RE-OS GEOCHRONOLOGY AND CHEMOSTRATIGRAPHY OF THE MAIKOP SERIES PETROLEUM SOURCE ROCKS OF EASTERN AZERBAIJAN

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Abstract

The Oligocene-Miocene Maikop Series is a world-class source interval that is the most important petroleum source rock for the petroleum systems of the South Caspian Basin (SCB) and surrounding region. The Maikop is a thick (up to 3 km) succession of silty mudstones with intervals containing up to 15% total organic carbon (TOC). Despite years of study, correlation of organic-rich intervals within the South Caspian Basin and beyond to basins of the Eastern Paratethys is problematic. Current age constraints are based primarily on microfaunal assemblages, but the assemblages are lacking in precision and are sparsely dispersed between intervals.

This study provides a much-needed numerical age datum in Maikopian strata that may be used to improve correlation of organic-rich intervals both locally and regionally. The numerical age date obtained in this study was produced via Re-Os isotope geochronology. Of the five sample suites analyzed in this study, one Re-Os data set yielded an isochron of 17.2 ± 3.2 Ma. Re-Os data sets that failed to produce statistically meaningful isochrons provide qualitative age constraint by comparing calculated initial $^{187}Os/^{188}Os$ ratios from these samples to the geologic history of $^{187}Os/^{188}Os$ ratios in seawater through time. Additionally, geochemical analysis of the sample suites used for Re-Os geochronology was performed to better understand the redox conditions and sediment source at the time of deposition. Relative enrichment in detrital elements (e.g. Ti, Al), enrichment factors and ratios of redox-sensitive trace metals (to indicate oxic, suboxic, or anoxic conditions), and pyrolysis characterization were performed on all samples. The most notable results indicate that the sample suite dated at 17.2 Ma was deposited in a suboxic to anoxic environment where the anoxia may have been the result of limited basin isolation resulting from tectonics influencing relative sea-level change and sediment provenance.

Introduction

The Oligocene-Miocene Maikop Series was deposited in the ancient Paratethys Sea, an epicontinental sea that evolved from the unrestricted Tethys Ocean. The Maikop Series was deposited throughout the ancient Paratethys, making deposits of the Maikop identifiable across an extensive region, from as far west as the Eastern Black Sea and as far north as the northern portion of the central Caspian region (Green et al., 2009). Due to its association with the Paratethys Sea, the Maikop is often studied to unlock clues pertaining to the evolution of the Paratethys and the factors that affect it, including climate, tectonics, eustacy, etc. (Rogl, 1999; Popov et al., 2008; Hudson et al., 2008; Johnson et al., 2009). Furthermore, the Maikop Series is considered the primary source rock for numerous petroleum systems in basins throughout the Paratethys (see Sachsenhofer et al., *this issue*).

A prime area in which to study the Maikop Series is in eastern Azerbaijan, where deposits of the Maikop may be found plentifully in outcrop along the flanks of the Greater Caucasus Mountains. Additionally, the South Caspian and Kura Basins of eastern Azerbaijan produce large volumes of hydrocarbons primarily sourced from the Maikop Series (Isaksen et al., 2007; Bechtel et al., 2014), making the study of the Maikop in this area key to understanding organic matter preservation, maturation, and hydrocarbon migration associated with these accumulations. However, problems with correlating organic-rich intervals of Maikop strata still persist after decades of study. As discussed in Sachsenhofer et al., *this* issue, results between studies of organic-rich intervals of Maikopian strata in this region do not yield a consistent timing of deposition (Hudson et al., 2008; Johnson et al., 2009; Bechtel et al., 2014). The differences in timing may be due to major lateral variability in source rock parameters, or they may reflect problems with age dating (Sachsenhofer et al., *this issue*).

Problems with constraining the age and lateral connectivity of Maikopian strata arise from the nature of Maikopian lithology. The Maikop Series is composed primarily of mudstones largely barren of microfauna, with only sparse intervals bearing diagnostic microfaunal assemblages. This makes the Maikop notoriously difficult to constrain stratigraphically and geochronologically through traditional methods. To address this problem, this study has produced a numerical age date through Re-Os isotope geochronology of organic-rich mudstones in order to provide an age datum for an event of high organic-matter preservation. This age constraint provides a much-needed datum for previous (and future) stratigraphic efforts in the SCB and beyond. Furthermore, this study constrains the depositional conditions present at the time of deposition in order to increase the utility of these sample suites in correlation to other localities where extensive geochemical characterization has been done. Geochemical analyses of the sample suites give clues as to the detrital input, organic-matter type and preservation, bottom-water oxygenation, and the connectivity of the Kura Basin with the open ocean during time of deposition. However, in this extended abstract, only the numerical and qualitative age dates produced via Re-Os geochronology will be discussed; the full results will be available in the complete article (Washburn et al., *in press*).

Materials and Methods

Samples of pre-Maikop (Koun) and Maikop strata were taken from three sample sites: Perikeshkul, Mount Islamdag, and Shikhzahirli (Figure 1). Sample sites were chosen from strata where work focused on microfaunal assemblages and chemostratigraphy has previously been performed (Popov et al., 2008; Hudson et al., 2008; Johnson et al., 2009). Samples were collected from dark, presumably organic-rich intervals in lower, middle, and upper stratigraphic horizons at each of the sample sites. In order to produce enough geochemical heterogeneity to produce an isochron in Re-Os geochronology, eight samples were taken from each horizon across a vertical range of 20-50 cm per sample suite. Nine sample suites were collected in total from the three localities, with at least eight samples from each suite. Care was taken in sample collection to avoid hydrothermal features and any surficial weathering, as these have been shown to alter the Re-Os geochemistry of the mudstones (Pierson-Wickmann et al., 2002; Georgiev et al., 2012).

Of the nine sample suites collected, five were selected for analysis of Re and Os based on their elevated organic matter content and their abundance of Mo (determined through XRF and ICP-OES analyses), which is commonly associated with Os. Sample suites chosen included suites I-1, I-3, P-1, P-3, and S-1 (Figure 2). Re and Os occur in organic-rich mudstones in ppb and ppt, respectively. They are strongly sidero- and chalcophilic, so great care was taken to ensure that samples were not contaminated or geochemically altered prior to analysis.

Samples selected for Re-Os geochemistry were larger (~50-100 g in size) to ensure their geochemical representation of the lithologic unit. As Re and Os are chalcophilic and siderophilic, samples were polished with silica carbide grit pads to remove any contamination with metal tools, then powdered in an alumina-ceramic shatterbox to yield 30-80 g of powdered sample. Samples were then digested in acid and the Re and Os isolated using a series of chemical washes using the process outlined in Selby and Creaser (2003). The resulting Re and Os was then analyzed using negative thermal ionization mass spectrometry (N-TIMS) in a Thermo Scientific Triton TIMS instrument, which allows measurement of Re and Os at the nanogram to subnanogram concentration, respectively, with accuracy up to ±0.5% 2σ (Volkening et al., 1991; Creaser et al., 1991).

Results

Of the five sample suites analyzed for Re-Os geochronology, only the Re-Os data for one sample suite successfully produced a geological meaningful age and uncertainty: the Islamdag I-1 sample suite. Collectively the Re-Os data for the Islamdag I-1 possess $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ values of ~2000-6000 and ~1.0 and 2.3, respectively that are positively correlated. The entire sample set yield a Re-Os date of 17.2 ± 3.2 Ma, with an initial $^{187}Os/^{188}Os$ of 0.71 ± 0.23. However, significant scatter is exhibited by the data set about the best-fit line as described by the exceptionally high mean square of weighted deviates (MSWD) value of 660. However, samples plot at regular intervals above and below the line of best fit that describes the isochron. When split into two subsets, one representing those that regularly plot above the line of best fit, and the other representing those that plot below the line of best fit, two statistically meaningful isochrons are produced. The two subsets yield Re-Os dates of 16.9 ± 2.2 Ma (initial $^{187}Os/^{188}Os$ = 0.80 ± 0.14, MSWD = 33) and 18.3 ± 1.7 Ma (initial $^{187}Os/^{188}Os$ = 0.56 ± 0.13, MSWD = 21). Both date determinations are identical within uncertainty.

Discussion

Re-Os geochronology, though only successful for one of the five sample suites, provides important new data in the South Caspian and Kura Basins. An age date of ~17.2 Ma for the lower Islamdag sample suite provides a datum of reference for the extensive bio-, chemo-, chrono-, and lithostratigraphic data that has been collected throughout the Kura Basin and possibly the SCB. The only puzzling aspect of the Re-Os geochronology is the production of two isochrons of identical date, but differing initial $^{187}Os/^{188}Os$ compositions. The reason for the split is unknown, as there are apparently no other elements analyzed in this study that show the same separation pattern between samples. It may be possible that the differences are the result of rapid, dynamic changes within the hydrodynamics of the basin at the time of deposition. These rapid changes may be the result of increases and decreases in restriction in the SCB caused by tectonics, relative sea level change, or a combination of the two.

Despite the failure of the other sample suites to produce statistically meaningful isochrons, the information obtained from their Re-Os geochemistry is useful. Using the amounts of radiogenically decayed versus undecayed Os isotopes ($^{187}Os/^{188}Os$, respectively), a qualitative age of deposition was determined for each of the sample suites. This was done by comparing the values of calculated initial $^{187}Os/^{188}Os$ with values from the global seawater $^{187}Os/^{188}Os$ ratios through time (Figure 3; Peuker-Ehrenbrink & Ravizza, 2012). For example, analyzed pre-Maikopian (Koun) strata results displayed an $^{187}Os/^{188}Os$ ratio of 0.39 (Figure 2). This low ratio compares strongly with the Os excursion that took place near the Eocene-Oligocene Transition (EOT), thereby providing strong evidence that the Maikop did not begin depositing until after the EOT. The $^{187}Os/^{188}Os$ ratio of 0.74 from suite P-3 is similar to the ratio produced by suite I-1 and corresponds to a long period of stability from the Oligocene through the Middle Miocene. Suites P-3 and I-1 are correlated based on this similarity (Figure 2). Suite S-1 has an $^{187}Os/^{188}Os$ ratio of 0.80, which correlates strongly with ratios from the late Middle Miocene, suggesting it is the youngest sample suite analyzed. Correlations in Figure 2 were strengthened using cluster analysis of geochemical analyses on each sample; these results are discussed in detail in Washburn et al. (*in press*).

In addition to qualitative age dates, comparison of the $^{187}Os/^{188}Os$ ratios with global seawater values through time provide an indicator of basin restriction. Restriction leads to either the relative enrichment or depletion of Os isotopes, resulting in a significant deviation of $^{187}Os/^{188}Os$ ratios from the geologic record (Figure 3). The correlation between $^{187}Os/^{188}Os$ ratios from Miocene Maikopian strata of the Kura Basin and global oceanic ratios indicates that the Kura Basin was actively communicating with open marine waters during much of the Miocene. Only one sample suite showed a significant variation in Os isotope ratios: sample I-3. This sample is stratigraphically younger than the 17.2 Ma sample (I-1) at the same outcrop (Figure 2), leading to an interpretation, consistent with Popov (2008) and others, that it is middle Miocene in age. The measured $^{187}Os/^{188}Os$ ratio for this sample suite is inconsistent with global open marine Miocene values (Figure 3), indicating that the Kura Basin was periodically restricted in the middle Miocene.

Conclusion

A new numerical age date constraining an organic-rich interval of Maikop deposition at ~17.2 Ma has been developed using Re-Os geochronology. This numerical age date is a valuable tool for improving past and future correlations of the Maikop in the Kura and South Caspian Basins, and possibly between other deposits of the Maikop (and equivalent formations) throughout the ancient Paratethys Sea. The matching of $^{187}Os/^{188}Os$ ratios of Maikop in the Kura Basin with those of open marine deposits provides qualitative age dates and suggests that the Kura Basin was in open communication with marine waters throughout most of the Miocene, with periodic restriction becoming more common at the top of the section. Further geochemical analyses of these age-constrained sample suites allows better correlation with other outcrops across the basin, and will soon be released in Washburn et al., *in press*.

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