E
167°5'E
167°10'E
0 1.5 3 6 9
km
N
Thompson Sound
Secretary Island
Bradshaw Sound
Malaspina Reach
Doubtful Sound
First Arm
Crooked Arm
Deep Cove
Hall Arm
14
15
16
17
13
20
11
12
9
8
10
7
4
3
1
6
45°15'S
45°20'S
45°25'S
45°30'S


POLARIS II


Average of > 7 m of rainfall each year

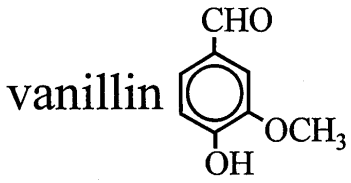
Lignin



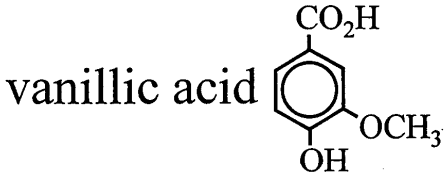
Lignin Biomarkers

CuO oxidation products

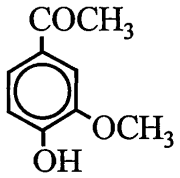
Vanillyl compounds



vanillin

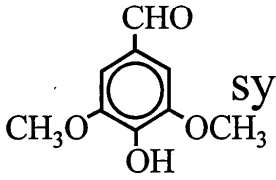


vanillic acid

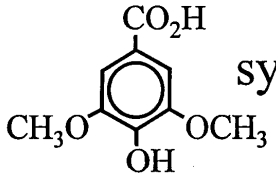


acetovanillone

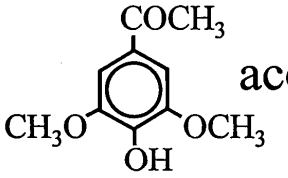
Syringyl compounds



syringaldehyde

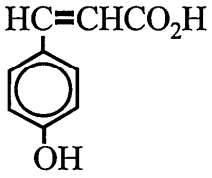


syringic acid

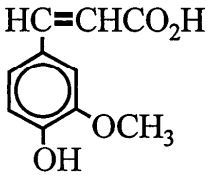


acetosyringone

Cinnamyl Compounds



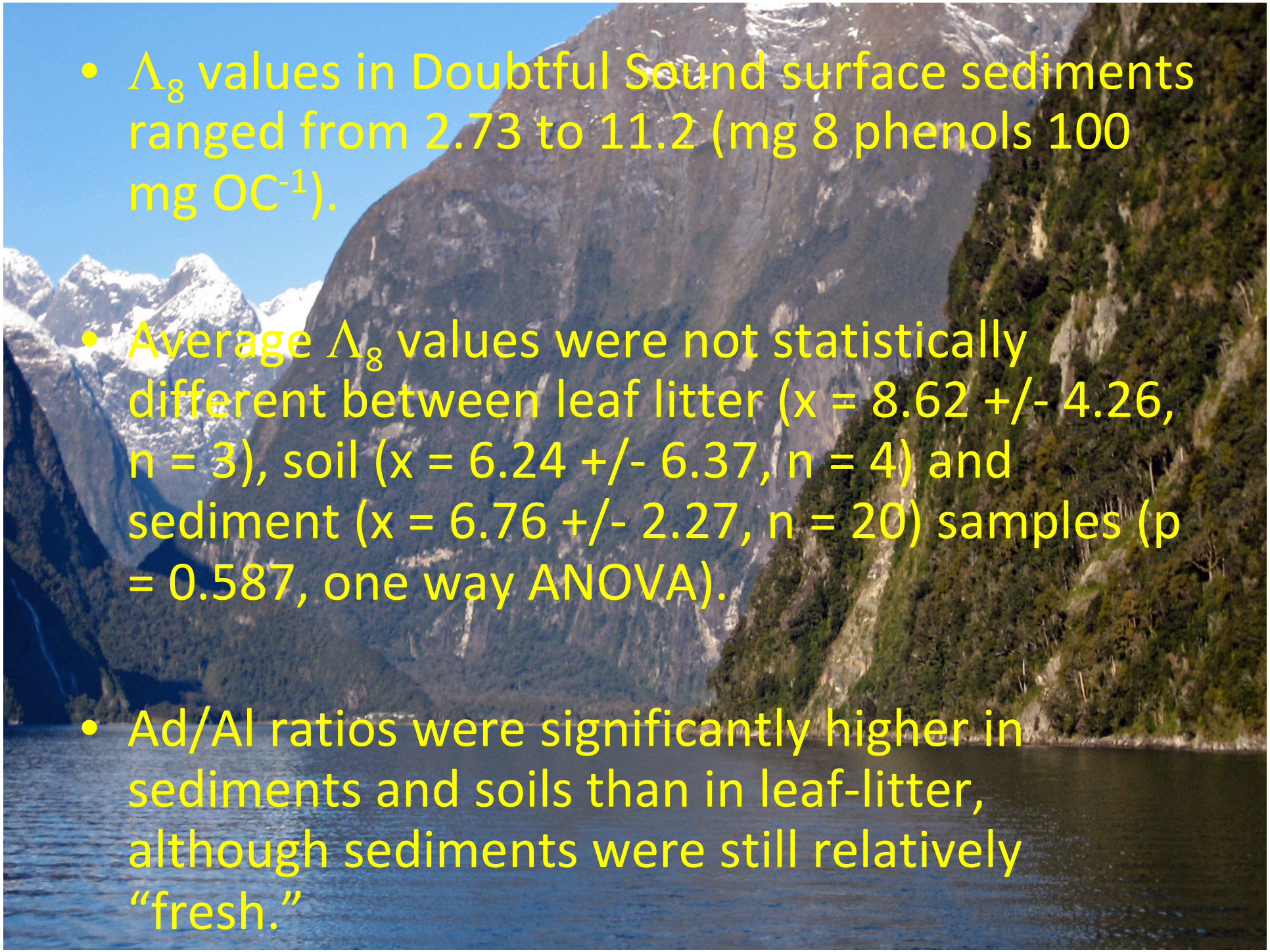
p-coumaric acid



ferulic acid

Lignin Analysis

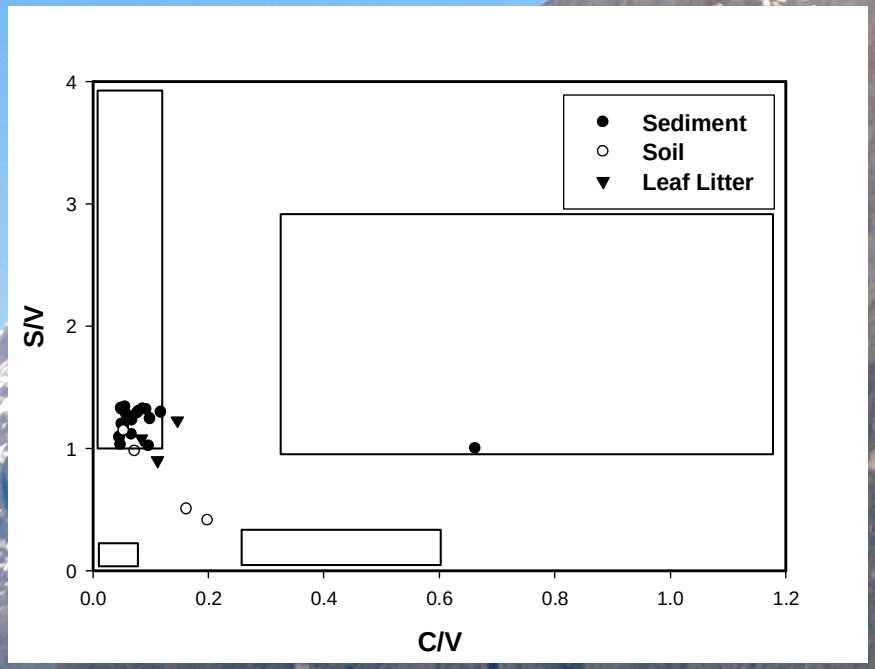
- LOP were created and removed from sediments using the cupric oxide (CuO) oxidation method (Hedges and Ertel 1982)
- The sums of syringyl, vanillyl, and cinnamyll phenols per 100 mg organic carbon (Λ_8) were used as indicators of lignin abundance
- Vanillic acid to vanillic aldehyde (Ad/Al)v and syringic acid to syringic aldehyde (Ad/Al)s ratios were used as proxies of lignin degradation state
- Syringyl to vanillyl (S/V) and cinnamyl to vanillyl (C/V) ratios were used as lignin source indicators



- Λ_8 values in Doubtful Sound surface sediments ranged from 2.73 to 11.2 (mg 8 phenols 100 mg OC^{-1}).

- Average Λ_8 values were not statistically different between leaf litter (x = 8.62 +/- 4.26, n = 3), soil (x = 6.24 +/- 6.37, n = 4) and sediment (x = 6.76 +/- 2.27, n = 20) samples (p = 0.587, one way ANOVA).

- Ad/Al ratios were significantly higher in sediments and soils than in leaf-litter, although sediments were still relatively "fresh."

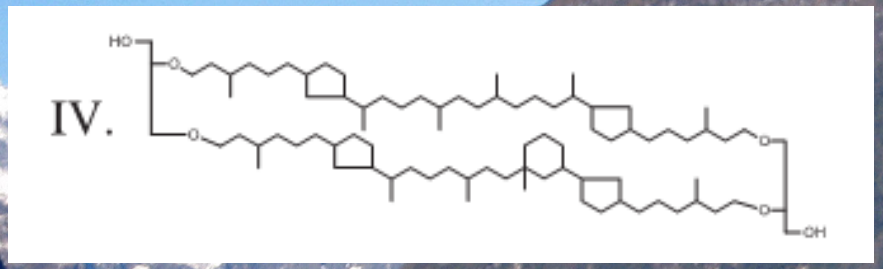


End-Member and Sediment Analyses

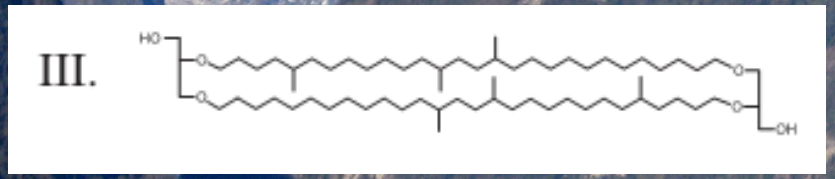
- High concentrations of syringyl and low concentrations of cinnamyl, relative to vanillyl phenols, indicated the predominant source of lignin to sediments was woody angiosperm material.
- Leaf litter fell into this same range, although with slightly elevated cinnamyl concentrations.
- Soil samples fell into this range with the exception of two samples, which indicate some variability in source signatures.

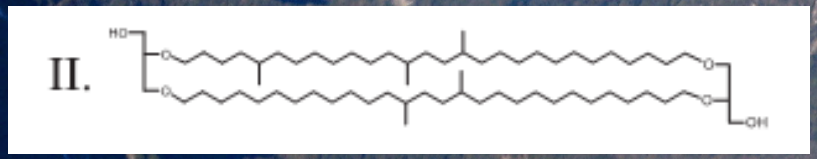
Tetraethers in BIT index

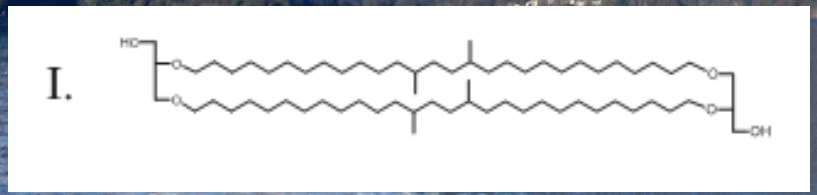
Marine (crenarchaeol)

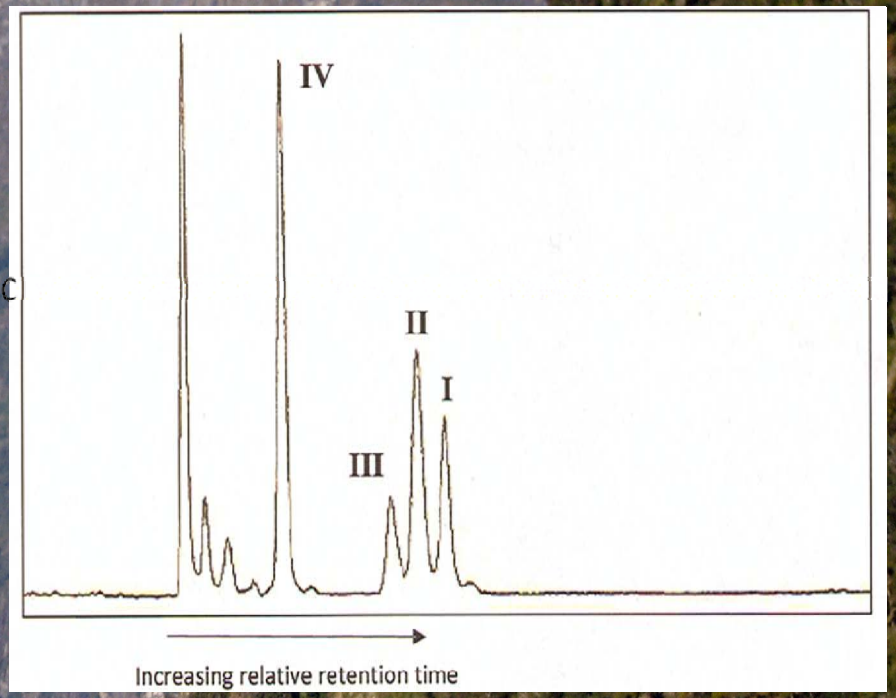


Soil









BIT = [I + II + III]/ [I + II + III] + [IV]

Structures from Hopmans et al. 2004

Archaea…..

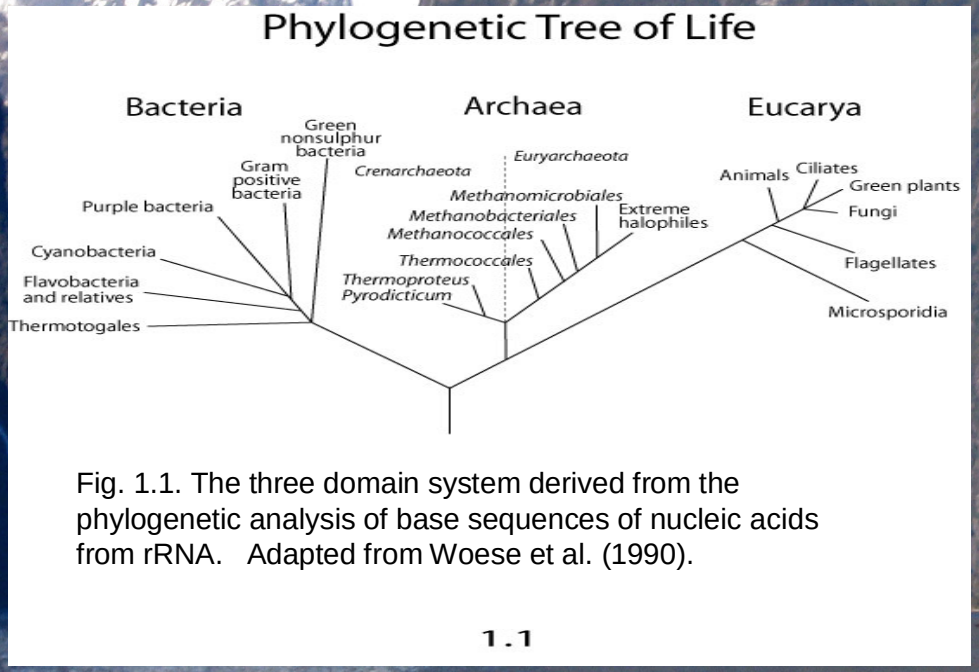
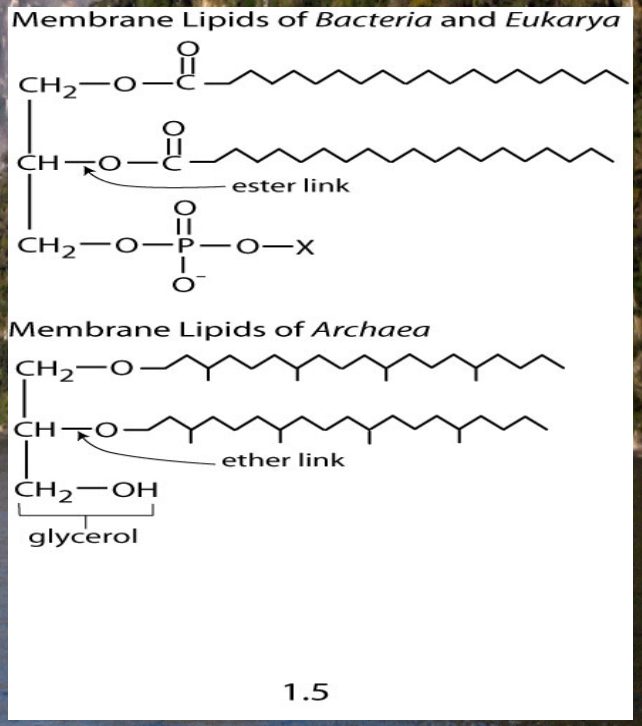
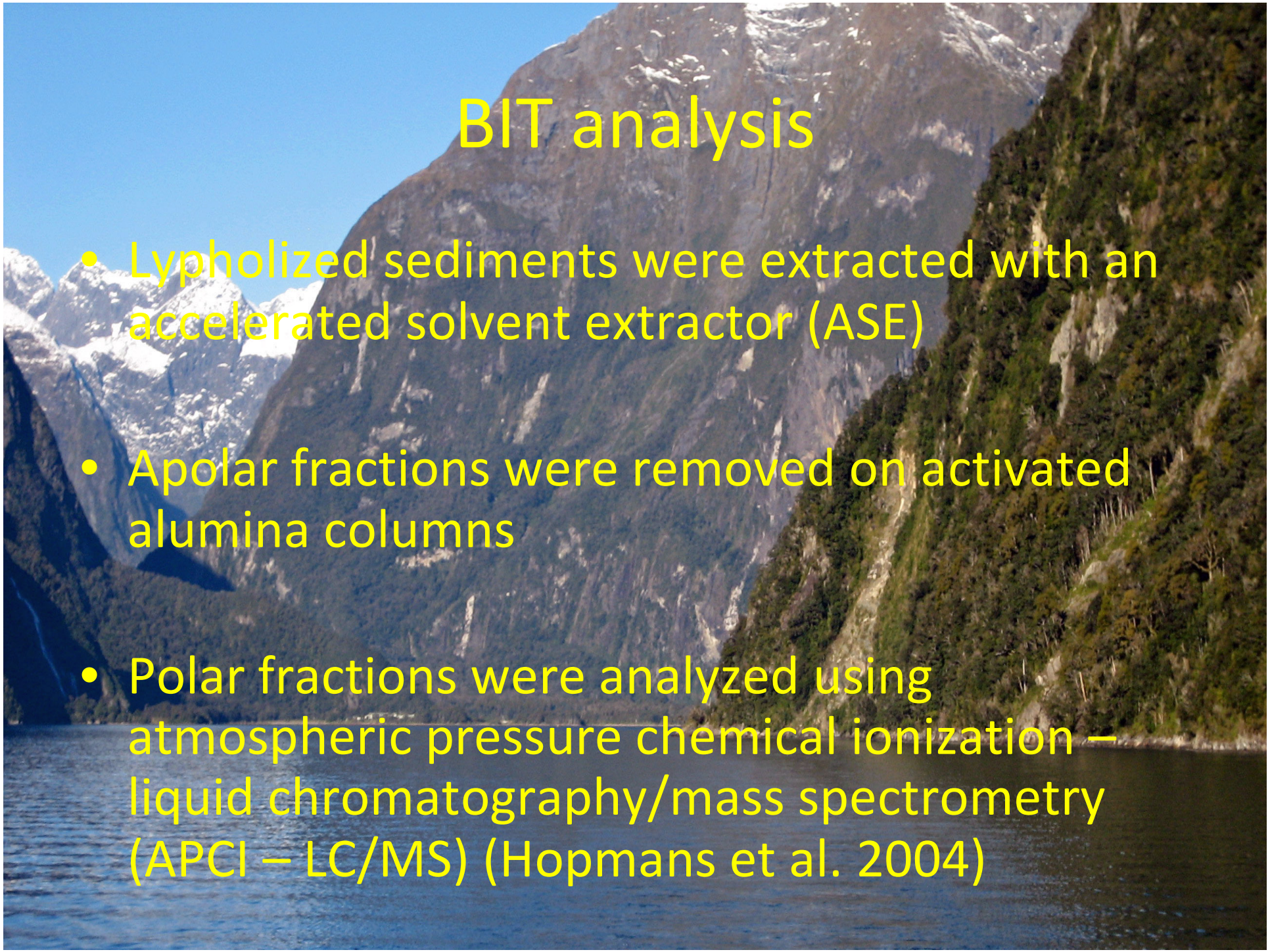


Fig. 1.1. The three domain system derived from the phylogenetic analysis of base sequences of nucleic acids from rRNA. Adapted from Woese et al. (1990).



From Bianchi and Canuel (2010) Chemical Biomarkers in Aquatic Ecosystems (In press) Princeton University Press, 612 pp.



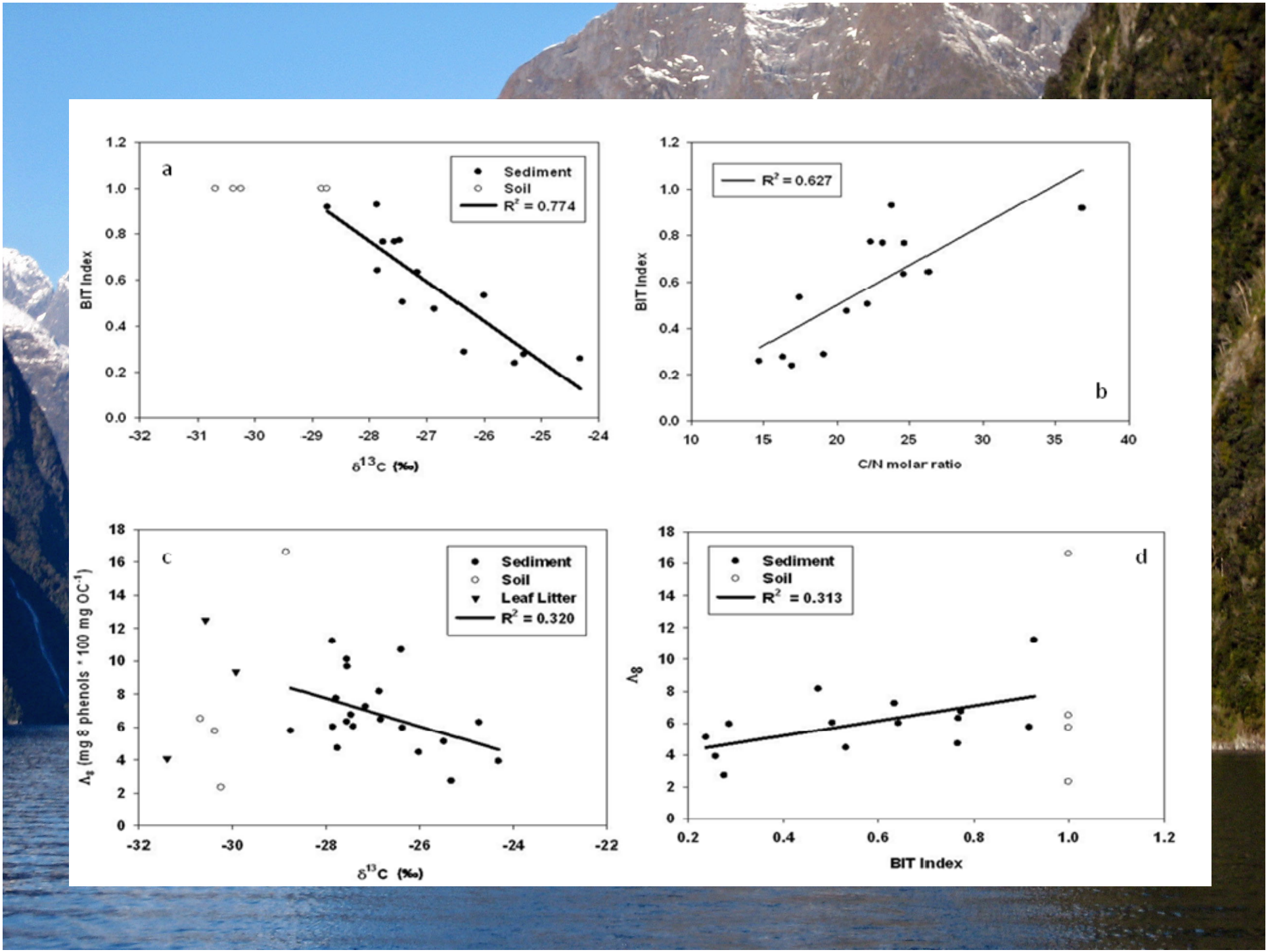
BIT analysis

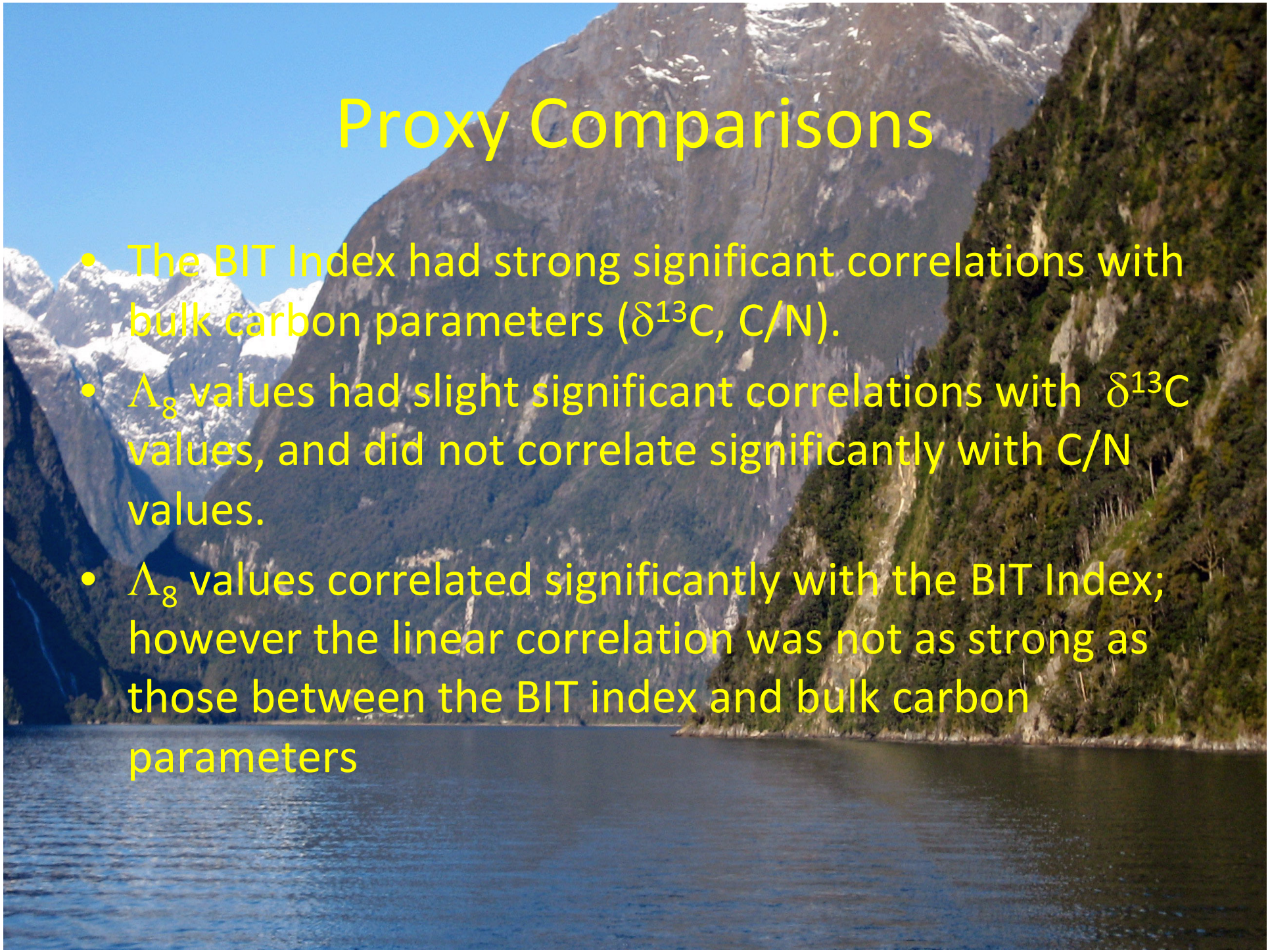
- Lypholized sediments were extracted with an accelerated solvent extractor (ASE)
- Apolar fractions were removed on activated alumina columns
- Polar fractions were analyzed using atmospheric pressure chemical ionization – liquid chromatography/mass spectrometry (APCI – LC/MS) (Hopmans et al. 2004)

BIT Index

- BIT values in Doubtful Sound surface sediments ranged from 0.24 to 0.93 (x = 0.57 +/- 0.24)

- Soil end-members contained no crenarchaeol (BIT = 1).


a
Sediment
Soil
R² = 0.774
BIT Index
δ13C (‰)
b
R² = 0.627
BIT Index
C/N molar ratio
c
Sediment
Soil
Leaf Litter
R² = 0.320
Λ8 (mg ε phenols * 100 mg OC-1)
δ13C (‰)
d
Sediment
Soil
R² = 0.313
Λ8
BIT Index

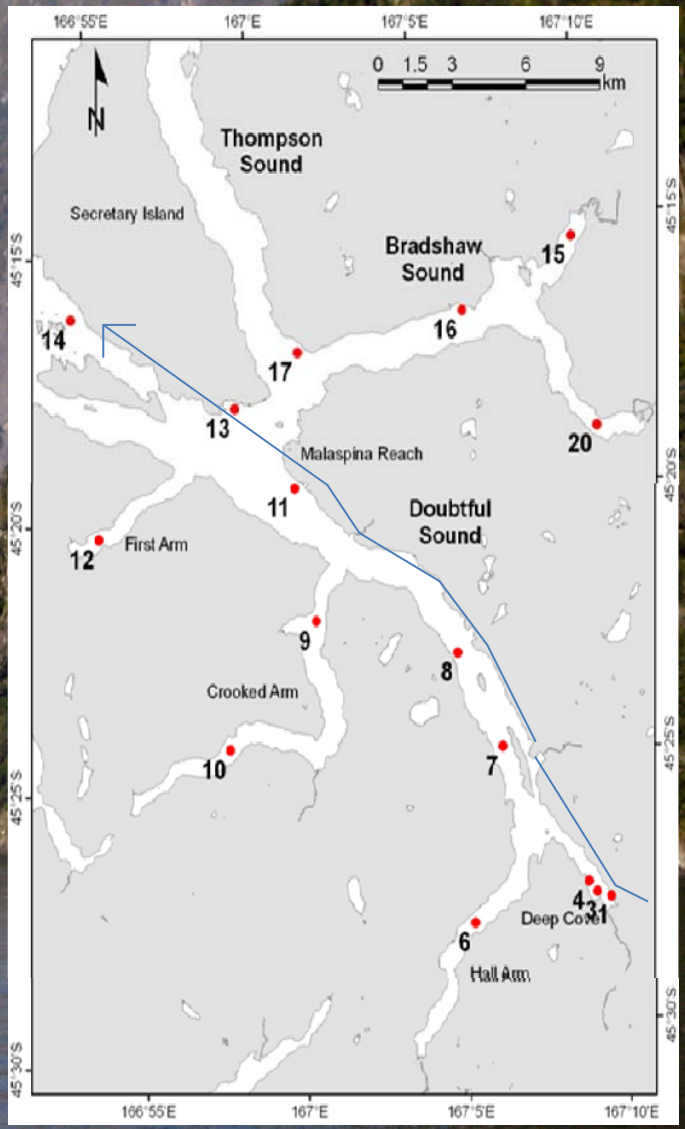


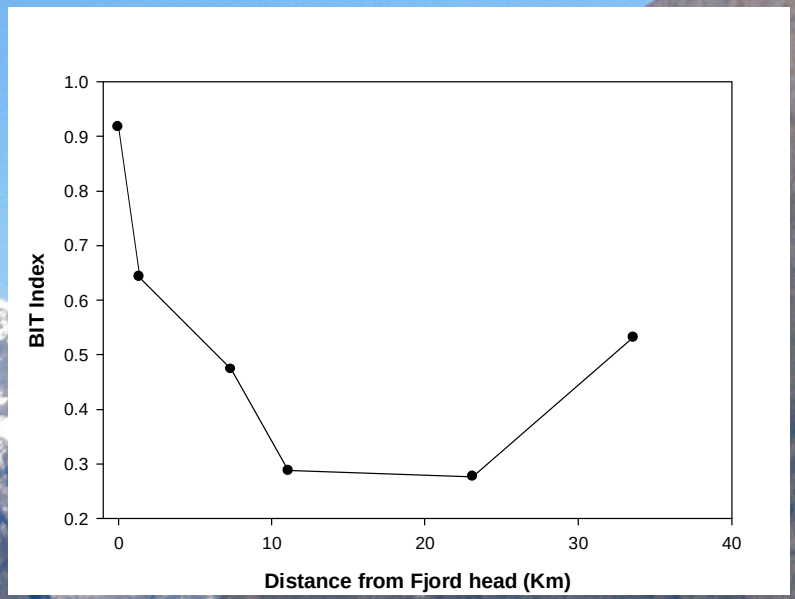
Proxy Comparisons

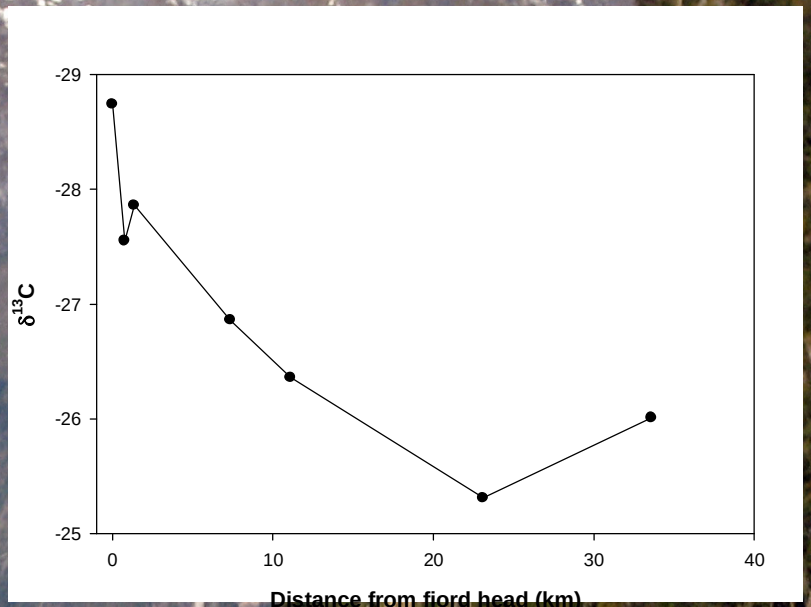
- The BIT Index had strong significant correlations with bulk carbon parameters ($\delta^{13}C$, C/N).
- Λ_8 values had slight significant correlations with $\delta^{13}C$ values, and did not correlate significantly with C/N values.
- Λ_8 values correlated significantly with the BIT Index; however the linear correlation was not as strong as those between the BIT index and bulk carbon parameters

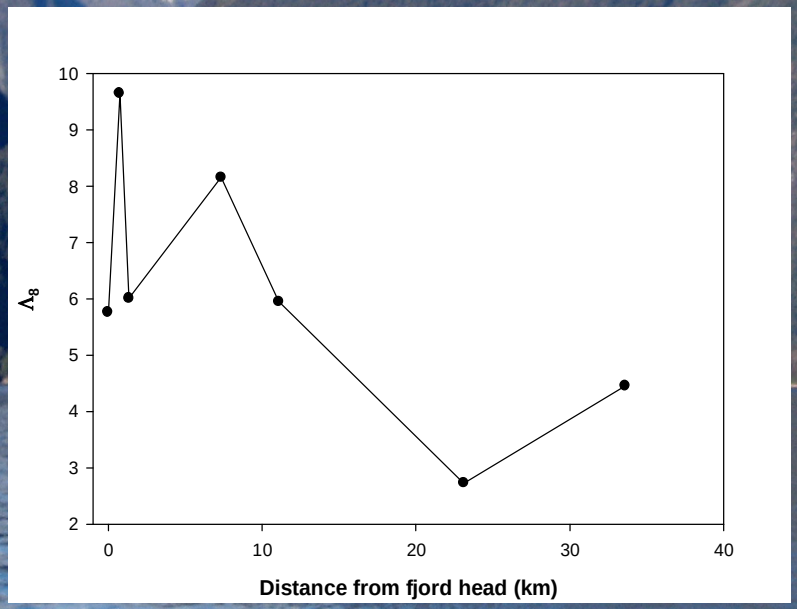
Spatial Trends

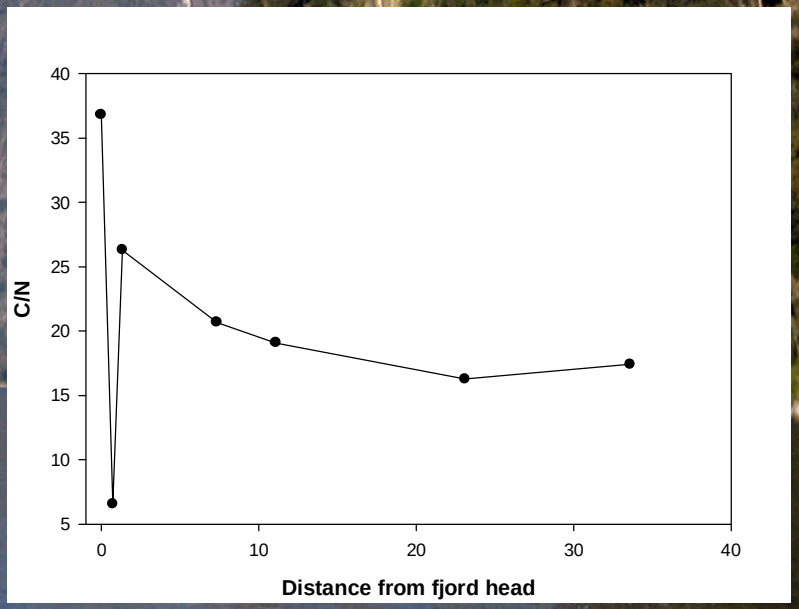
- To assess differences in hydrodynamic sorting of biomarkers and bulk proxies, a transect was chosen from the input site of a headwater stream (DS01) to the site closest to the mouth of the fjord (DS14).




BIT Index
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0
10
20
30
40
Distance from Fjord head (Km)


δ13C
-29
-28
-27
-26
-25
0
10
20
30
40
Distance from fjord head (km)

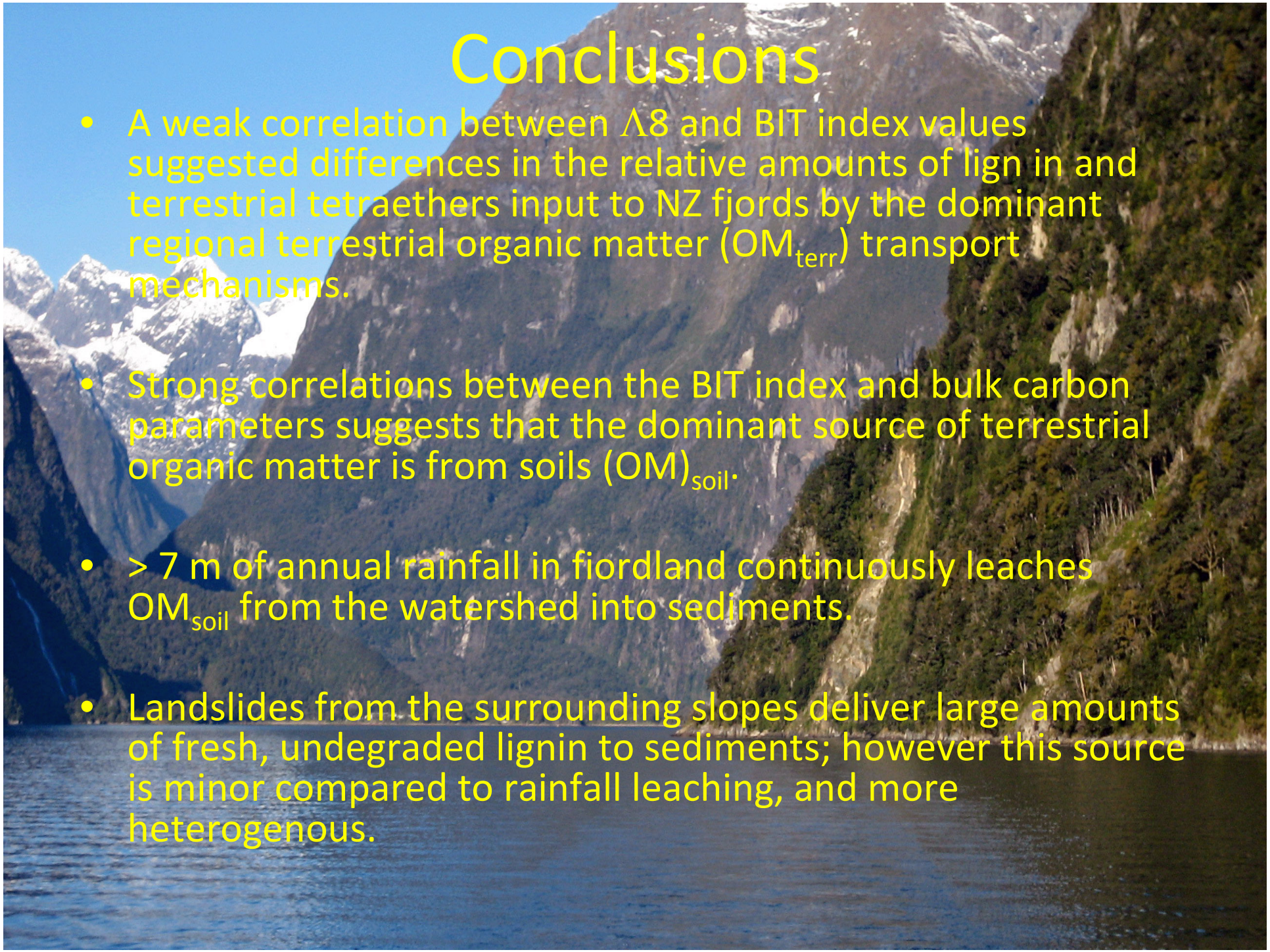

Λ8
10
9
8
7
6
5
4
3
2
0
10
20
30
40
Distance from fjord head (km)


C/N
40
35
30
25
20
15
10
5
0
10
20
30
40
Distance from fjord head

Water Depth Trends

		Depth*	BIT*	$\Lambda 8$	$(Ad/Al)_v$	% OC	C/N	$\delta^{13}C$
Shallow	Avg	50.8	0.70	7.73	6.74	5.5	24.5	-27.3
	Std. Dev.	21.3	0.23	2.23	2.24	3.6	6.6	1.4
Deep	Avg	158.9	0.44	6.10	5.30	5.5	19.6	-26.5
	Std. Dev.	59.3	0.19	2.16	2.68	4.1	3.1	0.9
t-test	*p*	0.0007	0.036	0.189	0.2	0.97	0.096	0.218

* Indicates parameters that show significant differences between shallow and deep sites



Conclusions

- A weak correlation between $\Lambda 8$ and BIT index values suggested differences in the relative amounts of lign in and terrestrial tetraethers input to NZ fjords by the dominant regional terrestrial organic matter (OM_{terr}) transport mechanisms.
- Strong correlations between the BIT index and bulk carbon parameters suggests that the dominant source of terrestrial organic matter is from soils $(OM)_{soil}$.
- > 7 m of annual rainfall in fiordland continuously leaches OM_{soil} from the watershed into sediments.
- Landslides from the surrounding slopes deliver large amounts of fresh, undegraded lignin to sediments; however this source is minor compared to rainfall leaching, and more heterogenous.


Jasmina
Photo by Apse (2007)