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Evolution of the thermal properties of ocean aqueous solutions from Archean chemical compositions to modern seawaters

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Introduction

Chemical composition of Earth seawater has changed with time. Despite the uncertainties, there is an agreement that the first seawaters formed on Earth were in balance with a primitive atmosphere rich in carbon dioxide (CO_2). They were anoxic, poor in sulfate, and with a concentration in bicarbonate (HCO_3^-) higher than calcium (Ca^{2+}), resulting in an alkaline brine where the precipitation of carbonate minerals such as nahcolite and trona was propitious. Later, the decrease in temperature favored the continental crust formation and the weathering of the CO_2, probably causing the acidification of the ocean to a neutral state. The following "Great Oxidation Event" introduced the oxygen (O_2) to the environment and subsequently sulfate (SO_4^{2-}) concentration started to increase from around 10 m in the Silurian to 29 m nowadays. The ratio HCO_3-/Ca^{2+} inverted, promoting the precipitation of gypsum instead of carbonates. Attending to the Mg/Ca ratio from the Phanerozoic, it has occurred a periodically exchange between brines rich in Ca and brines rich in Mg, for instance, this ratio was around 1.5 at Silurian times while currently it has a mean value of 5.2 [1,2 and references therein].

With these premises, the goal of this study is to determine the effect on the thermal properties of the solutions of: A) The balance between CO_2 and CO_3^{2-} dissolved according to the temperature and pressure, B) The addition of SO_4^{2-} ion, and the increase in its concentration, C) The change in the Mg/Ca ratio.

Changes in the thermal properties of the seawater affect the interaction among the atmosphere-crust-ocean and, consequently, the cycles of energy and some elements and the habitability conditions during the planet's history. In some cases, data can be applied to other planetary oceans.

Experimental Procedure

Starting from an aqueous solution simulant of modern seawater chemical composition, we prepare series of solutions with decreasing $MgSO_4$ concentration while keeping the other salt concentration constant (KCl, NaCl, $CaCl_2$). In these series we study the influence of points B and C at 1 bar. For point A, we change $MgSO_4$ by $MgCO_3$, and perform a second series of runs with the alkaline solution mineral concentrations constant but adding CO_2(g) at pressures up to 1000 bar.

The high pressure µDSC7 evo calorimeter (SETARAM Instrumentation, France) allows the direct determination of the specific heat (Cp) in a temperature range from 228 to 293 K.

Objective A is complemented with Raman spectroscopy under high pressure. The setup composed by the iHR550 Raman spectrometer (Horiba JobinYvon, France) coupled to a homemade high-pressure cell that has been already shown and validated for the kind of study proposed in previous works [3-5].

Results

Specific heat and thermal conductivity data of present composition seawater at different salinities, and under wide range of temperature and pressure is available in the literature for comparison [6, 7 and references therein].

As an example, we show in Figure 1 three tests performed for the calculation of Cp in pure H_2O, NaCl eutectic composition aqueous solution (23.3 wt% NaCl, melting point 252 K) and $MgSO_4$ eutectic composition aqueous solution (17.0 wt% $MgSO_4$, melting point 269 K), before and after melting. Cp varies with temperature and suffers dramatic shifts when there is a physical change of the sample. The data obtained in previous works [8] for NaCl solution at 24 wt% is added to the plot to demonstrate the validation of the calorimeter.

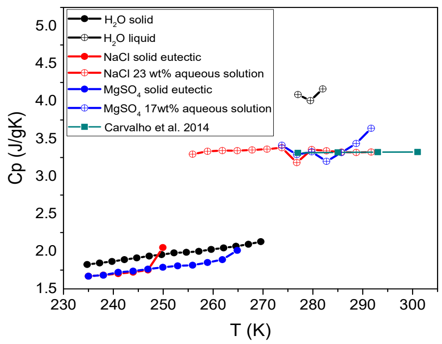

Figure 1. Cp vs. T for H_2O, NaCl and $MgSO_4$ solutions.

Acknowledgements

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