

## ***Interactive comment on “Seasonal pH and aragonite saturation horizons in the Gulf of Alaska during the North Pacific Survey, 1956–1957” by S. McKinnell and J. R. Christian***

### **Anonymous Referee #2**

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Anonymous Referee Comments on: “Seasonal pH and aragonite saturation horizons in the Gulf of Alaska during the North Pacific Survey, 1956–1957” by S. McKinnell and J. R. Christian, *Biogeosciences Discuss.*, 6, 4587–4602, 2009 [www.biogeosciences-discuss.net/6/4587/2009](http://www.biogeosciences-discuss.net/6/4587/2009).

### General Comments

McKinnell and Christian utilized an extensive data set of pH measurements collected by the Pacific Oceanographic Group of the Fisheries Research Board of Canada in the Gulf of Alaska collected in summer of 1956 and winter of 1957 to estimate aragonite saturation levels in the subarctic North Pacific in summer and winter. Using a number of

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assumptions and calculations based on this data set they suggested that the aragonite saturation estimates indicated that undersaturated water was a common feature of the surface mixed layer north of 51° N latitude in the winter of 1957. The North Pacific Survey data were compared with the results of a summer 2007 survey of the west coast of North America where pH levels were ~0.1 pH units lower than was found in the summer of 1956. The authors made a number of assumptions in making these calculations that, in some instances, are contradicted by the recent scientific literature. Furthermore, the authors chose to ignore much of the previous research studies on carbonate saturation in the North Pacific, which do not appear to support their findings. I recommend that the manuscript be returned to the authors for major revisions (see specific comments below).

### Specific Comments

Page 4591. What is the accuracy of the pH measurements and how was it determined? How did the authors deal with the potential biases caused by the changes in liquid junction potential that occurs when standards of one ionic strength are compared with seawater samples of a significantly different ionic strength? What is the alkalinity-salinity relationship and what are the uncertainties associated with this estimate? What are the major uncertainties in the aragonite saturation calculations and how were they determined? Does the precision in the 1956-57 pH data contribute to the uncertainty in the aragonite saturation calculation? If so, how much? Are there any biases between the 1956-57 datasets relative to the recent data?

Pages 4591-92. The author's aragonite saturation calculations are based on the assumption that alkalinity does not change over time due to anthropogenic CO<sub>2</sub> uptake and carbonate mineral dissolution. This assumption is made despite the fact that the uptake of anthropogenic CO<sub>2</sub> is decreasing the saturation state to values below 1.0 in subsurface waters and also in surface waters in wintertime north of 51° N! The authors do not make reference to the work of Sarma et al (2002) that showed that aragonite saturation horizon (ASH) shoaled significantly by 25 to 155 m in the North Pacific over

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the last two decades. Over the same time interval, DIC increased from 12.5 to 36.8  $\mu\text{mol kg}^{-1}$  in the vicinity of ASH in the Pacific and total alkalinity increased significantly by 5 to 10  $\mu\text{mol kg}^{-1}$  in the Pacific at the ASH, most likely as a result of aragonite dissolution. The authors need to address these results that contradict their fundamental assumption.

Page 4593. The authors state that their profiles of aragonite saturation as a function of depth indicate widespread undersaturation in the Gulf of Alaska in wintertime, especially in the north where median values of aragonite saturation state were  $<1$  at all depths. Furthermore, their data suggest that the upper layer was supersaturated in summer in both the northern and southern Gulf of Alaska. Why are these results so different from the 1985 results published in Feely et al (1988) for the same region? Feely et al (1988) show that the surface waters were supersaturated with respect to both aragonite and calcite in both winter and summer to depths greater than 100 m? Feely et al (1988) go on to suggest that surface water  $\text{pCO}_2$  values in excess of 650  $\mu\text{atm}$  are required before undersaturation with respect to aragonite will be achieved. Did the authors calculate surface water  $\text{pCO}_2$  values for their 1956-57 data set? Is that consistent with wintertime  $\text{pCO}_2$  values for the region based on their work and other results for the Gulf of Alaska in winter?

Page 4593. Discussion. The authors state that "Few surveys of carbonate parameters have been made in the Gulf of Alaska which limits our understanding of its state and rate of change." Is it not appropriate then for the authors to compare their results with the "few" previous studies that have addressed this problem for this region of the North Pacific? Why were the Feely et al., 1982, 1984, 1988; Chen et al., 1988 papers not discussed in this paper?

Page 4594. The authors state that "Along the North American upwelling region, Feely et al. (2008) found  $\text{Oarag} < 1$  at pH 7.75 in waters with potential densities of 26.2 at relatively shallow depths (40–120 m). In the winter of 1957, this combination of pH and potential density was found near the surface ( $<30$  m) in the northwestern Gulf

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of Alaska. At depths below 30 m, a pH of 7.75 on this potential density layer was characteristic of winter pH with average values of 7.65 (Fig. 4). In the summer of 1956, 42 of 44 pH values were  $>7.75$  on this density layer. Considering only the samples collected south of 51 N in summer, the minimum pH observed on the 26.15–26.25 layer at all stations was 7.83 ( $n=23$ , mean pH=8.00; mean depth of layer=136 m). These results suggest that the pH measured on samples taken in July 2007 would have been observed very rarely, if at all, during the summer of 1956." If the water that is upwelled along the coast of North America does not come from the same source as the water on the same density surface in the Gulf of Alaska, I am not sure that this comparison is valid. I would think that the two water masses with different sources could have distinctly different pH, DIC and TA values before even considering the anthropogenic  $\text{CO}_2$  additions over time.

Figure 6 and in the text. What are the uncertainties of the aragonite saturation estimates calculated by the procedures employed in this paper?

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