Seasonal variations in the chromium isotopic composition of seawater in the Celtic Sea

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Recent studies have shown that the chromium (Cr) isotopic composition of seawater is variable, with $\delta^{53/52}$Cr values ranging from 0.4 to 1.6‰ [1, 2]. Although rivers are the principal source of Cr to the oceans, these values are considerably higher than continental crust (0.12±0.10‰; [3]). This has been attributed to fractionation of Cr isotopes during oxidative weathering, and it has been asserted that relatively high $\delta^{53/52}$Cr values in banded iron formations are indicative of elevated atmospheric and surface ocean oxygenation before the Great Oxidation Event [4].

The processes that cause the variations in seawater $\delta^{53/52}$Cr are, however, as yet poorly understood. Studies of Cr speciation indicate that Cr oxidation state can vary substantially over the seasonal cycle, with strong positive correlations between Cr(III):Cr(VI) and both bacterial biomass and primary productivity [5]. To assess the potential importance of these redox transformations on the Cr isotopic composition of seawater, we have determined Cr concentration and $\delta^{53/52}$Cr for a suite of seawater samples collected over the course of a seasonal cycle from the Celtic Sea as part of the UK Shelf Seas Biogeochemistry Program. Preliminary results for the winter months (December and March) indicate that Cr concentrations range between 2.2 and 2.6 nM. A speciation study for March indicates that 3-54% of this is present as Cr(III). $\delta^{53/52}$Cr values are generally within the range of those reported for other coastal and shelf environments (1.0 - 1.2‰), although one sample taken from 25 m water depth has a value of 2.1‰. We will also present data for the same sites for April and July, revealing the extent of seasonal variations in seawater $\delta^{53/52}$Cr for the first time.

[1] Bonnand*, et al.* (2013), *Earth. Planet. Sci. Lett.* **382**, 10-20. [2] Scheiderich*, et al.* (2015), *Earth. Planet. Sci. Lett.* **423**, 87-97. [3] Schoenberg*, et al.* (2008), *Chem. Geol.* **249**, 294-306. [4] Frei*, et al.* (2009), *Nature* **461**, 250-253. [5] Connelly*, et al.* (2006), *Deep Sea Res.* **53**, 1975-1988.