Application of Chemostratigraphy and Re-Os Geochronology to the Maikop Series of Eastern Azerbaijan: Constraining Kura and South Caspian Basin Evolution

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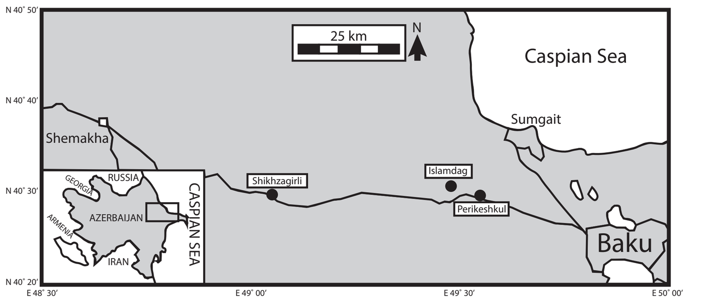
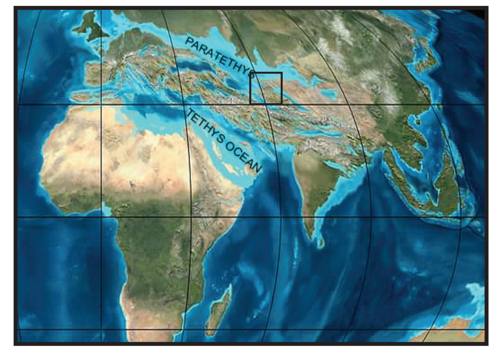
Introduction

- Organic-rich intervals of the Maikop Series of the Paratethys Sea record a critical change in the paleogeographic evolution of the Paratethys Sea related to isolation and development of anoxia in its subsequent basins
- However, the Maikop Series is largely devoid of diagnostic microfaunal assemblages, so the timing of deposition and stratigraphic correlation of the Maikop is under-developed
- This hampers our ability to resolve the evolution of the Paratethys Sea and to model the preservation, generation, and migration of hydrocarbons in its basins
- To resolve these problems, we present:
  (1) Sampling location and background on the complexities of the South Caspian Basin where the Maikop is a key source rock interval
  (2) Chemostratigraphic constraints of onshore sections of the Maikop developed via statistical analysis of rock geochemistry
  (3) Source rock characterization of Maikop samples via pyrolysis
  (4) Maikop depositional oxygen conditions via redox-sensitive trace metal ratios
  (5) Re-Os isotope geochronologic constraints on organic-rich intervals of the Maikop
  (6) Conclusions
- We show that the Maikop may be accurately stratigraphically constrained and resolve the timing of the periodic isolation of the Paratethys Sea

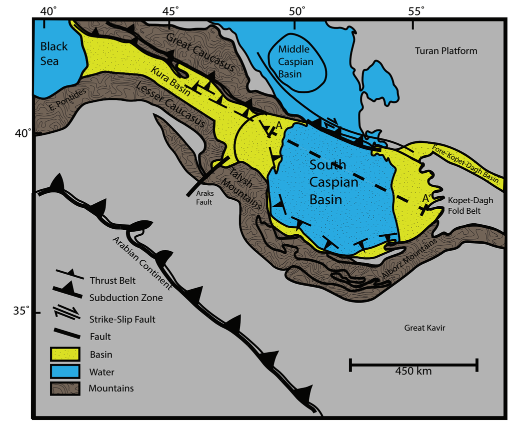
1 Geologic Setting



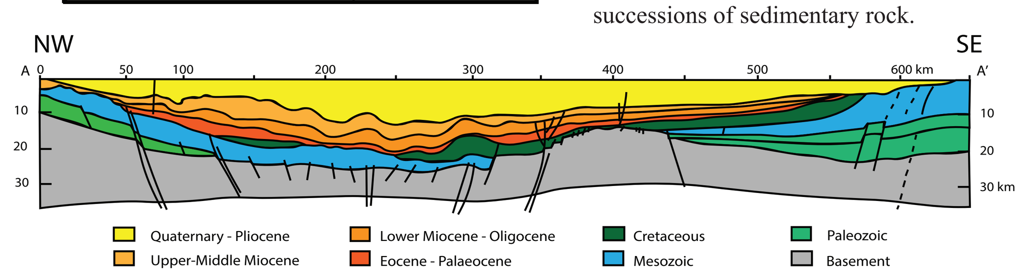
Simplified map of Eastern Azerbaijan showing the three Maikop outcrop sampling locations used in this study, modified from Hudson et al., (2008). Outcrops were selected from previous work done on the Maikop.



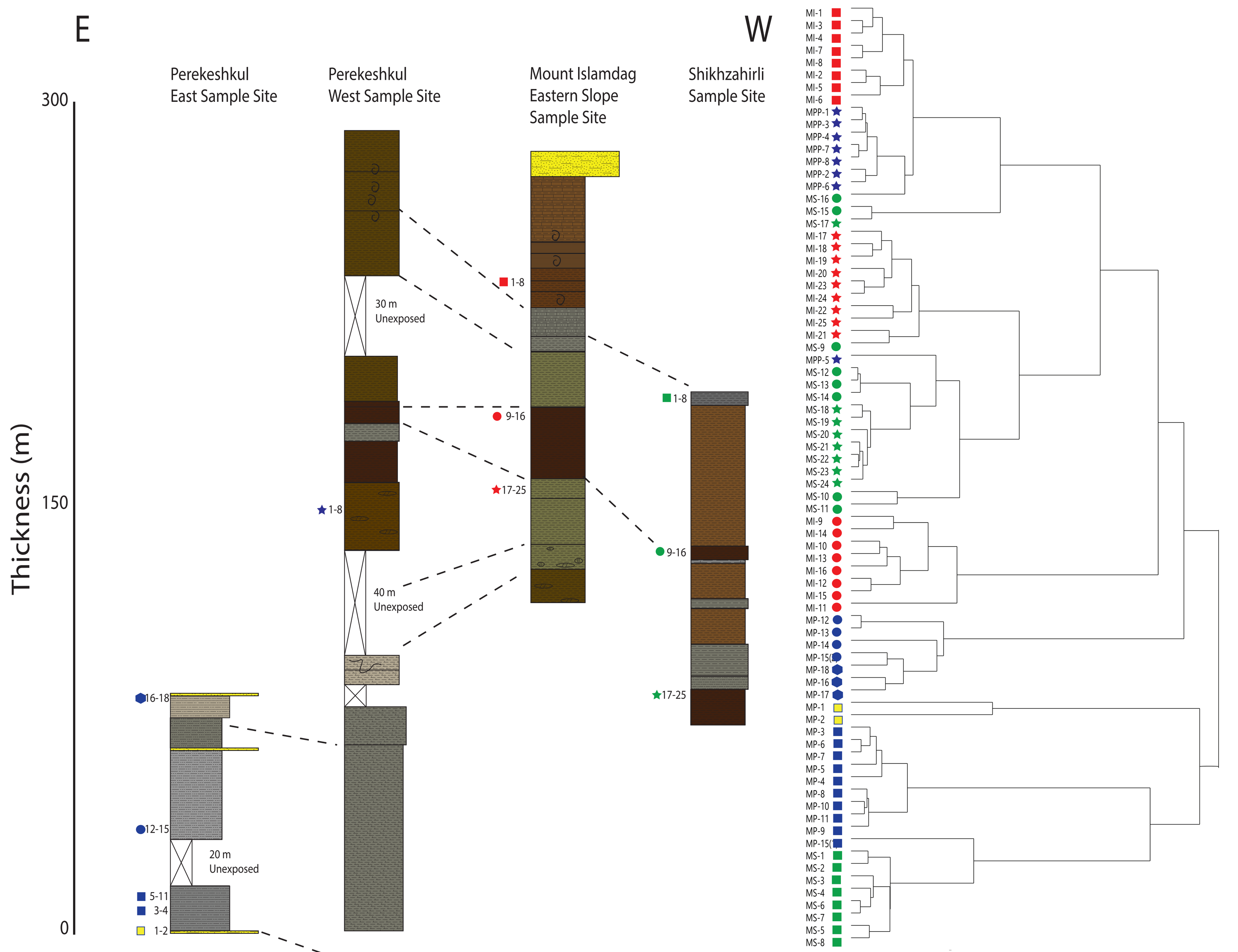
Paleogeographic representation of the Paratethys Sea near the Eocene-Oligocene Transition (EOT), from Ron Blakey (www2.nau.edu). Approximate location of the paleo-Caspian Sea is marked. Upon restriction of the Tethys Ocean by continental tectonics, the Paratethys evolved as a restricted sea with one primary connection to the ocean to the west. Closure of this seaway occurred due either to global eustacy or continued plate tectonic movement.



[Left] Modern tectonic setting of the South Caspian (SCB) and Kura Basins, modified from Brunet et al., (2009). Complex plate tectonic interactions resulted in oceanic crust flooring the SCB, rapid uplift of mountains and subsidence of basins, and complex folding and faulting throughout the basins. [Below] Simplified cross section of the SCB, modified from Brunet et al., (2009). The SCB is one of the deepest sedimentary basins in the world, with rapid subsidence and sedimentation resulting in young, thick, overpressured successions of sedimentary rock.



2 Maikop Stratigraphy



Maikop stratigraphic correlations over four measured sections. Perekeshkul West and Mount Islamdag Eastern Slope measured sections modified from Popov et al. (2008). Maikop lithology is primarily composed of silty claystones and shales, with varying levels of calcium carbonate in some intervals. Stratigraphic correlations were based on the biostratigraphic work of Popov et al. (2008) and the statiscal analysis of geochemical elements obtained from XRF and ICP-OES analysis. The results of the statistical heirarchal cluster analysis are displayed on the right with symbols indicating sampling locations within the stratigraphic columns. Statistics indicate that the SCB was a dynamic, rapidly changing basin at the time of Maikop deposition, as evidenced by regional variability of geochemical signatures. Further stratigraphic analysis and constraint will be completed as more data (specifically Re-Os dates, sulfur analysis, and platinum group element analysis) is received.

References

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Brunet, M., Korotaev, M.V., Ershov, A.V., Nikishin, A.M., (2003). The South Caspian Basin: a review of its evolution from subsidence modelling. Sedimentary Geology; 156, pp. 119-148.

Hudson, S.M., Johnson, C.L., Efendiyeva, M.A., Rowe, H.D., Feyzullayev, A.A., Aliyev, C.S., (2008). Stratigraphy and geochemical characterization of the Oligocene-Miocene Maikop Series: Implications for paleogeography of Eastern Azerbaijan. Tectonophysics, 451, 40-55.

Jones, B., & Manning, A.C., (1994). Comparison of geochemical indices used for the interpretation of palaeoredox conditions in ancient mudstones. Chemical Geology; 111, pp. 111-129.

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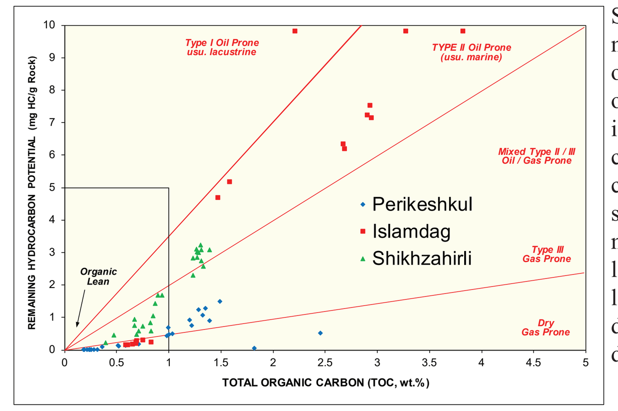
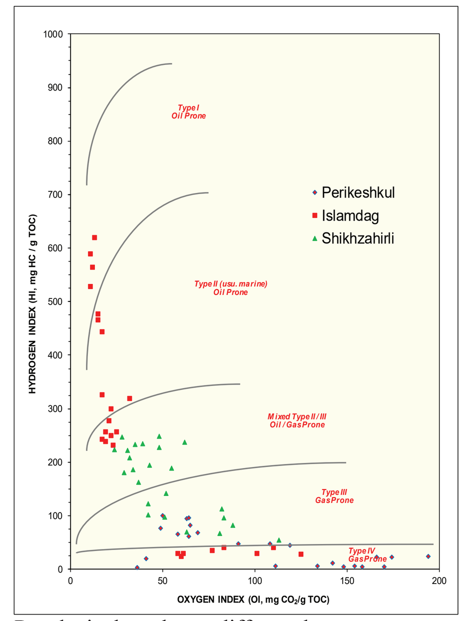
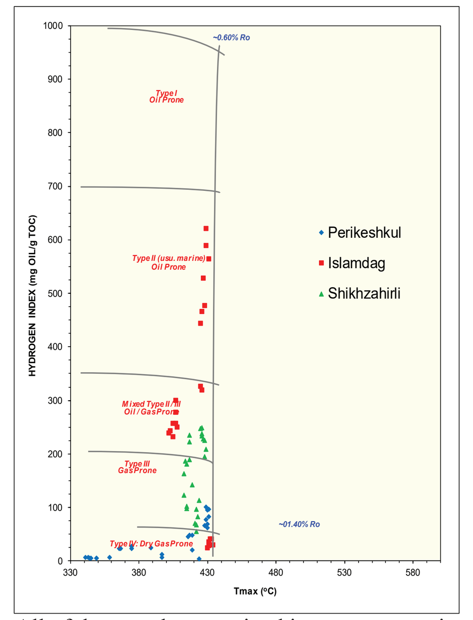
3 Source Rock Characterization



Source rock kerogen quality as measure by pyrolysis. About half of the samples were found to be organic lean, indicating that organic matter in the onshore Maikop is concentrated moslty in thin, discreet intervals of black shale (Hudson, 2008). These thin intervals may correspond to periods of isolation of the Paratethys Sea that led to restriction of circulation and development of anoxic water conditions.

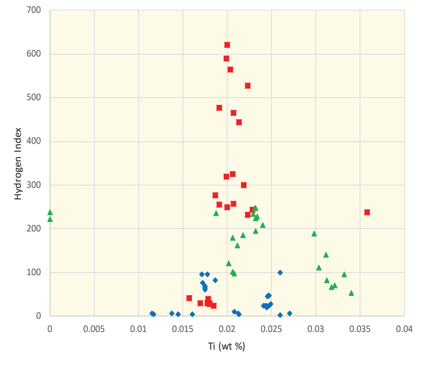


Pyrolysis data shows different kerogen types related to varying types of organic matter. Samples contain mixed-source marine and terrestrial organic matter. Organic matter type may influence Re & Os abundances in samples.



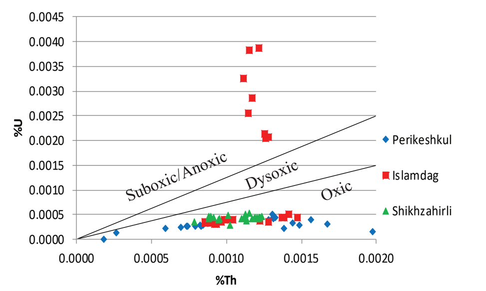
All of the samples contained immature organic matter due to insufficient burial and temperature. This is ideal for sample collecteion because it ensures that no carbon cracking has occurred that would cause the hydrogen index to be unreliable.

Hydrogen Index and Production Index plotted on a logarithmic scale display a strong negative correlation. Type III kerogen dominant samples show the strongest production index values, related to higher terrestrial organic matter input.

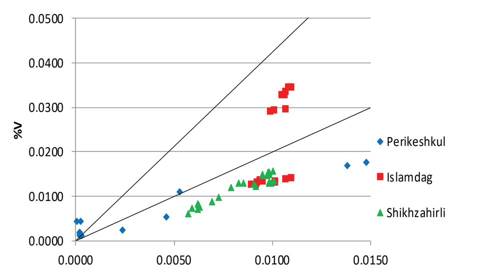


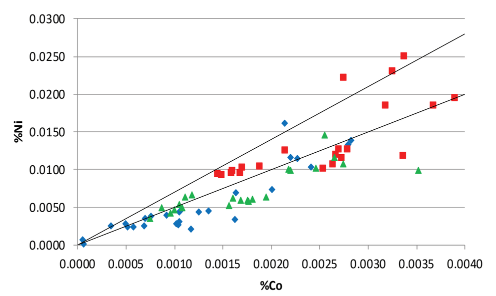
A weak correlation exists between the hydrogen index (HI) and Ti (wt %). An increase of terrestrial organic matter input raises the relative abundance of Ti and reduces the HI of the sample.

4 Maikop Depositional Oxygen Conditions

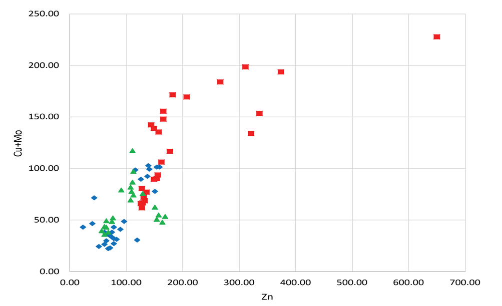


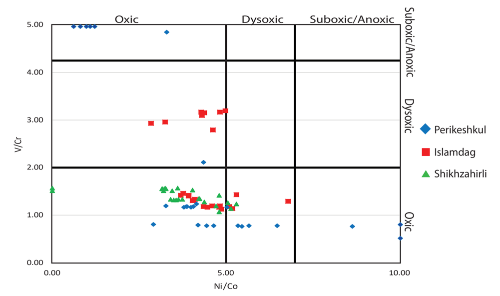
Ratios of redox-sensitive trace metals indicate whether sediments were deposited in oxic, dysoxic, or anoxic water conditions. Ratio values for each subsequent condition are from Jones & Manning (1994).
[Left] U/Th ratios indicate that one sample suite from Islamdag was deposited under anoxic conditions; oxic conditions prevailed in the rest.
[Right] V/Cr ratios support U/Th ratios, save for the Islamdag anoxic suite; V/Cr ratios indicate this suite to be deposited in dysoxic to anoxic water.



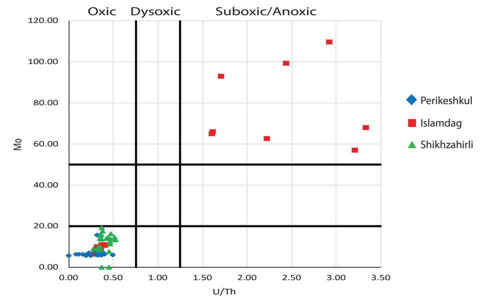


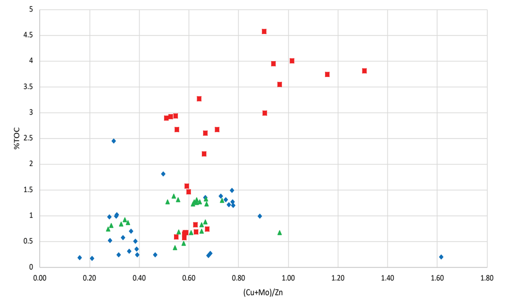
[Left] Ni/Co was shown by Jones & Manning (1994) to be a reliable indicator of oxygen water conditions. Ni and Co both increase with increasing organic matter in these samples, resulting in more scattered results.
[Right] (Cu+Mo)/Zn has been discussed as an unreliable indicator of reducing bottowm-water conditions (Jones & Manning, 1994). However, data from this study indicate a strong correlation, indicating this as a reliable ratio for reducing condition interpretation.



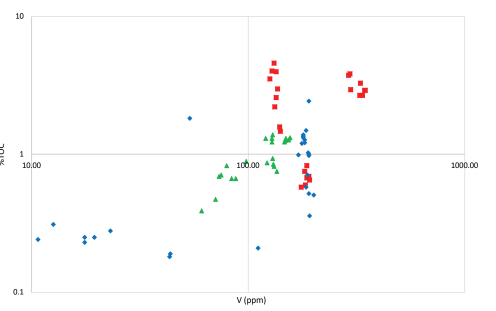


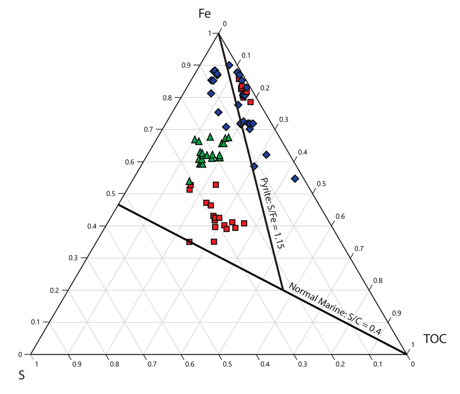
Plotting ratio indicators of oxygen water conditions highlights disagreements between ratios.
[Left] Comparison between Ni/Co and V/Cr suggests that most samples may reliably be considered to have been deposited in oxic conditions.
[Right] Data plotted between U/Th and Mo enrichment suggest a link between anoxic deposition and Mo enrichment. Higher Mo is useful for identifying prime samples for Re-Os geochronology.



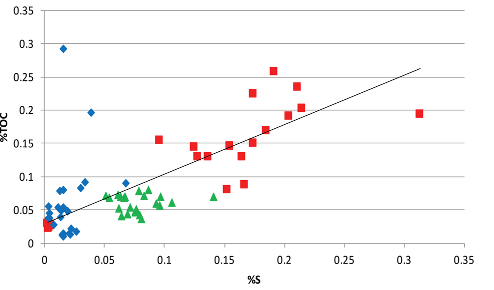


[Left] Geochemical indicator of reducing depositional conditions (Cu+Mo)/Zn) plotted against TOC show a good positive correlation between reducing water conditions and the preservation of organic matter, indicating that organic matter preservation is a result of anoxic, reducing conditions as opposed to over-production of organic matter.
[Right] V plotted against TOC shows a weak positive correlation, indicating higher preservation of marine organic matter.

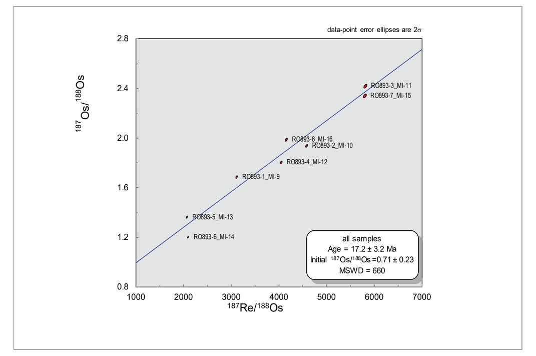




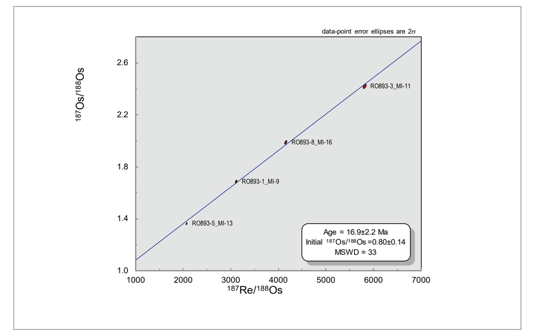
[Left] C-S-Fe relationships suggest iron enrichment in most samples, indicating that not all of the iron is bound in pyrite. Normal marine trend lines from Hudson et al. (2008).
[Right] Sulfur is shown to be strongly correlated with TOC, indicating strongly reducing water conditions during deposition of organic matter.

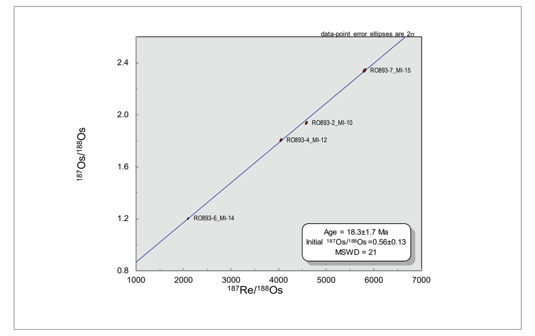


5 Re-Os Isotope Geochronology



Isotope geochronology for the middle Islamdag sample suite reveals a depositional age well within the Miocene. Prior studies based on microfaunal assemblages have placed this sction within the Late Oligocene.
The MWSD value indicates there is a high degree of scatter about the best-fit line (isochron), which most likely relates to variable initial osmium isotope compositions in the sample set.
All samples are extremely enriched in Re and 192Os, the implications for which are not yet understood.





Cyclic variability in the sample isotope ratios suggest variable initial Os isotope compositions. When broken into two separate isochrons, the MSWD is reduced to 33 and 21, respectively. Given the identical age of the two isochrons (within error), variations in initial Os probably relates to environmental changes in a very dynamic basin.

6 Conclusions

- The bulk of samples were deposited in oxic conditions, with one sample suite from Islamdag deposited in dysoxic to anoxic conditions. This supports the conclusions of Hudson et al., (2008) that most of the Maikop in the Kura Basin was deposited in oxic water conditions, with anoxic conditions reflected in thin, discreet intervals of black shale.
- The thin intervals of black shale are thought to correspond with the initial periodic isolation of the Paratethys Sea. The anoxic Islamdag suite showed an Re-Os isochron age of deposition in the Miocene, indicating that the Paratethys Sea was still undergoing periodic isolation well into the Miocene and had not yet been terminally isolated from open water circulation.
- Periodic isolation of the Paratethys Sea into the Miocene resolves that terminal isolation was not the result of the large climate-induced seawater drop at the Eocene-Oligocene Transition. It is likely that terminal isolation occurred as the Arabian Plate continued to converge with the Eurasian Plate, resulting in upwelling and closure of ocean seaways.
- Correlations between TOC and redox-sensitive metal ratios indicate that organic matter preservation in the SCB was the result of the development of suboxic to anoxic bottom-water conditions, not from a high flux of terrestrial organic matter or marine organic matter over-production.
- The application of chemostratigraphy to the Maikop added resolution to the stratigraphic correlations of the Maikop regionally.

Future Work

- More accurate sulfur analysis will be obtained via Leco Sulfur Analysis, and further sulfur analysis will be performed.
- Platinum group elements (Pt, Pd, Rh, Ir, Ru, Au, Re, and Os) analysis will be performed. These elements will be useful for constraining paleoclimate based on enrichment values compares to average continental crust.
- Os isotopes will be examined for correlations to the Os excursion that occurred around the Eocene-Oligocene Transition on rocks argued to be deposited around that time interval
- Four more Re-Os isochron ages will be obtained for samples on the lower and upper portions of the stratigraphic sections in order to further develop stratigraphic correlations, basin evolution, and paleo-environmental conditions.