

Quantitative mineralogy of the Yukon River system: Changes with reach and season, and determining sediment provenance

D. D. EBERL

U.S. Geological Survey, 3215 Marine St., Suite E-127, Boulder, Colorado 80303, U.S.A.

ABSTRACT

The mineralogy of Yukon River basin sediment has been studied by quantitative X-ray diffraction. Bed, beach, bar, and suspended sediments were analyzed using the RockJock computer program. The bed sediments were collected from the main stem and from selected tributaries during a single trip down river, from Whitehorse to the Yukon River delta, during the summer of 2001. Beach and bar sediments were collected from the confluence region of the Tanana and Yukon Rivers during the summer of 2003. Suspended sediments were collected at three stations on the Yukon River and from a single station on the Tanana River at various times during the summers of 2001 through 2003, with the most complete set of samples collected during the summer of 2002.

Changes in mineralogy of Yukon River bed sediments are related to sediment dilution or concentration effects from tributary sediment and to chemical weathering during transport. Carbonate minerals compose about 2 wt% of the bed sediments near Whitehorse, but increase to 14 wt% with the entry of the White River tributary above Dawson. Thereafter, the proportion of carbonate minerals decreases downstream to values of about 1 to 7 wt% near the mouth of the Yukon River. Quartz and feldspar contents of bed sediments vary greatly with the introduction of Pelly River and White River sediments, but thereafter either increase irregularly (quartz from 20 to about 50 wt%) or remain relatively constant (feldspar at about 35 wt%) with distance downstream. Clay mineral content increases irregularly downstream from about 15 to about 30 wt%. The chief clay mineral is chlorite, followed by illite + smectite; there is little to no kaolinite. The total organic carbon content of the bed sediments remains relatively constant with distance for the main stem (generally 1 to 2 wt%, with one exception), but fluctuates for the tributaries (1 to 6 wt%).

The mineralogies of the suspended sediments and sediment flow data were used to calculate the amount of mineral dissolution during transport between Eagle and Pilot Station, a distance of over 2000 km. We estimate that approximately 3 wt% of the quartz, 15 wt% of the feldspar (1 wt% of the alkali and 25 wt% of the plagioclase), and 26 wt% of the carbonates (31 wt% of the calcite and 15 wt% of the dolomite) carried by the river dissolve in this reach.

The mineralogies of the suspended sediments change with the season. For example, during the summer of 2002 the quartz content varied by 20 wt%, with a minimum in mid-summer. The calcite content varied by a similar amount, and had a maximum corresponding to the quartz minimum. These modes are related to the relative amount of sediment flowing from the White River system, which is relatively poor in quartz, but rich in carbonate minerals. Suspended total clay minerals varied by as much as 25 wt%, with maxima in mid July, and suspended feldspar varied up to 10 wt%. Suspended sediment data from the summers of 2001 and 2003 support the 2002 trends.

A calculation technique was developed to determine the proportion of various sediment sources in a mixed sediment by unmixing its quantitative mineralogy. Results from this method indicate that at least three sediment sources can be identified quantitatively with good accuracy. With this technique, sediment mineralogies can be used to calculate the relative flux of sediment from different tributaries, thereby identifying sediment provenance.

INTRODUCTION

The Yukon River basin, the fourth largest in North America, drains an area of about 855 000 km² and has a total length of over 3000 km [for an excellent overview of the Yukon system, see Brabets et al. (2000)]. The river begins in northern British Columbia and flows in a northwesterly direction into Alaska, where it turns near the confluence with the Porcupine River to

flow generally southwest to the Bering Sea. The mean annual water discharge is about 2×10^{11} m³ per year at Pilot Station, and sediment discharge into the Bering Sea is about 55 million metric tons per year, most of which is deposited in the summer months. About 18 million metric tons are deposited annually on flood plains. The Yukon River has several large tributaries (Fig. 1), but just two tributaries contribute the largest amounts of sediment (Table 1): the White River, and its tributary the Donjek River, carries sediment from the glaciated Wrangell-St. Elias

* E-mail: ddeberl@usgs.gov

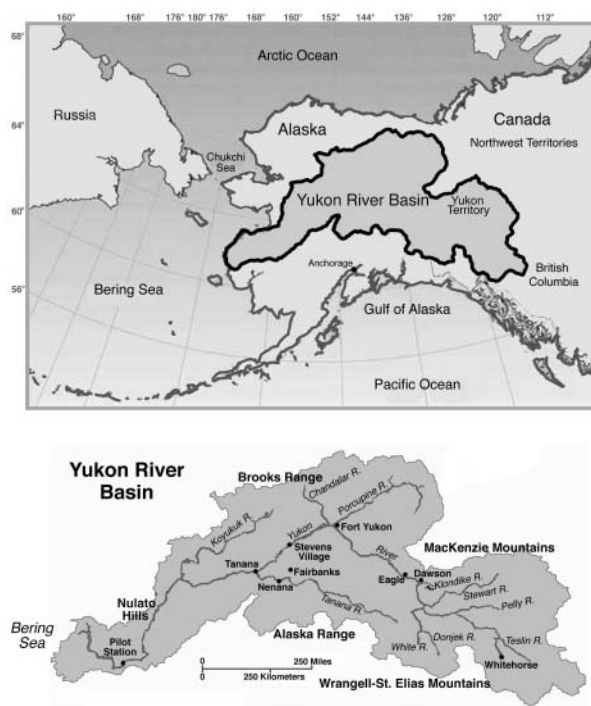


FIGURE 1. Location map of the Yukon River basin.

Mountains to the south, and the Tanana River drains the glaciated Alaska Range to the southeast. Three other sources contribute significant amounts ($>10^6$ metric tons annually) of sediment to the Yukon River, the Pelly River, the Porcupine River and the Koyukuk River. Many tributary basins, such as the Porcupine and the Koyukuk, are underlain by continuous permafrost (see Table 5 in Brabets et al. 2000).

The U.S. Geological Survey (USGS) initiated a project to study the Yukon River system in 2001 as a part of the National Stream Quality Accounting Network (NASQAN) program (<http://water.usgs.gov/nasqan/>). The project will establish baseline values for water quality in the basin in order to detect changes that may occur during possible permafrost melting in response to climate change. As a part of this project, six stations in Alaska (at Eagle, Stevens Village, and Pilot Station on the Yukon River, with other stations at the Porcupine River, the Koyukuk River, and at Nenana on the Tanana River) were established to sample water and suspended sediment at intervals during the summer months (May through September; Table 2), although only the stations on the Yukon and Tanana Rivers were sampled intensively. In addition, river sediments were sampled by two USGS volunteers in the summer of 2001 during a kayaking trip from the city of Whitehorse (Yukon Territory, Canada) to the Bering Sea. They collected 50 river bed samples from the main stem of the Yukon River and from its tributaries (Table 3). Also, beach and bar sediments from the Tanana River-Yukon River confluence region were collected in August, 2003 to measure patterns of sediment mixing between the main stem and this tributary (Table 4).

The quantitative mineralogy of the sediments was studied to learn how mineralogy may change during transport in a long river

TABLE 1. Estimated annual suspended-sediment loads for selected sites in the Yukon River basin (first two columns from Brabets et al. 2000), and measured and calculated ratios for sediment sources

Name (YT is Yukon , Territory and the others are from Alaska) (1)	Annual load (metric tons) (2)	Measured proportion of Yukon suspended sediment* (3)	Calculated proportion of Yukon bed sediment† (4)
Yukon at Whitehorse, YT	56,000		
Pelly R., YT	1,100,000	0.05	0.00
Yukon R. above White R., YT	3,180,000		
White R. + Donjek R., YT	14,500,000 + 11,420,000‡	0.11	0.16
Stewart R., YT	900,000		
Yukon R. at Dawson, YT	30,000,000		
Yukon R. at Eagle	30,000,000		
Porcupine R., Chandalar R.	7,200,000 900,000	0.81	0.96
Yukon R. at Rampart	30,000,000		
Tanana R.	34,500,000	0.47	0.50 (0.54)§
Yukon R. at Ruby	60,000,000		
Koyukuk R.	1,800,000	0.97	1.00
Yukon R. at Pilot Station	54,500,000		

* Proportion = weight of downstream Yukon suspended sediment/(weight of upstream Yukon suspended sediment + weight of tributary suspended sediment) using data from column 2.

† Same proportion as above, but calculated by unmixing of XRD quantitative mineral data for bed sediment (see text).

‡ Donjek data calculated by difference from Table 10 in Brabets et al. (2000).

§ Parenthesis refers to suspended sediment, unmixed from the Yukon River at Pilot Station using XRD quantitative mineral data for suspended samples for the Yukon River at Stevens Village and for the Tanana River. These suspended samples were collected at approximately the same time.

TABLE 2. Suspended-sediment samples collected during the 2002 season, and the presence of smectite in the sediment

Sample - no. YRS	Location	Date collected	Time collected	Smectite present?
32	Yukon R. at Eagle	5/22/02	1420	no
41	Yukon R. at Eagle	7/10/02	1120	yes
47	Yukon R. at Eagle	8/1/02	1150	yes
48	Yukon R. at Eagle	8/1/02	1200	yes
55	Yukon R. at Eagle	8/28/02	1340	yes
30	Porcupine R. at Fort Yukon	6/6/02	1500	–
31	Porcupine R. at Fort Yukon	6/26/02	1310	–
35	Yukon R. at Stevens Village	6/4/02	1630	no
36	Yukon R. at Stevens Village	6/24/02	1330	no
44	Yukon R. at Stevens Village	7/18/02	1400	yes
46	Yukon R. at Stevens Village	7/30/02	1510	yes
53	Yukon R. at Stevens Village	8/23/02	1440	yes
54	Yukon R. at Stevens Village	8/24/02	1450	yes
57	Yukon R. at Stevens Village	9/5/02	1450	yes
33	Tanana R. at Nenana	5/14/02	1500	no
34	Tanana R. at Nenana	5/29/02	1550	no
42	Tanana R. at Nenana	7/16/02	1430	yes
45	Tanana R. at Nenana	7/29/02	1310	yes
51	Tanana R. at Nenana	8/21/02	1330	yes
52	Tanana R. at Nenana	8/22/02	1340	yes
56	Tanana R. at Nenana	8/30/02	1450	yes
37	Yukon R. at Pilot Station	6/12/02	1340	no
38	Yukon R. at Pilot Station	6/20/02	1850	no
40	Yukon R. at Pilot Station	7/1/02	1900	yes
43	Yukon R. at Pilot Station	7/16/02	1130	yes
49	Yukon R. at Pilot Station	8/8/02	1420	yes
50	Yukon R. at Pilot Station	8/8/02	1430	yes
58	Yukon R. at Pilot Station	9/24/02	1630	yes

Note: Suspended sediment data for the 2001 and 2003 seasons can be found at <http://brrcftp.cr.usgs.gov/pub/ddeberl/>.

TABLE 3. Location of bed-sediment samples collected by kayakers during the 2001 season

Sample number: YR-	Location	km from Whitehorse
1	Yukon R. at Whitehorse	0
2	Yukon R. above Teslin R.	111
3	Teslin R.	118
4	Yukon R. below Teslin R.	126
5	Yukon R. above Pelly R.	333
6	Pelly R.	337
7	Yukon R. below Pelly R.	344
8	Yukon R. above White R.	485
9	White R.	493
10	Yukon R. below White R.	495
11	Yukon R. below Stewart R.	502
12	Yukon R. above Dawson	606
13	Yukon R. below Dawson	613
14	Forty Mile R.	644
15	Yukon R. at Eagle	764
16	Tatonduk R.	817
17	Nation R.	862
18	Kandik R.	921
19	Charles R.	944
20	Coal Creek	967
21	Wood Chopper Creek	980
22	Yukon R. at Circle	1079
23	Yukon R. above Porcupine R.	1211
24	Porcupine R.	1222
25	Yukon R. below Porcupine R.	1229
26	Birch Creek	1281
27	Beaver Creek	1392
28	Tributary, name unknown	1406
29	Yukon R. at Dalton Bridge	1602
30	Hess Creek	1666
31	Yukon R. above Tanana R.	1837
32	Tanana R.	1851
33	Yukon R. below Tanana R.	1868
34	Tozitna R.	1880
35	Nowitna R.	2018
36	Melozitna R.	2098
37	Yukon R. at Ruby	2102
38	Yukon R. at Galena	2210
39	Yukon R. above Koyukuk R.	2260
40	Koyukuk R.	2272
41	Yukon R. below Koyukuk R.	2302
42	Nulato R.	2334
43	Yukon R. at Kaltag	2408
44	Yukon R. at Grayling	2721
45	Annk R.	2754
46	Yukon R. at Holy Cross	2796
47	Innoko R.	2799
48	Yukon R. at Russian Mission	2915
49	Yukon R. at Pilot Station	3111
50	Andreafsky R.	3151

system, how main stem mineralogy is influenced by tributaries, and how the mineralogy of suspended sediment may change with the season. In addition, a method was developed for modeling sediment flux in the system by quantitatively unmixing sediment sources from mixed sediments. Knowledge about such changes in mineralogy in a major river system that exists largely in its natural state may improve our understanding of how water quality may vary with sediment fluxes and with weathering rates related to climate change.

METHODS

Suspended sediments (data for 2002 in Table 2) were collected during the 2001 through 2003 seasons according to standard USGS protocols. The methods described by Edwards and Glysson (1988) were used for the collection of flow-integrated samples at all stations, following the protocols of Horowitz et al. (1994). The suspended samples were processed according to established USGS protocols (USGS 1997–1999). The kayakers' bed sediments (Table 3) were collected by hand from the river bottoms below the waterline. Sediments from the Tanana-Yukon confluence were collected from bars and beaches, generally above the waterline. All

TABLE 4. Location of beach and bar sediments collected from the Tanana-Yukon confluence area in 2003

Sample number	River	Sample coordinates		
Y1	Yukon above confluence	N65° 25'	W150° 47'	00.7"
Y2	Yukon above confluence	N65° 10'	W151° 36'	58.1"
Y3	Yukon above confluence	N65° 44'	W149° 50'	23.3"
Y4	Yukon above confluence	At Dalton Highway		
Y5	Yukon above confluence	N65° 44'	W149° 50'	45.6"
Y6	Yukon above confluence	N65° 27'	W150° 15'	10.1"
T1	Tanana above confluence	N65° 06'	W151° 44'	49.1"
T2	Tanana above confluence	N65° 06'	W151° 47'	63.0"
T3	Tanana above confluence	N65° 06'	W151° 48'	34.3"
T4	Tanana above confluence	N65° 09'	W151° 53'	45.1"
T5	Tanana above confluence	N65° 09'	W151° 55'	34.8"
YT1	Yukon below confluence	N65° 11'	W152° 43'	42.5"
YT2	Yukon below confluence	N65° 11'	W152° 42'	48.9"
YT3	Yukon below confluence	N65° 08'	W152° 36'	47.0"
YT4	Yukon below confluence	N65° 08'	W152° 36'	56.2"
YT5	Yukon below confluence	N65° 08'	W152° 37'	27.2"
YT6	Yukon below confluence	N65° 08'	W152° 31'	27.1"
YT7	Yukon below confluence	N65° 07'	W152° 31'	22.8"
YT8	Yukon below confluence	N65° 08'	W152° 22'	30.9"
YT9	Yukon below confluence	N65° 08'	W152° 22'	56.9"
YT10	Yukon below confluence	N65° 09'	W152° 15'	45.0"
YT11	Yukon below confluence	N65° 10'	W152° 15'	39.7"

bed, beach, and bar sediments were dried, and then passed through a 500 μ m sieve, thereby recovering almost all of the sample except for some pebbles in samples collected from the upper reaches of the Yukon River near Whitehorse.

Quantitative mineralogy was determined by X-ray diffraction (XRD) for all sample sets. The samples were prepared for analysis according to the methods described by Šrodoň et al. (2001). Briefly described here, 3 g of sample was mixed with 0.333 g of an internal standard (zincite). The mixture was then ground with 4 mL of methanol in a McCrone mill for 5 minutes, oven dried at 85 °C, passed through a 4 mm sieve, and then side-loaded (by tapping) into an aluminum holder. Samples were X-rayed from 5 to 65° 2 θ with CuK α radiation (40 kV, 30 mA) using a Siemens D500 X-ray diffraction system with a graphite monochromator, 1° slits, a step size of 0.02° 2 θ , and a counting time of 2 s per step. A typical XRD pattern is presented in Figure 2.

The XRD data were converted into wt% minerals using the RockJock computer program (Eberl 2003). Briefly, the program compares integrated X-ray intensities for minerals present in a sample with that of an internal standard (zincite), and weight percents are calculated from previously measured mineral intensity factors (MIFs; also termed reference intensity ratios, RIRs). Integrated X-ray intensities for individual minerals were determined by fitting stored XRD patterns for pure minerals to the measured XRD pattern by using the Solver option in Microsoft Excel. The Solver option minimized the degree of fit parameter between measured and calculated patterns by varying the intensities of the stored standard patterns by multiplying each of these patterns by a separate factor. This analysis was carried out for two regions of the XRD pattern, 20–65° 2 θ for non-clay analysis, and 58–65° 2 θ for clay mineral analysis. All samples were analyzed for the same mineral suite, and three examples of bed sample analyses are given in Table 5. The complete data set and the RockJock program are available from the U.S. Geological Survey at <ftp://brrcrftp.cr.usgs.gov/pub/ddeberl/>.

The RockJock technique has been checked for accuracy using artificial mixtures, and generally gives results that are within 1 or 2 wt% of actual values (Eberl 2003). A sum for an analysis that is close to 100% is a further check because weight percents for each mineral are calculated independently with respect to the zincite internal standard. The RockJock program earned third place in an international quantitative analysis competition that used complex mineral mixtures (the Reynolds Cup; McCarty 2002), finishing closely behind the winner (cumulative bias for three samples for RockJock was 45 vs. 32 for the winner). The program has since been improved to the point that it would have won the previous competition.

The results of carbonate mineral (calcite + magnesian calcite + dolomite) quantitative XRD analyses were checked using a carbon analyzer, with good results (Fig. 3; correlation coefficient $r^2 = 0.92$). In this method, total inorganic carbon (TIC) was determined by acidification (CM5130 Acidification Module) and measurement of CO₂ contained in the gas stream. The calcite wt% was calculated by multiplying TIC by 8.3333. Some of the discrepancy between the two methods (Fig. 3) results from attributing all of the carbonate from the carbon analyzer determinations to the mineral calcite, whereas, on average, samples contain about 1.4 times as much

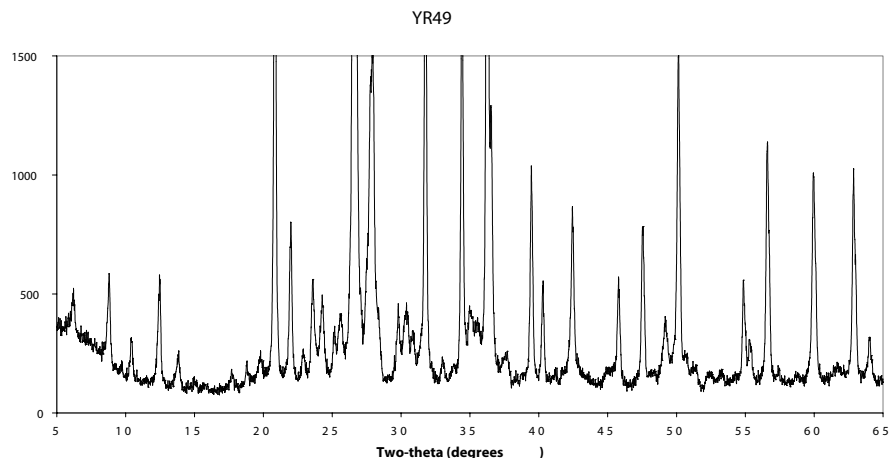


FIGURE 2. XRD pattern of Yukon River bed sample YR49 from Pilot Station.

TABLE 5. Sample RockJock analyses for Yukon River system bed sediments

Minerals	YR8	YR9	YR10
Non-clays:			
quartz	51.0	18.4	23.7
microcline (ordered)	1.8	0.5	1.8
microcline (intermediate)	2.4	2.2	2.3
sanidine	2.4	1.5	1.3
orthoclase	0.0	0.0	0.0
anorthoclase	5.2	10.3	10.4
albite	5.6	7.1	7.4
oligoclase	4.1	3.9	2.4
andesine	2.5	0.0	0.0
labradorite	1.8	10.4	10.2
bytownite	1.5	5.2	5.2
anorthite	0.0	0.0	0.0
calcite	0.4	7.5	6.8
Mg-calcite	0.7	1.0	0.4
dolomite	2.7	5.5	5.1
amphibole	2.1	2.1	1.8
pyroxene	0.3	2.0	1.9
magnetite	0.0	0.3	0.0
hematite	0.0	0.5	0.3
goethite	0.5	0.3	0.2
Total non-clays	84.9	78.8	81.4
Clays:			
kaolinite	0.0	0.7	2.1
ferruginous smectite	0.3	0.9	4.5
illite (+ Al-smectite)	5.9	5.5	0.0
chlorite CCa-1	0.0	0.0	0.0
chlorite CCa-3	0.1	0.0	0.0
chlorite CCM	0.0	0.0	0.0
chlorite CO	0.1	0.1	0.0
chlorite Tusc	8.1	8.9	4.1
chlorite A	2.8	3.3	2.8
Total clays:	17.3	19.2	13.6
Total:	102.2	98.0	95.0
Non-clay degree of fit:	0.077	0.074	0.072
Clay degree of fit:	0.045	0.039	0.037

calcite as dolomite. Total carbon (TC) was determined by combustion using a CM5120 Furnace Apparatus. The wt% total organic carbon (TOC) was calculated using the equation: $TOC = (TC - TIC) \times 1.724$.

Sediment mineralogy was unmixed quantitatively using the MinUnMix program (program and instructions available at the ftp site given above). This procedure quantitatively determines the fractions of component sediments in a mixture. For example, quantitative mineralogy was measured for bed sediments collected from the Yukon River and a tributary above their confluence, and from sediment collected below the confluence. The concentration in wt% of each min-

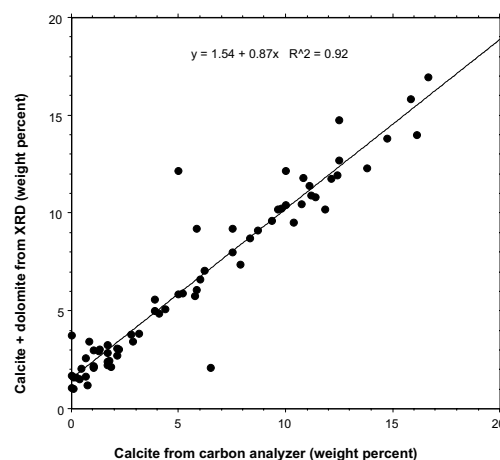


FIGURE 3. Comparison between X-ray diffraction and carbon analyzer methods for determining wt% carbonates in Yukon River

eral in the upstream Yukon sediment was multiplied by a factor (f), and that in the tributary was multiplied by a second factor (g). The factors were constrained to be positive, and to sum to unity. The concentrations of each mineral (multiplied by the factors) in the upstream samples then were summed, and the sums were compared to the measured mineralogy of the downstream Yukon sediment by having the Solver option in Excel minimize a degree of fit parameter between the measured and calculated quantitative mineralogy by varying the factors. The degree of fit is defined as the sum of absolute value of the difference in concentration between the measured and calculated mineralogy, divided by the sum of the weight percent of the measured mineralogy. The method was extended to unmix from 2 to 5 sediment sources.

Illite crystallite thicknesses were measured by Fourier analysis of the (001) X-ray diffraction peak shape according to the Bertaut-Warren-Averbach peak-broadening method (Drits et al. 1998) using the MudMaster computer program (Eberl et al. 1996). Samples were treated with the polymer polyvinylpyrrolidone (PVP-10) to remove swelling from the illite particles prior to XRD analysis (Eberl et al. 1998a).

RESULTS AND DISCUSSION

Bed sediments

The concentrations of the major minerals in the bed sediments were plotted against distance from Whitehorse. The carbonates near Whitehorse make up about 2 wt% of the sediment (Fig. 4a). With entry of the White River tributary at 493 km this value increases to approximately 14 wt%. The White River itself carries about 14 wt% carbonate sediment, indicating that the sudden

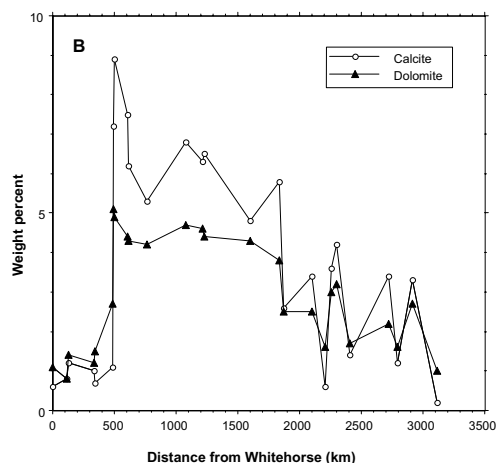
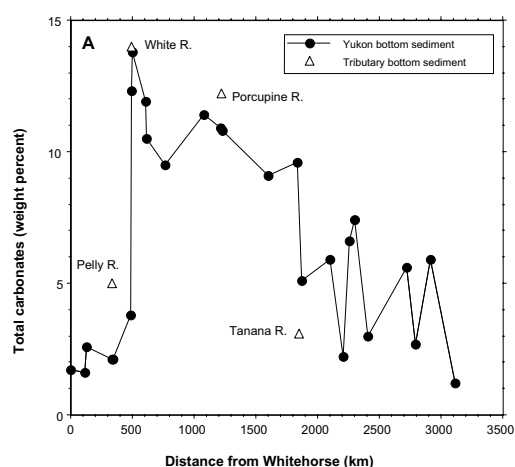


FIGURE 4. (a) Wt% total carbonates in bed sediments with distance from Whitehorse. (b) Same plot for calcite and dolomite.

increase in Yukon carbonate is related to mixing with sediment from this tributary. Thereafter, the total carbonate in the Yukon bed sediments decreases quickly to about 10 wt%, after which the carbonate content remains approximately constant at 10 wt% with distance downstream until the Tanana River, which carries about 3 wt% carbonate, enters the Yukon River at 1851 km. Here the carbonate content of the Yukon sediment decreases by half. Downstream from the Tanana confluence, the calcite content varies between 1 and 7 wt%, finally finishing with a value at Pilot Station that is close to its initial value at Whitehorse. The percentages of calcite and dolomite roughly track each other throughout the course of the river (Fig. 4b).

Quartz concentration (Fig. 5) starts at a value of about 35 wt% near Whitehorse, suddenly increases to 65 wt% with the entry of the Pelly River, and then decreases to about 20 wt% with the entry of the White River. Throughout the rest of the reach, the quartz content gradually increases to a value of about 50 wt% at Pilot Station.

Feldspar content initially has the opposite trend (Fig. 6a), starting at about 45 wt%, then decreasing to 15 wt% with the entry of the Pelly River, and then increasing again to about 45

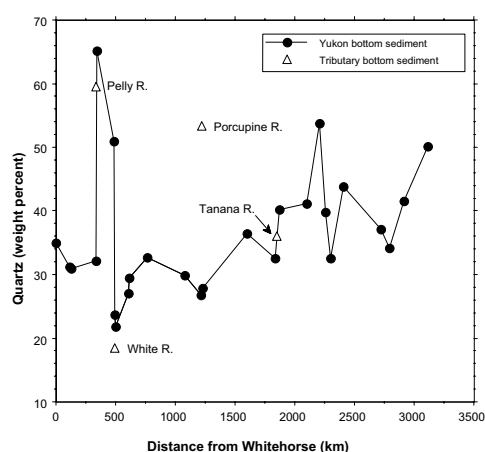


FIGURE 5. Wt% quartz in bed sediments with distance from Whitehorse.

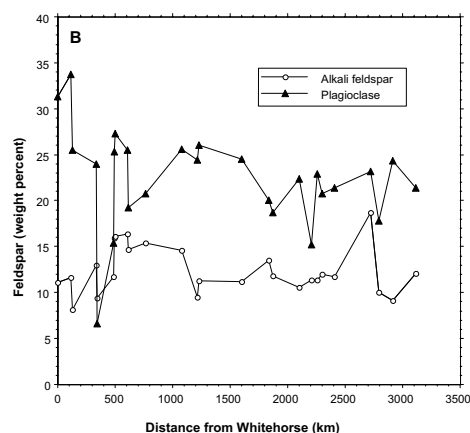
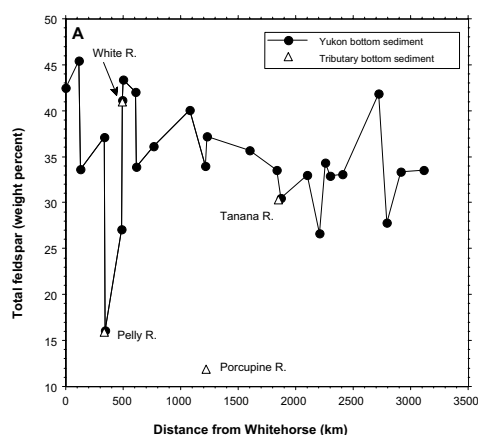


FIGURE 6. (a) Wt% total feldspar in bed sediments with distance from Whitehorse. (b) Same plot for alkali feldspar and plagioclase.

wt% at the confluence of the White River. Thereafter feldspar remains roughly constant between 30 and 40 wt%. The bed sediment generally contains about twice as much plagioclase

as alkali feldspar (Fig. 6b).

Total clay mineral content (Fig. 7a) starts at about 15 wt%, and increases irregularly downstream, ending at about 27 wt% at Pilot Station. A regression analysis of total clay mineral concentration and distance downstream from Whitehorse resulted in an r^2 value of 0.55. The clays are dominated by chlorite, with subordinate illite + smectite, and very little kaolinite (Fig. 7b). The lack of kaolinite is expected for an arctic region where weathering is mostly mechanical rather than chemical (e.g., Eberl 1984).

Total organic carbon (TOC) content, plotted for the main stem and tributaries as a function of distance from Whitehorse (Fig. 8), indicates that the bed sediments in the tributaries are, on average, twice as rich in TOC than the sediments in the main stem, and, generally, TOC in the tributary sediments is more variable.

Suspended sediments

According to Brabets et al. (2000), the suspended sediments are the most significant part of the overall sediment load carried by the Yukon River and its tributaries. For example, the bedload of the Tanana River near Fairbanks is only 1 to 2 wt% of the suspended load. The discussion here will emphasize suspended

sediment data for the summer of 2002, which is the most complete data set. Data for the summers of 2001 and 2003 can be found at the ftp site.

The change in suspended-sediment concentrations for May through September 2002 is shown in Figure 9 for three stations on the Yukon River (Eagle, Stevens Village, and Pilot Station), and for the station on the Tanana River at Nenana. All stations have a maximum in suspended sediment concentration near the end of July or in August, which is most pronounced for the main stem at Eagle. The Tanana River has two maxima, one in May, and another probably near the end of July. The first peak likely is in response to snow melt runoff, and the second less pronounced peak results from glacial melt. Sediment concentration in the Tanana River is much larger than that found for the main stem.

The weight percents of the suspended minerals, listed in Table 2, are plotted for the same stations for various sampling times during the 2002 season. Quartz content varies by about 20% during the sampling season, and has minima at all stations

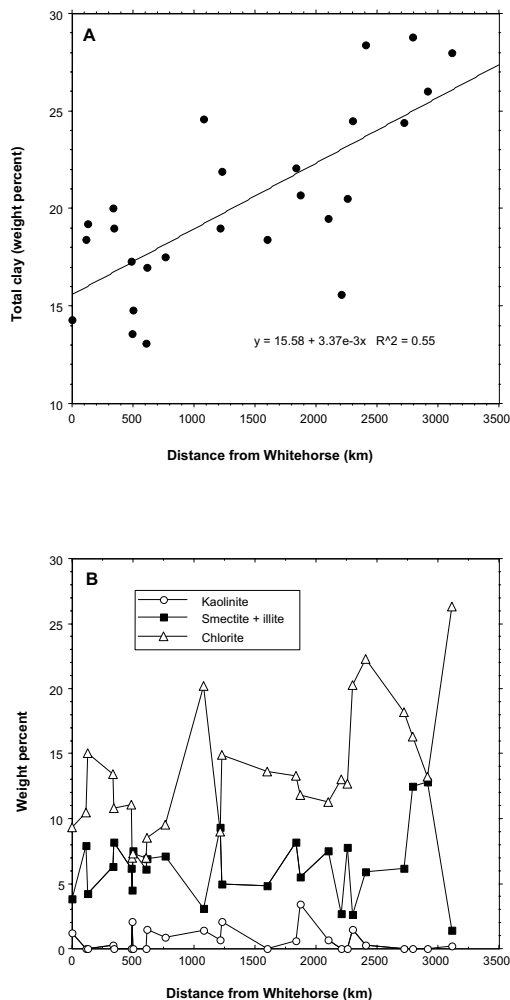


FIGURE 7. (a) Wt% total clay in bed sediments with distance from Whitehorse. (b) Same plot for kaolinite, smectite + illite, and chlorite.

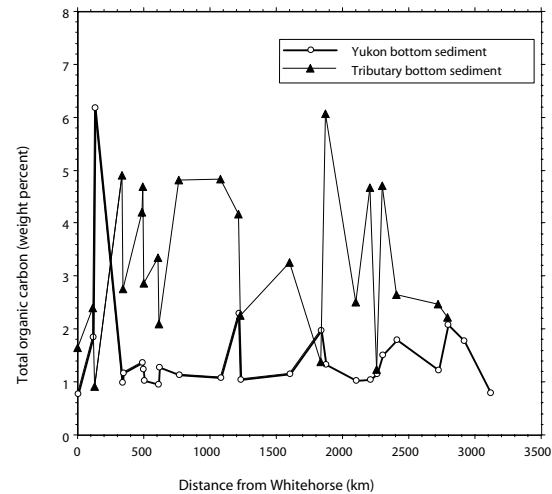


FIGURE 8. Wt% total organic carbon with distance from Whitehorse for bed sediments.

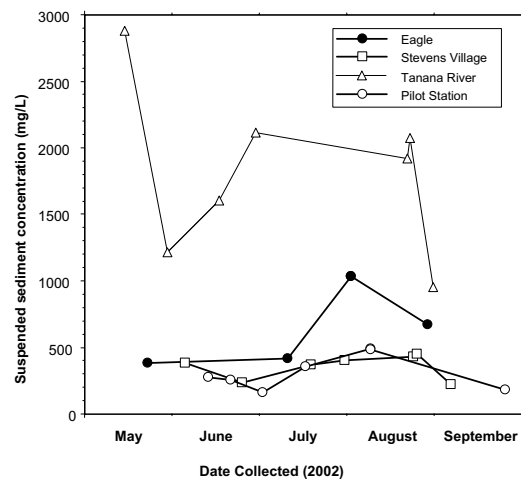


FIGURE 9. Change in suspended sediment concentrations in river water for the 2002 season for four fixed stations.

in mid-summer (Fig. 10). These minima appear to correlate neither with sediment concentration (Fig. 9), nor with maximum discharge, which occurs in early June (see Fig. 21 in Brabets et al. 2000), but do correlate with carbonate maxima for the Yukon River samples (Fig. 11), and to a clay mineral maximum for the Tanana River samples (Fig. 12). A current velocity of about 5 km/h (a reasonable value) can be calculated from the migration of the quartz minimum (Fig. 10) for the stations on the Yukon River.

The concentration of suspended carbonates remains steady with the changing season at 2 wt% for the Tanana River, but show maxima in early July for the Eagle and Stevens Village stations (Fig. 11). As was discussed above, these maxima correlate with the minima for quartz (Fig. 10). The maximum for the Pilot Station samples appears toward the end of September (Fig. 11), when it has a similar suspended carbonate content as suspended sediments from the other Yukon stations. The Pilot Station maximum may be related to reduced flow of calcite-poor sediment from the Tanana River system during the fall, leading to a smaller dilution effect.

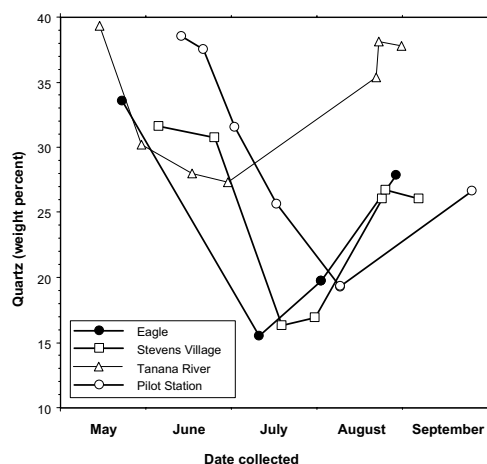


FIGURE 10. Change in wt% quartz in suspended sediment for the 2002 season for four fixed stations.

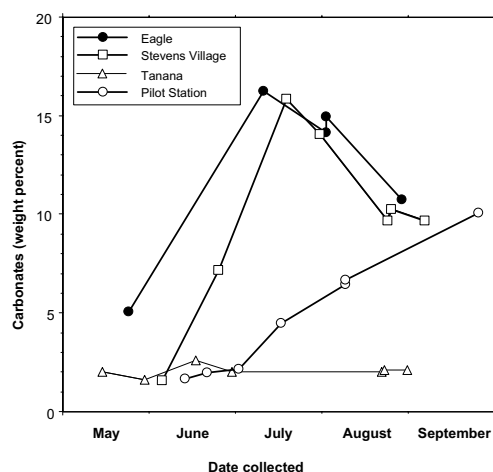


FIGURE 11. Change in wt% carbonates (XRD data) in suspended sediment for the 2002 season for four fixed stations.

Suspended feldspars are fairly constant (at about 31 wt%) for the Tanana River during the 2002 sampling season (Fig. 13). However, the Eagle sediment shows a feldspar maximum (at about 37 wt%) at the end of July, whereas the Stevens Village sediment decreases slightly (from 30 to 27 wt%) in feldspar during the summer months. The Pilot station sediment has a feldspar maximum (33 wt%) in June, and a minimum (24 wt%) in July.

The total clay mineral content has a maximum in mid-July for all stations (Fig. 12). The type of clay also changes. Early in the season significant amounts of smectite are not found in the suspended sediments (Table 2, last column). Smectite first appears together with calcite at Eagle in the 7/10/02 sample, and thereafter is found in the suspended sediments at this station throughout the remainder of the season (Table 2). Smectite first appears about a week later at Stevens Village, together with calcite (Table 2 and Fig. 14). The simultaneous appearance of calcite with smectite at these stations may indicate that this smectite

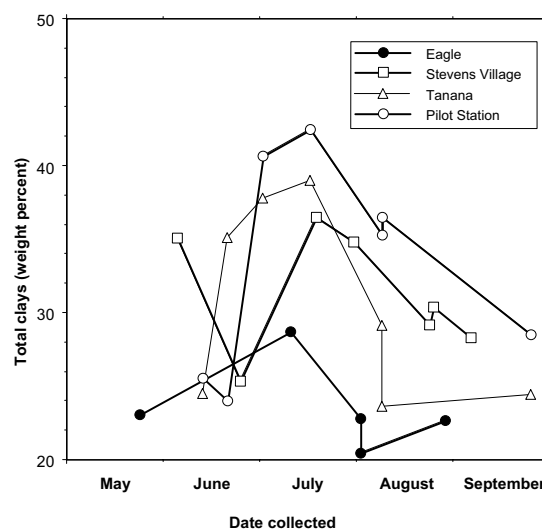


FIGURE 12. Change in wt% total clays in suspended sediment for the 2002 season for four fixed stations.

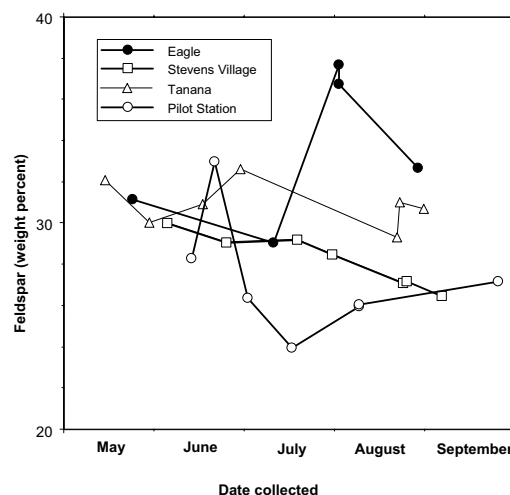


FIGURE 13. Change in wt% total feldspar in suspended sediment for the 2002 season for four fixed stations.

is coming from the calcite-rich White River system. Smectite first appears in the Tanana River suspended sediment sometime between 6/20/02 and 7/16/02, and at Pilot Station in the 7/1/02 sample. The timing indicates that the initial Pilot Station smectite may come from the Tanana River system.

Patterns of changes in suspended sediment mineralogy with season for the summer of 2003 are nearly identical to those described above for 2002. For the summer of 2001, however, the quartz minima (and carbonate maxima) are later in the summer (mid-August).

COMPARISON BETWEEN BED AND SUSPENDED SEDIMENTS

Figure 15 compares the non-clay mineral concentration for bed and suspended (average value) sediments for the four stations where suspended sediment was collected. The non-clays generally are more highly concentrated in the bed sediments, although for the Tanana River the bed and suspended sediments have nearly equal amounts of non-clays.

Unmixing sediment sources

When the main stem and a tributary merge, sediment from each source is mixed downstream from the confluence. Suspended sediments and dissolved load from the two sources may not mix completely for hundreds of kilometers below the confluence (Stallard 1987), which is why it is necessary to collect width- and depth-integrated samples to characterize the suspended load, as was done in this study. Bed sediments, however, may undergo cross-channel mixing over a much shorter distance (Johnsson et al. 1991). Sediments also may enter and leave the river through exchanges with the flood plain (Dunne et al. 1998).

It is possible to calculate the proportion of each upstream source in the downstream sediment from quantitative mineralogy using the MinUnMix program described in the Methods section. This calculation assumes that the upstream sediments are mineralogically representative of the river sediments from which they were collected, that they were well mixed below the confluence, and that winnowing and sorting has not significantly changed the mineralogy.

As an example of this calculation, the mineralogy of sample

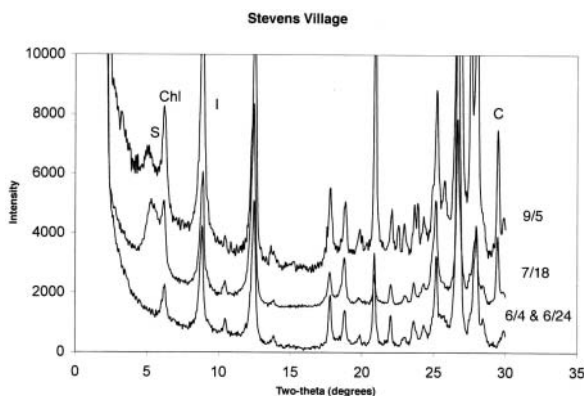


FIGURE 14. X-ray diffraction patterns of oriented, ethylene glycol solvated, suspended sediment samples taken from the Yukon River at Stevens Village. S = smectite, Chl = chlorite, I = illite, and C = calcite.

YR10, which was collected downstream from the mixing zone, should be a mixture of that found in samples YR8 and YR 9, which were collected from the Yukon River and the White River, respectively, upstream from their confluence (Table 5). These calculated proportions are compared with actual measurements of sediment load to test the method (columns 3 and 4 in Table 1). For example, the proportion of Yukon River sediment downstream from the White River-Yukon River confluence calculated from the annual sediment load [Table 1; $3\,180\,000 / (3\,180\,000 + 14\,500\,000 + 11\,420\,000) = 0.11$] compares well with the value of 0.16 calculated from the values given in Table 5 using the MinUnMix program. Similar calculations were made where possible for other confluences with comparable results (Table 1). The proportions match surprisingly well, especially considering that the measured proportions were calculated from the suspended load, and that most of the unmixed proportions were calculated from the mineralogy of the bed sediments. Artificial mixtures were prepared from the bed sediments, X-rayed, their mineralogies determined using RockJock, and then the mineralogies were unmixed using MinUnMix to further test the method, with good accuracy (Table 6). The data show that the unmixing method can be tested using artificial mixtures of end-members. One can accurately unmix up to three samples, but the method becomes inaccurate, at least for the samples chosen here, if 4 and 5 samples are used in the mixtures (Table 6).

The sources for suspended sediments were unmixed using bed sediment mineralogies in an attempt to explain the quartz minimum and calcite maximum (Figs. 10 and 11) in the suspended sediment data. Using the sediment fractions given in Figure 16, which were determined from MinUnMix calculations using samples YR8 and YR9 as the sediment sources, the minimum and maximum for quartz and carbonates could be modeled (Fig. 17). Similar calculations for the Stevens Village (using the same sediment sources) and Pilot Station (using White River sediment, YR9, and Tanana River sediment, YR32, as the sources) also indicate that the general shape of the quartz minima

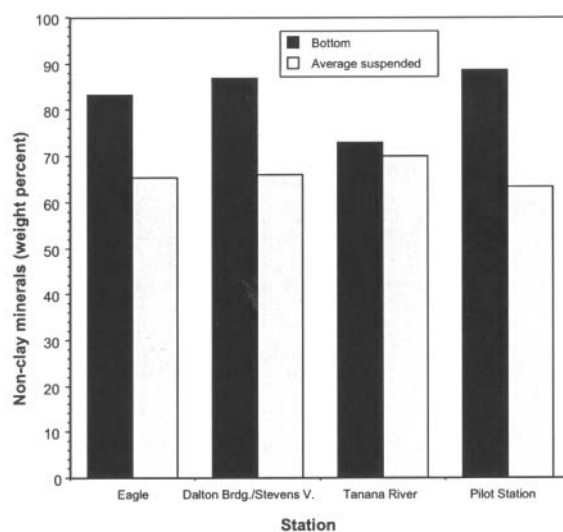


FIGURE 15. A comparison between wt% non-clays in bed and suspended sediments for four fixed stations. The values for the suspended sediments are average values for the 2002 season.

and carbonate maxima (Figs. 10–11) could be modeled, but the feldspar and clay data could not.

The assumptions that sediments are well mixed below the confluence, and that the upstream sediments are representative of the river as a whole were tested by collecting beach and bar samples from the Tanana River-Yukon River confluence region (Table 4). Eleven samples were collected from opposite sides of the Yukon River to a distance of approximately 43 km below the confluence (YT samples). In addition, five samples were collected from the Tanana River and seven samples from the Yukon River sediments (T and Y samples, respectively) upstream from the confluence. If the sediments are well mixed below the confluence, then sediments from both sides of the river should contain the same fraction of Tanana River and upstream Yukon River sediment. If the upstream sediments are representative of their rivers, then it should not matter which upstream sediment is chosen as a source for unmixing the mineralogies below the confluence. In other words, any combination of upstream sediments in MinUnMix should give the same fraction for samples collected below the confluence.

The seven plus five upstream samples and the eleven mixed samples from below the confluence led to a matrix of 35×11 MinUnMix solutions, which are summarized as average values in Table 7. The sample pairs collected closest to the confluence (YT11 and YT10 at 14 km) contain different proportions of Yukon sediment (0.70 and 0.15, respectively), and therefore the Tanana and Yukon River sediments are not well mixed at this distance. Non-island samples 35 km from the confluence (YT3

and YT5), however, give approximately the same value for each side of the river (0.63 and 0.59) indicating that the sediment sources may be well mixed at this distance, if island sediments are avoided. The relatively large standard deviations for the MinUnMix solutions, however, indicate a need for extreme caution in applying the technique, especially when only a few samples are used as end-members in the analyses. The consistent results found for unmixing the kayakers' bed samples (Tables 1 and 6) vs. the large standard deviation for the beach and bar samples collected from the confluence (Table 7) may result from sampling differences: the kayakers sampled bed sediments below the

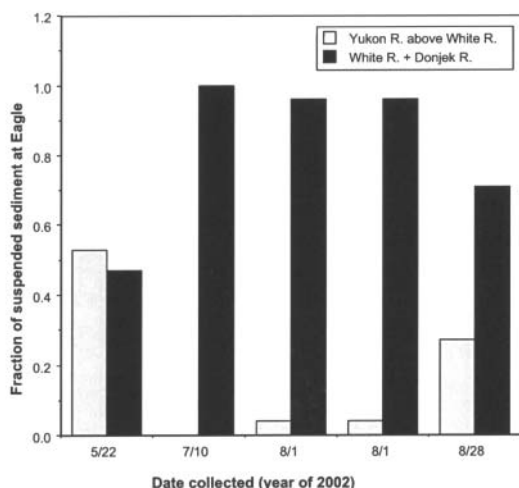


FIGURE 16. Fraction of sediment sources, calculated using Yukon River bed sediment collected above the White River and White River bed sediment in MinUnMixer, as a function of time of year for suspended sediment collected at Eagle in 2002.

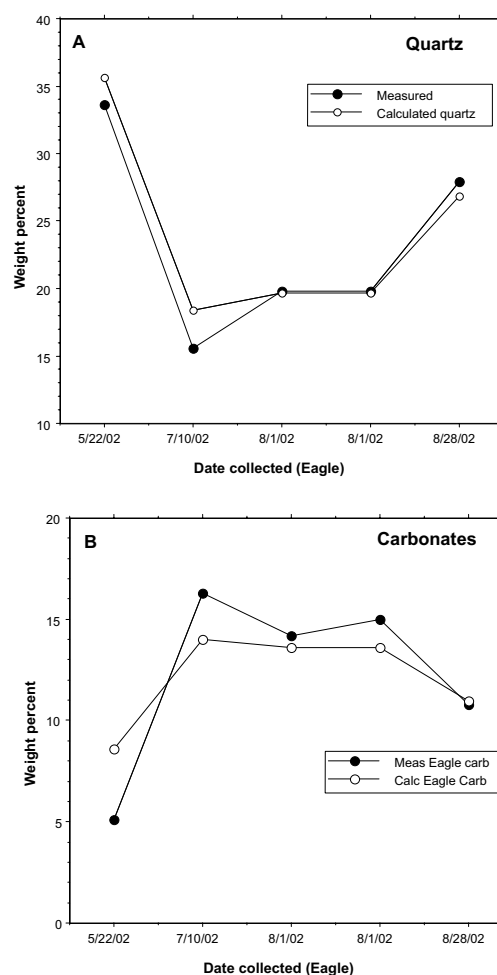


FIGURE 17. Measured mineralogies (XRD) (proportions from Fig. 16) in relation to calculated changes in mineralogy with season for the Eagle fixed station. (a) quartz; (b) carbonates.

TABLE 6. Analyses of artificial mixtures by the mineralogical unmixing technique (see text)

Samples mixed	Proportions artificially mixed	Unmixed proportions from artificial mixtures
YR2 + YR3	0.40 + 0.60	0.30 + 0.70
YR8 + YR9	0.20 + 0.80	0.19 + 0.81
YR23 + YR24	0.90 + 0.10	0.92 + 0.08
YR31 + YR32	0.50 + 0.50	0.55 + 0.45
YR9 + YR24 + YR32	0.33 + 0.33 + 0.33	0.39 + 0.29 + 0.32
YR9 + YR24 + YR32 + YR40	0.25 + 0.25 + 0.25 + 0.25	0.16 + 0.10 + 0.55 + 0.19
TR6 + YR9 + YR24 + YR40 + YR50	0.2 + 0.2 + 0.2 + 0.2 + 0.2	0.44 + 0.28 + 0 + 0.03 + 0.26

TABLE 7. Results of unmixing of beach and bar sediments collected below the Tanana-Yukon River confluence

Sample number	km from confluence (approximate river distance)	Side of river sampled	Mean proportion Yukon R. sediment	Standard deviation
YT2	43	North	0.66	0.25
YT1	43	South (island)	0.32	0.26
YT3	35	North	0.63	0.22
YT4	35	Island	0.29	0.21
YT5	35	South	0.59	0.38
YT6	31	North (island)	0.73	0.29
YT7	31	South	0.48	0.36
YT9	21	North	0.75	0.29
YT8	21	South	0.59	0.35
YT11	14	North	0.70	0.29
YT10	14	South	0.15	0.17

waterline, whereas the confluence was sampled from bars and beaches above the waterline. Beach and bar sediments could be subject to weeks or months of leaching and winnowing before being refreshed by the deposition of new sediment.

Although sediment source modeling is a promising technique, further modeling was not attempted because of the many uncertainties involved in the calculation, especially the assumption that bed sediment composition approximates suspended sediment mineralogy. This assumption cannot be completely valid, because suspended sediment changes mineralogy with season (Figs. 10–13 and 16–17). More exact results could be obtained if “primary” suspended sediment sources in the Yukon system were identified. Such a source would be a tributary in which the suspended sediment does not change in relative proportions of minerals through the season, although the concentration of sediment could vary. Once such primary suspended mineralogies have been measured, the large suspended sediment flows and sources in the Yukon system could be modeled more precisely.

Illite thickness measurements

The mean thicknesses and thickness distributions of illite crystallites were measured for suspended and bed sediment using the Bertaut-Warren-Averbach XRD method (MudMaster computer program; Eberl et al. 1996, 1998a). A typical distribution shape is shown in Figure 18a. An α - β^2 plot (Eberl et al. 1998b) for the distributions is shown in Figure 18b. The α term is defined as the mean of the natural logarithms of the thicknesses, and β^2 is their variance. The data form a linear trend to the left of the field expected for illite crystal growth in hydrothermal or diagenetic systems (Bove et al. 2002; Środoń et al. 2000). With further study, it may be possible to use such plots to distinguish between authigenic and detrital illites in rocks. Detrital illites should have a larger variance for a given mean thickness because they may be composed of mixtures of illites from a variety of sources. Generally, illites from Yukon suspended sediments have a larger variance for a given mean thickness than do those found for bed sediments (Fig. 18b).

Mean illite crystallite thicknesses for suspended sediments change with the season (Fig. 18c). The suspended illites at Eagle have a relatively constant thickness with the season, varying from 5 to 6 nm, but thicknesses in suspended sediments in the Tanana

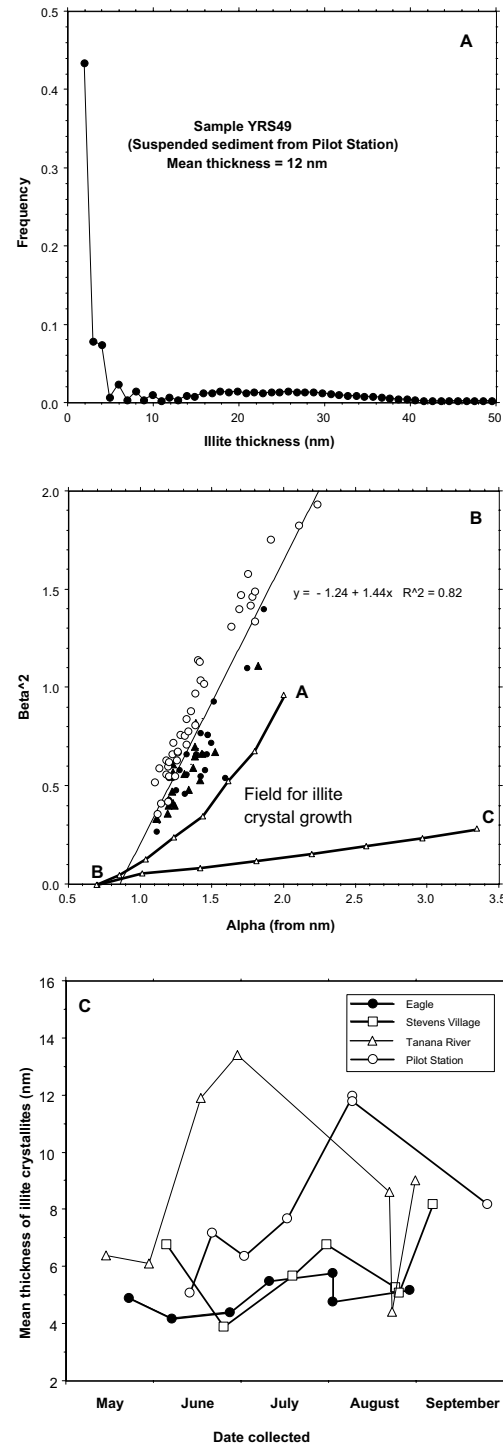


FIGURE 18. (a) Typical illite crystallite size distribution measured from a suspended sediment using an X-ray peak broadening technique (see text). (b) Plot of α and β^2 values for crystallite size distributions for illites found in suspended sediments (open circles), Yukon River bed sediments (filled circles), and tributary bed sediments (filled triangles). $\alpha = \sum f(T) \ln(T)$ and $\beta^2 = \sum [\ln(T) - \alpha]^2 f(T)$, where T is illite crystallite thickness, and $f(T)$ is the frequency of the thickness. (c) Change in mean illite crystallite thicknesses in suspended sediment for the 2002 season for four fixed stations.

River seem to vary with total clay content of the suspended sediment (compare Figs. 12 and 18c). The illites in the Tanana River have the greatest range in thicknesses, changing by a factor of about 2 to 3 during the collecting season. The changes in suspended illite thicknesses at Pilot Station reflect changes in illites released from the Tanana River (Fig. 19c), and demonstrate the influence of the composition of Tanana River sediment on sediment at the mouth of the Yukon River.

Weathering of minerals during river transport

An approximate mass-balance calculation, using average percentages for the minerals in suspended sediments from the fixed stations (data for all three years were used in the averages) and sediment flow data (Table 1, including a correction for sediment overbank losses), indicates that approximately 1.2×10^6 metric tons of suspended carbonate, roughly 1/4 of that carried by the river, may dissolve between Eagle and Pilot Station each year. This total includes about 30 wt% of the suspended calcite and 15 wt% of the suspended dolomite. Similarly, roughly 3×10^6 metric tons of feldspar dissolve. This includes approximately 1 wt% of the alkali feldspar carried by the river between Eagle and Pilot Station, and 25 wt% of the plagioclase. Roughly 6×10^6 metric tons of quartz dissolves over the same reach, or 3 wt% of that carried. It is estimated that 10 wt% of the yearly calcium ion load for the river comes from the dissolution of carbonates and plagioclase between Eagle and Pilot Station.

ACKNOWLEDGMENTS

The author thanks kayakers W. Barber and J. Klink for collecting bed sediments, A. Horowitz and J. Smith for supplying the suspended samples, A. Blum, P. Schuster, and R. Striegl for reviewing the original manuscript, D. Kile for analyzing some of the samples, L. Eberl, P. Erhart, and R. Snyder for their help in the field, W. Freeman for carbon analyses, and K. Eberl for help with the graphics. The use of trade names is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

REFERENCES CITED

- Bove, D.J., Eberl, D.D., McCarty, D.K., and Meeker, G.P. (2002) Characterization and modeling of illite crystal particles and growth mechanisms in a zoned hydrothermal deposit, Lake City, Colorado. *American Mineralogist*, 87, 1546–1556.
- Brabets, T.P., Wang, B., and Meade, R.H. (2000) Environmental and hydrologic overview of the Yukon River Basin, Alaska and Canada. U.S. Geological Survey Water-Resources Investigations Report 99-4204, 74 p.
- Drits, V., Eberl, D.D., and Šrodoň, J. (1998) XRD measurement of mean thickness, thickness distribution and strain for illite and illite/smectite crystallites by the Bertaut-Warren-Averbach technique. *Clays and Clay Minerals*, 46, 38–50.
- Dunne, T., Mertes, L.A.K., Meade, R.H., Richey, J.E., and Forsberg, B.R. (1998) Exchanges of sediment between the flood plain and channel of the Amazon River in Brazil. *Geological Society of America Bulletin*, 110, 450–467.
- Eberl, D.D. (1984) Clay mineral formation and transformation in rocks and soils. *Philosophical Transactions of The Royal Society of London A*, 311, 241–257.
- (2003) User guide to RockJock—A program for determining quantitative mineralogy from X-ray diffraction data. U.S. Geological Survey Open-File Report, OF 03-78, 40 p.
- Eberl, D.D., Drits, V., Šrodoň, J., and Nüesch, R. (1996) MudMaster: A program for calculating crystallite size distributions and strain from the shapes of X-ray diffraction peaks. U.S. Geological Survey Open-File Report, 96-171, 46 p.
- Eberl, D.D., Nüesch, R., Sucha, V., and Tsipursky, S. (1998a) Measurement of fundamental illite particle thicknesses by X-ray diffraction using PVP-10 intercalation. *Clays and Clay Minerals*, 46, 89–97.
- Eberl, D.D., Drits, V.A., and Šrodoň, J. (1998b) Deducing crystal growth mechanisms for minerals from the shapes of crystal size distributions. *American Journal of Science*, 298, 499–533.
- Edwards, T.K. and Glysson, G.D. (1988) Field methods for measurement of fluvial sediment. U.S. Geological Survey Open-File Report, 86-531, 118 p.
- Horowitz, A.J., Demas, C.R., Fitzgerald, K.K., Miller, T.L., and Rickert, D.A. (1994) U.S. Geological Survey protocol for the collection and processing of surface-water samples for the subsequent determination of inorganic constituents in filtered water. U.S. Geological Survey Open-File Report, 94-539, 57 p.
- Johnsson, M.J., Stallard, R.F., and Lundberg, N. (1991) Controls on the composition of fluvial sands from a tropical weathering environment: Sands of the Orinoco River drainage basin, Venezuela and Columbia. *Geological Society of America Bulletin*, 103, 1622–1647.
- McCarty, D.K. (2002) Quantitative mineral analysis of clay-bearing mixtures: The “Reynolds Cup” contest. *Committee on Powder Diffraction Newsletter*, 27, June 2002, p. 12–16, <http://www.iucr.org/iucr-top/comm/cpd/Newsletters>.
- Šrodoň, J., Eberl, D.D., and Drits, V.A. (2000) Evolution of fundamental-particle size during illitization of smectite and implications for reaction mechanism. *Clays and Clay Minerals*, 48, 446–458.
- Šrodoň, J., Drits, V.A., McCarty, D.K., Hsieh, J.C.C., and Eberl, D.D. (2001) Quantitative mineral analysis by powder X-ray diffraction from random preparations. *Clays and Clay Minerals*, 49, 514–528.
- Stallard, R.F. (1987) Cross-channel mixing and its effect on sedimentation in the Orinoco River. *Water Resources Research*, 23, 1977–1986.
- U.S. Geological Survey (1997–1999) National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chapters, A1–A9, 2 v., variously paged. (Chapters were published from 1997–1999; updates and revisions are ongoing and can be viewed at: <http://water.usgs.gov/owq/FieldManual/mastererrata.html>)

MANUSCRIPT RECEIVED OCTOBER 1, 2003

MANUSCRIPT ACCEPTED MARCH 6, 2004

MANUSCRIPT HANDLED BY LEE GROAT