**Biogeosciences
Discussions**

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

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Anonymous Referee #1 (Referee comments in bold)

(1) It is appropriate to spend a significant amount of time discussing the pH scales used, but that is not the only potential problem with data like this. The pH measurements were almost certainly made using a glass electrode although this is never actually acknowledged in the paper. Glass electrodes have liquid junction potentials that effect accuracy because the ionic strength of the buffers used is different than seawater. This causes a significant accuracy error that should have at least been acknowledged here.

Yes the measurements were made using a glass electrode. The reviewer is correct that there is a potential error here. After considering this and other reviewer comments carefully, we have attempted to make a correction for this error. The referees raised questions about the pH data, about the alkalinity estimates (from regression on T and S using modern data), and about the improbably low carbonate ion concentrations derived from these (aragonite undersaturation in surface waters in winter). We examined both the alkalinity regression and the pH data in hope of identifying the reasons why the [CO3–] concentrations were so low, and concluded that the problem was largely in the pH, not the TA. By comparing to modern data at depths where we expect relatively little pH change due to anthropogenic carbon, we found that there was a significant offset: the mean pH was almost 0.2 units lower in the depth interval from 1000-2000 m in the older data. We applied the mean difference from contemporary values as a correction to the old pH data across the board. We really should have done this prior to the initial submission and thank the reviewers for their diligence in identifying the problem.

(2) Another serious problem with the saturation calculations is the estimation of the alkalinity using the salinity-temperature regressions. (What regression was used?) If you take a look at alkalinity data from the North Pacific published by Wong et al in this decade you do not see nice trends with salinity in surface waters, presumably because it is an area of CaCO3 formation. Thus, extrapolating a trend from this area today to 50 years ago could easily be very wrong, depending on the extent of CaCO3 formation in the surface waters at these two times.

Salinity-normalized alkalinity is not constant, especially in high latitude waters. Note that this is not simply a regression on salinity but on both salinity and temperature, although the temperature provides relatively little additional information. We used all of the information available in the early data to make the best possible estimate of another of the "four pillars" (alkalinity in this case being the only conceivable candidate). This approach does not require us to assume that calcification and calcite dissolution

are negligible, only that the rates of these processes, relative to other hydrographic and ecosystem processes, are stationary over time. This assumption is not particularly robust, but it is the best we can do with the data available. As noted above, we looked carefully at the alkalinity estimates as a possible source of the improbable results derived, and found that errors of this sort were not a very plausible explanation.

The alkalinity regression was derived using data from the Line P program collected by Dr. C.S. Wong over the period 1985-2001. These data are not yet in the public domain but have been submitted to CDIAC as part of a North Pacific data synthesis effort coordinated by PICES and will be opened when this process is completed (`http://pices.int/publications/annual_reports/Ann_Rpt_07/2007%20CC-S_f.pdf`). Initial quality control has been performed on these data and only data flagged as 'good' were used here. In the revised MS we will provide more detail e.g., depth range, the actual regression equation.

(3) Finally, I am not sure of the usefulness of comparing data at sigma theta 26.2 in near surface waters of the subarctic pacific with similar data on this density horizon along the coast of North America. What is the surface origin of waters that upwell on the coast? How different is the history of waters from these two regions? It is likely that the respiration history of these two waters is different, which would make their carbonate ion concentrations different - even without the effects of anthropogenic CO2. In spite of these criticisms, I find this paper very interesting for the historical content and for the insight it brings to the carbonate chemistry of the region around one of the world's most important time series locations.

This is a good point that will be given careful consideration in revision, perhaps refocusing more closely on comparisons with contemporary data beyond the shelf where the 1950s data were collected.

<center>C1375</center>

Anonymous Referee #2

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?

After considering this comment and those of the other reviewers, we looked for biases relative to modern data at depths where we expect relatively little pH change due to anthropogenic carbon. We found that there was significant offset: the mean pH was almost 0.2 units lower in the depth interval from 1000-2000 m in the older data. We also examined carefully the possibility that bias in the alkalinity estimates could have resulted in the improbable results obtained, and found that bias in the pH was a more likely explanation. We therefore applied a correction to the pH based on the difference in means for the 1000-2000 m depth interval. We really should have done this prior to the initial submission and thank the reviewers for their diligence in identifying the problem. The aragonite saturation and carbon chemistry calculations use well-established methods. If the result is in error it results from error in the pH data or the alkalinity estimates, not the subsequent calculations

The author's aragonite saturation calculations are based on the assumption that alkalinity does not change over time due to anthropogenic CO2 uptake and carbonate mineral dissolution. This assumption is made despite the fact that the uptake of anthropogenic CO2 is decreasing the saturation state to values below 1.0 in subsurface waters and also in surface waters in wintertime north of 51 N!

<center>C1376</center>

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 C511 the last two decades. Over the same time interval, DIC increased from 12.5 to 36.8 μmol kg-1 in the vicinity of ASH in the Pacific and total alkalinity increased significantly by 5 to 10 μmol 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.

We are familiar with the work of Sarma and agree that calcite dissolution due to anthropogenic CO2 is a potential source of error in our calculations. However, we do believe that it is a large one. The regression equation includes data from the surface to 500 m depth, and the inputs of alkalinity from aragonite dissolution described by Sarma occur over a much more limited depth range. If this depth were at one or the other end of our range this might be a serious problem, but it is not. The reviewer is correct that the alkalinity regression depends on several unverifiable assumptions, but it is the only option. We need to estimate another of the "four pillars" and DIC is obviously out of the question. There are several possible biases arising from this approach that have been identified by the reviewers, and these are detailed in the revised manuscript.

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 pCO2 values in excess of 650 uatm are required before undersaturation with respect to aragonite will be achieved.

The near-surface undersaturation is now much less as a result of the correction applied to the pH data. We agree that some very important earlier work on carbon in the GoA was overlooked, and thank the reviewer for pointing this out. The data shown in Feely et al 1988 show that the ASH is barely more than 100 m deep at latitudes north of 50 degrees (their Figure 3a), and note that "the first instance of undersaturation should occur in subarctic waters in wintertime when surface temperatures are coldest and pCO_2 concentrations are enriched from respiration and upwelling" (p. 239). We are not suggesting that undersaturation actually began in the 1950s, but the differences between their data and ours are not that great. In the revised calculation we still get some undersaturated points near the surface, but most of our data for the upper 100 m are supersaturated. A linear or polynomial regression fit to the rather noisy data actually estimates the ASH to be more than 200 m, although visual inspection clearly indicates that undersaturation starts to become common below 100 m. If the ASH is only around 100 m depth we wonder if it is that implausible that surface water undersaturation could occasionally be observed in winter. This region of the ocean has unusually small winter mixing depths for its latitude, but winter mixed layers in excess of 100 m do occur, and research ships are rarely present in winter. A review of 669 winter density profiles from Project Argo data indicates that mixed layer depths ($>$ 100m) appeared in the Gulf of Alaska ($>$=51˚N, -160 to -135˚W) about 20% of the January profiles, 30% in the February profiles, and 40% in March profiles, from 2003-2008 inclusive. In this case MLD was determined as the depth of a density difference exceeding 0.0125.

Did the authors calculate surface water pCO2 values for their 1956-57 data set? Is that consistent with wintertime pCO2 values for the region based on their work and other results for the Gulf of Alaska in winter?

This is an excellent suggestion, and confirms the necessity of the correction applied to the pH data. With the correction, pCO_2 is a bit too high ($\sim$420 μatm), but without the correction it is much higher ($>$600).

Interactive comment on Biogeosciences Discuss., 6, 4587, 2009.

C1379