

Advances in the study of Mg from living coccolithophores and echinoderms carbonate: new optimizations, applications, and trends at high $p\text{CO}_2$ Mario Lebrato¹, Sonia Blanco-Ameijeiras², Heather M. Stoll³, Ana Mendez-Vicente³, Debora Iglesias-Rodriguez², Andreas Oschlies¹, Marius N. Müller⁴, Scarlett Sett¹, Kai G. Schulz¹¹ IFM-GEOMAR. Kiel, Germany² National Oceanography Centre, Southampton. University of Southampton, Southampton, UK³ University of Oviedo. Department of Geology, Oviedo, Asturias, Spain⁴ Laboratoire Oceanographique de Villefranche-sur-mer (LOV). CNRS-UPMC. Villefranche-sur-mer Cedex, France

Coccolithophore calcification has been extensively studied in the past decades: from the molecular basis to the global scale role of carbonates in models and the responses at the ecophysiological level in a high CO_2 world. Coccolithophores are also used in paleoceanography studies of productivity (Sr:Ca ratio), palaeothermometry (through the Sr:Ca, alkenone biomarkers and possibly with the Mg:Ca ratio), and are involved in studies of reconstructing past CO_2 conditions (alkenones). However, the easier handle of foraminifera e.g. in terms of size and cleaning protocols has fostered an extensive use of this taxa instead of coccolithophores (echinoderm calcites have also been used owing to their easy handling). Ironically, the poor use made from coccoliths is a consequence of the Mg present in organic forms in the calcite (mainly from the chlorophyll isocyclic ring and the bound to organic molecules of ATP and ADP among others), which contaminates measurements from the inorganic Mg fraction. We investigated in detail the intraspecific variability in physiological and biogeochemical properties of the cosmopolitan coccolithophore *Emiliana huxleyi* by using 13 strains isolated from contrasting ocean basins and latitudes in semicontinuous cultures at constant conditions of temperature, irradiance, salinity, nutrients and water carbonate system. For each *E. huxleyi* strain and also for 1 strain of *Calcidiscus leptoporus* and *Gephyrocapsa oceanica* we present calcification (CaCO_3 production alone), MgCO_3 (production combining CaCO_3 and Mg:Ca), PIC:POC, Mg:Ca and Sr:Ca data. We optimized several organic Mg cleaning protocols by deliberately contaminating pure powder CaCO_3 samples with *Chlorella autotrophica* grown in the laboratory and then recovering the known Mg:Ca from the pure calcite with a 99% success in one of the protocols (oxidation-reduction-rinsing). The Mg:Ca data from the 15 strains used (all) indicates that rather than the protocols *per se* avoiding accurate Mg:Ca determinations, it is the PIC:POC ratio and especially the amount of POC present per sample the cause of the contamination. To assess contamination we used phosphorus (P:Ca), iron (Fe:Ca), and sodium (Na:Ca) as indicators. By making use of the EPOCA database we compared our results with another 10 strains from *E. huxleyi* (some overlap with our strains), and we conclude that the range of calcification (0 to 15 $\text{pg C cell}^{-1} \text{d}^{-1}$) and PIC:POC (0 to 1) found within the concept of species at similar culturing conditions could cause misunderstanding in the responses at high $p\text{CO}_2$ if considering wild populations (strains mixed). We finally present results on the Mg:Ca and Sr:Ca trend in *G. oceanica* calcites in a gradient of $p\text{CO}_2$ using artificial seawater from pre-industrial to future scenarios, showing linear trends, which open new questions into the use of the elemental ratios in biogeochemical studies.