Click to view video of Arctic PCA scores

Circum-Arctic Petroleum Systems Defined Using Biomarkers, Isotopes, and Chemometrics*

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Abstract

Because petroleum systems involve multiple elements and processes, traditional exploration to find subsurface traps is prone to error. Costly exploration failures, such as the Mukluk well in Alaska, show that large traps may lack oil and gas. Understanding the link between petroleum and the source rock reduces risk. For example, identification of the source rock for accumulations suggests migration pathways and whether nearby structures might have filled. Unfortunately, conventional oil-to-source rock correlation and studies of mixed oils are commonly unreliable because they are based on few parameters and lack statistical evaluation of uncertainty.

This paper describes two new chemometric methods that use geochemical data to define petroleum systems and de-convolute oil mixtures in the circum-Arctic. Source- and age-related biomarker and isotope data were measured for ~1000 oil samples collected above ~55^{o}N latitude. A multi-tiered chemometric decision tree identified 31 circum-Arctic oil families based on a training set of 622 oil samples. 'Decision-tree chemometrics' uses principal component analysis (PCA) and other multivariate statistical tools to classify and assign confidence limits for oil and source-rock extract samples. For example, the method identifies seven oil families in West Siberia, four in East Siberia, and two in the Volga-Ural basin and the corresponding source rocks.

Seventy-four of the above oil samples from the Barrow Arch on the Alaska North Slope were studied to assess relative volumetric contributions from different source rocks to the giant Prudhoe Bay Field. Alternating least squares of concentration data (ALS-C) for

46 biomarkers was used to de-convolute the mixtures. ALS-C results for 23 oil samples from the prolific Ivishak Formation reservoir in the field indicate similar contributions from Triassic Shublik Formation and Cretaceous Hue-GRZ source rocks (37% each), and less from the Jurassic Kingak Shale (26%). These results differ from published interpretations that most oil in the field originated from the Shublik Formation. Unlike conventional methods to assess mixtures, ALS-C does not require that pure end member oils be identified prior to analysis or that laboratory mixtures of these oils be prepared to evaluate mixing. Further application of these methods could significantly improve understanding of the origins of crude oil in other areas of the circum-Arctic, thus reducing exploration risk.

References

Kontorovich, A.E., 1984, Geochemical methods for the quantitative evaluation of the petrolen potential of sedimentary basins: AAPG Memoir, v. 35, p. 79-109.

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Peters, K.E., C.C. Walters, and J.M. Moldowan, 2005, The Biomarker Guide: Cambridge University Press, Cambridge, U.K., 1155 p.

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Peters, K.E., F.D. Hostettler, T.D. Lorenson, and R.J. Rosenbauer, 2008, Families of Miocene Monterey crude oil, seep, and tarball samples, coastal California: AAPG Bulletin, v. 92, p. 1131-1152.

Peters, K.E., L.S. Ramos, J.E. Zumberge, Z.C. Valin, and K.J. Bird, 2008, De-convoluting mixed crude oil in Prudhoe Bay field, North Slope, Alaska: Org. Geochem., v. 39, p. 623-645.

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Theme II 10:45 am Wednesday

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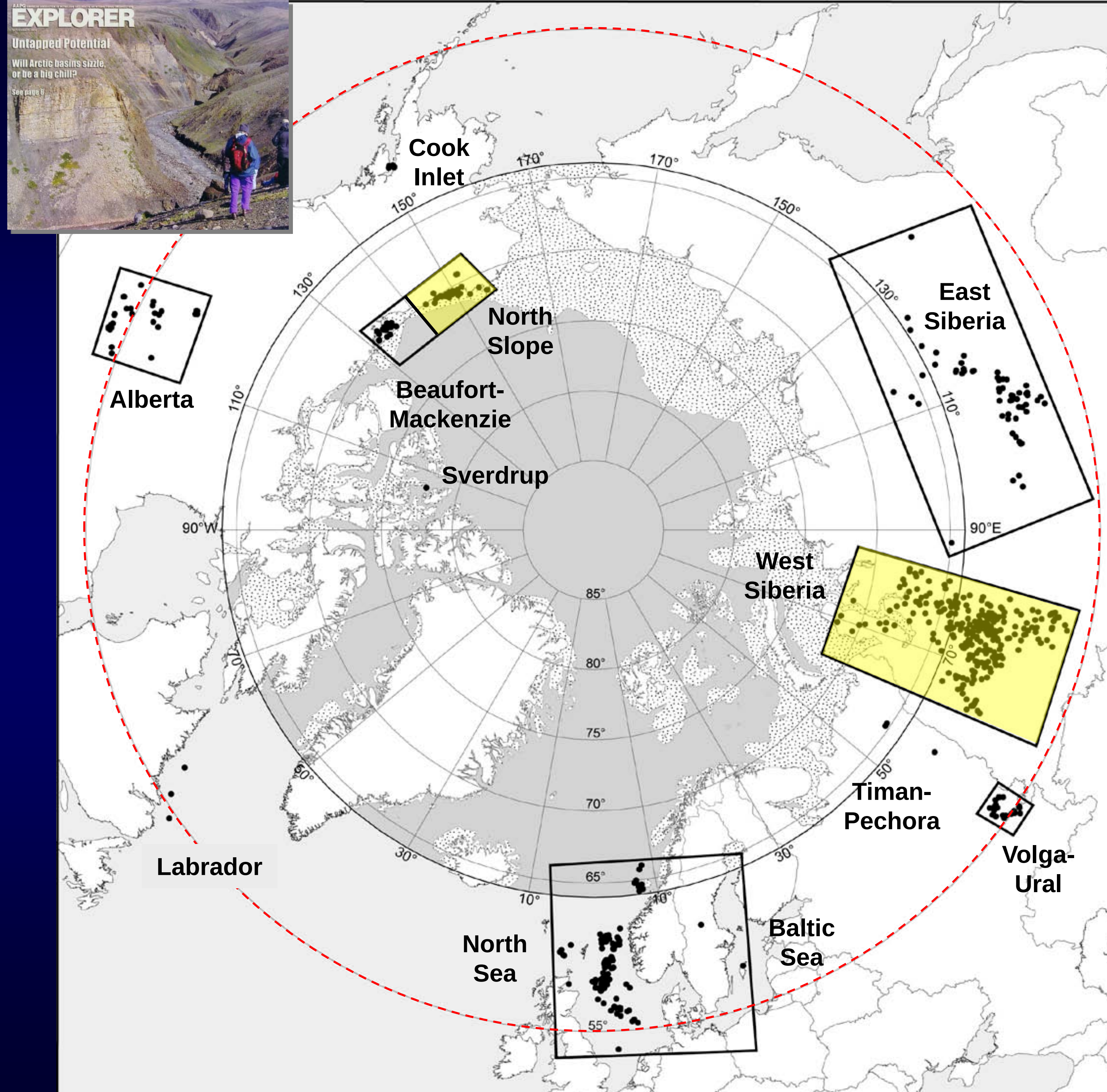
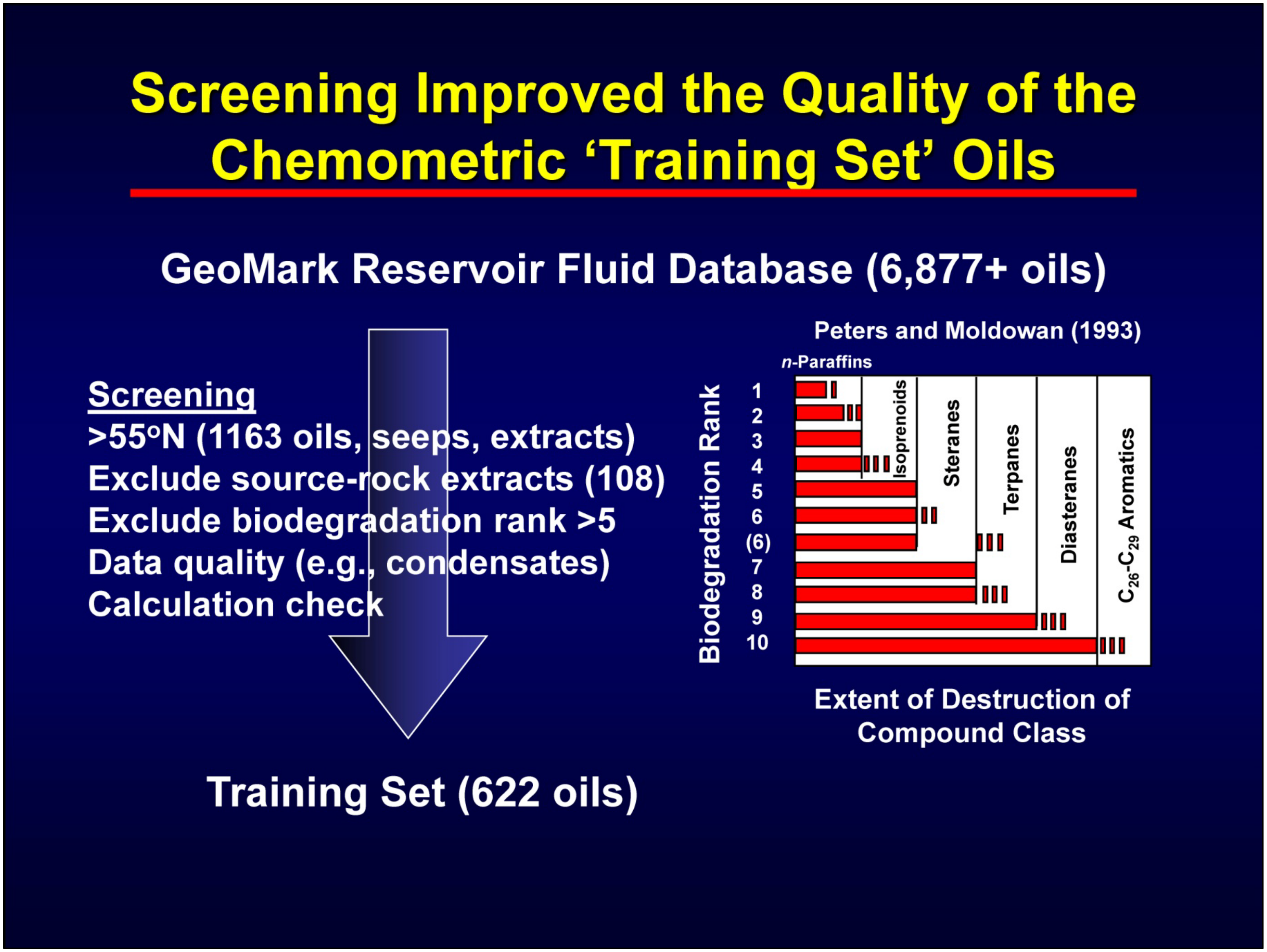
Purpose of Circum-Arctic Study

- Correlate crude oils into genetic families (oil-oil correlation); build predictive model
- Identify the source rock for each oil sample (oil-source rock correlation)
- De-convolute mixed crude oils

Circum-Arctic Oil and Seep Samples



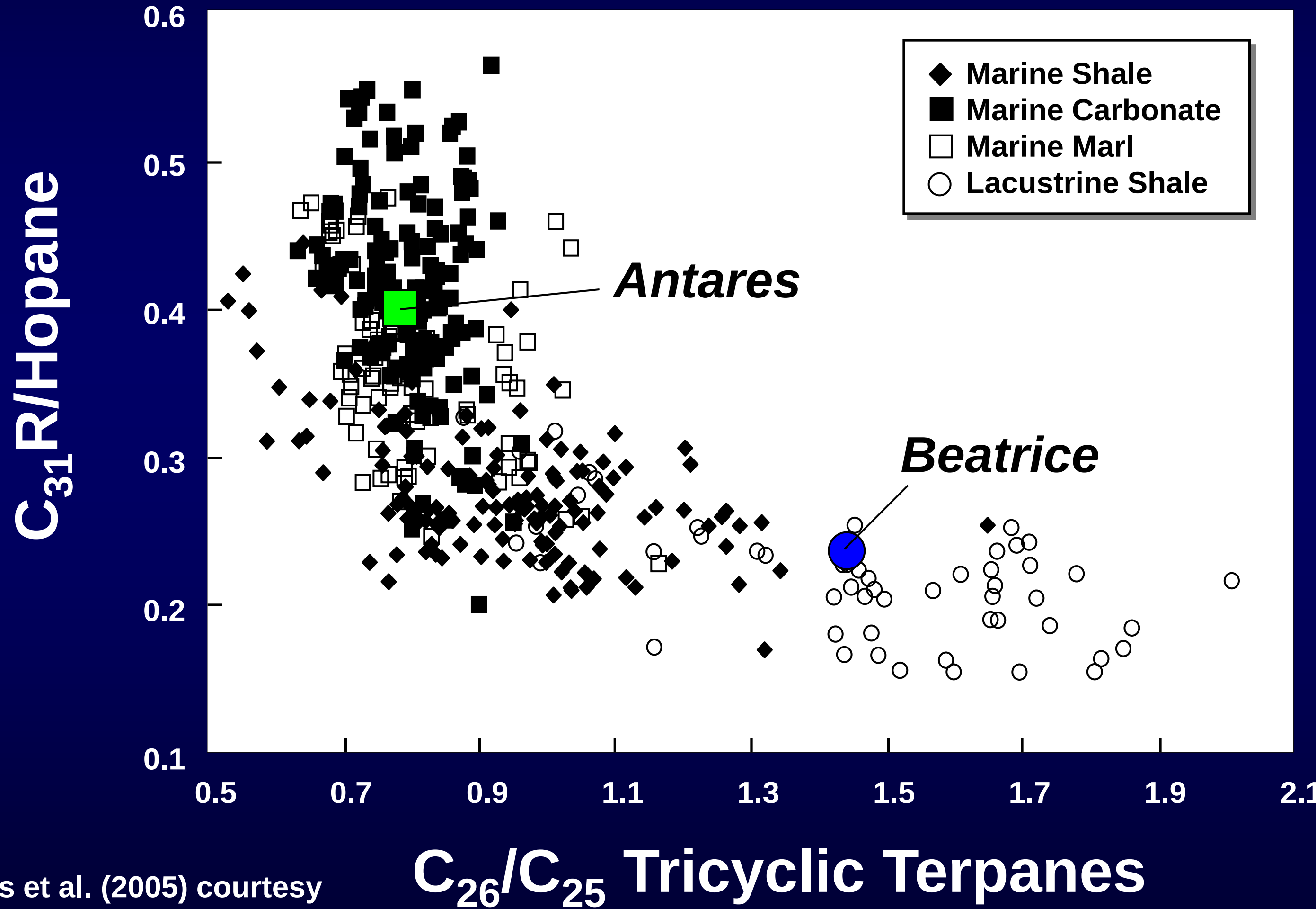


Notes by Presenter: Additional samples were screened from the original dataset if they lacked both inferred age and lithology from the geochemistry. Two very large groups of related samples, mainly from Upper Jurassic source distal marine source rock in Russia were reduced in size using [Scott Ramos program]. The samples eliminated from the Pirouette model were retained in an Excel file for use in a test of the InStep model. Other samples for tests of the InStep model included extracts of known source rocks, and problematic oil samples eliminated from the Pirouette model during screening.

~20 Independent Source-Related Variables Characterize the Training Set

Oil Samples	Terpanes														Steranes				Isotopes	
	C_{19}/C_{23}	C_{22}/C_{21}	C_{24}/C_{23}	C_{26}/C_{25}	Tet/C_{23}	$C_{27}T/C_{27}$	C_{28}/H	C_{29}/H	X/H	Ol/H	$C_{31}R/H$	Ga/$C^{31}R$	$C_{35}S/C_{34}S$	$C_{26}T/Ts$	S/H	%C_{27}	%C_{28}	%C_{29}	δ^{13}Csat	δ^{13}Caro
A92P_PDMS	2.01	0.38	0.82	0.94	1.39	0.35	0.14	0.48	0.06	0.20	0.23	0.08	0.49	0.19	0.30	18.8	37.1	44.0	-28.42	-27.34
A118T_MC	0.04	0.73	0.55	0.78	0.22	0.03	0.08	1.01	0.04	0.01	0.40	0.36	1.28	2.03	0.16	30.6	28.8	40.6	-30.04	-29.94
EB1PC_MM	0.03	0.30	0.78	0.91	0.21	0.35	0.31	0.71	0.05	0.03	0.35	0.23	1.22	2.78	1.06	13.2	19.0	67.7	-34.45	-34.34
R21UJ_DMS	0.08	0.40	0.90	0.66	0.39	0.23	0.06	0.54	0.05	0.02	0.36	0.10	1.02	0.64	0.73	38.4	32.1	29.5	-32.03	-31.83
NWE34D_FL	0.20	0.26	0.65	1.44	0.51	0.01	0.03	0.62	0.20	0.01	0.23	0.34	0.51	0.56	0.20	21.2	39.7	39.1	-32.27	-30.72

Indirect Correlation: Biomarkers in Oil Characterize the Source Rock (EDA)



Peters et al. (2005) courtesy of GeoMark Research, Inc.

Chemometrics Extracts Information From Multivariate Chemical Data

Visual

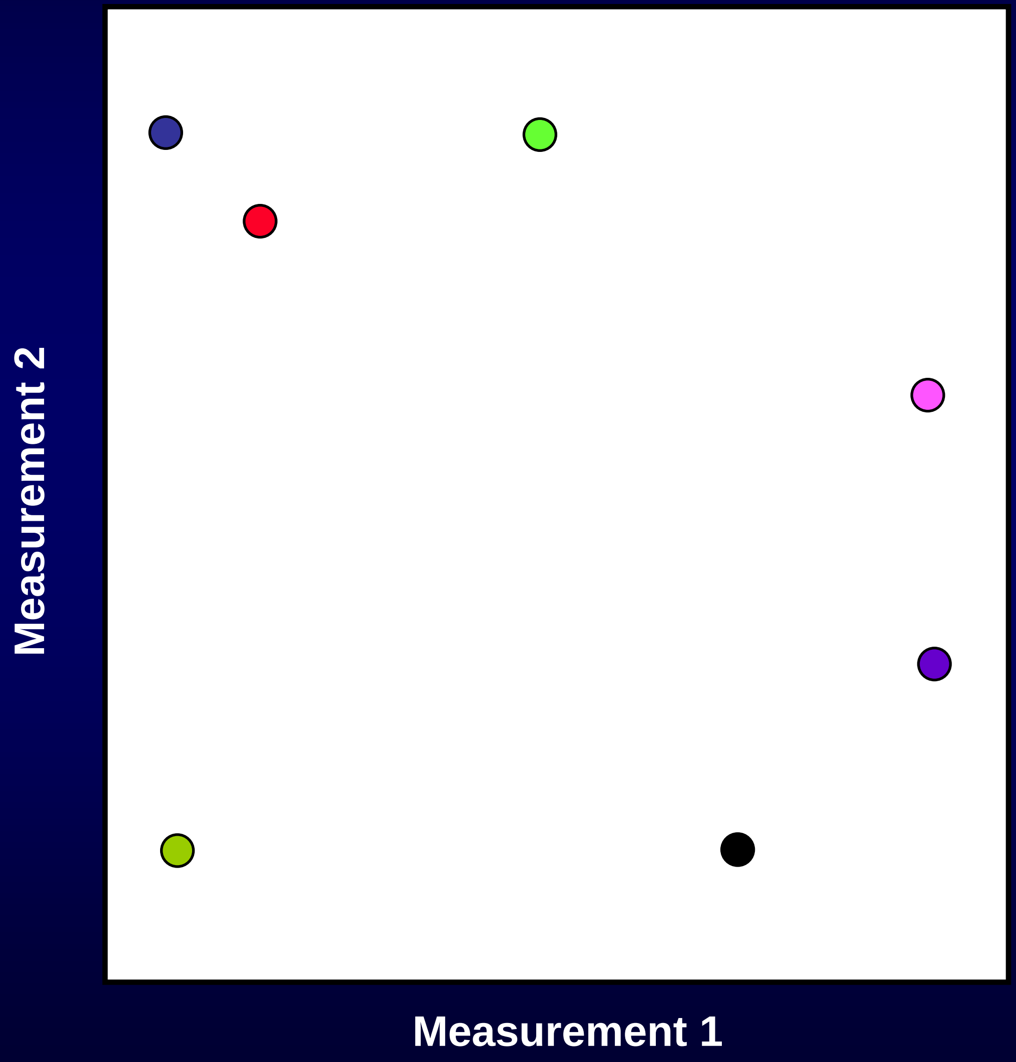
- **Hierarchical Cluster Analysis (HCA)**

Modeling

- **Principal Components Analysis (PCA)**
- **K-Nearest Neighbor (KNN)**
- **PCA Modeling of Class (SIMCA*)**

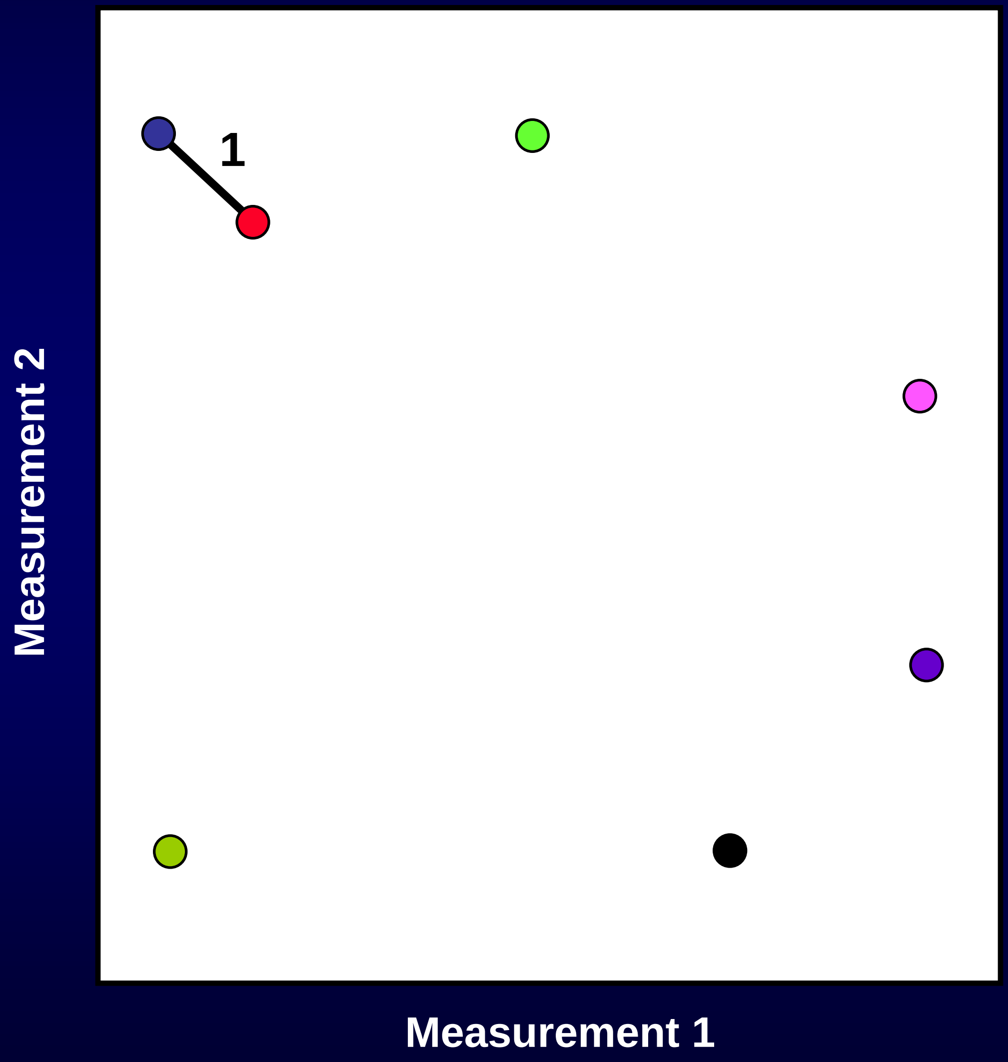
*Soft Independent Modeling of Class Analogy

How Similar Are Samples? Calculate Distance in Two or *n*-Dimensions

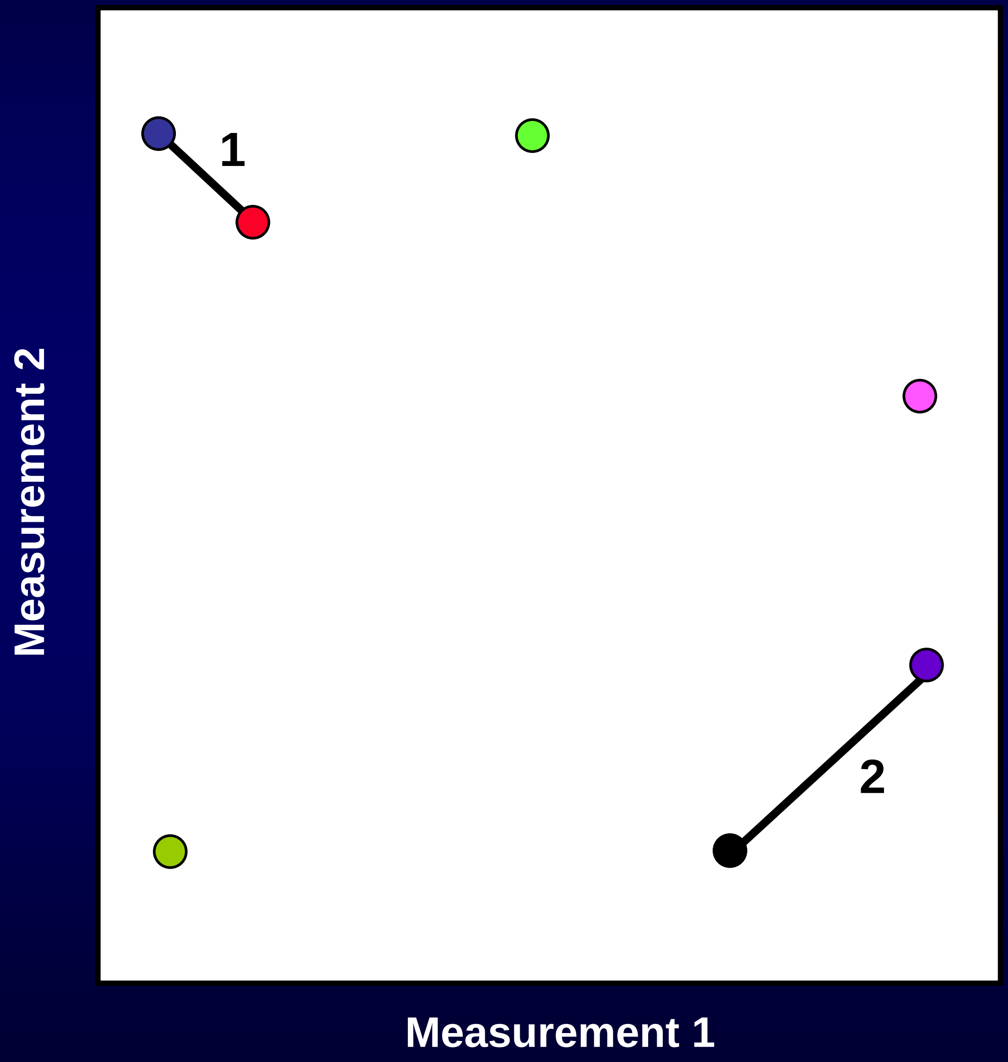


A simple example with 2 measurements on 7 samples.

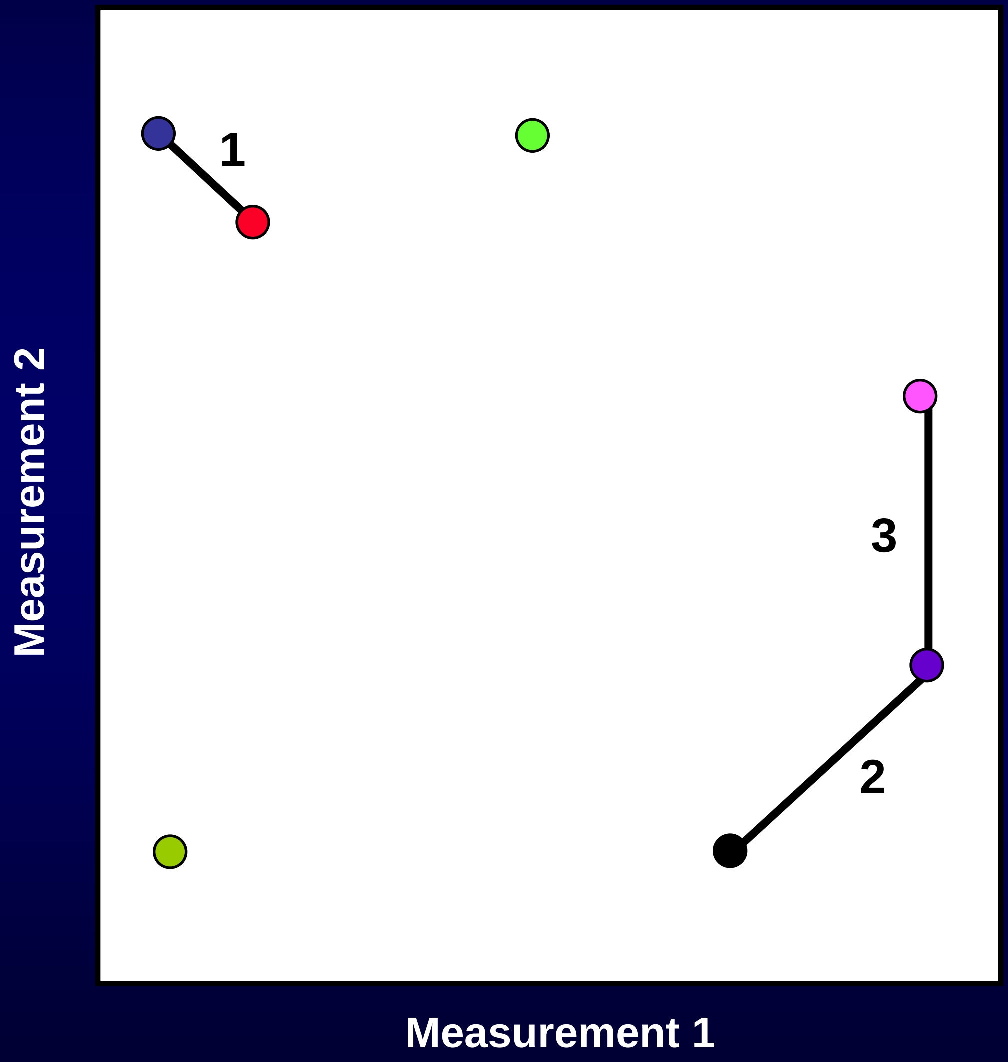
Calculate the Distance Between Points



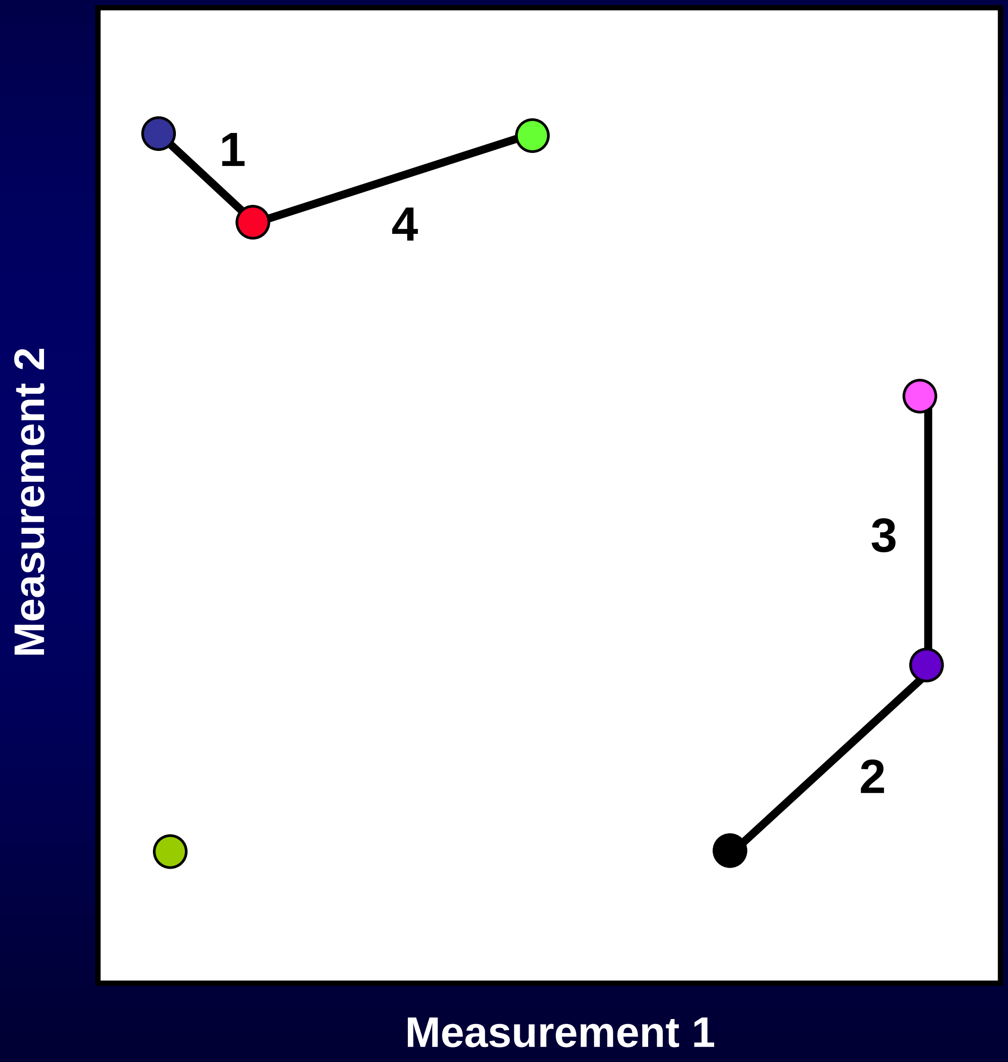
Calculate the Distance Between Points



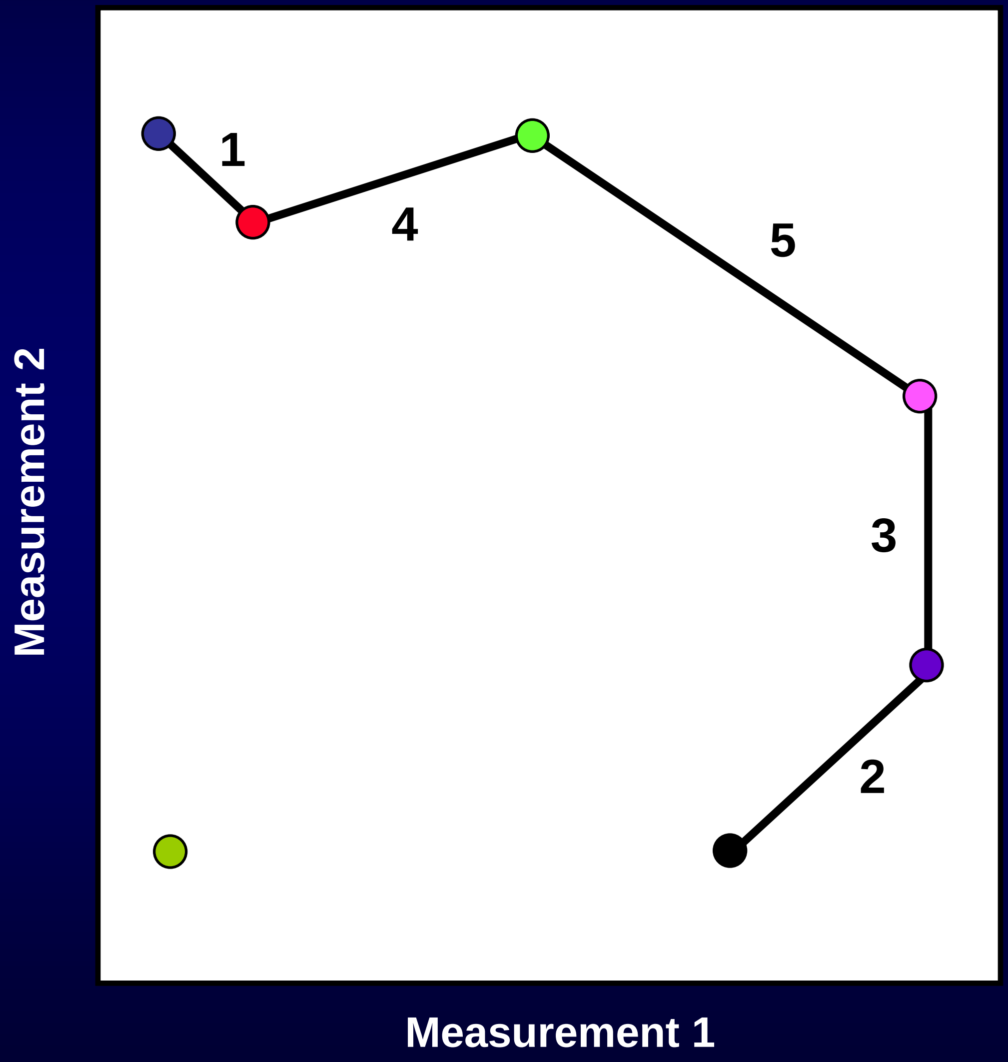
Calculate the Distance Between Points



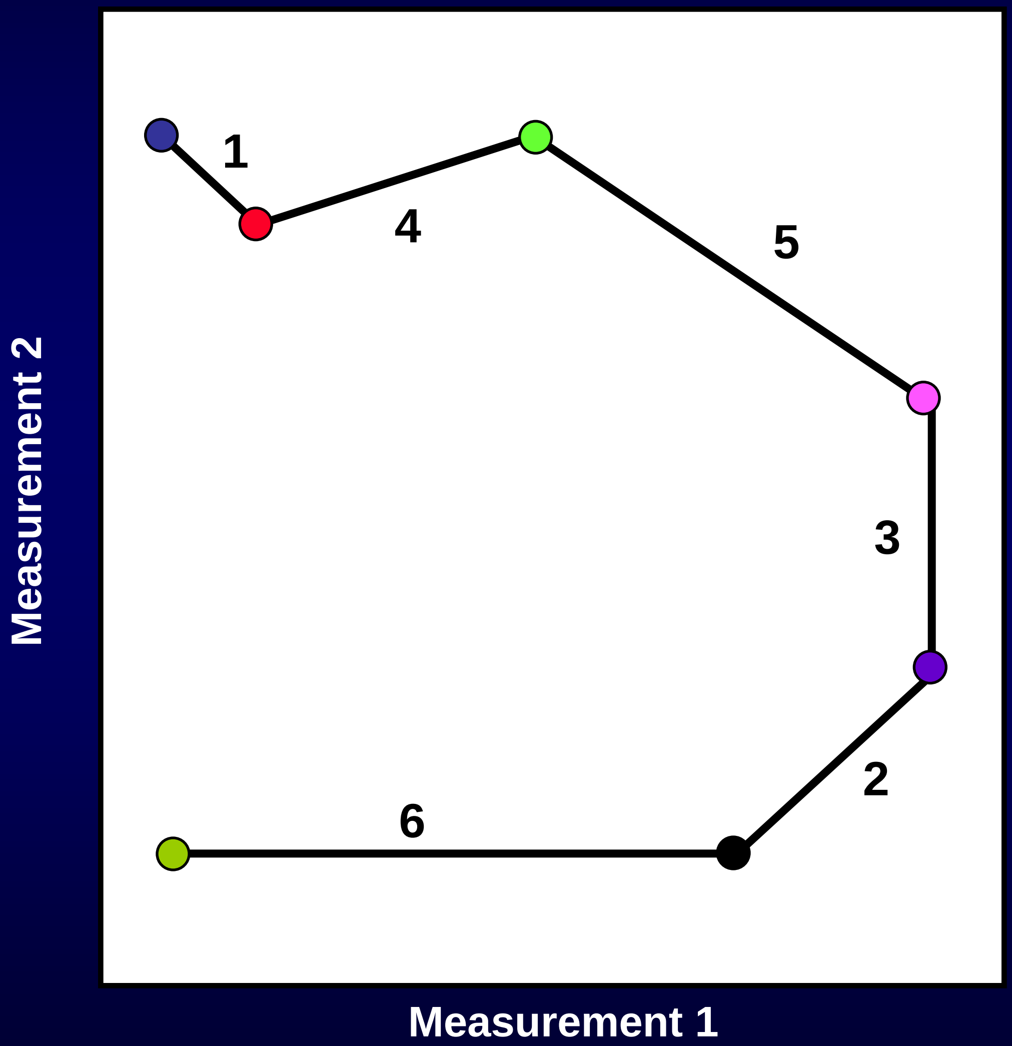
Calculate the Distance Between Points

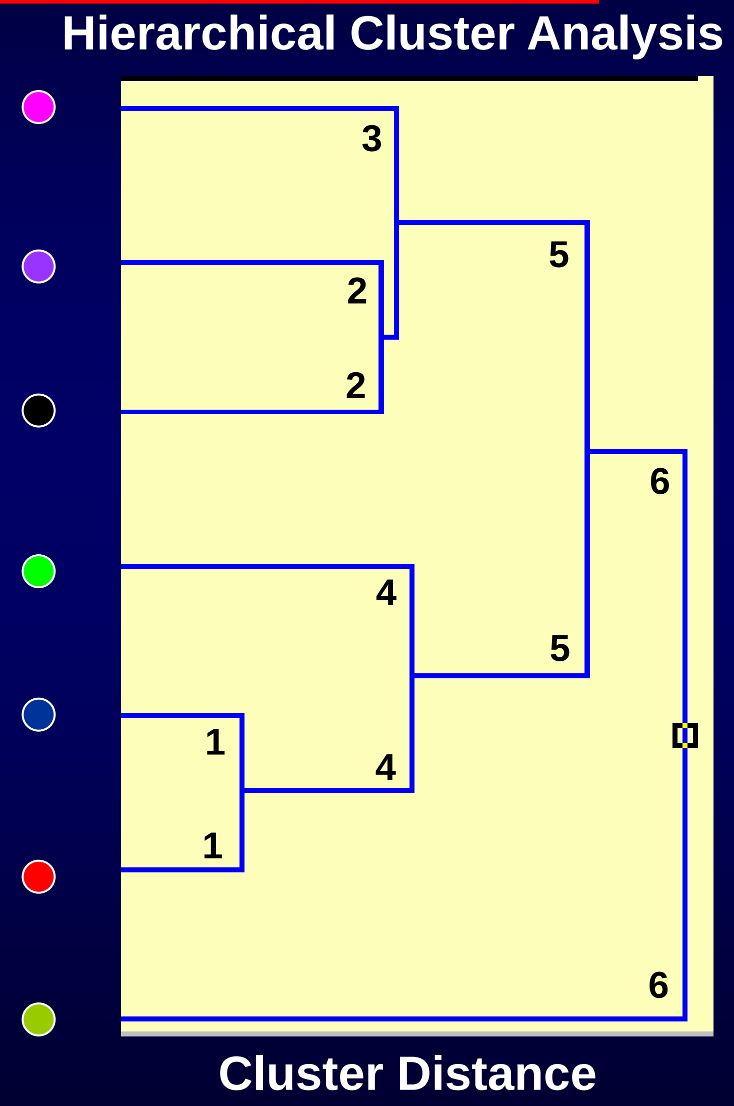


Calculate the Distance Between Points

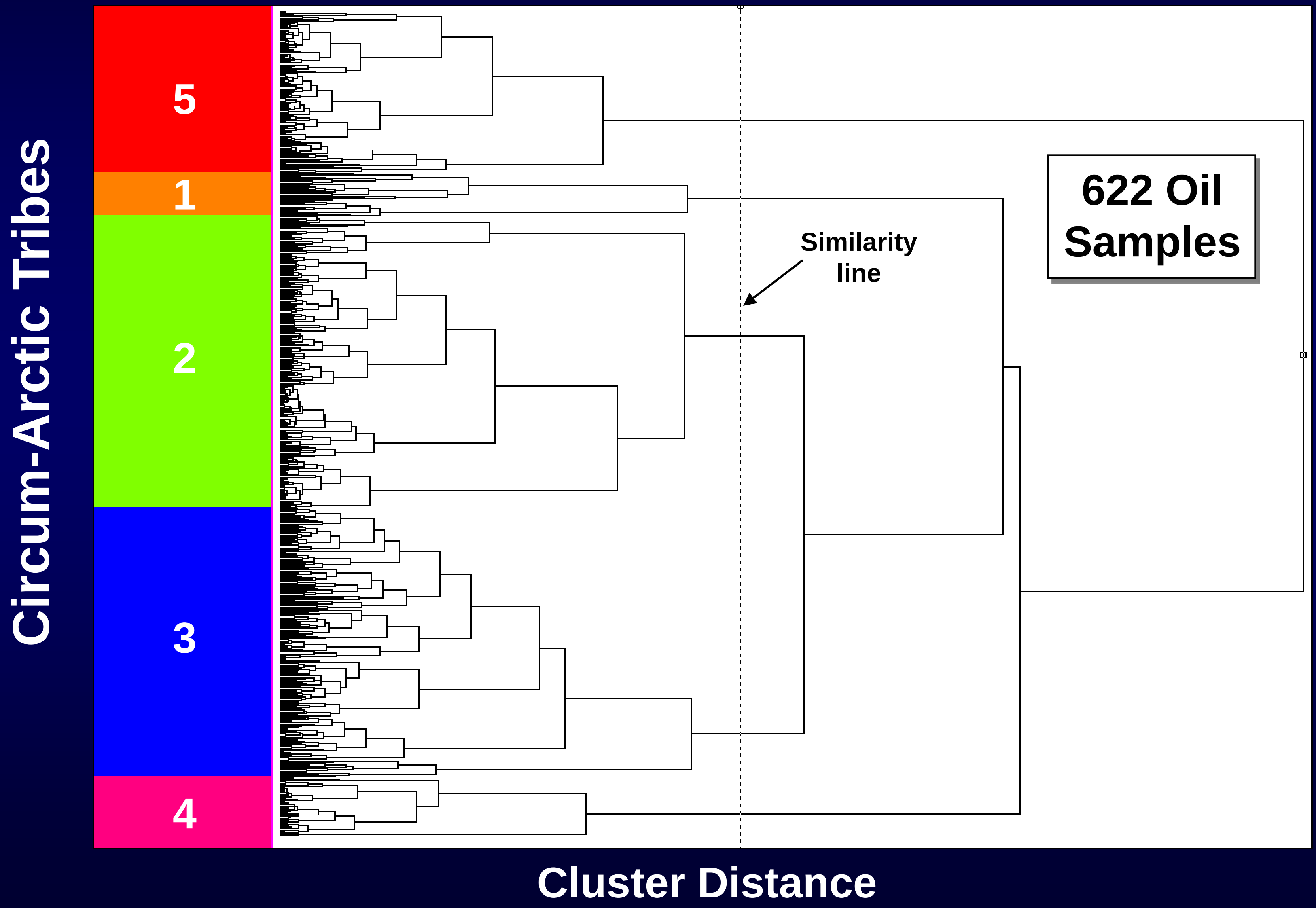


HCA Dendrograms Are Based on Measured Cluster Distance in *n*-Space

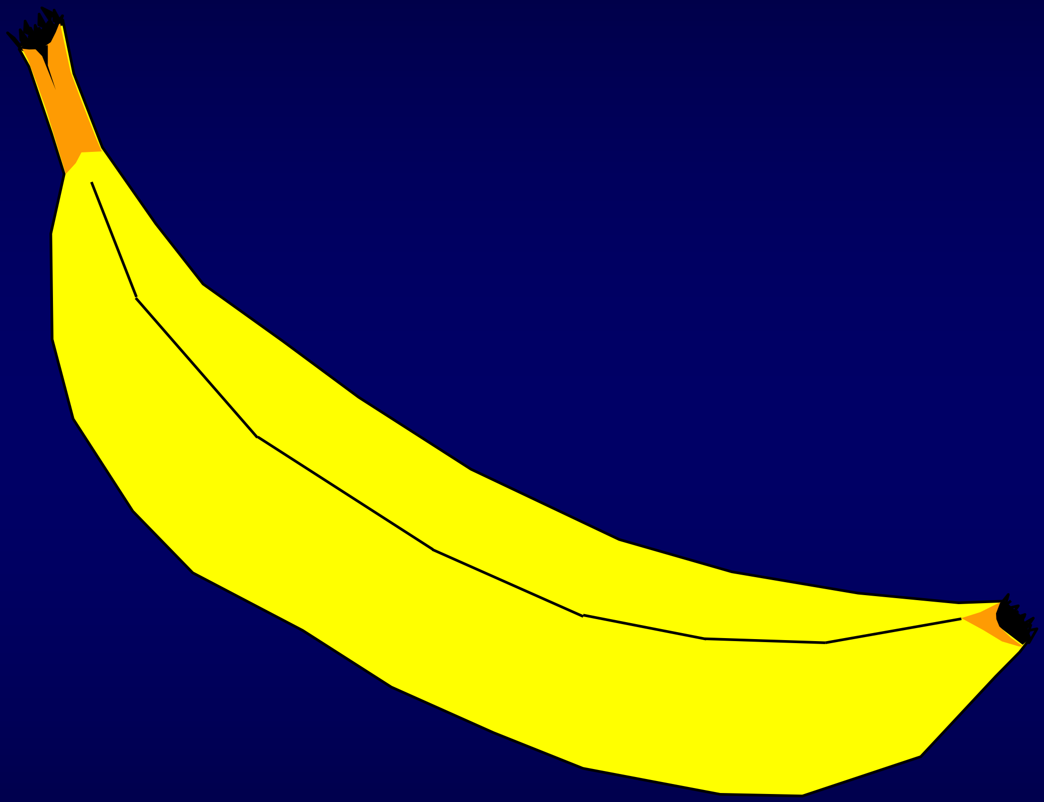




Hierarchical Cluster Analysis (HCA) is a Distance-Based Classification

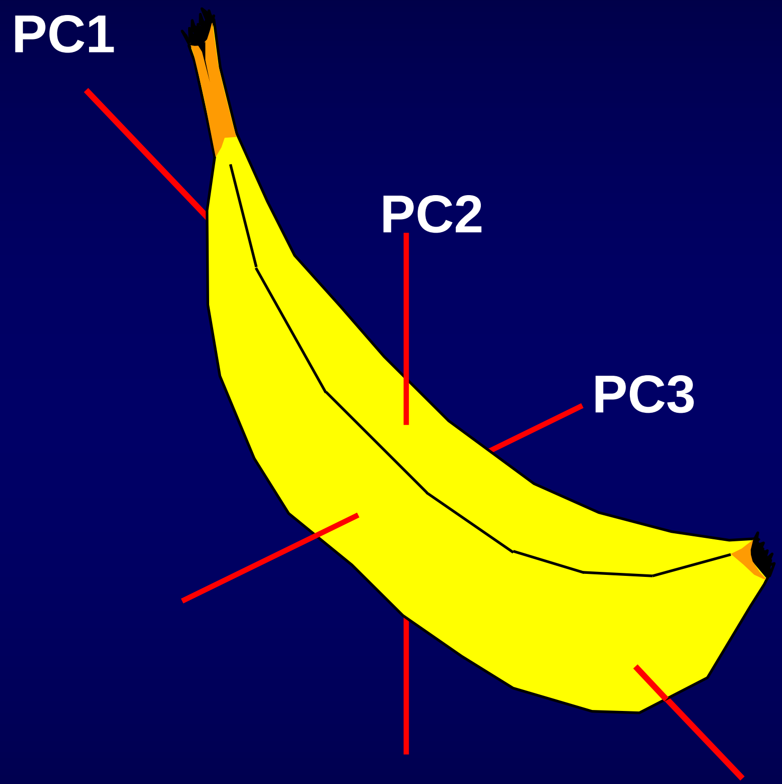


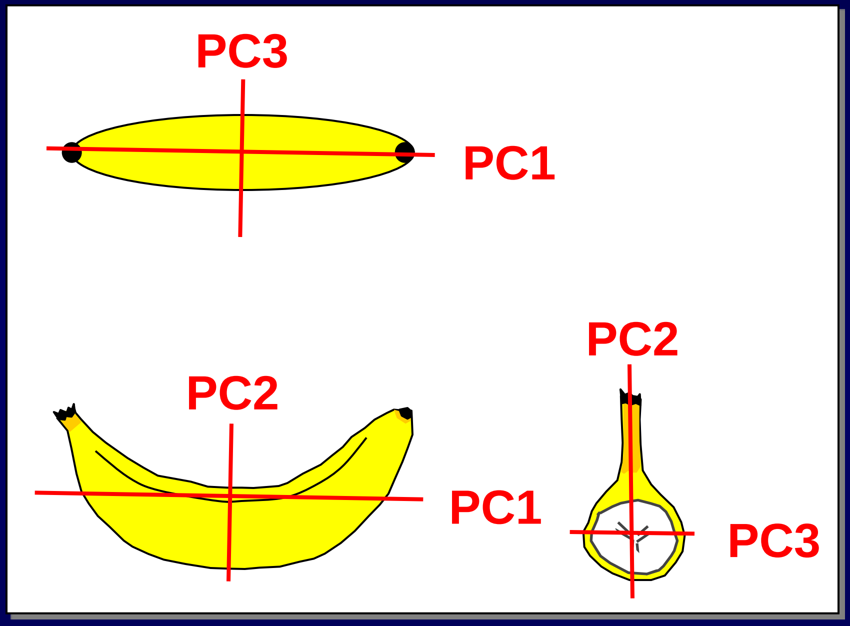
Placing a Banana in Perspective (Principal Components of a Banana)



Suppose you can look only at 2D plots. To reduce this 3D object to an informative 2D plot, use PCA.

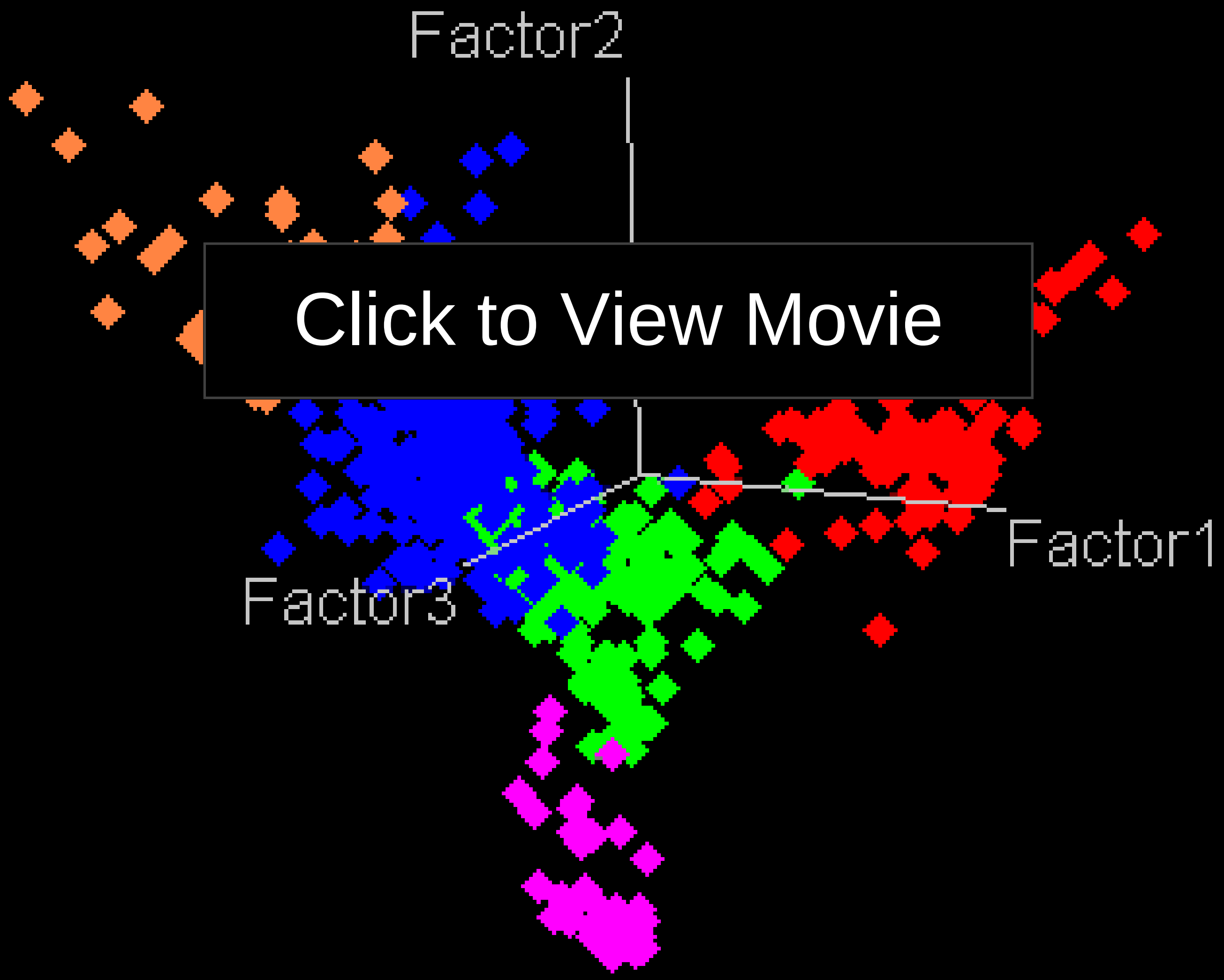
Principal Components Analysis: New Axes Span Maximum Data Variation





If you had to identify a banana by its shadow (*i.e.*, from a 2D projection), which view above would be most informative?

Principal Components Analysis: New Axes Span Maximal Variation in Data



Oil Tribe

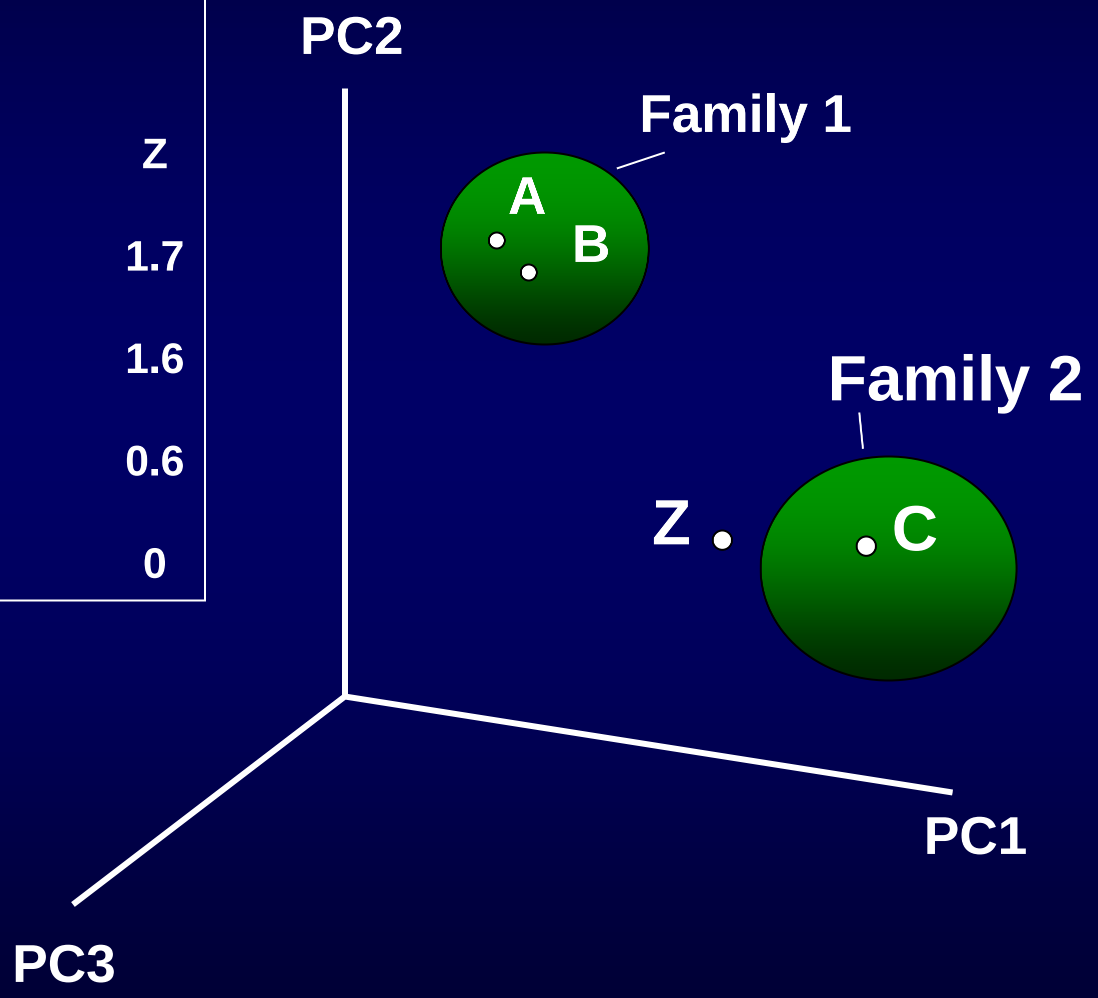
1
2
3
4
5

KNN Assigns New Sample to Family to Which Its K-Nearest Neighbors Belong

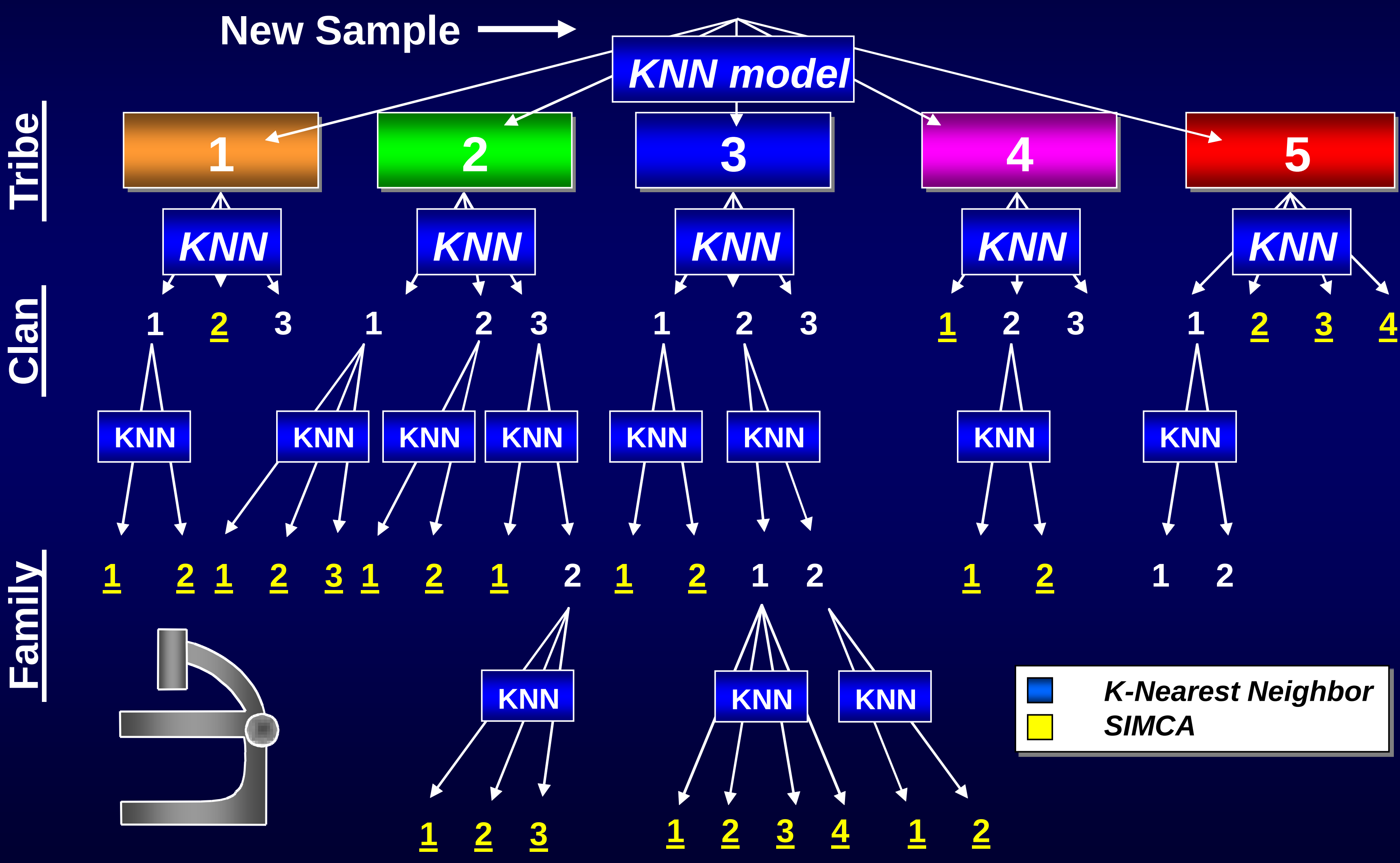
Distance Matrix

	A	B	C	Z
A	0	0.2	1.6	1.7
B		0	1.4	1.6
C			0	0.6
Z				0

K value	Predicted Family
1	2
2	2
3	1



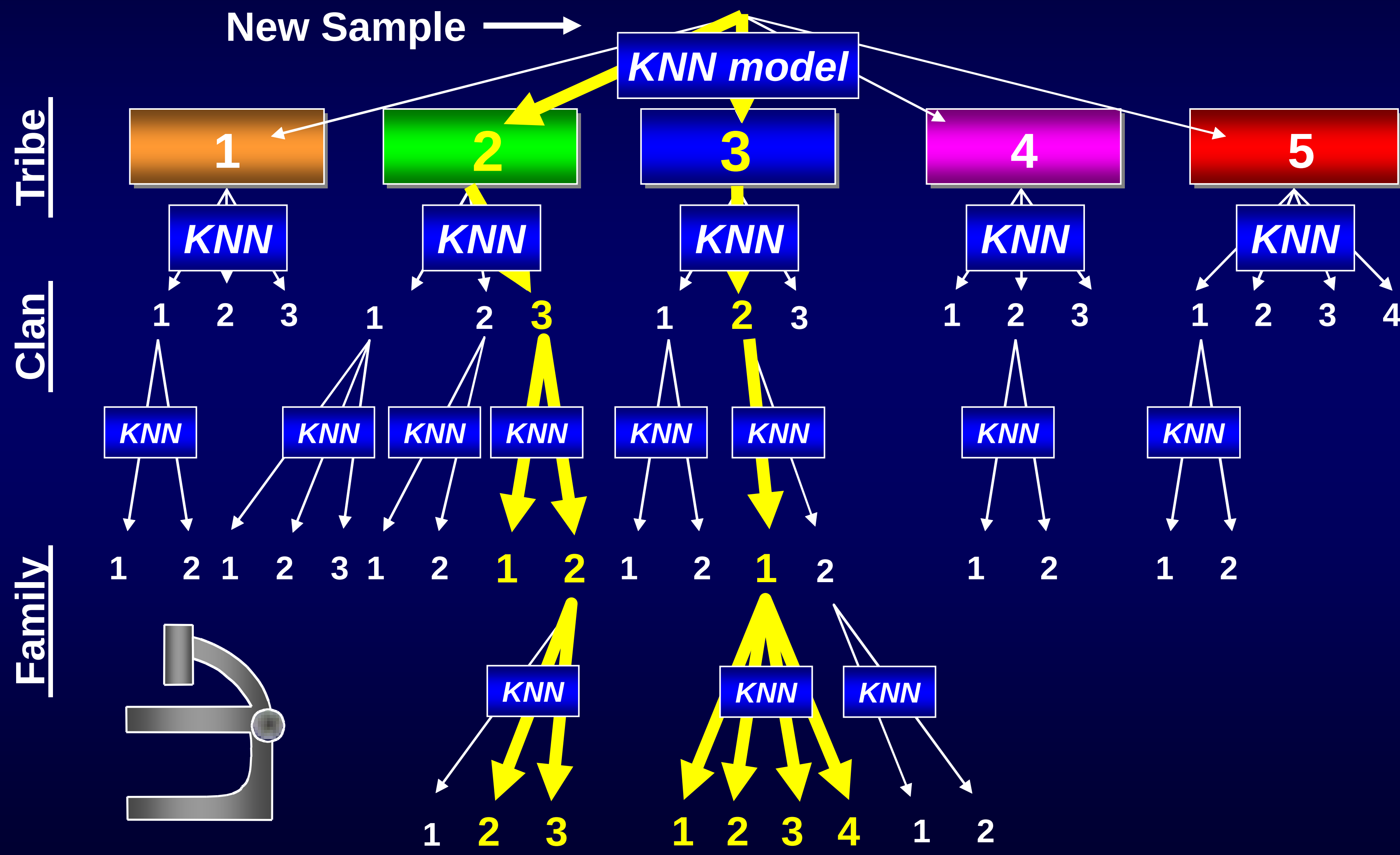
Decision Tree Fine-Tunes the Pattern Recognition of Circum-Arctic Samples



Tribe	Family	Samples		Location	Inferred Setting	Inferred Age	~Age, my	Inferred Source
1	111	33	13	West Siberia	Paralic Deltaic Marine Shale	L.-M. Jurassic	183	Tyumen
	112		5	Lena-Vilyuy		Jurassic (Permian?)	183 (270?)	Jurassic
	12		13	Beaufort-Mackenzie		Paleogene(?)	45	Paleogene(?)
	13		2	West Siberia		L.-M. Jurassic	183	Tyumen
2	211	364	39	North Slope	Marine Marl	Mixed (Triassic-Cretaceous)	104-224	Shublik-Hue
	212		10			Cretaceous	104	Hue
	213		3			M.-U. Triassic	224	Shublik
	221		9	Alberta	Marine Carbonate	Devonian-Miss.	372	Exshaw
	222		24	North Slope		M.-U. Triassic	224	Shublik
	231		212	West Siberia	Distal Marine Shale	Upper Jurassic	151	Bazhenov
	2321		7	N. Slope, Cook Inlet		Jurassic	170, 191, 224	Kingak, Tuxedni
	2322		13	North Sea		U. Jurassic	151	Kimmeridge
	2323		47	West Siberia				Bazhenov
3	311	333	7	West Siberia	Paralic Deltaic Marine Shale	L.-M. Jurassic	183	Tyumen
	312		17	Alberta, Timan-Pechora	Marine Marl	Devonian	386	Duvernay, Domanik
	3211		42	West Siberia	Distal Marine Shale	Upper Jurassic	151	Bazhenov
	3212		17	North Sea				Kimmeridge
	3213		141					
	3214		92	N. Sea, Labrador, N. Slope, W. Siberia		L. Cret.-U. Jurassic	121, 151	Kimm., pebble, Bazenhov
	3221		8	N. Slope, Beaufort-Mackenzie		U. Cret.-Tertiary	50, 82	Canning
	3222		7	Alberta		U. Cretaceous	82	2nd White Speck
	33		2	North Sea	Freshwater-Lacustrine Shale	Devonian	386	Old Red Sandstone
4	41	42	5	Alberta	Marine Carbonate	Devonian	386	Keg River
	421		11	Volga-Ural				Domanik
	422		24					
	43		2	North Slope		Carboniferous	322	Lisburne
5	511	122	2	Sweden (Baltic Sea)	Distal Marine Shale	Cambrian-Ordovician	494	Alum
	512		2	Sweden (Siljan)		Ordovician	469	Tretaspis
	52		27	East Siberia	Marine Marl	Precambrian	>600	Iremken
	53		68					
	54		23					

Notes by Presenter: NEW (30 groups)

Families From Upper Jurassic Source: 231, 2322, 2323, 3211, 3212, 3213, 3214



West Siberia Oil Families Show a Concentric Pattern

TOC, wt.%

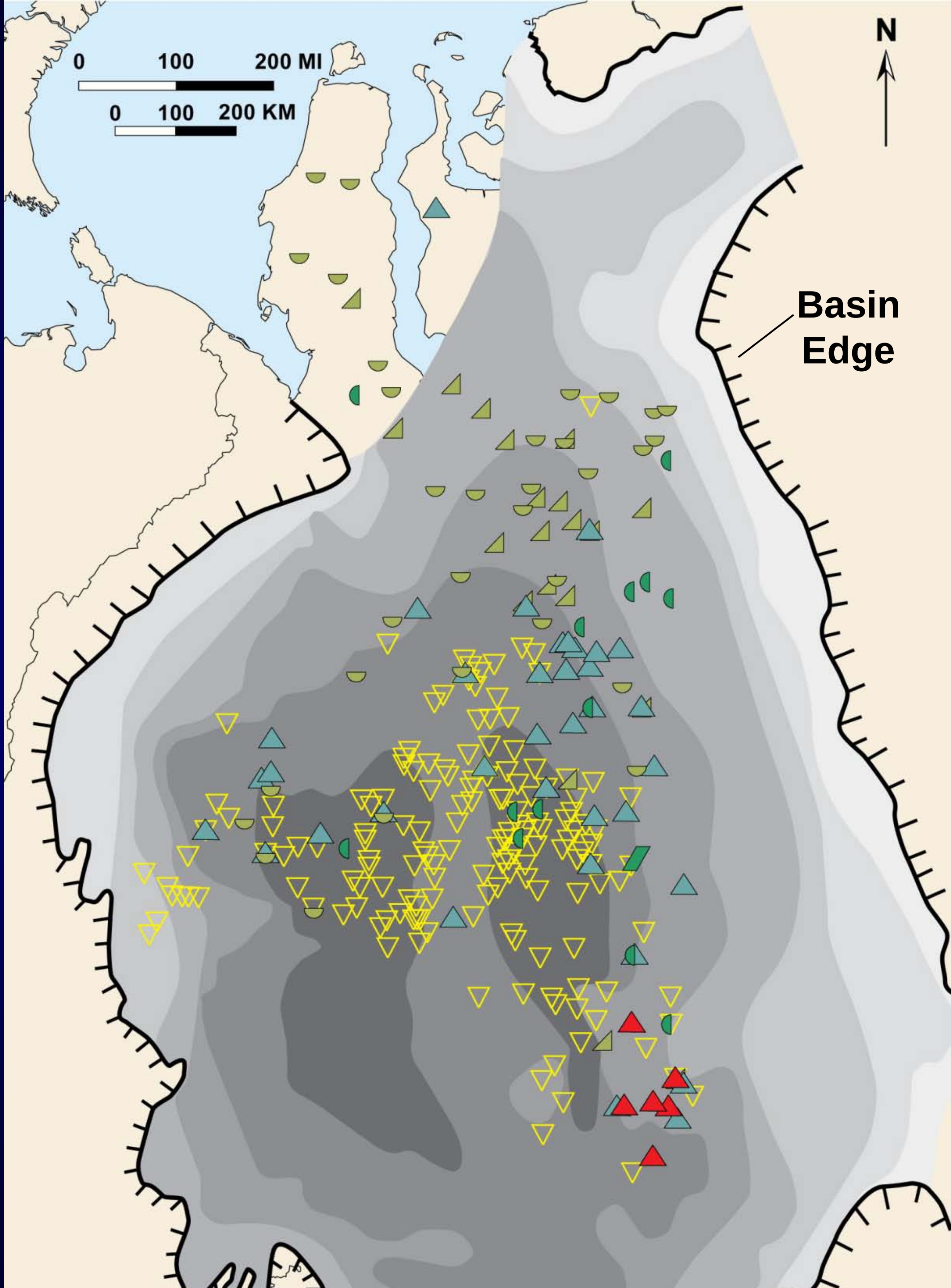
- <1
- 1-2
- 2-3
- 3-5
- 5-7
- 7-10
- >10

Family

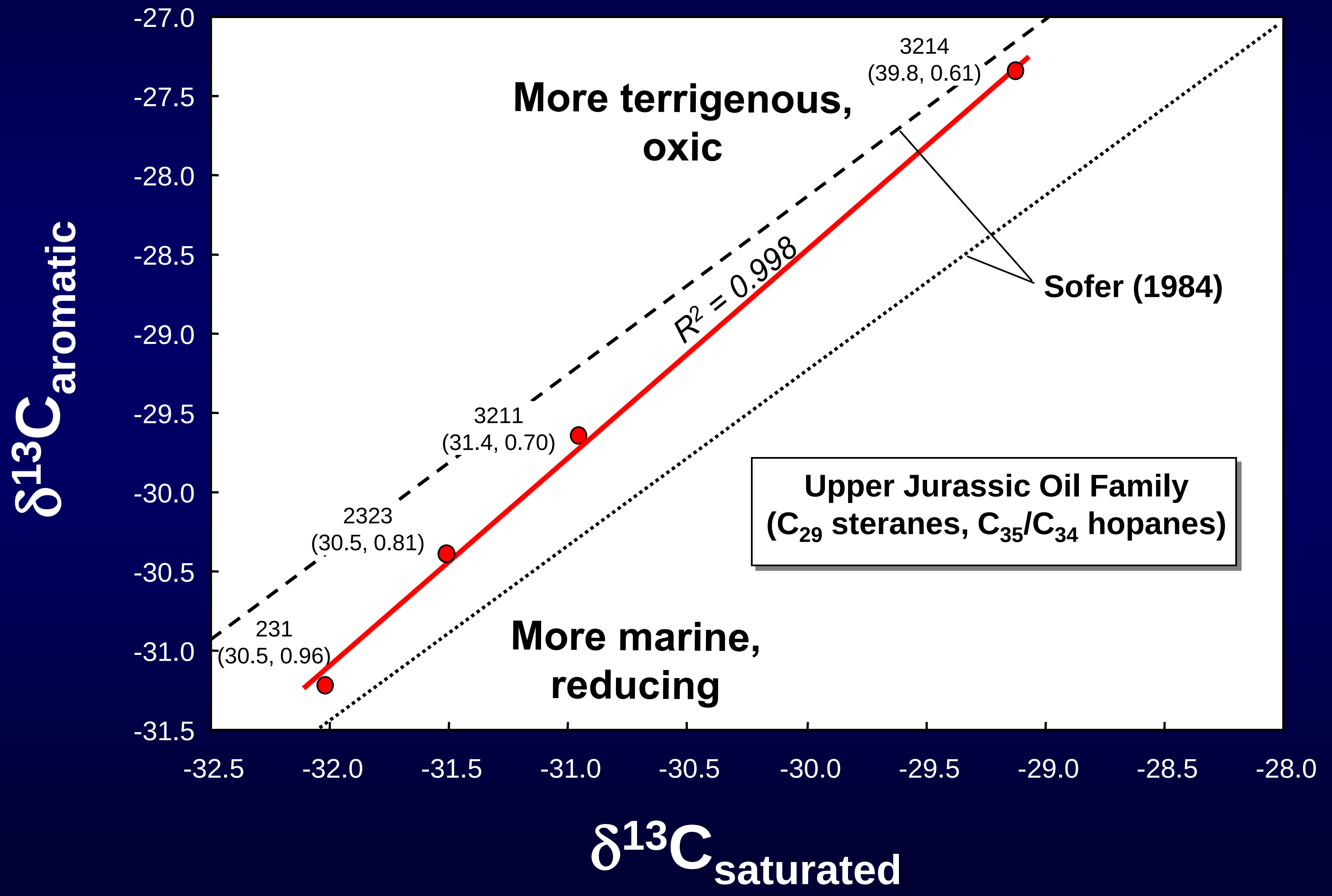
L-M Jurassic Tyumen:
- 111
- 13
- 311

U Jurassic Bazhenov:
- 231
- 2323
- 3211
- 3214

Kontorovich (1984)



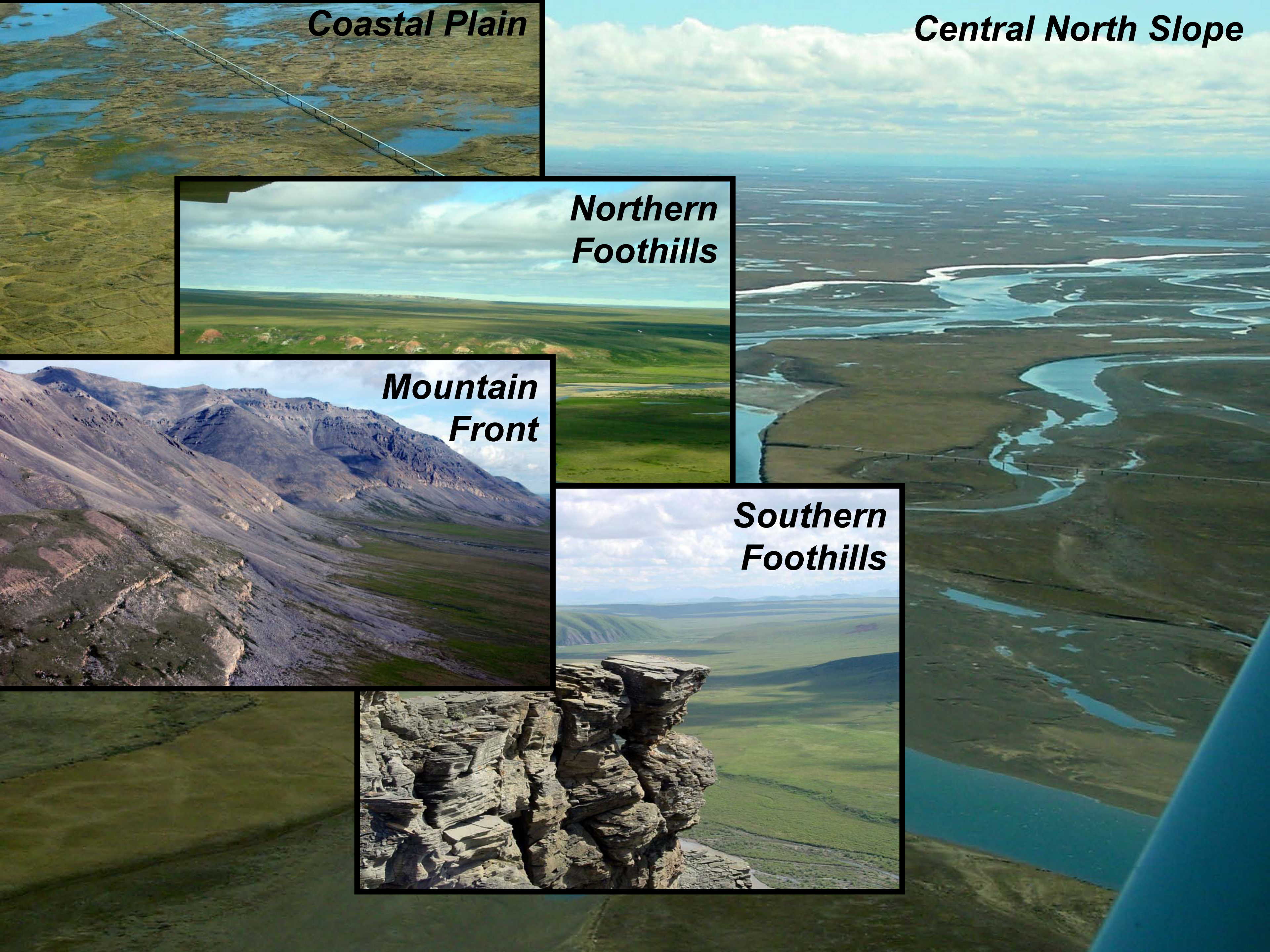
West Siberian Oil Geochemistry Varies According to Source-Rock Organofacies



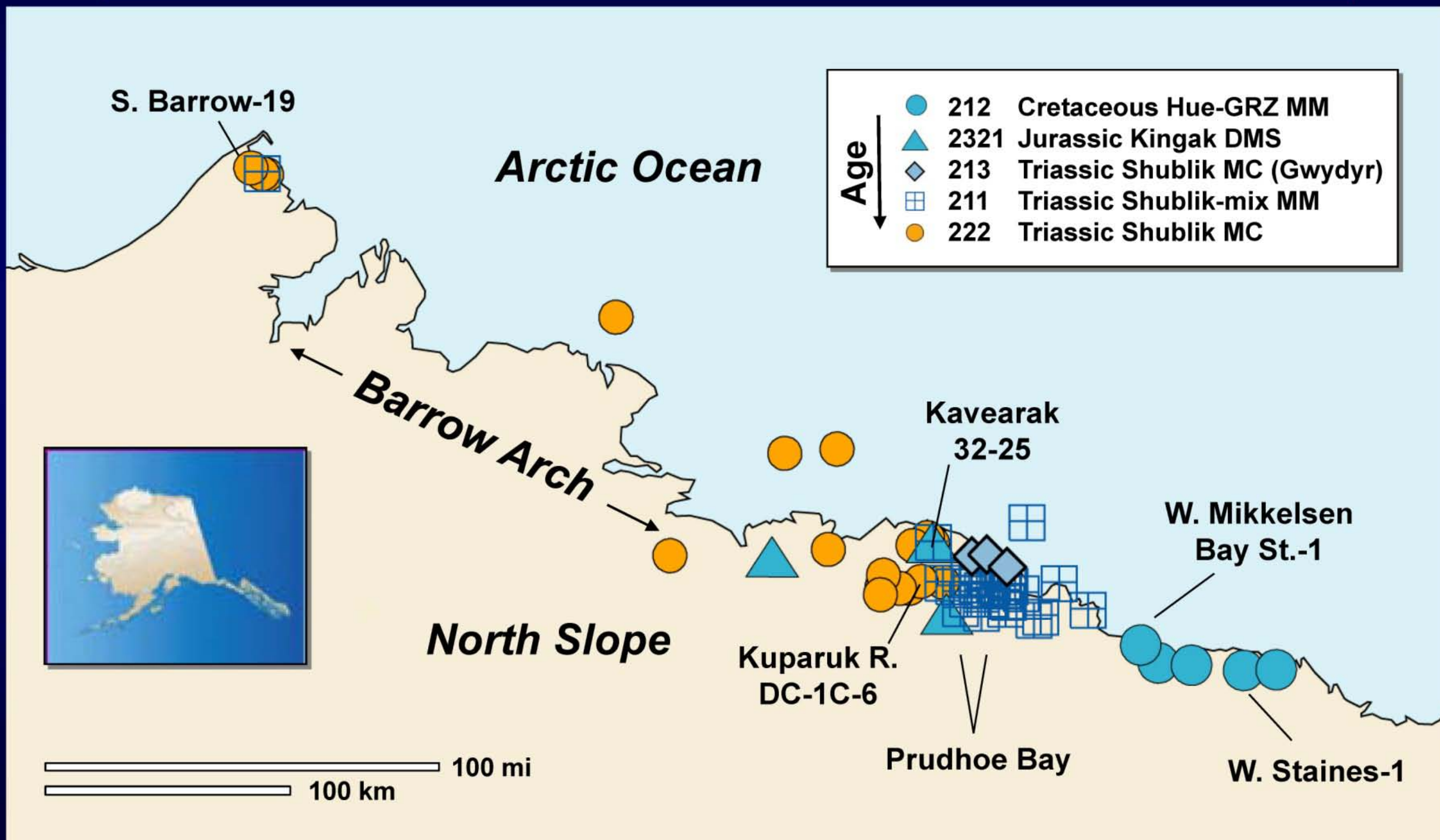
Direct Correlation: Predicted Origins of Rock Extracts Are Agree With Geology

<table>
<tr><th>Sample</th><th>Sample Age/Origin</th><th>Inferred Source Rock</th><th>Inferred Location</th><th>Family</th><th>SIMCA Fit</th></tr>
<tr><td>XRU3</td><td rowspan="4">U Jurassic Bazhenov Fm., West Siberia</td><td rowspan="4">U Jurassic distal marine shale</td><td rowspan="4">Russia</td><td rowspan="2">231</td><td>Good</td></tr>
<tr><td>XRU5</td><td rowspan="3">Excellent</td></tr>
<tr><td>XRU10</td><td rowspan="2">2323</td></tr>
<tr><td>XRU11</td></tr>
<tr><td>XUK8</td><td rowspan="4">U Jurassic Kimmeridge Clay, N. Sea</td><td rowspan="4">U Jurassic distal marine shale</td><td rowspan="2">U.K.-Norway</td><td rowspan="2">3213</td><td rowspan="2">Excellent</td></tr>
<tr><td>XUK28</td></tr>
<tr><td>XUK26</td><td rowspan="2">U.K-Norway (and other)</td><td rowspan="2">3214</td><td>Good</td></tr>
<tr><td>XUK36</td><td>Excellent</td></tr>
<tr><td>XRU15</td><td rowspan="3">L-M Jurassic Tyumen Fm., West Siberia</td><td rowspan="3">L-M Jurassic paralic deltaic marine shale</td><td rowspan="3">Russia</td><td rowspan="3">111</td><td>Good</td></tr>
<tr><td>XRU22</td><td rowspan="2">Excellent</td></tr>
<tr><td>XRU32</td></tr>
</table>

Decision Tree Prediction

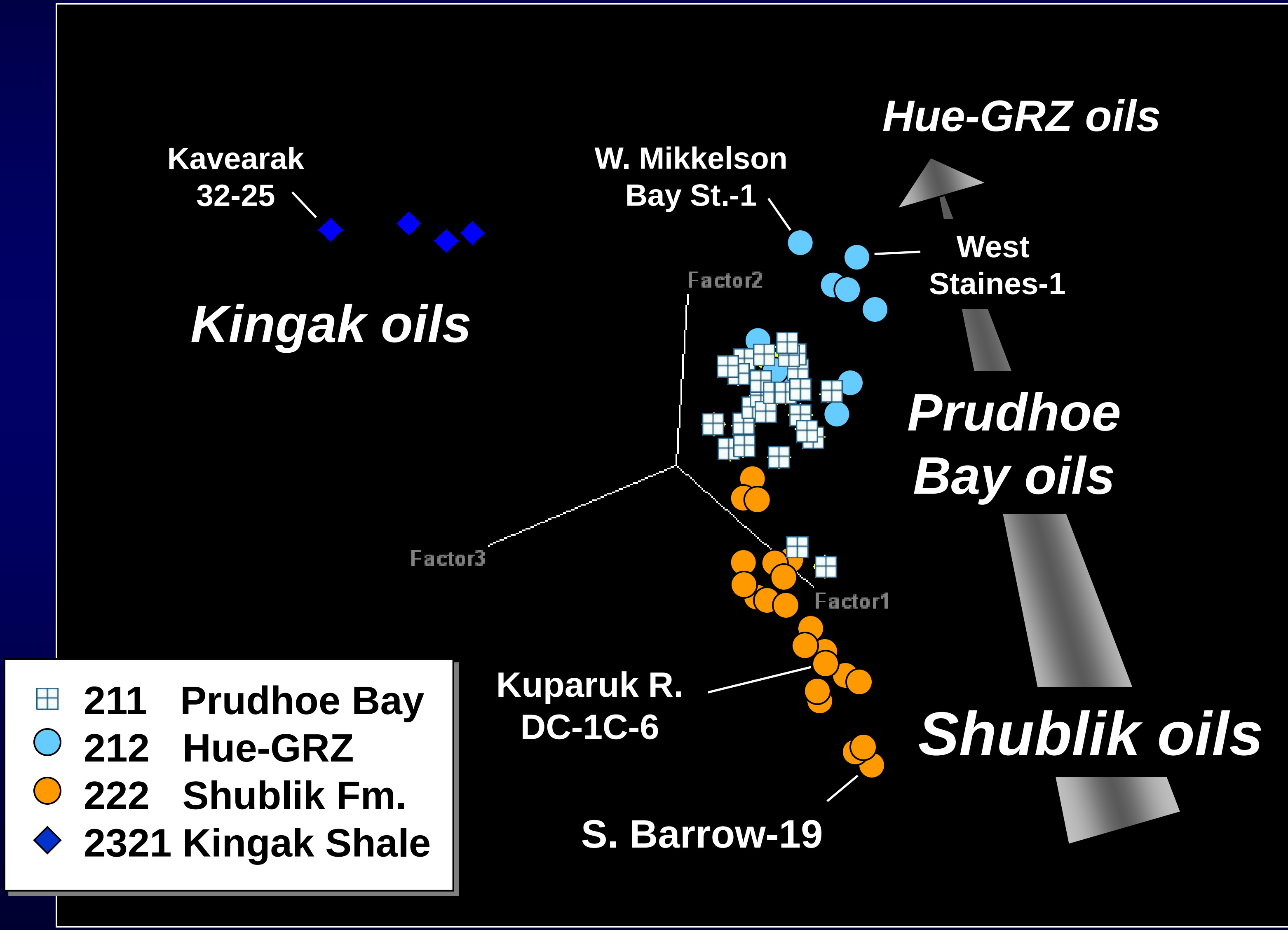

Central North Slope
Coastal Plain
Northern Foothills
Mountain Front
Southern Foothills

Can Prudhoe Bay Oil Mixtures Be De-convoluted Using Chemometrics?

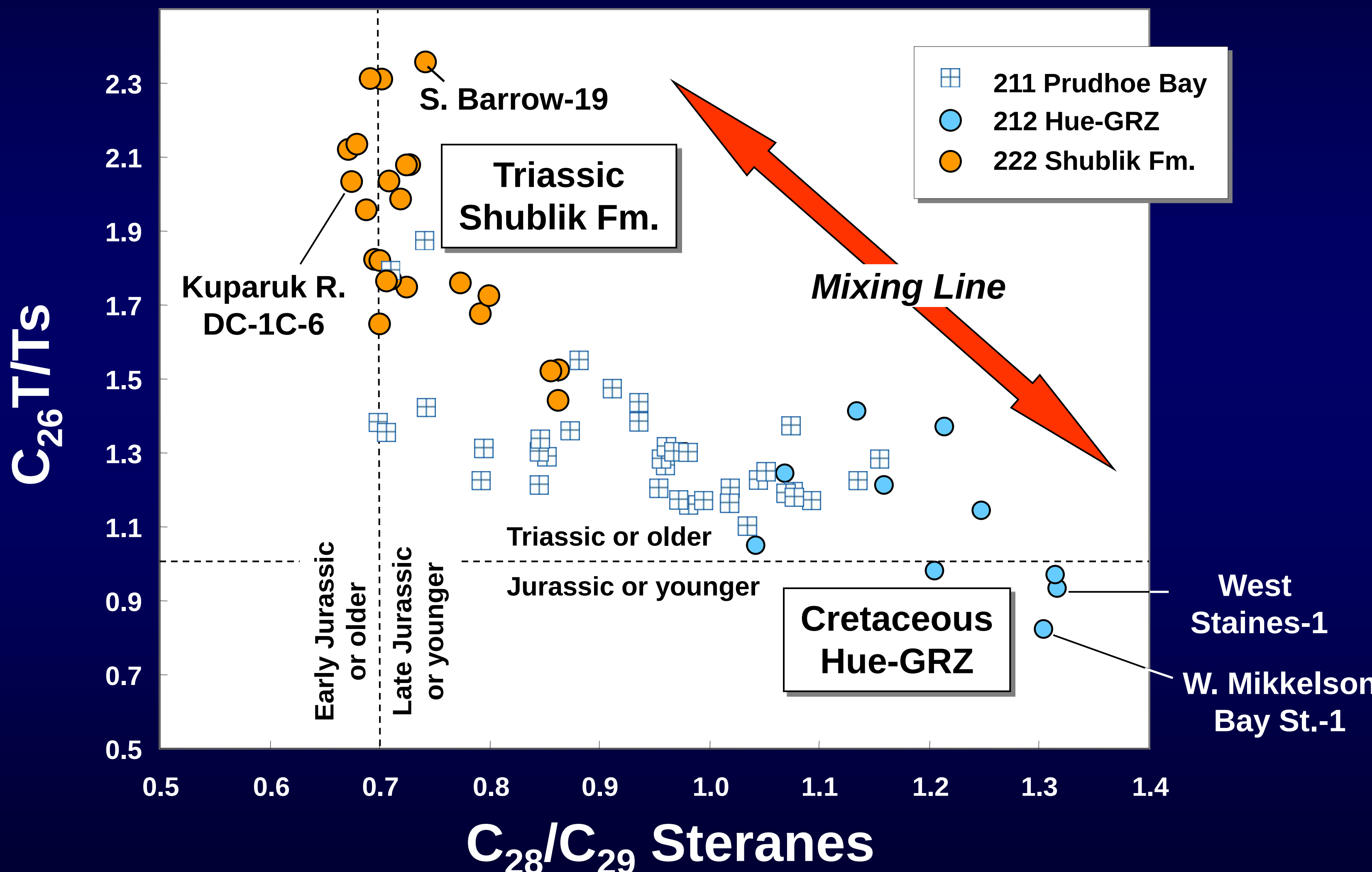


Notes by Presenter: Wicks et al. (1991) concluded that Endicott Field (offshore E of Prudhoe Bay Field) originated mainly from Cretaceous Hue-GRZ with lesser input from Triassic Shublik and Jurassic Kingak source rocks based on 13C isotopes of oils and source-rock extracts and pyrolyzates. Shublik/Kingak dominant: Eileen West End, Kuparuk; Intermediate: Prudhoe Bay; Hue-GRZ dominant: Endicott.

PCA Suggests Mixing of Oils From Shublik and Hue-GRZ at Prudhoe Bay

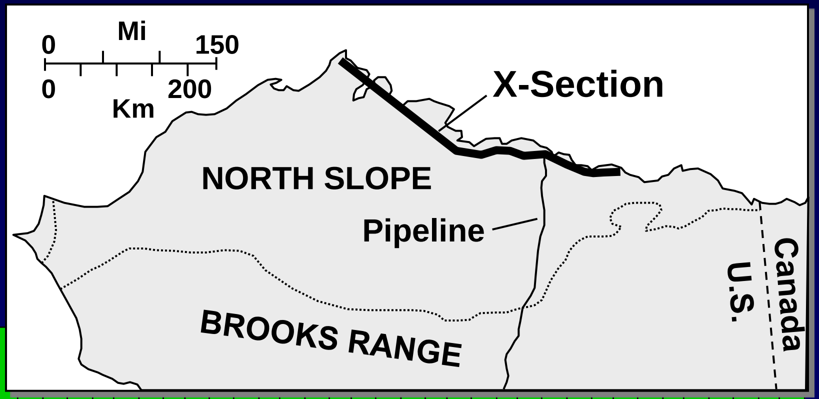


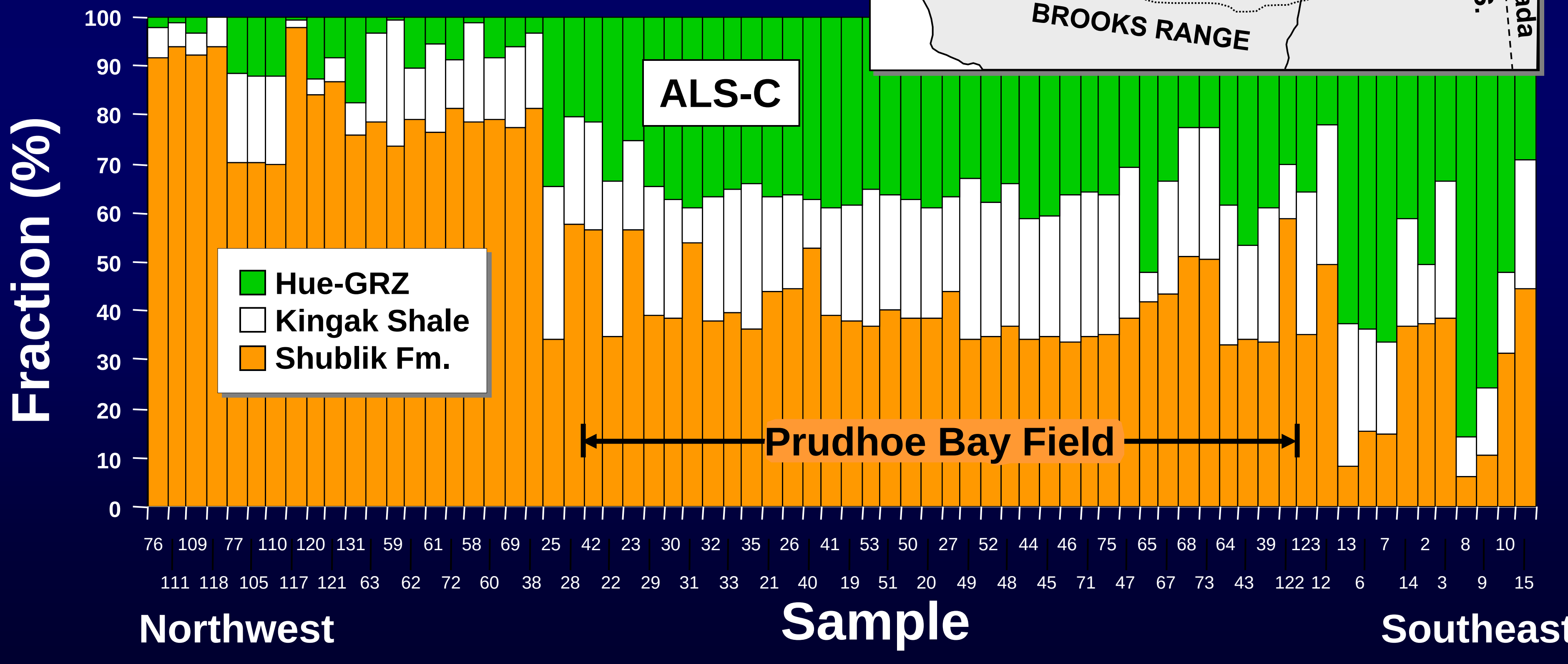
Age-Related Biomarkers Support Mixing of Triassic and Cretaceous Oils at Prudhoe Bay



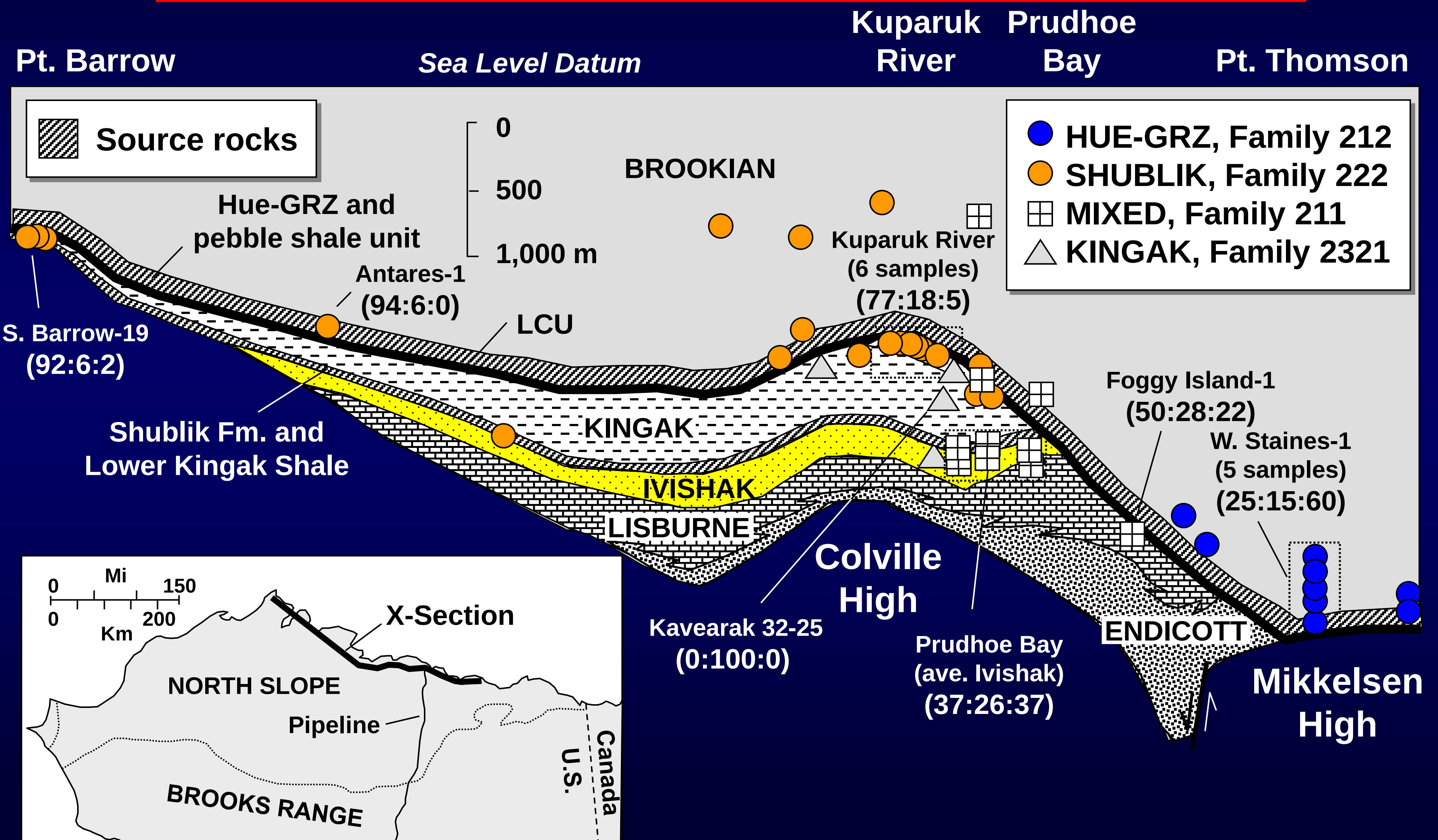
Alternating Least Squares Analysis (ALS) De-convolutes North Slope Oil Mixtures

Peters et al., 2008, De-convoluting mixed crude oil in Prudhoe Bay field, North Slope, Alaska. Organic Geochemistry 39: 623-645.

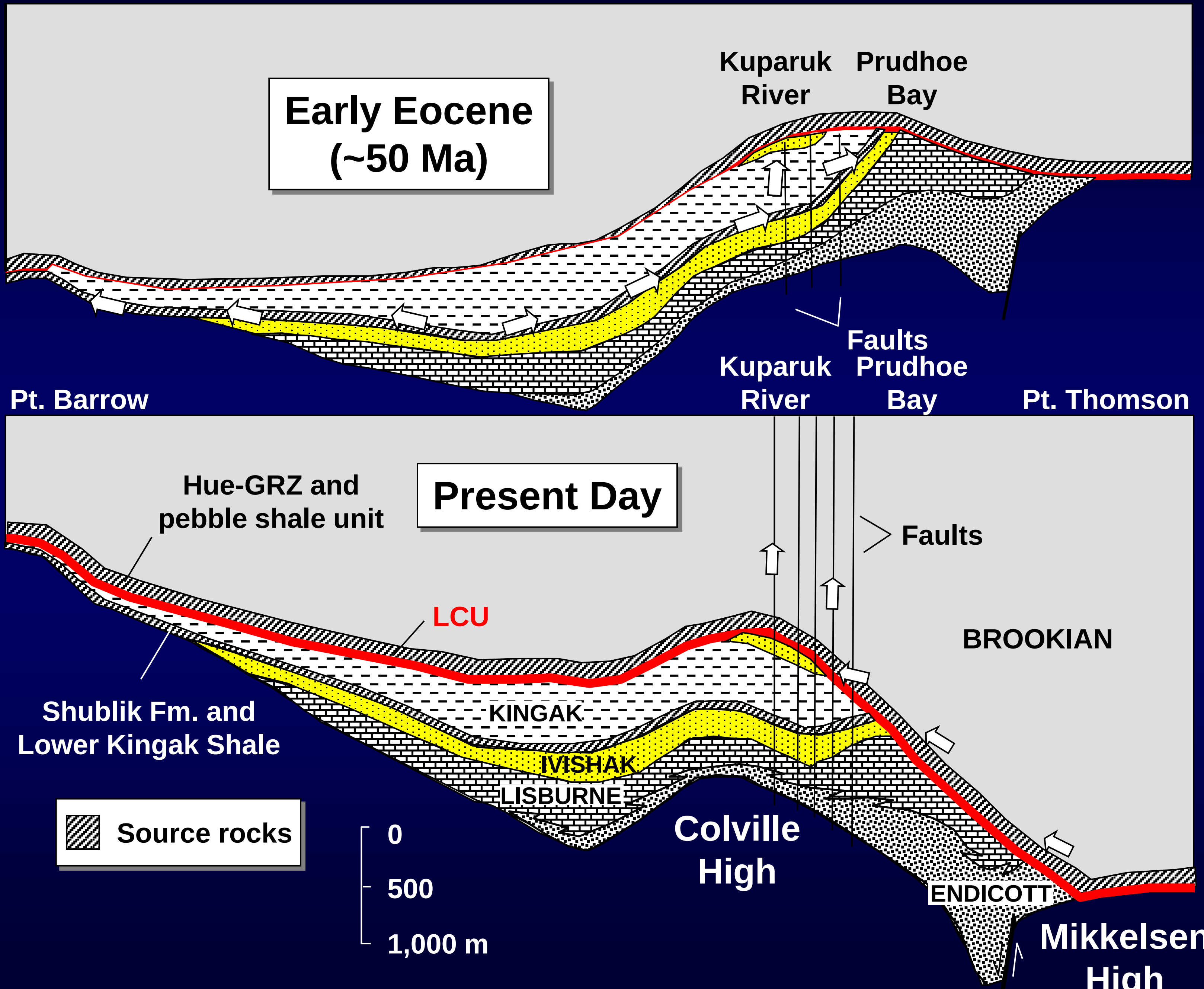




Mixed Prudhoe Bay Oils Imply Updip, Down-Section Migration of Hue-GRZ Oil



Late Hue-GRZ Oil Mixed With Shublik Oil at Prudhoe Bay



Conclusions: Circum-Arctic

- **Chemometrics separates >1000 Circum-Arctic oil samples into 31 families (9 families on the North Slope; PCA)**
- **Geochemistry indicates source-rock organofacies, depositional environment, lithology, age *(indirect correlation)***
- **'Decision-tree chemometrics' classifies new samples *(direct correlation)* and assigns level of certainty to correlation**
- **PCA and biomarkers suggest mixing of Triassic Shublik marine carbonate oils with Jurassic and Cretaceous marine shale oils**
- **Oil mixtures can be de-convoluted (ALS); Prudhoe Bay oils are mixtures dominated by Hue-GRZ and Shublik Formation in ~equal proportions**

References on the Use of Chemometrics to Establish Petroleum Systems

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Alternating Least Squares (ALS) Analyses Show Good Repeatability

Oil Sample	% Shublik Formation	% Hue-GRZ	% Kingak Shale
Fish Creek-1 (2949-3008 ft)	71	12	17
Fish Creek-1 (2920-3060 ft)	70	12	18
Fish Creek-1 (2925-3060 ft)	70	11	19
Phoenix-1 DST 1	84	13	3
Phoenix-1 DST 3	87	9	4
West Kuparuk-1 DST 2	58	20	22
West Kuparuk-1 DST 6	57	21	22

Notes by Presenter: Four end-member model shows that pebble shale contribute little to any oil except Simpson-Umiat oils (Cape Simpson and three Umiat samples) and Kingak oils (Alpine and two Hemi Springs State oils); justifies three end-member model.

Hue-GRZ Input is More Important at Prudhoe Bay Than Previously Recognized

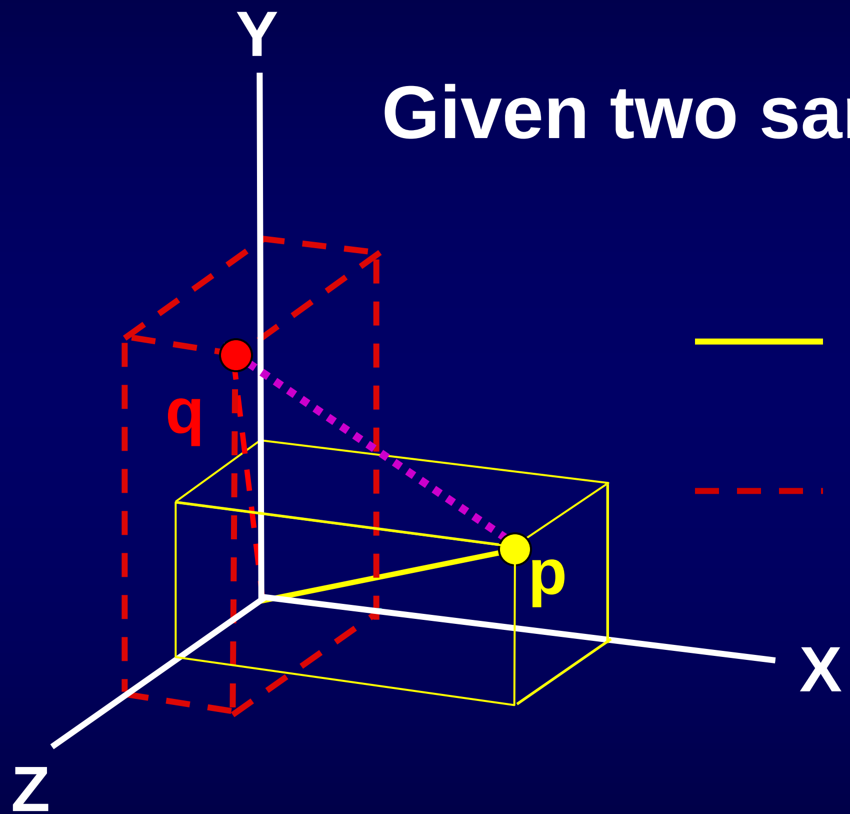
Oil Samples	% Shublik Formation	% Hue-GRZ	% Kingak Shale
Prudhoe Bay (Masterson, 2001)	59	28	13
DS-1-1 (Prudhoe Bay)	34	47	19
G-2 (Prudhoe Bay)	34	41	25
B-2 (Prudhoe Bay)	35	41	24
C-1 (Prudhoe Bay)	34	36	30
E-5 (Prudhoe Bay)	39	31	30
Ave. 30 oils Prudhoe Bay	37	37	26

This Study

Notes by Presenter: Five examples are all from Sadlerochit reservoirs at Prudhoe Bay. Mastersons' Hue includes pebble shale unit. Masterson made some assumptions about thickness and organic richness of SRs in the fetch area for Prudhoe Bay to calculate relative contributions of the different SR…using the calculated proportions of oil contributed by each SR and measured sulfur contents of representative end-member oils, he calculated reasonable sulfur contents compared to measured sulfur contents in Prudhoe Bay oils.

Calculate the Multivariate Distance Between Two Points in Three-Space

Given two samples p and q:



$$\mathbf{p} = a_1x + b_1y + c_1z$$

$$\mathbf{q} = a_2x + b_2y + c_2z$$

$$d_{qp} = [(a_1 - a_2)^2 + (b_1 - b_2)^2 + (c_1 - c_2)^2]^{1/2}$$