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 187Re to 187Os provides a radiometric clock that records the time of shale deposition and the 187Os/188Os 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 187Os/188Os through time, thereby recording changes in global patterns of oxidative weathering and Os influx and defining the resolution of the 187Os/188Os tracer; and (3) determine Re-Os systematics in migrated hydrocarbons and source rocks, thereby documenting the time of isotopic homogenization of hydrocarbons and establishing 187Os/188Os 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.
Re-Os dating of black shales: timing and duration of sedimentary processes

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Crustal Processes – Geological Survey of Norway
Rhenium (Re) and Osmium (Os) 
redox-sensitive metals

Platinum Group Elements

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$^{185}\text{Re} = 37.398\%$

$^{187}\text{Re} = 62.602\%$

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

$\lambda^{187}\text{Re} = 1.666 \times 10^{-11} \text{ yr}^{-1}$ (Smoliar et al. 1996)

$^{184}\text{Os} = 0.02\%$

$^{186}\text{Os} = 1.60\%$

$^{187}\text{Os} = 1.51\%$

$^{188}\text{Os} = 13.3\%$

$^{189}\text{Os} = 16.2\%$

$^{190}\text{Os} = 26.4\%$

$^{192}\text{Os} = 41.0\%$
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 $^{187}\text{Os}/^{188}\text{Os}$ in crust over time.
Geochemistry of Re and Os

**Average crust**
- Re/Os $\approx 10$
- Present day $^{187}\text{Os}^{188}\text{Os} \approx 1$

**Mantle and meteorites**
- Re/Os $\approx 1$
- Present day $^{187}\text{Os}^{188}\text{Os} = 0.127$
Major sources of Re and Os in seawater


(Micro)meteorites:
$^{187}\text{Os}/^{188}\text{Os} = 0.127$,
low Re/Os ratio, high [Os]

Input to seawater from (micro)meteorites

Riverine input to seawater from continental crust

Mn crusts:
low [Re], high [Os]

Metalliferous sediments:
low [Re], mod. [Os]

Organic-rich sediments:
high [Re], [Os] & Re/Os ratios

Crust:
high Re/Os ratio, low [Os]
Old crust: $^{187}\text{Os}/^{188}\text{Os} \approx 1.9$
Young crust: $^{187}\text{Os}/^{188}\text{Os} > 0.127$

MOR hydrothermal vents (young crust input to seawater)

Mantle: $^{187}\text{Os}/^{188}\text{Os} = 0.127$,
low Re/Os ratio, high [Os]
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 $^{187}\text{Os}/^{188}\text{Os}$**

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

  **Increasing $^{187}\text{Os}/^{188}\text{Os}$ with time**

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

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

Changes in seawater Re-Os over time

- Os more sensitive than Sr to short-term changes
  - Global variation in $^{187}\text{Os}/^{188}\text{Os} \gg$ than $^{87}\text{Sr}/^{86}\text{Sr}$
  - Os residence time in seawater $\ll$ for Sr

Seawater $^{187}\text{Os}/^{188}\text{Os}$ 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 \( \text{CrO}_3 \cdot \text{H}_2\text{SO}_4 \)**

- **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 \textit{Selby et al., 2007}
  - Small \textit{but measurable} in migrated hydrocarbons

\begin{tabular}{|l|l|}
\hline
\textbf{Asphaltene} & Re \approx 1-300 ppb \\
 & Os \approx 20-1500 ppt \\
\hline
\textbf{Maltenes} & Re \approx 0.03-2 ppb \\
 & Os \approx 0.2-20 ppt \\
\hline
\textbf{Minimal difference in }^{187}\text{Os}/^{188}\text{Os} \\
\hline
\end{tabular}
\[
\begin{align*}
\left( \frac{^{187}\text{Os}}{^{188}\text{Os}} \right)_p &= \left( \frac{^{187}\text{Os}}{^{188}\text{Os}} \right)_i + \frac{^{187}\text{Re}}{^{188}\text{Os}} e^{\lambda t} - 1
\end{align*}
\]

\[y = b + (x) m\]

\[\text{Tracer Os initial ratio}\]

\[\frac{^{187}\text{Os}}{^{188}\text{Os}}\]

\[\frac{^{187}\text{Re}}{^{188}\text{Os}}\]

Shale #1, Shale #2, Shale #3, Shale #4

\[t > 0 \text{ (isochron)}\]

\[t = 0\]
Assumptions behind the isochron method:

1) All phases isotopically equilibrated at the same time

2) All phases had the same initial $^{187}\text{Os} / ^{188}\text{Os}$ ratio

3) No subsequent gain, loss, or redistribution of Re or Os

*Necessary condition:* Spread in $^{187}\text{Re} / ^{188}\text{Os}$ 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)

Synsedimentary pyrites from the Rooihoogte and Timeball Hill Formations, Transvaal Basin, South Africa

Model 1 Age = 2316.8 ± 5.1 Ma
Initial $^{187}\text{Os}/^{188}\text{Os} = 0.1119 ± 0.0013$
MSWD = 0.37, n = 4

Rooihoogte only

Age with $\lambda$ uncertainty = 2316 ± 7 Ma
Model 1 Age = 2315.8 ± 4.3 Ma
Initial $^{187}\text{Os}/^{188}\text{Os} = 0.1121 ± 0.0012$
MSWD = 0.43, n = 7

Regression of Rooihoogte samples alone yields same result. Isochron not controlled by two data clusters.
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
Longitudinal- and cross-sections through Pechenga Greenstone Belt

Member C (Lammas):
- Ultramafic tuff and tuffite
- Eruptive ultramafic breccia
- Gritstone and conglomerate

Member B:
- $C_{org}$ and S-rich turbidites and basaltic tuff
  - finely laminated rhythmites with pyritic layers
- Gritstone and conglomerate

Member A:
- $C_{org}$ and S-bearing arkosic and lithic sandstone and siltstone
- Drillhole

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
"Productive" Formation, Pechenga Greenstone Belt, Kola Penninsula, NW Russia

Organics + Sulfide Isochron
Model 3 Age = 2003.8 ± 8.9 Ma
Initial $^{187}\text{Os}/^{188}\text{Os} = 0.133 \pm 0.020$
$\text{MSWD} = 7.2, n = 13$

Chemically extracted organics
Model 3 Age = 2006 ± 26 Ma
Initial $^{187}\text{Os}/^{188}\text{Os} = 0.130 \pm 0.042$
$\text{MSWD} = 4.3, n = 8$

Sulfidic layers, pyrite rich
Model 3 Age = 2004 ± 20 Ma
Initial $^{187}\text{Os}/^{188}\text{Os} = 0.133 \pm 0.058$
$\text{MSWD} = 17, n = 5$

187\text{Re}/188\text{Os}

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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
Typical Joy Lake slates

Drilled $C_{\text{org}}$-rich slate, avoiding pyrite and carbonate veins
Joy Lake Sequence, Wawa Subprovince, Superior Province, Northern Minnesota

Drill hole 26503

data points are much larger than uncertainties

Oldest sedimentary unit dated by Re-Os

Model 1 Age = 2695 ± 14 Ma
Initial $^{187}\text{Os}/^{188}\text{Os} = 0.15 ± 0.16$
MSWD = 0.80, $n = 5$
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
Moelv Tillite, central Norway – How old is it?

Shale clast
Ring conglomerate overlies Biri on erosional surface. Moelv grades into Ekre, with gradual grain size decrease in transgressive sequence. There is NO CAP CARBONATE.
Collecting Biri Shale
Biri Formation - Djupdalsbekken - "Bridge Section"

Data-point error ellipses are $2\sigma$.

Age = 560.6 ± 4.4 Ma

Initial $^{187}$Os/$^{188}$Os = 1.099 ± 0.025

MSWD = 0.53, n = 7
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
Moelv tillite at Øvre Rendal with dropstones
Biri Formation at Øvre Rendal

Sample site

After excavation

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Model 3 Age = 303 ± 12 Ma
Initial $^{187}\text{Os}/^{188}\text{Os} = 1.13 ± 0.25$
MSWD = 106, n = 6
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

Svalbard

Botneheia Formation
Blanknuten Member

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**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 Osₐ 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
- $^{187}\text{Os}/^{188}\text{Os}$ records seawater Os composition and fingerprints hydrocarbons
  - Linking seawater $^{187}\text{Os}/^{188}\text{Os}$ evolution to global tectonic and climatic events
  - Tracing and correlating hydrocarbons
- Isochron age and initial $^{187}\text{Os}/^{188}\text{Os}$ for hydrocarbons
  - Permits modeling of source and timing of migration

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Selected References


