

# GEOCHEMISTRY OF THE APUK GAS SEEP ALONG THE COLVILLE RIVER—EVIDENCE FOR A THERMOGENIC ORIGIN

by  
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## INTRODUCTION

The Brooks Range Foothills of Alaska's North Slope are generally considered gas prone with mean estimates of undiscovered, technically recoverable natural gas reported in the tens of trillions of cubic feet (Houseknecht and Bird, 2006; Garrity and others, 2005; Bird and Houseknecht, 2002; Schuenemeyer, 1999). Despite the large size of this assessed resource, the province remains underexplored and more data are required to evaluate details of the gas component of the petroleum system (for example, Nelson and others, 2006; Burruss and others, 2003).

This report summarizes new data from the Aupuk gas seep along the Colville River (Ikpiukuk River Quadrangle; fig. 1). The gas seep was discovered by a U.S. Navy geological field party in 1945 near Kakvuiyat Bend upstream of the confluence of Aupuk Creek with the Colville River (figs. 1 and 2). The area was revisited in 1946, 1947, and 1950 by U.S. Geological Survey (USGS) field parties (Chapman and others, 1964). Compositional data from samples analyzed in 1946 were reported by Chapman and others (1964) and indicated the seep was dominated by methane, although available technology did not allow them to assess whether the gas was biogenic or thermogenic.

During recent stratigraphic investigations of the Albian–Cenomanian Nanushuk Formation (LePain and others, 2008, this volume), we were able to relocate the still active seep and sample it for modern geochemical analyses. Three gas samples were collected from the seep during 2005 and 2006 and analyzed for both molecular composition and stable isotopic data.

## SEEP DESCRIPTION AND SAMPLE COLLECTION

The seep is located in a small meander scar lake shown in figure 2. Rubbly exposures of Nanushuk Formation sandstone form the moderately steep slope immediately south of the seep. During the first visit in 2005, gas bubbles emanated from a single point in water less than 60 cm deep on the south side of the lake, approximately 12 m from

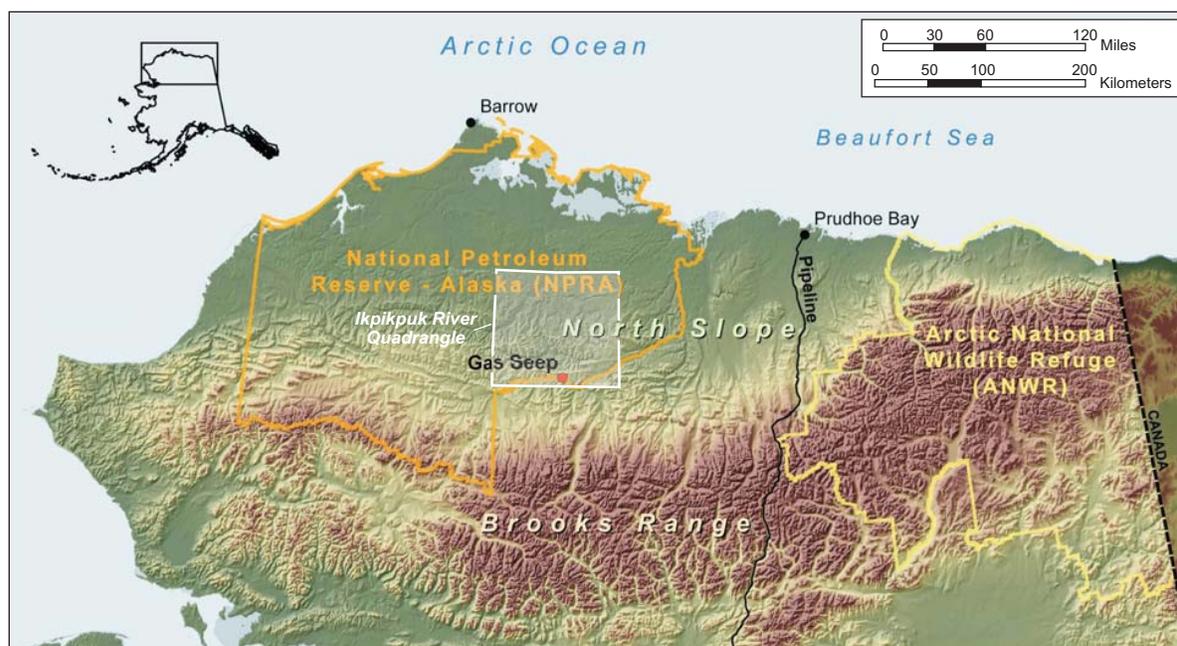


Figure 1. Regional map of northern Alaska showing location of the Aupuk gas seep. See figure 2 for more detailed map and coordinates.

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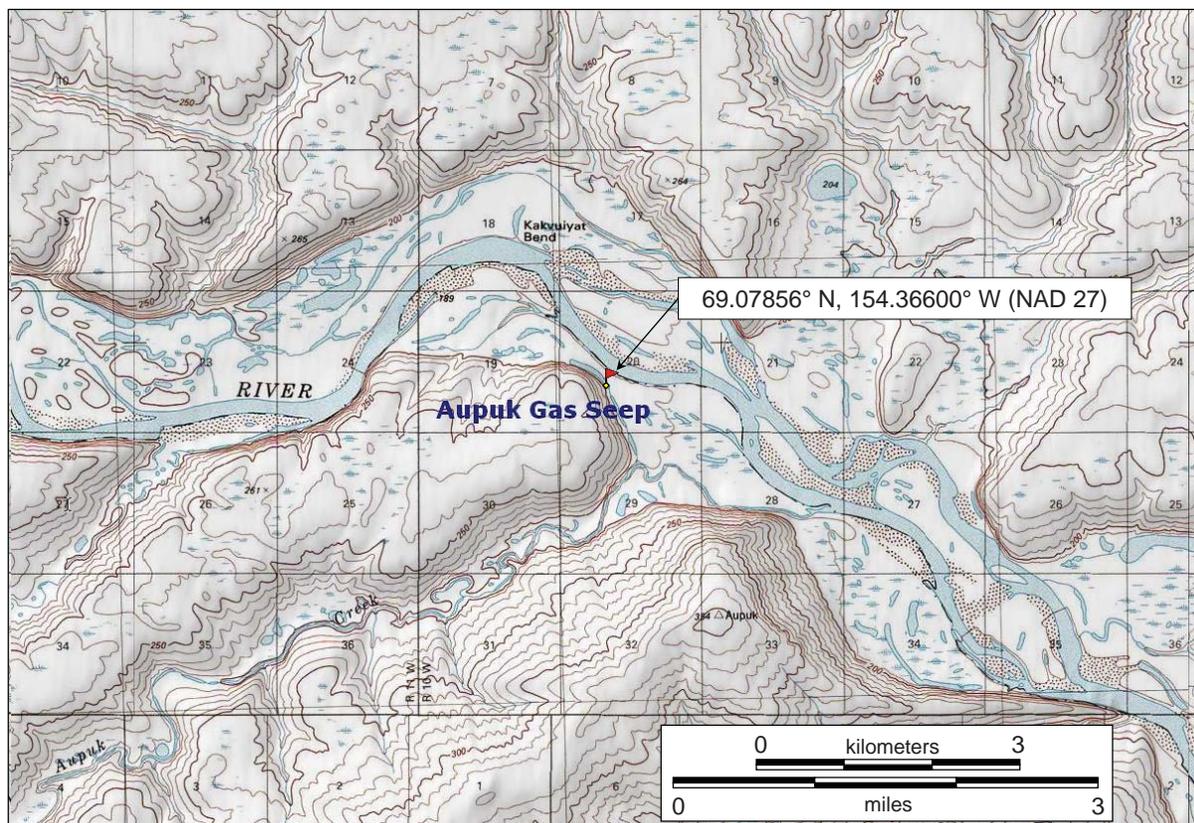


Figure 2. Location of the Aupuk gas seep sampled during the 2005 and 2006 field seasons, between Kakvuiyat Bend and the confluence of Aupuk Creek on the Colville River.

the southeast end (fig. 3). Bubbles rose from the lake bottom in continuous streams lasting 2–3 seconds with no more than 15 seconds between subsequent episodes<sup>3</sup>. In 2006, the seep was far more active, with approximately 20 bubble streams observed within a ~15 m radius, a level of activity analogous to that observed in the early USGS investigations (Chapman and others, 1964). The 2006 samples were collected from what appeared to be the same vent as the 2005 sample. All samples were collected by allowing the bubbles to displace approximately 200 ml of water from an inverted 250 ml I-Chem amber glass sample bottle (fig. 3d).

The 2005 sample was analyzed for composition at CoreLab in Calgary, Alberta, then forwarded to the Department of Earth and Ocean Sciences at the University of Victoria in Victoria, British Columbia, for methane isotope analysis. Two additional gas samples were collected in 2006 and analyzed at Intertek Westport Technology Center, Houston, Texas.

## COMPOSITION AND METHANE ISOTOPIC ANALYSIS

Table 1 presents results for all known analyses of the Aupuk gas seep, including data from 1946 reported in Chapman and others (1964). Because of known or suspected air leakage into their samples, Chapman and others (1964) reported the gas composition in two columns: column A gives the composition on a dry basis but including air, and column B gives results on a dry, air-free basis. No specific explanation is given for how the air-free results were derived, but the nitrogen, oxygen, and argon values in column B appear to have been recalculated by assuming all the oxygen in column A was due to air leakage, and adjusting the nitrogen and argon values in direct proportion to their ratios with oxygen in air. In any event, their compositions range from approximately 95 percent methane (including air, column A) to approximately 99 percent methane (on a dry, air-free basis, column B), with traces of nitrogen, carbon dioxide, argon, and heavier gas species.

<sup>3</sup>See 19-second QuickTime movie clip illustrating the nature and rate of gas seepage during the 2005 visit <<http://www.dggs.dnr.state.ak.us/pubs/pubs?reqtype=citation&ID=16084>>.



Figure 3. Field photos of the Aupuk gas seep near Kakvuiyat Bend on the Colville River. (a) View to northeast of small meander scar lake immediately south of Colville River. (b) View to northwest at sample location on south shore of lake. During the 2005 visit, the gas bubbles emanated from a single point in water less than 60 cm deep near the south side of the lake approximately 12 m from the southeast end [arrows in (a) and (b)]. In 2006, numerous bubble streams were active within a radius of approximately 15 m from sample location. Gas samples were collected by allowing bubble stream (c) to displace approximately 200 ml of water from an inverted 250 ml I-Chem amber glass sample bottle (d).

Similar to other analyses of gas in the Brooks Range Foothills (Burruss and others, 2003), data from the Aupuk seep indicate a very dry gas, containing mostly methane with negligible ethane and heavier hydrocarbons (table 1). However, all three of our recent samples yielded significantly higher nitrogen content than gas sampled from the same seep in 1946 (table 1). The reason for the high nitrogen content is not clear. Most natural gases from the North Slope contain less than 4 mole percent nitrogen (Burruss and others, 2003), and air contamination is blamed for higher nitrogen content in some cases. However, the ratio of nitrogen to oxygen in sample 05PD034 (235:1) is orders of magnitude higher than the ratio in air (3.25:1), so only a small fraction of the nitrogen can be readily explained by air leakage alone. Sample 06PD004a yielded a much lower methane and much higher nitrogen content than any of the other compositional analyses from this seep (table 1), and is believed to have been contaminated by air. However, the results for the 2006 analyses did not distinguish between oxygen and argon, making it impossible to calculate the nitrogen:oxygen ratio to establish air contamination.

Isotope analysis of the nearly 87 percent methane fraction in sample 05PD034 yielded a  $\delta^{13}\text{C}$  ratio of -39.3 per mil, and  $\delta^2\text{H}$  ratio of -195 per mil (table 1). These data are plotted on the natural gas characterization plot (fig. 4; format after Schoell, 1983), and indicate the Aupuk gas seep is clearly thermogenic rather than biogenic in origin, and appears to be a condensate- or oil-associated product generated at oil-window maturity. The 2006 samples were not analyzed for deuterium isotopes, although the two additional carbon isotopic measurements were nearly identical to the 2005 sample (table 1) and appear to be representative of actual current seepage.

Table 1. Composition and methane isotopic data, Aupuk gas seep

	This Study			Chapman and others, 1964	
	05PD034 <sup>a</sup>	06PD004A <sup>b</sup>	06PD004B <sup>b</sup>	A <sup>c</sup>	B <sup>c</sup>
<b>Composition (mole %)</b>					
Methane	86.98	77.51	87.06	95.40	98.80
Ethane	tr	n/a	n/a	0.06	0.07
Nitrogen	11.77	18.78	11.51	3.30	0.70
Oxygen	0.05	n/a	n/a	0.70	n/a
Argon	--	n/a	n/a	0.10	0.06
Carbon Dioxide	1.20	n/a	n/a	0.40	0.40
Argon & Oxygen	0.05	3.70	1.43	0.80	n/a
	100.00	99.99	100.00	99.96	100.03
<b>Methane Isotopes (per mil)</b>					
$\delta^{13}\text{C}$ , Carbon	-39.3	-39.1	-39.3		
$\delta\text{D}$ , Deuterium	-195	n/a	n/a		

<sup>a</sup>2005 sample: Compositional analysis by CoreLab, Calgary; isotopic analyses by Michael Whiticar and Paul Eby, Dept. of Earth and Ocean Sciences, University of Victoria, B.C.; sample shipping, analytical costs, and oversight courtesy of Petro-Canada.

<sup>b</sup>2006 samples: analyses by Intertek Westport, Houston, TX; analyses did not differentiate or did not separately report argon and oxygen, and do not mention either ethane or carbon dioxide, which were presumably not detected.

<sup>c</sup>USGS samples: Analyzed in 1946, and were reported on a dry basis, but including air (column A), and on a dry, air-free basis (column B). Isotope analyses were not possible at that time.

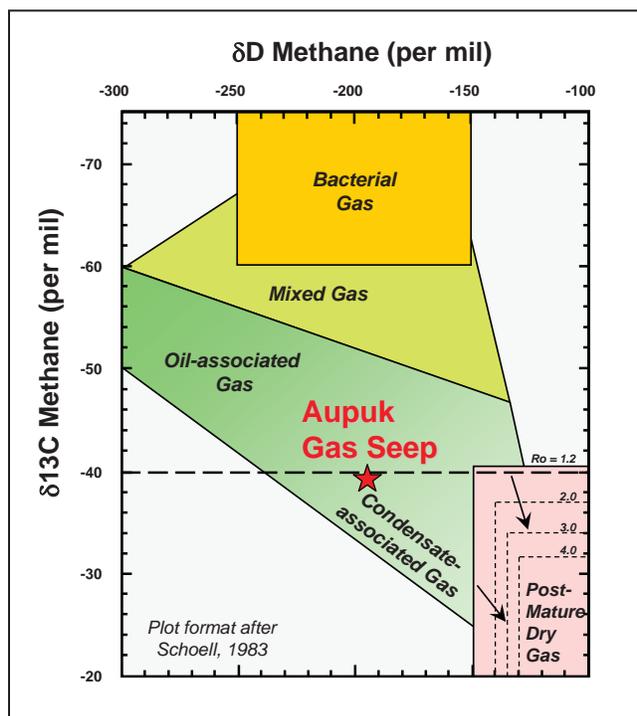


Figure 4. Natural gas characterization plot showing carbon and deuterium isotope measurements of methane from the 2005 Aupuk gas seep sample. Analysis of the nearly 87 percent methane fraction yielded a  $\delta^{13}\text{C}$  ratio of -39.3 per mil, and  $\delta\text{D}$  ratio of -195. The gas plots firmly in the thermogenic field, and appears to be an oil- or condensate-associated product generated at oil-window maturity. Carbon isotope values of the 2006 samples were essentially the same as the 2005 value; deuterium isotopes were not measured on 2006 samples.

## DISCUSSION AND CONCLUSIONS

The presence of a surface gas seep suggests there is a slowly leaking, thermogenic gas accumulation reservoir in Nanushuk Formation sandstones at depth. The source of this gas is difficult to assess because natural gases do not contain the large, complex biomarker molecules that allow liquid hydrocarbons to be tied back to their specific source rocks. On the basis of its apparent oil-window thermal maturity, it is speculated that the Aupuk seep is probably sourced from gas-prone terrestrial kerogen in the Torok Formation. If migration occurred early in the burial history, then the gas could also be a relict charge from several deeper source rocks that are likely now at much higher maturation levels. These include the Lower Cretaceous gamma ray zone (GRZ, also known as highly radioactive zone, HRZ) and/or pebble shale unit, Jurassic Kingak Formation, and Triassic Shublik Formation, and perhaps other intervals. Finally, given the possibility that polyphase deformation affected this area (O'Sullivan and others, 1997; Finzel and others, 2003), the Aupuk seep could reflect an accumulation of re-migrated hydrocarbons from an earlier episode of trapping.

The trapping mechanism and timing of hydrocarbon migration for the Aupuk gas is unknown, although consideration of local and regional data offers some constraints. Chapman and others (1964) noted that the seep was located near the east end of the Aupuk anticline (fig. 5). The position of the seep near the axis of the structure, as well as evidence for local faulting, support the hypothesis that the gas is leaking from a structurally trapped accumulation. Subsequent mapping in the southern Ikpikpuk Quadrangle by Mull and others (2005) reported additional strike and dip data, further constraining the nature of the Aupuk anticline (fig. 5). Most wells targeting the Nanushuk Formation in the foothills were drilled on structural highs (Mull, 1989) and all the Nanushuk foothills gas discoveries (undeveloped) are reported to be trapped in structural closures (Meade, Square Lake, Wolf Creek, East Umiat, Gubik, and East Kurupa are summarized in Kumar and others [2002]; Oumalik is described in Robinson [1956] and Schindler [1988]).

The timing for the development of this and other folds in the foothills belt could be either mid-Cretaceous (Albian–Cenomanian) or Paleocene. Timing the formation of structural traps in this area is significant because the younger deformation event postdates the principal mid- to Late Cretaceous phase of hydrocarbon generation suggested by burial and thermal history modeling (Burns and others, 2002). In assessing structural plays within NPRA, Potter and Moore (2003) interpreted all of the folding within the Nanushuk belt to reflect deformation at approximately 60 Ma, an episode that is widely recorded by apatite fission track data (Moore and others, 2004; O'Sullivan and others, 1997). However, the presence of an earlier phase of mid-Cretaceous folding cannot be ruled out. In fact, there are select fission track data from the central Brooks Range foothills, south of the Nanushuk outcrop belt, that preserve evidence for cooling at 90–110 Ma (Duncan and others, 2006; Cole and others, 1997; O'Sullivan and others, 1997). It is possible that this mid-Cretaceous cooling event affected Nanushuk rocks, but that subsequent burial reset the apatite thermochronometer, potentially erasing any record of pre-60 Ma cooling events (uplift and folding).

The Kurupa anticline (south of the Awuna syncline shown in fig. 5) is approximately 21 km south of the Aupuk seep and houses the undeveloped East Kurupa gas accumulation within the Torok and/or Fortress Mountain Formations (Kumar and others, 2002). In a study of the thermal maturity of the Torok and Nanushuk Formations involved in this fold, Bird and Pawlewicz (2006) concluded from vitrinite data that folding likely occurred prior to maximum burial, presumably in the mid-Cretaceous. On the basis of seismic and field evidence, other workers have also suggested portions of the Nanushuk Formation were influenced by mid-Cretaceous folding (Wallace, 2003; Finzel and others, 2003; Mull and others, 2000; Cole and others, 1997; Detterman and others, 1963). If additional new data confirm an episode of mid-Cretaceous folding, it would increase the probability of structurally trapped oil and gas accumulations across the Brooks Range Foothills.

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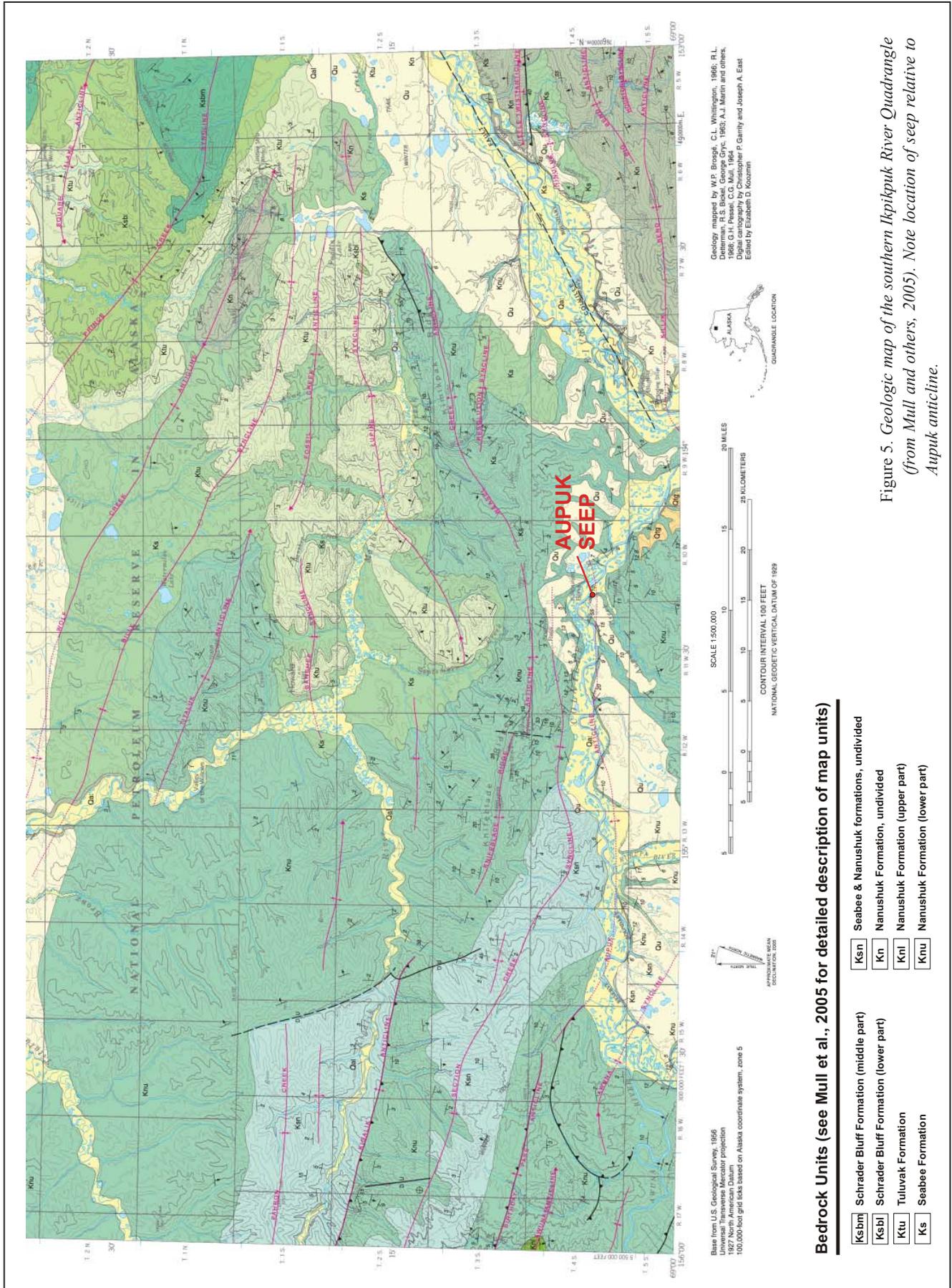


Figure 5. Geologic map of the southern Ikpikpak River Quadrangle (from Mull and others, 2005). Note location of seep relative to Aupuk anticline.

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