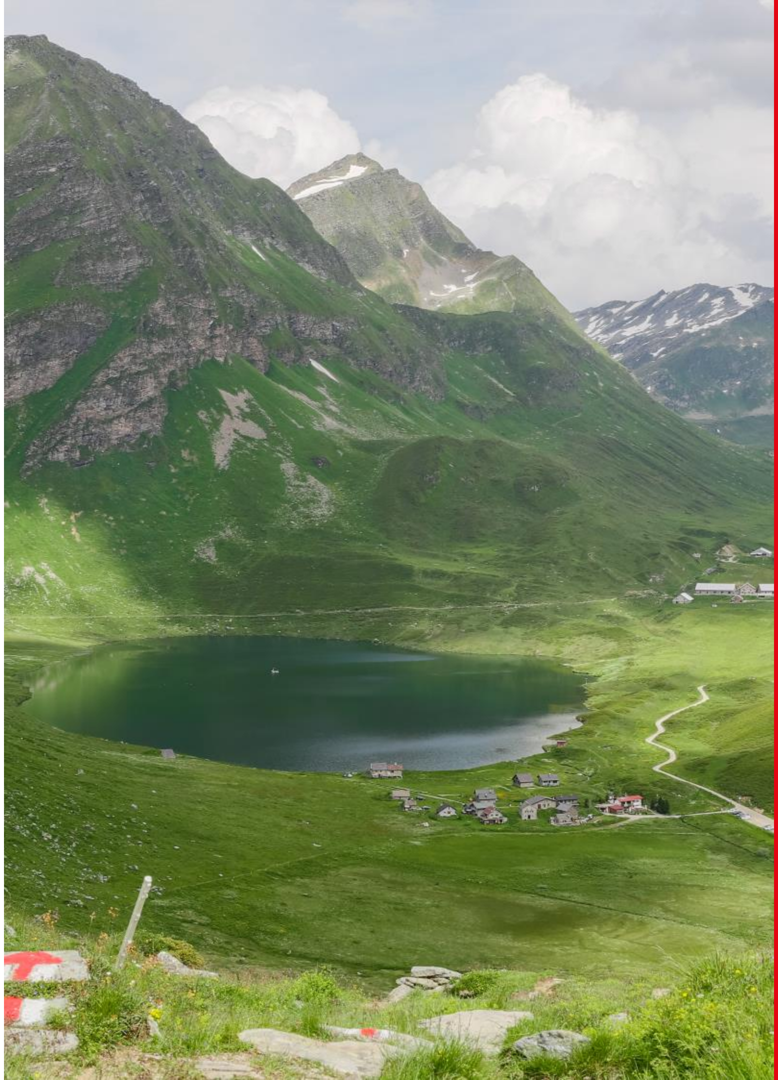

Chemistry of natural waters I

ENV-200 Week 8

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Learning objectives

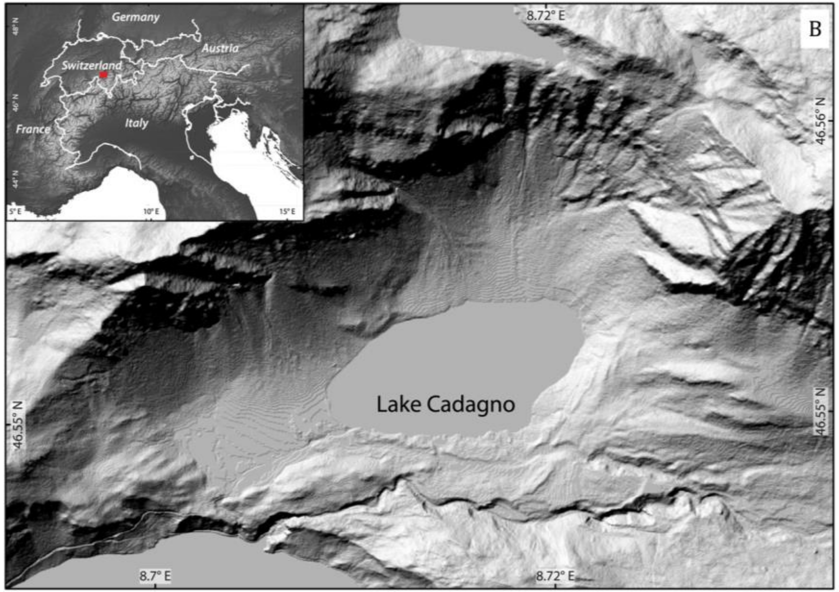
You should be able to use the concepts we covered in the past few weeks to interpret the **chemistry of a real lake**. Based on observations of the chemical conditions, you should be able to conclude which **reactions** and **processes** are occurring in the lake.

Lake Cadagno

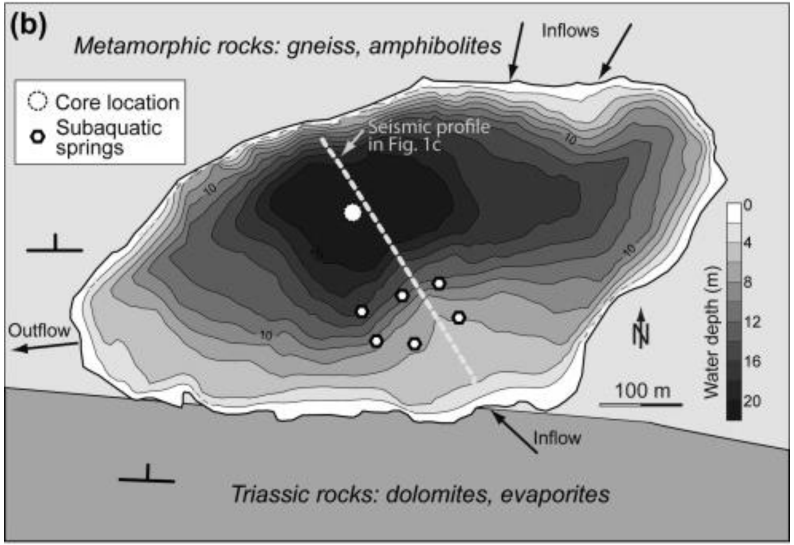
Lake Cadagno is located at 1921 m elevation. It is a 21 m deep crenogenic meromictic alpine lake with a permanent chemocline near 13 m depth.

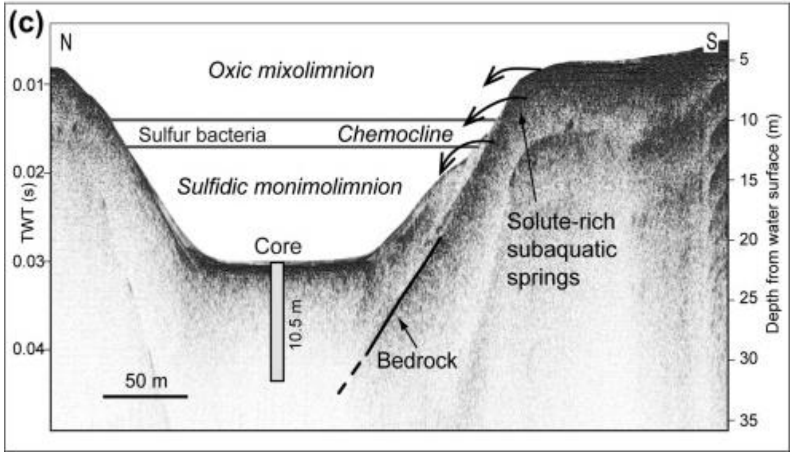
- A meromictic lake is a lake which has layers of water that do not intermix.
- The chemocline is the border at which water layers with different chemistries meet.

Janssen, DJ et al., AGU Geophys Res Let, ***2022****, 49, e2022GL099154.*



Lake Cadagno

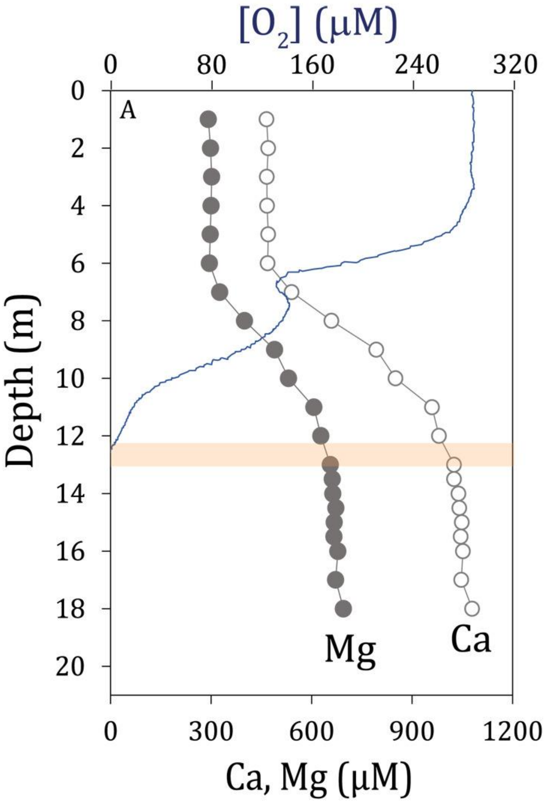




- The catchment basin is characterized by sulfate containing rocks.
- Weathering processes transport significant amounts of sulfate into Lake Cadagno.
- Underwater springs feed substantial amounts of leached sulfate into the hypolimnion of lake Cadagno (crenogenic meromixis). This sulfate-rich, heavier water rests at the bottom of the lake and prevents mixing during spring and fall.

*Wirth, SB et al., Geochim Cosmochim Acta, **2013**, 120, 220-238.*

Water column



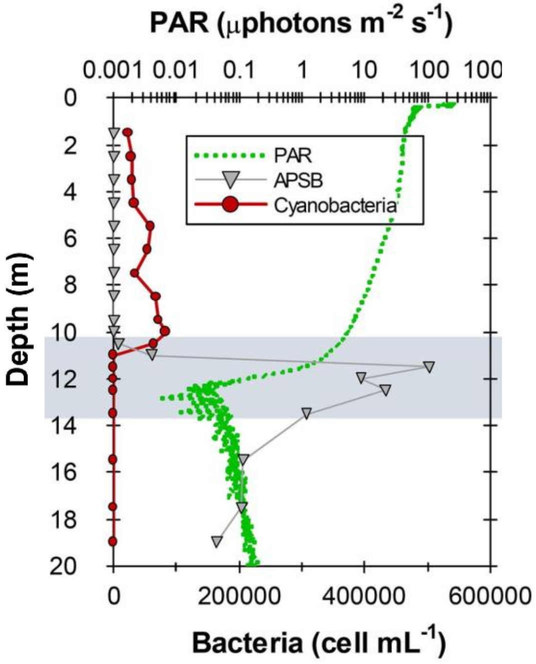
The chemocline separates the upper, oxygenated layer (above 13 m depth) and the lower, anoxic layer (below 13 m depth).

a. Why do bottom waters become anoxic?

b. What differences in water chemistry do you expect for these two layers?

Janssen, DJ et al., *AGU Geophys Res Let*, ***2022***, *49, e2022GL099154.*

Water column



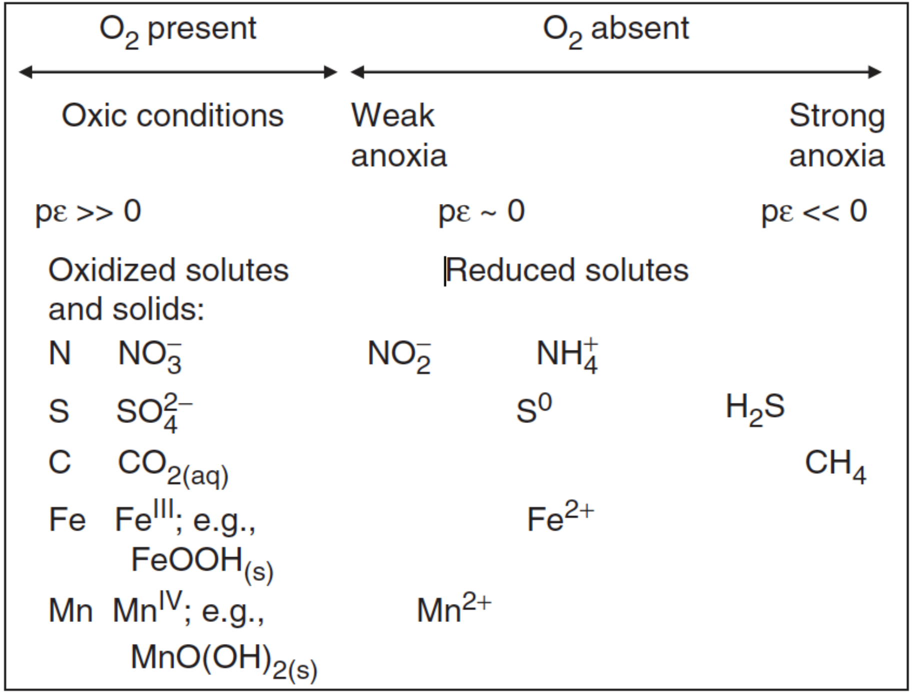
Why do bottom waters become anoxic?

- High primary production in the surface layer (cyanobacteria)
- Formed organic matter sinks downward and is degraded in the chemocline and below
- Step-wise consumption of electron acceptors

PAR = photosynthetically active radiation
APSB = anaerobic phototrophic sulfur bacteria

*Ellwood, MJ et al., Geochim Cosmochim Acta, **2019**, 255, 205-221.*

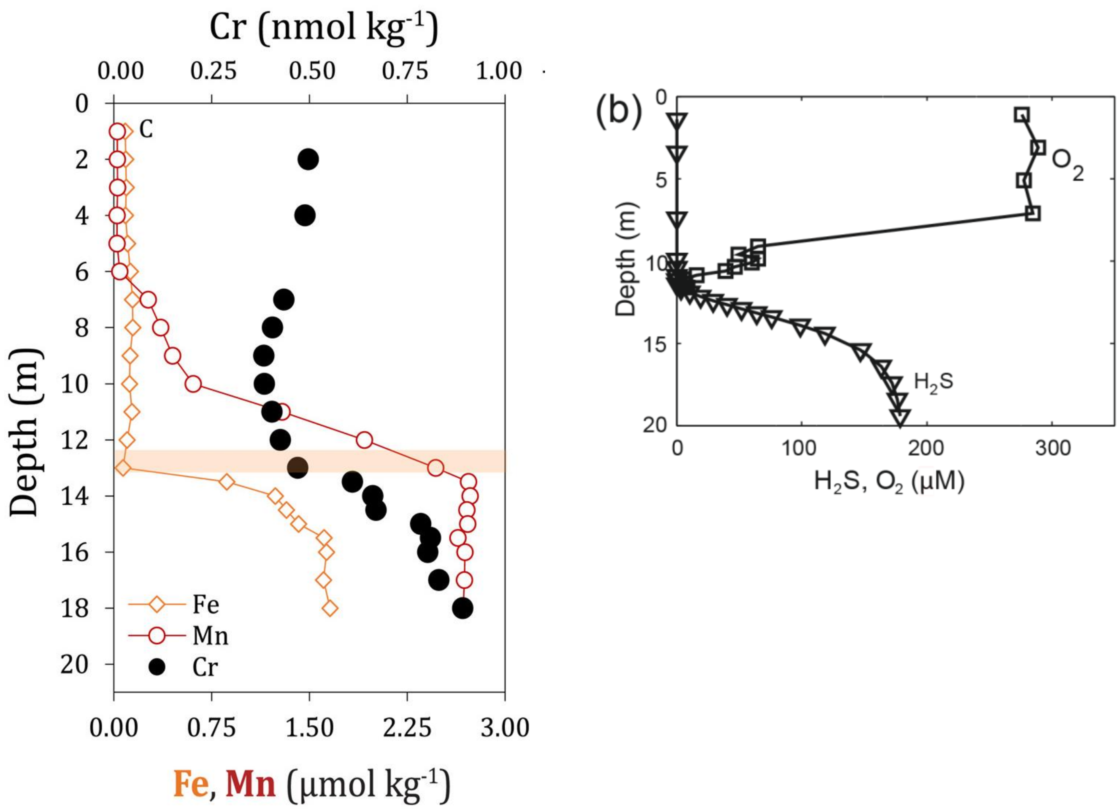
Water column



What variations in water chemistry do you expect for these two layers?

- Oxic layer: oxidized solutes and solids
- Anoxic layer: elevated concentrations of reduced Mn, Fe, H_2S

Water column



Do concentration profiles follow the expected redox sequence?

*Janssen, DJ et al., AGU Geophys Res Let, **2022**, 49, e2022GL099154. Dahl, TW et al., Geochim Cosmochim Acta, **2010**, 74, 144-163.*

Sulfur cycling at the chemocline

Sulfate (SO_4^{2-}) from gypsum is delivered horizontally by subaquatic springs

- **Dissimilatory sulfate reduction:** Form of anaerobic respiration that uses sulfate as the terminal electron acceptor to produce hydrogen sulfide

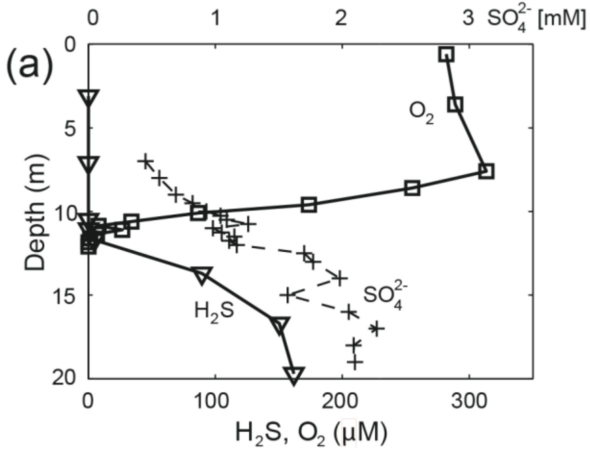
$$C_2H_3O_2^- + SO_4^{2-} + 3H^+ \rightarrow 2CO_2 + H_2S + 2H_2O$$

Anoxygenic photosynthesis: H_2O oxidation to sulfur or sulfate by phototrophic sulfur bacteria

$$HCO_3^- + 2H_2S + hv \rightarrow CH_2O + 2S^0 + H_2O + OH^-$$

$$2HCO_3^- + H_2S + hv \rightarrow 2CH_2O + SO_4^{2-}$$

- The sulfidocline shows diurnal fluctuations between 11 and 13 m



Purple and green sulfur bacteria cultures.
*Kushkevych, I. et al., Front. microbiol, **2024**, 15*

*Del Don, C. et al., Aquatic Sciences, **2001**, 63(1), 70-90. Dahl, TW et al., Geochim Cosmochim Acta, **2010**, 74, 144-163.*

Iron cycling at the chemocline

As iron(II) diffuses upward within the chemocline, it is oxidized to iron(III) and precipitates as iron(III) hydroxides

- **Biotic Fe(II) oxidation**: fixation of inorganic carbon to form organic matter by iron-oxidising anoxygenic phototrophs (termed photoferrotrophs)

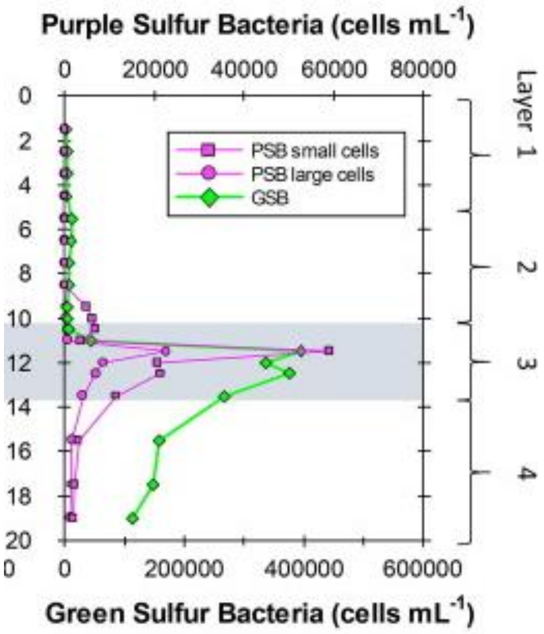
  $HCO_3^- + 4Fe^{2+} + 10H_2O + hv = CH_2O + 4Fe(OH)_3 + 7H^+$

  Green and purple sulfur bacteria

- **Abiotic iron(II) oxidation**: reaction with dissolved oxygen or particulate manganese

  $2Fe^{2+} + O_2 + 4H_2O = 2Fe(OH)_3 + 2H^+$

  $2Fe^{2+} + MnO_2 + 4H_2O = 2Fe(OH)_3 + Mn^{2+} + 2H^+$



*Ellwood, MJ et al., Geochim Cosmochim Acta, **2019**, 255, 205-221.*

Iron cycling at the chemocline

The formed iron(III) hydroxides sink through the chemocline and are immediately reduced.

- **Biotic iron reduction**: dissimilatory iron(III) reduction and dissolution reactions

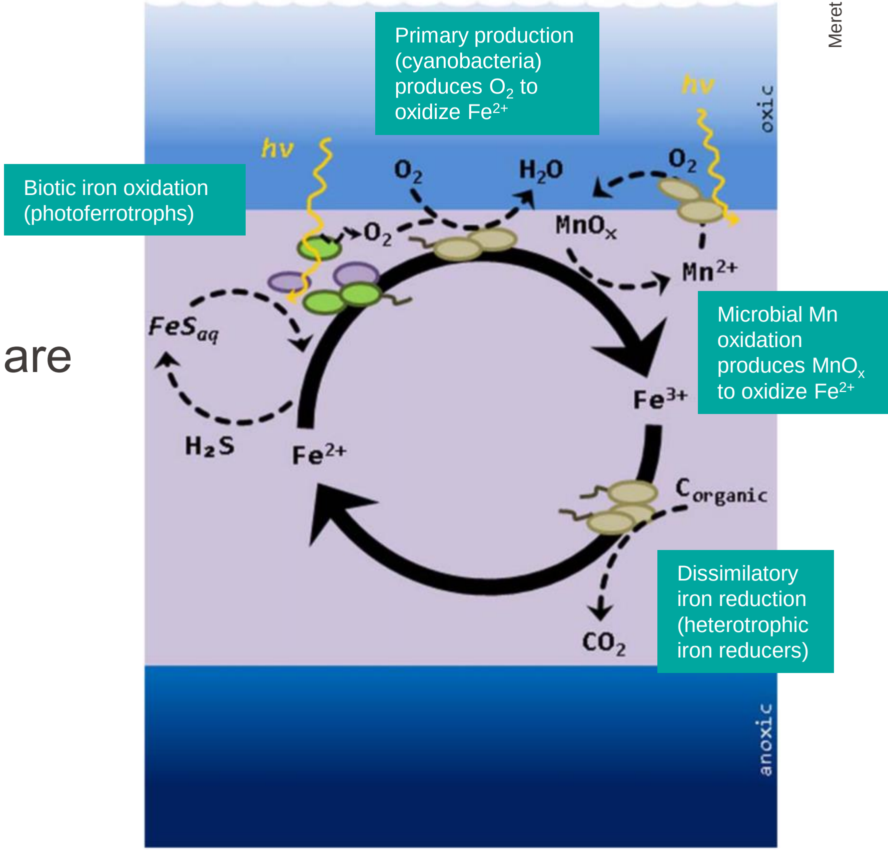
  $C_2H_3O_2^- + 8Fe^{3+} + 4H_2O = 2HCO_3^- + 2Fe^{2+} + 2H^+$

  $HCOO^- + 2Fe^{3+} + H_2O = HCO_3^- + 2Fe^{2+} + 2H^+$

  Heterotrophic iron-reducing bacteria

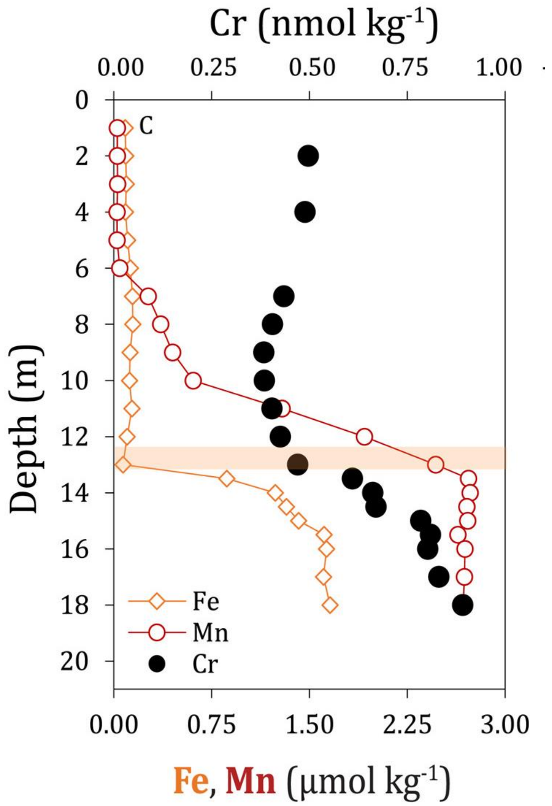
Iron cycling at the chemocline

Rapid oxidation and reduction of iron results in "cryptic" cycling: iron oxides are not detected because they are immediately reduced



Berg, JS et al., Environ Microbiol, **2016**, 18(12), 5288-5302.

Water column



We can explain the Fe and Mn trends with the redox profile. But what about Cr?

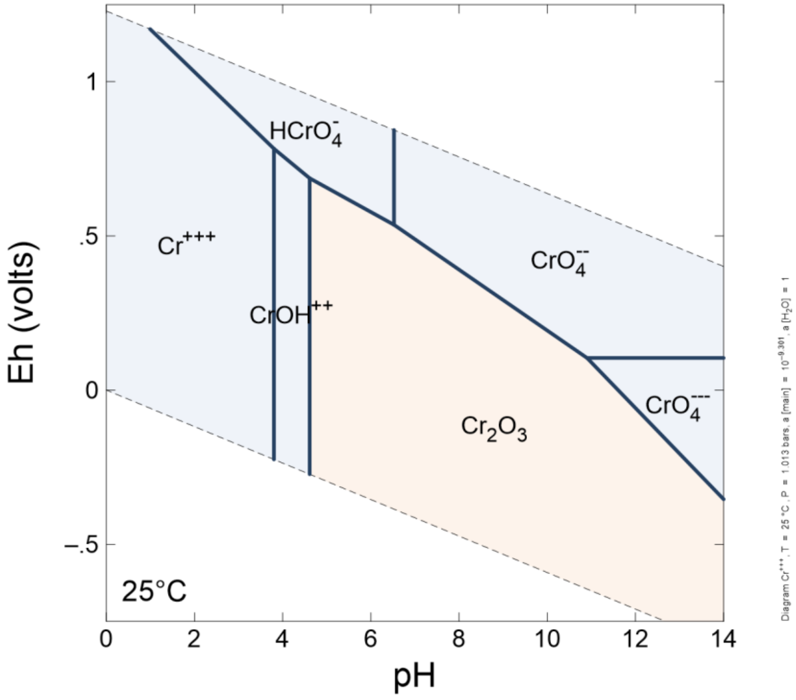
Cr likely comes into the lake through surface water input resulting from oxidative terrestrial weathering.

Which processes could result in these trends in concentration?

*Janssen, DJ et al., AGU Geophys Res Let, **2022**, 49, e2022GL099154.*

Biogeochemistry of chromium (Cr)

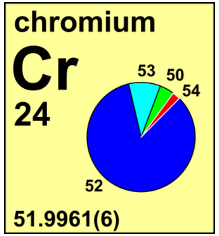
- Chromium (Cr) is a redox-sensitive metal element with two natural oxidation states
  - Cr(VI)
    - Soluble
    - Commonly as oxyanions
    - Very toxic
  - Cr(III)
    - Insoluble
    - Cr (III)-compounds
    - Less toxic



*Wei, W. et al., Chemical Geology, **2020**, 541.*

The Cr isotope system

- Chromium has four stable isotopes with different abundances:
  - ^{50}Cr 4.35 %
  - **^{52}Cr 83.79 %**
  - **^{53}Cr 9.50 %**
  - ^{54}Cr 2.36 %



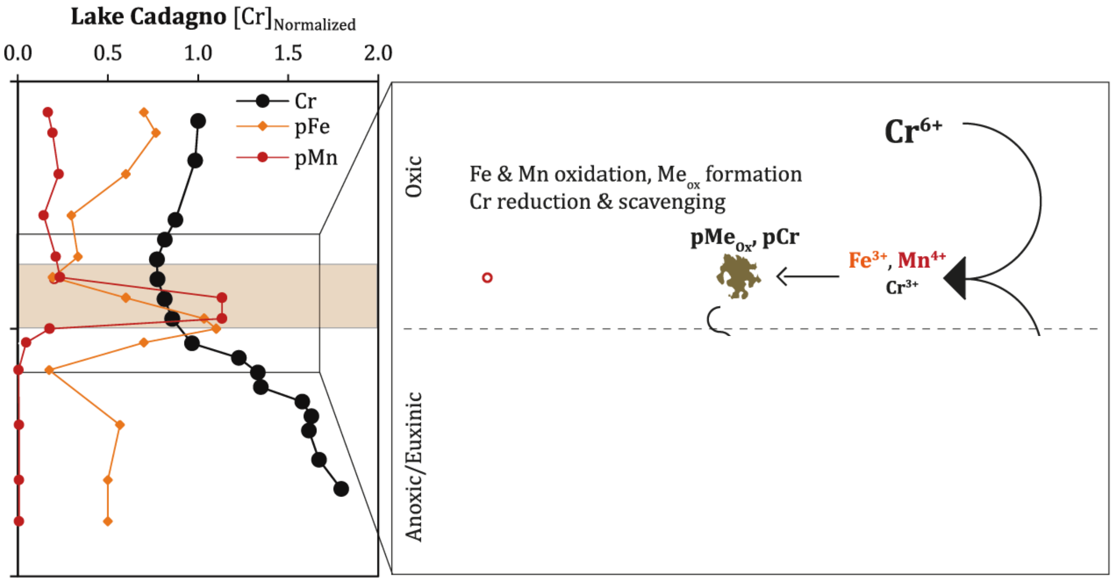
- Isotope ratios offer a third dimension:
  - Concentration => How much?
  - Speciation => In which form?
  - Isotope ratios => What's the history? (Sources, processes)

- Cr isotope fractionation occurs during Cr redox reactions as well as other redox-independent processes

Cr isotopes as a paleo proxy

- Chromium (Cr) isotopes are increasingly used as a **paleoproxy** to understand changes in Earth's **redox conditions**, **oxygenation history**, and **biogeochemical cycles** over geologic time.
- Paleo-reconstructions using **sedimentary δ^{53}Cr records** apply the assumption that Cr is efficiently sequestered into sediment phases under reducing conditions
- Complete Cr redox conversion prevents isotopic fractionation, resulting in sediment-hosted authigenic δ^{53}Cr equivalent to the overlying water column
- Lake Cadagno acts as an “ocean analog” to study the processes affecting the δ^{53}Cr signature in the water column

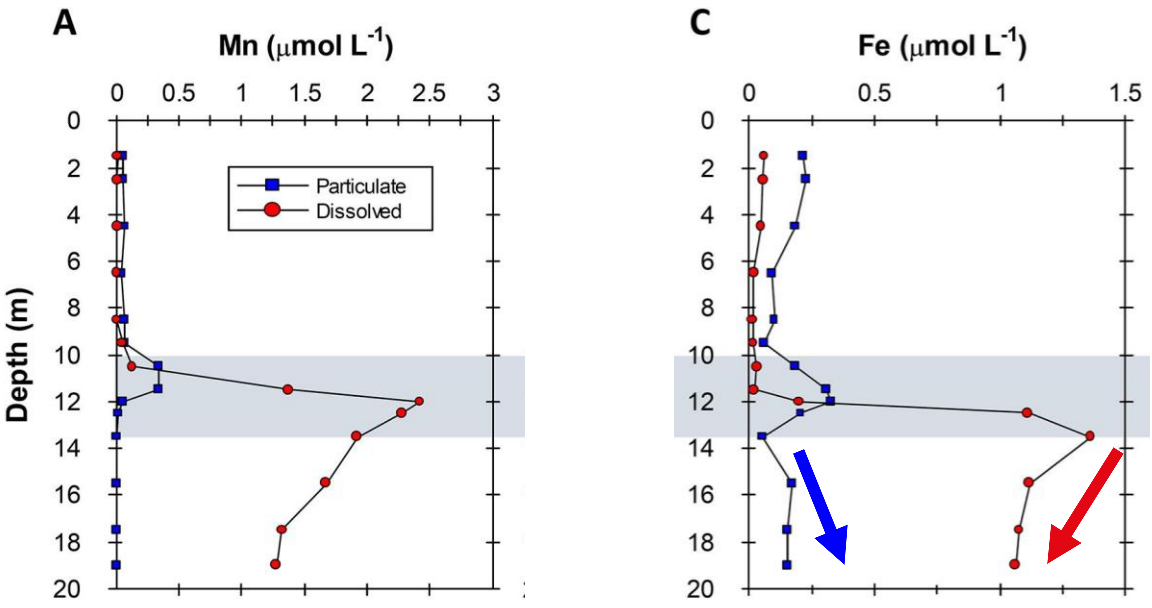
Redox processes at the chemocline



- Fe and Mn oxides form within and above the chemocline, driven by upward transport of dissolved Fe(II)
- Fe(II) reduces Cr from Cr^{6+} to Cr^{3+}
- Cr^{3+} is scavenged onto metal oxides
- Sinking particles transport Cr^{3+} down- reductive dissolution of iron oxides results in release of Cr

*Janssen, DJ et al., AGU Geophys Res Let, **2022**, 49, e2022GL099154.*

Particulate and dissolved concentrations

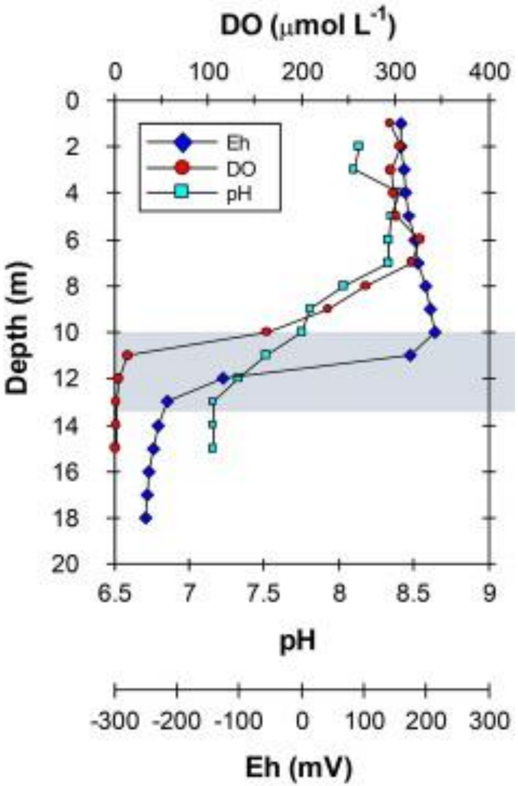


Iron(III) compounds are reductively dissolved in the anoxic zone. Why do we see an increase in particulate iron and decrease in dissolved iron below the chemocline?

*Ellwood, MJ et al., Geochim Cosmochim Acta, **2019**, 255, 205-221.*

Iron redox processes

- The decrease in dissolved and increase in particulate Fe concentrations suggest that iron phases are precipitating.
- Which method could you use to figure out which phases are precipitating?



*Ellwood, MJ et al., Geochim Cosmochim Acta, **2019**, 255, 205-221.*

E_H-pH stability diagram to the rescue!

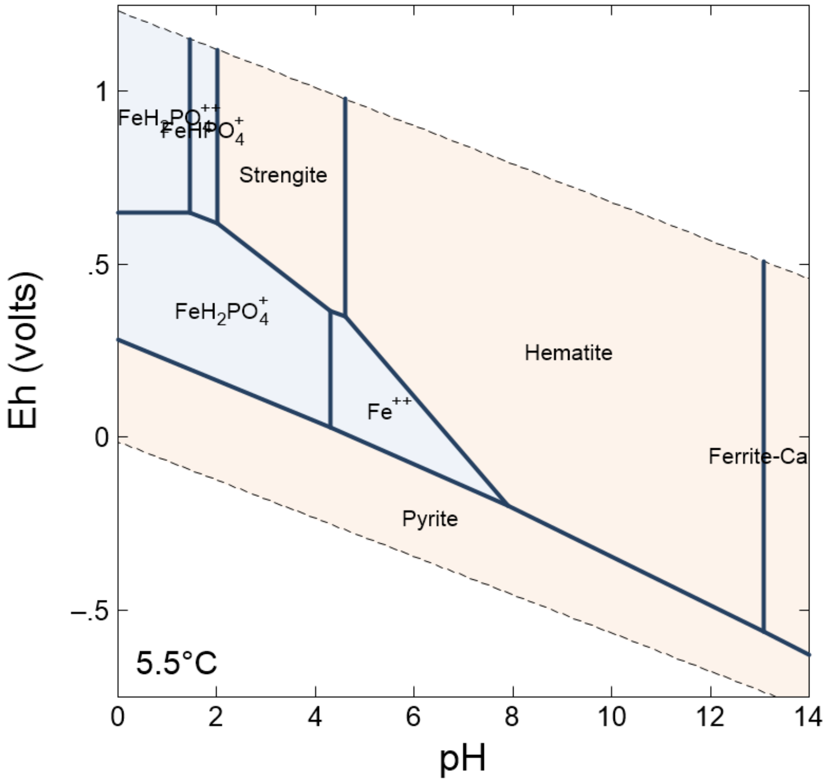
Which parameters do you need? (These are given in the paper referenced below)

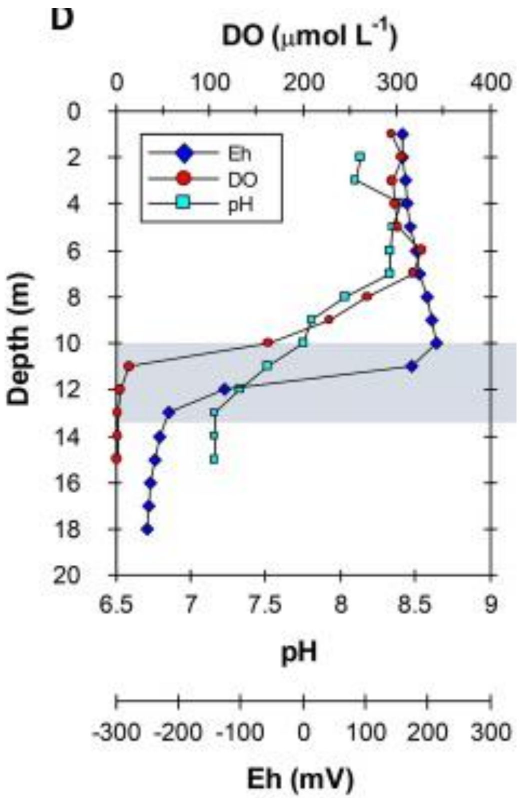
- Temperature: 5.5 °C
- Pressure: 1 bar
- Total iron concentration: 1 µmol/L
- Bicarbonate: 1 mmol/L
- Calcium: 1 mmol/L
- Sulfate: 3 mmol/L
- Phosphate: 3 µmol/L

=> We will learn how to use modeling tools to create Eh-pH diagrams next week

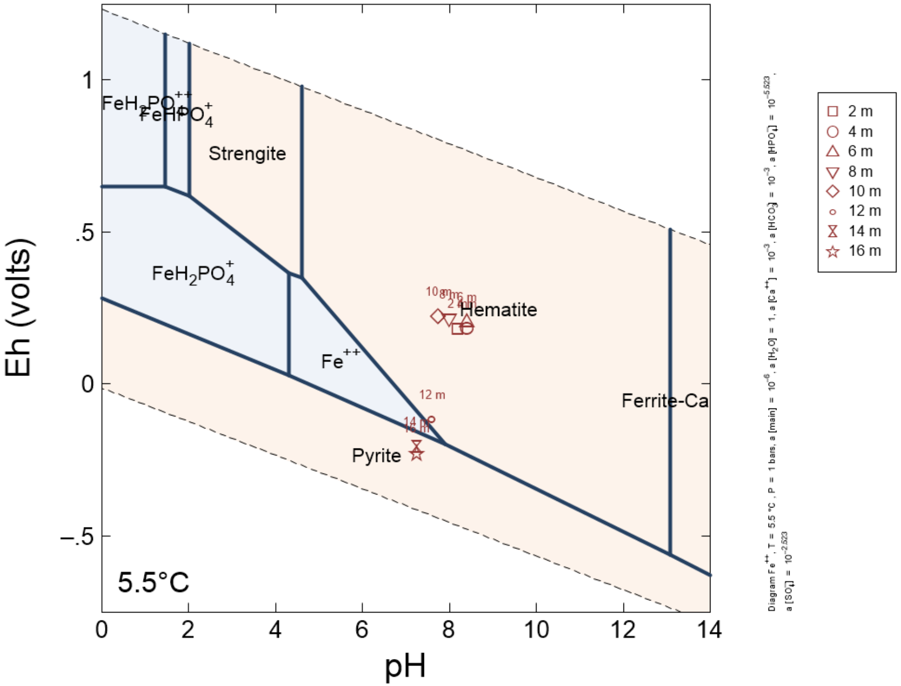
Ellwood, MJ et al., Geochim Cosmochim Acta, ***2019****, 255, 205-221.*

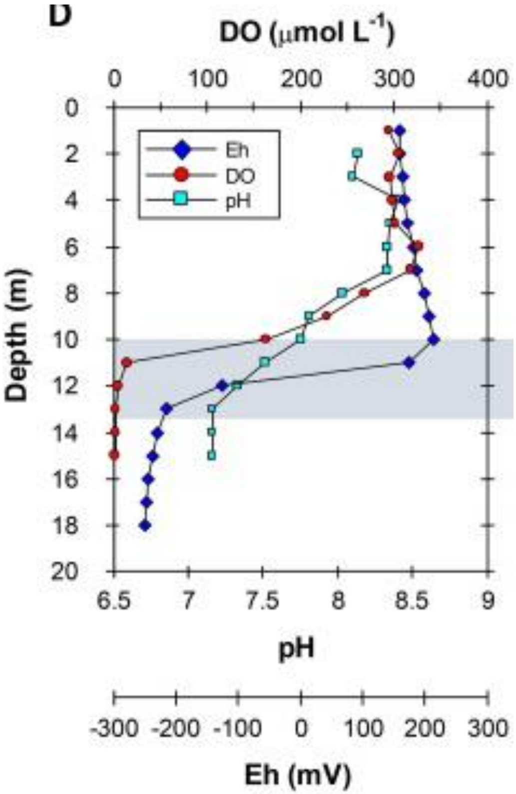
E_H-pH stability diagram





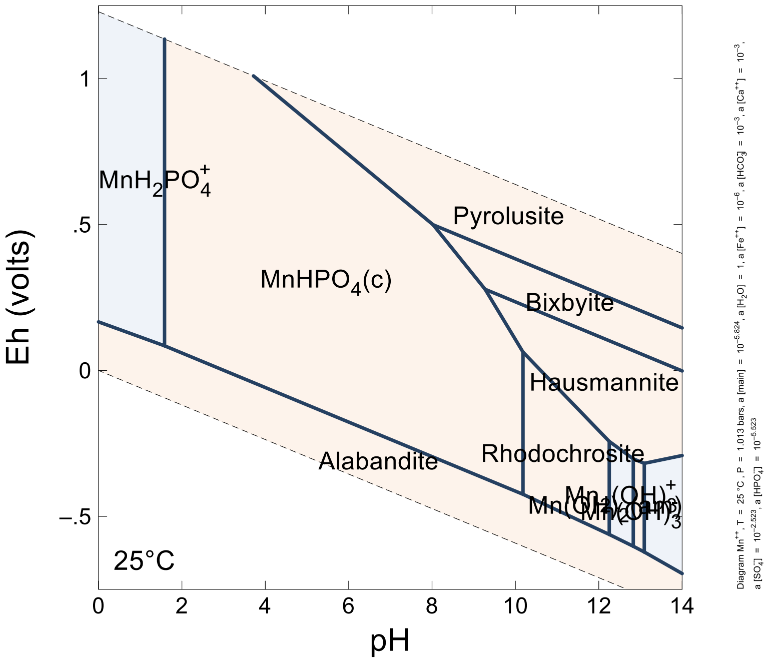
E_H-pH stability diagram: Solution

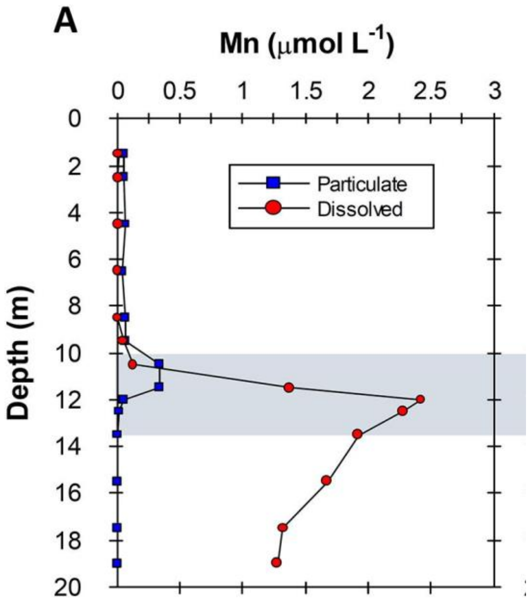




FeS is expected to precitipate in the anoxic zone and likely causes the increase in particulate concentrations we observed.

E_H-pH stability diagram: Solution

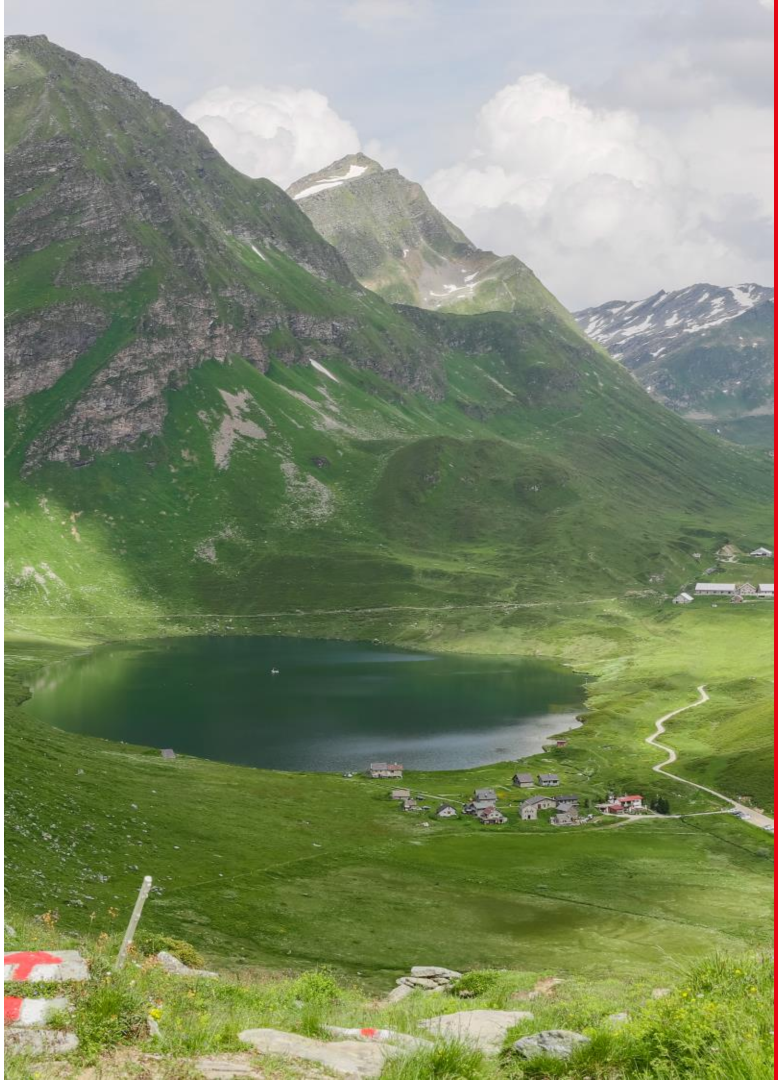




Why is there no increase in particulate Mn?

Summary

1. Lake Cadagno has a permanent chemocline that separates oxic surface from anoxic bottom waters. This setting allowed us to discuss many of the processes covered in class in a natural setting: dissolution and precipitation processes, metal speciation, microbially mediated and abiotic redox processes.
2. We further realized how geochemical modeling can be useful to make sense of some of the water column data for Lake Cadagno reported in the literature.



Chemistry of natural waters II

ENV-200 Week 8

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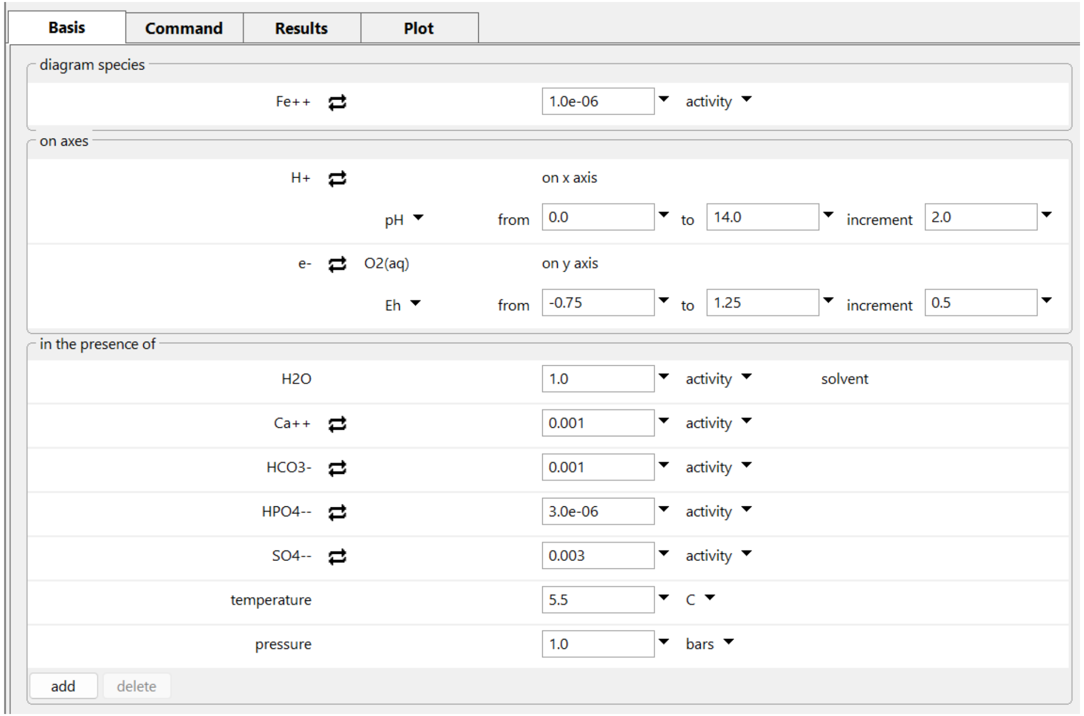
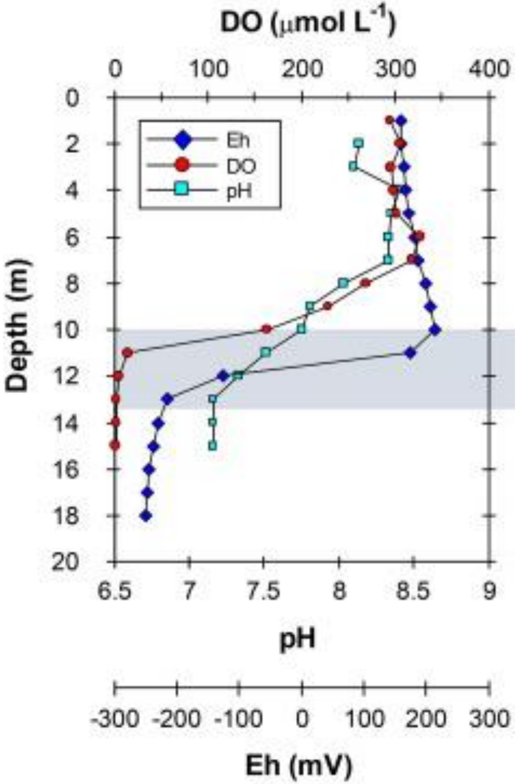
E_H-pH stability diagram: Solution



E_H-pH stability diagram: Solution

- Now add the data from the figure on the right into your E_H-pH diagram.
- To do so, create a GSS file, add the data, and then drag and drop it into your E_H-pH diagram.



Ellwood, MJ et al., *Geochim Cosmochim Acta*, ***2019***, *255, 205-221.*