1. Introduction
   1. Current decrease average 0.1 pH units in ocean due to uptake of anthropogenic C, predicted to be 0.14-0.35 units over 21st century on different scenarios (IPCC 2007)
   2. No evidence that the ocean pH was more than 0.6 units less than today’s over past 300 million years with projected max ocean surface reduction of 0.77 by 2300 (Caldeira & Wickett 2003)
   3. When changes in CO2 occur on the timescale of < 10^4 years, ocean pH is sensitive; if occurs >10^5 years changes can be buffered through interactions with carbonate minerals (Caldeira & Wickett 2003)
   4. Resilience of many ecosystems likely to be exceeded in the 21st century due to climate change, its associated disturbances, and global change drivers (land-use, pollution, habitat fragmentation, increased resource use) (IPCC 2007)
2. Basic Chemical reactions of OA – What are the characteristics of OA caused by increased CO2
   1. Anthropogenic CO2 in ocean increases [CO2] and DIC but not charge balance and TA (Schulz et al. 2009)
      1. Increase [HCO3] and [H+]
      2. Decrease [CO3] and Ω calcite and aragonite
   2. All IPCC emissions scenarios lead to Ω aragonite undersaturation in the surface Southern Ocean by 2100 and global pH decrease from 0.3-0.5 units (Caldeira and Wickett 2005).
   3. As dissolved CO2 increases, additional CO2 reacts with CO3 to make more HCO3, yielding more CO2 and HCO3 and less CO3 (Dickson in Riebesell et al. 2010)
   4. Information needed for composition of CO2 in seawater: salinity, T, and 2 of DIC, TA, pH, or pCO2 (Dickson in Riebesell et al. 2010)
   5. Best choice of parameters: pH using the spec and total DIC using infrared – allow description of CO2 systems alone without other coexisting acid-base systems (Dickson in Riebesell et al. 2010)
3. Evidence of Anthropogenic OA
   1. Global greenhouse gas emissions have increased since pre-industrial, up 70% 1970-2004 (IPCC 2007)
      1. CO2 is the majority of GHG and amounts have been increasing even more rapidly the past couple of decades
   2. Global atmospheric concentrations of CO2, CH4, N2O are now much greater than ice core values from 1000s of years – mostly fossil fuel use then land-use change for CO2 increase (IPCC 2007)
   3. Evidence of human-mediated pH change at surface-150 m in North Pacific; upper OA is proportional to anthropogenic increase in atmospheric CO2 (Byrne et al. 2010)
   4. Highest [CO2] is in near-surface waters (Sabine et al. 2004)
   5. Expect ocean pH to fall at an accelerating rate if atm CO2 continues to rise (Byrne et al. 2010)
   6. If ocean surface pCO2 continues to increase proportionally to atmospheric CO2, then at 2x atm CO2 (based on preindustrial levels) there will be a 30% decrease in [CO3] and 60% increase in [H+]; as [CO3] decreases so does the ocean’s ability to absorb more CO2 (Sabine et al. 2004)
   7. Shoaling of aragonite and calcite saturation horizons in the Atlantic through Indian and Pacific oceans due to higher DIC:TA in intermediate to deep water of the Indian and Pacific relative to Atlantic caused by enrichment of DIC (Feely et al. 2004)
   8. Shallow depth undersaturation with respect to aragonite in all 3 oceans from anthropogenic CO2 (Feely et al. 2004)
4. Dissolved Inorganic Carbon
   1. DIC = [CO2 (aq)] + [HCO3] + [CO3]
      1. Measure by acidifying sample, extract and measure unionized CO2 (Dickson in Riebesell et al. 2010)
   2. Changing DIC at constant TA (Gattuso et al. in Riebesell et al. 2010)
      1. Aeration at target pCO2
         1. pH-stat: pH monitored continuously, controller opens/closes valves of gas delivery of, pH threshold measured by pCO2 and TA and allows compensation for changes in carbonate chemistry from photosynthesis or respiration but difficult for system to reach equilibrium with high biological activity
            1. air + pure CO2
            2. CO2-free air + pure CO2: CO2-free air from molecular sieves or CO2 scrubbers
            3. Air, CO2-free air, pure CO2
         2. bubbling with premixed gases
      2. Addition of high-CO2 seawater
         1. DIC and TA are conservative: mixed water = sum of amounts in 2 water sources
      3. Addition of strong acid and CO3 and/or HCO3
         1. CO3 and HCO3 elevate DIC and acid balances change in TA – mimics changes from CO2
   3. Addition of CO3 and/or HCO3 (Gattuso et al. in Riebesell et al. 2010)
      1. DIC and TA increased by adding N2CO3 (CO3) or NaHCO3
      2. Changes in DIC depend on changes in [ion]
      3. Changes in TA depend on changes in charge x [ion]
   4. Samples poisoned for storage (Dickson et al. 2007)
   5. CO2 extraction from seawater: water reacted with phosphoric acid in borosilicate glass stripping chamber. Stripped of CO2 gas (Dickson et al. 2007)
   6. Coulometry is the use of electricity to convert all of a chemical species to a different chemical state. For total CO2, CO2 is converted to a weak acid (hydroxyethylcarbamic): 2CO2 + 2NH2(CH2)2OH -> 2HO(CH2)2NHCOOH. OH- ions (strong base) are electrogenerated by the reduction of H2O and used to titrate the weak acid. The equivalence point is detected photometrically with the indicator dye thymolphthalein, which turns to blue from colorless. (Johnson et al. 1985)
   7. DIC = ((Ns-b\*t-a)/c)\*(1/(Vs\*ρ)) (Dickson et al. 2007)
      1. Ns = coulometer reading for the sea water sample
      2. A = acid blank
      3. B = background level of the system
      4. C= coulometer calibration factor
      5. T=time required to measure water sample
      6. Vs=volume of sea water sample at temp of use
      7. Ρ=density of sea water sample
   8. Estimation of changes in DIC from anthropogenic sources (Byrne et al. 2010)
   9. To calculate contribution of anthropogenic CO2 to the ocean, need: (Gruber et al. 1996)
      1. Ocean sample total C, alkalinity, dissolved O2, T, and salinity
      2. Water age
      3. History of atmospheric CO2 levels
   10. To separate anthropogenic CO2 from natural background variability need to eliminate contributions from (Gruber et al. 1996)
       1. soft-tissue pump (photosynthesis, respiration, biomineralization) by eliminating C proportional to O2 used
       2. carbonate pump using alkalinity distribution corrected for nitrate cycling
       3. then correct for O2 saturation concentration, alkalinity, pre-industrial [C], and water age/depth
   11. Certified reference materials for DIC and TA, pH, and f(CO2) (Dickson et al. 2007)
5. Total Alkalinity
   1. TA = number of moles of H+ equivalent to the excess of proton acceptors over proton donors in 1 kg of sample (Dickson et al. 2007)
   2. TA = [HCO3] + 2[CO3] + [B(OH)4-] + [OH0 + [HPO42-] + 2[PO4-3] + [H3SiO4-] + [NH3] + [HS-] – [H3PO4] – [H+]free – [HSO4-] – [HF] (Schulz et al. 2009)
   3. TA = [HCO3] + 2[CO3] + [B(OH)4] + [OH] – [H+]
      1. Measure by acidimetric titration (Dickson in Riebesell et al. 2010)
   4. Seawater contains a number of acid-base species (aside from CO2, boric acid and water) that are mostly derived from minor nutrients and contribute to TA. They are mostly in deep water, but can be upwelled. These nutrients are of concern in the lab and mean that may not be able to reliably determine the contribution of CO2 to TA (Dickson in Riebesell et al. 2010)
   5. Changing TA but not DIC: addition of strong acids & bases; acid decreases TA, base increases TA (Gattuso et al. in Riebesell et al. 2010)
   6. Decreased TA causes increased seawater CO2 (Schulz et al. 2009)
      1. Important for comparisons with changes in DIC
      2. At high CO2 less [HCO3] is important, but at low CO2 more [CO3] is important
   7. Closed cell titration allows assumption that DIC remains constant (Dickson et al. 2007)
   8. Open cell titration: 2-stage, seawater acidified to 3.5-4 and stirred to allow escape of CO2 then to pH 3. Allows assumption that total DIC is ~0 from pH 3-3.5 (Dickson et al. 2007)
   9. Titration progress monitored with an electrode (Dickson et al. 2007)
   10. Pontentiometric titration = HCl titration with pH determined equivalence point. HCl is added past carbonic acid endpoint – add enough acid to change voltage to a preassigned increment. The HCl solutions are made to have the same ionic strength as seawater. TA is determined from proton balance at the alkalinity equivalence point. For equation in a, substitute for TA = (V0\*TA – V\*N)/(V0+N) where V0 = initial volume of sample, N = normality of acid titrant, V = volume of acid added). Computer program to calculate assuming nutrients are negligible, which only works for surface waters. (Millero et al. 1993)
6. pH
   1. pH = -log[H+]
      1. measure with electrode or spectrophotometer with indicator dye (Dickson in Riebesell et al. 2010)
   2. glass/reference electrode cell (Dickson et al. 2007)
      1. total [H+] in seawater includes contribution from sulfate ion: [H+] ~ [H+]f + [HSO4-]
      2. standard buffers in synthetic seawater (same T as sample)
   3. spectrophotometric method (Clayton & Byrne 1993) uses molecular properties of pH indicator meta-cresol purple (Byrne et al. 2010)
      1. small amount of dye added to each sample and absorbance measured at 434 and 578 nm and at a non-absorbing wavelength against reference of pure seawater (wavelengths correspond to absorption maxima of acid HI- and base I2- forms, respectively, Dickson et al. 2007)
      2. pH is calculated from absorbance ratios
   4. indicator dye: dye is an acid-base compound; the spectrophotometer depends on acid and base forms having substantially difference absorbance spectra (Dickson et al. 2007)
      1. pH=pK(HI-) + log[I2-]/[HI-]
      2. double-beam spectrophotometer
      3. 0.05-0.1 mL dye to produce absorbance peaks between 0.4 and 1.0
      4. also measure at non-absorbing wavelength 730 nm
      5. pH calculated based on absorbances for each wavelength, extinction coefficients, equ’m constant function of salinity and T for m-cresol purple
      6. correct for addition of acid-base dye
7. pCO2
   1. pCO2 = x(CO2)p
      1. x(CO2) = mol fraction of CO2 in air
      2. p = total pressure
      3. direct measure of air, estimate fugacity (Dickson et al. 2007)
   2. pCO2 in a discrete sample of sea water: known amount of seawater and known volume of air (with known initial amount of CO2) in a closed system at constant T and pressure – water and air reach equilibrium sample of air analyzed for CO2 using gas chromatograph or infrared CO2 detector. Then used to calculate pCO2 (Dickson et al. 2007)
      1. 250-2000 ppm
      2. temperature important
      3. calibrate with 3 calibration gases of well-known CO2 concentrations that span range of measured values
      4. samples must be collected and poisoned
   3. pCO2 in air in equ’m with continuous stream of seawater: suitable for 250-550 ppm; fixed volume air equilibrated with stream of seawater that goes through the equilibrator, CO2 content of air will adjust to be in equ’m with flowing seawater; air is sent through a non-dispersive infra-red analyzer to measure CO2 (analyzer calibrated); this measures fCO2 (Dickson et al. 2007)
      1. fCO2 = fugacity of carbon dioxide in gas phase, not pCO2 – non-ideal nature of gas phase
      2. fugacity coefficient = ratio of fugacity to partial pressure, function of T and gas phase composition
8. Calcite and aragonite saturation
   1. Aragonite and calcite are polymorphs of CaCO3 with aragonite 1.5x more soluble than calcite at 25C. Magnesian calcite has Mg randomly substituted for Ca and is solubility between arag and calc (Dickson in Riebesell et al. 2010)
   2. Ω depends on T, salinity , and pressure (Feely et al. 2004)
      1. Ω = [Ca][CO3]/Ksp, where [Ca] is estimated from salinity and [CO3] is calculated from DIC and TA
   3. [CO3] is the main driver for changes in Ω (Feely et al. 2004)
   4. calculated from DIC and TA using CO2SYS developed by Lewis and Wallace 1998, using Mehrbach et al. 1973 carbonate constants that had been refit by Dickson and Millero 1987 (Feely et al. 2010)