# Brewing Water

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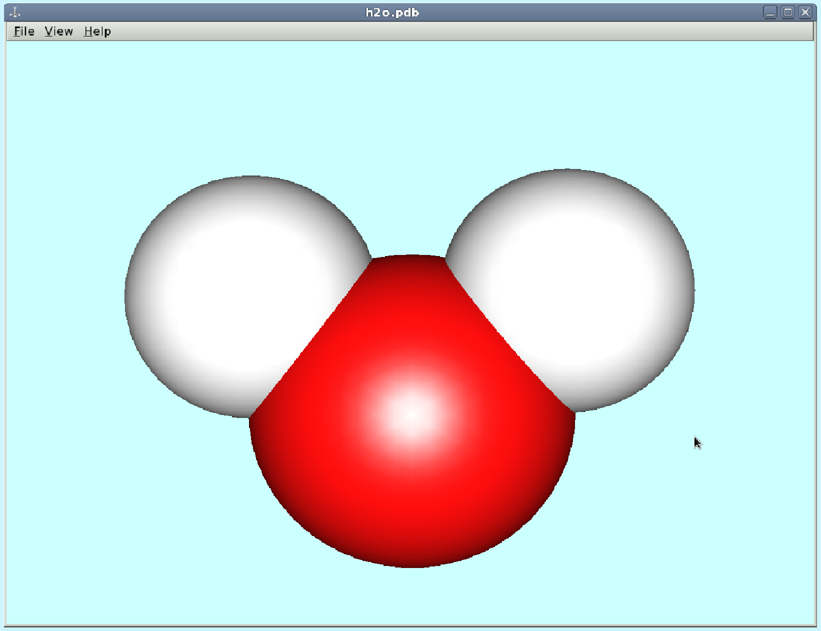
# Brewing Water Chem is Intricate

- The point of this presentation is to discuss concepts
- There is limited coverage of the detailed calculations
- Web links and references cover the arcane calculation in detail with nice spreadsheets & java scripts.

# Water is simple

- $H_2O$ – two Hydrogen one Oxygen
- Molecular weight (2*1 + 16 =) 18 Dalton
- 18 grams, ~0.6 ounce (~1 ice cube) is one Mole



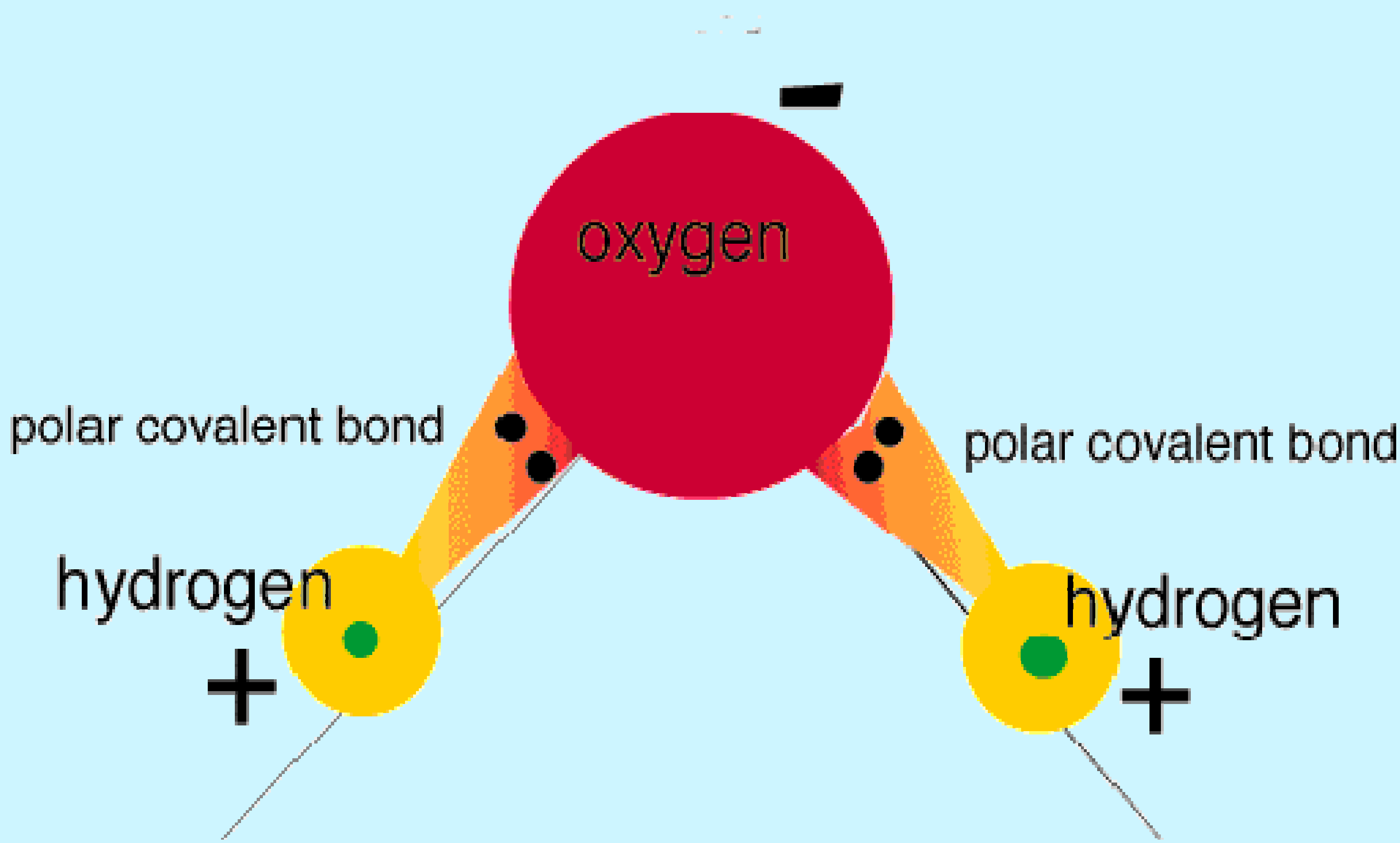
# Water has one trick, dissociation

- $H_2O$ => $H^+$ and $OH^-$
- $H^+$ + $H_2O$ => $H_2O_2^+$

splits into a hydrogen or hydronium and a hydroxyl

- Temperature dependent !
- A liter of 25C(77F) neutral water has $10^{-7}$ Mol of hydronium (pH = 7). At mash temp 65C(155F) there are 2.5 times more hydronium (pH= ~6.6).

# But things dissolve in water, Water is a 'strong' polar solvent



# Ions we may find in tap water

- Calcium
- Magnesium
- Sodium
- Potassium
- Iron, Nickel, Copper
- Nitrogen (nitrate) ?
- Carbonate (tbd)
- Sulfate, Sulfite, Sulfide
- Silicate
- Chloride, Chlorine
- Fluoride
- Phosphate ?
- ... more ...

# Basic concepts ...

- pH – a measure of the concentration of free hydrogen ions (acids). $H^+$ or hydronium $H_2O_2^+$
- Alkalinity – a measure of how much buffering (carbonates) exist in water. It's tested by measuring the amount of acid needed to drive pH to 4.3.
- Hardness – the concentration of Calcium and Magnesium ions in water

# Why we care about water ?

- Water ions impact ...
  - Mash conversion
  - Yeast performance
  - Beer stability & haze
  - Beer flavor
- Water pH impacts ...
  - Mash conversion, Hops extraction, Yeast performance
- Water infections impact flavor !

# Why we care about solutes/ions and acids ?

- **MASH**
  - Small amounts of Calcium needed for alpha-amylase activity (enzyme co-factor).
  - Enzyme activity is pH dependent. (5.1-5.5 @ mash temp or 5.5-5.9 @ room temp)
  - High pH extracts bad phenolic flavors from malt.
  - High pH causes stuck sparge (mushy grist)
  - Water is used up in hydrolysis.  10gal of 12P wort uses ~220gm (1 cup) of water for conversion !

# Enzyme shape impact activity.
# co-factors & pH

# Why we care about solutes/ions and acids ?

- **Fermentation**
  - Yeast need water (duh!)
  - Most nutrition is from malt, but water may contain "fertilizer" N-P-K (nitrogen, phosphorus, potassium)
  - Yeast manage wort/beer pH, but prefer a starting point < 6.
  - Some minor ions enhance fermentation in TINY quantity (copper, zinc)
  - Some minor ions harm yeast (zinc, arsenic)
  - Too many ions reduce water activity (Ac).

# Is there fertilizer in your water ?

- Common agricultural fertilizer is labeled N-P-K (nitrate, phosphate, potassium salts)
- Yeast need these too.
- These are usually sequestered in plants and animals, and rare in water sources.
- If present they may come from runoff, composting plants, algae kills, or excrement
- Has bad implications for your water source.

# Are there 'bugs' in your water ?

- Bacteria and fungi are common in all natural water sources. Brewers mostly care about lactobacilli, acetobacteria and wild yeasts.
- Municipal water supplies add hypochlorite ($ClO^-$) ions (bleach) to water to oxidize(burn) the bugs. Also chloramine $ClNH_2^-$ . *Note chloride (Cl-) ions differ.*
- Upside – suppresses infection
- Downside – chlorite is reactive and the products are flavorful/bad. (medicinal & phenolic flavor)

# Why we care about solutes/ions and acids ?

- **Hopping**
  - pH impacts hop extraction.
  - Too high (>6) means more beta-lupulones, coarse bitterness.
  - Too low (<4.5) means poor isomerization – low bitterness.
  - Sulfate ($SO_4^{--}$) ions enhance hop bitterness

# Why we care about solutes/ions and acids ?

- **Beer Stability & Haze**
  - Sulfite ($SO_3^{--}$) are excellent antioxidants
    - Reduced mash color
    - Reduces beer oxidation
    - Produces sulfate when oxidized.
  - Iron and Copper ($Fe^{++}$, $Cu^{++}$) cause oxidation & staling & haze !
    - The only way to manage iron are 'green clay' filtration or oxidation & sedimentation.
    - FDA wants copper out of tuns.

# Why some well water smells of rotten eggs

- Iron is the cause !
- Some bacteria convert Iron and sulfate into rust + hydrogen sulfide for energy !
- Chlorinating the well kills the bacteria, stops rotten egg stink.
- Iron is still a big brewing problem – find another water source.

# Why we care about solutes/ions and acids ?

- **Beer Flavor**
  - Yeast control beer pH,so acidity in water isn't very important beer pH. (The tongue tastes alkalinity !)
  - A large number of ions have an impact on final beer flavor and mouthfeel, so difficult, complex to analyze.
  - ......

# The easy cases

- We assume your water is potable
  - Iron, Tin, Silicate, Manganese, Chlorite – just plain bad, <0.01 ppm
  - Zinc – needed at ~0.1ppm, acceptable at < 0.5ppm
  - Sodium(Na) smooth flavor enhancing to 150ppm, but adds harshness with sulfate. Go easy on Na.
  - Chloride(Cl) adds fullness & sweetness to 250ppm
  - Sulfate($SO4^{--}$) - adds crisp edge and enhances bitterness (up to 350ppm in big IPAs)

# Where do we stand in these ?

| Cleveland | Copley | range | comment |
|---|---|---|---|
| 1 ppm Chlorine | 0 ppm | <20ppb | Must remove, filter, boil |
| 10.7 ppm Na | 5.1 ppm Na | 0-150 ppm | Increase desirable. |
| 18 ppm Cl | 16 ppm Cl | 0-250 ppm | Increase desirable |
| 36 ppm sulfate | 30 ppm sulfate | 50-100 normal<br>100-350 IPA+ | Ok, but increase for bitter beers |

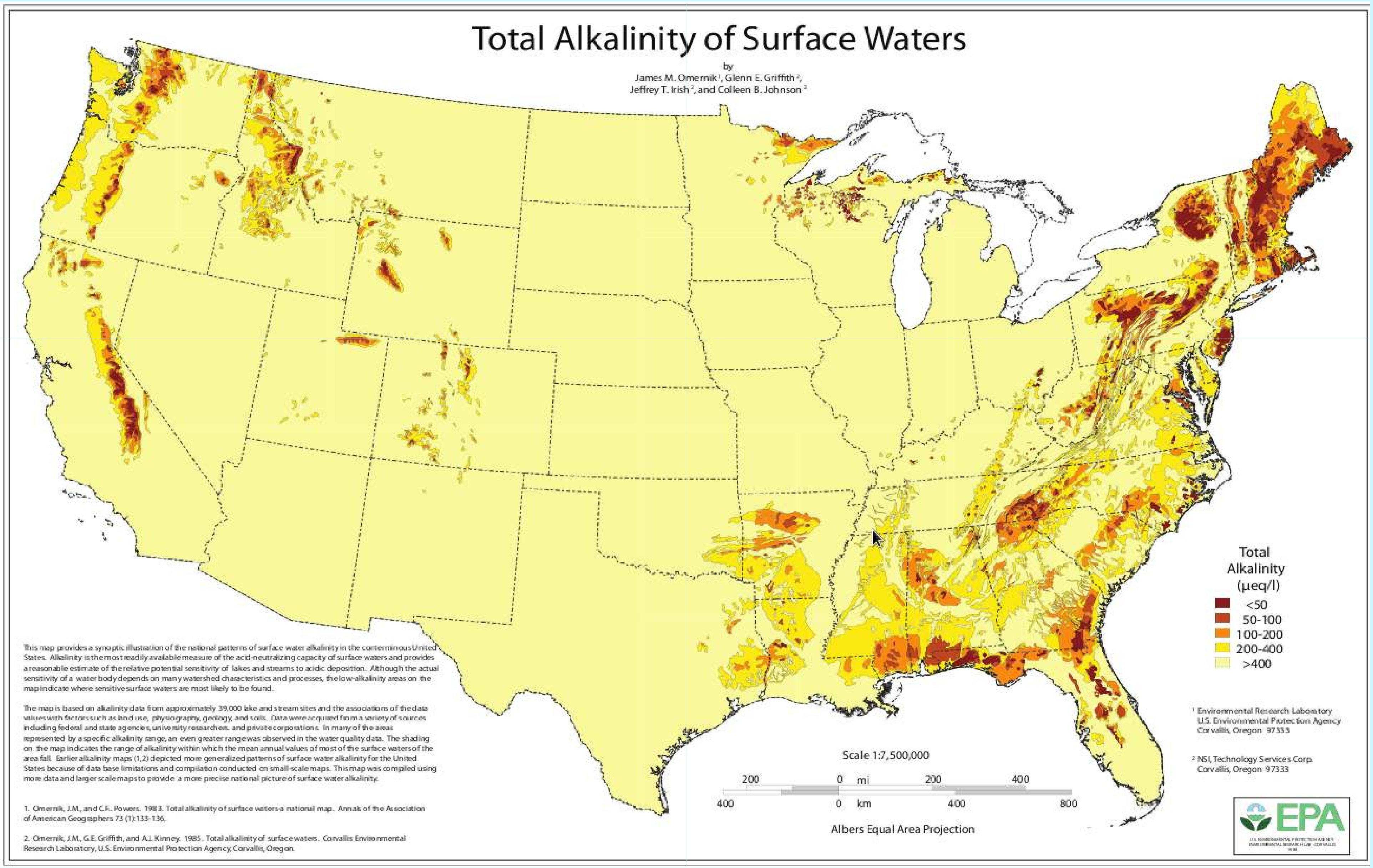
# The hard cases

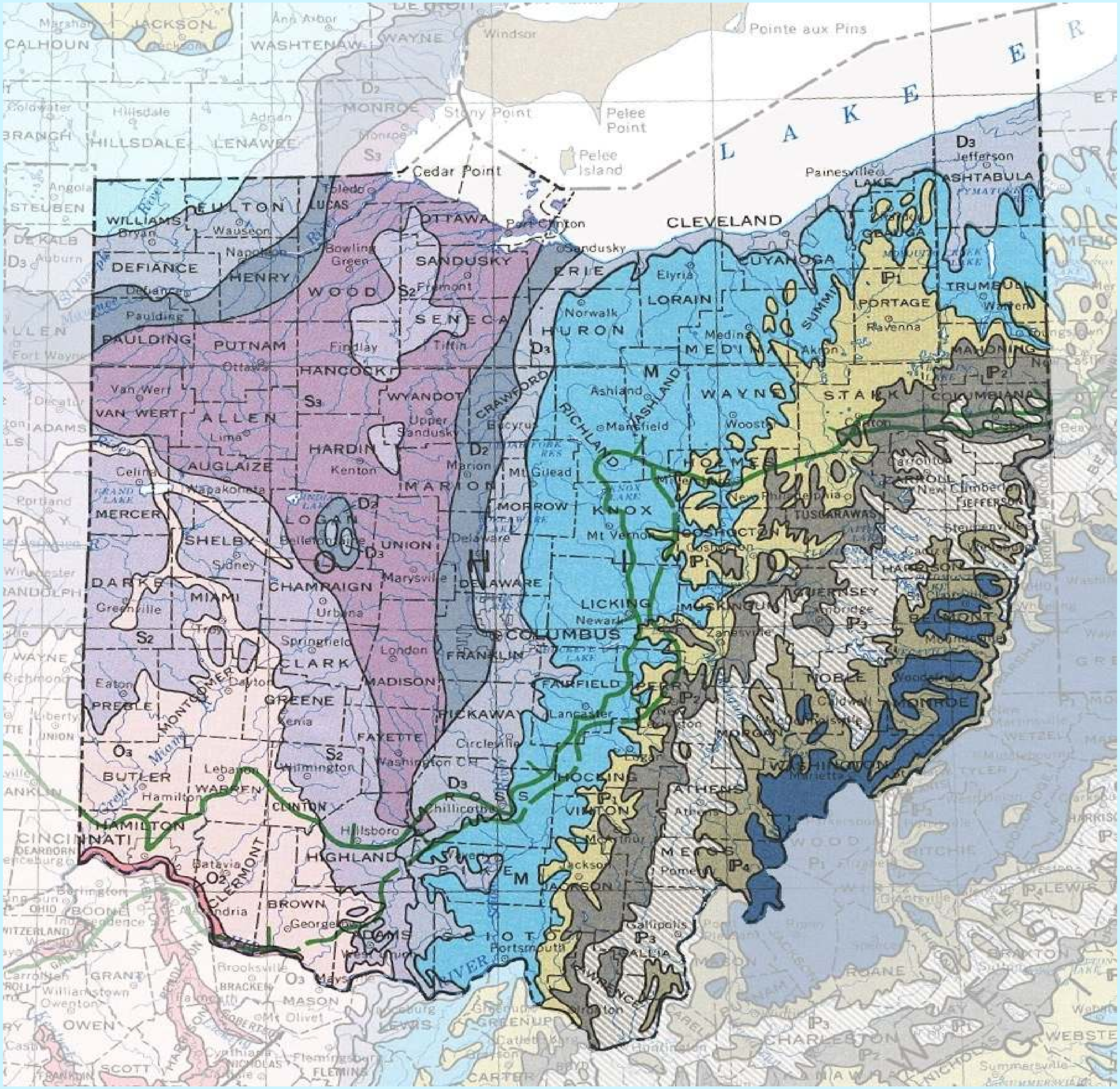
- Calcium & Magnesium (Ca, Mg) = hardness
  - Ca 50-150 ppm
  - Mg 10-30 ppm
- Carbonate (mostly bicarb, $HCO_3^-$) = alkalinity
  - 0-50 ppm bicarb for light color beers
  - 50-150 ppm bicarb for dark beers
  - Mash pH is the issue !!!

# Where do we stand in these ?

| Cleveland | Copley | range | comment |
|---|---|---|---|
| 33 ppm Ca | 63 ppm Ca | 0-150 ppm | good |
| 7.1 ppm Mg | 18 ppm Mg | 10-30 ppm | good |
| 120ppm Alk ~145ppm bicarb | 96 ppm Alk, 116 pm bicarb | 0-50 ppm pale 50-150 dark | **<u>Only dark beers w/o treatment</u>** |

# The Big Picture




LAKE ERIE
Pointe aux Pins
Windsor
Stony Point
Pelee Point
Pelee Island
Cedar Point
Port Clinton
Sandusky
Toledo
CLEVELAND
Painesville
Jefferson
ASHTABULA
LAKE
GEAUGA
CUYAHOGA
TRUMBULL
Warren
PORTAGE
Ravenna
SUMMIT
Akron
LORAIN
Elyria
MEDINA
Medina
MAHONING
STARK
Canton
COLUMBIANA
WAYNE
Wooster
ASHLAND
Ashland
RICHLAND
Mansfield
HOLMES
KNOX
Mt Vernon
COSHOCTON
Coshocton
TUSCARAWAS
New Philadelphia
CARROLL
Carrollton
JEFFERSON
Steubenville
HARRISON
GUERNSEY
Cambridge
BELMONT
MUSKINGUM
Zanesville
LICKING
Newark
COLUMBUS
FRANKLIN
FAIRFIELD
Lancaster
PERRY
NOBLE
MONROE
Woodsfield
MORGAN
WASHINGTON
Marietta
ATHENS
Athens
HOCKING
Logan
VINTON
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JACKSON
Jackson
LAWRENCE
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Portsmouth
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ROSS
Chillicothe
PICKAWAY
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London
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Hillsboro
ADAMS
BROWN
CLERMONT
Batavia
CLINTON
Wilmington
WARREN
Lebanon
BUTLER
Hamilton
HAMILTON
CINCINNATI
GREENE
Xenia
MONTGOMERY
Dayton
PREBLE
Eaton
CLARK
Springfield
CHAMPAIGN
Urbana
MIAMI
Troy
DARKE
Greenville
SHELBY
Sidney
LOGAN
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UNION
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DELAWARE
Delaware
MORROW
Mt Gilead
MARION
Marion
HARDIN
Kenton
WYANDOT
Upper Sandusky
CRAWFORD
Bucyrus
HURON
Norwalk
ERIE
SENECA
Tiffin
SANDUSKY
Fremont
OTTAWA
WOOD
Bowling Green
HANCOCK
Findlay
PUTNAM
Ottawa
ALLEN
Lima
AUGLAIZE
Wapakoneta
MERCER
Celina
VAN WERT
Van Wert
PAULDING
Paulding
DEFIANCE
Defiance
HENRY
Napoleon
FULTON
Wauseon
WILLIAMS
Bryan
LUCAS
MICHIGAN
CALHOUN
JACKSON
WASHTENAW
WAYNE
MONROE
Monroe
Hillsdale
HILLSDALE
Adrian
LENAWEE
BRANCH
Coldwater
STEUBEN
Angola
DE KALB
Auburn
ALLEN
Fort Wayne
ADAMS
Decatur
Portland
Winchester
RANDOLPH
WAYNE
Richmond
Liberty
UNION
FRANKLIN
DEARBORN
BOONE
GRANT
OWEN
SCOTT
BRACKEN
MASON
Maysville
LEWIS
GREENUP
CARTER
FLEMING
CHARLESTON
WOOD
RITCHIE
TYLER
WETZEL
ROANE
Summersville
WEBSTER
S2
S3
D2
D3
M
O2
O3
P1
P2
P3
P4

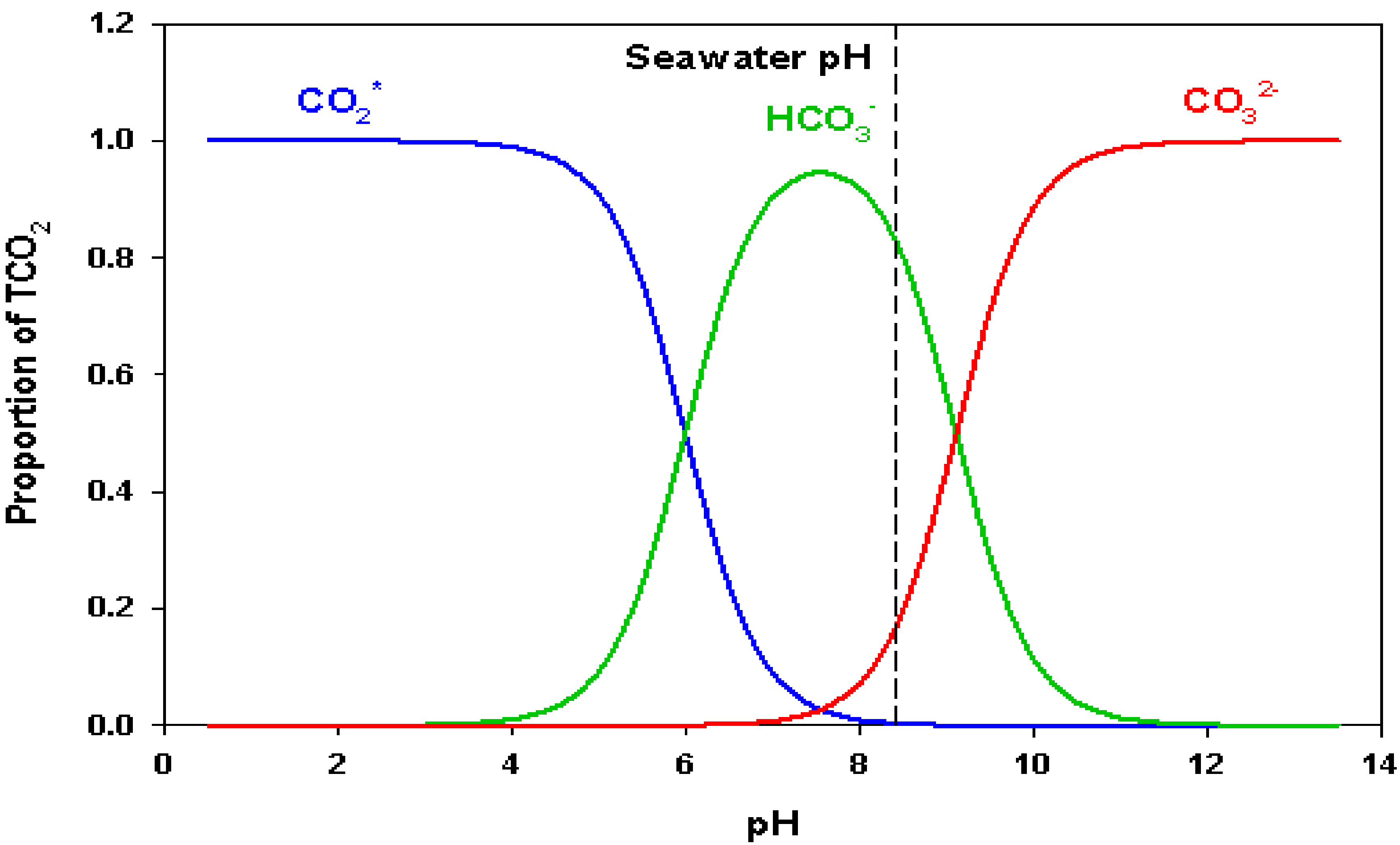
# Common Soluble Minerals

- calcite, aragonite, limestone, marble - $CaCO_3$
- dolomite - $Ca.Mg(CO_3)_2$
- gypsum - $CaSO_4.(H_2O)_2$
- anhydrite - $CaSO_4$
- epsomite - $Mg.SO_4.(H_2O)_7$
- halite - NaCl
- Others ... Iron, Fluoride, Potassium various metals

# So what is Alkalinity ?

- Answers the question – how much acid (hydronium ions) does it take to drive the pH to 4.3 ?
- Expressed “as $CaCO_3$” [very misleading!]
- $CaCO_3 \Rightarrow Ca^{++} + CO_3^{--}$ [almost insoluble]
- $CO_3^{--} + H^+ \Rightarrow HCO_3^-$ [bicarbonate, soluble]
- $HCO_3^- + H^+ \Rightarrow CO_2 + H_2O$ [effervesces]

# The moment of Steve's awakening



# Example Calculation

- Cleveland Water:

Alkalinity (Alk) = 120 ppm (??) *as-*$CaCO_3$

120ppm CaCo3 = 1.18mMol

each carbonate requires 2 hydrogens to ...

Acid required = 2.36 mMol of H+, 2.36 meq.

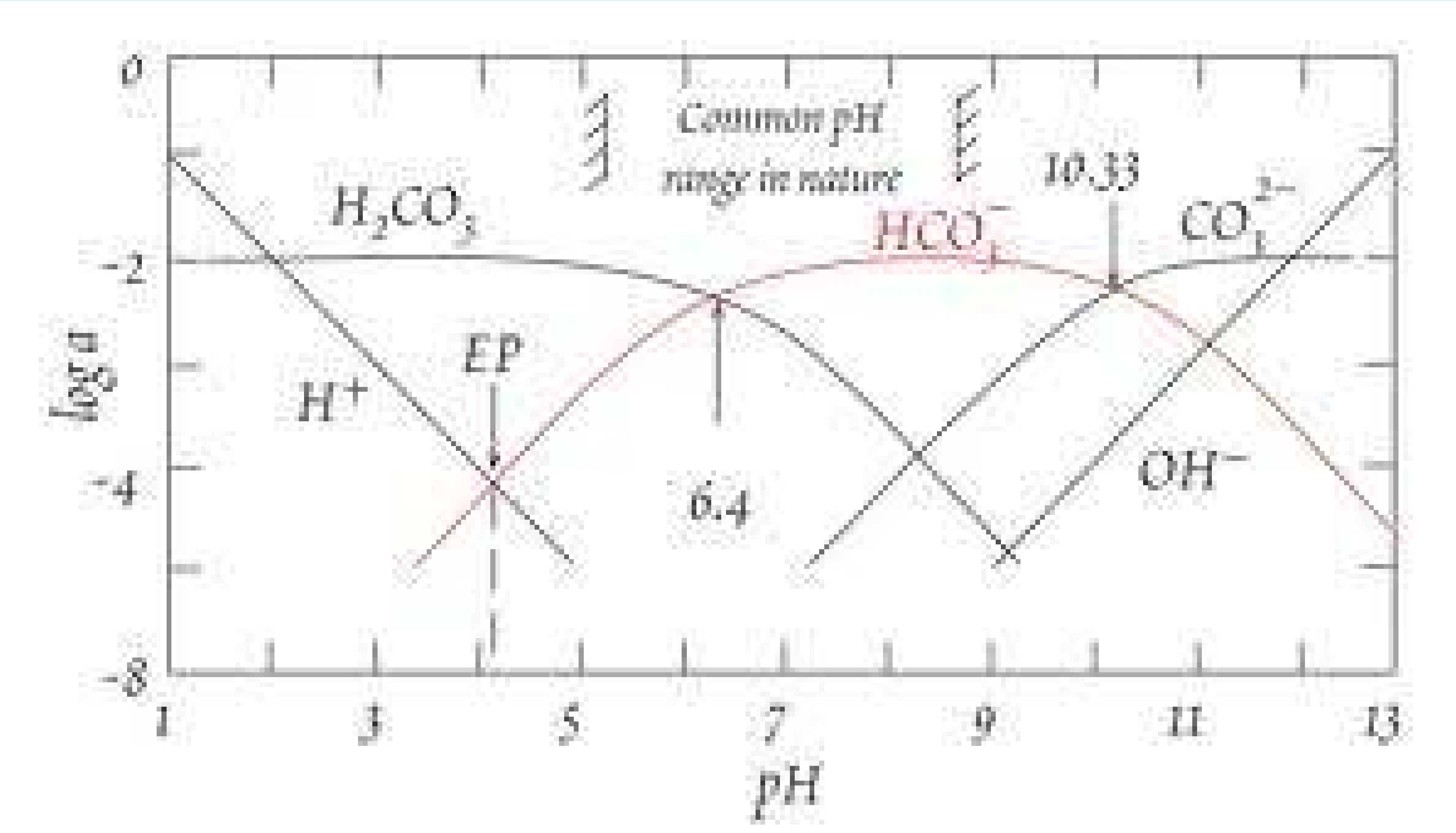
--

To acidify the water requires $10^{-4.5} - 10^{-7}$ = 0.031meq ... totally **negligible**.

# But this is misleading

- Cleveland water has pH=7.3, so it's effectively all **bicarbonate** !
- Our water has ~2.36 mM of bicarb [$HCO_3^-$]
- NOT    1.18 mM of carbonate [$CO_3^{--}$]

# This chart implies two solutions to alkalinity



# Ways to correct alkalinity

- **Boil and add oxygen** (how?)
  - Converts 2 bicarbs to 1 $CO_2$ + $H_2O$ and 1 $CaCO_3$
  - Precipitate chalk and decant, reduces Ca&Mg
  - Difficult, incomplete, expensive, time consuming
- **Add base** (pickling lime) to >pH 11
  - Chalk precipitates overnight, decant
  - Acidify (tiny addition)
  - Slow but cheap, reduces Ca&Mg

# More ways to correct alkalinity

- **Add acid** to pH = ~6, and stir to release CO2
  - Quick & easy, requires food grade acid
- **Reverse Osmosis filter**
  - Removes ~95% of all ions
  - So 120ppm Alk becomes ~6ppm
- **Dilute with distilled or RO water**
  - To get from 120ppm to 50ppm Alk requires
    - 42% CLV water + 58% Distilled

# Mash pH is the goal !

- Pure water + pale malt gives pH ~5.7 @68F GOOD!
- With 20% crystal malt gives pH ~5.2 @68F (too low)
- 100% caramel, roast gives pH 4.0-4.8 @68F (very low)
- Darker malts are acidic !

# Mash pH and alkalinty

- To produce "chalk" requires Ca or Mg
- Our water is deficient

33ppm Ca = 0.83 mM

7.1ppm Mg = 0.30 mM

- 1.13 mM of cations but 2.36mM of bicarb !
- We need another 1.23mM of Ca

- add gypsum $CaSO_4.2(H_2O)$

- or add $Ca(OH)_2$

# Phytin in malt reduces alkalinity !

- Kolbach determined phytin precipitated hardness(Ca & Mg) and produces acid.
- 50.5 ppm of Alk (as CaCO3) is counteracted when phytin reacts with 70ppm of Ca or 88ppm of Mg
- If CLV water has 120ppm of Alkalinity, then we can remove the alkalinity in the mash by with 166ppm Ca or 210ppm Mg.

# Phytin (cont)

- This means adding ~133ppm of Ca
  - Add 0.53g/L gypsum (adds ~300ppm of sulfate)
  - Add 0.45g/L calcium chloride (adds ~230ppm Cl)

  **DOESN'T WORK WELL**
- If Alkalinity is really 120ppm as $CaCO_3$ then use acid additions.

# References

- John Palmer's “How to Brew” online

http://howtobrew.com/sitemap.html

- http://www.brewersfriend.com/water-chemistry/
- HBD.org archives

http://hbd.org/archives.shtml

http://hbd.org/hbd/archive/2648.html

http://brewery.org/brewery/Library.html#Water

- Homebrew Talk Wiki

http://www.homebrewtalk.com/wiki/index.php