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## Title

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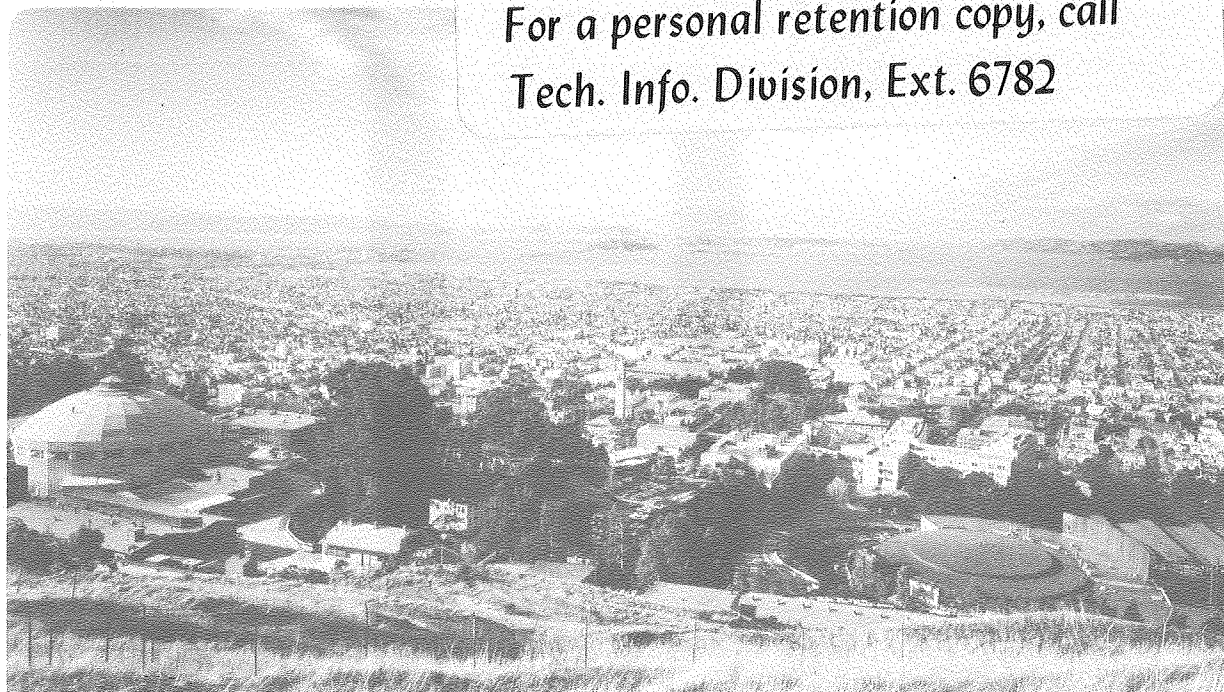
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AN INVESTIGATION OF METHODS FOR THE SELECTIVE REMOVAL  
AND CHARACTERIZATION OF TRANSITION METALS ASSOCIATED  
WITH SOLIDS IN THE MARINE ENVIRONMENT

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## EXECUTIVE SUMMARY

The operation of an OTEC plant will result in the mixing of large volumes of seawater from different depths within the ocean. Associated with this seawater will be suspended particulate material. This solid material is capable of both adsorbing and releasing transition metals. Because suspended particulate material is intimately involved in marine food webs and transition metals such as copper can have toxic effects, it is important to develop a sound methodology for characterizing and quantifying transition metals which will be associated with solid material passing through an OTEC plant.

The characterization of solid-phase associated transition metals in the marine environment has largely been directed at marine sediments. Studies of sediment-associated transition metals have generally indicated that it is not possible to uniquely identify the solid phases or chemical speciation of a given metal. There are many reasons for this difficulty, but the probable major analytical problems arise from the fact that many of the transition metals of interest are present only in trace concentrations as adsorbed species on amorphous oxides or as coprecipitates. These difficulties have led to an approach in which transition metals are classified according to how easily they are solubilized when exposed to different types of chemical attack, as defined in chemical extraction schemes.

There are at present a large number of different transition metal extraction schemes in use. Only rarely have these different techniques been carefully compared on a variety of solids from the marine environment. Consequently, it is often not possible to make a sound assessment of the results obtained by investigators who have used different extraction methods to characterize solid-phase associated transition metals or to select the most appropriate methodology for making measurements on a given type of solid material.

In this study, several of the most widely accepted techniques were compared for many of the most commonly measured transition metals. The use of a variety of marine sediments, rather than trapped suspended particulate matter, was necessitated by both the relatively large amount of material needed for an examination of all the methods and the lack of any OTEC program collected particulate material. In order to determine the true extraction efficiency of the methods studied, all solid concentrations have been normalized to total metal concentration values as obtained by neutron activation analysis and/or x-ray fluorescence measurements.

On weak, four intermediate strength and two strong metal extraction methods were studied individually. The weak method had the lowest extraction efficiency, but dissolved all solid carbonate phases. A potential problem with the weak method is that it does not retain extracted metals quantitatively in solution, but allows them to be adsorbed on remaining solids. The simplest of the four methods (0.5 N HCl) caused the release of lower amounts of most metals studied when compared to the other three intermediate methods. It cannot be classified as a weak method,

however, as it does attack some moderately resistant solid phases. Only one of the other three intermediate methods (a reducing acetic acid solution) was relatively free from analytical difficulties and it is preferred for this reason. The two strong extraction procedures are quite similar. Neither strong method yields true total metal concentrations.

The five step sequential extraction scheme of Tessler et al. (1979) was also evaluated. The results were generally good with regard to both metal phase fractionation and overall total extraction of available metals.

The general order of release of metals from all sediments is  $\text{Co} > \text{Mn} \sim \text{Co} > \text{Ni} > \text{Fe} > \text{Al}$ . Oxidized or very mildly reducing sediments are characterized by dominant metal release at the intermediate step from manganese associated species and the residual step from iron associated species. Reducing sediments are characterized by dominant metal release from the steps attacking the organic and residual phases.

Based on the results of this study, the sequential extraction scheme of Tessler et al. (1979) is the recommended method for the characterization of solid-phase associated transition metals. An increase of the reducing agent concentration in the intermediate step and temperature decrease with an additional HCl digestion in the residual step are recommended as improvements, based on the results of the individual extraction method studies.

## INTRODUCTION

Transition metals are among the most intensely studied chemical components in the marine environment. Their presence in this natural system and sensitivity to variations in environmental conditions make them ideal indicators of sedimentary processes. To make the most use of these metals, it is necessary to be able to accurately measure their absolute concentrations and chemical forms.

Studies of trace metals as dissolved species in marine waters (e.g. Kester et al., 1975; Brewer, 1975; Ahrlund, 1975; Bruland et al., 1978) have progressed rapidly in recent years. However, substantially less progress has been made in the characterization of the various forms of transition metals in the solid phases found in studies of suspended particulate matter and sediments (e.g. Gad and LeRiche, 1966; Chester and Hughes, 1967; Bodine and Fernalld, 1973; Bruland et al., 1974; Agemian and Chau, 1976; Tessler et al., 1979).

As sediments are the dominant sink for transition metals in the marine system, it is desirable to know the pathways by which the metals arrive and the physico-chemical states in which the metals exist in solid sediment phases. The determination of the chemical phases in which each metal can exist is a very difficult problem. It is complicated by the numerous phases which are found in marine sediments. These phases include weakly and strongly adsorbed metal ions, metal carbonates, sulfates, sulfides, oxides, hydroxides, phosphates and organometallic compounds. Many transition metals are present as minor or trace components in these phases. The problem is further complicated by the fact that many phases are not crystalline, but instead are amorphous (especially oxyhydroxides and

sulfides, Berner, 1964; Berner, 1967; Murray, 1975) or adsorbed (Donnelly and Merrill, 1977; Forbes et al., 1976; Murray, 1975; Krom and Sholkovitz, 1978; Lerman and Childs, 1973). Also, many phases form as coatings on other more abundant phases.

Because of these major difficulties, the concept of an operationally defined metal reactivity is generally used, rather than attempt to individually characterize each sedimentary phase. The relative reactivity has been defined by the strength of chemical attack necessary to liberate a fraction of a particular metal. Distinct chemical phases that respond similarly are, therefore, treated as equivalent phases. Using this approach, sediments and their trace metals can be characterized by comparative degree of susceptibility to chemical conditions rather than by the relative amounts of specific chemical phases within each. It should be noted, however, that this behavior can frequently be closely correlated with individual phases.

The major goal of this study was the evaluation and comparison of several of the most commonly used transition metal extraction techniques for several transition metals, when applied to a variety of major types of marine sediments. The extraction efficiency of each technique was evaluated by comparison to total metal concentration values, based on neutron activation and x-ray fluorescence analysis.

#### Development of Trace Metal Extraction Methods

Numerous methods have been devised to chemically characterize the solid components of sediments. As the number of techniques for trace metal characterization increased, it became obvious that techniques which were supposed to release equivalent compounds give significantly different

results (Agemian and Chau, 1976; Malo, 1977). Consequently, the common terminology used to describe solid trace metal extractability from sediments came to reflect the various methodologies (e.g. hot, concentrated HCl extractable). As variations in trace metal extractability became better known, investigations into the solid phases responsible for these variations increased. Wet chemical techniques were performed on sediments characterized by fusion techniques, x-ray diffraction, x-ray fluorescence or neutron activation. Bodine and Fernald (1973) compared before and after x-ray diffraction scans of sediments treated with an EDTA solution to show stability of normal clays to this attack. Malo (1977) compared several techniques using a sodium carbonate fusion technique as the normalizing method. These and many other techniques commonly used to analyze marine sediments originally were developed for all soil studies.

In addition to the use of acids of varying strengths, some investigators began using solutions of complexing agents, oxidizing agents, reducing agents, or combinations of these with acids. These methods were designed to be more representative of natural conditions and also were shown to be more specific extractors of certain metal phases, at least in some instances. One widely used example of this is the use of the reducing agent hydroxylamine hydrochloride for the dissolution of hydrogenous manganese oxides and hydroxides, as developed by Chester and Hughes (1967).

Other techniques which have been applied to sediment studies include the previously mentioned fusions, x-ray investigations and radioactive studies. Fusion, x-ray fluorescence and neutron activation provide good total elemental concentrations but cannot be used to characterize phases.

Combustion analyses are generally not favored in that they have no basis in natural systems and several metals can be volatilized and lost. X-ray diffraction is excellent for crystal phase determinations but cannot distinguish amorphous phases or adsorbed species which can be very abundant forms in some sediments.

The basic result of these solid phase investigations has been the delegation of most techniques into one, or a combination of several, classifications of metal phases. These are adsorbed, carbonate associated, hydrogenous, organic associated and silicate or residual. It has yet to be determined, however, that any of the presently used techniques uniquely and completely extract metals from a specific phase. The complicated nature of most sediments offers little hope for the successful absolute fractional extraction of its components.

The wet chemical extraction techniques used in this study are the result of a review of recent publications on this topic. Though application of most techniques to marine studies has been recent (since the 50's), the actual development of many of the techniques can be traced back through the soil science literature to the turn of the century. The original development of these techniques was with regard to plant nutrient studies, with the branching to use for trace metals coming as a side development. A good summary of the older techniques, along with a treatment of their historical development is found in Jackson (1958). Work such as that of Williams et al. (1976), make direct allusions to soil science research as the basis for techniques used. The direct development of trace metal techniques for marine sediments can be illustrated with a few notable examples. Chester and Hughes (1967) made popular the combination of a reducing agent (for the extraction of manganese oxides) with a moderate

acid (for the extraction of iron oxides) for the extraction of the complicated amorphous iron and manganese oxide mixtures commonly found in marine sediments. Bodine and Fernald (1973) proposed EDTA solutions as selective extractors of calcium and magnesium, carbonate and sulfate fractions. Gad and LeRiche (1966) proposed ammonium oxalate and hydrogen peroxide as an extractant of all non-detrital metals. They also proposed that the difference between this treatment and that from the use of only ammonium oxalate represented the proportion associated with sulfides and organics.

#### SAMPLE DESCRIPTION AND PREPARATION

##### Description

To determine the applicability of the different extraction methods to a wide variety of sediment types, each method used in this study was based on eight different major sediment types. These sediments were chosen to reflect several normally encountered types of marine environments from both shallow and deep sea zones. Each sediment is briefly described below and a summary is presented in Table 1.

The first sediment, labelled BA, is a shallow water, high carbonate, oxidizing, medium sand from the Bahama platform near the Bimini Islands. The sample was collected by hand with a polyethylene core tube in about 10 meters water depth. Upon retrieval, the sample was stored in whirl pak bags. After air removal and sealing, each sample was frozen until analysis was begun.

The second sediment, BB, is a shallow water, high carbonate, mildly reducing, medium to fine sand from Biscayne Bay, Florida. The sample was collected by coring with screw topped polyethylene bottles until

TABLE 1. DESCRIPTION OF SEDIMENTS STUDIED

| <u>DESIGNATION</u> | <u>DESCRIPTION</u>                                                                                              |
|--------------------|-----------------------------------------------------------------------------------------------------------------|
| BA                 | Shallow water calcium carbonate-rich oxidating sand from Bahama platform                                        |
| BB                 | Shallow water calcium carbonate-rich, mildly reducing sand from Biscayne Bay, Florida                           |
| FM                 | Shallow water mildly reducing low carbonate silty sand from Long Island Sound "FOAM" study site                 |
| HH                 | Shallow water strongly reducing low carbonate silty clay from the "Black Hole" of New Haven Harbor, Connecticut |
| CS                 | Continental slope mildly reducing clay from off the coast of North Carolina                                     |
| DH                 | Deep sea calcium carbonate-rich clay from the Mid-Atlantic Ridge                                                |
| DL                 | Deep sea calcium carbonate-poor red clay from the Nares Abyssal Plain                                           |
| TAG                | Deep sea manganese crust from the Transatlantic Geotraverse site on the Mid-Atlantic Ridge                      |

completely filled, following which, the sample bottle was sealed and taken immediately to the lab for analysis.

The third sediment, FM, is a mildly reducing, shallow marine, low carbonate silty sand. It is gray green and was collected at the FOAM study site (Goldhaber et al., 1977) in Long Island Sound. The sample was received in a sealed glass tube from R.A. Berner and was immediately prepared for analysis.

The fourth sediment, HH, is a strongly reducing silty clay. It is low carbonate, dark green in color and shallow marine, having been collected from the "Black Hole" of New Haven Harbor. This sample was provided by R.A. Berner and was immediately prepared for analysis.

The fifth sediment, CS, is a mildly reducing clay from the continental slope off the coast of North Carolina. The sample was collected from 1850 meters water depth by gravity core from the NOAA ship Researcher by John Morse. The core was sectioned and stored in sealed polyethylene bags for approximately two years prior to analysis.

Sediment six, DH, is a deep-sea high carbonate red clay from the flanks of the Mid-Atlantic Ridge at 4730 meters water depth. Sediment seven, DL, is a deep-sea low carbonate red clay from the Nares Abyssal Plain at 5370 meters water depth. These sediments were probably slightly reducing. Both were collected and stored the same as sediment five.

The final sediment, TAG, is a brownish black, oxidized, possibly hydrothermal (Rona, 1978) crusty sediment from the Transatlantic Geotraverse site on the Mid-Atlantic Ridge. The sediment was received already dried and was immediately prepared for analysis.

### Preparation of Samples

Each wet sediment was squeezed in a teflon lined squeezer with nitrogen gas at 40 psi to remove excess porewater. The sediment cake was then oven dried at 100°C overnight, ground to pass through a 125 mesh sieve, and stored in screw-topped polyethylene containers. Sediments were homogenized by shaking prior to sample withdrawal and samples were withdrawn by randomly scooping several times with a teflon-coated microspatula.

Organic carbon was determined for each sample by decomposition in a porcelain crucible at 500°C for one hour in a muffle furnace. Samples were dried for one hour at 110°C to remove any hydrated water within the sediments prior to the organic carbon determination.

Approximately 5 g subsamples of each sediment type were reground to pass 200 mesh for x-ray diffractometer, with the sediment being repacked between each run. Each sediment was scanned from 50 to 5 degrees 2 $\theta$  at 1°/min scan rate. Though the charts are not presented here, all of the sediments, including those stored for several years, displayed normal peak distribution patterns for typical marine sediments of similar source type.

One to two gram subsamples of the finely ground sediments were sent to Lawrence Berkeley Laboratory, Berkeley, California, for neutron activation analysis (NAA) and x-ray fluorescence (XRF) analysis. The analyses were performed by Drs. F. Asaro, H. Michel and R. Gaugu, and included the analysis of over 40 elements. Rare earth element patterns were plotted and were found to also be characteristic of normal marine sediments (F. Asaro, personal communication). This combined with the x-ray diffraction results lend support to the assumption that these sediments can be considered reasonably representative of several major types of common marine

sediments.

Results for the metals to be analyzed by wet chemical techniques in this study (Al, Fe, Mn, Cu, Co and Ni) are used as baseline total values to which all other values can be compared. However, within the TAG sediment, aluminum and copper could not be determined, and for BA, the copper value is highly suspect.

Though the original sediment compositions may have changed somewhat, due to storage prior to analysis (Thompson et al., 1979), all indications from rare earth patterns and x-ray analysis show no drastic modifications. As it is the prime objective of this work to characterize the methods and not primarily to make sediment composition determinations, small variations in sediment composition prior to analysis are not of major concern here.

## EXTRACTION PROCEDURES AND ANALYTICAL METHODS

### Individual Methods

Each of the individual extraction techniques was chosen to be representative of one of the three most commonly used categories; weak, intermediate and strong. They are summarized in Table 2. The three methods, of widespread use in recent studies, which were considered for use within the weak category are: 1) the EDTA complexing method of Bodine and Fernalld (1973), 2) the 0.5 N HCl leaching common to many investigators, and 3) the pH 5 acetic acid-sodium acetate buffer method of Froelich et al. (1977). All three methods are supposed to remove adsorbed metal ions as well as calcium carbonate, gypsum and anhydrite associated metals. Because of the observed severity of attack of the 0.5 N HCl solution on clay lattices (Ray et al., 1957; Bradshaw et al., 1974), this method is

TABLE 2. SUMMARY OF INDIVIDUAL EXTRACTION METHODS

| <u>METHOD</u> | <u>STRENGTH</u> | <u>DESCRIPTION</u>                                  |
|---------------|-----------------|-----------------------------------------------------|
| 1             | Weak            | pH 5 acetic acid-sodium acetate buffer              |
| 2             | Intermediate    | 0.5 N HCl                                           |
| 3             | Intermediate    | pH 3 buffer of oxalic acid and ammonium oxalate     |
| 4             | Intermediate    | pH 3 buffer of sodium citrate and sodium dithionate |
| 5             | Intermediate    | Hydroxylamine hydrochloride in 25% acetic acid      |
| 6             | Strong          | Hot concentrated HCl                                |
| 7             | Strong          | Nitric and perchloric acids in equal amounts        |

considered here to be more representative of intermediate strength methods than a weak method. The EDTA method was rejected for this study because of its extreme slowness of reaction (Chester and Hughes, 1967) and lack of specificity of attack (Agemian and Chau, 1977). Consequently, the only individual weak method studied was the pH 5 buffer solution of Froelich et al. (1977), referred to here generally as Method 1.

Four intermediate strength methods were selected for study from a large number of possible choices. Each method was selected because of its very widespread use or its favorability as expressed in previous comparison studies. The first is the 0.5 N HCl method mentioned above (Method 2). The second (Method 3) is a modification of the ammonium oxalate method of Gad and LeRiche (1966). The modification is a pH 3 buffer of oxalic acid and ammonium oxalate as described by Froelich et al. (1977). The third (Method 4) also a pH 3 buffer consisting of sodium citrate and sodium dithionite reagents, is used as described by Malo (1977). The fourth (Method 5) is the popular hydroxylamine hydrochloride in 25% acetic acid method as described in Chester and Hughes (1967), Malo (1977) and Agemian and Chau (1976).

Of the strong methods, which are designed to attack all solid phases, three were chosen for investigation. These three are by far the most commonly used strong techniques today. The first (Method 6) is the simple and widely used method of digestion by hot, concentrated (HCl) (e.g. Williams et al., 1976). The second (Method 7) is the method described in Agemian and Chau (1976), using a one to one mixture of nitric and perchloric acids as the digesting solution. The third, using perchloric and hydrofluoric acids as described by Tessler et al. (1979) is considered in the sequential scheme section, as this method is the final step in the

five step extraction scheme.

#### Sequential Extraction Scheme

Of several proposed sequential extraction schemes, the five step scheme of Tessler et al. (1979), is the one chosen for study here. It was selected because the authors have shown great care in the selection of each step. A summary of these steps is presented in Table 3. Alternate similar methods to those selected by them at each step are discussed and the reasons for the elimination of these other methods from consideration are presented. Complete descriptions of the procedures followed at each step can be found in their paper. A brief description is presented here.

Step One, which is designed to remove only exchangeable, or adsorbed metals, uses a pH 7 magnesium chloride solution to replace adsorbed metals with magnesium. Step Two uses a pH 5 acetic acid-sodium acetate solution very similar to that presented earlier. This step can then attack mineral species sensitive to pH fluctuations, such as carbonates and some easily soluble sulfates. Step Three uses hydroxylamine hydrochloride in 25% acetic acid (though at a much lower concentration than that used in the previously described Method 1) to release oxide associated metals and other species sensitive to low Eh conditions. The fourth step, using 30%  $H_2O_2$  and heating, is designed to remove organic associated and other high Eh sensitive species of metals. The fifth step, involving complete dissolution of the remaining residue with perchloric and hydrofluoric acids is designed to dissolve all remaining metals, predominantly those within silicate lattices.

#### Additional Considerations

While performing the seven selected individual extraction techniques,

TABLE 3. SUMMARY OF SEQUENTIAL EXTRACTION STEPS

| <u>STEP</u> | <u>DESCRIPTION</u>                              |
|-------------|-------------------------------------------------|
| 1           | pH 7 magnesium chloride solution                |
| 2           | pH 5 acetic acid-sodium acetate buffer          |
| 3           | Hydroxylamine hydrochloride and 25% acetic acid |
| 4           | 30% $H_2O_2$ heated                             |
| 5           | Perchloric and hydrofluoric acid digestion      |

certain operational difficulties had to be overcome. As overnight shaking required sealing of sample containers for several of the methods, it became necessary to dissolve as much carbonate as possible prior to sealing. Slow dissolution of carbonate, especially in very high carbonate samples, is also necessary to prevent foaming over of the sample as the organics present bind the bubbles into a durable foam mat. Dissolution was, therefore, accomplished by addition of the required volume of reagent in small portions over a period of 30 to 60 minutes. Samples were then sealed, shaken by hand, and checked after 10 to 15 minutes for pressure buildup. When no sample exhibited such buildup, all the samples were placed on the automatic shaker.

Filtration of the samples following extraction also involved some manipulation. To speed filtration and reduce sample loss or contamination by exposure to air for extended periods of time, solutions were syringe filtered through a dual set of Nuclepore filters in Swin-lock filter holders. The dual set of filters (1.0  $\mu\text{m}$  followed by 0.45  $\mu\text{m}$ ) reduced excessive clogging by particles to increase filtration efficiency, yet one problem arose which could not be easily solved. During filtration of acetic acid and oxalic acid buffered solutions, filtration efficiency was greatly decreased by a development of back pressure within the filter holders. This problem could not be reduced by occasional "reverse filtration flow" as it was not due to clogging by particulates. It could only be solved by frequent changing of filter membranes, resulting in substantially greater sample loss than anticipated.

In performing the five step extraction scheme of Tessler et al. (1979), the most critical difference between this technique and the individual extraction methods involved the absolute necessity of

preventing sample loss between steps. Centrifugation, rather than filtration, was used to separate the sample solution from the remaining sediment between each step. To prevent possible losses from numerous transfers of solutions from reaction vessels to centrifuge tubes, the first four steps were all performed using the centrifuge tubes as the reaction vessels.

Following each centrifugation, the solution was withdrawn with an adjustable pipet with disposable polyethylene tips. The remaining sediment was washed with 10 ml of double distilled deionized water, dispersed and centrifuged. The wash solution was removed in the same manner as sample solutions and was discarded. Following the fourth step, the remaining sediment samples were then transferred quantitatively to teflon beakers for the final acid digestion step.

Of the five steps in this scheme, two are directly comparable to previous methods mentioned. The second step involves the use of a pH 5 acetic acid-sodium acetate buffer similar to that of the weak individual method (1). The solution for the second step was prepared by adding acetic acid to a 1 M sodium acetate solution until the pH equalled 5. The solution for the individual method, however, was prepared by adding sodium acetate to a 0.5 N acetic acid solution until the pH equalled 5. Also, the third step is very similar to the individual method (5) containing hydroxylamine hydrochloride in that each involved dissolution of the reducing agent in 25% (v/v) acetic acid. They differed, however, in that the individual method used a final solution of 1 M hydroxylamine hydrochloride whereas the third step called for the concentration to be only 0.04 M.

## RESULTS AND DISCUSSION

### Composition of Sediments

The results of the wet chemical (weak extraction Method 1) and neutron activation analysis techniques for calcium are presented in Table 4. Each value represents the weight percent of each sediment consisting of  $\text{CaCO}_3$ , assuming all Ca measured was from this phase and neglecting the fraction of carbonate existing with Mg or Sr. The average values from both types of determinations agree very well, with values determined by NAA averaging 1% higher, probably due to the greater amount of oxide and silicate calcium measured by this method. These results indicate that the weak extraction method is effective in dissolving carbonate, but there is no evidence that this method does not attack other solids as well. There is also no indication whether carbonate associated metals are retained in solution by this method or whether some fraction of those metals released are readsorbed by the remaining sediment prior to filtration.

The weight percent of solid phase organic carbon was determined for each sediment, except TAG for which there was insufficient sample. These results are also presented in Table 4. The overall results are reasonable in that the most reducing sediment, HH, had the highest amount of organic carbon (9%) and in general the more reducing sediments had higher values than the other sediments. The one exception to this is the reducing sediment from the continental slope area, CS, which was one of the two sediments with the lowest amount of organic material. In comparison with previous analyses performed on an adjoining section of this cored sample, good agreement in percent organic carbon is noted with 0.7% from this study and 0.8% by Morse and Cook (1978). Thus, lack of input of organic material

TABLE 4

Major Sediment Components  
(By Weight)

| <u>Sediment</u> | <u>CaCO<sub>3</sub> (%)</u><br>(By Dissolution) | <u>CaCO<sub>3</sub> (%)</u><br>(By NAA) | <u>Organics (%)</u> | <u>Clay (%)</u> | <u>Silicate (%)</u> |
|-----------------|-------------------------------------------------|-----------------------------------------|---------------------|-----------------|---------------------|
| BA              | 95.4                                            | 93.5                                    | 1.5                 | -----           | 4 ± 2               |
| BB              | 57.4                                            | 58.1                                    | 2                   | -----           | 30 ± 10             |
| FM              | 9.6                                             | 12.7                                    | 4                   | 40 ± 10         | 40 ± 10             |
| HH              | 2.0                                             | 3.3                                     | 9                   | 50 ± 15         | 30 ± 10             |
| CS              | 10.6                                            | 11.1                                    | 0.7                 | 35 ± 10         | 45 ± 10             |
| DH              | 50.0                                            | 50.8                                    | 0.7                 | 25 ± 10         | 15 ± 5              |
| DL              | 1.3                                             | 1.0                                     | 3                   | 50 ± 15         | 35 ± 10             |
| TAG             | -----                                           | 3.6                                     | 0.5                 | 10 ± 5          | 15 ± 5              |

to the area, or the biogenic oxidation of organic material prior to sampling could be responsible for its relative depletion.

The percentages of clay and silicate components were qualitatively determined by x-ray diffraction. The silica peak was used to estimate silicate component percentages, while the various clay peak assemblages were used to estimate total clay component percentages. The results are presented in Table 4 with estimated errors allowing for non-standardized calculations. Although other components were detectable by x-ray analysis, they were quantitatively insignificant and are not included in the sediment component descriptions, except for TAG, in with the "other" (70 wt. %) is dominated by manganese oxides (Scott et al., 1978), and is calculated as  $\text{MnO}_2$  from the NAA manganese value.

Sediments BA and BB are unique in that they have no significant amount of clay material. The fact that they are predominantly carbonate and clean quartz sands also greatly reduces their metal retaining capacity. In subsequent analyses the release of most metals during weak extraction eliminated the need to use any strong methods. The very low concentrations of most metals in these sediments produced highly variable results when mathematically compared as duplicates. Therefore, to reduce the complexity of sediment comparisons and averages, these two sediments are not considered in further comparisons. Sediments FM and CS, which are both mildly reducing contained nearly equal amounts of clays and silicates. Sediment HH, DH and DL had a dominant, and remarkably constant, amount of clays relative to silicates. The variation in actual percentages for these three sediments (HH, DH and DL) is directly due to the variation in carbonate percentages, indicating the carbonate acts as a diluting component.

### Total Transition Metals

Results of the x-ray fluorescence and neutron activation analyses are available from the authors upon request. Each metal was determined by the method found to be most sensitive as determined by previous studies (F. Asaro, personal communication). Of the seven elements of principle interest here, only copper was determined by XRF. The rest (Ca, Mn, Fe, Co, Ni and Al) were measured by NAA.

The NAA and XRF values for Al, Fe, Mn, Cu, Co and Ni are presented in Table 5. These values are used as baseline total values, to which the results of the wet chemical analyses are compared to determine extraction efficiency relative to absolute amounts of the elements. It should be noted that the values for Al and Cu in sediment TAG could not be determined because of the extremely high Mn content of this sediment.

### Individual Extraction Techniques

Concentrations of the various metals extracted from each sediment are also available from the authors upon request. Percent variation between duplicate extractions is presented in Table 6 by metal for the seven different extraction techniques and six sediment types considered. To allow for minor inhomogeneities during sediment sampling and procedural analyses steps, it was decided that variations of 20% (approximately twice the analytical precision) or larger should be of concern. Of the 248 values presented in Table 6a, approximately one-eighth (32) are greater than or equal to 20. Of these, 13 are in the analysis of the TAG sediment for which many of the measured concentrations are very low. That comparison of low metal concentrations results in most of the high variations, is demonstrated in Table 6 by the fact that the largest number

TABLE 5

Total Element Concentrations  
(By Weight)

| <u>Sediment</u> | <u>Al(%)</u> | <u>Fe(%)</u> | <u>Mn(ppm)</u> | <u>Cu(ppm)</u> | <u>Co(ppm)</u> | <u>Ni(ppm)</u> |
|-----------------|--------------|--------------|----------------|----------------|----------------|----------------|
| FM              | 5.91 ± .10   | 3.09 ± .03   | 737 ± 15       | 32 ± 4         | 10.49 ± .20    | 25 ± 7         |
| HH              | 6.51 ± .14   | 3.99 ± .04   | 639 ± 13       | 260 ± 25       | 12.86 ± .23    | 44 ± 8         |
| CS              | 6.62 ± .17   | 3.66 ± .03   | 390 ± 8        | 23.6 ± 3.7     | 12.03 ± .21    | 32 ± 7         |
| DH              | 4.62 ± .10   | 2.85 ± .04   | 2689 ± 54      | 88 ± 9         | 38.3 ± .5      | 89 ± 7         |
| DL              | 9.74 ± .21   | 5.56 ± .05   | 5549 ± 157     | 118 ± 11       | 79.6 ± .9      | 130 ± 10       |
| TAG             | -----        | 0.046 ± .005 | 420,000 ± 8000 | -----          | 3.10 ± .13     | 399 ± 10       |

Errors are the larger of 1% of measured value or 1  $\sigma$

TABLE 6a

Individual Techniques: % Variation Between Duplicate Sediment Analyses

| <u>Al</u> |           |           |           |           |           |            | <u>Fe</u> |           |           |           |           |           |            |
|-----------|-----------|-----------|-----------|-----------|-----------|------------|-----------|-----------|-----------|-----------|-----------|-----------|------------|
|           | <u>FM</u> | <u>HH</u> | <u>CS</u> | <u>DH</u> | <u>DL</u> | <u>TAG</u> |           | <u>FM</u> | <u>HH</u> | <u>CS</u> | <u>DH</u> | <u>DL</u> | <u>TAG</u> |
| Method    |           |           |           |           |           |            | Method    |           |           |           |           |           |            |
| 1         | 0         | 24        | 38        | 9         | 18        | 0          | 1         | 2         | 2         | 3         | 0         | 0         | 20         |
| 2         | 6         | 32        | 2         | 5         | 5         | 18         | 2         | 3         | 0         | 2         | 52        | 0         | 17         |
| 3         | 7         | 5         | 5         | 0         | 5         | 7          | 3         | 0         | 0         | 1         | 14        | 5         | 6          |
| 4         | 0         | 6         | 4         | 5         | 12        | 0          | 4         | 4         | 6         | 0         | 3         | 0         | 7          |
| 5         | 0         | 22        | 13        | 0         | 10        | 5          | 5         | 3         | 6         | 37        | 7         | 1         | 0          |
| 6         | 0         | 4         | 4         | 4         | 4         | 5          | 6         | 2         | 2         | 2         | 5         | 1         | 6          |
| 7         | 8         | 18        | 0         | 4         | 0         | 5          | 7         | 2         | 6         | 0         | 0         | 0         | 0          |

| <u>Mn</u> |           |           |           |           |           |            | <u>Cu</u> |           |           |           |           |           |            |
|-----------|-----------|-----------|-----------|-----------|-----------|------------|-----------|-----------|-----------|-----------|-----------|-----------|------------|
|           | <u>FM</u> | <u>HH</u> | <u>CS</u> | <u>DH</u> | <u>DL</u> | <u>TAG</u> |           | <u>FM</u> | <u>HH</u> | <u>CS</u> | <u>DH</u> | <u>DL</u> | <u>TAG</u> |
| Method    |           |           |           |           |           |            | Method    |           |           |           |           |           |            |
| 1         | 4         | 0         | 11        | 3         | 14        | 40         | 1         | 5         | 51        | 23        | 14        | 5         | 0          |
| 2         | 2         | 4         | 9         | 54        | 3         | 4          | 2         | 9         | 6         | 10        | 4         | 0         | 6          |
| 3         | 7         | 6         | 8         | 1         | 0         | 2          | 3         | 20        | 2         | 200       | 4         | 6         | 15         |
| 4         | 0         | 6         | 3         | 0         | 5         | 30         | 4         | 4         | 2         | 16        | 2         | 0         | 3          |
| 5         | 5         | 2         | 0         | 3         | 0         | 9          | 5         | 0         | 5         | 6         | 2         | 2         | 30         |
| 6         | 4         | 0         | 2         | 3         | 3         | 4          | 6         | 3         | 4         | 22        | 2         | 0         | 6          |
| 7         | 3         | 3         | 5         | 6         | 7         | 5          | 7         | 0         | 1         | 0         | 0         | 0         | 21         |

| <u>Co</u> |           |           |           |           |           |            | <u>Ni</u> |           |           |           |           |           |            |
|-----------|-----------|-----------|-----------|-----------|-----------|------------|-----------|-----------|-----------|-----------|-----------|-----------|------------|
|           | <u>FM</u> | <u>HH</u> | <u>CS</u> | <u>DH</u> | <u>DL</u> | <u>TAG</u> |           | <u>FM</u> | <u>HH</u> | <u>CS</u> | <u>DH</u> | <u>DL</u> | <u>TAG</u> |
| Method    |           |           |           |           |           |            | Method    |           |           |           |           |           |            |
| 1         | --        | 40        | --        | --        | --        | 49         | 1         | 55        | 3         | 0         | 6         | 9         | 0          |
| 2         | 34        | 14        | 2         | 4         | 17        | 46         | 2         | 5         | 5         | 24        | 4         | 10        | 65         |
| 3         | 8         | 2         | 10        | 0         | 2         | 85         | 3         | 16        | 2         | 24        | 3         | 3         | 11         |
| 4         | 6         | 11        | 167       | 15        | 6         | 200        | 4         | 6         | 0         | 13        | 13        | 11        | 50         |
| 5         | 6         | 7         | 4         | 3         | 3         | 63         | 5         | 18        | 13        | 20        | 2         | 4         | 11         |
| 6         | 5         | 0         | 9         | 4         | 3         | 29         | 6         | 7         | 6         | 0         | 9         | 9         | 8          |
| 7         | 5         | 0         | 9         | 7         | 11        | 16         | 7         | 0         | 4         | 0         | 3         | 2         | 2          |

TABLE 6b

Individual Techniques: Number of Significant Variations

Total: 32 (of 248)

| <u>By Sediment</u> | <u>By Metal</u> | <u>By Method</u> |
|--------------------|-----------------|------------------|
| FM-3               | Al-4            | 1-9              |
| HH-5               | Fe-3            | 2-7              |
| CS-9               | Mn-3            | 3-4              |
| DH-2               | Cu-7            | 4-4              |
| DL-0               | Co-9            | 5-5              |
| TAG-13             | Ni-6            | 6-2              |
|                    |                 | 7-1              |

of high variations occurs in the weak method analyses (Method 1), the minor component metals (Cu, Co and Ni) and the TAG sediment. A greater degree of variability is to be expected for TAG, since the predominant constituents of TAG are manganese oxyhydroxides which can show pronounced inhomogeneity in metal constituents scavenged during or after precipitation.

Table 7 presents average metal concentrations of duplicate extraction solutions by each method for each sediment and also gives the percentage of each metal extracted by each method for each sediment when compared with NAA and XRF data. Table 8 presents results of weak extraction and the average of results for the intermediate methods and strong methods. It also presents values for these three groups averaged over all sediment types.

Except for cobalt from TAG, the weak extraction method (1), which is for adsorbed and carbonate associated metals, extracted a lower percentage of each metal compared to the other six methods. It extracted no detectable aluminum from any sediments. This indicates little or no attack on clay lattices or aluminosilicate structures. The intermediate methods (2, 3, 4 and 5) averaged 3.8%, 3.8%, 8.2% and 6.0%, aluminum release, respectively, with an overall averaged for all four methods of 5.5%. The strong methods, 6 and 7, did extract the most aluminum, 21.8% and 28.2% averages respectively, with a combined average of 25%. However, their yields are far less than they should be if they are to be considered for total element analysis.

Iron behaves very uniformly at each level of attack, the weak method averaged 2.8% extraction with a range of 0% to 9%. The intermediate method averaged 29.6%, 27%, 27% and 38% extraction individually when averaged over all sediment types, with a combined average of 31%. The strong methods (6

TABLE 7a

Average Al Release (mg/g)

| <u>Sediment</u> | <u>Method 1</u> | <u>Method 2</u> | <u>Method 3</u> | <u>Method 4</u> |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| FM              | 0.12            | 2.63 ± .08      | 2.32 ± .08      | 5.1             |
| HH              | 0.08 ± .01      | 3.09 ± .49      | 3.91 ± .09      | 6.4 ± .2        |
| CS              | 0.16 ± .03      | 2.96 ± .03      | 2.13 ± .05      | 5.2 ± .1        |
| DH              | 0.23 ± .01      | 1.85 ± .05      | 1.37            | 4.30 ± .10      |
| DL              | 0.11 ± .01      | 1.89 ± .05      | 2.96 ± .08      | 5.2 ± .3        |
| TAG             | 0 ± 0           | 0.33 ± .03      | 0.56 ± .02      | 0.39 ± 0        |

| <u>Sediment</u> | <u>Method 5</u> | <u>Method 6</u> | <u>Method 7</u> | <u>NAA</u> |
|-----------------|-----------------|-----------------|-----------------|------------|
| FM              | 2.80            | 10.9            | 12.3 ± .5       | 59.1 ± 1.0 |
| HH              | 4.15 ± .45      | 13.8 ± .3       | 16.6 ± 1.5      | 65.1 ± 1.4 |
| CS              | 3.95 ± .25      | 14.4 ± .3       | 16.0            | 66.2 ± 1.7 |
| DH              | 3.70            | 14.9 ± .3       | 14.4 ± .3       | 46.2 ± 1.0 |
| DL              | 4.85 ± .25      | 16.8 ± .3       | 39.4            | 97.4 ± 2.1 |
| TAG             | 0.41 ± .01      | 0.44 ± .01      | 0.43 ± .01      | -----      |

Fraction of Total Al Released (%)

| <u>Sediment</u> | <u>1</u><br><u>NAA</u> | <u>2</u><br><u>NAA</u> | <u>3</u><br><u>NAA</u> | <u>4</u><br><u>NAA</u> | <u>5</u><br><u>NAA</u> | <u>6</u><br><u>NAA</u> | <u>7</u><br><u>NAA</u> |
|-----------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| FM              | 0                      | 4                      | 4                      | 9                      | 5                      | 18                     | 21                     |
| HH              | 0                      | 5                      | 6                      | 10                     | 6                      | 21                     | 25                     |
| CS              | 0                      | 4                      | 3                      | 8                      | 6                      | 21                     | 24                     |
| DH              | 0                      | 4                      | 3                      | 9                      | 8                      | 32                     | 31                     |
| DL              | 0                      | 2                      | 3                      | 5                      | 5                      | 17                     | 40                     |
| TAG             | -                      | -                      | -                      | -                      | -                      | --                     | --                     |

± Values are the average differences between duplicate determinations

TABLE 7b

Average Fe Release (mg/g)

| <u>Sediment</u> | <u>Method 1</u> | <u>Method 2</u> | <u>Method 3</u> | <u>Method 4</u> |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| FM              | 0.95 ± .01      | 0.64 ± .01      | 4.0             | 10.2 ± .2       |
| HH              | 1.78 ± .02      | 13.4            | 9.8             | 15.9 ± .4       |
| CS              | 0.23 ± .01      | 8.4 ± .1        | 3.76 ± .01      | 11.0            |
| DH              | 0.02            | 11.5 ± 3.0      | 4.15 ± .29      | 6.9 ± .1        |
| DL              | 0.01            | 15.2            | 8.7 ± .2        | 12.0            |
| TAG             | 0.04 ± .01      | 0.24 ± .02      | 0.38 ± .02      | 0.06 ± .01      |

| <u>Sediment</u> | <u>Method 5</u> | <u>Method 6</u> | <u>Method 7</u> | <u>NAA</u> |
|-----------------|-----------------|-----------------|-----------------|------------|
| FM              | 7.3 ± .1        | 18.3 ± .2       | 21.3 ± .4       | 30.9 ± .3  |
| HH              | 12.7 ± .4       | 25.3 ± .2       | 28.4 ± .9       | 39.9 ± .4  |
| CS              | 12.6 ± 2.3      | 25.7 ± .2       | 24.7            | 36.6 ± .3  |
| DH              | 11.7 ± .4       | 22.6 ± .6       | 20.5            | 28.5 ± .4  |
| DL              | 18.6 ± .1       | 33.9 ± .2       | 37.7            | 55.6 ± .5  |
| TAG             | 0.30 ± 0        | 0.32 ± .01      | 0.36 ± 0        | 0.46 ± .05 |

Fraction of Total Fe Released (%)

| <u>Sediment</u> | <u>Weak</u>     | <u>Intermediate</u> |                 |                 |                 | <u>Strong</u>   |                 |
|-----------------|-----------------|---------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | <u>1</u><br>NAA | <u>2</u><br>NAA     | <u>3</u><br>NAA | <u>4</u><br>NAA | <u>5</u><br>NAA | <u>6</u><br>NAA | <u>7</u><br>NAA |
| FM              | 3               | 2                   | 13              | 33              | 24              | 59              | 68              |
| HH              | 4               | 34                  | 25              | 40              | 32              | 63              | 71              |
| CS              | 1               | 23                  | 10              | 30              | 34              | 70              | 67              |
| DH              | 0               | 40                  | 15              | 24              | 41              | 79              | 72              |
| DL              | 0               | 27                  | 16              | 22              | 33              | 61              | 68              |
| TAG             | 9               | 52                  | 83              | 13              | 65              | 70              | 78              |

TABLE 7c

Average Mn Release ( $\mu\text{g/g}$ )

| <u>Sediment</u> | <u>Method 1</u> | <u>Method 2</u>     | <u>Method 3</u>     | <u>Method 4</u>    |
|-----------------|-----------------|---------------------|---------------------|--------------------|
| FM              | 163 $\pm$ 3     | 253 $\pm$ 2         | 274 $\pm$ 9         | 295                |
| HH              | 180             | 278 $\pm$ 5         | 315 $\pm$ 10        | 327 $\pm$ 9        |
| CS              | 95 $\pm$ 5      | 110 $\pm$ 5         | 234 $\pm$ 9         | 173 $\pm$ 3        |
| DH              | 208 $\pm$ 3     | 179 $\pm$ 48        | 2045 $\pm$ 15       | 970                |
| DL              | 118 $\pm$ 8     | 383 $\pm$ 5         | 4050                | 523 $\pm$ 13       |
| TAG             | 52.6 $\pm$ 10.6 | 255,000 $\pm$ 5,000 | 371,000 $\pm$ 3,500 | 15,590 $\pm$ 2,330 |

| <u>Sediment</u> | <u>Method 5</u>      | <u>Method 6</u>     | <u>Method 7</u>      | <u>NAA</u>          |
|-----------------|----------------------|---------------------|----------------------|---------------------|
| FM              | 236 $\pm$ 6          | 383 $\pm$ 8         | 503 $\pm$ 8          | 737 $\pm$ 15        |
| HH              | 263 $\pm$ 3          | 423                 | 488 $\pm$ 8          | 639 $\pm$ 13        |
| CS              | 145                  | 298 $\pm$ 3         | 282 $\pm$ 7          | 390 $\pm$ 8         |
| DH              | 2385 $\pm$ 35        | 1813 $\pm$ 23       | 1755 $\pm$ 55        | 2689 $\pm$ 54       |
| DL              | 3720                 | 3665 $\pm$ 55       | 2025 $\pm$ 75        | 5549 $\pm$ 157      |
| TAG             | 386,000 $\pm$ 17,000 | 393,000 $\pm$ 8,000 | 385,000 $\pm$ 10,000 | 420,000 $\pm$ 8,000 |

TABLE 7c (continued)

Fraction of Total Mn Released (%)

| <u>Sediment</u> | <u>Weak</u>     | <u>Intermediate</u> |                 |                 |                 | <u>Strong</u>   |                 |
|-----------------|-----------------|---------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | <u>1</u><br>NAA | <u>2</u><br>NAA     | <u>3</u><br>NAA | <u>4</u><br>NAA | <u>5</u><br>NAA | <u>6</u><br>NAA | <u>7</u><br>NAA |
| FM              | 22              | 34                  | 37              | 40              | 32              | 52              | 68              |
| HH              | 28              | 44                  | 49              | 51              | 41              | 66              | 76              |
| CS              | 24              | 28                  | 60              | 44              | 37              | 76              | 72              |
| DH              | 8               | 7                   | 76              | 36              | 89              | 67              | 65              |
| DL              | 2               | 7                   | 73              | 9               | 67              | 66              | 36              |
| TAG             | 0               | 61                  | 88              | 4               | 92              | 94              | 92              |

TABLE 7d

Average Cu Released ( $\mu\text{g/g}$ )

| <u>Sediment</u> | <u>Method 1</u> | <u>Method 2</u> | <u>Method 3</u> | <u>Method 4</u> |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| FM              | 4.4 $\pm$ .1    | 22 $\pm$ 1      | 2.45 $\pm$ .25  | 8.45 $\pm$ .15  |
| HH              | 63 $\pm$ 16     | 132 $\pm$ 4     | 82 $\pm$ 1      | 105 $\pm$ 1     |
| CS              | 0.70 $\pm$ .08  | 10.5 $\pm$ .5   | 1.4 $\pm$ 1.4   | 3.8 $\pm$ .3    |
| DH              | 1.42 $\pm$ 1.0  | 51 $\pm$ 1      | 28.5 $\pm$ .5   | 44.5 $\pm$ .5   |
| DL              | 5.5 $\pm$ .15   | 63              | 3.40 $\pm$ .25  | 33              |
| TAG             | 0 $\pm$ 0       | 5.03 $\pm$ .15  | 3.40 $\pm$ .25  | 3.42 $\pm$ .05  |

| <u>Sediment</u> | <u>Method 5</u> | <u>Method 6</u> | <u>Method 7</u> | <u>NAA</u>     |
|-----------------|-----------------|-----------------|-----------------|----------------|
| FM              | 18              | 8.75 $\pm$ .15  | 21              | 32 $\pm$ 4     |
| HH              | 130 $\pm$ 3     | 95 $\pm$ 2      | 199 $\pm$ 1     | 260 $\pm$ 25   |
| CS              | 17.5 $\pm$ .5   | 5.4 $\pm$ 6     | 16              | 23.6 $\pm$ 3.7 |
| DH              | 87 $\pm$ 1      | 46.5 $\pm$ .5   | 57              | 88 $\pm$ 9     |
| DL              | 93 $\pm$ 1      | 30              | 81              | 118 $\pm$ 11   |
| TAG             | 1.41 $\pm$ .21  | 4.20 $\pm$ .13  | 8.76 $\pm$ .92  | -----          |

Fraction of Total Cu Released (%)

| <u>Sediment</u> | <u>Weak</u>            | <u>Intermediate</u>    |                        |                        |                        | <u>Strong</u>          |                        |
|-----------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
|                 | <u>1</u><br><u>XRF</u> | <u>2</u><br><u>XRF</u> | <u>3</u><br><u>XRF</u> | <u>4</u><br><u>XRF</u> | <u>5</u><br><u>XRF</u> | <u>6</u><br><u>XRF</u> | <u>7</u><br><u>XRF</u> |
| FM              | 14                     | 69                     | 8                      | 26                     | 56                     | 27                     | 66                     |
| HH              | 24                     | 51                     | 32                     | 40                     | 50                     | 37                     | 77                     |
| CS              | 3                      | 44                     | 6                      | 16                     | 74                     | 23                     | 68                     |
| DH              | 16                     | 58                     | 32                     | 51                     | 99                     | 53                     | 65                     |
| DL              | 5                      | 53                     | 13                     | 28                     | 79                     | 25                     | 69                     |
| TAG             | --                     | --                     | --                     | --                     | --                     | --                     | --                     |

TABLE 7e

Average Co Release ( $\mu\text{g/g}$ )

| <u>Sediment</u> | <u>Method 1</u> | <u>Method 2</u> | <u>Method 3</u> | <u>Method 4</u> |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| FM              | 0               | 4.45 $\pm$ .75  | 2.4 $\pm$ .1    | 3.2 $\pm$ .1    |
| HH              | 1.0 $\pm$ .2    | 7.2 $\pm$ .5    | 43.5 $\pm$ .05  | 5.6 $\pm$ .3    |
| CS              | 0               | 9.9 $\pm$ .1    | 4.0 $\pm$ .2    | 2.4 $\pm$ 2.0   |
| DH              | 0               | 50 $\pm$ 1      | 36              | 6.6 $\pm$ .5    |
| DL              | 0               | 69 $\pm$ 6      | 85 $\pm$ 1      | 9.6 $\pm$ .3    |
| TAG             | 1.81 $\pm$ .44  | 5.36 $\pm$ 1.22 | 1.23 $\pm$ .52  | 0.29 $\pm$ .29  |

| <u>Sediment</u> | <u>Method 5</u>  | <u>Method 6</u> | <u>Method 7</u> | <u>NAA</u>      |
|-----------------|------------------|-----------------|-----------------|-----------------|
| FM              | 1.75 $\pm$ .05   | 7.3 $\pm$ .2    | 8.6 $\pm$ .2    | 10.49 $\pm$ .20 |
| HH              | 4.15 $\pm$ .15   | 11              | 11              | 12.86 $\pm$ .23 |
| CS              | 5.2 $\pm$ .1     | 11.5 $\pm$ .5   | 11.5 $\pm$ .5   | 12.03 $\pm$ .21 |
| DH              | 38.5 $\pm$ .5    | 23.5 $\pm$ .5   | 122 $\pm$ 4     | 38.3 $\pm$ .5   |
| DL              | 72 $\pm$ 1       | 74 $\pm$ 1      | 38 $\pm$ 2      | 79.6 $\pm$ .9   |
| TAG             | 10.77 $\pm$ 3.41 | 4.07 $\pm$ .60  | 5.80 $\pm$ .47  | 3.10 $\pm$ .13  |

Fraction of Total Cu Released (%)

| <u>Sediment</u> | <u>Weak</u>     | <u>Intermediate</u> |                 |                 |                 | <u>Strong</u>   |                 |
|-----------------|-----------------|---------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | <u>1</u><br>NAA | <u>2</u><br>NAA     | <u>3</u><br>NAA | <u>4</u><br>NAA | <u>5</u><br>NAA | <u>6</u><br>NAA | <u>7</u><br>NAA |
| FM              | 0               | 42                  | 23              | 31              | 17              | 70              | 82              |
| HH              | 8               | 56                  | 34              | 44              | 32              | 86              | 86              |
| CS              | 0               | 82                  | 33              | 20              | 43              | 96              | 96              |
| DH              | 0               | 131                 | 94              | 17              | 101             | 61              | 319             |
| DL              | 0               | 87                  | 107             | 12              | 90              | 93              | 48              |
| TAG             | 58              | 173                 | 40              | 9               | 347             | 131             | 187             |

TABLE 7f

Average Ni Release ( $\mu\text{g/g}$ )

| <u>Sediment</u> | <u>Method 1</u> | <u>Method 2</u> | <u>Method 3</u> | <u>Method 4</u> |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| FM              | 1.1 $\pm$ .3    | 8.2 $\pm$ .2    | 1.85 $\pm$ .15  | 6.9 $\pm$ .2    |
| HH              | 6.9 $\pm$ .3    | 20.5 $\pm$ .5   | 10.0 $\pm$ .1   | 16              |
| CS              | 3               | 12.5 $\pm$ 1.5  | 5.9 $\pm$ .7    | 10.4 $\pm$ .6   |
| DH              | 9.7 $\pm$ .3    | 56 $\pm$ 1      | 34.5 $\pm$ .5   | 23.5 $\pm$ 1.5  |
| DL              | 3.35 $\pm$ .15  | 82 $\pm$ 4      | 72 $\pm$ 1      | 38 $\pm$ 2      |
| TAG             | 0 $\pm$ 0       | 526 $\pm$ 170   | 491 $\pm$ 27    | 231 $\pm$ 58    |

| <u>Sediment</u> | <u>Method 5</u> | <u>Method 6</u> | <u>Method 7</u> | <u>NAA</u>   |
|-----------------|-----------------|-----------------|-----------------|--------------|
| FM              | 8.0 $\pm$ .7    | 14.5 $\pm$ .5   | 14              | 25 $\pm$ 7   |
| HH              | 15 $\pm$ 1      | 32 $\pm$ 1      | 24.5 $\pm$ .5   | 44 $\pm$ 8   |
| CS              | 10.9 $\pm$ 1.1  | 22              | 19              | 32 $\pm$ 7   |
| DH              | 46.5 $\pm$ .5   | 43 $\pm$ 2      | 35.5 $\pm$ .5   | 89 $\pm$ 7   |
| DL              | 82.5 $\pm$ 1.5  | 110 $\pm$ 5     | 57.7 $\pm$ .5   | 130 $\pm$ 10 |
| TAG             | 445 $\pm$ 24    | 476 $\pm$ 20    | 514 $\pm$ 4     | 399 $\pm$ 10 |

Fraction of Total Ni Released (%)

| <u>Sediment</u> | <u>Weak</u>     | <u>Intermediate</u> |                 |                 |                 | <u>Strong</u>   |                 |
|-----------------|-----------------|---------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | <u>1</u><br>NAA | <u>2</u><br>NAA     | <u>3</u><br>NAA | <u>4</u><br>NAA | <u>5</u><br>NAA | <u>6</u><br>NAA | <u>7</u><br>NAA |
| FM              | 4               | 33                  | 7               | 28              | 32              | 58              | 56              |
| HH              | 16              | 47                  | 23              | 26              | 34              | 73              | 56              |
| CS              | 9               | 39                  | 18              | 33              | 34              | 69              | 59              |
| DH              | 11              | 63                  | 39              | 26              | 52              | 48              | 40              |
| DL              | 3               | 63                  | 55              | 29              | 63              | 85              | 44              |
| TAG             | 0               | 132                 | 123             | 58              | 112             | 119             | 129             |

TABLE 8

Metals Released When Averaged for all Weak (W),  
Intermediate (I), and Strong (S) Individual Methods  
(By Weight)

| <u>Sediment</u> | <u>Al</u> |          |          | <u>Fe</u> |          |          | <u>Mn</u> |          |          |
|-----------------|-----------|----------|----------|-----------|----------|----------|-----------|----------|----------|
|                 | <u>W</u>  | <u>I</u> | <u>S</u> | <u>W</u>  | <u>I</u> | <u>S</u> | <u>W</u>  | <u>I</u> | <u>S</u> |
| FM              | 0         | 5.5      | 20       | 3         | 18       | 65       | 22        | 36       | 60       |
| HH              | 0         | 6.8      | 24       | 4         | 33       | 68       | 28        | 46       | 71       |
| CS              | 0         | 5.3      | 23       | 1         | 24       | 69       | 24        | 42       | 75       |
| DH              | 0         | 6.0      | 33       | 0         | 30       | 76       | 8         | 52       | 67       |
| DL              | 0         | 3.8      | 29       | 0         | 25       | 65       | 2         | 39       | 52       |
| TAG             | -         | ---      | --       | 9         | 53       | 75       | 0         | 61       | 93       |

| <u>Sediment</u> | <u>Cu</u> |          |          | <u>Co</u> |          |          | <u>Ni</u> |          |          |
|-----------------|-----------|----------|----------|-----------|----------|----------|-----------|----------|----------|
|                 | <u>W</u>  | <u>I</u> | <u>S</u> | <u>W</u>  | <u>I</u> | <u>S</u> | <u>W</u>  | <u>I</u> | <u>S</u> |
| FM              | 14        | 40       | 47       | 0         | 28       | 76       | 4         | 25       | 57       |
| HH              | 24        | 43       | 57       | 8         | 42       | 86       | 16        | 35       | 65       |
| CS              | 3         | 35       | 46       | 0         | 45       | 96       | 9         | 31       | 64       |
| DH              | 16        | 60       | 59       | 0         | 86       | 191      | 11        | 45       | 45       |
| DL              | 5         | 43       | 47       | 0         | 74       | 71       | 3         | 53       | 65       |
| TAG             | --        | --       | --       | 58        | 142      | 159      | 0         | 106      | 124      |

Averaged Over All Sediment Types

| <u>Metals</u> | <u>W</u>    | <u>I</u>  | <u>S</u> |
|---------------|-------------|-----------|----------|
| Al            | 0 ± 0       | 5.5 ± 0.7 | 26 ± 4   |
| Fe            | 2.8 ± 2.5   | 31 ± 9    | 70 ± 4   |
| Mn            | 14.0 ± 10.7 | 46 ± 7    | 70 ± 10  |
| Cu            | 12.4 ± 6.7  | 44 ± 6    | 51 ± 5   |
| Co            | 11.0 ± 15.7 | 70 ± 30   | 113 ± 41 |
| Ni            | 7.2 ± 4.8   | 49 ± 20   | 70 ± 18  |

and 7) average 67% and 70.8% individually and 70% combined for iron extraction efficiency. Though still not very close to 100%, strong methods would much better for iron, which is less likely to be as predominant as Al in lattice structures, than for aluminum.

The weak method extracted 14% of the manganese on average, principally due to high values for FM (22%), HH (28%) and CS (24%), which are all reducing sediments. They can be reasonably expected to have significant amounts of manganese present in very labile forms. That this weak method does not significantly attack manganese oxide phases is evidenced by the low efficiencies of extraction from DH (8%), DL (2%), (both oxidized sediments) and especially that insignificant (0%) manganese was extracted from TAG, of which 42% of the entire sediment is manganese. The intermediate methods (2, 3, 4 and 5) averaged 30%, 64%, 31% and 60% extraction efficiencies respectively for manganese, with an overall average of 46%. The strong attack of the reducing, acetic acid method (3) and the citrate-dithionite method (5) on manganese oxides is shown by the 88% and 92% extraction respectively, of the manganese from TAG. The strong methods (6 and 7) averaged 70% and 68% respectively, and 70% overall. Again, the averages are higher than for the weaker methods, but not close to 100%.

Copper extraction is variable for all sediments. The weak method extracted an average of 12.4% with a range from 3% to 24% for the different sediment types. The highest value was found in sediment FM which contains the most organics and is the most reducing. It possibly indicates that the copper extracted from this type of sediment may be loosely associated with organics as adsorbed rather than structurally bound species. The intermediate methods (2, 3, 4 and 5) averaged 55%, 18.2%, 32.2% and 71.6% respectively, with an overall average of 44%. The higher average of the

oxalate (2) and citrate-dithionite (5) methods probably reflect more favorable conditions for oxidizing organic material because of the non-reducing complexing agents present in each. The association of copper with manganese and iron oxides in the TAG sample could not be determined with certainty since copper could not be determined in this sample by NAA or XRF analyses, and therefore, no extraction efficiencies for copper could be determined. However, the copper values for TAG by the reducing acetic acid method (3) are substantially lower than those by either strong method, indicating only minor possible associations, of copper with these oxides. The strong methods (6 and 7) averaged 33% and 69% respectively, and 51% overall. The concentrated HCl method was consistently lower than the HCl:HNO<sub>3</sub> method, indicating problems for copper analysis by this method. Again, both methods are well below 100% efficient.

Cobalt is the most randomly variable element determined. The weak method extracted cobalt from only two sediments, HH and TAG. The overall average was 11% however, but only because of the 58% extraction for TAG which exhibited high variability. This could be indicative of significant amounts of Co present as adsorbed species on the surface of iron and manganese oxides in the TAG sample. The intermediate methods (2, 3, 4 and 5) averaged 95%, 55%, 22% and 81% efficiencies respectively, with an overall average of 70%. The oxalate method (2) gives the most uniform extractions for all sediment types. The oxalate (2) reducing acetic acid (3) and citrate-dithionite (5) methods all extracted approximately 100% for both deep sea samples. The lower value of the reducing acetic acid method (3) for TAG is very similar to the value by the weak method. The extremely high values (>> 100%) for the oxalate and citrate-dithionite method, indicates that the cobalt is probably loosely adsorbed to oxides or

contained within other phases, rather than held within the oxide phases. However, the >> 100% values may also indicate errors in the NAA cobalt values for DH and TAG, severe problems with the oxalate and citrate-dithionite methods for cobalt or analytical problems. The strong methods averaged 90% and 136% efficiencies, with an average of 113%. It would seem that, on average, both these methods are capable of extracting the great majority of cobalt. Again, the consistent >> 100% values for the  $\text{HCl:HNO}_3$  method may indicate problems with this method in the analysis of cobalt.

The results for nickel were more uniform than for other elements. The weak method averaged 7.2% extraction efficiency. The high value of 16% in sediment HH may reflect labile nickel phases from anthropogenic inputs. The intermediate methods (2, 3, 4 and 5) averaged 63%, 44%, 35% and 54.5% efficiencies and 49% overall. All these methods extracted significant amounts of nickel from TAG indicating nickel's apparent affinity for strong associations with oxides. The strong methods (6 and 7) averaged 75.3% and 64% individual and 70% overall efficiencies. Again, these two methods fall short of 100% efficiency.

#### Sequential Extraction by Tessler et al. (1979) Method

In comparing the results of the sequential scheme of Tessler et al. (1979) to those of the individual extraction method study, it must be remembered that the scheme steps are performed sequentially on the residue from the previous step, whereas the other studies' results are based on the original sediment samples. This requires the summation of the values from all previous steps and the step being compared be performed, before comparison of results from the individual methods can be made.

Extracted concentrations of the various metals by each step for the

different sediments are available from the authors upon request. Two subsamples of each sediment was again analyzed. Each subsample was analyzed at least twice by atomic absorption spectrophotometry until values obtained for that subsample agreed to better than 5%.

The percent variation between analyses between subsample is presented in Table 9. Again, variation of 20% or greater is deemed of concern as previously explained. Fifty-two of the 280 variation numbers (29%) are significantly variant, though seven of these are due to the difference between one small value and zero. The numbers are closely distributed by sediment type from a low of six (HH)m to a high of ten (FM, CS and TAG). DH and DL have eight each. Distribution by step and by element are not as even. By step, over half are confined to the adsorbed (1) and carbonate (2) steps (19 and 13, respectively) with a steady decrease by step to the residual step with 5. By element, Ni and Co, when summed (15 and 13, respectively) produce as many significant total variations between duplicates as do the sum of Cu, Al, Fe and Mn (8, 7, 6 and 5, respectively).

Despite many major differences by step, when the totals in all five step analyses are averaged, only one of the 36 concentrations exceeds 20% in the difference of subsamples. This indicates that the high variations tend to cancel each other when summed and that each total metal concentration in each sediment is relatively homogeneous. However, each sediment subsample may not contain the same phase distribution of each element, or each attack is not uniformly successful at removing the appropriate phases or maintaining these phases in solution.

Table 10 presents the results from each step normalized to the NAA or XRF values for each metal in each sediment and the total of all five steps normalized to the NAA values. In the analysis of aluminum, all eight

TABLE 9

Sequential Scheme : % Variation  
Between Duplicate Sediment Analyses

| <u>Metal</u> | <u>Step</u> | <u>FM</u> | <u>HH</u> | <u>CS</u> | <u>DH</u> | <u>DL</u> | <u>TAG</u> |
|--------------|-------------|-----------|-----------|-----------|-----------|-----------|------------|
| Al           | 1           | 1         | 42        | 13        | 45        | 1         | 0          |
|              | 2           | 41        | 13        | 10        | 13        | 32        | 2          |
|              | 3           | 5         | 16        | 24        | 5         | 1         | 6          |
|              | 4           | 11        | 1         | 11        | 8         | 1         | 38         |
|              | 5           | 29        | 11        | 6         | 10        | 14        | 1          |
|              | Total       | 24        | 10        | 4         | 10        | 12        | 0          |

| <u>Metal</u> | <u>Step</u> | <u>FM</u> | <u>HH</u> | <u>CS</u> | <u>DH</u> | <u>DL</u> | <u>TAG</u> |
|--------------|-------------|-----------|-----------|-----------|-----------|-----------|------------|
| Fe           | 1           | 16        | 3         | 43        | 49        | 13        | 200        |
|              | 2           | 40        | 13        | 19        | 28        | 18        | 0          |
|              | 3           | 1         | 8         | 7         | 3         | 1         | 200        |
|              | 4           | 4         | 1         | 6         | 10        | 4         | 13         |
|              | 5           | 18        | 1         | 7         | 0         | 8         | 7          |
|              | Total       | 9         | 2         | 3         | 1         | 7         | 8          |

| <u>Metal</u> | <u>Step</u> | <u>FM</u> | <u>HH</u> | <u>CS</u> | <u>DH</u> | <u>DL</u> | <u>TAG</u> |
|--------------|-------------|-----------|-----------|-----------|-----------|-----------|------------|
| Mn           | 1           | 7         | 5         | 2         | 3         | 0         | 69         |
|              | 2           | 9         | 10        | 2         | 12        | 75        | 11         |
|              | 3           | 1         | 11        | 3         | 1         | 4         | 2          |
|              | 4           | 2         | 1         | 13        | 28        | 2         | 5          |
|              | 5           | 9         | 0         | 4         | 5         | 12        | 3          |
|              | Total       | 4         | 1         | 0         | 2         | 4         | 0          |

TABLE 9 (continued)

| <u>Metal</u> | <u>Step</u> | <u>FM</u> | <u>HH</u> | <u>CS</u> | <u>DH</u> | <u>DL</u> | <u>TAG</u> |
|--------------|-------------|-----------|-----------|-----------|-----------|-----------|------------|
| Cu           | 1           | 18        | 3         | 200       | 4         | 200       | 0          |
|              | 2           | 18        | 13        | 37        | 11        | 8         | 0          |
|              | 3           | 15        | 19        | 9         | 6         | 12        | 18         |
|              | 4           | 17        | 5         | 35        | 2         | 4         | 24         |
|              | 5           | 28        | 25        | 1         | 6         | 8         | 20         |
|              | Total       | 18        | 8         | 16        | 1         | 9         | 18         |

| <u>Metal</u> | <u>Step</u> | <u>FM</u> | <u>HH</u> | <u>CS</u> | <u>DH</u> | <u>DL</u> | <u>TAG</u> |
|--------------|-------------|-----------|-----------|-----------|-----------|-----------|------------|
| Co           | 1           | 200       | 26        | 200       | 200       | 87        | 19         |
|              | 2           | 45        | 10        | 78        | 60        | 4         | 31         |
|              | 3           | 35        | 7         | 26        | 4         | 21        | 4          |
|              | 4           | 19        | 4         | 14        | 1         | 44        | 32         |
|              | 5           | 11        | 1         | 28        | 13        | 6         | 10         |
|              | Total       | 12        | 1         | 18        | 5         | 2         | 12         |

| <u>Metal</u> | <u>Step</u> | <u>FM</u> | <u>HH</u> | <u>CS</u> | <u>DH</u> | <u>DL</u> | <u>TAG</u> |
|--------------|-------------|-----------|-----------|-----------|-----------|-----------|------------|
| Ni           | 1           | 43        | 70        | 57        | 30        | 111       | 50         |
|              | 2           | 50        | 32        | 7         | 12        | 46        | 7          |
|              | 3           | 111       | 92        | 8         | 26        | 8         | 50         |
|              | 4           | 1         | 5         | 6         | 3         | 6         | 0          |
|              | 5           | 2         | 5         | 5         | 2         | 5         | 0          |
|              | Total       | 4         | 9         | 2         | 17        | 5         | 1          |

TABLE 10

Fraction of Total Metal (%)  
Released at Each Step of Sequential Scheme

| <u>Sediment</u> | <u>Metal</u> | <u>St. 1</u><br>NAA | <u>St. 2</u><br>NAA | <u>St. 3</u><br>NAA | <u>St. 4</u><br>NAA | <u>St. 5</u><br>NAA | <u>Total</u><br>NAA |
|-----------------|--------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| FM              | Al           | 0                   | 0                   | 0.9                 | 5.1                 | 42.8                | 48.9                |
|                 | Fe           | 0.1                 | 0.1                 | 8.8                 | 23.2                | 39.4                | 71.6                |
|                 | Mn           | 1.7                 | 9.8                 | 22.1                | 24.6                | 34.9                | 93.1                |
|                 | *Cu          | 5.2                 | 6.5                 | 2.0                 | 88.5                | 23.8                | 126.0               |
|                 | Co           | 4.4                 | 3.7                 | 3.1                 | 29.6                | 95.5                | 136.2               |
|                 | Ni           | 0.2                 | 1.4                 | 0.4                 | 21.1                | 53.0                | 76.1                |
| <u>Sediment</u> | <u>Metal</u> | <u>St. 1</u><br>NAA | <u>St. 2</u><br>NAA | <u>St. 3</u><br>NAA | <u>St. 4</u><br>NAA | <u>St. 5</u><br>NAA | <u>Total</u><br>NAA |
| HH              | Al           | 0                   | 0                   | 1.0                 | 5.9                 | 48.0                | 55.0                |
|                 | Fe           | 0                   | 0.5                 | 14.0                | 22.3                | 38.1                | 75.0                |
|                 | Mn           | 18.8                | 5.7                 | 11.7                | 24.2                | 34.2                | 94.6                |
|                 | *Cu          | 1.2                 | 31.7                | 15.2                | 10.3                | 29.6                | 88.1                |
|                 | Co           | 4.0                 | 5.0                 | 8.8                 | 27.9                | 90.4                | 136.0               |
|                 | Ni           | 1.5                 | 1.2                 | 8.9                 | 13.8                | 31.4                | 56.9                |

\*Cu by XRF

TABLE 10 (Continued)

| <u>Sediment</u> | <u>Metal</u> | <u>St. 1</u><br>NAA | <u>St. 2</u><br>NAA | <u>St. 3</u><br>NAA | <u>St. 4</u><br>NAA | <u>St. 5</u><br>NAA | <u>Total</u><br>NAA |
|-----------------|--------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| CS              | Al           | 0                   | 0                   | 0.7                 | 4.2                 | 37.7                | 42.6                |
|                 | Fe           | 0                   | 0                   | 4.3                 | 15.5                | 46.0                | 65.9                |
|                 | Mn           | 1.3                 | 11.9                | 17.2                | 14.4                | 34.5                | 79.3                |
|                 | *Cu          | 0                   | 0.6                 | 2.6                 | 43.6                | 45.5                | 91.0                |
|                 | Co           | 2.4                 | 4.4                 | 14.2                | 23.7                | 88.1                | 132.7               |
|                 | Ni           | 0.1                 | 0.8                 | 6.1                 | 14.9                | 37.1                | 59.0                |

| <u>Sediment</u> | <u>Metal</u> | <u>St. 1</u><br>NAA | <u>St. 2</u><br>NAA | <u>St. 3</u><br>NAA | <u>St. 4</u><br>NAA | <u>St. 5</u><br>NAA | <u>Total</u><br>NAA |
|-----------------|--------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| DH              | Al           | 0                   | 0                   | 1.0                 | 3.8                 | 56.7                | 61.6                |
|                 | Fe           | 0                   | 0                   | 7.6                 | 6.7                 | 57.2                | 71.6                |
|                 | Mn           | 0                   | 0.3                 | 73.6                | 5.6                 | 3.7                 | 83.3                |
|                 | *Cu          | 1.5                 | 4.7                 | 45.3                | 9.1                 | 77.9                | 138.5               |
|                 | Co           | 1.1                 | 1.0                 | 72.9                | 12.8                | 23.5                | 111.2               |
|                 | Ni           | 0.3                 | 0.6                 | 16.4                | 3.4                 | 17.3                | 38.1                |

\*Cu by XRF

TABLE 10 (Continued)

| <u>Sediment</u> | <u>Metal</u> | <u>St. 1</u><br>NAA | <u>St. 2</u><br>NAA | <u>St. 3</u><br>NAA | <u>St. 4</u><br>NAA | <u>St. 5</u><br>NAA | <u>Total</u><br>NAA |
|-----------------|--------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| DL              | Al           | 0                   | 0                   | 0.4                 | 3.6                 | 26.9                | 31.0                |
|                 | Fe           | 0                   | 0                   | 4.6                 | 7.0                 | 44.9                | 56.5                |
|                 | Mn           | 0                   | 0                   | 62.6                | 23.6                | 3.6                 | 89.8                |
|                 | *Cu          | 0                   | 3.6                 | 29.6                | 10.0                | 72.8                | 116.1               |
|                 | Co           | 0.4                 | 1.1                 | 58.4                | 16.4                | 23.4                | 99.6                |
|                 | Ni           | 0                   | 0.7                 | 16.4                | 7.8                 | 16.7                | 41.7                |

| <u>Sediment</u> | <u>Metal</u> | <u>St. 1</u><br>NAA | <u>St. 2</u><br>NAA | <u>St. 3</u><br>NAA | <u>St. 4</u><br>NAA | <u>St. 5</u><br>NAA | <u>Total</u><br>NAA |
|-----------------|--------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| TAG             | Al           | ----                | ----                | ----                | ----                | ----                | ----                |
|                 | Fe           | 0.4                 | 0                   | 0.4                 | 5.8                 | 36.7                | 43.2                |
|                 | Mn           | 0                   | 0                   | 16.0                | 30.3                | 36.4                | 82.7                |
|                 | *Cu          | ----                | ----                | ----                | ----                | ----                | ----                |
|                 | Co           | 17.9                | 47.3                | 13.6                | 0                   | 0                   | 78.8                |
|                 | Ni           | 0.1                 | 0.2                 | 9.4                 | 9.6                 | 9.8                 | 29.0                |

\*Cu by XRF

sediments released essentially 0% in both the adsorbed (1) and carbonate (2) steps. The hydrogenous step (3) released between 0.4% and 1.0% indicating very mild or no lattice attack. The organic step (4) released between 3.6% and 5.9% indicating mild lattice attack, while the step (5) released 27% to 57%. The weaker four steps, therefore, show little or no attack of aluminosilicate framework structures. However, the final step either does not fully attack these structures, or causes significant fractions of the released aluminum to be inefficiently measured.

The adsorbed (1) and carbonate (2) steps also extracted very little iron from any of the sediments, with a maximum of 0% by the carbonate step for sediment HH. The hydrogenous step (3) extracted an average of 6.6% with a range of 0.4% to 14%, the maximum again being for sediment HH. An average of approximately 7% of the iron in the marine sediments studied occurs as oxides or hydroxides. The amount of iron oxide in the TAG sediment is much lower (approximately 0.5%), indicating insignificant accumulation of iron phases in this sediment. The organic step extracted 6% to 23% of the iron. This indicates that significant portions of iron are bound to organics and other Eh sensitive species. The 37% to 57% of the iron extracted by the residual step (5) also indicates that the silicate lattices contain appreciable iron. When the steps are summed, however, the total iron extracted averages only 64%. The total average metal extraction efficiency is greater than for aluminum, but the deviation is still significant.

Manganese extracted by the adsorbed step (1) is very low, 0% to 1.7%, except for sediment HH, from which almost 91% of the manganese was removed. Again, as this is the most reducing sediment, and it is likely that much of the manganese would be in a labile state. The carbonate step (2) extracted

0% to 12% of the manganese, with the high value from the reducing sediment CS and the low values from the deep sea sediments DH, DL and TAG. The hydrogenous step (3) values range from lows of 12% and 16% in HH and TAG sediments, to highs of 63% and 74% for DL and DH sediments. The low value in HH reflects the loss of Mn to the labile phases while the low TAG value may indicate that the concentration of the reducing agent in this solution is insufficient to liberate the large amount of Mn present. This step significantly extracted Mn from CS (17%) and FM (22%) and was the dominant step for DL (63%) and DH (74%). The organic step (4) extracted 5.6% to 30% of the Mn, with an average of 20%. This represents a significant portion of manganese as organic associated species. Four to 36% extraction of Mn by the residual step (5) represents substantial lattice associated manganese. It also brought the sums of all five methods within measurement error limits of 100%. The total Mn values ranged from 79% to 95%, with an average of 87%.

Copper was also found to be at low concentrations in weakly adsorbed species, being extracted 0% to 5% by the adsorbed step (1). Copper is generally very low in the carbonate step (2) when extracted (0.6% to 6.5%) except for sediment HH from which 32%, the largest value of the five steps, was obtained. This may show the tendency for copper to become mobile under strongly reducing conditions, though not to the extent of manganese. The hydrogenous step (3) extracted 2% to 45% of the total copper, with an average of 19%. The high values were obtained from the two deep sea samples DH and DL (45% and 30% respectively). The organic extraction step (4) Cu values were relatively low, 9.1% to 10.3%, except for CS (44%) and FM (89%). The high values for these probably represent the great percentage of organic bound copper not yet released from the mildly

reducing sediments. The 24% to 78% range and 50% average of the residual step (5) values further indicate the variability of phases in which copper may be found in substantial quantities. Again, the highest values are from sediments DH and DL, presumably due to binding within the clay lattices under oxidizing conditions. The total extraction values averaged 96%, indicating good analytical recovery.

Cobalt is more abundant as weakly adsorbed species, as evidenced by the 0.4% to 18% range and 5% average extraction efficiencies found in the adsorbed step (1). The carbonate step (2) values were generally low (2% to 5%) except for TAG from which 47% was extracted. The hydrogenous step (3) extraction efficiencies were high for DH (73%) and DL (58%), with the value for TAG (13.6%) accounting for all remaining Co in this sediment. Cobalt's behavior may be attributed to a late stage addition as a highly mobile component of the manganese-rich sediment, and the principal association with the oxide phases of deep sea sediments. The organic step (4) produced moderately low extraction efficiencies (0% to 30%, 18% average). The residual step (5) liberated the dominant fraction of Co from the three reducing sediments, CS (88%), FM (96%) and HH (90%). Overall, it is observed that cobalt is in mobile phases in oxidizing sediments and very resistant to chemical attack in reducing sediments.

Nickel is another element difficult to quantitatively account for, as evidenced by the 29% to 76% range and 50% average extraction efficiency for the totals of all five steps. The adsorbed (1) and carbonate (2) steps extracted very little nickel, with a 0.3% to 2.7% range and 0.8% average extraction. The hydrogenous step (3) extracted moderate amounts of nickel, extracting the highest percentage from the deep sea sediments DH and DL (16.4%) averaging 9.6% for all sediments. The organic step was highest for

the reducing sediments CS (14.9%), HH (13.8%) and FM (21%) relative to the other sediments (3.4% to 9.6%, average). The final step (5) resulted in the lowest average extraction efficiency of any method, 28%. For deep sea oxidizing sediments nickel appears to be equally distributed between oxides and silicates, with organics of significant but varying importance. In reducing sediments, silicates and other insoluble phases are the dominant nickel containing phases, organics, a distant second, and the other phases of minor importance.

#### COMPARISON OF DATA

To compare results from these groups of wet chemical methods it is necessary to condense the number of values to be examined. The metals studied here are found in widely variable amounts within the different sediment phases, and low extraction efficiencies of some metals and high efficiencies of others are most desirable for many methods. Consequently, it may be misleading to condense the data by averaging values for all metals within each sediment type. To observe which methods work best for all sediment types, it was decided that averaging should be done for each metal over all six sediment types as an indication of each method's general applicability. However, it should be emphasized that much important information is obscured by doing so.

The averages calculated are presented in Table 11 along with the average deviation from the mean and the percent of the deviation. Table 11a presents the averages for each of the seven methods and for each metal as indicated above. Table 11b presents the same type of data for each of the five sequential extraction scheme steps. The average values from these tables have also been plotted in Figures 1a and 1b. To enable

TABLE 11a

Metal Release by Individual  
Methods (%), Averaged Over All Six Sediment Types

| <u>Metal</u> | <u>1</u><br>NAA    | <u>2</u><br>NAA   | <u>3</u><br>NAA   | <u>4</u><br>NAA   |
|--------------|--------------------|-------------------|-------------------|-------------------|
| Al           | 0 ± 0              | 3.8 ± 0.7 (18%)   | 3.8 ± 1.0 (26%)   | 8.2 ± 1.4 (17%)   |
| Fe           | 2.8 ± 2.5 (89%)    | 29.7 ± 12.3 (41%) | 27.0 ± 18.7 (69%) | 27.0 ± 7.3 (27%)  |
| Mn           | 14.0 ± 10.7 (76%)  | 30.2 ± 16.2 (54%) | 63.8 ± 15.2 (24%) | 30.7 ± 16.1 (52%) |
| Cu           | 12.4 ± 6.7 (54%)   | 55.0 ± 6.8 (12%)  | 18.2 ± 11.0 (60%) | 32.2 ± 10.6 (33%) |
| Co           | 11.0 ± 15.7 (143%) | 95.2 ± 37.9 (40%) | 55.2 ± 30.2 (55%) | 22.2 ± 10.2 (46%) |
| Ni           | 7.2 ± 4.8 (67%)    | 62.8 ± 23.2 (37%) | 44.2 ± 29.9 (68%) | 35.0 ± 8.0 (23%)  |

| <u>Metal</u> | <u>5</u><br>NAA   | <u>6</u><br>NAA   | <u>7</u><br>NAA   |
|--------------|-------------------|-------------------|-------------------|
| Al           | 6.0 ± 0.8 (13%)   | 21.8 ± 4.1 (19%)  | 28.2 ± 5.8 (21%)  |
| Fe           | 38.2 ± 9.9 (26%)  | 67.0 ± 6.9 (9%)   | 70.8 ± 2.8 (4%)   |
| Mn           | 59.7 ± 23.0 (39%) | 70.2 ± 9.9 (14%)  | 68.2 ± 11.8 (17%) |
| Cu           | 71.6 ± 14.9 (21%) | 33.0 ± 9.6 (29%)  | 69.0 ± 3.2 (5%)   |
| Co           | 105 ± 80.7 (77%)  | 89.5 ± 17.2 (19%) | 136 ± 78 (57%)    |
| Ni           | 54.5 ± 22.0 (40%) | 75.3 ± 17.9 (24%) | 64.0 ± 21.7 (34%) |

Percentages in parentheses are percent standard deviation of the percent extracted.

TABLE 11b

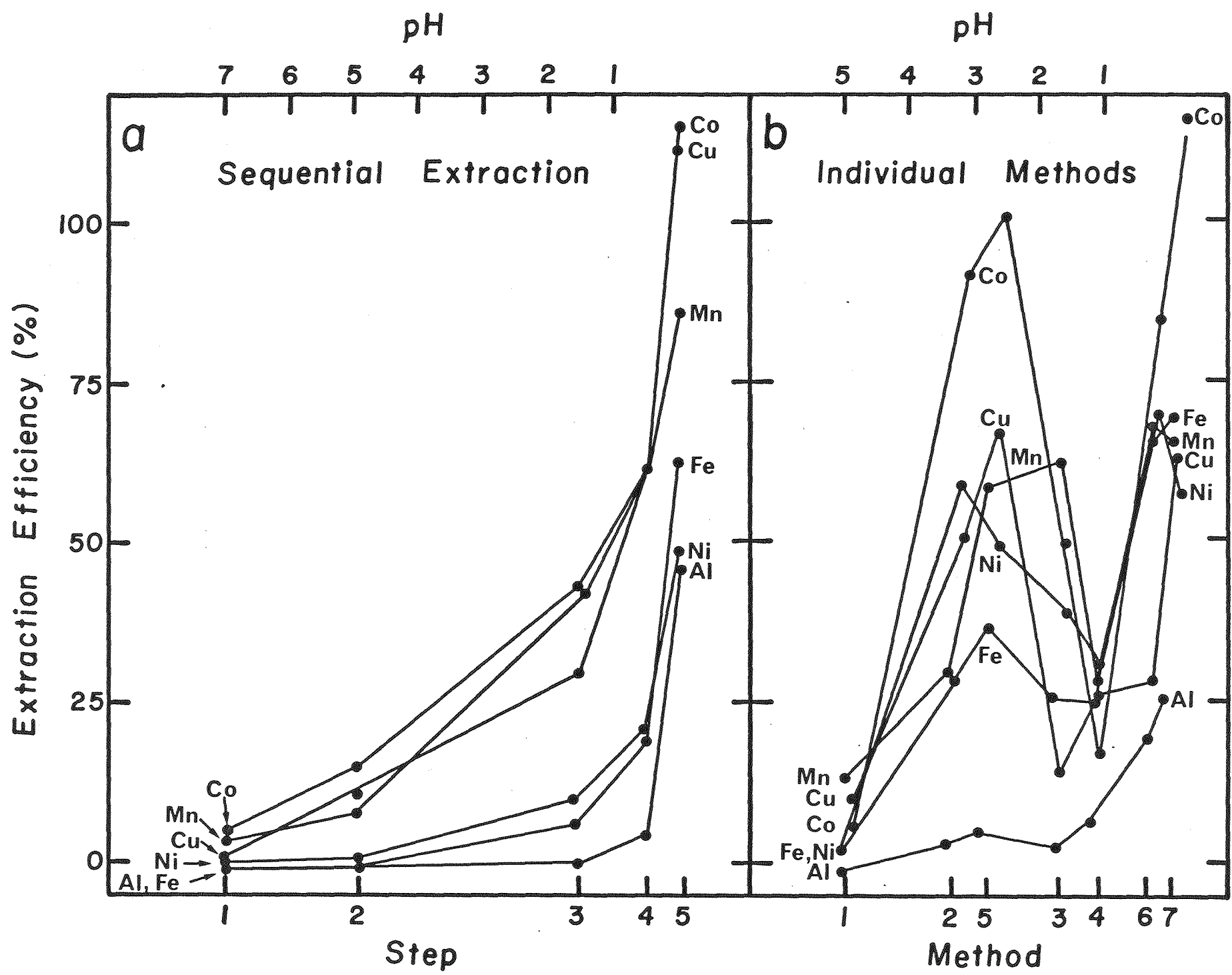
Metal Released (%) at Each Step of the  
Sequential Scheme, Averaged Over All Six Sediment Types

| <u>Metal</u> | <u>St.1</u><br>NAA | <u>St.2</u><br>NAA | <u>St.3</u><br>NAA | <u>St.4</u><br>NAA |
|--------------|--------------------|--------------------|--------------------|--------------------|
| Al           | 0 ± 0              | 0 ± 0              | 0.8 ± 0.2 (25%)    | 4.5 ± 0.8 (18%)    |
| Fe           | 0.1 ± 0.1 (100%)   | 0.1 ± 0.1 (100%)   | 6.6 ± 3.5 (53%)    | 13.4 ± 6.9 (51%)   |
| Mn           | 3.6 ± 5.0 (139%)   | 4.6 ± 4.5 (98%)    | 33.9 ± 22.8 (67%)  | 20.5 ± 7.0 (34%)   |
| Cu           | 1.6 ± 1.5 (94%)    | 9.4 ± 8.9 (95%)    | 18.9 ± 14.8 (78%)  | 32.3 ± 27.0 (84%)  |
| Co           | 5.0 ± 4.3 (86%)    | 10.4 ± 14.0 (135%) | 28.5 ± 24.8 (87%)  | 18.4 ± 8.7 (47%)   |
| Ni           | 0.4 ± 0.4 (100%)   | 0.8 ± 0.3 (38%)    | 9.6 ± 4.5 (47%)    | 11.8 ± 4.8 (41%)   |

| <u>Metal</u> | <u>St.5</u><br>NAA | <u>Sum Total</u><br>NAA |
|--------------|--------------------|-------------------------|
| Al           | 42.4 ± 8.1 (19%)   | 47.8 ± 8.8 (18%)        |
| Fe           | 43.7 ± 5.7 (13%)   | 64.0 ± 9.4 (15%)        |
| Mn           | 24.6 ± 13.9 (57%)  | 87.1 ± 5.4 (6%)         |
| Cu           | 49.9 ± 20.3 (41%)  | 111.9 ± 17.9 (16%)      |
| Co           | 53.5 ± 37.9 (71%)  | 115.8 ± 19.2 (17%)      |
| Ni           | 27.6 ± 13.0 (47%)  | 50.1 ± 13.9 (28%)       |

#### FIGURE CAPTION

Figure 1. Extraction efficiencies for different metals by technique, scaled by the pH of the extraction technique. Presented extraction efficiencies are averages over all six sediment types. Figure 1a presents the results for the different steps in the sequential extraction scheme of Tessler, et al. (1979). The results for the individual extraction techniques are presented in Figure 1b.



direct visual comparison between results, the abscissa has been scaled by pH. The pH of each method and each sequential scheme step solution was measured directly, and the values were used to place each method and sequential scheme step at its appropriate location along the abscissa. This scaling of the figure allows trends to be compared in two dimensions.

The features of particular interest from the sequential scheme step patterns of Figure 1a are the high final extraction percentages. The similarity of extraction patterns and the division of the six patterns into two distinct groups. Mn, Cu and Co behave similarly, as do Al, Fe and Ni.

The results of the individual methods are presented for each metal in Figure 1b and averaged for all similar strength methods in Figure 2. The weak method extracts higher Fe, Ni and Mn concentrations than the comparable sequential scheme method. The copper value is similar to the sequential scheme value. Cobalt is slightly depressed relative to the values for the scheme method. Attack on aluminum silicate lattices by this method is slight, if at all, as reflected by the undetectable release of aluminum. The averaged intermediate method values of Figure 2 are well ordered. Attack on aluminum is small, iron is released to a significant, but not dominant, degree; copper, manganese and nickel are released at a comparable level of 40% to 50%, and cobalt is released at the highest percentage of approximately 70%.

When looking at the individual results, however, the picture is more complicated. Aluminum confining phases are attacked least by the weak, oxalate and reducing acetic acid individual methods, and extracted by the 0.5 N HCl method to more than twice the values of the oxalate or reducing acetic acid methods. Iron is extracted to a similar extent by the intermediate methods, with slightly higher extraction efficiency by the

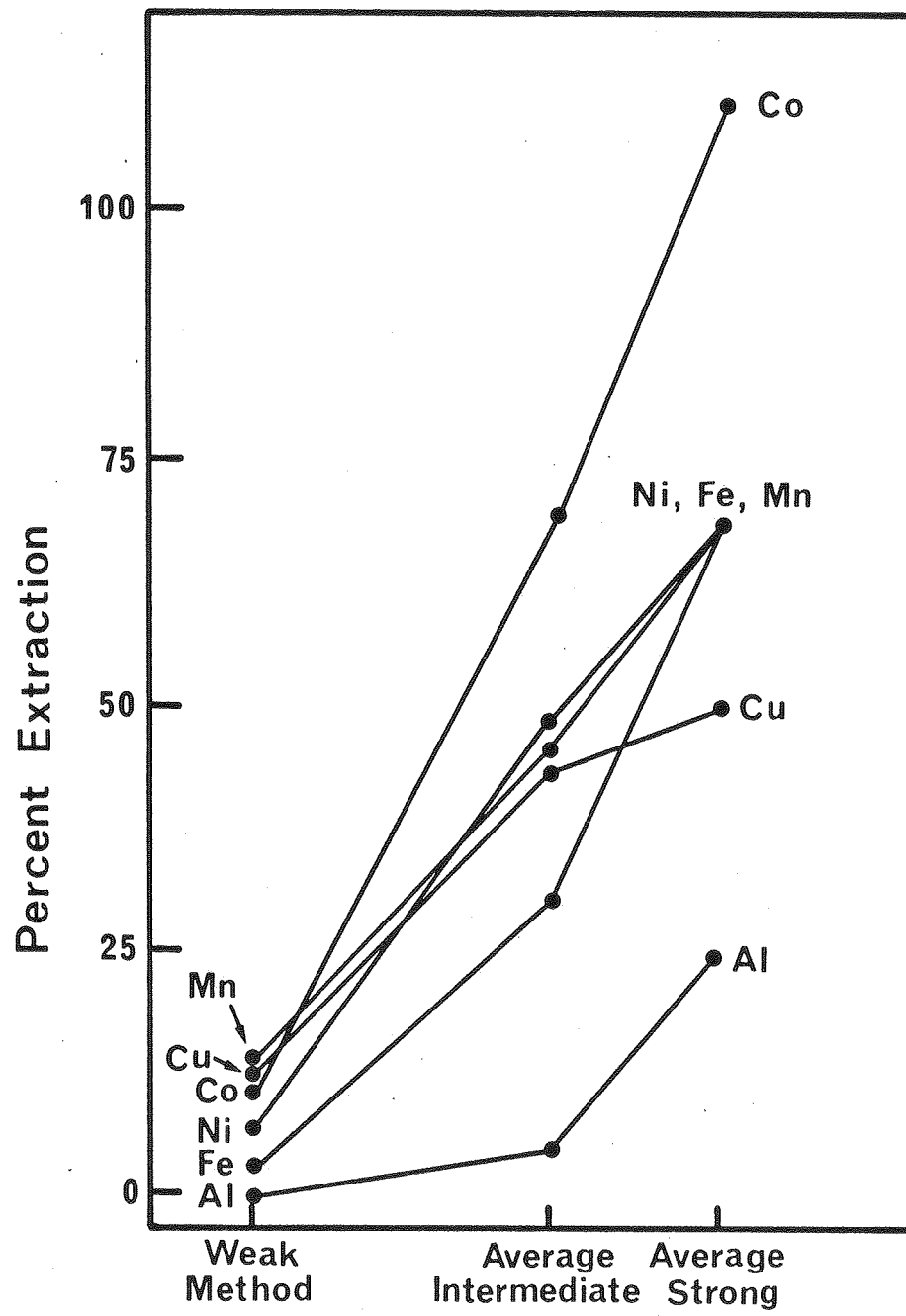


Figure 2. Extraction efficiencies for the various metals from all sediments averaged for similar methods.

citrate-dithionite method. The oxalate and 0.5 N HCl methods extract uniformly low manganese concentrations while the reducing acetic acid and citrate-dithionite methods extract uniformly high manganese concentrations. For cobalt, copper and nickel, the oxalate and citrate-dithionite methods extract much higher concentrations than the reducing acetic acid or 0.5 N HCl methods concentration. Values obtained by the 0.5 N HCl method are generally low. As noted previously cobalt is less favorably extracted from all sediments by reducing solutions, and is dominantly found in resistant phases of reducing sediments. Copper and nickel may be less efficiently extracted because the reducing solution will not attack organic associated phases as well as the oxalate or citrate complexing agents in the solutions of the other intermediate methods.

The comparison between the results of the reducing acetic acid method and those found for the very similar method of the hydrogenous step in the sequential scheme reflects the difference in concentration of the reducing agent in each solution. The reducing acetic acid solution extracts a slightly higher concentration of aluminum and cobalt, while the higher concentration of the reducing agent in this solution reduces the amount of copper extracted relative to the hydrogenous step solution. The substantially higher extraction efficiencies found for manganese, iron and nickel also reflect the stronger reducing conditions of the acetic acid solution.

The only metal to be completely extracted by the strong methods is cobalt. The moderately high average results for Fe, Mn and Ni are reflected by quite uniform extraction by both methods. A low, but uniform, average value for Al extraction was observed. The low average extraction efficiency for Cu is largely due to the very low extraction by the

concentrated HCl method. This is simply a more concentrated acid solution than the 0.5 N HCl method, which also extracted relatively low concentrations of Cu. In comparison to the strong method of the sequential scheme, these strong methods have significantly lower extraction efficiencies, except for iron and nickel. The iron results are comparable for all methods. Both the concentrated HCl and HCl:HNO<sub>3</sub> methods are more efficient in extracting nickel than the final step used in the sequential extraction scheme.

### CONCLUSIONS

The individual methods are not preferred for the determination of the order of metal release, as the relative amounts of each metal released vary at each level of attack depending on the method used. Instead, the individual methods make it possible to evaluate the relative susceptibility of different trace metals to removal from sediments under a specific set of chemical conditions. The weak method appears to efficiently remove such expected labile species as manganese from the strongly reducing sediment and cobalt from the manganese oxide-rich sediment, as well as the carbonate associated metals, without significantly attacking other species.

All of the metals studied (except aluminum) are released in very similar patterns from reducing sediments for all four intermediate strength methods. The major variations in extraction efficiency between the intermediate strength methods was observed for the oxidized or very mildly reducing sediments. In general, the solutions with complexing agents obtained higher levels metal release than the acid only solution which does not release most trace metals. This difference may reflect a

greater ability of the complexing agents to retain the metals in solution. The oxalate method is less efficient in releasing manganese and iron, while the reducing acetic acid method and the citrate-dithionite method have very similar and higher efficiencies. The reducing acetic acid method is preferred because the citrate-dithionite method attacks the mineral lattices to a slightly greater degree, as reflected by increased extraction of aluminum.

Both strong individual methods are more variable for most elements than the strong method from the sequential extraction scheme. Based on sediment type, the reducing sediments again show greater uniformity, while the wide variations are principally due to the oxidizing sediments.

The order of metal release using the sequential scheme of Tessler et al. (1979) varies by sediment type. All metals, except aluminum, from the reducing sediments follow a similar pattern of release, with very minor amounts released over the first three steps and the majority released by the organic and residual steps. As was found in the individual extraction methods, large variabilities for the sediment-averaged metal release values arise primarily from the results obtained for the oxidizing or very mildly reducing sediments. Iron, copper and nickel are released in a manner similar to that found for the reducing sediments. In most sediments studied, manganese and cobalt show a rapid release prior to the organic associated steps (Step 4) and generally less release by the later two steps.

To reduce sediment (or particulate matter) dependent variabilities and maintain appropriate extraction efficiencies for all metals of interest, it is recommended that the sequential scheme of Tessler et al. (1979) be used. The technique also has the advantage of giving a more

detailed type of information on metal distribution in a sample and requiring less sample for overall characterization. The following modifications are recommended. For the third step, it is recommended that the concentration of the reducing agent be increased to 0.5 M, to increase manganese, iron and nickel extraction efficiencies without changing the efficiencies for cobalt and copper. For the fifth step, it is recommended that a third digestion, using a 2 to 3 N HCl solution, be used to eliminate any excess anionic species from the solution that may interfere with the atomic absorption analyses for nickel and iron.

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