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Assessment of the Tessier and BCR sequential extraction procedures for elemental partitioning of Ca, Fe, Mn, Al, and Ti and their application to surface sediments from Chinese continental shelf

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Abstract

Surface sediments can integrate a wide variety of information of seawater in marginal seas, e.g., the Quaternary sedimentary shelf such as the East China Sea (ECS) and Yellow Sea (YS). The Tessier and BCR sequential extraction procedures (SEPs) have been widely applied for extraction of various geochemical phases from sediments. To choose a suitable SEP for phase extraction of sediments from the above Quaternary sedimentary shelf, efficiency and selectivity experiments were conducted on typical individual minerals and the applicability of each SEP was assessed for natural sediments (the natural sediment standard GSD-9 and three surface sediment samples). The geochemical represented elements (Ca, Fe, Mn, Al, and Ti) were measured using both SEPs. Both SEPs have good dissolution efficiency and selectivity for the targeted geochemical phases; the optimized extractant volume for each fraction was determined. The Tessier SEP is particularly recommended for the study of adsorption-desorption process. The application of the Tessier SEP to surface sediments can furnish valuable information, including the productivity conditions (via the reducible fraction Mn) and sedimentary environments (via the carbonate fraction Ca). These results confirm that the Tessier SEP is suitable for elemental fractionation in sediments from the Chinese continental shelf.

Key words: elemental fractionation, surface sediments, Tessier SEP, BCR SEP, efficiency, selectivity

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1 Introduction

Quaternary sedimentary shelves are characterized by complicated ocean circulation (Lie and Cho, 2002), hypoxia (Chen et al., 2007; Rabalais et al., 1991), and large inputs of terrigenous sediment (Walter et al., 2000). The sediments deposited on these shelves are important records of this information (Li et al., 2017; Ding et al., 2017). With regard to rapid variations in seawater hydrology, if the sedimentation rate is sufficiently high, sediments can provide integrated information concerning seawater dynamics over a period of several years in estuaries and on continental shelves. The sedimentary record can reflect sediment provenance, physical processes (adsorption-desorption), chemical processes (oxidation-reduction) and biological processes. To investigate these different types of information and processes, different components in marine sediments must be extracted separately, including carbonates, hydrous metal oxides, organic substances and crystalline minerals (Szefer et al., 1995).

Chemical fractionation is an efficient approach for speciation analysis. The separation and analysis of individual mineral fractions has been used for studying trace element partitions (Chao, 1972; Chester and Hughes, 1967; Choi et al., 2015; Ray et al., 1957; Gutjahr et al., 2007, 2014; Leleyter and Probst, 1999; Poulton and Canfield, 2005; Song and Choi, 2009; Yang et al., 2002; Zhang et al., 2015; Zhu et al., 2006, 2012). Sequential extraction procedures (SEPs) are designed to isolate specific fractions of the sediments. The Tessier and BCR (Bureau Community of Reference) SEPs are most widely applied to metal fractionation in sediments and soil samples (Rauret et al., 1999; Sahuquillo et al., 1999; Tessier et al., 1979; Usero et al., 1998; Lin et al., 2014; Liu et al., 2016; Esmaeilzadeh et al., 2016). The accuracy and validity of SEPs for trace metal speciation have been extensively examined. However, few studies have assessed SEPs for elemental partitioning in sediments from Quaternary sedimentary shelves, such as the East China Sea (ECS) and Yellow Sea (YS). Assuring the selectivity and efficiency of each step and validating SEPs in this environment remains an important challenge.

The purpose of this study was to choose a proper SEP and optimize the extraction conditions with the methodology to be ap-

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plied to marine sediments on Chinese continental shelf to accurately determine the diverse origins of sediments and interpret various biogeochemical processes. Typical individual minerals (carbonate minerals, Fe-Mn oxides and clay mineral) were extracted to verify the efficiency and selectivity of the extractants. The Changjiang natural sediment standard GBW07309 (GSD-9) was selected and treated using both SEPs to assess their applicability. Finally, further assessment of the Tessier SEP was conducted using marine surface sediments from the Chinese continental shelf in relation to different sedimentary environments and productivity levels.

2 Materials and methods

2.1 Samples and reagents

The studied samples include typical individual minerals and natural sediments.

Efficiency and selectivity experiments were conducted on the following typical individual minerals: carbonate minerals (calcite, dolomite, rhodochrosite, and siderite), Fe-Mn oxides (pyrolusite, hematite, magnetite, amorphous $Fe(OH)_3$) and clay mineral (kaolinite). Amorphous $Fe(OH)_3$ was synthesized in laboratory, and the remaining chemicals and minerals were purchased. Calcite and dolomite were obtained from the Wuhan Iron and Steel Research Institute; MnCO₃ from the State Bureau of Building Materials Geological Institute; siderite from the Wuhan Iron and Steel Corporation; Fe minerals from the Geophysical and Geochemistry Research Institute; and kaolinite from Tianjin Ruijin Chemical Co. LTD.

The natural sediment standard GSD-9 (from Changjiang) was purchased to determine the optimum volume of extractant for each fraction in both SEPs. Three surface sediment samples collected in July 2013 were used for validity assessment (ME3 from south of the Changjiang Estuary, C05 from the Central Yellow Sea, and MT1 from southwest of Cheju Island).

MgCl₂, hexahydrate (>99%, ACS reagent) and HClO₄ (70%, ACS reagent) were purchased from Acros Organics. NH₂OH-HCl (Reagent Plus) and HNO₃ (≥65%, ISO. Reag. Ph. Eur.) were purchased from Sigma. NaAc (ACS, Reag. Ph. Eur.), NH₄Ac (ACS, Reag. Ph. Eur.), HAc (glacial, 100%, ACS, Reag. Ph. Eur.), H₂O₂ (30%), and HF (70%, ACS reagent) were purchased from Merck.

2.2 Extraction procedures

The extraction procedures of BCR (Rauret et al., 1999) and Tessier (Tessier et al., 1979) SEPs used in this study are summarized as follows:

BCR SEPs: (1) carbonate fraction (0.11 mol/L HAc), (2) Fe-Mn oxides fraction (0.5 mol/L NH₂OH-HCl), (3) organic matter fraction (30% H₂O₂), and (4) residual fraction (HNO₃, HF, HClO₄).

Tessier SEPs: (1) exchangeable fraction (1 mol/L MgCl₂), (2) carbonate fraction (1 mol/L NaAc-HAc), (3) Fe-Mn oxides fraction (0.04 mol/L NH₂OH-HCl), (4) organic matter fraction (30% H₂O₂), and (5) residual fraction (HNO₃, HF, HClO₄).

2.2.1 Efficiency and selectivity experiments on typical individual minerals

To study the efficiency and selectivity of both SEPs, typical individual minerals were extracted separately with the various extractants; these minerals included natural calcite, dolomite, rhodochrosite, siderite, pyrolusite, hematite, magnetite, synthetic amorphous Fe(OH)₃, and clay mineral (kaolinite). For the efficiency experiment, a series of different mass of each mineral was separately treated with a constant extractant volume in each fraction to determine the maximum mass that could be dissolved. For selectivity experiments, the initial mass of all minerals were 0.25 g, the extractant volume was used as determined in the efficiency experiment. After extraction, the percentages of the elements extracted were used to assess the efficiency and selectivity of the SEPs. The percentage of elements in each fraction was calculated based on the total concentration of each element which was determined by total digestion. If the percentage in the extract was close to 100%, the corresponding mass was considered to be the largest mass that could be dissolved completely. If the mineral content in the samples exceed the maximum mass, this demonstrates that a larger extractant volume should be used. For the exchangeable fraction, all minerals were treated to test the efficiency and selectivity. For the carbonate fraction, calcite and dolomite were utilized to evaluate the efficiency, and Fe-Mn oxides and kaolinite were used to assess selectivity. For the Fe-Mn oxides fraction, MnO₂ and amorphous Fe(OH)₃ were used to evaluate the efficiency, and hematite, magnetite, and kaolinite were used for selectivity assessment.

2.2.2 Applicability of both SEPs to the natural sediment standard

Different elements are associated with specific phases in natural sediment. To differentiate between these phases with minimal impact from other phases, the optimized extractant volume for each fraction was evaluated for the Tessier and BCR SEPs. A 0.25 g sample of GSD-9 was successively treated with different volumes of extractant for each SEP. Each fraction was subjected to leaching after the completion of the last-step extraction. Representative elements (Ca, Fe, Mn, Al, and Ti) were quantified in each fraction: Ca and Mn for exchangeable dissolution, Ca for carbonate dissolution, Fe and Mn for oxide dissolution, Al and Ti for silicates dissolution. Each supernatant solution was separated by centrifugation at 4 000 r/min for 20 min and then transferred to a polytetrafluoroethylene (PTFE) bottle. The residue was washed once with Milli-Q H₂O and decanted into a polyethylene (PE) bottle. The combined supernatant solution was dried to near dryness, 2 mL HNO₃ was added, and the solution was dried again to a HNO3 matrix. All fractions were brought up to volume in 2% HNO₃ before analysis.

2.2.3 Applicability of the Tessier SEP to surface sediments on the Chinese continental shelf

Different from the natural sediment standard, in view of different geographical environments, sedimentary environments, sedimentation rates and productivity levels, three surface sediments from the Chinese continental shelf were extracted using the Tessier SEP to further validate the applicability. These samples were collected from south of the Changjiang Estuary (ME3); the central YS (C05); and southwest of Cheju Island (MT1).

2.3 Instrumentation

The Ca, Fe, Mn, Al, and Ti concentrations were determined using an inductively coupled plasma atomic emission spectrometer (ICAP 6300, Thermo Fisher Scientific, USA), and the instrument's reproducibility was less than 3%.

3 Results and discussion

3.1 Efficiency and selectivity evaluation using typical individual minerals

The efficiency and selectivity results obtained using the BCR and Tessier SEPs are discussed separately.

3.1.1 Efficiency

(1) BCR SEP: 7.5 mL of 0.11 mol/L HAc can completely dissolve 0.04 g calcite and 0.025 g dolomite; 7.5 mL of 5 mol/L NH_2OH -HCl can fully dissolve 0.15 g MnO_2 and 0.025 g amorphous Fe(OH)₃.

(2) Tessier SEP: 0.25 g calcite and 0.125 g dolomite could be completely dissolved by 8 mL 1 mol/L NaAc-HAc. Leleyter et al. (1999) also found that sodium acetate (pH=5) was not efficient for dolomite dissolution. 7.5 mL of 0.04 mol/L NH₂OH-HCl could dissolve 0.01 g MnO₂ and 0.04 g amorphous Fe(OH)₃.

Compared with the results using 0.5 mol/L NH₂OH-HCl (pH=1.5), a solution of 0.04 mol/L NH₂OH-HCl in 25% HAc more effectively dissolved the amorphous Fe oxide while 0.5 mol/L NH₂OH-HCl (pH=1.5) more efficiently dissolved MnO₂.

Good efficiency usually ensures acceptable selectivity. Selectivity experiments were performed, and the results are listed below.

3.1.2 Selectivity

(1) BCR SEP: As presented in Table 1, the low percentages extracted from the Fe-Mn oxides and kaolinite imply that 7.5 mL of 0.11 mol/L HAc does not dissolve oxides and silicates. The high dissolution percentage of carbonate minerals indicates that 0.11 mol/L HAc has good selectivity for distinguishing between carbonates and non-carbonate minerals. 0.5 mol/L NH₂OH-HCl also has poor dissolution efficiency for hematite, magnetite and kaolinite. However, 42% MnO₂ and 11% Fe(OH)₃ were dissolved. This finding indicates that 0.5 mol/L NH₂OH-HCl has a greater extraction efficiency for amorphous Fe-Mn oxides than for crystalline oxides.

(2) Tessier SEP: As shown in Table 1, the low dissolution percentage of each mineral indicates that $MgCl_2$ only dissolved the absorbed elements without contamination from other phases (carbonate phase and Fe-Mn oxides). The leachable elements were adsorbed due to the permanent charge (Leleyter and Probst, 1999).

When treated with 8 mL of 1 mol/L NaAc-HAc, carbonate minerals, but not Fe-Mn oxides, were dissolved. Moreover, 100% calcite, 45% dolomite, and 10%-30% MnCO₃ were dissolved. Siderite is not the main carbonate mineral in the ECS (Zou et al., 2008), so only a negligible (0.99%) dissolution of siderite here has little effect. Rongemaille et al. (2011) also reported that siderite was not easily dissolved by 2% and 5% HAc.

When 0.25 g individual mineral was leached with 7.5 mL of 0.04 mol/L NH₂OH-HCl, 6.4% MnO₂ and 42% Fe(OH)₃ were leached. This liberation did not occur for the exchangeable and carbonate fractions.

In summary, both the BCR and Tessier SEPs have good dissolution efficiency and selectivity for the targeted minerals. When the natural sediment with mixture minerals was studied, the applicability was assessed as follows.

3.2 Applicability of both SEPs to the natural sediment standard (GSD-9)

The data are furnished in Fig. 1 and Fig. 2, respectively. The results are discussed below.

3.2.1 BCR SEP

(1) Fraction I_B : carbonate fraction

As shown in Fig. 1a, approximately 85% Ca and 35% Mn were

Table 1.	The dissolution se	electivity of carbonate	minerals, Fe-Mn oxides	and kaolinite of extrac	ctants in the Tessier and BCR SEPs

Mineral	BCR SEP		Tessier SEP		
	Carbonate/%	Fe-Mn oxides/%	Exchangeable/%	Carbonate/%	Fe-Mn oxides/%
Calcite	26.0	_	1.8	100.0	_
Dolomite	18.0	-	1.3	45.0	-
Rhodochrosite	10.0	-	0.1	12.0	-
MnCO ₃	14.0	-	0.3	31.0	-
Siderite	1.4	-	ND	1.0	-
MnO_2	ND	42.0	0.1	ND	6.4
Hematite	0.2	2.6	ND	0.1	7.8
Magnetite	ND	1.7	ND	0.2	2.3
Fe(OH) ₃	ND	11.0	0.1	0.5	42.0
Kaolinite	1.2	1.2	0.1	0.3	1.7

Note: % means the percentage of mineral dissolved, ND not detected, and - not extracted. The mass of all mineral was 0.25 g.

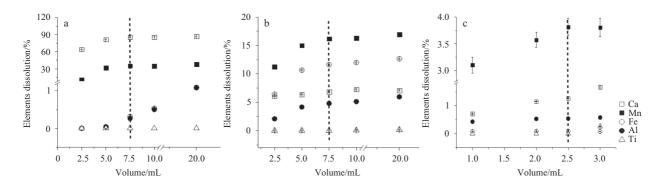


Fig. 1. Effect of extractant volume on the dissolution of Ca, Fe, Mn, Al, and Ti in various fractions of GSD-9 using the BCR SEP. a. Carbonate fraction, b. Fe-Mn oxides fraction, and c. organic matter fraction.

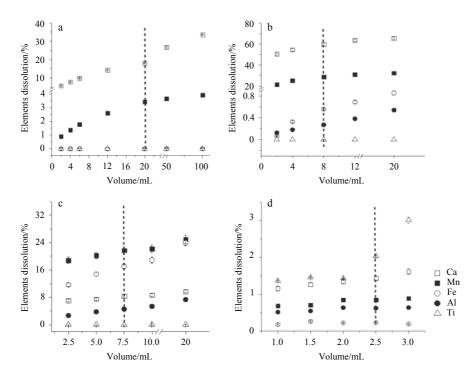


Fig. 2. Effect of extractant volume on the dissolution of Ca, Fe, Mn, Al, and Ti in various fractions of GSD-9 using the Tessier SEP. a. Exchangeable fraction, b. carbonate fraction, c. Fe-Mn oxides fraction, and d. organic matter fraction.

leached when the extractant volume was 7.5 mL, similar amounts of Ca and Mn were dissolved when using a larger volume. Notably, carbonates were sufficiently solubilized. The high percentage of Mn (approximately 35%) in this fraction can be attributed to the dissolution of manganese carbonate, which was demonstrated by the treatment of rhodochrosite and $MnCO_3$ with 0.11 mol/L HAc. The low percentages of Al and Fe indicated that the attack of silicate was minimal. The proportions of Al and Fe increased with the increase of extractant volume (over 7 mL), indicating enhanced contributions from the detrital and oxide phases. Previous results have also indicated that the enhanced extractant volume would lead to the dissolution of non-carbonate minerals (Freslon et al., 2014; He et al., 2015).

Therefore, 7.5 mL of 0.11 mol/L HAc was recommended for the extraction of carbonate phase.

(2) Fraction II_{B} : Fe-Mn oxides fraction

The results are shown in Fig. 1b. Approximately 13% Fe and 16% Mn were removed and the percentages were nearly constant when the volume exceeded 7.5 mL, indicating the dissolution of the reactive Fe-Mn oxides and poor crystalline hydroxides, such as Fe(OH)₃. The low percentage of Al indicated only a slight breakdown of silicates. Thus, 7.5 mL of 0.5 mol/L NH₂OH-HCl was chosen to extract the reactive Fe-Mn oxides and poor crystalline hydroxides.

(3) Fraction III_{B} : organic matter fraction

The dissolved amounts of Ca, Fe, Mn, Al, and Ti are presented in Fig. 1c. Small portions of each element were extracted, implying these elements rarely existed in the organic matter fraction. The percentages of Ca and Mn did not change when the volume exceeded 2.5 mL, except with an increasing amounts of Al and Ti. Consequently, 2.5 mL H_2O_2 was chosen.

Based on the above experimental work, the optimal volume of each extractant was chosen as follows: 0.25 g GSD-9 was treated progressively with 7.5 mL of 0.11 mol/L HAc at room temperature for 16 h; 7.5 mL of 0.5 mol/L NH₂OH-HCl (pH=1.5) at room

temperature for 16 h; 2.5 mL of 30% H_2O_2 (pH=2) at room temperature for 1 h, then at 85°C for 1 h, an additional 2.5 mL of 30% H_2O_2 (pH=2) at 85°C for 1 h and 20 mL of 1 mol/L NH₄Ac (pH=2) at room temperature for 16 h.

3.2.2 Tessier SEP

(1) Fraction I_T : exchangeable fraction

According to the concentration plots in Fig. 2a, a logarithmic relationship was observed for Ca and Mn when the volume increased from 2 mL to 20 mL. After an initial rapid increase, the percentage of Mn approached a dynamic balance although there was a slight increasing trend. The low percentages of Al, Fe, and Ti in all extracts implied that $MgCl_2$ treatment did not affect the silicates. The concentration of Ca slowly increased as the volume was larger than 20 mL, indicating minimal attack of the carbonates. Consequently, 20 mL of 1 mol/L $MgCl_2$ (pH=7) was selected.

(2) Fraction II_T : carbonate fraction

The percentages of Ca, Fe, Mn, Al, and Ti are illustrated in Fig. 2b. The Ca and Mn concentration curves show that the carbonates were adequately dissolved at a volume of 8 mL. Previous studies have indicated that carbonates cannot be fully dissolved if the sediment/solvent volume weight ratio is too high (Tessier et al., 1979). The high percentage of Mn (approximately 30%) in this fraction could also be attributed to the dissolution of manganese carbonate, which was proved by the extraction of rhodochrosite and MnCO₃. The low levels of Al and Fe indicate that silicate dissolution is minimal. Therefore, 8 mL of 1 mol/L NaAc-HAc was chosen to efficiently extract the carbonate phase.

(3) Fraction III_T : Fe-Mn oxides fraction

Variations in the amounts of Ca, Fe, Mn, Al, and Ti are presented in Fig. 2c. Similar to the BCR extraction, approximately 18% Fe and 20% Mn were removed and the percentages were constant at a volume of 7.5 mL, indicating the dissolution of reactive Fe-Mn oxides. The low percentage of Al indicates only a slight dissolution of silicate occurred. The Fe content was higher with an increase in volume, indicating partial attack of the crystalline Fe oxides and detrital silicate-rich minerals. Consequently, 7.5 mL of 0.04 mol/L NH₂OH-HCl in 25% HAc was chosen.

(4) Fraction IV_T : organic matter fraction

The amounts of Ca, Fe, Mn, Al, and Ti are shown in Fig. 2d. Small portions of each element extracted in this fraction implied that these elements rarely occurred in the organic matter fraction. The percentages of Mn, Fe, Ca, and Al did not change when the volume exceeded 2.5 mL, except with an increasing percentage of Ti. Hence, 2.5 mL of 30% H₂O₂ was chosen.

Based on the above discussion, the optimal volume of each extractant was presented as follows: 0.25 g GSD-9 was successively extracted with 20 mL of 1 mol/L MgCl₂ (pH=7) at room temperature for 1 h; 8 mL of 1 mol/L NaAc-HAc (pH=5) at room temperature for 5 h; 7.5 mL of 0.04 mol/L NH₂OH-HCl in 25% HAc at 96°C for 6 h; 2.5 mL of 30% H₂O₂ at 85°C for 5 h and 5 mL of 3.2 mol/L NH₄Ac (pH=2) at room temperature for 0.5 h.

The sums of the individual fractions for both SEPs agree well with the pseudo-total element analyses, ranging from 94% to 106% for the various elements, and the error is within 2% for most elements as shown in Fig. 3a and Fig. 3b, similar dissolution percentages of Fe, Al, and Ti were extracted from each fraction using both SEPs. The distinct difference between the Tessier and BCR SEPs was the exchangeable fraction in the Tessier SEP. Approximately 18% Ca and 4% Mn existed in the exchangeable fraction, the dissolution of this fraction is usually accompanied by the release of nutrient elements, which is important when studying element cycling in estuaries and on continental shelf areas.

Based on the similarities and differences discussed above between the Tessier and BCR SEPs, we offer several recommendations with regard to the applicability of each SEP to various biogeochemical processes: The Tessier SEP is recommended for the study of the following processes: (1) adsorption-desorption process (exchangeable Ca in estuaries and exchangeable Mn in marine sediments), (2) authigenous origin (carbonate Ca) and carbon cycle, and (3) biogeochemical process of Mn in marine sediments. Both the Tessier and the BCR SEPs can be used for the study of the following processes: (1) oxidation-reduction processes and hypoxia conditions, and (2) clastic rocks and terrigenous sediment provenance.

3.3 Characterizing the difference of surface sediments from various geographical environments on the Chinese continental shelf

Based on the application recommendations for each SEP, three surface sediments (ME3, south of the Changjiang Estuary; C05, the central YS; and MT1, southwest of Cheju Island) were extracted using the Tessier SEP. The percentages and concentrations of Ca, Fe, Mn, Al, and Ti are shown in Fig. 4 and Fig. 5, respectively. Ti (>98%) was mainly present in the residual fraction, indicating a terrigenous source. Al (>95%) was in the residual fraction, which agrees with previous results (Yuan et al., 2004). The bulk Al/Ti ratio was likely to be used as a sensitive tracer of particle flux and export production (Kryc et al., 2003; Wei et al., 2003). The Al/Ti ratio was found higher in ME3 (16.8), MT1 (18.4)

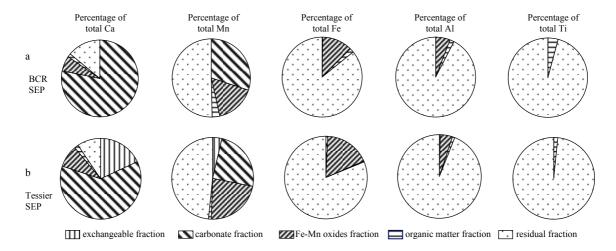


Fig. 3. Ca, Fe, Mn, Al, and Ti distributions for GSD-9 using the BCR (a) and Tessier (b) SEPs.

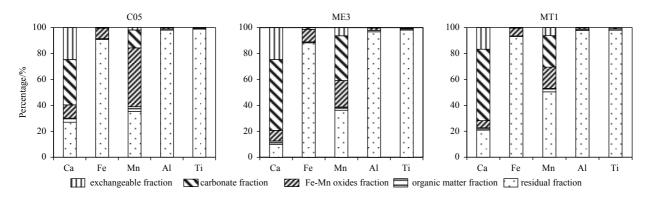


Fig. 4. Ca, Fe, Mn, Al, Ti distributions for C05, ME3, MT1 using the Tessier SEP.

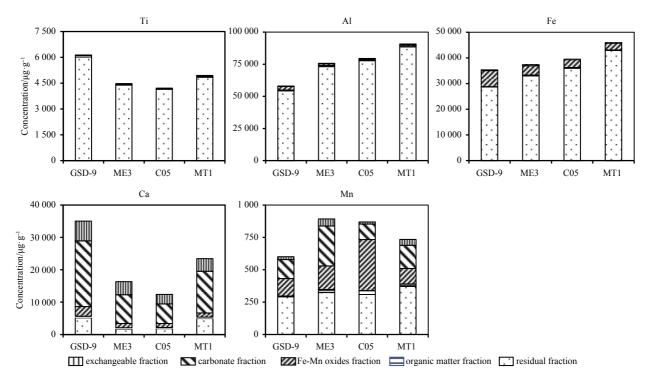


Fig. 5. Ca, Fe, Mn, Al, and Ti concentrations for GSD-9, ME3, C05, and MT1 using the Tessier SEP.

and C05 (18.1) than in the Changjiang (10.5) and Huanghe (16.4) sediments (Zhang et al., 1998), suggesting Al scavenging process by particles. Dou (2007) and Wei et al. (2003) found the excess Al in the ECS and South China Sea (SCS), respectively, suggesting that the excess Al can indicate biogenic matters flux on the shelf area. A total of 80%-90% of Fe was in the residual fraction, followed by 10%-20% Fe in Fe-Mn oxides fraction, agreeing with the results of previous studies (Kryc et al., 2003; Reid et al., 2011). This fraction of Fe arises from oxidation and deposition of Fe in seawater (Huang et al., 1997). About 20%-50%, 20%-40%, 20%-50%, and 2%-5% Mn were in residual, carbonate, reducible, and exchangeable fraction, respectively. The concentration (600 $\mu g/g$) and percentage (50%) of Mn in reducible fraction in C05 is higher than that in ME3 and MT1 (100-250 μ g/g and 20%-30%, respectively). The excess Mn may result from scavenging of dissolved Mn onto particles settling in high productivity areas near the Yellow Sea Cold Water (Lin et al., 2005). About 30%-60% Ca was associated with carbonates, and 10%-25% was in the exchangeable fraction. This is dissolution of absorbed Ca by electrostatic interaction, poor crystalline Ca and carbonate forms. The concentration of Ca in C05 was lower than that in ME3 and MT1, as a result of the lower concentration of carbonates in the YS (Chen et al., 2000).

4 Conclusions

To choose a suitable SEP for elemental fractionation in Quaternary sediments, the efficiency and selectivity, and application recommendations of the Tessier and BCR SEPs were evaluated.

(1) The extractants used in the BCR and Tessier SEPs have good dissolution efficiency and selectivity for the targeted phases.

(2) The optimal extractant volume for each fraction was determined for each SEP.

(3) To investigate various biogeochemical processes (different elements in specific experimental fraction) the application recommendations for each SEP are given.

(4) The application of the Tessier SEP to the surface sediments on the Chinese continental shelf provides a variety of information including productivity conditions (via higher Al/Ti ratio and the reducible fraction Mn) and sedimentary environments (via carbonate fraction Ca), which further demonstrates the suitability of the Tessier SEP.

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