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Quantitative compensation of grain-size effects in elemental concentration: A Korean coastal sediments case study

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ABSTRACT

Element concentrations ($C_{element}$) of the sediments in the diverse Korean coastal environments were constrained strongly by the grain-size effect (GSE), especially after compensation for metal-free carbonate and organic material contents. However, the GSE in some elements (especially metallic elements) was not completely offset by conventional Al-normalization ($C_{element}/C_{Al}$ ratio), and further the best-fit regression lines between the concentrations of Al and elements may not be linear, but instead curved, and also cannot pass through the origin point (0, 0). The results suggest the presence of conventional GSE (primary GSE) as well as another GSE (i.e., secondary GSE), which was well supported by the factor analysis for the variable of $C_{element}/C_{Al}$ ratios. Such primary and secondary GSEs are likely caused by physical and chemical processes, respectively, such as the quartz-dilution effect by metal-free, coarse-grained sediments and diagenetic reactions in organic-rich, fine-grained sediments. Furthermore, these GSEs in Korean coastal sediments can be quantitatively normalized by a quadratic equation: $C_{element} = a_0 \cdot C_{Al} + a_1 \cdot (C_{Al})^2$, where a_0 and a_1 are constants for the primary and the secondary GSEs, respectively.

1. Introduction

Elemental concentrations of siliciclastic sediments in aquatic environments are constrained primarily by sediment grain size (Horowitz, 1985, 1991; Herut and Sandler, 2006, and many references therein). Accordingly, elemental concentrations of coastal sediments around the Yellow Sea and the northern East China Sea have been found to significantly correlate with sediment grain size (Kim et al., 1998; Cho et al., 1999; Lin et al., 2002; Zhang and Liu, 2002). Indeed, the sediment grain-size effect (GSE) has been considered widely in the interpretation of sediment metal pollution, discrimination of sediment provenance, and many other biogeochemical phenomena (Horowitz and Elrick, 1987; Jung et al., 1996; Cahoon et al., 1999; Yang et al., 2003; Lim et al., 2013).

Most of elements, especially metallic elements, are generally concentrated in fine-grained sediments and, consequently, positive correlations occur in pair diagrams between mean grain size (Mz) and the concentrations of elements (Cho et al., 1999; Herut and Sandler, 2006; Lim et al., 2006). To remove the GSE reflected in the elemental concentrations, various methods have been suggested and applied, including physically separating the fine-grained sediments (e.g., <63 μm) by standard sieving or chemically normalizing the elemental concentrations by the concentrations of conservative metallic elements such as Al, Li, and Fe (Oliver, 1973; Bruland et al., 1974; Loring, 1991; Kim et al., 1998; Birch, 2003). Among them, the Al-normalization method ($\mathbf{C}_{element}/\mathbf{C}_{Al}$ ratio), obtained by dividing the elemental concentration ($\mathbf{C}_{element}$) by the Al concentration ($\mathbf{C}_{Al}$), has been widely adopted (Windom et al., 1989; Rubio et al., 2000; Swarzenski et al., 2006; Wang et al., 2011; Ho et al., 2012; Mil-Homens et al., 2013) and has also been used in many recent studies of Yellow Sea and East China Sea sediment geochemistry (Cho et al., 1999; Yang et al., 2003; Lim et al., 2006; Zhang et al., 2009). The conventional Al-normalization method has the advantages of the unusual input of anthropogenic Al, the conservative behavior of Al in normal marine environments, and the analytical convenience of Al in bulk sediments (Herut and Sandler, 2006).

However, the Al-normalization method rationally presumes that metal-free quartz grains are abundant in coarse-grained

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sediments and that metal-rich clay minerals are enriched in fine-grained sediments (the so called quartz-dilution effect; Kim et al., 1998). Also, mean sediment grain size is assumed to be represented by the Al concentrated in fine-grained sediments. On the basis of this two end-member mixing concept, a linear relationship line is expected in pair diagrams between the concentrations of Al and elements. Nonetheless, more than one linear relationship line occurs unexpectedly in such pair diagrams, and thus pivot points between the linear relationship lines in the diagrams or an alternative origin point in the diagrams have been defined functionally without a specific rationale (Herut and Sandler, 2006; Lim et al., 2006). Indeed, best-fit linear regression lines in these pair diagrams commonly do not pass through the origin point (0, 0) (Lim et al., 2006). In this study, we explained why linear regression of X and Y cannot extend to the origin, and further discussed the validity of the conventional Al-normalization method. And also, we tried to quantitatively normalize the grain-size effects in the elemental concentrations.

2. Materials and methods

In total, 157 surface sediment samples were collected from the western and southern coasts of Korea using a Smith-McIntyre grab sampler during the years of 2006–2010 (Fig. 1). The western coast of Korea belongs to the eastern part of the Yellow Sea, a tide-dominated epicontinental shelf environment with broad and monotonously flat seafloor morphology, which was post-glacially submerged after the last glacial maximum (LGM) (Park and Khim, 1992). The deepest trough, with water depth of approximately 90 m, is located in the southeastern part of the Yellow sea (Fig. 1). The southern coast of Korea also is a typical transgressive epicontinental shelf environment with water depths of 45–130 m. The area is covered with sediments that accumulated during the sea level rise following the LGM (Yoo et al., 2002; Yang et al., 2003). Most of these coastal areas were exposed during the LGM period, and paleo-channels of several Chinese and Korean rivers have been observed (Park and Gong, 2001; Yoo et al., 2003).

Grain-size analysis was carried out using a standard sieving method for the sand fractions (>63 μm), and a pipetting method was used for the mud fractions (<63 μm). For elemental compositions, bulk sediment samples were oven-dried overnight at 60 °C and then powdered with an agate mortar. Total carbon (TC) contents of the powdered sediments were measured using a CHN elemental analyzer (Thermo Scientific, model FLASH 2000). Total inorganic carbon (TIC) contents were measured using a CO_2 coulometer (UIC, model CM5014). The analytical accuracies for these elements were within 5% based on standards and replicate samples. Total organic carbon (TOC) concentrations were estimated as the difference between the TC and TIC contents. TIC was converted to calcium carbonate ($CaCO_3$) content as a weight percentage using the multiplication factor of 8.3333. The powdered samples were dissolved by two separate methods, one involving a mixture of hydrofluoric and perchloric acids and the other by fusion with lithium metaborate. These two prepared solutions were then

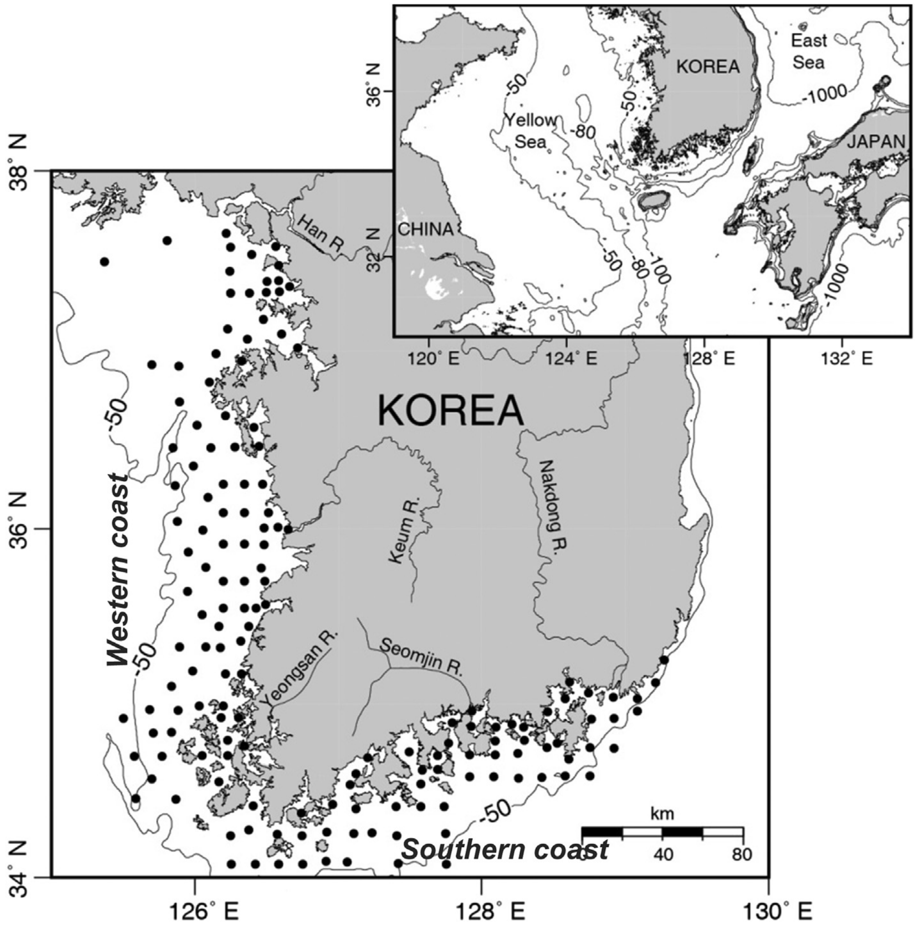

Fig. 1. Map showing the sampling sites of surface sediments from the western and southern coasts of Korea. In total, 157 sampling stations were designed and investigated according to the long-term Korean Water Survey Program by the Government of Korea. The numbers are water depths (m).