

GEOCHEMICAL EVIDENCE FOR TWO STAGES OF HYDROCARBON EMPLACEMENT AND THE ORIGIN OF SOLID BITUMEN IN THE GIANT TENGIZ FIELD, KAZAKHSTAN

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Tengiz is a giant oil field on the northeastern coast of the Caspian Sea in Kazakhstan that produces a high gravity, H₂S-rich oil from a reservoir containing abundant solid bitumen. Several lines of geochemical and petrographic evidence suggest there were at least two stages of petroleum migration into the Tengiz reservoir, both generated off-structure from a marine source rock. The initial charge gave rise to solid bitumen, perhaps by a deasphalting process. Bitumen formation was followed by a period of hydrothermal activity which thermally matured the bitumen to an insoluble pyrobitumen, produced bitumen-free pores, precipitated calcite on the bitumen, and mineralized portions of the Tengiz flank. Finally, a second petroleum charge, most likely from the same source at higher maturity, accompanied by a significant influx of H₂S arising from thermochemical sulfate reduction (TSR) deep in the basin, filled Tengiz with its present-day oil.

The Tengiz reservoir consists of Carboniferous and Devonian limestones with mostly grainstone and packstone textures that define an isolated mound with a central platform and surrounding flank. Dolomitization and silicification are rare; cements are sparry calcite. The reservoir is divided into Unit 1 (~3,950 - ~4,500m), Unit 2 (~4,500 - ~5,100m), and Unit 3 (~5,100 - >5,600). Porosity average is 7% BV (range 0-20%). Where solid bitumen is abundant it typically occupies 3% BV (range 0-15%), but bitumen occupies <1% BV in large parts of the reservoir. Bitumen is commonly encapsulated with calcite cement. Typically production preferentially enters bore-holes from a few meters-thick intervals. Top reservoir temperature is 105°C and initial pressure was 11,500 psi.

Tengiz Oil

Tengiz reservoir fluid with density = 0.63 g/cc, GOR = 2,700 scf/stb, and Bo = 2.14 rb/stb consist of 13 mol.% (8.1 wt.%) H₂S, 44 mol.% CH₄, 14 mol.% C₂₋₃, 11 mol.% C₄₋₇, 18 mol.% C₈₊, δ³⁴S [CDT] of the H₂S is estimated at +14 to +16‰ based on five samples of waste sulfur resulting from quantitative removal of H₂S prior to export, Tengiz export crude is a 46.5⁰ API gravity light oil.

Well-head oils display remarkable homogeneity. Analysis of 27 oils show that compositional variation is within analytical error for bulk (API [-42⁰], sulfur [0.5 wt.%,] δ¹³C [-29‰ δ¹³C {PDB}], δ³⁴S [+11 to +14‰], and compound class) and molecular properties (C₇ isomers, sterane biomarkers, and atomic sulfur distributions). Group type separation typical of light oils, is dominated by saturated hydrocarbons with moderate aromatic content, a few percent NSO resins, and no asphaltenes (Table. 1). Detailed gas chromatograms are unable to differentiate the oils (Fig. 1). The star diagram in Figure 1 shows only minor differences between 12 non-paraffin pick ratios among the 27 oils. C₇ and biomarker data suggest that the present-day Tengiz oil was generated from a marine algae source rock at a late stage of thermal maturity.

Table1. Group Type Separation of 17 Tengiz Well-Head Liquids (weight %).

Saturates	Aromatics	NSO Resins	Asphaltenes	API Gravity
75 to 79	19 to 22	2 to 4	nil	40 to 45 ⁰

Organic sulfur species are dominated by dibenzothiophenes with moderate amounts of benzothiophenes and small amounts of thiophenes and thiols (mercaptanes). The chromatogram in Figure 2 shows the distribution of organic sulfur compounds measured using an atomic emission detector. Compositional groups defined using organic sulfur chromatograms are not robust. For example, native

sulfur (S₈) occurs in the 0.01-0.2 wt.% level in about half our samples, but its occurrence is not consistent in samples collected from the same well-head 18 month apart. These data can not be used as a guide to reservoir compartmentalization, rather they may be related to differences in sampling, well production, and/or well-bore chemical reactions.

More than 10 vol.% of well-head oil precipitates at room temperature as <1 x 10 micrometer-size wax crystals with a molecular composition, measured by high temperature gas chromatography, showing *n*-paraffins near C₄₀ with an even-over-odd carbon-number preference, and *n*-paraffins near C₆₀ with an odd-over-even carbon-number preference (Figure 3). Similar preferences occur in oils sourced from the Devonian Duvernay calcareous marine shale source in Alberta, Canada. Waxes as heavy as C₉₀ occur in minute quantities.

Solid Bitumen

Solid organic matter that fills about one-third of the potential porosity is bitumen – i.e., secondary solidified petroleum, and not primary kerogen. The bitumen is a pyrobitumen based on its: (1) vanishingly small solubility in toluene and methylene chloride, (2) overall high reflectivity, (3) low H/C atomic ratio, and (4) occurrence of mosaic reflectivity texture. Solid bitumen occurs in: (1) microporosity within foraminifera tests, oolites, and other carbonate particles, (2) interparticle porosity and moldic vugs, and (3) fractures and stylolites.

Two key petrographic observations are: (1) occurrence within bitumen-filled rocks of bitumen-free vugs suggesting post-bitumen dissolution, and (2) sparry calcite cement over bitumen indicating post-bitumen calcite precipitation. Both observations are confirmed by most workers who examined Tengiz core and thin sections (e.g., Mitch Harris and Ray Garber, personal communication). These observations require multiple hydrocarbon migration events at Tengiz because the reservoir must be oil-saturated for bitumen to form, subsequently brine-saturated for post-bitumen vugs and sparry calcite cement to form, and finally oil-saturated a second time to account for the present-day oil.

Bitumen abundance ranges from 0 to 15 vol.%; there are a few 1-m occurrences of 50% bitumen. General bitumen distribution does not appear systematic. Bitumen is generally more abundant in Unit 1 relative to Unit 2, and generally more abundant in platform rim and flank wells (1 to 7 vol.%) relative to platform interior wells (<2 vol.%). Bitumen occupies 0-100% of the potential porosity (defined as measured core porosity plus measured core bitumen, Figure 4). Bitumen appears to occupy a larger fraction of potential porosity in Bashkirian (upper-most ~90 m) relative to deeper formations, but some low porosity intervals in Unit 2 display 100% bitumen filling.

Systematic sampling of Tengiz bitumen demonstrates that it is quite homogeneous with 81.6 wt.% C, 8.1 wt.% S, H/C atomic ratio of 0.81 (Table 2); $\delta^{13}\text{C} = -30$, and $\delta^{34}\text{S} = +7$ to $+9\text{‰}$ (Table 3). Solubility is ~1% in toluene and methylene chloride, but significant solubilities are reported in cocktails of more polar organic solvents. Pyrolysis-gas chromatograms of Tengiz bitumen yield molecular patterns quite similar to present-day oil.

Table 2. Chemical Composition of 29 Isolated Bitumen Samples from Tengiz-8

Element	C (wt.%)	H (wt.%)	O (wt.%)	N (wt.%)	S (wt.%)	H/C (atomic)
Normalized Mean	81.6	5.5	3.7	~1	8.1	0.81
Standard Deviation	1.7	0.3	1.7	~	0.78	0.04

Paleothermometry

The best paleothermometric information from bitumen reflectivity is provided by the occurrence of mosaic texture that suggests “rapid” heating. Attempts to use bitumen reflectivity like vitrinite reflectivity to estimate paleothermometry are not successful because of the complexity of bitumen reflectivities. Bitumen reflectivities from a single sample may range from 0.2% to over 1.5%, commonly with several modes (Figure 5). Multiple modes are in conflict with bitumen H/C ratios that are homogenous throughout Tengiz because higher reflectivities are caused by aromatization which decreases H/C ratio. Some individual large bitumen grains contain a high reflectivity core with a low reflectivity rim. Fine-grained bitumen always displays low reflectivity. These relations suggest that the low reflectivities are an alteration product, due to absorbed present-day oil but does not constrain a sample’s “correct” reflectivity.

Fluid inclusions from wells Tengiz-8 and Tengiz-22 yield abundant petroleum and aqueous fluid inclusion from Units 1 and 2. Aqueous inclusions (from all depths studied) yield homogenization temperatures (*Th*): from 78 to 120⁰C with a major mode at 85-95⁰C and a minor mode at 112-116⁰C (Figure 6); final melting temperatures indicate 1-5 wt.% NaCl equivalent salinities.

Petroleum inclusions display a range of fluorescence from blue to yellow. *Th* ranges from 25-45⁰C in blue fluorescing inclusions and 45-60⁰C in yellow fluorescing inclusions. Yellow fluorescing inclusions typically contain asphaltic precipitates. API gravity for most inclusions are 44-50⁰ (close to the export crude), but PVT considerations suggest that petroleum inclusions are not simply-trapped present-day oil. Gas chromatograms of crushed fluid inclusions yield molecular patterns quite similar to bitumen pyrolysate and present-day oil.

History of Tengiz Hydrocarbons

Geochemical and petrographic evidence suggest a complex history for bitumen formation and oil entrapment in Tengiz. Although there is no geochemical or petrographic data that absolutely proves our model for two stages of oil emplacement in Tengiz, there are supporting and consistent observations. These include:

- Bitumen-free pores and sparry calcite cement after bitumen require formation after or simultaneous with bitumen emplacement. After the first reservoir filling and solid bitumen formation, there must have been a period of brine saturation, followed by a second-stage of filling of present-day oil.
- Bitumen probably formed by deasphalteening from first generation oil (modeled by the yellow fluorescence inclusions). The high sulfur in bitumen (8 wt%) is consistent with sulfur enrichment from an oil higher in sulfur than present-day oil.
- The nearly identical, $\delta^{13}\text{C}$ and similar chromatograms suggest bitumen and present-day oil are genetically related. $\delta^{34}\text{S}$ of H_2S and present-day oil are similar, but differ from bitumen. Bitumen formed from petroleum should display only a small $\delta^{34}\text{S}$ fractionation – but we observe a large $\delta^{34}\text{S}$ difference (+4‰) suggesting that the sulfur in the oil has a contribution from another sulfur source, likely TSR. Hydrous pyrolysis experiments (Z. Aizenshtat, personal communication) show -7 to -16 $\delta^{34}\text{S}$ fractionation between (light) H_2S and (heavy) oil- but we observe Tengiz H_2S heavier than the oil by a few ‰, again suggesting independent sources.
- The large amount of H_2S in Tengiz (8 wt.% of the reservoir fluid) demands an inorganic source for the sulfur. Thermochemical sulfate reduction (TSR) is the obvious process. But there is essentially no anhydrite cement in Tengiz, and Tengiz is too cool (present temperatures = 105-

123⁰C in the upper km, and fluid inclusions suggest the temperature was never higher) to sustain TSR within the reservoir. We suggest TSR between second-stage migrating Tengiz oil and sulfate-rich aqueous fluids (derived from the overlying evaporite) took place downdip in the basin near the oil's source where temperatures were considerable hotter. The TSR not only added H₂S to the migration oil, but increased the oil's $\delta^{34}\text{S}$ distinguishing second-stage (present-day) oil from first-stage oil that produced the bitumen.

- Yellow fluorescence hydrocarbon fluid inclusions typically contain solid organic matter. Since the chemical composition of oil within these inclusions was fixed, the solid hydrocarbon probably precipitated during core recovery. This suggests that despite the similar gravity between yellow and blue fluorescing inclusions. We suggest that the oil in the yellow fluorescing inclusions represents the first generation migrated oil, and that oil contained enough heavy components to form a bitumen.

Following bitumen formation, the Tengiz reservoir was breached, probably by faulting the salt seal; brine replaced first generation oil causing observed calcite dissolution and precipitation. After an unknown interval, the reservoir is resealed and filled with second generation. Present-day oil, probably from the same, or similar, evolving source but now affected by TSR, as suggested by the similarity of bitumen and present-day oil's $\delta^{13}\text{C}$ and molecular pattern, and $\delta^{34}\text{S}$ systematics described above.

An alternate suggestion is that the reservoir was breached before bitumen formation allowing hydrothermal solutions to pass through the reservoir transforming residual oil to solid bitumen and causing calcite dissolution and precipitation (Bill Hallager, personal communication, 1997). Although we do not completely reject this suggestion, we note that the fluid inclusion temperatures are not high enough to crack residual oil and homogeneity of bitumen chemical composition is not consistent with hot spots expected along pathways of hydrothermal flow.

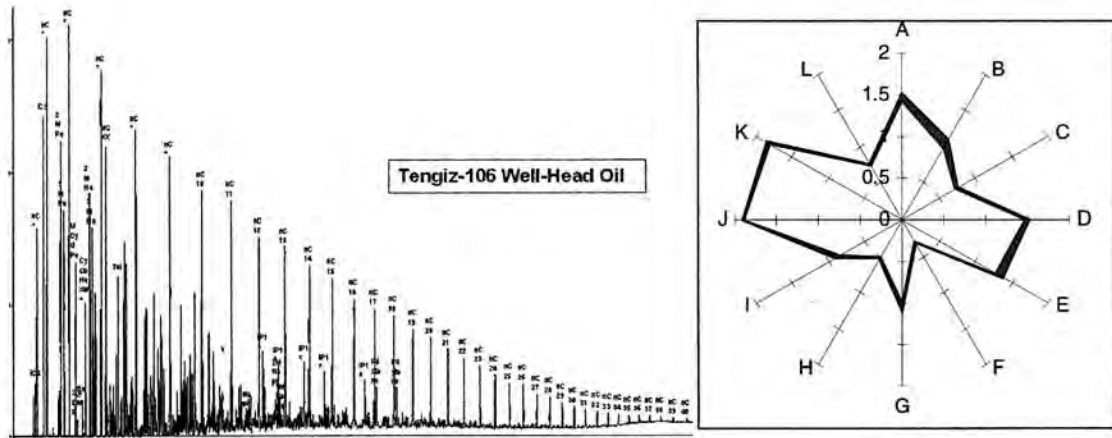


Figure 1. Molecular composition of Tengiz well-head oil. Left is a typical gas chromatogram. Right is a star diagram that illustrates oil's homogeneity as evidenced by small range of values along each of 12 axes that represents different peak ratios.

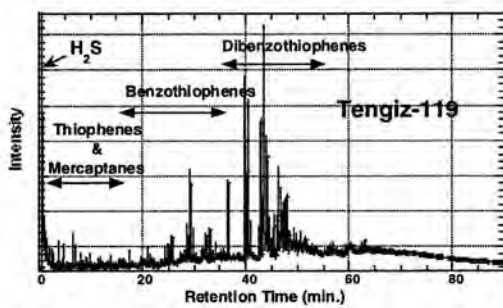


Figure 2. Sulfur fingerprint for Tengiz-119 well-head oil.

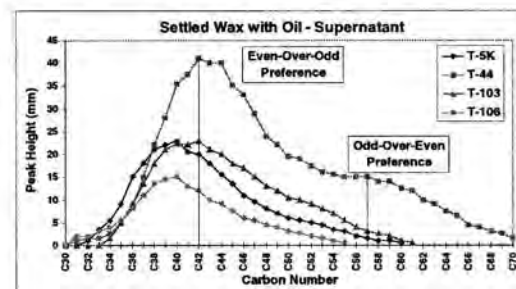


Figure 3 n-Paraffin distribution in wax precipitated from Tengiz oil.

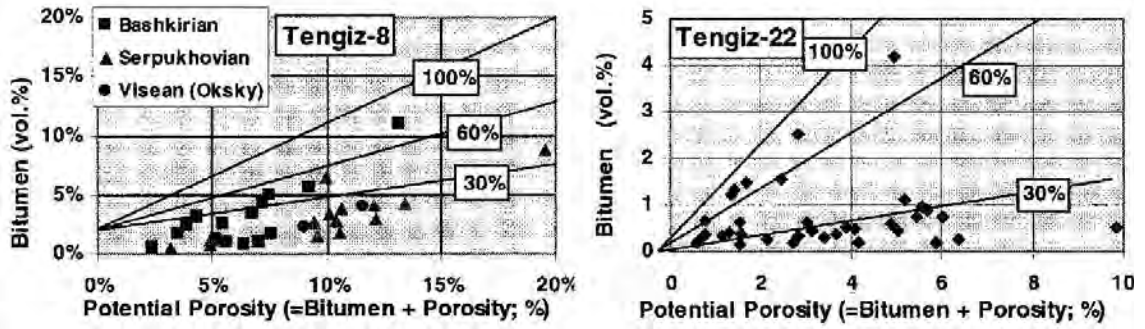


Figure 4. Bitumen in relation to potential porosity is similar in wells with different overall porosity. Tengiz-8 is a platform rim well and Tengiz-22 is a platform interior well.

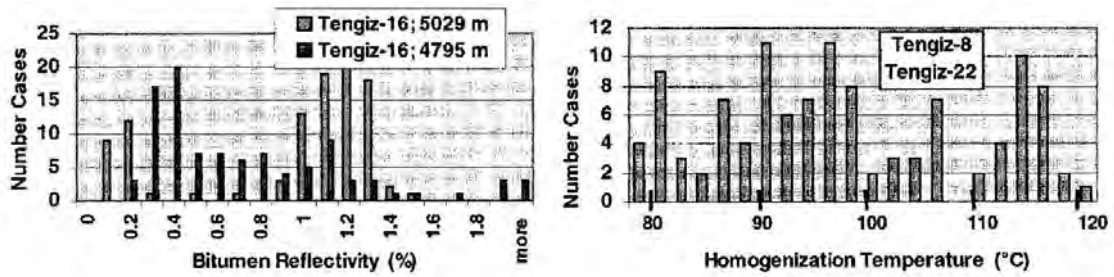


Figure 5. Bitumen reflectivities from 2 samples.

Figure 6. Aqueous fluid inclusion Th from 2 samples.