



Short communication

Secondary grain-size effects on Li and Cs concentrations and appropriate normalization procedures for coastal sediments

Hoiso Jung ^a, Dhongil Lim ^{b, c, *}, Zhaokai Xu ^d, Kapsik Jeong ^a^a Geology and Geophysics Division, Korea Institute of Ocean Science & Technology, 787 Haean-ro, Ansan, 426-744, South Korea^b South Sea Research Institute, Korea Institute of Ocean Science & Technology, Geoje, 656-830, South Korea^c Department of Marine Environmental Sciences, University of Science and Technology, Daejeon, 305-320, South Korea^d Key Laboratory of Marine Geology and Environment, Institute of Oceanology, Chinese Academy of Sciences, Qingdao, 266071, China

ARTICLE INFO

Article history:

Received 10 December 2015

Received in revised form

11 March 2016

Accepted 28 March 2016

Available online 30 March 2016

Keywords:

Coastal sediments

Grain-size proxy

Metal concentrations

Yellow sea

ABSTRACT

The sediment grain-size effect (GSE), a fundamental factor relevant to the interpretation of elemental concentrations and isotopic compositions, has been normalized using conservative elements such as aluminum (Al), cesium (Cs), and lithium (Li) ($C_{(Al, Cs, Li)}$), which serve as proxies for the natural metal-controlling variables of grain size, mineralogy, and organic matter. However, a secondary GSE reportedly remains even after compensation by the Al-normalization procedure, particularly for the concentrations of transition metals ($C_{T.M.}$). This secondary effect also occurred in the $C_{(Li, Cs)}/C_{Al}$ ratios of the Korean coastal sediments examined in this study. The primary and secondary GSEs on Cs and Li concentrations can be explained by the quartz-dilution effect and the Cs- and Li-incorporation effect of phyllosilicate minerals, respectively, based on a model involving three component end-members: a Cs- and Li-free sand-dominated sediment component consisting mostly of quartz and feldspar, a Cs- and Li-bearing silt-dominated component of mica, and a Cs- and Li-enriched clay-dominated component of illite. Although the primary and secondary GSEs on the concentrations of transition metals (particularly Cu and Ni) in coastal sediments might be normalized by dividing the metal concentrations by the square of the Al concentration ($C_{T.M.}/(C_{Al})^2$), the GSEs can also be normalized by dividing the concentrations by the exact Cs (or Li) concentration ($C_{T.M.}/C_{Cs}$).

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Sediment grain size is a crucial consideration when interpreting sediment contamination and provenance discrimination, sediment dynamics and stratigraphy, and even ecology of benthic animals. It is a fundamental part of many sedimentological and geochemical studies on aquatic sediments (e.g., Cahoon et al., 1999; Feng et al., 2004; Lim et al., 2006; Ho et al., 2012). Sediment grain size is a primary factor constraining elemental concentrations in siliciclastic sediments (Horowitz, 1985, 1991; Herut and Sandler, 2006 and references therein), because different grain-size groups have different mineralogical compositions, resulting in different geochemical compositions. Therefore, it is necessary to normalize sediment grain size, particularly when clarifying the elemental

compositions of sediments. In general, metallic elements are concentrated in fine-grained sediments but depleted in coarse-grained sediments; consequently, significant correlations generally emerge between grain size and metal concentrations of sediments (Horowitz and Elrick, 1987; Windom et al., 1989; Jung et al., 1996; Zhang et al., 2009). Various normalization methods have been used to normalize the grain-size effect (GSE) on metal concentrations in diverse marine sediments, including Korean coastal sediments. For example, researchers have applied practical sediment grain-size separation using standard sieving, as well as theoretical calculations of metal concentrations using the concentrations of conservative elements (e.g., Al, Fe, Cs, and Li) (Oliver, 1973; Bruland et al., 1974; Loring, 1991; Song et al., 2014). Normalization methods are based on the assumption that the concentrations of conservative elements, which are also enriched in fine-grained sediments, are diluted by metal-free quartz grains that are abundant in coarse-grained sediments (the quartz-dilution effect; Kim et al., 1998). Based on the two end-member mixing concept, a linear relationship is expected between the

* Corresponding author. South Sea Research Institute, Korea Institute of Ocean Science & Technology, Geoje, 656-830, South Korea.

E-mail address: oceanlim@kiost.ac.kr (D. Lim).

concentrations of conservative and metallic elements. However, more than one linear regression line has been reported in these element pair diagrams, so pivot points between the linear relationship lines in the diagrams or an alternative origin point in the diagrams have been functionally defined without an original rationale for the nonlinearity (Herut and Sandler, 2006; Lim et al., 2006; Song et al., 2014).

Recently, Jung et al. (2014) reported the existence of a significant nonlinear, quadratic relationship between Al and metallic elements (e.g., Cu, Ni, and Sc). They concluded that this curved line is caused by the primary and the secondary GSEs on metal concentrations, which were interpreted as being caused by the physical quartz-dilution effect by metal-free coarse-grained sediments, and the chemical diagenetic effect that occurs in organic-rich fine-grained sediments, respectively. Unfortunately, however, the newly introduced concept of secondary GSE considers only the diagenetically reactive transition metals in sediments, and not alkali or alkaline earth metals such as Cs and Li. In the present study, Korean coastal sediments were evaluated to assess the secondary GSEs of the concentrations of two conservative alkali metals (Cs and Li), which are strongly recommended for use in normalizing the GSE (Loring, 1990; Aloupi and Angelidis, 2001; Roussiez et al., 2005; Song et al., 2014). Appropriate GSE normalization procedures were also explored, and are presented.

2. Materials and methods

The surface sediment sampling sites (157 in total), analytical methods, and regional settings used in this study were described previously (Jung et al., 2014). Briefly, to analyze elemental compositions, bulk sediment samples were oven-dried overnight at 60 °C and then powdered using an agate mortar. The powdered samples were dissolved by two separate methods, one involving a mixture of HF and HClO₄ and the other by fusion with LiBO₂, particularly to analyze Si. Then these two prepared solutions were analyzed to determine the concentrations of elements using ICP-ES and ICP-MS. The accuracies of the analytical methods were monitored by repeated analysis of a standard reference material (MAG-1) together with a batch of sediment samples. The relative deviations between measured and known values were generally less than 10%, indicating satisfactory recoveries for the elements in this study.

3. Results and discussion

3.1. Relationship between elemental concentrations and secondary GSE

The sediment samples were typical aluminosilicate materials (SiO₂ + Al₂O₃ ≈ 78%) supplemented with other major elements (Fe₂O₃ + K₂O + Na₂O + CaCO₃ + MgO ≈ 16%) and accessory materials (≈ 6%), exhibiting broad variation in mean grain size (Mz) ranging from -0.8 to 8.9 φ (average 5.0 ± 2.5 φ). The concentrations of all metals (C_{met}) were recalculated to compensate for the dilution effect resulting from the inclusion of metal-free materials (CaCO₃, organic materials, and/or interstitial water) and then expressed as C_{met}' in the figures (Figs. 1–3), as described in detail in Jung et al. (2014).

A clear linear relationship ($r^2 = 0.98$) emerged between the concentrations of Al and Si, except for some scattered samples (Fig. 1). The linear relationships between the concentrations of Al and alkali- and alkaline-earth metals (Li, K, Rb, Cs and Ba) were less distinct (Fig. 1): overall, Cs, Li, and Rb concentrations were positively correlated with Al concentrations and negatively correlated with Ba. Interestingly, K concentrations appeared to be scattered in

coarse-grained sediments, with less than ~7% Al, but positively correlated in fine-grained sediments, with more than ~7% Al (Fig. 1). The relatively high concentrations of K and Ba in the coarse-grained sediments, as shown in Fig. 1, may have been due to abundant feldspar grains; Cho et al. (1999) and Lim et al. (2013) previously pointed out that elevated concentrations of both of these elements in the coarse-grained sediments of Korean coastal zones could be attributed to the wide occurrence of feldspar. Thus, the concentrations of Cs, Li, and many other transition metals in coarse-grained sediments are likely diluted not only by quartz but also by feldspar minerals (particularly K-feldspar).

If we assume that sediments are a simple mixture of two end members, a metal-free component (e.g., quartz) and a metal-rich component (e.g., clay minerals enriched with Al and other metals), the intercept with the X-axis in a pair diagram between the concentrations of Al and other alkali- and alkaline-earth elements should be zero. As shown in Fig. 1, however, the X-intercepts in the pair diagrams between the concentrations of Cs (or Li) and Al are not 0% Al, but rather approximately 2% Al. The X-intercepts between the concentrations of Al and transition metals also occur at about 2–3% Al (Jung et al., 2014). These findings clearly suggest that coarse-grained sediments with less than 2% Al consist only of metal-free quartz, whereas sediments with more than 2% Al are a mixture of quartz with feldspar and other mineral grains composed of Al, Li, Cs, and other metallic elements.

Although a linear relationship is expected between the concentrations of Li and Cs and Al, the relationship between them exhibits a curved pattern rather than a linear pattern, because Li and Cs are particularly depleted or enriched in sand-dominant or clay-dominant sediments, respectively (Fig. 1). Alkali metals such as Li and Cs are major cations, together with Al, Fe, Mg, and Ti composing mica (Polubeshova and Nir, 1999; Sparks, 2003). In addition, Li and Cs are reportedly sorbed or exchanged with K ions during weathering of mica, resulting in hydrous mica (illite; Starkey, 1982; McKinley et al., 2001; Zhuang et al., 2003), which is the most abundant clay mineral (~60%) in the Yellow Sea and the northern East China Sea (Yang et al., 2003; Li et al., 2014a, 2014b). Choi et al. (2010) reported that illite in Yellow Sea sediment is the weathering product of biotite, primarily from the Huanghe River, and of muscovite from the Changjiang and Korean rivers. Therefore, the enrichment of Li and Cs in clay-dominant sediments might be due to the abundant illite in fine-grained Korean coastal sediments.

The nonlinear relationships between the concentrations of Cs and Li and Al were confirmed by the first derivative of Cs and Li by Al concentrations ($C_{(Cs, Li)}/C_{Al}$), as shown in Fig. 2. The ratios of C_{Cs}/C_{Al} and C_{Li}/C_{Al} were not constant with increasing Al concentrations but increased linearly (Fig. 2b and d), indicating that the relationships between these elements are curved rather than linear. This quadratic relationship has previously been reported between the concentrations of Al and transition metals, including Cu and Ni, in Korean coastal sediments (Jung et al., 2014); the primary and secondary GSEs were explained as a quartz dilution effect and a chemical diagenetic reprecipitation effect, respectively. Early diagenetic reactions such as organic matter degradation, oxygen consumption with remobilization of transition metals from organic complexes and/or oxide precipitates under suboxic and/or anoxic conditions, and subsequent reprecipitation of the remobilized metals in pore fluids are possible diagenetic reactions that are likely to be more active in organic-rich, fine-grained sediments. However, Cs and Li are alkali metals that are remobilized or concentrated by late diagenesis or (reverse) weathering, not by early diagenesis, and thus they are sorbed into phyllosilicate mineral lattices (Stoffyn-Egli and Mackenzie, 1984; Martin et al., 1991; Sparks, 2003; Misra and Froelich, 2012). Therefore, the secondary GSE on Cs and Li concentrations, particularly in fine-grained sediments, is likely

Download English Version:

<https://daneshyari.com/en/article/4539240>

Download Persian Version:

<https://daneshyari.com/article/4539240>

[Daneshyari.com](https://daneshyari.com)