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CLAY MINERALOGY OF THE LOWER COLVILLE RIVER DELTA, NORTH ARCTIC ALASKA

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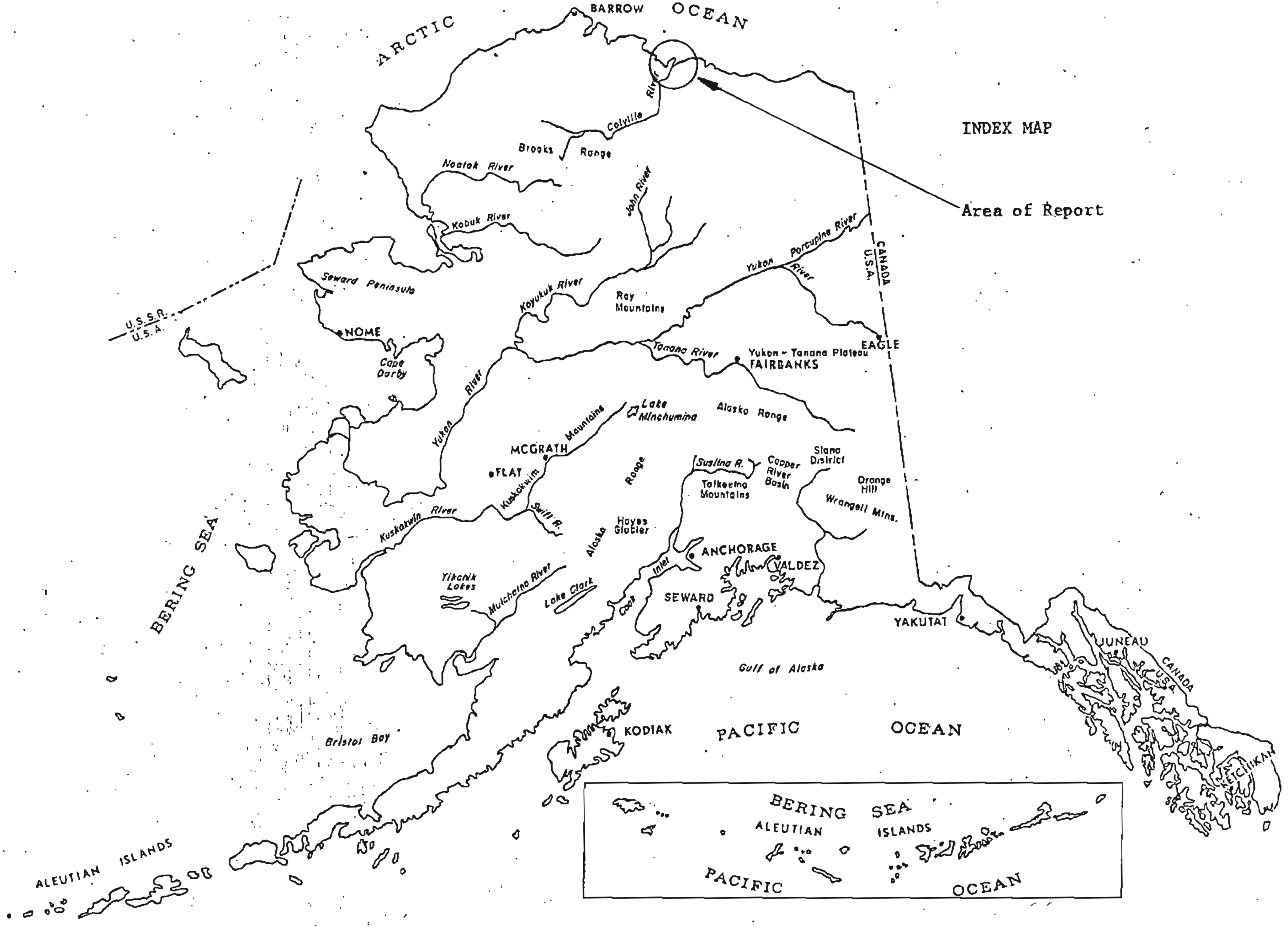


INDEX MAP

Area of Report
ARCTIC
BARROW
OCEAN
Colville River
Brooks Range
Noatak River
Kobuk River
John River
Seward Peninsula
U.S.S.R.
U.S.A.
NOME
Cape Darby
Koyukuk River
Ray Mountains
Yukon River
Porcupine River
CANADA
U.S.A.
EAGLE
Tanana River
Yukon - Tanana Plateau
FAIRBANKS
Lake Minchumina
Alaska Range
Yukon River
MCGRATH
Mountains
FLAT
Kuskokwim
Swift R.
Kuskokwim River
Range
Susitna R.
Copper River Basin
Slana District
Orange Hill
Talkeetna Mountains
Wrangell Mtns.
Hayes Glacier
Alaska
ANCHORAGE
VALDEZ
Cook Inlet
SEWARD
Tikchik Lakes
Mulchatna River
Lake Clark
BERING SEA
YAKUTAT
JUNEAU
CANADA
USA
Gulf of Alaska
KODIAK
PACIFIC
OCEAN
KETCHIKAN
Bristol Bay
ALEUTIAN ISLANDS
BERING SEA
ALEUTIAN ISLANDS
PACIFIC OCEAN

INTRODUCTION

The need for the preservation of continental and marine environments in as unpolluted a state as possible has long been recognized. However, in order to detect pollution in an environment it is necessary to have in hand baseline ecological data relative to that environment in its pristine or unpolluted state. The foregoing has special relevance to the continental, deltaic and shallow marine environments of Arctic Alaska. Although this region is apparently relatively free from any appreciable pollution at present, potential problems may arise in the future as a result of increased development in that area, especially of the large petroleum reserves. Realizing this various Federal, State and private agencies have undertaken to further our environmental knowledge of this region. This report presents preliminary results of some baseline studies of the mineralogy of sediments from the continental margin and the adjacent shallow marine regime of this region.

DESCRIPTION OF ENVIRONMENTS

The deltaic region of north Arctic Alaska is one of the few transitional natural environments on earth of which we have very limited knowledge. The area under study extends from Harrison Bay in the west to Maguire Island in the east, and from the North Slope coast oceanward to approximately the 10 fathom line (Figure 1).

The transitional environment between Cape Halkett and Canning River mouth (Figure 1) consists of a complex of several river estuaries, distributary channels, bays, lagoons, barriers, bars, coastal beaches and deltaic plain consisting of tundra. Several large rivers (e.g. Colville, Kuparuk,

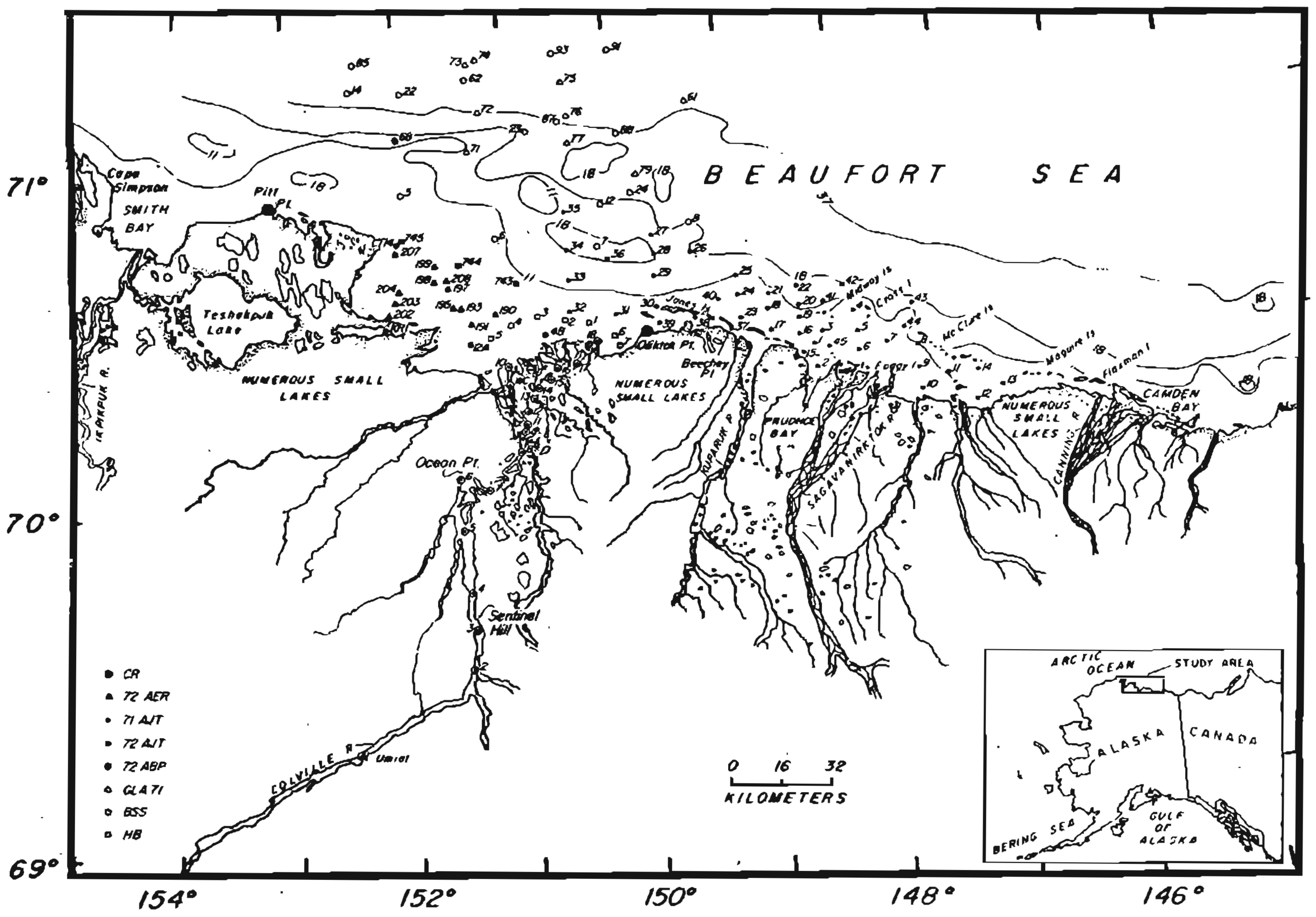


Figure 1. Map of study area, Arctic Alaska

Sagavanirktok and Canning) have built deltas which coalesce laterally to form a complex of deltas. The most prominent of the deltas in this region is that of the Colville River, and it greatly influences sedimentation in the nearshore. As such it merits special mention.

The Colville River has a course of approximately 600 km, and has built a 560 km^2 delta at the mouth. Several distributaries break off from the main channel at the delta head, and as a result several lobate islands have formed in the far downstream end. Most of these islands in the estuary are elongated parallel to the distributary channels. All river channels of the North Slope are highly braided, presumably because of the great seasonal variations in sediment and water discharge. Arnborg et al. (1962) have calculated that the most striking feature of the Arctic rivers is the great concentration of activity in a short period of time. For example, in 1962 43% of the annual discharge ($16 \times 10^9 m^3$) and 73% of the total inorganic suspended load (5.8×10^6 tons) were discharged from the Colville River during a three-week period around the spring breakup (Arnborg et al., 1962). The bulk of this sediment-laden fluvial discharge initially flows oceanward over sea ice situated off the river mouths, and settles on the ice as a deposit ranging from 1 to 8 inches in thickness. Finally this sediment finds its way to the bottom through drain holes in sea ice (Walker, 1972) and/or by melting of the ice. According to Reimnitz and Bruder (1972), most of this fluvial sediment outfall is deposited on the steeper slopes seaward of the 2 m depth contour off the Colville River mouth; this area represents the delta front.

Some detailed morphological and hydrographical attributes of the North Slope river deltas - especially that of Colville River - were recently presented by Walker and McCloy (1969), Lewellen (1972), Kinney et al. (1972) and Walker (1972), and therefore, particulars of these attributes will not be enumerated here. However, it should be noted that the morphologies of the North Slope deltas do not exactly conform to any of the delta prototypes mentioned in the literature; the closest resemblance, at best, is probably to the arcuate delta type. All North Slope rivers are truly Arctic rivers inasmuch as they arise, flow and discharge in Arctic Alaska, which is characterized by permafrost terrain. All these rivers are partly or wholly frozen almost eight months of the year.

The mean lunar tidal range in the north Alaskan arctic coast is comparatively very low, roughly 1' (Matthews, 1970). Kinney et al. (1972), have reported that in the lagoons and nearshore during the summer surface currents may range from 0 to 37 cm/sec (0 to 0.75 knots). Dygas et al. (1972), while observing a good correlation of strength and directions of water currents and wind, concluded that in the Simpson Lagoon the bottom current velocity is in the order of 17.3 cm/sec. However, as a result of storm surge sea level in the coastal area may vary as much as 5 ft within a short time (Matthews, 1970; Kinney et al., 1972). Although tidal flats are not extensive in the north coast of Alaska because of low tidal range, some low lying deltaic areas may often become water-logged during the sea level rise resulting from storm surge.

Salinities of waters in the Colville Delta and adjacent continental margin region range from 10°/oo to 65.9°/oo (Kinney et al., 1972; Schell and Hall, 1972; Walker, 1972). Presumably, the unusually high saline waters are formed as a result of great concentration of ions in water bodies entrapped between grounded ice; the ionic supply being from deionization of saline ice. Primary productivity in the lagoonal area is relatively low, most values ranged around 1 ug C-hr (Alexander and Billington, 1972).

The continental facies of the North Slope Deltas is dominated by the coastal beaches, Harrison Bay, Simpson Lagoon, the far offshore and near-shore barriers. The lagoon and Harrison Bay are shallow, having a depth range of 0.8 to 3.5 m. The barriers and bars are oriented roughly parallel to the deltaic coastline, and locations of all barriers in the area of study are confined to the east of the Colville River confluence. The barrier surfaces consist predominantly of gravels. With the exception of the areas near river mouths, the coastal beach essentially has gravelly and sandy deposits, the size distributions of which have been described by Naidu et al. (1970) and Dygas et al. (1971). The open marine deltaic faces and the adjacent shelf surface is presently being, and/or been modifified, by ice gouging (Reimnitz et al, 1972), and some of the offshore bars seem to have originated by ice push. Comparative aerial photographic studies (Dygas et al., 1972) reveal large scale morphological changes in the Pingok and Thetis Islands over the past 20 years. The Arctic deltaic environment under description differs from the low-latitude deltas in several ways. The more notable differences are the absence of extensive sand dunes, flood plains, tidal flats and mangrove swamps, together with the common presence of coastal gravel deposits, a deltaic plain dominated by tundra, and subjection of the entire area to strong ice stress conditions for the major part of the year, as well as to thermal erosion.

DETAILED CLAY MINERALOGIC STUDIES

INTRODUCTION

Results presented in this report are based on analyses of surface sediment samples that were collected during various phases of activities related to continuing projects of the Institute of Marine Sciences, University of Alaska, in the North Slope area. Details have been given elsewhere (Naidu, 1972; Naidu and Mowatt, 1973 a,b).

In an attempt at elucidating the mineralogic relationships, detailed studies have been made of materials from selected sample stations along the lower course of the Colville River (locations CR3, CR5, CR7, CR8, figure 2), as well as from the Harrison Bay area (KR1, figure 2). Similar work to that described below is currently in progress on materials from locations CR4, CR6, CR9, CR17 and CR18, and will also be done on other selected stations offshore as our preliminary results indicate areas of particular interest.

Our principal approach in these detailed studies has been to investigate the mineralogy within sub-fractions of the less-than two micron equivalent spherical diameter ("e.s.d.") particle-size range for each sample locality. It was anticipated that this would permit more definitive characterization of the clay mineral types present, and thus enable investigations of relationships between the sample localities to be based on an increased degree of resolution with respect to mineralogies. Further, the relationships among the different particle-size fractions of each sample location was deemed to be of interest in increasing our understanding with respect to matters of sediment transport, deposition, and possible changes in the nature of the clay minerals during the sedimentary regimen. Finally, an appraisal of different modes of sample preparation and treatment was made on materials from each of three particle size ranges from one station, CR5, in order to evaluate applicability to this type of study. The comparative behavior of various sizes of clay minerals in response to these treatments was noted, and will be discussed further in the section describing the mineralogy of locality CR5.

The results on the five locations studied to date indicate the desirability of performing detailed studies of this nature, in addition to the routine investigation of the less-than two micron e.s.d. size fraction in toto (the "bulk

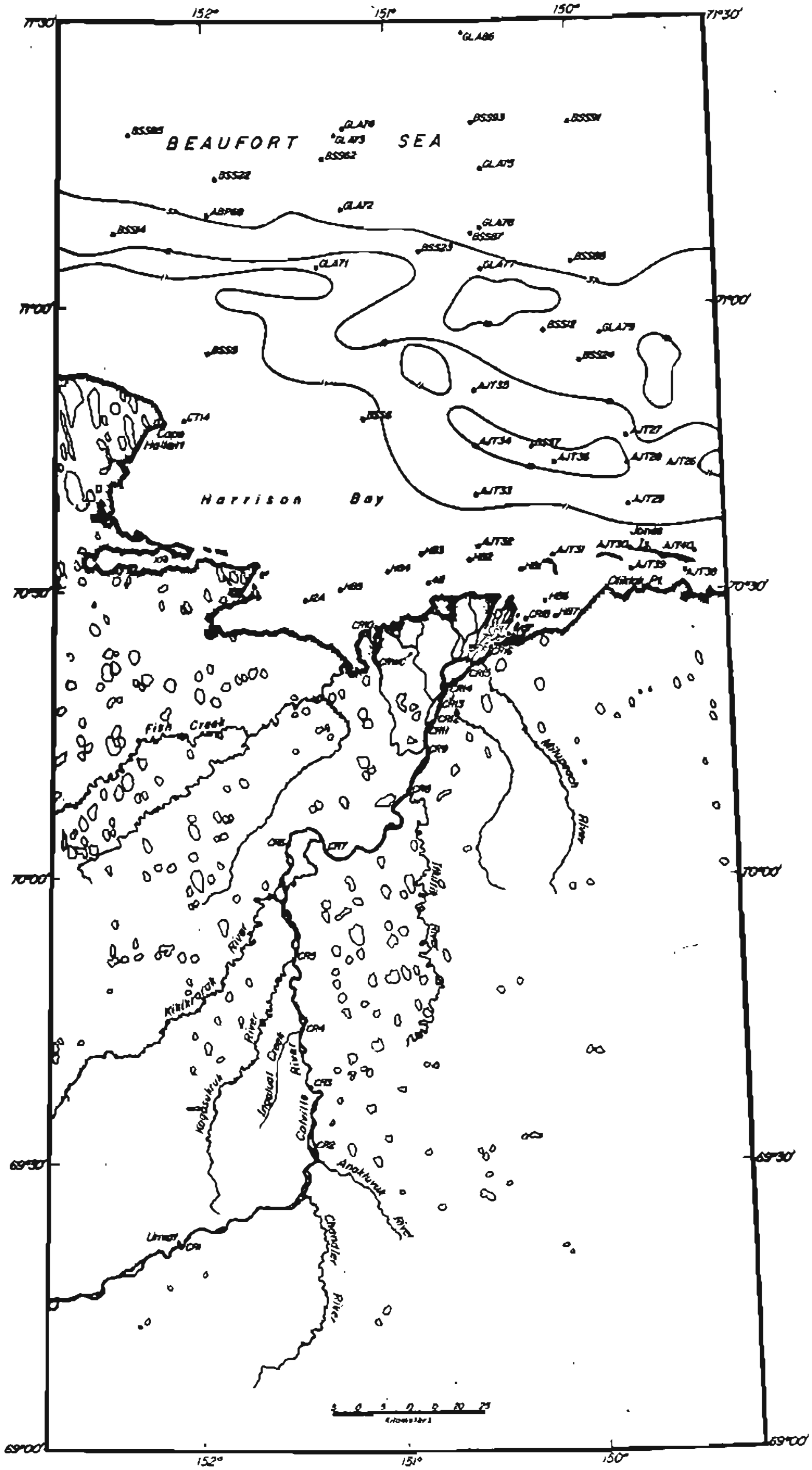


Figure 2. Colville River and Delta area, Arctic Alaska.

clay mineralogy," ie). The gross aspects of sedimentologic relationships are normally characterized fairly well by the latter information, but often there are ambiguities left unresolved without more detailed analysis. In some instances hitherto unsuspected mineralogic subtleties are brought to light as well, which is cause for some concern regarding interpretations and generalizations made on the basis of the more cursory examinations routinely performed. Admittedly the more detailed studies involve a considerably greater expenditure of time and effort, and are less amenable to routine work on a great number of samples. However, based on preliminary apprisal of a given area by means of the bulk clay mineralogy, samples of critical importance may be selected for the additional in-depth studies which appear to be essentially the next higher level of sophistication. Given the expense attendant to collection of samples, along with the interest regarding mineralogy-geochemistry-sedimentology of the geographic areas represented, this increased degree of analytical resolution appears worth striving for.

The value of this approach has been amply demonstrated elsewhere; M.L. Jackson in his various soil mineralogy studies (cf. Jackson, 1956, 1964, etc.) was one of the earlier advocates, for example.

Sample Preparation

Separate portions of the sample material from each of the locations previously described were treated according to the following procedural scheme.

1. The bulk sample was wet-sieved with deionized water, using a 230 mesh (62.5μ) stainless steel sieve.

2. The resultant$<$62.5μ e.s.d. material was treated with H_2O_2, using the method described by Jackson, 1956, pages 35-36, in order to remove organic material. This permits study of the inorganic phases present, without the uncertainties and ambiguities which arise in the presence of appreciable organic material. Although this obviously leads away from a true understanding of the geochemical-mineralogic-sedimentologic relationships in the natural environment, it appears necessary in order to clearly characterize the clay mineral phases present. Thus, at least an enhanced understanding of one facet of the natural system is attained, admittedly at some sacrifice in terms of the natural context. As per the suggestion of Douglas and Fiessinger, 1971, the pH was monitored during this treatment on each sample. The most acidic value observed was 6.6, which suggests little likelihood of significant clay mineral modification resulting from this treatment.

3. The resultant sedimentary material was suspended in 1000 ml. graduated cylinders, in deionized water, and the $< 2\mu$ e.s.d. size material was removed by differential settling of the coarser material ($> 2\mu$ e.s.d., ie.). The suspended$<2\mu$ material was removed by siphoning, additional deionized water was added to the residual material in the cylinder, the mixture was stirred and re-suspended, and any remaining $< 2\mu$ material removed as before. This procedure was repeated until the supernatant material was clear to the eye, at which stage presumably most if not all of the$<2\mu$ sediment originally present in the sample had been removed for further study. No dispersant chemicals were added, as flocculation did not appear to present any problem with these materials, presumably due to the use of deionized water, as well as because of effective rinsing of the mixture by the repeated re-suspensions.

4. The resultant $<2\mu$ material was subjected to further particle-size fractionation, using centrifugal sedimentation, following the methods described by Jackson, 1956, pages 127 ff. The $<0.3\mu$ e.s.d. size fraction was removed first, followed successively by the $0.3 - <1.0\mu$ e.s.d. size fraction, and then the $1.0 - <2.0\mu$ e.s.d. size fraction. It is realized, given the compromises necessary relative to generalizations regarding particle shape and particle density, as well as physical parameters regarding fluid dynamics and particle settling, gravitational effects as a function of geographic latitude, etc., that these particle-size values are only nominal in any absolute sense. Hopefully, however, they are valid in a relative sense within the framework of studies in one laboratory. The results of our work to date seem to support this latter appreciation of the situation, at least.

5. For the resultant materials from station CR5, each of the particle-size fractions obtained was divided into two portions. One aliquot was reserved for analysis as described below, the second aliquot was first subjected to the treatment described by Jackson, 1956, pages 57-58, for the removal of "free-iron oxide" material from sediment. An evaluation of the effects of this treatment was made in comparison to the other aliquots, in order to ascertain the desirability of utilizing this procedure. Of interest also was the effect of this treatment, which involves the use of $Na_3C_6H_5O_7 \cdot 2H_2O$, $NaHCO_3$, and $Na_2S_2O_4$, at temperatures of 75-80°C, on the various particle-sizes. The results are discussed in the section describing the mineralogy of location CR5. Additionally, this "free-iron oxide removal" treatment was used on the $0.3 - <1.0\mu$ size fraction from location CR3, after it became apparent that the X-ray diffraction patterns of the untreated material were unintelligible, due to the presence of appreciable amounts of iron oxide. The results of this are discussed in the section dealing with station CR3.

Analytical Procedures

General Discussion -

The principal objective of our studies to date has been to investigate the nature of the clay minerals present in each of the size fractions, and to attempt to understand the relationships within each sample locality, as well as between localities. X-ray diffraction has been the basic analytical method used, although chemical studies are in progress or planned as well. In X-ray diffraction work, the following analytical scheme was utilized.

For each particle-size fraction, for each sample location, seven specimens were prepared by placing aqueous suspensions on porous ceramic plates (American Olean Co. Bisques, cut to size). By means of vacuum applied to the underside of each plate, the suspended clay material was sedimented onto the surface of the plate in such a manner that the basal planes of the layer silicate minerals are predominantly aligned parallel to the surface of the plate. This is essentially the method of Kinter and Diamond, 1956, as also described and evaluated by Gibbs, 1965. This method is preferred as it permits various further treatments to be performed on the clay materials after they are thus mounted on the plates. Additionally, the ubiquitous presence of diffraction maxima ("peaks", ie.) attributable to the alpha-quartz present in the ceramic plate material, far from being any great hindrance, actually serves the useful purpose of a built-in internal standard for each sample, with respect to absolute positions of the diffraction maxima from the clay minerals with respect to Bragg angles. The quartz peaks thus used are located at 26.64°2θ (3.34Å) and 20.842θ (4.26Å) for copper K-alpha radiation, which was used throughout the course of our work.

Mineralogic determinations

Various further treatments were performed on the various plate mounts of each particle-size fraction of each sample, followed by X-ray diffraction analysis. A Philips Electronics Norelco X-ray Diffractometer was employed, the samples being analyzed at varying scanning speeds as appropriate, using Nickel-filtered copper K-alpha radiation. These treatments are described individually below, in conjunction with discussions of the criteria used for recognition of the various clay mineral species. A certain amount of such definition seems unavoidable here, in view of inconsistencies in usage, disagreements in terminology, and so forth, with which the literature is unfortunately replete. Much of this confusion is due to the difficulties inherent in attempting an assessment of complex assemblages of fine-grained materials. More complete discussions of the theoretical and practical aspects of clay mineralogic analysis can be found in standard reference works such as Brown, 1961, Grim, 1968, Carrol, 1970, etc. All of the work described in the present study was carried out at room temperature and relative humidity. Each of the cation saturation treatments was followed by two rinses with deionized water. The X-ray diffraction work was performed on mounts which had been air-dried under laboratory conditions. The instrumental parameters used routinely, unless otherwise specified, were 2°2θ per minute scan speed, time constant 2, with 1°-0.006" slits.

Specific Treatments and Clay Mineralogic Analysis

1. Saturation with ethylene glycol - This permits the detection of the presence of materials (eg. smectites and some vermiculites, as well as mixed-layered phases containing either of these as component layers) into which molecules of glycol may associate themselves in interlayer structural sites. Reynolds, 1965, discussed this effect quite thoroughly. The resultant interplanar basal repeat distance for smectites is in the neighborhood of 17Å.

2. Saturation with KCL (1N) - This procedure affords the opportunity for exchange of K+ onto such appropriate interlayer structural sites as may exist in any of the mineral phases present. The present consensus of opinion regarding this phenomenon seems to be that materials variously described (often somewhat nebulously) as "stripped, weathered, degraded" illites or micas, "soil vermiculites," etc. will readily accept K+ ions into interlayer structural sites formerly occupied by K+ prior to the "degradation" process. This results in the "collapse" of the degraded structure, and is reflected in the X-ray diffraction analysis as a shift in basal spacings from somewhere>10Å to approximately the 10Å region. The term "illite" might be used to collectively designate materials of this sort, but other studies (Hower and Mowatt, 1966) have indicated that there are other aspects relative to this problem which are difficult to distinguish in working with polyphase assemblages such as the present study. Thus, our present usage of the term "illite" in describing the mineralogy should not be construed as other than a generalization to describe material with gross x-ray diffraction effects similar to those described by Hower and Mowatt. Actually, as in the present studies, some term of a more descriptive nature, such as "10Å material," might well be adopted, at least in those instances where more definitive information is lacking. In essence, since the term illite has been interpreted variously by many investigators, for our purposes we will either use it in a very general descriptive sense, or avoid its use, with the understanding that the problem essentially is one of interfacing terminology, previous usages, and limits of resolution for analytical techniques currently available. This further leads to the necessity here for a brief discussion of our handling of the matter of "interstratified," or "mixed-layer" materials. In view of the problems already cited regarding the unraveling of diffraction effects from polycomponent assemblages, together with

the obvious complexity of the problem, it seems best to merely generalize in a descriptive manner with respect to mixed-layer materials in our samples, rather than attempt to present detailed interpretations whose dubious validity seem to outweigh their possible usefulness. The matter of mixed-layering has been dealt with recently by Reynolds, 1967, Reynolds and Hower, 1970, and Hower, 1967, treating the problem of varying degrees of ordering within these materials, for simplified cases. The natural assemblages, particularly those representing materials whose properties result from a combination of heritage, weathering, and cation exchange in the lacustrine/marine environment, are undoubtedly more complex, and thus even less amenable to clear understanding with our present methods. As pointed out by Mills and Zwarich, 1972, the recognition and interpretation of interstratifications in clay mineral assemblages is often extremely difficult, and in the fine clay fractions attention must also be given to line-broadening effects on diffraction maxima resulting from very small particle sizes.

Smectitic materials are those which possess residual interlayer charges resulting from deviations from electrostatic neutrality within the "basic lattice" of the minerals such that equilibrium exchange of K+ coordinated with water molecules into the interlayer sites is manifested by a basal spacing in the 12.5Å region by X-ray analysis, under our experimental conditions. In "degraded" micas, etc., this residual interlayer charge is somewhat higher (of a more negative character, ie.), such that K+ ions enter the exchange sites without the water molecules, leading to the smaller (∿10Å, ie.) interplanar distances observed. Prior to K+ exchange, some of these latter materials may also show varying degrees of apparent structural tolerance for, uptake of, and resultant "expandability" with, ethylene glycol, and thus may be confused with smectitic materials if more detailed work is not done. However, once saturated with K+, vermiculites and degraded micaceous materials commonly show little or no tendency to "re-expand" upon saturation with ethylene glycol. Thus, the differences in behavior of clay mineral samples subjected to various treatments offer clues in attempting to obtain greater insight into the nature of the assemblages, and in assessing the properties of the phases present. The other treatments described in this section are further examples of this approach.

3. Saturation with NaCl(1N) - This is done in order to ascertain the effects of the interaction between Na+ions, the various clay mineral phases, and the aqueous phase. The Na+ion as such is apparently not as stable in the interlayer sites of degraded micas as the large K+ion, and its relationship to degraded phases is not clearly defined under our experimental conditions. However, smectitic materials effect an equilibrium with Na+ and coordinated water molecules such that basal spacings in the 12.5Å region are observed by X-ray analysis.

4. Saturation with $MgCl_2$(1N) - Although both vermiculitic and smectitic phases appear to adopt an equilibrium with Mg++ and water such that a basal spacing of about 14Å results, the smectitic materials will subsequently re-equilibrate with ethylene glycol in such a manner that a basal spacing in the neighborhood of 17Å results, whereas vermiculites do not seem to show the same effect. "Degraded" chlorites, representing the chloritic analogs of vermiculites and "degraded" micas, also readily equilibrate with Mg++ ions and the aqueous phase, with a 14Å basal periodicity the result.

5. Saturation with $Ca(C_2H_3O_2)_2(1N)$ - Smectites, Ca++, and water equilibrate in such a manner that a basal spacing of about 15Å results, whereas the behavior of vermiculites and degraded micas is somewhat indeterminate. Although this treatment was not overly useful in itself in delineating clay mineral species, it served as a necessary antecedent in effecting exchange of the same ion onto smectite phases in all samples prior to further heat treatments of these samples. The latter treatments did prove to be quite informative.

6. Saturation with filtered sea water - This treatment was performed in order to investigate the mutual equilibrium relationships among the major cations present in sea water, the aqueous phase, and the clay mineral phases, having analogous data from the other treatments described above for individual cations.

7. Saturation with ethylene glycol of each cation saturated sample, after X-ray diffraction analysis - In order to compare the effects of the various cation treatments, each specimen was saturated with ethylene glycol, and re-analyzed by X-ray diffraction. The resultant differences, for a given sample, in peak positions and intensities, were quite informative with respect to characterizing the mineral phases.

8. Heat treatment, one hour at 300°C - After X-ray analysis, each calcium acetate treated specimen was heated in a muffle furnace for one hour at 300°C, and re-analyzed by X-ray diffraction. This treatment drives off the loosely bound interlayer water molecules from smectitic and vermiculitic materials, but has no appreciable effect on illitic, kaolinitic, or chloritic components. The resultant basal spacing for smectites and vermiculites coincides, in

general, with that of illites and micas, in the neighborhood of 10Å. A useful comparison is possible here between the efficacy of KCL treatment and the 300°C treatment, for a given sample, in "collapsing" the hydrated "expandable" smectitic-vermiculitic layers present to this 10Å periodicity.

9. Heat treatment, one hour at 430°C - The same specimens previously heated to 300°C were heated for an additional one hour period at 430°C, and re-analyzed by X-ray diffraction. This heating is made with the intent of attempting to monitor structural changes in any of the clay minerals present, particularly any chloritic and/or kaolinitic phases of relatively low thermal stability. It is often difficult, at best, to discern such changes in individual members of polyphase assemblages such as those under study here, but the attempt was made nevertheless.

10. Heat treatment, one hour at 550°C - Kaolinites generally break down to amorphous materials under this treatment, and the basal spacing in the 7Å region due to kaolinite in the sample disappears under X-ray examination. Any contribution to a diffraction maximum in the 7Å region due to the presence of a chloritic phase also disappears under these conditions, but the presence of such material is confirmed by the enhancement in intensity of a diffraction maximum in the 14Å region, often shifted toward the 13.8Å neighborhood somewhat. Thus, a measurement of the relative intensities of these various diffraction maxima, as well as those in the 10Å region, provide useful indications as to the nature and relative amounts of the minerals present. The same Ca++ saturated specimens previously heated at 300°C and 430°C were utilized in this step of our analytical scheme.

11. Slow-scanning, 20° to 28°2θ - In an attempt to assess the presence and relative amounts of chlorite and kaolinite, each KCL saturated specimen was re-analyzed by X-ray diffraction, with the goniometer scanning at 1/2°2θ per minute, over the 2θ range of 20° to 28°, with the recorder chart speed set at one inch per minute. The resultant diffraction traces readily permit the resolution of discreet diffraction peaks in the 3.52 - 3.54Å region and the 3.58Å region, and these are most likely attributable to chloritic and kaolinitic components, respectively. Whenever possible, in the present study, the relative areas of the peaks were determined, for a given specimen, in order to estimate the relative amounts of these phases present.

12. HCL treatment - Aliquots of each particle size from samples KR1 and CR7 were subjected to treatment with 1 N HCL at 80°C for 24 hours, porcelain plate mounts were prepared of the rinsed residual solids, which were then analyzed by X-ray diffraction, using the "slow-scanning" procedure. This treatment appears to attack (cf. Ross, 1969) the chloritic phases present, leaving any kaolinite present as an enhanced component of the residual sample material, as seen by the subsequent diminuition or complete absence of the 3.52 - 3.54Å region diffraction maximum. Coincident with this, the peak in the 3.58Å region is much more clearly defined, verifying the presence of this phase in the samples studied to date. Similar work is in progress on the materials from localities CR3, CR5, and CR8, and will also be done on samples from localities CR4, CR6, CR9, CR17, and CR18, which are currently under study.

13. Random powder analysis - In order to complete the X-ray analyses, each particle-size fraction of each sample was analyzed using a random (non-oriented ie.) mounted powder sample. Information resulting from such analysis might be anticipated to be of some significance with respect to elucidation of poly-

types of the various clay minerals present. However, the fact that the samples consist of polycomponent mixtures results in sufficient overlap of diffraction maxima from the several phases present that sufficient ambiguities arise to largely negate the usefulness of this approach.

Analytical Data

Method of interpretation and presentation.

On the basis of past experiences of the present investigators, as well as those of other workers with whom we are aquainted, we are in strong agreement with the discussion and commentary given by Pierce and Siegel, 1969, with respect to attempts at quantification in clay mineral studies. In accordance with this philosophy, we have not attempted to assess in any sort of "quantitative" or "semi-quantitative" manner the abundances of the various phases present in the samples under study here. Rather, as suggested by Pierce and Siegel, we have determined the areas of the various diffraction peaks of interest by measurement with a compensating polar planimeter, and have presented these, as ratios, in tabular form as our basic data. We have also calculated various other ratios of peak areas of interest, and used these in attempting to elucidate clay mineral relationships.

These data are discussed in the following sections, for each sample locality, and then the relationships among the localities are dealt with, in a separate section. The localities are shown on figure 2.

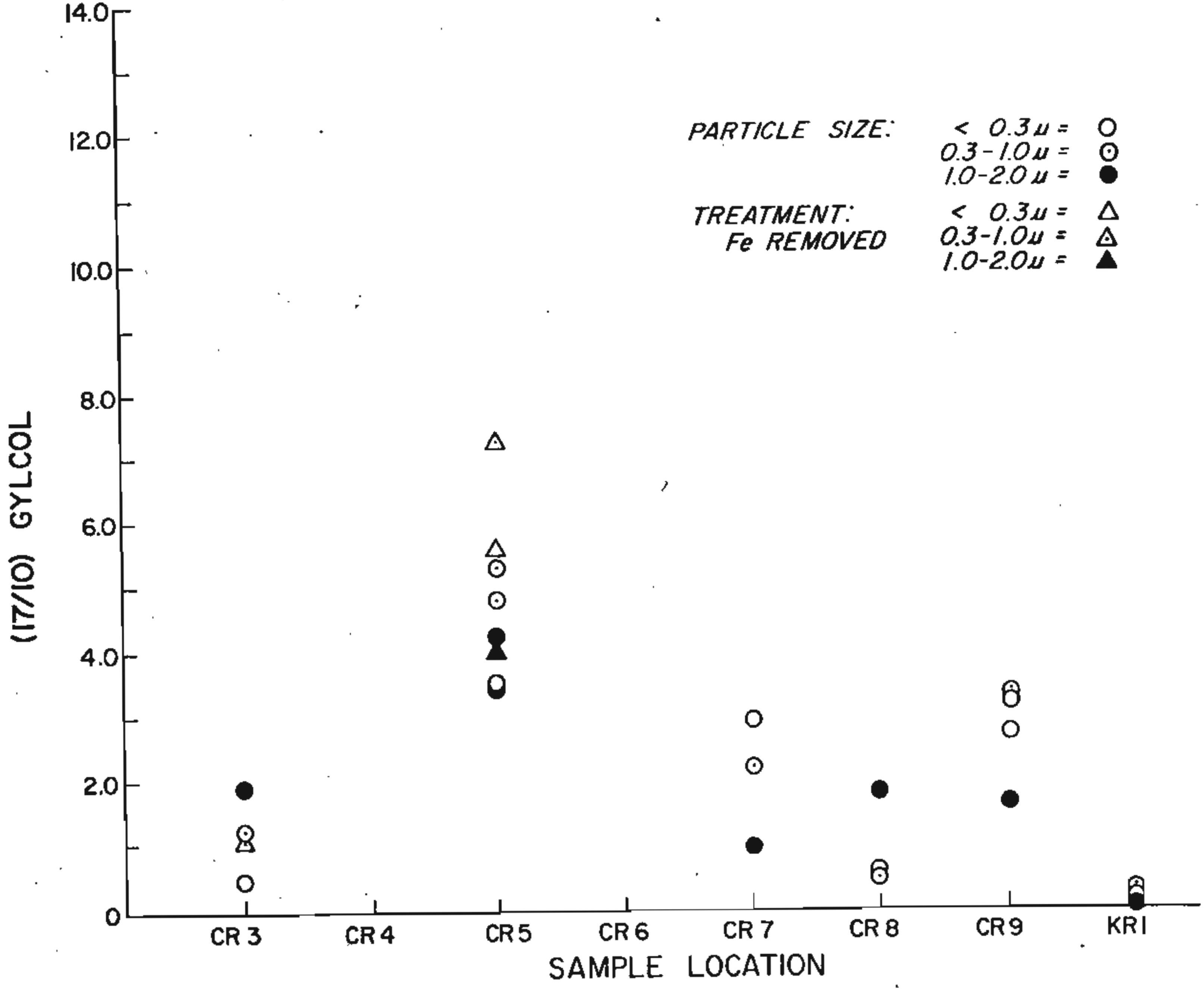
Thorough discussion of the diffractometer traces and their probable significance regarding the mineralogic relationships will not be presented in the present report, but will be deferred until work currently underway on the other samples has been completed.

Sample Location CR3 -

Representing material furthest upstream of those sites investigated, the mineralogic relationships unfortunately were not as clearly definable as we might have hoped. This material was characterized by an unusually high amount of iron oxide/hydroxide component, coating the other mineral particles, and causing the X-ray diffraction effects to be somewhat difficult to interpret. This was due to the high background resulting from fluorescence of iron caused by the copper K-alpha radiation employed, as well as to the poorly crystalline nature of the ferruginous material, and the masking effect of coatings on the grains of the clay minerals. In order to deal with this problem, the treatment to remove free iron oxides described by Jackson, 1956, and alluded to earlier in this paper, was resorted to. While this procedure did indeed result in improved x-ray diffraction effects from the residual materials, there was cause for concern regarding its effect on the clay mineral phases present, notably the chloritic materials, particularly in the finer particle-size ranges. Thus, we present our data for this locality with some misgivings with respect to their validity vis-a-vis the natural assemblages, and with respect to comparison with materials from other localities which were not subjected to this treatment. As the data on some of the CR-3 samples, as well as for those from locality CR-5 indicate, it is likely that some modifications are effected in the clay mineralogy as a result of this procedure. As the extent of these changes is difficult to assess for any given sample without comparative data on untreated aliquots, the treatment was not used routinely in the further course of this investigation.

Figures 3 through 10 graphically depict some of the diffraction peak area relationships for the data which seem to be most reliable, based on the quality of the diffraction tracings. Replicate analyses were made of samples selected at random, entailing separate preparation of plates and separate treatments, in order to evaluate the reproducibility of the experimental procedures. The results of these analyses appear as duplicate plottings of various points on several of the figures, and allow some estimation to be made regarding experimental error and analytical precision. Given the other complexities of analyses of this sort, it was not deemed appropriate to explore this matter in a more sophisticated manner in the present study.

As can be seen for these data, the glycol-expandable and non-expandable 2:1 layer lattice silicate components (the smectite, 17Å and "illite", 10Å, respectively) do not vary greatly within the particle size ranges examined. Furthermore, the 17/10 ratio does not exceed 2.0, which suggests, based on attempts by other workers, (Johns, Grim, and Bradley, 1954; Biscaye, 1965) to semiquantitatively appraise clay mineral abundances, that the smectite/illite ratio is rather low in these materials. Somewhat surprisingly, this value is lowest in the finest size fraction, which presumably represents a sedimentologic effect at this sample site, since commonly the expandability of smectitic materials increases with decreasing particle size (cf. Jonas and Roberson, 1960). The 7/10 ratio in unglycolated specimens, which is interpreted to represent a measure of the amount of combined chlorite plus koalinite (7Å peak) relative to the amount of illite plus vermiculitic material (10Å peak) is lower for the finest particle size fraction, and somewhat higher and essentially constant for the two coarser size intervals. This represents another example of the predominance of chloritic and kaolinitic phases in the coarser size



SAMPLE LOCATION

SAMPLE LOCATION

Figure 5.

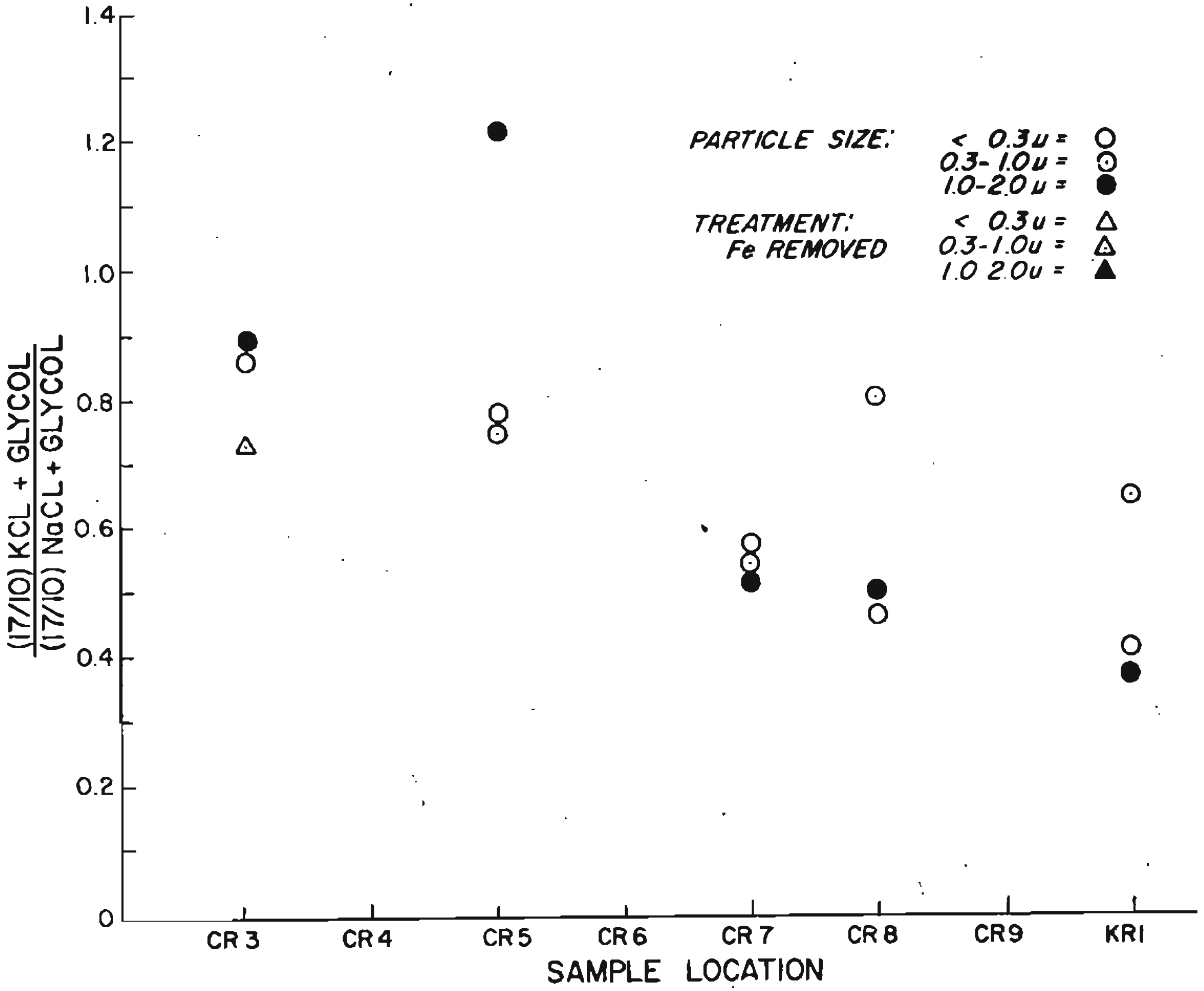
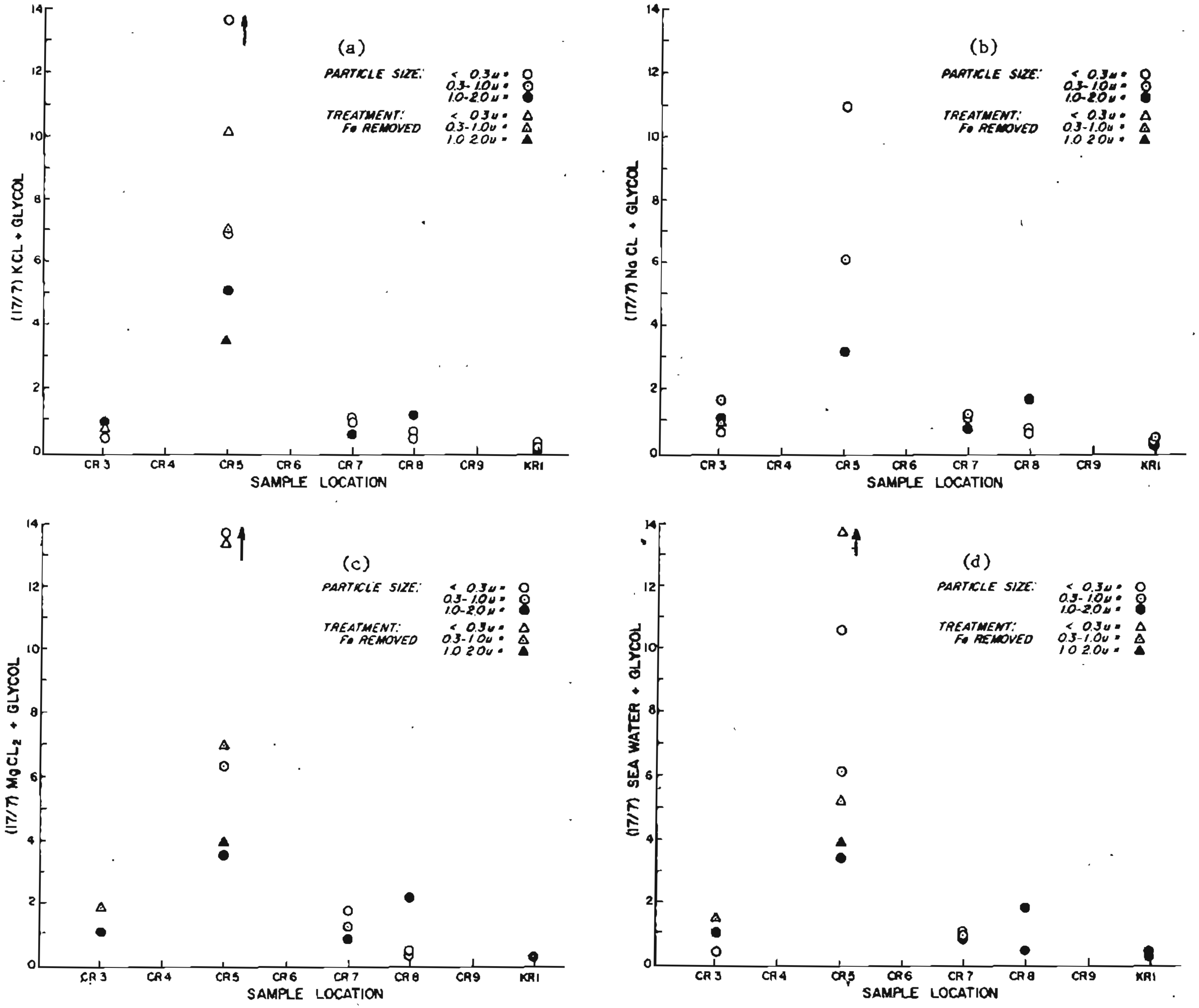
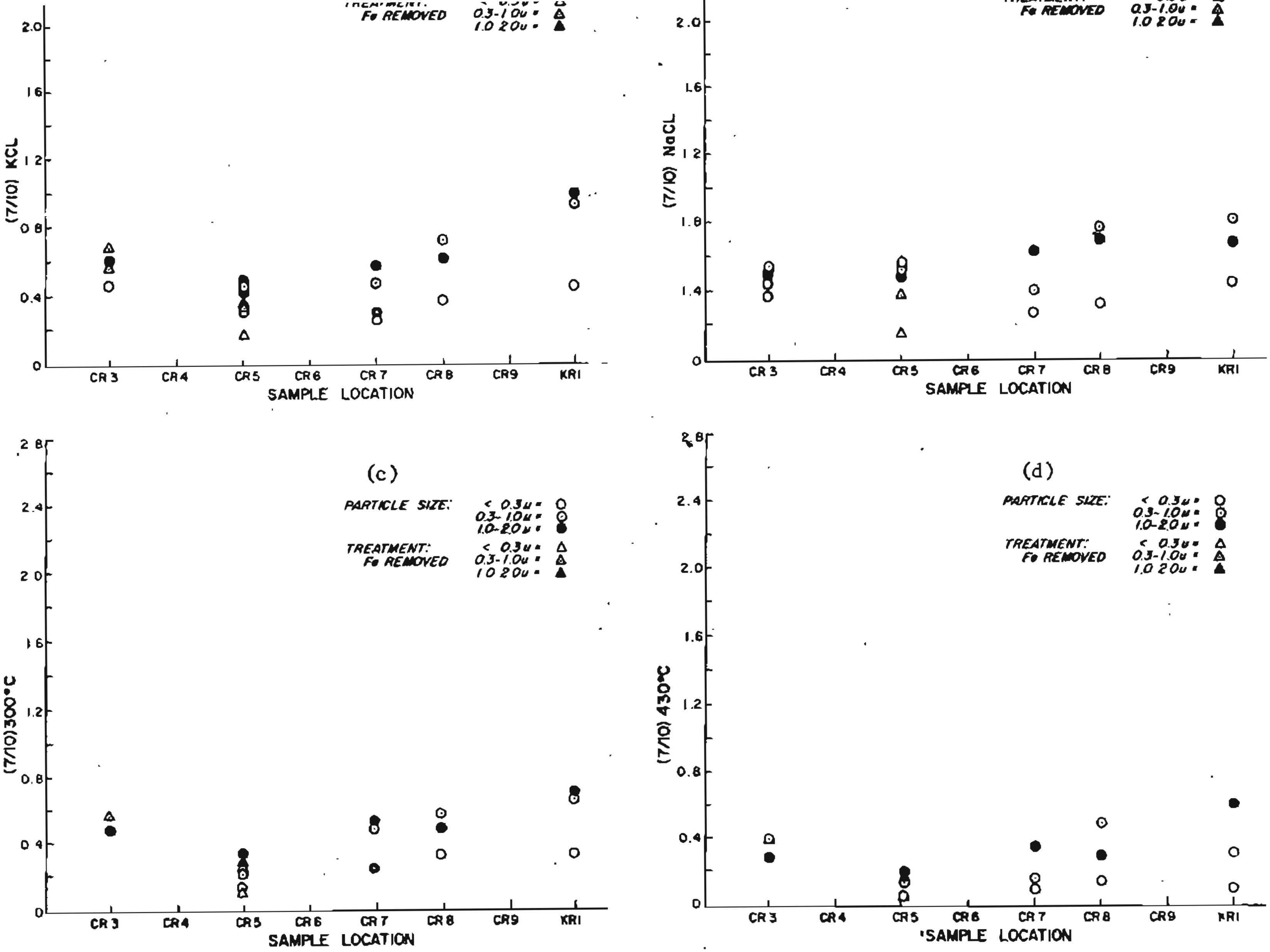

PARTICLE SIZE:
< 0.3u = ○
0.3-1.0u = ⊙
1.0-2.0u = ●
TREATMENT: Fe REMOVED
< 0.3u = △
0.3-1.0u = ◬
1.0 2.0u = ▲
(17/10) KCL + GLYCOL / (17/10) NaCL + GLYCOL
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
CR 3
CR 4
CR 5
CR 6
CR 7
CR 8
CR 9
KR1
SAMPLE LOCATION

Figure 6.


(a)
(17/7) KCL + GLYCOL
PARTICLE SIZE: < 0.3u = ○ 0.3-1.0u = ◎ 1.0-2.0u = ●
TREATMENT: Fe REMOVED < 0.3u = △ 0.3-1.0u = △ 1.0 2.0u = ▲
0 2 4 6 8 10 12 14
CR 3 CR 4 CR 5 CR 6 CR 7 CR 8 CR 9 KR1
SAMPLE LOCATION
(b)
(17/7) Na CL + GLYCOL
PARTICLE SIZE: < 0.3u = ○ 0.3-1.0u = ◎ 1.0-2.0u = ●
TREATMENT: Fe REMOVED < 0.3u = △ 0.3-1.0u = △ 1.0 2.0u = ▲
0 2 4 6 8 10 12 14
CR 3 CR 4 CR 5 CR 6 CR 7 CR 8 CR 9 KR1
SAMPLE LOCATION
(c)
(17/7) $MgCL_2$ + GLYCOL
PARTICLE SIZE: < 0.3u = ○ 0.3-1.0u = ◎ 1.0-2.0u = ●
TREATMENT: Fe REMOVED < 0.3u = △ 0.3-1.0u = △ 1.0 2.0u = ▲
0 2 4 6 8 10 12 14
CR 3 CR 4 CR 5 CR 6 CR 7 CR 8 CR 9 KR1
SAMPLE LOCATION
(d)
(17/7) SEA WATER + GLYCOL
PARTICLE SIZE: < 0.3u = ○ 0.3-1.0u = ◎ 1.0-2.0u = ●
TREATMENT: Fe REMOVED < 0.3u = △ 0.3-1.0u = △ 1.0 2.0u = ▲
0 2 4 6 8 10 12 14
CR 3 CR 4 CR 5 CR 6 CR 7 CR 8 CR 9 KR1
SAMPLE LOCATION


TREATMENT:
Fe REMOVED
0.3-1.0u = △
1.0 2.0u = ▲
(7/10) KCL
2.0
1.6
1.2
0.8
0.4
0
CR 3
CR 4
CR 5
CR 6
CR 7
CR 8
CR 9
KR1
SAMPLE LOCATION
TREATMENT:
Fe REMOVED
0.3-1.0u = △
1.0 2.0u = ▲
(7/10) NaCL
2.0
1.6
1.2
1.8
1.4
0
CR 3
CR 4
CR 5
CR 6
CR 7
CR 8
CR 9
KR1
SAMPLE LOCATION
(c)
PARTICLE SIZE:
< 0.3u = ○
0.3-1.0u = ⊙
1.0-2.0u = ●
TREATMENT:
Fe REMOVED
< 0.3u = △
0.3-1.0u = △
1.0 2.0u = ▲
(7/10)300°C
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0
CR 3
CR 4
CR 5
CR 6
CR 7
CR 8
CR 9
KR1
SAMPLE LOCATION
(d)
PARTICLE SIZE:
< 0.3u = ○
0.3-1.0u = ⊙
1.0-2.0u = ●
TREATMENT:
Fe REMOVED
< 0.3u = △
0.3-1.0u = △
1.0 2.0u = ▲
(7/10) 430°C
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0
CR 3
CR 4
CR 5
CR 6
CR 7
CR 8
CR 9
KR1
SAMPLE LOCATION

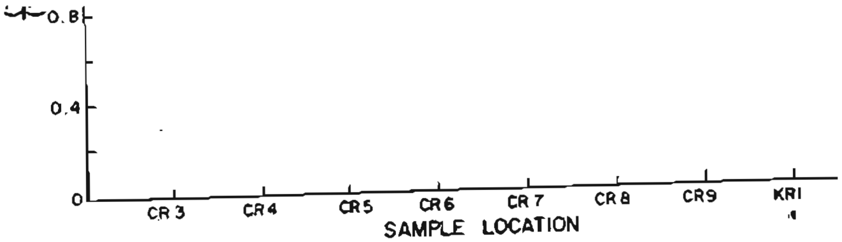

0.8
0.4
0
CR 3
CR 4
CR 5
CR 6
CR 7
CR 8
CR 9
KR1
SAMPLE LOCATION

Figure 9.

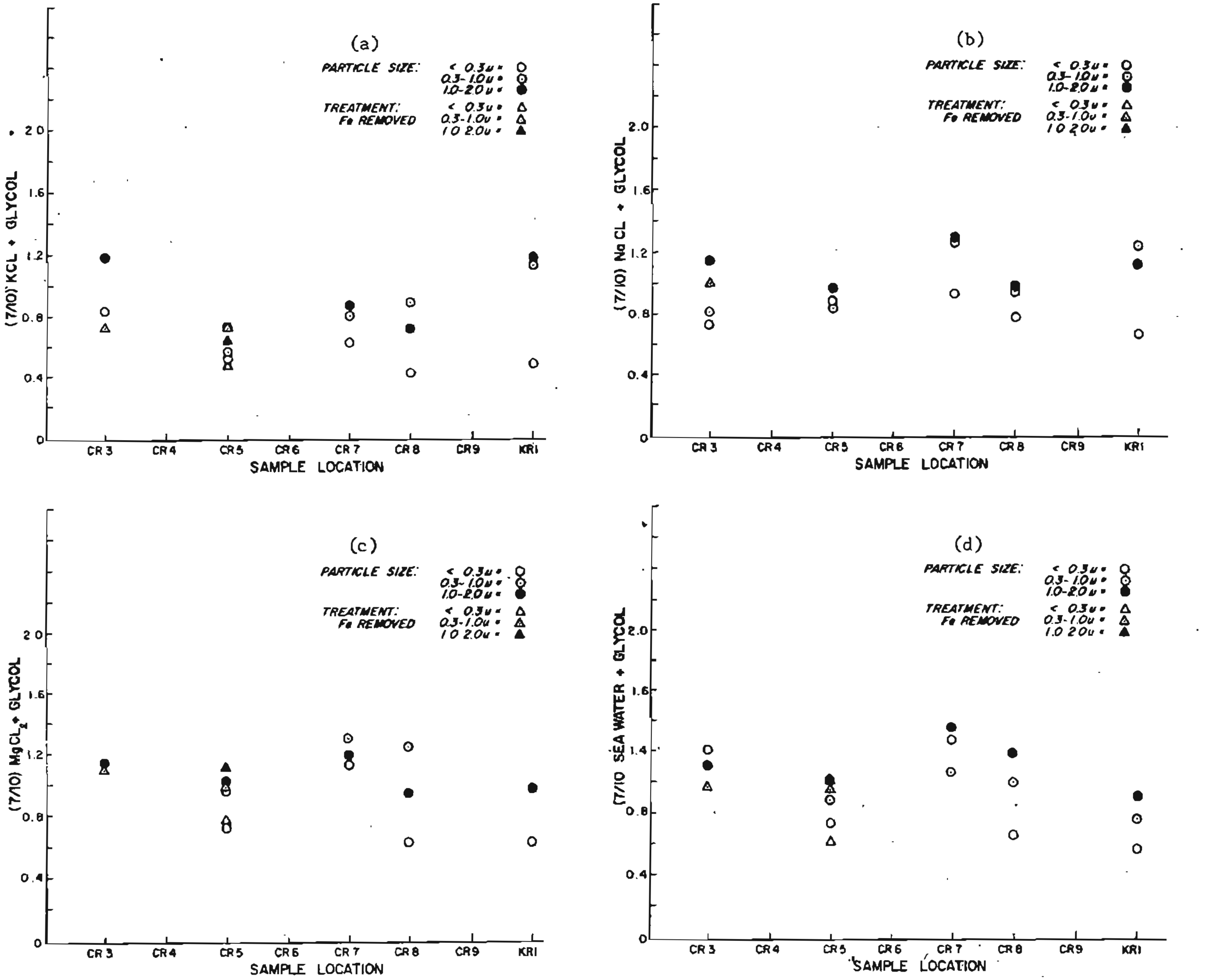
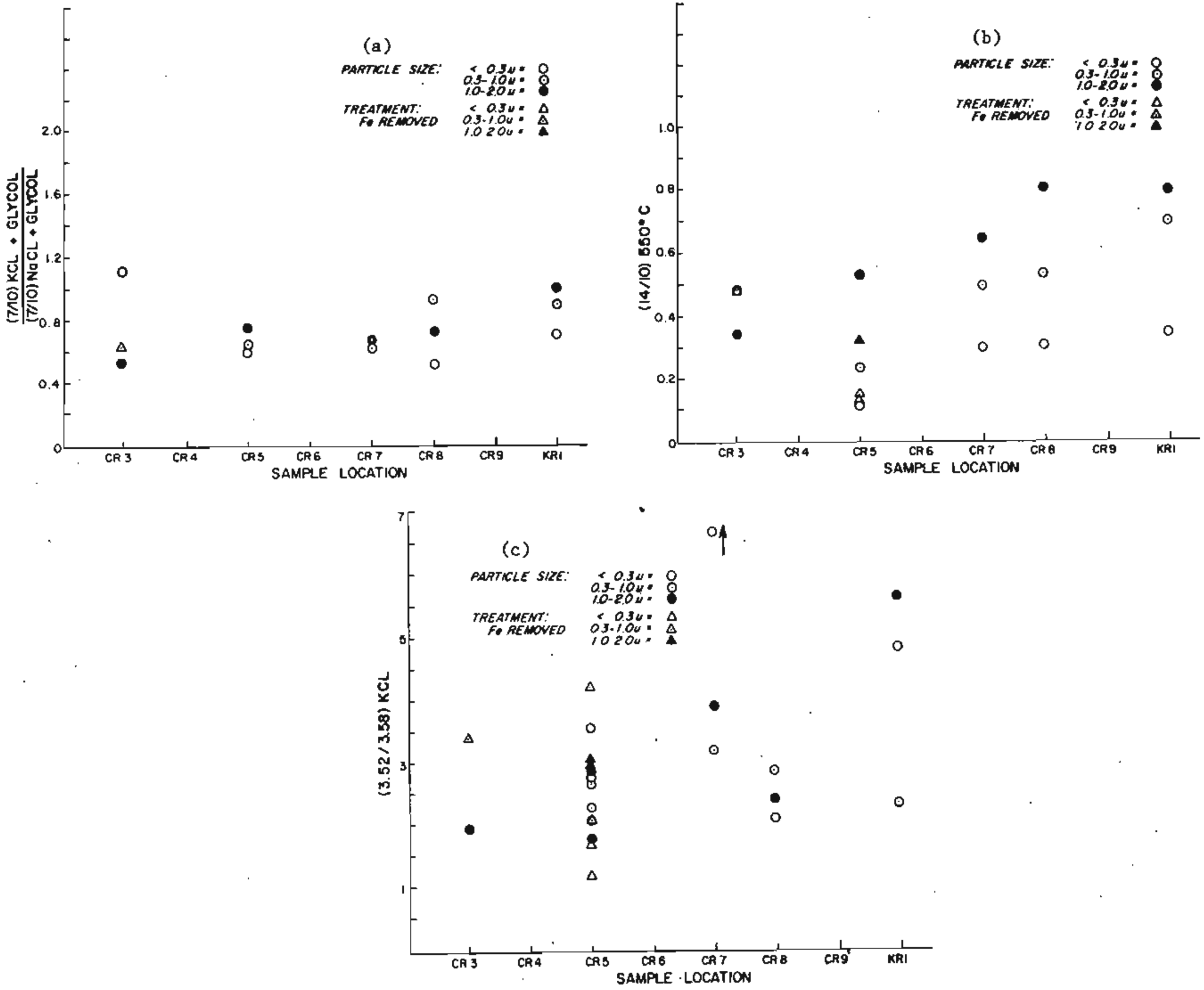

(a)
PARTICLE SIZE: < 0.3u = ○ 0.3-1.0u = ⊙ 1.0-2.0u = ●
TREATMENT: Fe REMOVED < 0.3u = △ 0.3-1.0u = △ 1.0 2.0u = ▲
(7/10) KCL + GLYCOL
2.0
1.6
1.2
0.8
0.4
0
CR 3
CR 4
CR 5
CR 6
CR 7
CR 8
CR 9
KR1
SAMPLE LOCATION
(b)
PARTICLE SIZE: < 0.3u = ○ 0.3-1.0u = ⊙ 1.0-2.0u = ●
TREATMENT: Fe REMOVED < 0.3u = △ 0.3-1.0u = △ 1.0 2.0u = ▲
(7/10) Na CL + GLYCOL
2.0
1.6
1.2
0.8
0.4
0
CR 3
CR 4
CR 5
CR 6
CR 7
CR 8
CR 9
KR1
SAMPLE LOCATION
(c)
PARTICLE SIZE: < 0.3u = ○ 0.3-1.0u = ⊙ 1.0-2.0u = ●
TREATMENT: Fe REMOVED < 0.3u = △ 0.3-1.0u = △ 1.0 2.0u = ▲
(7/10) MgCL2 + GLYCOL
2.0
1.6
1.2
0.8
0.4
0
CR 3
CR 4
CR 5
CR 6
CR 7
CR 8
CR 9
KR1
SAMPLE LOCATION
(d)
PARTICLE SIZE: < 0.3u = ○ 0.3-1.0u = ⊙ 1.0-2.0u = ●
TREATMENT: Fe REMOVED < 0.3u = △ 0.3-1.0u = △ 1.0 2.0u = ▲
(7/10 SEA WATER + GLYCOL
2.0
1.6
1.4
0.8
0.4
0
CR 3
CR 4
CR 5
CR 6
CR 7
CR 8
CR 9
KR1
SAMPLE LOCATION

Figure 10.


(a)
PARTICLE SIZE: < 0.3u = ○
0.3-1.0u = ◎
1.0-2.0u = ●
TREATMENT: Fe REMOVED < 0.3u = △
0.3-1.0u = △
1.0-2.0u = ▲
(7/10) KCL + GLYCOL / (7/10) NaCL + GLYCOL
0
0.4
0.8
1.2
1.6
2.0
CR 3
CR 4
CR 5
CR 6
CR 7
CR 8
CR 9
KR1
SAMPLE LOCATION
(b)
PARTICLE SIZE: < 0.3u = ○
0.3-1.0u = ◎
1.0-2.0u = ●
TREATMENT: Fe REMOVED < 0.3u = △
0.3-1.0u = △
1.0-2.0u = ▲
(14/10) 550° C
0
0.2
0.4
0.6
0.8
1.0
CR 3
CR 4
CR 5
CR 6
CR 7
CR 8
CR 9
KR1
SAMPLE LOCATION
(c)
PARTICLE SIZE: < 0.3u = ○
0.3-1.0u = ◎
1.0-2.0u = ●
TREATMENT: Fe REMOVED < 0.3u = △
0.3-1.0u = △
1.0-2.0u = ▲
(3.52 / 3.58) KCL
1
3
5
7
CR 3
CR 4
CR 5
CR 6
CR 7
CR 8
CR 9
KR1
SAMPLE LOCATION

ranges of sediments, which has been noted in many other studies reported in the literature. The replicate analyses of the KCL and NaCL treated specimens shown on figure 8 provide a useful feeling for the significance of variations in the ratios. On this basis, the 7/10 ratios of the glycolated specimens appear to be significantly higher, for each particle size fraction, which is most likely attributable to glycolation and expansion of a certain amount of the components recorded as "10Å material" in the unglycolated specimens. The sense of trend is somewhat different for the glycolated specimens, in that the coarsest fraction shows the highest 7/10 ratio, while the two finer fractions are somewhat lower. However, the overall trend of increasing 7/10 ratio with increasing particle size is discernible in these glycolated specimens. It is noteworthy that, in each instance, the 7/10 ratio is higher for the KCL vs. the NaCL treated samples, for a given particle size interval, for each of the glycolated or non-glycolated suites. This strongly suggests that the 10Å component in these materials does not contain appreciable amounts of vermiculitic material. Indeed, if the differences in the data are significant, as their consistency in sense seems to suggest, this behavior with K+ and Na+ exchange is difficult to rationalize on theoretical grounds. It is suggested that perhaps the treatment for removal of free iron oxide may have had some effect here. This topic will be discussed further under the sections dealing with other samples which were not subjected to such free iron oxide removal.

The 1/2° 2θ per minute scans endeavoring to resolve the 3.52Å and 3.58Å (chlorite and kaolinite, respectively) peaks were intelligible only for the two coarser size ranges; neither of these peaks was discernible for the $<0.3\,\mu$ specimen. However the mere detection of kaolinite in the coarser size intervals provides useful information within the context of the present study.

Heat treatments were not performed on some of the specimens from CR3, due to the limited amount of sample available.

Examination of diffraction traces of the CR3 specimens resulted in ambiguities of interpretation of these assemblages due to the rather ill-defined peaks and low peak to background relationships, particularly in the $<0.3\mu$ size range. However, a few brief comments on these traces appear warranted. There are indications of small but detectable amounts of "mixed-layer" materials present in each of the particle size ranges, although further assessment of this is difficult given the nature of the problem. At least it appears that "mixed-layered" phases resulting from inheritance-weathering-fluvial reconstitution effects are not dominant in this sample. Rather, the minerals present tend to be more representative of "end-member" types, although the relationships are less than well-defined, particularly in the finest size fraction, where line-broadening effects combine with the iron oxide problem to complicate interpretations.

Sample location CR5 -

As mentioned previously, materials from each particle size interval from this locality were divided into two aliquots, in order to assess the effects of the free iron oxide removal treatment. First the data from the routinely prepared specimens will be discussed, next the analogous specimens which were treated for the removal of free iron oxide will be dealt with, and then comparisons between the treatments will be made.

As can be seen on figures 3 and 4, the smectite/10Å material component appears to decrease with increasing particle size. Since the 17Å peak area was very large in comparison to the 10Å peak in these specimens, some of the apparent deviations may have been caused by consequent over-emphasis of the unavoidable errors in peak area measurements. Certainly the materials in each of these particle size ranges contain considerable amounts of smectite, ranging from a predominant amount in the <0.3μ size, through dominant in the 0.3-<1.0μ range, to perhaps sub-equal amounts of smectite, 10Å, and combined 7Å materials in the 1.0 -<2.0μ range. The information on the other Figures (5-10) further emphasizes these relationships. Noteworthy are the lower 7/10 ratios for the KCL+glycol specimens versus the other cation+glycol specimens, for a given size fraction. This relationship is maintained for the KCL versus the NaCL treated non-glycolated specimens as well, and strongly suggests that an appreciable portion of the 10Å component consists of "degraded mica/Vermiculite" material. Figure 10-C illustrates the relative proportions of 3.52-3.54Å/3.58Å scattering phases present; the replicate analyses give some indication of the precision of the analytical method. Essentially the ratio appears to be fairly constant among the three particle size ranges, at a value suggesting a considerably greater proportion of the chloritic material, but definitely indicating the presence of appreciable kaolinite as well.

In the analogous specimens which were subjected to the free-iron oxide removal procedure, the same sense of trends are shown, although there do seem to be several differences in ratio values sufficiently great to cause some concern regarding the effect of this treatment on clay mineral structures, particularly in the finest particle size range. In particular, the NaCL and KCL treated specimens appear to have had their characteristics somewhat altered, and in such a manner that it is suggested here that fine-grained chloritic phases may well be preferentially susceptible to attack by the reagents employed to remove the "free iron oxide". This might be anticipated, particularly for chlorites containing appreciable iron. Therefore, due to these effects, as well as uncertainties regarding aspects relative to different clay mineral compositions, the free-iron oxide removal procedure was not utilized further during the present study.

This sample station, CR5, is located at the mouth of the Kogasukruk River, where it enters the Colville River. The Kogasukruk River has its headwaters to the south, in the region northeast of the settlement of Umiat. This is the area in which the "Umiat Bentonite", a well developed montmorillonitic smectite, with certain beidellitic affinities, outcrops. This material has been studied by Anderson and Reynolds, 1966, who thoroughly characterized its mineralogic, chemical, and physical properties. Reference to this work, together with personal communications between Reynolds and Mowatt, 1972, affirm that the material represented at sample locality CR5 contains an appreciable amount of this bentonite component. Thus, an opportunity is afforded to monitor the sedimentologic, mineralogic, and geochemical behavior of this well-defined smectite during the course of its subsequent sojurn in the sedimentary regime from this locality, downstream in the Colville River, to the Colville Delta, and into the marine environment. It is felt that this is potentially a valuable parameter to consider in any attempt to delineate trends and mechanisms of sedimentation and sediment transport in this region, as well as in endeavoring to elucidate mineralogic-geochemical relationships regarding possible diagenetic effects in these environments. The Colville is a truly Arctic river, having its drainage basin entirely north of the Arctic Circle, and this furnishes uniqueness to the setting which was further incentive to the present and planned detailed work.

With regard to the diffractometer traces obtained from CR5 specimens, discussion will be limited in this report to the following observations. Detectable amounts of mixed-layer materials appear to be present in each of the particle size intervals, being particularly apparent in the heat-treated specimens. The data suggest that these phases represent interlayered "illite/chlorite", "vermiculite/chlorite", and/or "smectite/chlorite" components, presumably representing materials resulting from the effects of heritage and weathering prior to deposition at locality CR5. The large amount of well-defined smectite in these samples precludes clearer elucidation of the nature of the mixed-layer components by the various cation exchange treatments in this instance. However, there does seem to be noticeably less mixed-layer material in the coarsest size fraction, which seems to further support the above contention as to the nature and origin of these components. The X-ray diffraction manifestations of the mixed-layer phases are, if anything, somewhat more clearly defined in the specimens which were subjected to the free-iron oxide removal treatment, presumably due to the "cleaning-up" effect relative to the iron oxide. It is difficult to assess any effect of this treatment on the mixed-layer materials themselves, although such effects might be anticipated. It is also entirely possible that an appreciable amount of mixed-layered illite/smectite, a commonly occurring material geologically, might be present in these sediments, but not be detectable due to the high content of discreet smectite.

Sample location CR7.

As shown by figures 3-6, the relative amount of smectite to 10Å and combined 7Å materials is considerably less at this sample station, as compared to location CR5 upstream. However, although less striking, the same sense of trend of decreasing 17/10 and 17/7 ratios with increasing particle size is seen at locality CR7. Similarly, again the KCL+glycol treated specimens show consistently lower 17/10 and 17/7 ratios than their particle-size equivalents which have been treated with NaCL, $MgCL_2$, or sea water. This again suggests the presence of a significant component of "degraded mica/vermiculite" in each size fraction of this sample. This is emphasized by the 7/10 relationships shown on figures 9 and 10, for the KCL+glycol versus the other cation+glycol specimens. The other data, with the exception of the somewhat erratic pattern given by the sea water+glycol specimens, demonstrate a well-defined trend of increasing 7/10 ratios with increasing particle size, again reflecting increased proportions of the combined chlorite plus kaolinite component relative to the 10Å materials in the larger size ranges. Since the data presented indicate a predominant amount of chlorite relative to kaolinite, the further interpretation of the 7/10 trend as primarily representing increased amounts of chloritic material relative to "illitic" phases as a function of increasing particle size suggests itself. This is further supported by the trend of the 14/10 ratios shown on figure 10-b.

The diffractometer again indicate the presence of a detectable amount of mixed-layer material in each particle size range, although the proportion is lowest in the coarsest interval. Due to the considerably lower amount of smectite in these samples, as compared to those from CR5, the interstratified phases are discernible in some of the cation-treated specimens, as well as in the heat-treated specimens. Again, the interpretation is that the mixed-layer materials represent a vermiculite-illite-smectite/chlorite phase, or combination of such phases. Due to their low concentrations in these multicomponent samples, better definition of their nature does not seem feasible. The presence of interstratified illite/smectite is suggested by the X-ray traces, but difficult to verify more substantially.

Sample location CR8.

Interestingly, figures 3-6 portray a definable trend of increasing 17/10 and 17/7 ratios with increasing particle size. This might be interpreted as reflecting increasing amounts of expandable "degraded mica/vermiculite" as a function of particle size, given the relatively low amount of expandable component in the <0.3 range, as compared to the materials from locations CR5 and CR7. However, this trend might also be interpreted as representing a sedimentologic effect, resulting from non-deposition of finer grained smectitic materials at locality CR8. These relationships will be discussed subsequently in the present paper, but must be appreciated at the present time in order to attempt an evaluation of the clay mineral assemblage at this locality. The data of figures 7-10 suggest that the maximum in 7/10 ratios in the intermediate particle size interval, 0.3-$<1.0_{\mu}$ represents a greater proportion of chloritic component relative to 10Å phases. The KCL+glycol versus NaCl-, MgCL$_2$,or sea water+glycol relationships shown suggest that an appreciable portion of this 10Å material represents somewhat expansible degraded illite-mica-vermiculite, the presence of which is most noticeable in the coarsest size fraction, 1.0-$<2.0_{\mu}$. The parallel 7/10 ratios of the KCL+glycol versus MgCL$_2$+glycol and sea water+glycol specimens, is worthy of note, although a clearer understanding of its significance demands further study, currently in progress. It is tentatively suggested that an appreciable amount of "degraded" chlorite may be present in the 0.3-$<1.0_{\mu}$ size range, with resultant "reconstitution" to a better-defined chloritic material attendant upon MgCL$_2$ saturation, and that this material may show a degree of analogous behavior upon KCL saturation. In other words, it may be difficult, with KCL treatment alone, to differentiate between some degraded micas, and degraded chlorites. If this interpretation is correct, the usefulness of the variety of treatments used in the present work is further affirmed. The 14/10 ratios confirm the increased proportions of chlorite to illite plus smectite plus other 10Å phases in the coarser size ranges.

The diffractometer traces indicate the presence of mixed-layer materials in each of the particle size intervals. The phases are more readily discernible in this sample as representing a vermiculite-illite-smectite/chlorite component together with probably vermiculite-illite/smectite as well.

Sample location KR1.

It is clear that these materials are quite low in smectite, as shown by the 17/10 and 17/7 ratios of figures 3-6. Resort to an expanded data portrayal would be necessary to delineate any trends as a function of particle size, and such trends might be felt to be more apparent than real. Due to insufficient sample material, the $MgCL_2$ saturation treatments were not made of this sample, but the relationships seem to be reasonably interpreted nevertheless. The general trend is one of increasing 7/10 ratio with increasing particle size. The data seem to suggest an appreciable decrease in the relative proportions of chlorite to kaolinite in the 0.3-<1.0μ size range, together with roughly sub-equal amounts of total 7Å/ total 10Å components in the 0.3 -<1.0μ versus the 1.0 -<2.0μ size intervals. Thus, a significant concentration of kaolinite is seen in the 0.3 -<1.0μ size range, superimposed upon the afore-mentioned 7/10 trend as a function of particle size. In the three-size intervals, the contribution to the total 10Å components of any degraded mica/vermiculite materials in not detectable, which is not surprising, given the fact that this sample station represents a marine locality, and, hence, a departure from the fluvial/deltaic materials previously discussed. The apparently "deviant" behavior of the NaCL treated 1.0-<2.0μ specimen most likely represents an analytical "anomaly", given the apparent cogency of the remainder of the data. Thus, an apparent slight maximum in smectite relative to the other phases is seen in the 0.3-<1.0μ size range, together with a somewhat more noticeable maximum in kaolinite. As clearly demonstrated by the 550°C treated materials, the chlorite/10Å materials proportions increase with increasing particle size. This sense of trend is common to the other localities as well, and appears to be a characteristic feature of these assemblages.

The diffractometer traces indicate small but significant amounts of mixed-layer components in each of the particle size ranges, again representing a vermiculite-illite-smectite/chlorite and a probable vermiculite-illite/smectite phase, apparently persisting in the marine environment at this locality.

Comparative Mineralogy

In this section, an attempt is made to demonstrate and discuss the observed relationships among the clay mineral assemblages representing the five sample sites investigated to date. Certain trends are discernible from figures 3-10 presumably reflecting differences in clay mineral suites resulting from various sedimentologic and geochemical factors. Careful scrutiny of some of these data appears to warrant further, more specific comments.

Figures 3 and 4 portray the 17/10 ratios, and figure 5 compares the 17/10 ratios for KCL + glycol versus NaCL+glycol specimens. The latter plot shows a decided trend towards a decrease in the values of this parameter as one proceeds from locality CR3 to KR1. Interestingly, this trend, as well as the absolute values for the parameter, in general track quite nicely for the various particle sizes as well. Even the three apparently somewhat "anomalous" high values off this main trend appear to define a sub-trend parallel to the primary one. Admittedly the data are not that abundant to permit a vigorous defense of these apparent relationships, but the trends do seem to be real. Inspection of the figures shows that, with the exception of the materials from locality CR5, where the Umiat bentonite smectite dominates the assemblage, the 17/10 ratios range in value from a maximum of 2.2 on down to the 0.1 neighborhood. This certainly suggests that the sediments studied are composed of a greater proportion of 10Å materials, relative to smectitic phases, for each of the particle size intervals. This may be primarily a reflection of non-deposition of smectite, due to various sedimentologic effects, since the abundance of expandable clay minerals appears higher in marine sediments offshore from the Colville Delta than in sediments from adjacent portions of the Beaufort Sea area. Part of our further work, now underway, involves study of suspended load material from each of these sample sites, for comparative purposes, in order to more clearly define the sedimentologic and geochemical situation. The fact that the value of the parameter 17/10 for KCL+glycol versus NaCL+glycol specimens is less than 1.0 is strong evidence for the presence of a significant amount of degraded 10Å material, in each of the particle size ranges, for every sample (the sole exception is the 1.0-<2.0μ size at station CR5), and the sense of trend further suggests that this material increases in relative amount with distance downstream. However, this may be illusory, in that the same data might be interpreted as representing more effective exchange of ions from saline water, given the fact that locality KR1 is a marine site, and shows the lowest values for this trend. In other words, degraded materials which had not yet been exposed to saline water may behave in a somewhat different manner, under our experimental conditions of attempted cation exchange, relative to materials which have had a previous opportunity to effect (or at least approach) equilibrium under saline conditions.

This argument is further strengthened by the relationships shown on figure 4-d in which there appears to be a rather abrupt difference in the 17/10 sea water + glycol specimens between localities CR7 (fresh water) and CR8 (which may have been periodically exposed to influx of the salt-water wedge coming upstream from the river mouth). Actually, in view of these complexities, it is apparent that a clearer appreciation of the situation awaits the results of our further studies now in progress. In concluding the comments on the 17/10 relationships for the present, we might point out the consistent behavior of the 1.0 - <2.0μ size, relative to the finer size materials, at station CR8 under NaCL, $MgCL_2$, and sea water exchange and reglycolation. The interpretation is tentatively advanced here that the coarsest material here is composed of an unusually high amount of degraded micaceous-illitic material, relative to the smaller particles at this site, when comparison of its interaction with KCL+glycol is made. This might be further indicative of the fresh/saline water relationships discussed above, in that it would be anticipated that the finer particles would react more rapidly in effecting exchange equilibrium with the environment of deposition. Thus, this rather subtle feature may be quite important in gaining added insight into the overall relationships. However, alternatively, and perhaps likelier, it may merely represent influx of materials from the Itkillik River, which enters the Colville River at site CR8.

Figure 6 portrays the 17/7 ratios for the various cation + glycol treated specimens, and is presented more for the sake of completeness of data than for any particularly striking relationships discernible. The trends are consistent with the 17/10 ratios just discussed. Noteworthy is the similar behavior of the coarsest size fraction of location CR8 with respect to the accompanying smaller particles in this assemblage. The absolute values of the

17/7 ratio for station CR5 show the dominance of the smectite component in those materials, the remaining stations investigated yield 17/7 ratios more indicative of subordinate amounts of expandable components in proportion to total chlorite plus kaolinite. Station KR1, marine, shows the lowest value, and may result from various environmental differences. Winnowing and/or non-deposition of smectite, as well as formation of authigenic chloritic material in the marine environment are possible reasons, but differing source materials is another potential factor to be considered. This will be pursued further below.

In order to obtain the maximum amount of information from our data, we have presented in figures 7 through 10 quite a few of the available 7/10 relationships, for various treatments, and combinations thereof. It is felt that unique definition of the relationships is more likely the more thorough such graphical portrayal of data is attempted. Again, certain trends seem readily discernible, while some subtleties may be variously interpreted, and will remain somewhat unclear until more work is done. These figures show the effects of K+, Na+ and heat treatments. Evident is the consistently lower 7/10 ratio for the $<0.3\mu$ size range of a given locality, denoting lesser amounts of chlorite plus kaolinite relative to 10Å material in this finest size fraction. Further, a trend of increased 7/10 values progressively from CR5 through KR1 is seen, for each size interval, which suggests increased chlorite plus kaolinite proportions, with greatest amount in the marine sample location, KR1. At the latter site, the difference in 7/10 between the 300°C and 430°C treatments of the finest and intermediate particle size materials may reflect a significant amount of authigenic chloritic material, of lower thermal stability than the more usual detrital chlorites, which are generally of metamorphic or igneous heritage, and, thus, more stable under the 430°C treatment than a chloritic material formed under sedimentary conditions. It would be further anticipated that such authigenic phases as might be present would be predominantly in the finer grain sizes, due to probable low growth rates in the temperature-pressure regimen of the sedimentary environment.

The general sub-equal values for CR3, CR7, and CR8 suggest that the CR5 assemblage is somewhat unusual and, in effect is a "diluent" to the other suites represented by our sample sites upstream from the delta proper. These latter materials appear to exhibit the "characteristic" 7/10 relationships of Colville River fluvial sediments.

Again, the relationships shown by the figure which portrays the 7/10 ratios for KCL versus NaCL treated specimens indicate the presence of an appreciable component of degraded 10Å material in the samples studied. However, the fact that those values, except for the $<0.3\mu$ smectite-rich specimen for location CR5, are mainly clustered in the 1.2-1.0 region suggests that this degraded 10Å contribution is relatively minor. Figure 8-b compares the 7/10 ratios for KCL versus 300°C treated specimens, and illustrates the general similarities for stations CR3, CR7 and CR8. The exceptions once again occur at CR5, where the finer size fractions show the dominance of the Umiat smectite, which is not affected by KCL as much as it is by heat treatment. Interestingly, the KR1 material departs in the same sense as those CR5 finer materials, from the main sequence of values on figure 8-b. Also noteworthy is the agreement, well within the experimental error, of the values for each of the three particle size intervals at station KR1. This degree of similarity in behavior among the size ranges of one particular sample may merely be fortuitous. However, it seems sufficiently unusual that, in endeavoring to explain this situation, we tentatively suggest that it may represent an effective equilibrium situation having been attained with respect to K+ exchange at this site in the marine environment such that similar responses (more precisely lack of response) to K+ exchange under our experimental conditions has resulted. This is perhaps a somewhat outrageously speculative suggestion, but we nevertheless advance it here, fully aware of its uncertainty. It is difficult to either corroborate or contradict this assertion with respect to K+ specifically, upon examination of the data shown in figure 8-C, which similarly portrays the 7/10 ratios for NaCL versus 300°C treated specimens. The overall trends among the sample localities are analogous to those in figure 8-b, but the three particle size ranges at sample station KR1 are no longer identical in behavior to one another. This may mean that the NaCL saturation under our expermental conditions was sufficient to disturb the postulated equilibrium, although KCL treatment did not have the same effect. Data are not available for the 7/10 ratios of non-glycolated $MgCL_2$ or sea water treated specimens, so comparisons are not possible at this time, although this will be investigated further. Figures 9 and 10 show the 7/10 ratios for the various cation+glycol treated specimens. The consistent dominance of the 7Å phases with respect to 10Å materials in the coarser size fractions of a given sample is apparent, with the sole exception of the sea water treated material in the $<0.3\mu$ interval at station CR7. It is difficult to discern any really well-defined trends, although the coarser KR1 materials appear to be somewhat enriched in 7Å components once again. It might be further gleaned from figure 10-a, in which the 7/10 ratios for KCL+glycol versus NaCL+glycol samples are compared, that the relative amounts of combined chlorite plus kaolinite versus 10Å materials do not vary greatly among the samples studied, although it would seem that the marine locality, KR1 has characteristics somewhat different from the fluvial sediments.

Figure 10-b portrays the 14/10 ratios for specimens heated for one hour at 550°C. The data from station CR3 are somewhat suspect, in view of the problems cited earlier regarding the presence of significant amounts of ferruginous materials, attempts at its removal, and consequent uncertainties regarding the nature of the residual assemblages vis-a-vis the natural ones. Thus, we have not considered these data in the following discussion, although the data are shown on figure 10-b for completeness. Discernible is a trend toward increasing chlorite relative to 10Å materials (in this case the latter represents total smectite, illite, and degraded micas-vermiculites) downstream, with the maximum value in the marine locality, KR1. This trend is well defined, and equally shown for any given size range among the sample stations, as well as in a broad sense for each entire assemblage. This is quite interesting, and presumably represents the effect of sediment transport and deposition, combined with possible considerations of source material differences, as well as authigenesis in the marine environment. Although our data are insufficient at present to lend strong support to any of these variables, as shown earlier there are some suggestions that a moderate amount of authigenic formation of chloritic material may in fact be occurring in the marine milieu. The apparently lower 7/10 values for $MgCL_2$ + glycol and sea water+glycol specimens at KR1 might also suggest that some of this chloritic component may represent a degraded chloritic component in the river, which subsequently has re-equilibrated with Mg^{++} in the marine environment to form a "reconstituted" chlorite. This

is little more than speculation at the present stage of our studies, and will be pursued further. Certainly, the relationships are nicely delineated with the 550°C treatment, due to removal of the "chlorite plus kaolinite = 7Å material" problem.

Regarding this latter problem, figure 10-C portrays the data resultant from our attempts to resolve the "3.52/3.58Å doublet" resulting from X-ray diffraction maxima for chloritic versus kaolinitic phases, respectively. The lack of apparent trends might suggest little success in this attempt, but, with one exception, the reproducibility represented by the replicate samples shown indicates that the technique inherently has a useful degree of precision. The values for the free-iron oxide removal treated $< 0.3\mu$ fraction of sample CR5 suggest an appreciable degree of destruction of fine grained chloritic material. No consistent relationships are apparent from the data presently on hand, but the information portrayed is felt to be valid in itself, within a given sample site, as well as between sites. Difficulties in objectively obtaining these data can best be appreciated by reference to the diffractometer traces obtained experimentally. An additional complication is the possibility of shifts of the chlorite peak toward the 3.56-3.58Å area, depending upon structual and compositional effects.

Conclusions

Detailed studies of mineral assemblages in sedimentary materials seem to be potentially quite useful in enabling an enhanced degree of certainty regarding characterization of the constituent phases. This in turn permits appraisal of geochemical and sedimentologic relationships to be made with better insight into the nature of the materials involved. With this insight, more reliable predictions may be ventured as to the potential behavior, reactivity, ect. of these materials under various geologic-geochemical conditions, as well as with regard to the probable reaction of these materials in the context of the activities of man.

With regard to the materials discussed in this paper, the ubiquitous presence of smectitic and degraded 10Å phases in the sediments suggests that a reasonably high degree of "activity" might be anticipated in their natural environment, with respect to exchange of cations and/or foreign organic matter. However, it must be remembered that the materials studied required "removal" of organic material with hydrogen peroxide in order to permit meaningful X-ray analysis. Thus, the sample data represent material no longer in the natural state. However, the ease of exchanging various cations, as well as ethylene glycol, onto the clays in the laboratory suggests the likelihood of analogous behavior in their natural state as well. Additionally, it should be noted that although smectite is ubiquitous, it is not present in predominant proportions in any of the localities downstream from station CR5 studied to date (however, work in progress suggests that location CR9 is fairly rich in smectite as well, possibly as the result of a sedimentologic effect in this area). Thus, the absolute level of "activity" of any of these sediments remains to be assessed quantitatively. Furthermore, the one marine locality studied, KR1, is notably lower in any expandable phases, which would lead one to predict a coincidentally lower "activity" for these sediments relative to exchange phenomena. Physical adsorption onto clay surfaces, rather than the exchange into interlayer structural sites discussed in the present work, would be an additional mechanism potentially available to add to such "activity" of a sediment, and, for the clay minerals, would be predictable primarily on the basis of a quantitative assessment of particle size distribution within a sediment. Greater activity, in general, would be anticipated with sediments containing greater proportions of finer-grained constituents.

The present study has resulted in a rather detailed characterization of the sediments along the lower Colville River and Delta, and should be useful in endeavoring to elucidate sedimentologic and geochemical relationships in the adjacent areas offshore, along the Alaskan coast, and into the deeper Arctic Basin. This latter work is currently in progress, utilizing the methods described in the present study. Results to date have been published elsewhere (Naidu and Mowatt, 1973a,b; Naidu, Mowatt, Hawkins, and Hood, 1973; Naidu and Mowatt, 1974).

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