Re-Os Dating of Black Shales: Timing and Duration of Sedimentary Processes*

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Abstract

Re and Os are redox-sensitive elements fixed in organic material and sulfides in muds deposited in anoxic or euxinic marine environments. Decay of ^{187}Re to ^{187}Os provides a radiometric clock that records the time of shale deposition and the ^{187}Os/^{188}Os of seawater at that time. Recent studies yield robust ages for shales as old as 2.7 Ga, with resolution comparable to biostratigraphy in Phanerozoic rocks. This new instrument in the isotope geochemist's toolbox permits us to: (1) place absolute time pins in the sedimentary record, thereby refining the global time scale, constraining the duration of sedimentologic and paleontologic events, and correlating events at different localities in absolute time; (2) establish variations in seawater ^{187}Os/^{188}Os through time, thereby recording changes in global patterns of oxidative weathering and Os influx and defining the resolution of the ^{187}Os/^{188}Os tracer; and (3) determine Re-Os systematics in migrated hydrocarbons and source rocks, thereby documenting the time of isotopic homogenization of hydrocarbons and establishing ^{187}Os/^{188}Os as a tracer for hydrocarbon migration. Case studies demonstrate use of the Re-Os system to (1) date the rise of atmospheric oxygen at >2.32 Ga; (2) record dominance of chondritic, hydrothermal Os in the 2.04 Ga Pechenga rift basin, (3) provide a maximum age of 560 Ma for the Moelv tillite, Norway, and (4) link hydrocarbon maturation and migration to elevated heat flow in the Oslo rift at ~300 Ma. Re-Os dating of black shales complements U-Pb dating of ash layers, providing a new geochronologic method of comparable reliability and precision. Absolute time pins acquired with these two chronometers define rates in sedimentary systems. The Re-Os chronometer offers new potential for addressing fundamental questions in sedimentology, tectonics, paleogeography, paleoecology, and paleoclimatology.

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Crustal Processes – Geological Survey of Norway

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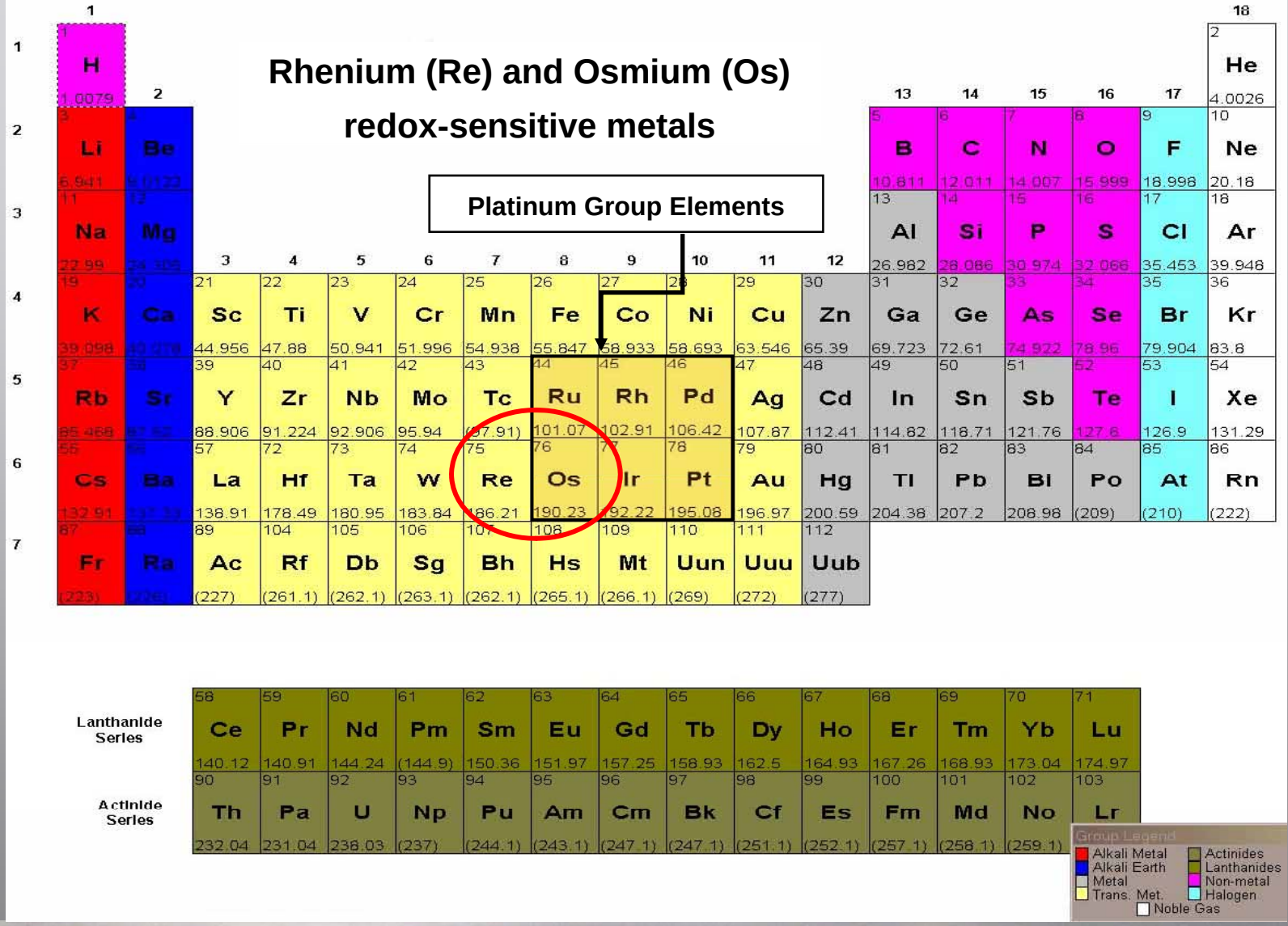
Rhenium (Re) and Osmium (Os) redox-sensitive metals

Platinum Group Elements



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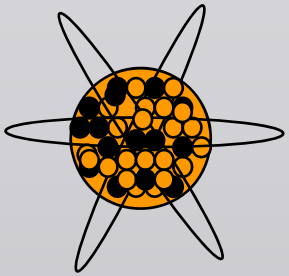


$^{185}Re = 37.398\%$

$^{187}Re = 62.602\%$

$^{184}Os = 0.02\%$

$^{186}Os = 1.60\%$

$^{187}Os = 1.51\%$

$^{188}Os = 13.3\%$

$^{189}Os = 16.2\%$

$^{190}Os = 26.4\%$

$^{192}Os = 41.0\%$

Half-life = $t_{1/2}$ = 41.6 Ga

$\lambda^{187}Re = 1.666 \times 10^{-11}\ yr^{-1}$

(Smoliar et al. 1996)

Geochemistry of Re and Os

- **Chalcophile elements**
  - **Concentrated in sulfides**
- **Large fractionation between mantle and crust**
  - **Os strongly compatible in mantle minerals**
  - **Re less compatible**

Re/Os in crust >> Re/Os in mantle.

High $^{187}Os/^{188}Os$ in crust over time.

Geochemistry of Re and Os

Average crust

Re/Os ≈ 10

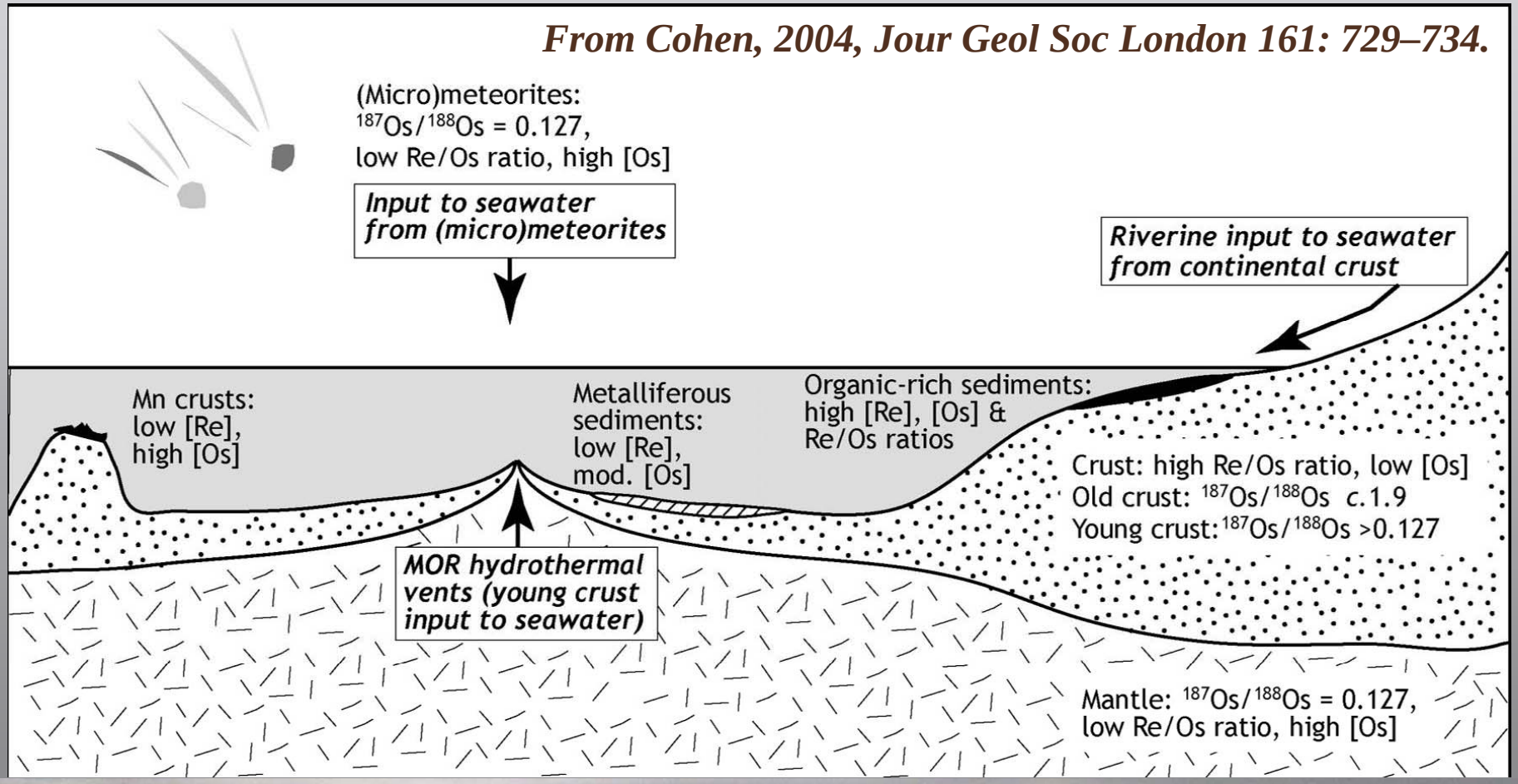
Present day $^{187}Os/^{188}Os \approx 1$

Mantle and meteorites

Re/Os ≈ 1

Present day $^{187}Os/^{188}Os = 0.127$

Major sources of Re and Os in seawater



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Changes in seawater Re-Os over time

- **Archean – anoxic atmosphere**
  - **Negligible transport of Re and Os in anoxic waters**
  - **Seawater dominated by hydrothermal and cosmic sources**

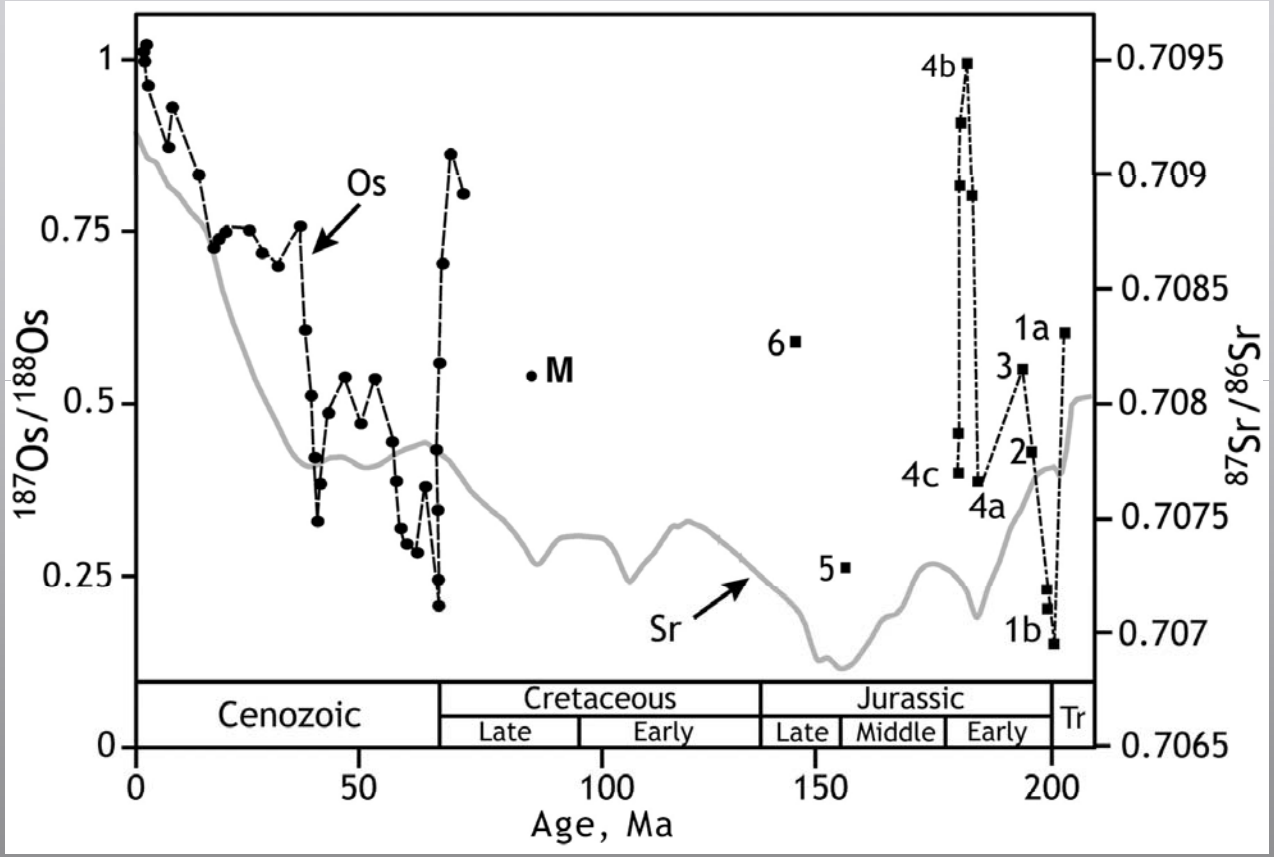
Chondritic $^{187}Os/^{188}Os$

- **Post-Archean – rise of atmospheric oxygen**
  - **Increasing input of dissolved Re and Os from continents**

Increasing $^{187}Os/^{188}Os$ with time

How much does seawater $^{187}Os/^{188}Os$ vary?

Compare to $^{87}Sr/^{86}Sr$



From Cohen, 2004, Jour Geol Soc London 161: 729–734.

Changes in seawater Re-Os over time

- **Os more sensitive than Sr to short-term changes**
  - **Global variation in $^{187}Os/^{188}Os$ >> than $^{87}Sr/^{86}Sr$**
  - **Os residence time in seawater << for Sr**

Seawater $^{187}Os/^{188}Os$ is a useful tracer

Where do Re and Os reside in shales?

Major sources

- **Sulfides**
  - **Syndepositional, diagenetic, or metamorphic**
- **Organics**
  - **Re and Os adsorbed on organics**
  - **Migrated hydrocarbons**

Minor sources

- **Detrital components**
  - **Transported weathering products**
  - **Aeolian dust**
  - **Cosmic dust**

Targeting hydrogenous Os

Drill out or mechanically separate sulfides

- **Advantage**
  - **Targets specific generation**
- **Disadvantage**
  - **Re-Os systematics may be disturbed by diagenetic or metamorphic mobilization**

Dissolve organics and sulfides in $CrO_3 \cdot H_2SO_4$

- **Advantage**
  - **Does not attack Re-Os in detrital minerals**
- **Challenge**
  - **Mixes Re and Os from organics and sulfides**

Effect of hydrocarbon maturation and/or migration?

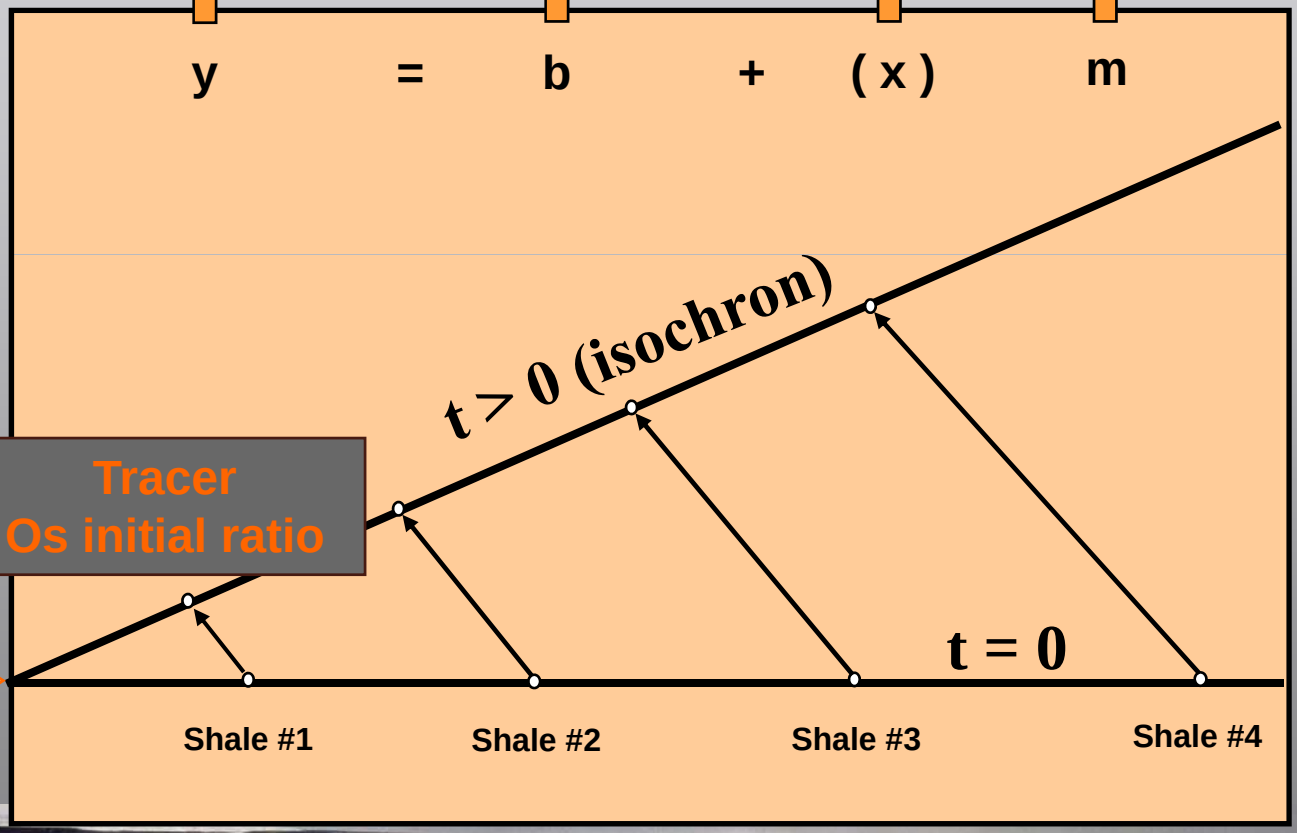
- **Fractionated into heavy hydrocarbons**
  - **Retained in source rocks** *Selby et al., 2007*
  - **Small *but measurable* in migrated hydrocarbons**

Asphaltenes	**Re ≈ 1-300 ppb**
	Os ≈ 20-1500 ppt
Maltenes	**Re ≈ 0.03-2 ppb**
	Os ≈ 0.2-20 ppt

Minimal difference in $^{187}Os/^{188}Os$

$$\left(\frac{^{187}Os}{^{188}Os}\right)_p = \left(\frac{^{187}Os}{^{188}Os}\right)_i + \frac{^{187}Re}{^{188}Os}\left[e^{\lambda t} - 1\right]$$

y = b + (x) m



$\frac{^{187}Os}{^{188}Os}$

Tracer Os initial ratio

$\left(\frac{^{187}Os}{^{188}Os}\right)_i$

$\frac{^{187}Re}{^{188}Os}$

Assumptions behind the isochron method:

1) **All phases isotopically equilibrated at the same time**
2) **All phases had the same initial $^{187}Os/^{188}Os$ ratio**
3) **No subsequent gain, loss, or redistribution of Re or Os**

Necessary condition:

Spread in $^{187}Re/^{188}Os$ ratios

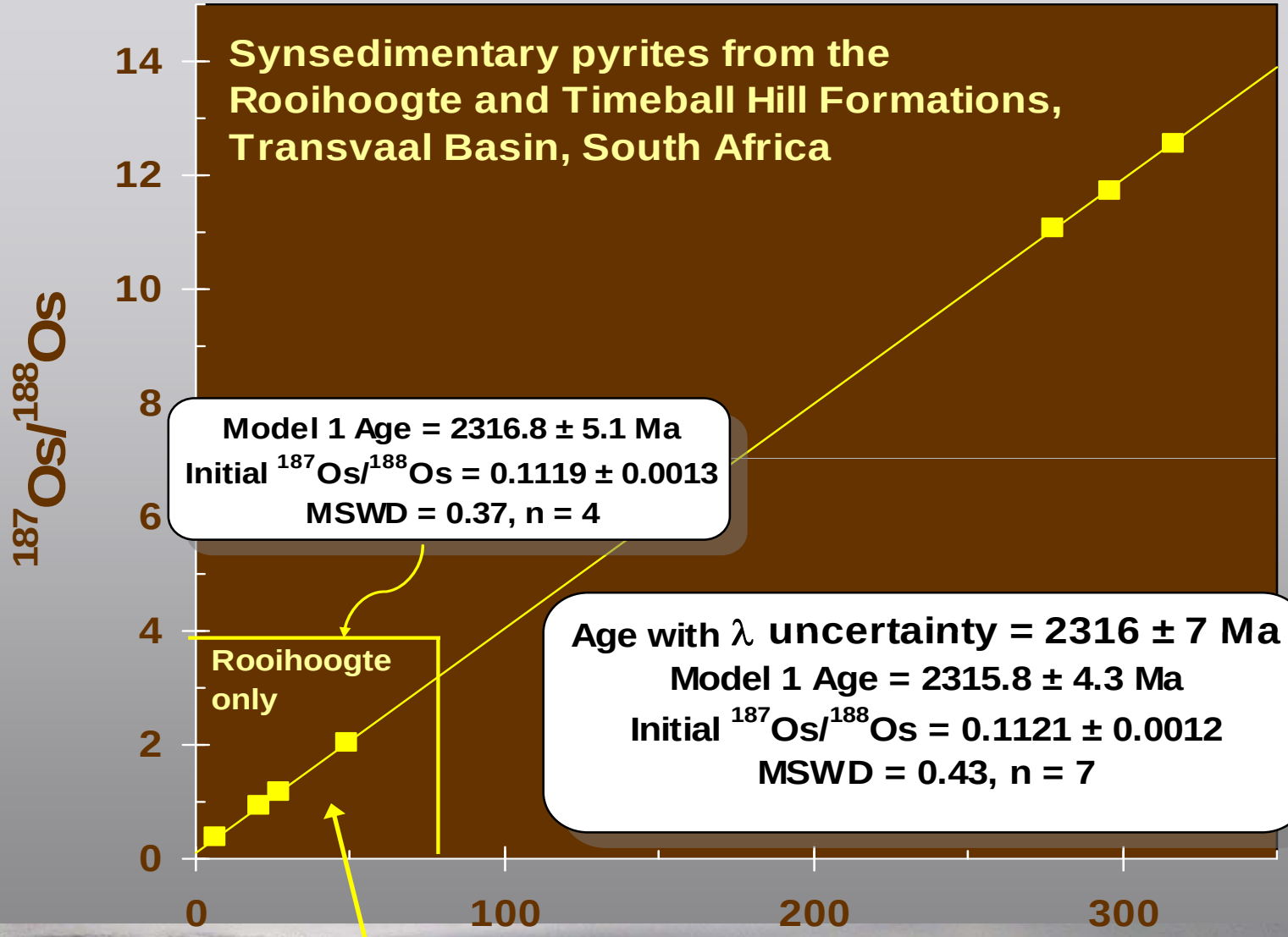
Does it work? Case study #1

Transvaal Basin – South Africa

- **Rooihoogte and Timeball Hill Formations**
  - **Carbonaceous shales with poorly constrained age**
- **Evidence for syn-depositional or early diagenetic pyrite**
- **Sulfur isotope data from pyrite documents oxic atmosphere (postdates Great Oxidation Event)**

Hannah et al., 2004, Earth and Planetary Science Letters 225: 43-52.

Hannah et al., 2004, Earth and Planetary Science Letters 225: 43-52.



Regression of Rooihoogte samples alone yields same result. Isochron *not* controlled by two data clusters.

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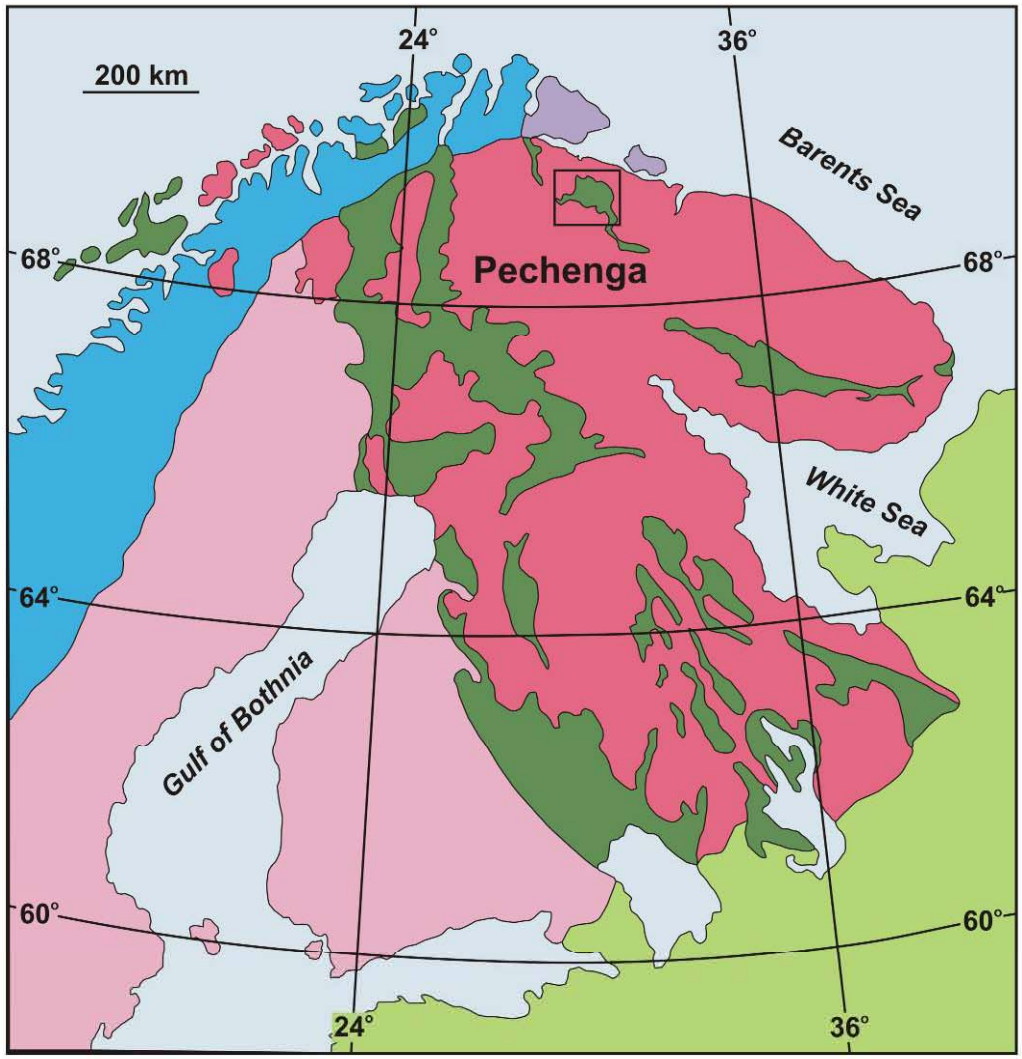
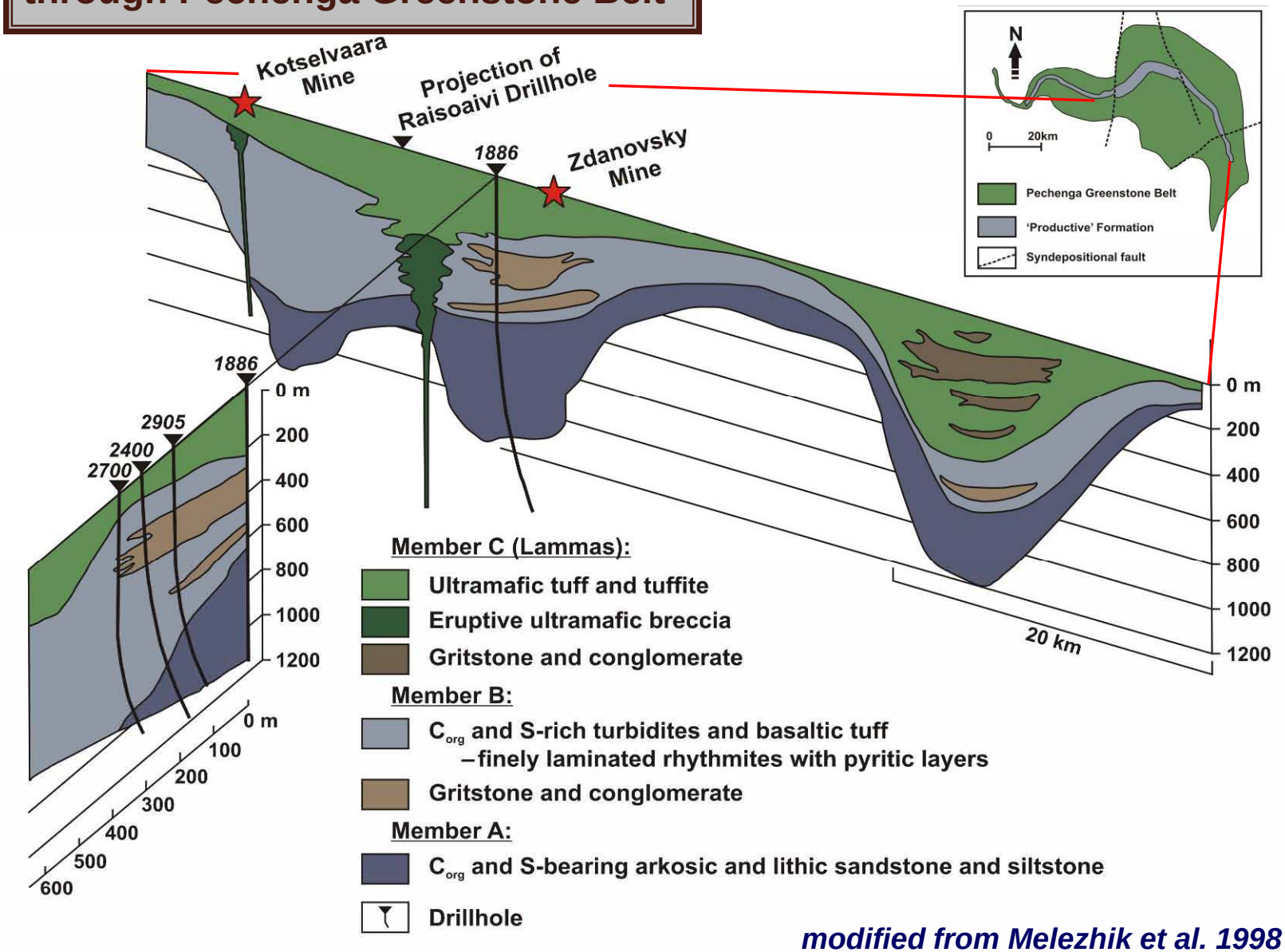
What about organics? Case study #2

Pechenga Greenstone Belt, Kola, Russia

- **Pilgujärvi Sedimentary Formation**
  - **Carbonaceous shales with sulfidic layers**
    - **Euxenic depositional environment**
- **Sampling**
  - **Diagenetic sulfide concretions**
  - **Syn-sedimentary sulfide layers**
  - **Organic-rich, sulfide-poor horizons**


200 km
24°
36°
68°
64°
60°
Barents Sea
White Sea
Gulf of Bothnia
Pechenga
Phanerozoic
Caledonides
Neoproterozoic
Svecofennian
Paleoproterozoic
Archean

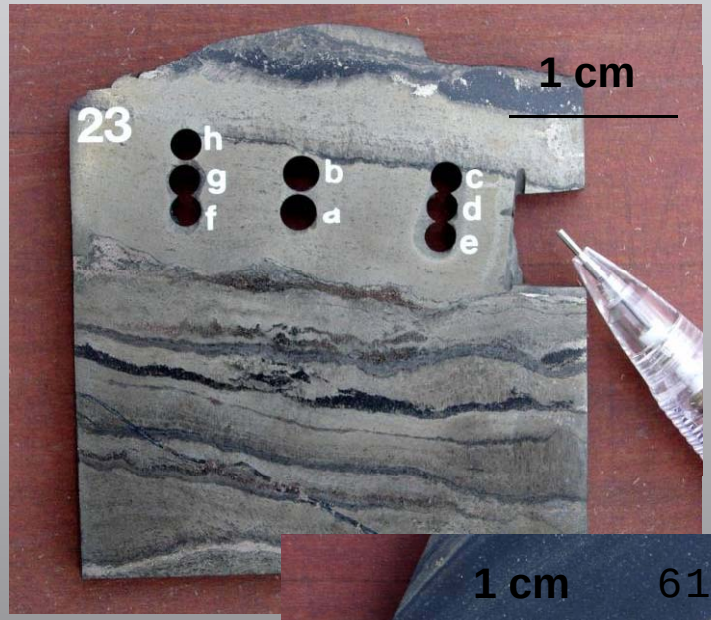
Longitudinal- and cross-sections through Pechenga Greenstone Belt

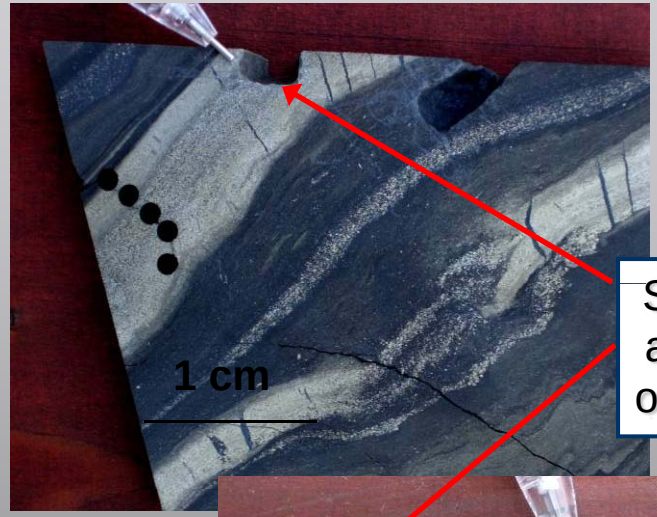


modified from Melezhik et al. 1998

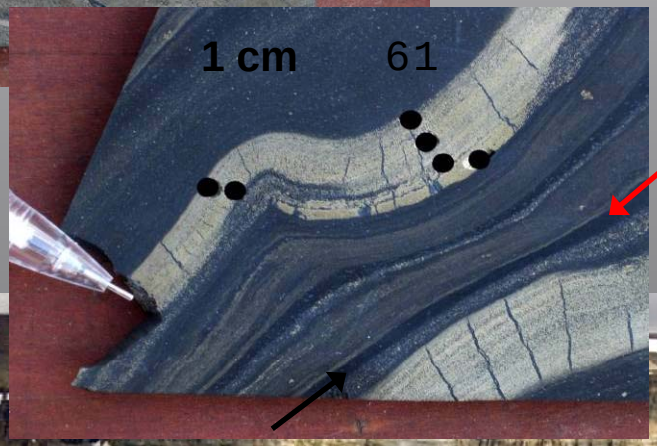
Organic material and synsedimentary sulfides –

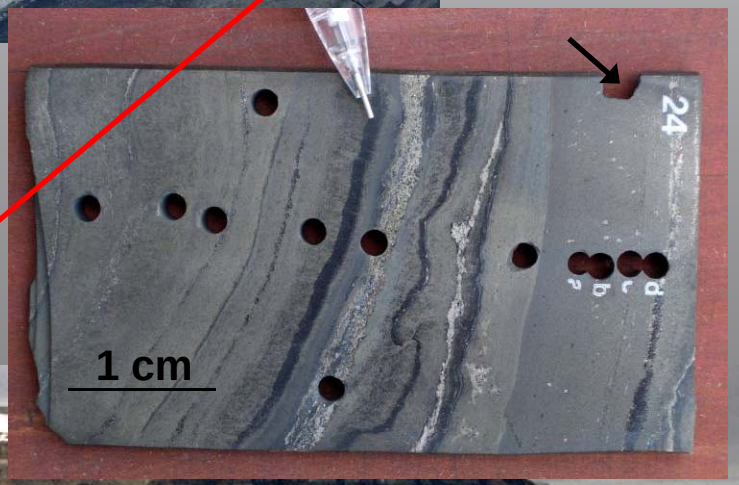
"Productive" Formation, Pechenga, Kola Peninsula



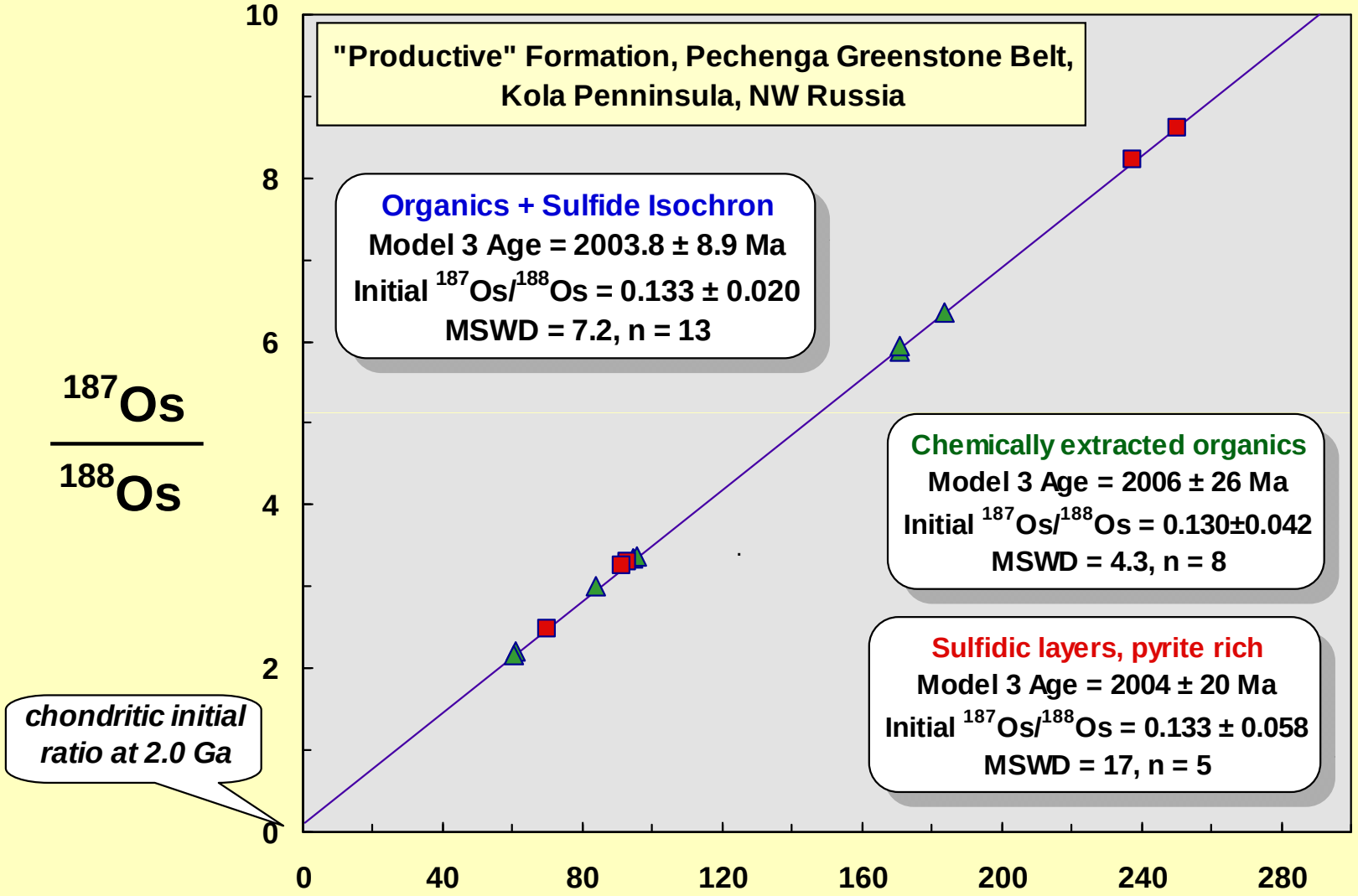


Synsedimentary pyrite and organic layers cut out for Re-Os analyses





Re-Os dating yields depositional age of Paleoproterozoic shale



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Colorado State University
Hannah et al., 2006

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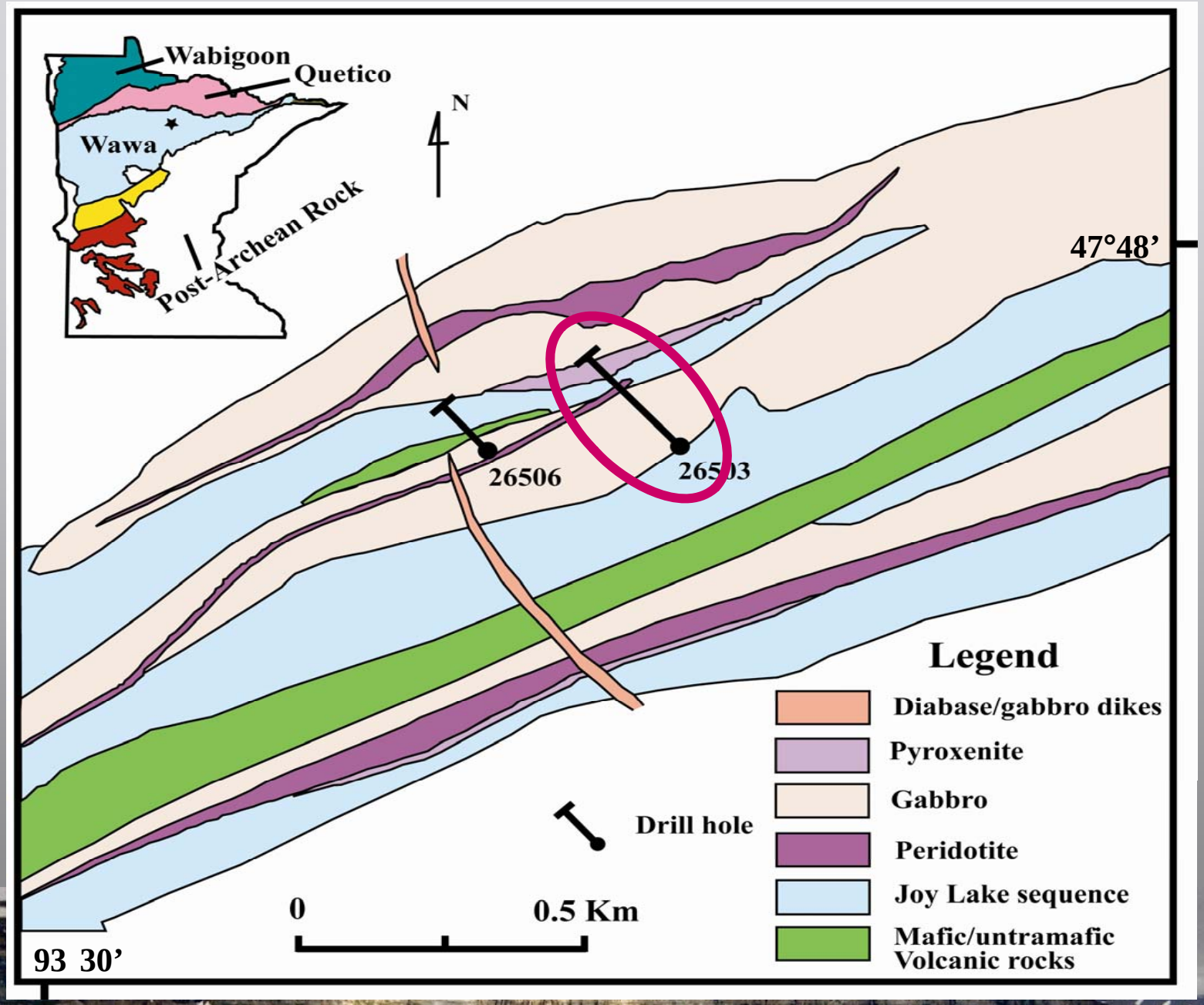
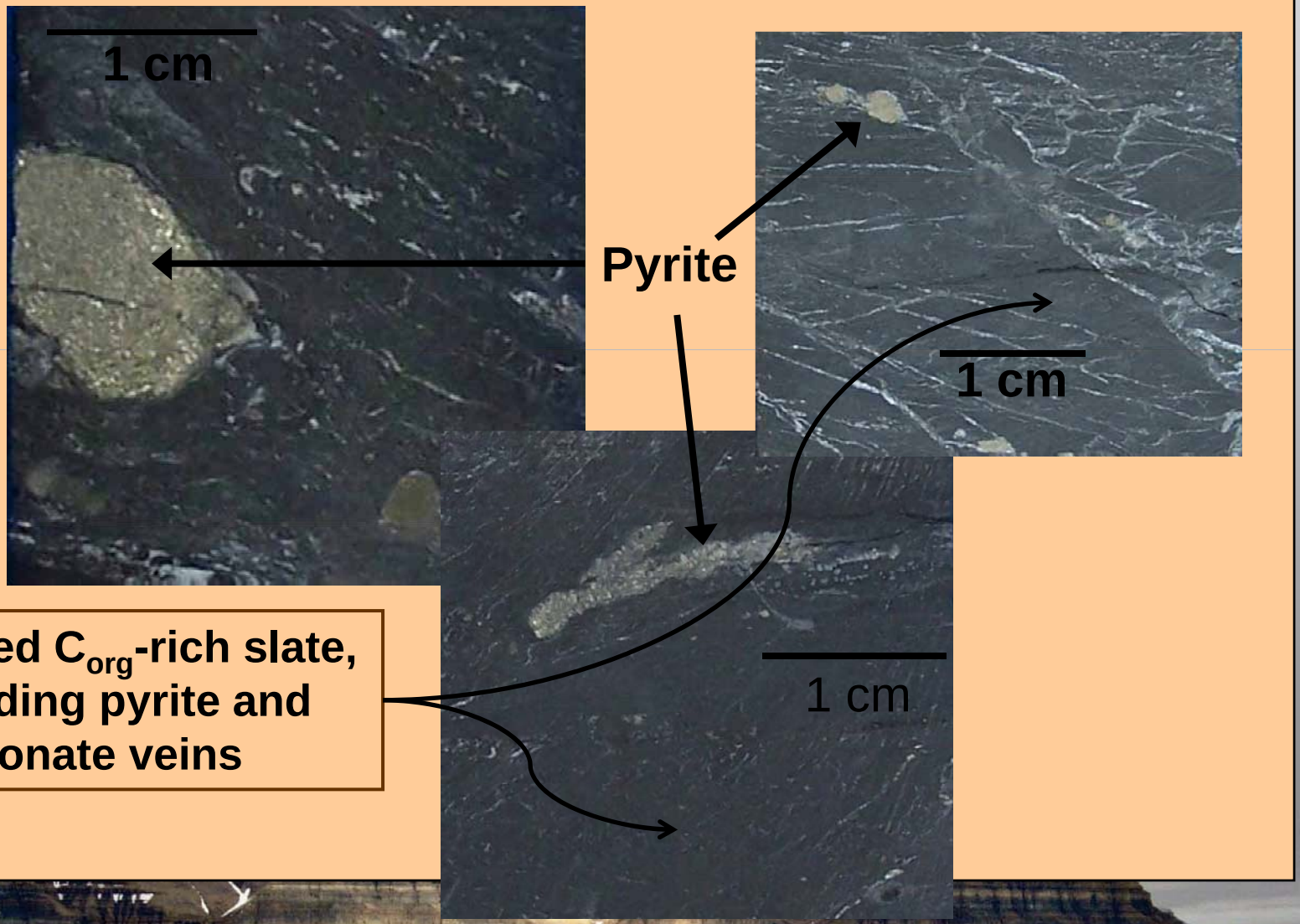
But metamorphism? Case Study #3

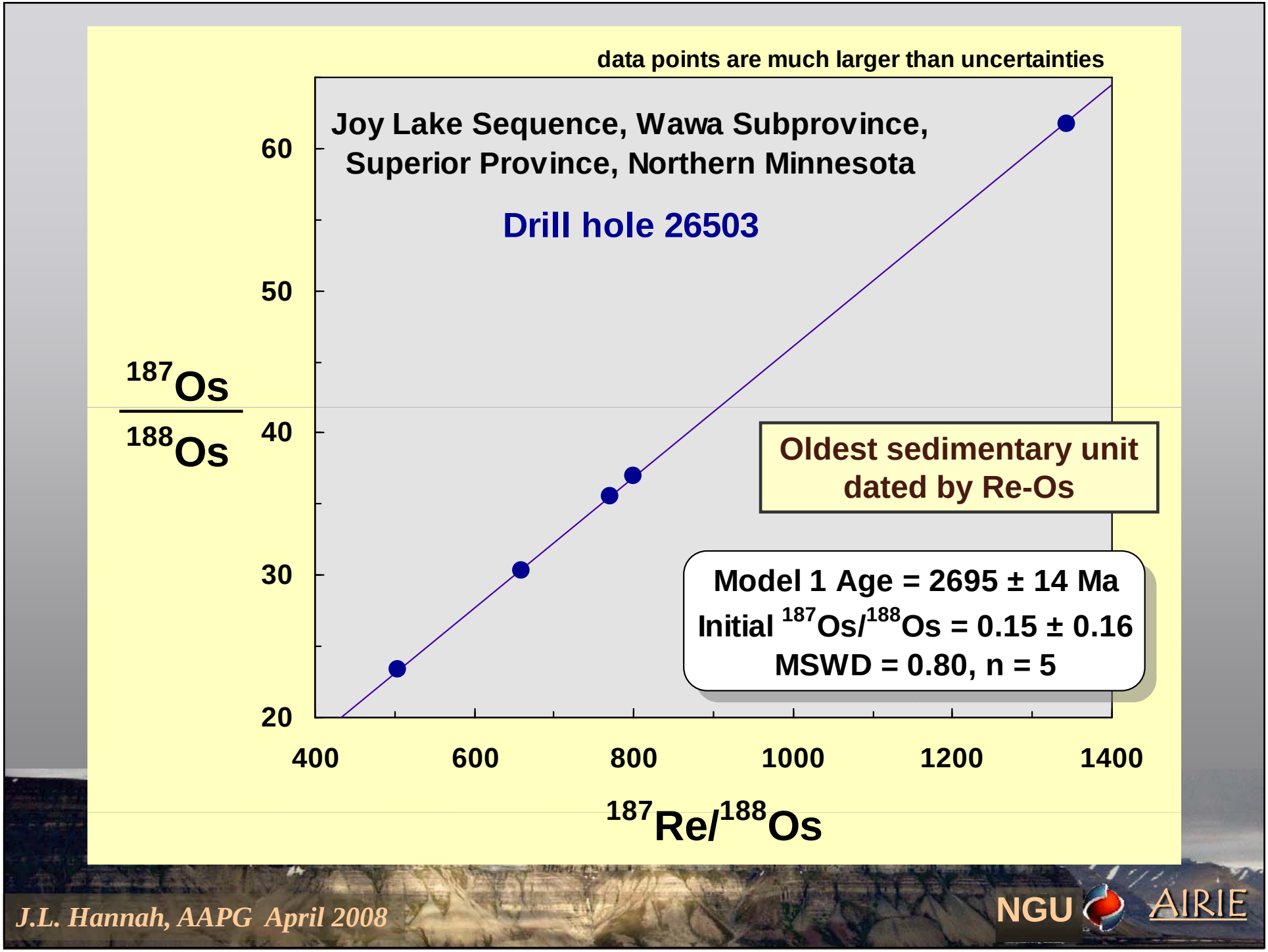
Supracrustal rocks, Superior Province

- **Refine Re-Os systematics in the Archean**
  - **Test application of Re-Os chronometer in C-rich *slates***
  - **Confirm limited Re and Os cycling prior to rise of atmospheric oxygen**
  - **Confirm limited input of radiogenic Os from continents to oceans in Archean**
- **Establish geochronologic framework for western Wawa subprovince**
  - **Hindered by poor exposure and limited geochronology**


Wabigoon
Quetico
Wawa
Post-Archean Rock
N
47°48’
26506
26503
Legend
Diabase/gabbro dikes
Pyroxenite
Gabbro
Peridotite
Joy Lake sequence
Mafic/untramafic Volcanic rocks
Drill hole
0
0.5 Km
93 30’

Typical Joy Lake slates

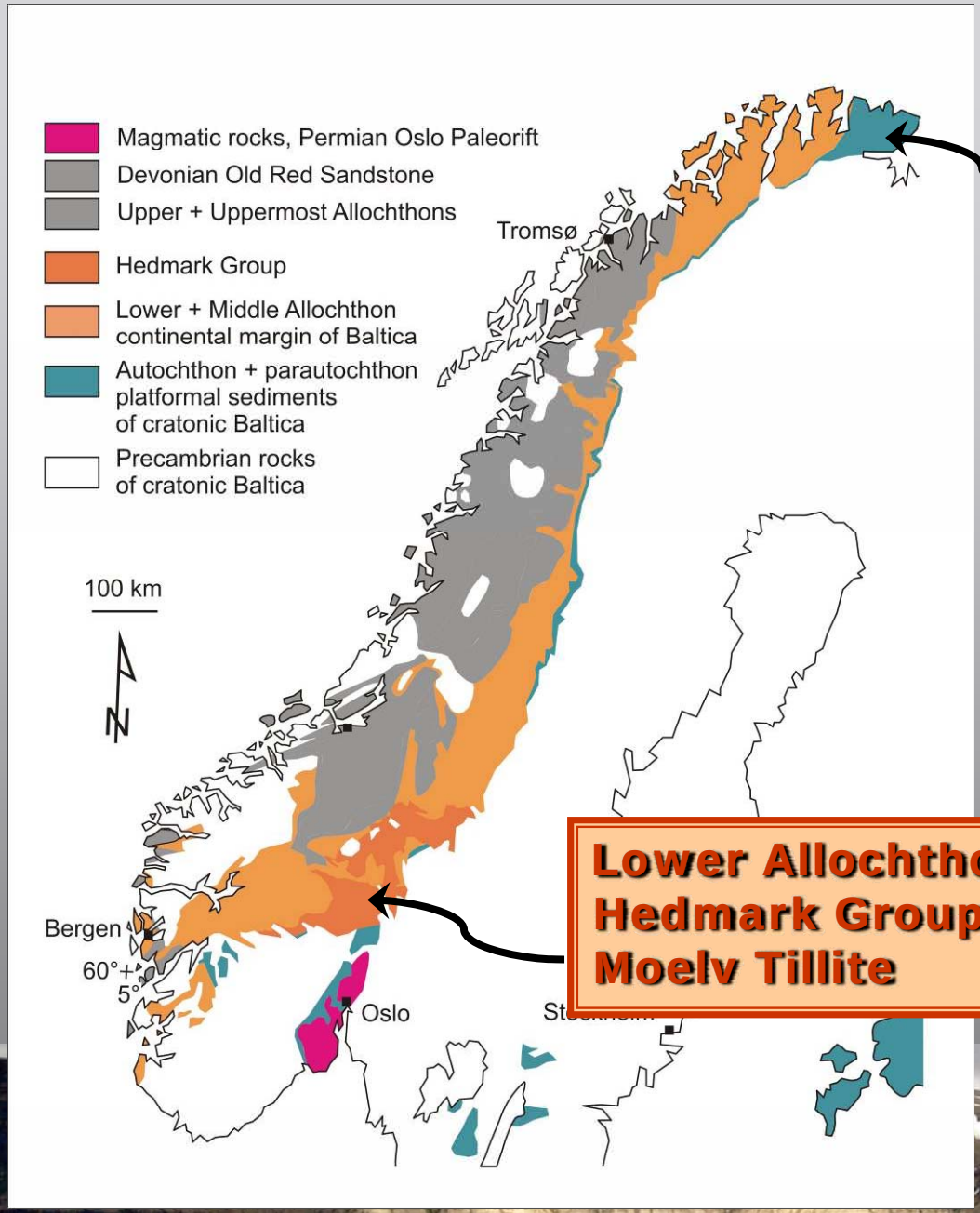



data points are much larger than uncertainties
Joy Lake Sequence, Wawa Subprovince,
Superior Province, Northern Minnesota
Drill hole 26503
Oldest sedimentary unit dated by Re-Os
Model 1 Age = 2695 ± 14 Ma
Initial 187Os/188Os = 0.15 ± 0.16
MSWD = 0.80, n = 5
187Os/188Os
187Re/188Os
60
50
40
30
20
400
600
800
1000
1200
1400

Case study #4 – Two correlative outcrops:

Neoproterozoic Biri Formation, S. Norway

- **Refine timing of Varanger glaciation**
  - **How are Baltica glaciation(s) related to others in the Neoproterozoic?**
    - **Sturtian ~720 Ma**
    - **Marinoan ~630 Ma**
    - **Gaskiers ~580 Ma**
  - **Tests for "Snowball Earth"**
    - **Was Varanger glaciation contemporaneous with other glacial events?**
    - **Was the Varanger a low-latitude event?**



Varanger Peninsula
Vestertana Group
Mortensnes Formation

Lower Allochthon
Hedmark Group
Moelv Tillite

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Moelv Tillite, central Norway – How old is it?

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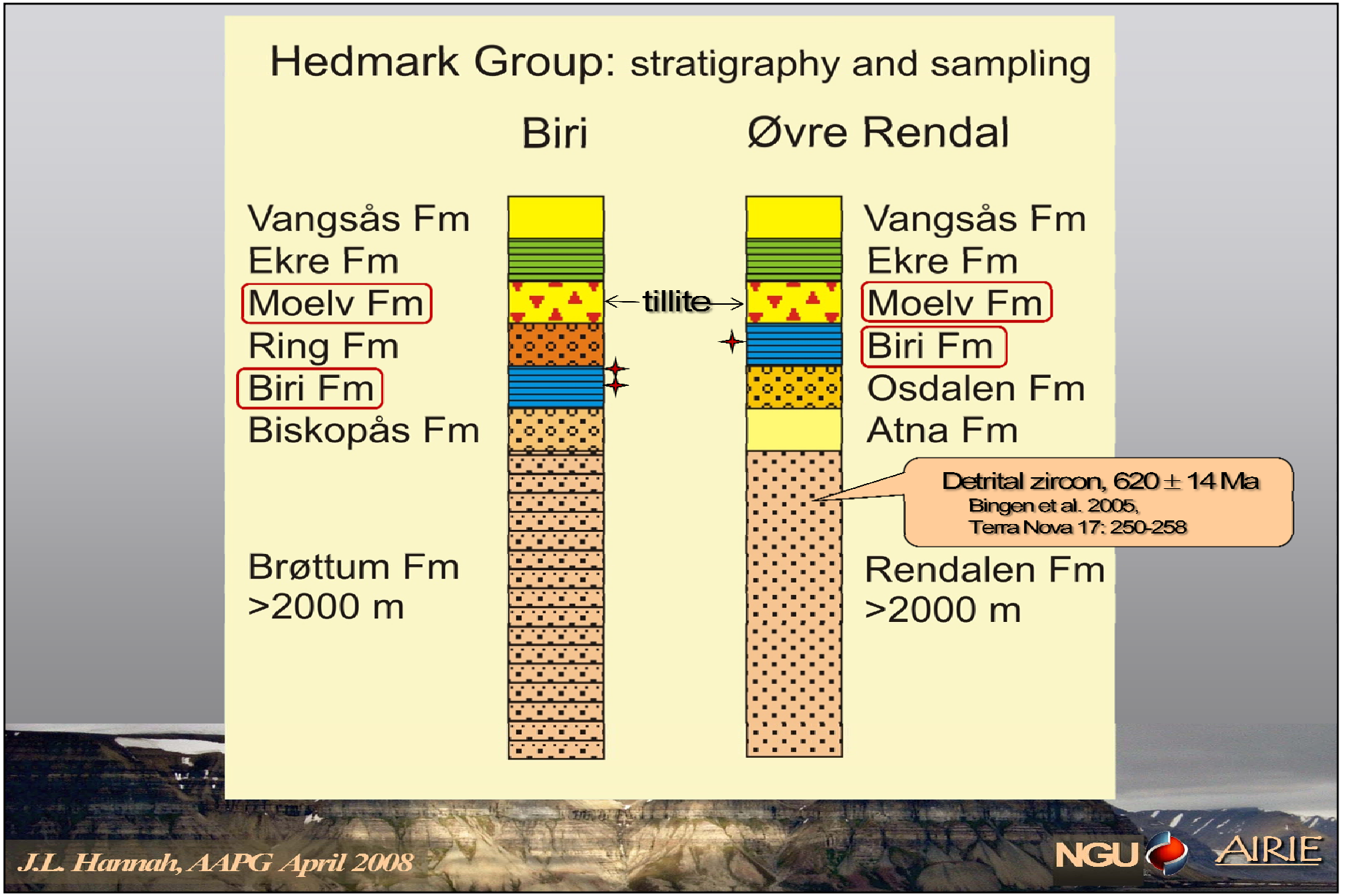
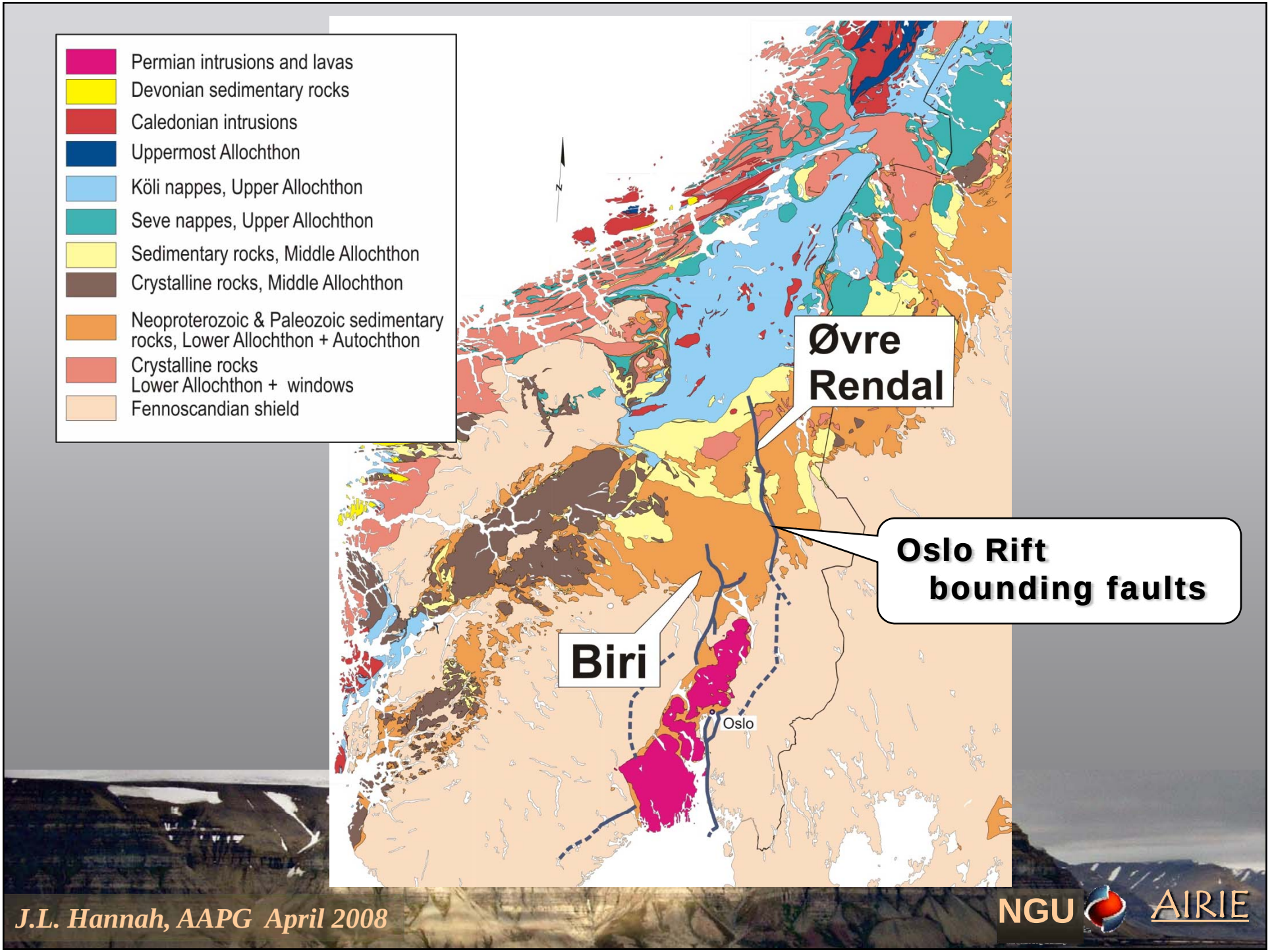


Ring conglomerate overlies Biri on erosional surface. Moelv grades into Ekre, with gradual grain size decrease in transgressive sequence. There is NO CAP CARBONATE.


Permian intrusions and lavas
Devonian sedimentary rocks
Caledonian intrusions
Uppermost Allochthon
Köli nappes, Upper Allochthon
Seve nappes, Upper Allochthon
Sedimentary rocks, Middle Allochthon
Crystalline rocks, Middle Allochthon
Neoproterozoic & Paleozoic sedimentary rocks, Lower Allochthon + Autochthon
Crystalline rocks Lower Allochthon + windows
Fennoscandian shield
N
Øvre Rendal
Oslo Rift bounding faults
Biri
Oslo

Collecting Biri Shale

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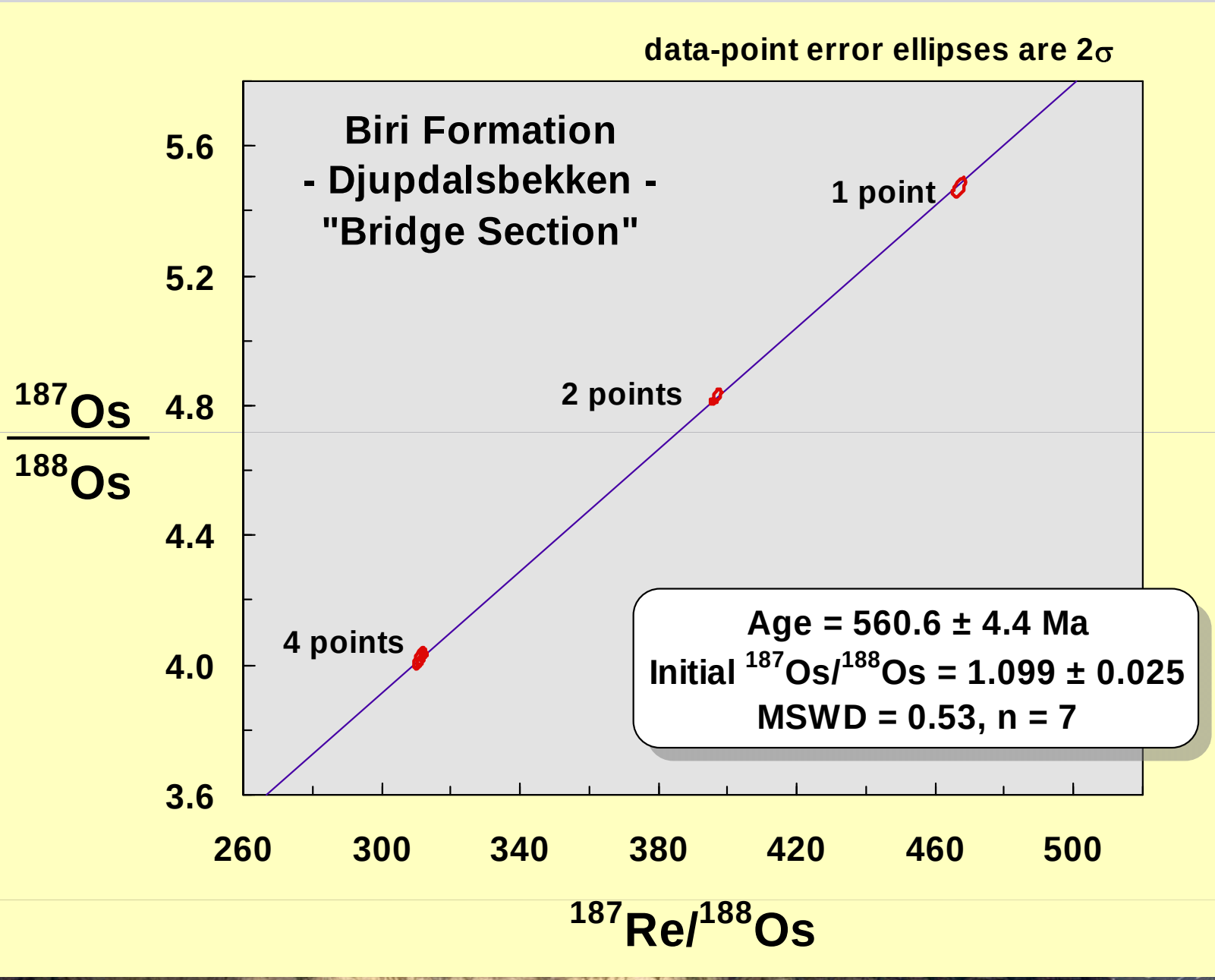
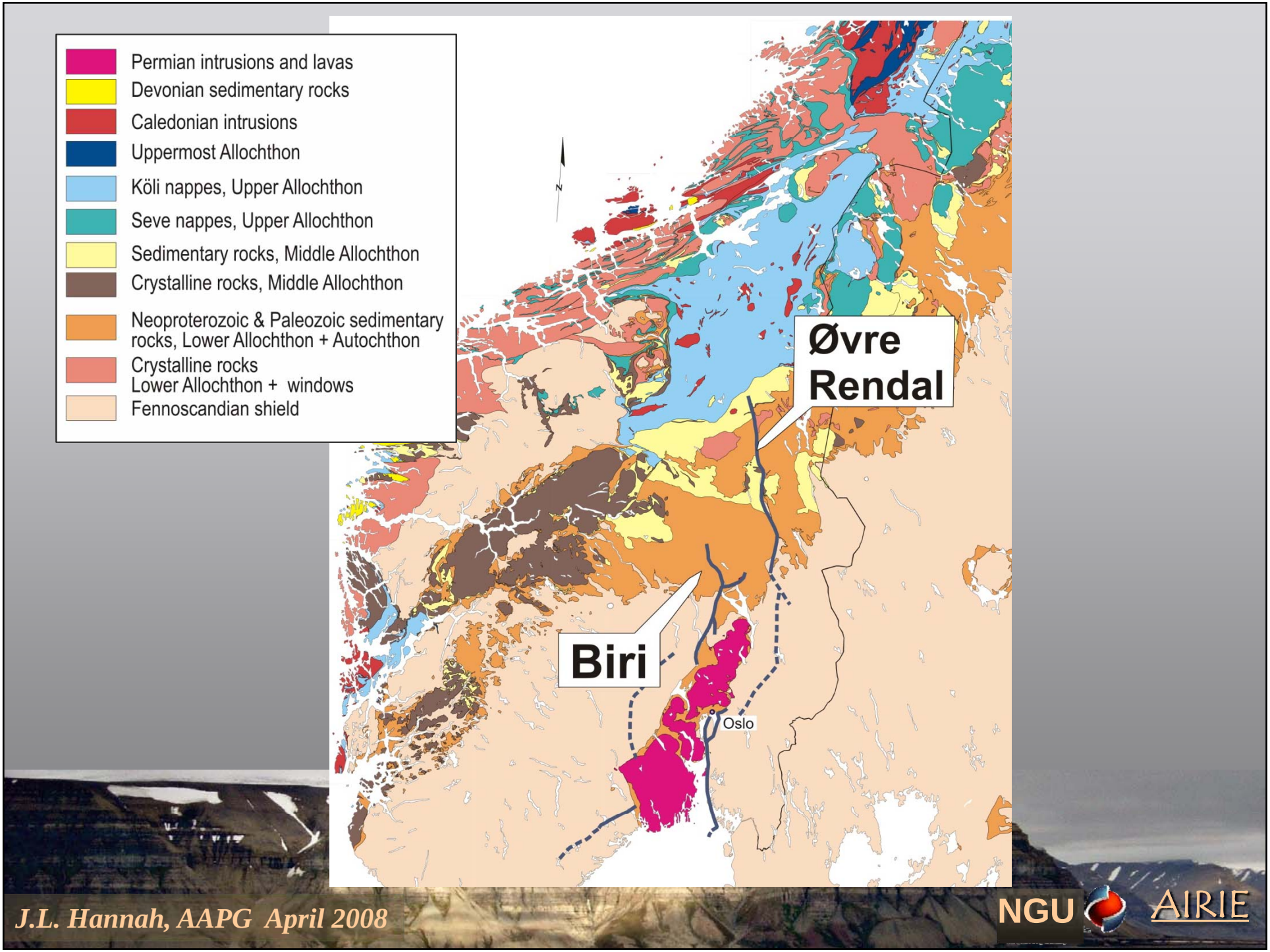

data-point error ellipses are 2σ
Biri Formation
- Djupdalsbekken -
"Bridge Section"
1 point
2 points
4 points
Age = 560.6 ± 4.4 Ma
Initial 187Os/188Os = 1.099 ± 0.025
MSWD = 0.53, n = 7
187Os / 188Os
5.6
5.2
4.8
4.4
4.0
3.6
260
300
340
380
420
460
500
187Re/188Os

What can we conclude?

- **Neoproterozoic glaciation apparently younger than Gaskiers event**
  - **Previous data for Varanger glaciation permissive of this younger age**
  - **Supports probability of *more than three* Neoproterozoic glacial events**
  - **Latitude of section at ~560 Ma poorly constrained**
    - **Lack of cap carbonate suggests temperate climate**



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Moelv tillite at Øvre Rendal

with dropstones

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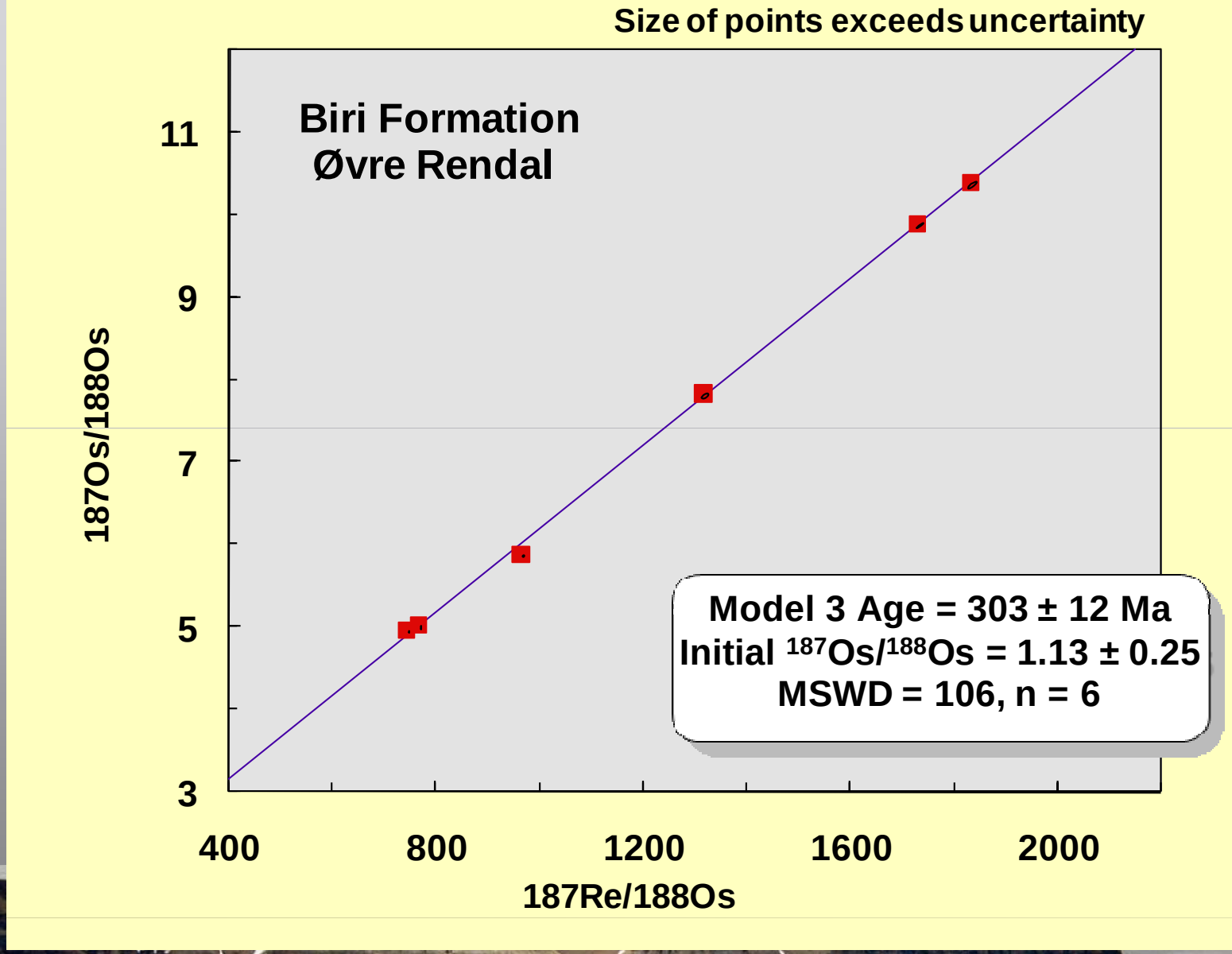
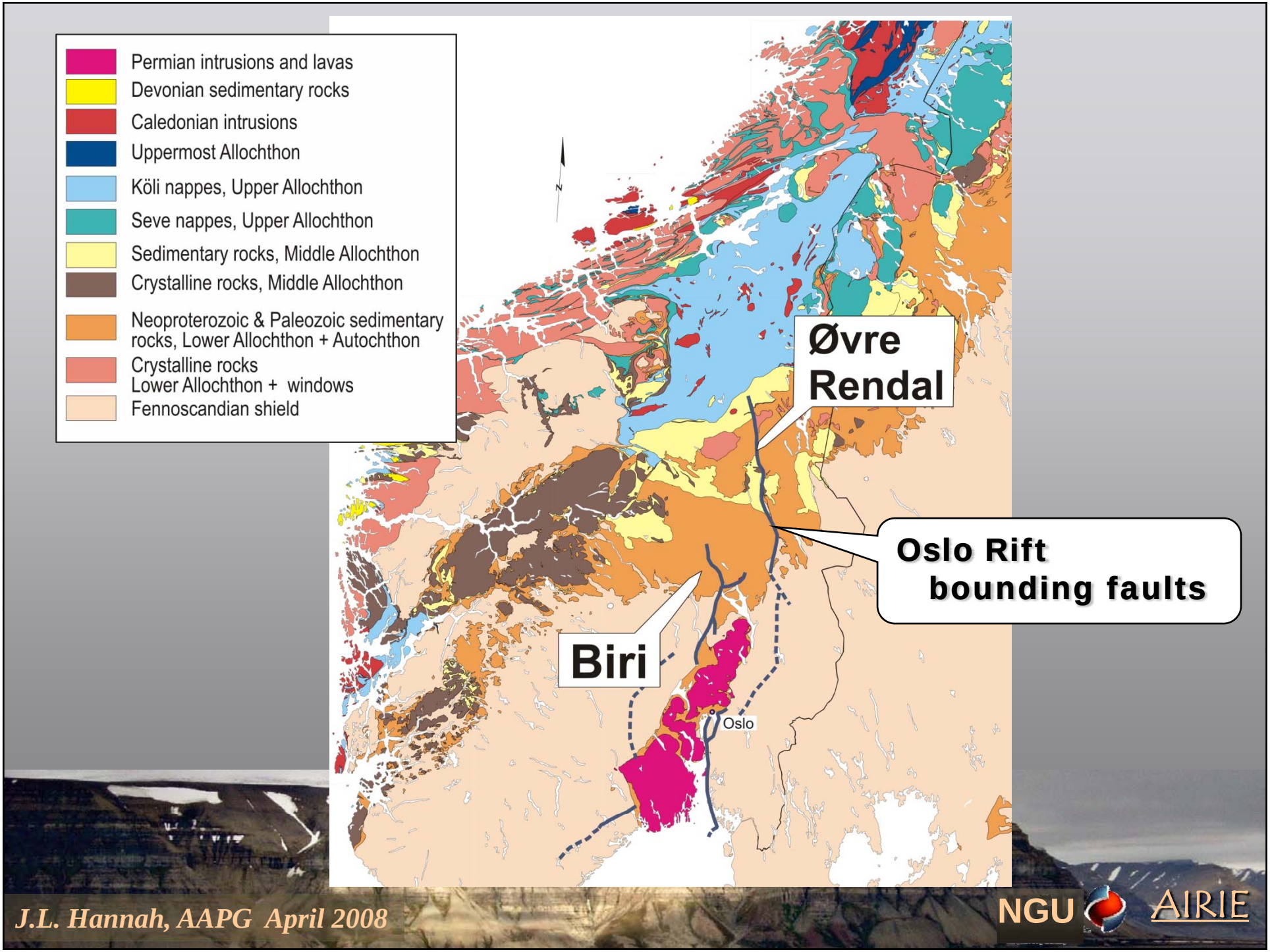
Biri Formation at Øvre Rendal

Sample site

After excavation


Size of points exceeds uncertainty
Biri Formation
Øvre Rendal
187Os/188Os
11
9
7
5
3
400
800
1200
1600
2000
187Re/188Os
Model 3 Age = 303 ± 12 Ma
Initial 187Os/188Os = 1.13 ± 0.25
MSWD = 106, n = 6


Permian intrusions and lavas
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Uppermost Allochthon
Köli nappes, Upper Allochthon
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Crystalline rocks Lower Allochthon + windows
Fennoscandian shield
N
Øvre Rendal
Oslo Rift bounding faults
Biri
Oslo

What can we conclude?

- **Hydrocarbons mixed, isotopically equilibrated during maturation and migration at ~300 Ma**
  - **Infiltration of hydrocarbons into mature shale**
    - **Age controlled by Re-Os systematics of hydrocarbons**
    - **Overwhelms Re and Os in residual kerogen/asphaltenes**

Case study #5 – Triassic source rocks

Breaking news –

- **First Blanknuten analyses**
  - **Ammonite zones indicate Anisian stage**
  - **Reasonable model age of ~245 Ma for initial $^{187}Os/^{188}Os$ of 1.0**
  - **Precise age and initial ratio await next week's analyses . . . and more**

Fingerprinting hydrocarbons

- **Establish Os_i seawater curve for depositional periods of proposed source rocks**
- **Construct isochrons from hydrocarbon analyses**
- **Model permissible source and timing of migration**

Summary:

- **High precision data obtained from shale with < 1% TOC.**
- **Ages robust through at least chlorite-grade metamorphism.**
  - **Dates and rates for sedimentary processes**
  - **Dates and rates for biogenic processes**
  - **Calibration of Earth's time scale**
- **$^{187}Os/^{188}Os$ records seawater Os composition and fingerprints hydrocarbons**
  - **Linking seawater $^{187}Os/^{188}Os$ evolution to global tectonic and climatic events**
  - **Tracing and correlating hydrocarbons**
- **Isochron age and initial $^{187}Os/^{188}Os$ for hydrocarbons**
  - **Permits modeling of source and timing of migration**

Selected References

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