

Silica and germanium cycling in a coastal shelf environment: Insights from northern Gulf of Mexico

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The Ge/Si ratio recorded in sedimentary opal covaries with glacial-interglacial cycles as far back as the Mid-Miocene [1], demonstrating its potential as a proxy for Si cycling. However, there are multiple mechanisms potentially influencing the Ge/Si recorded. These include the intensity of terrestrial rock weathering, variations in the size of the diagenetic Ge sink, and biological fractionation by marine silicifiers.

We have measured Ge and Si concentrations in the water column and sediment pore waters in the Gulf of Mexico (GOM). Results indicate extensive fractionation, enriching the shelf surface water Ge/Si to 2.3 (all Ge/Si ratios are in $\mu\text{mol/mol}$), significantly higher than the main Si source - the Mississippi River (Ge/Si = 1.5). Preliminary box model calculations predict a fractionation factor of $R_{\text{biogenic silica}}/R_{\text{water}} = 0.5-0.6$, where R is Ge/Si ratio. GOM deep water (500-2100 m Ge/Si = 0.82-0.86) is also enriched relative to the published global ocean values (Ge/Si = 0.70-0.76). Porewater observations in coastal sediments (Ge/Si = 0.3-0.7) and modelling suggest that 10-30% of Ge is diagenetically sequestered into an unidentified (possibly iron-rich) authigenic precipitate.

[1] Shemesh *et al.* (1989) *Paleoceanography*, **4**(3), 221–234.

Ferrian chromite formation in podiform chromitites from south-central Chile

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The metamorphic basement of the Coastal Cordillera in south-central Chile comprises two units with contrasting characteristics. The Eastern series is characterized by high T/low P conditions, whereas the Western Series represent high P/low T metamorphic conditions [1]. These units have been interpreted as an accretionary prism, where the Eastern series formed by frontal accretion and the Western series was produced by basal accretion [2]. The Western series comprises mainly metapsammopelitic rocks, metabasites and minor serpentized ultramafic rocks. The serpentinite bodies are scattered within the Western series and show variable degrees of serpentization. Although most of these serpentinites have accessory chromian spinels, only in one locality podiform chromitites have been found. Here we present the chemical composition of these chromitites determined using electron microprobe analysis (EMPA) in order to provide some insights on the formation of ferritchromite as an alteration product of chromite.

Chromitites are highly brecciated with a matrix completely altered to Cr-rich chlorite. Chromite spinel grain cores are high-Al in content, whereas ferrian chromite (i.e., ferritchromite) is Fe^{+3} rich and usually formed along cracks and margins. The observed pattern of alteration is similar to that described for other locations [3] with volume reduction associated with dissolution of chromite and formation of porous chromite. Unaltered chromite cores show Cr# [Cr/(Cr + Al) atomic ratio] = 0.65–0.70, Mg# [Mg/(Mg + Fe^{+2}) atomic ratio] = 0.50–0.70, and $\text{Fe}^{+3}/(\text{Fe}^{+3} + \text{Fe}^{+2}) < 0.15$. The chemical composition of chromites evolved towards higher #Cr (0.75–0.95), lower #Mg (0.40–0.10), and higher #Fe (0.20–0.40). The observed trend is consistent with a reaction of chromite with olivine to produce chlorite. The alteration process is concomitant with mass loss and development of a porous texture in chromite.

[1] Aguirre *et al.* (1972) *Kristalinikum* **9**, 7–19. [2] Willner *et al.* (2005) *J Petrology* **46**, 1835–1858. [3] Gervilla *et al.* (2012) *Contrib Mineral Petrol* **164**, 643–657.