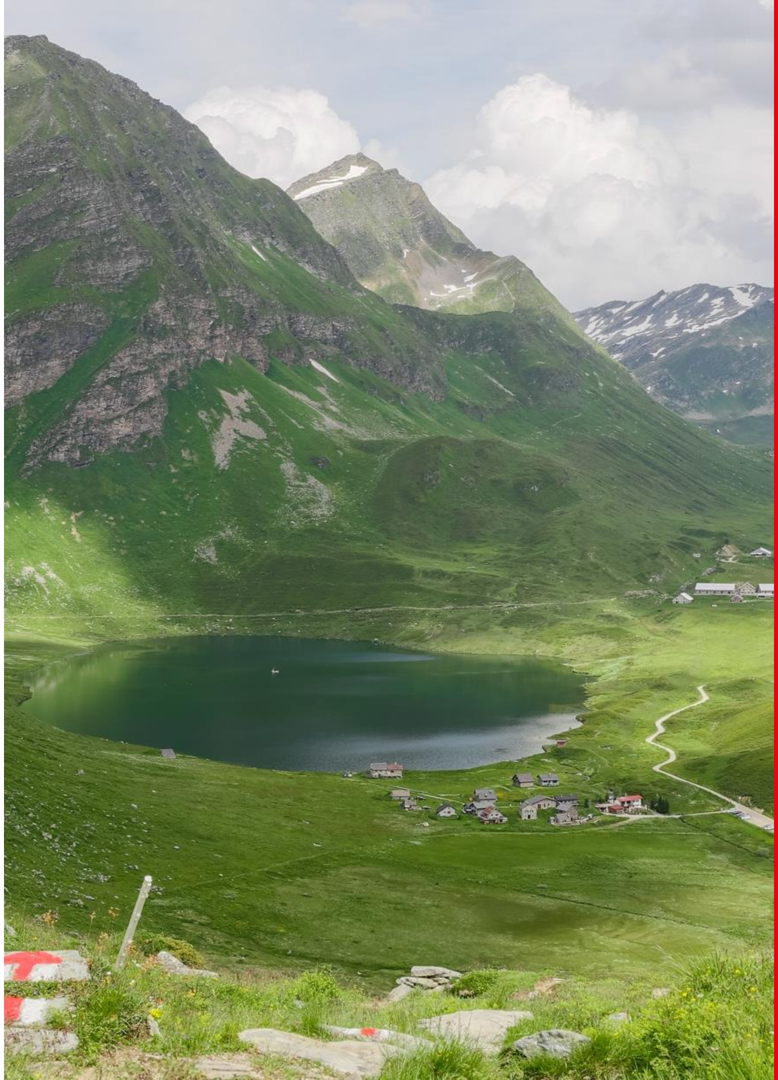

Chemistry of natural waters II

ENV-200

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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

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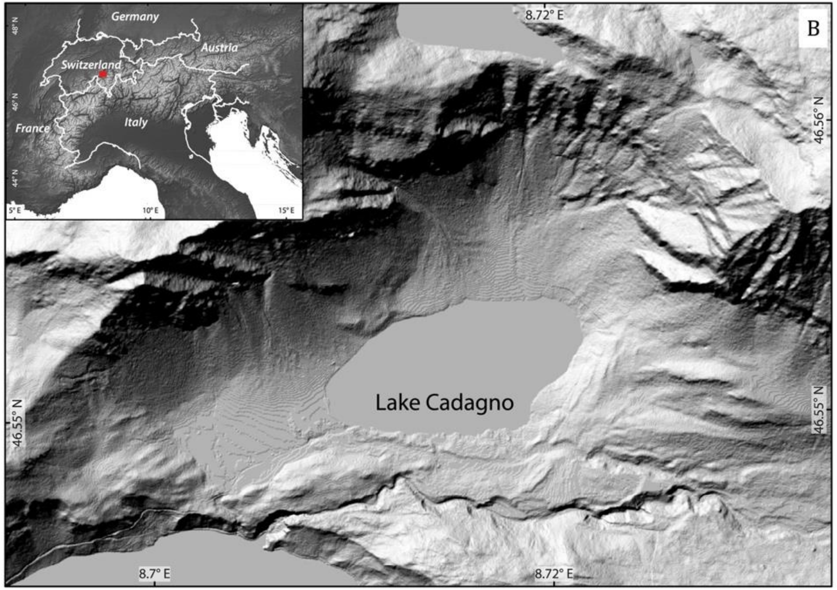
Lake Cadagno is located at 1921 m elevation. It is a 21 m deep meromictic alpine lake with a permanent chemocline near 13 m depth.

- 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

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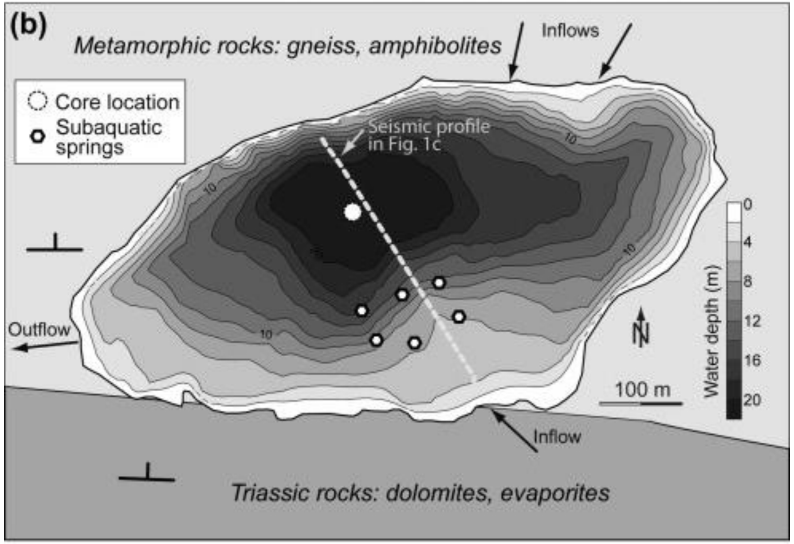
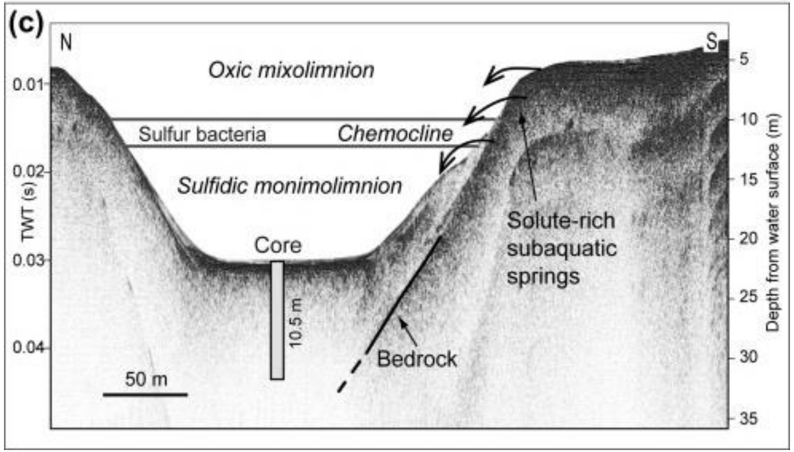
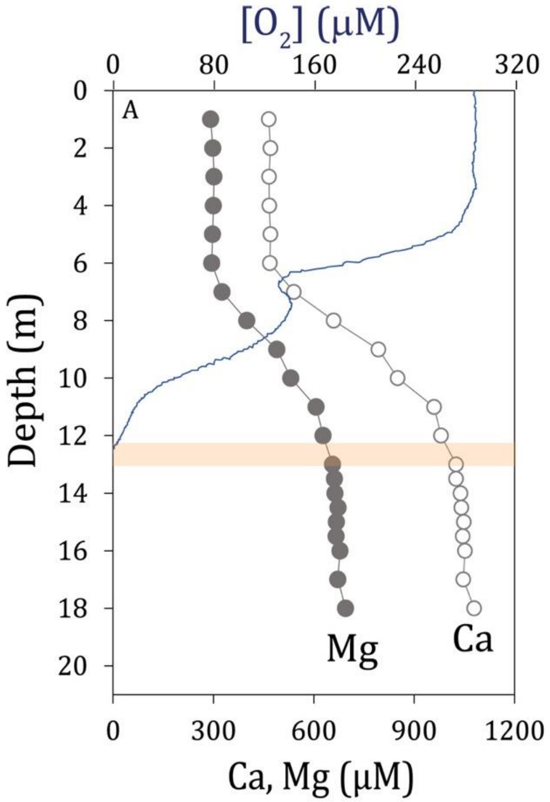




- The catchment basin is characterized by sulfate-containing rocks.
- Weathering processes transport significant amounts of sulfate into Lake Cadagno.
- Underwater springs feed substantial amounts of leached sulfate into the hypolimnion of lake Cadagno (crenogenic meromixis). This sulfate-rich, heavier 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).

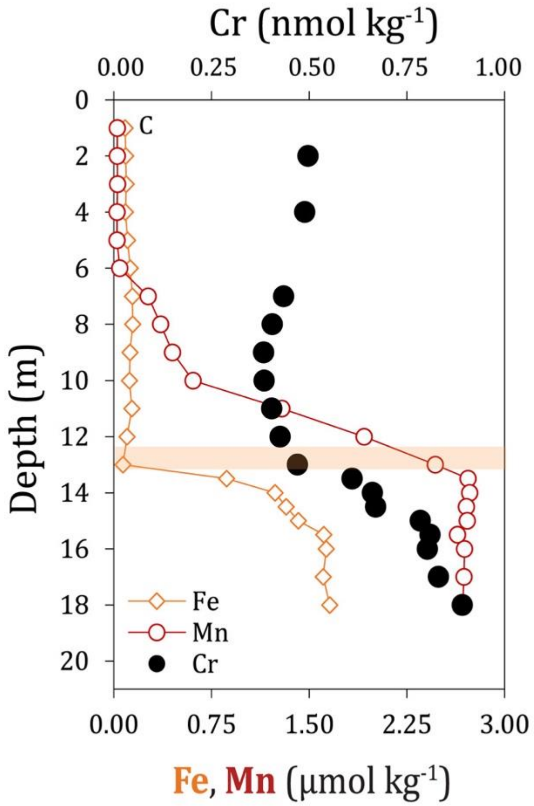
a. Why do bottom waters become anoxic?

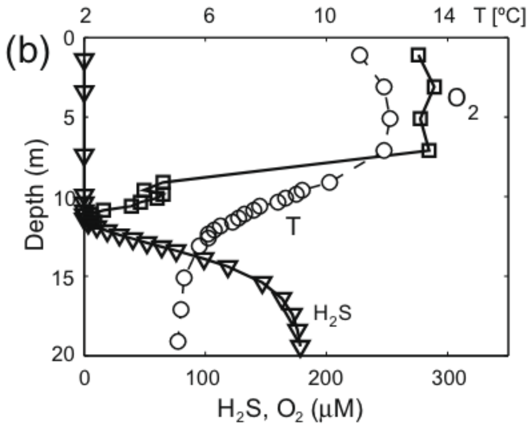
b. What differences in water chemistry do you expect for these two layers?

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

EPFL

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.*

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)

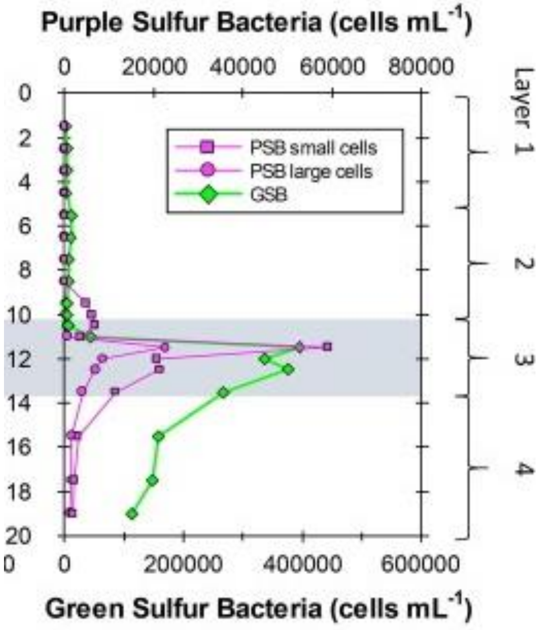
  $HCO_3^- + 4Fe^{2+} + 10H_2O + hv = CH_2O + 4Fe(OH)_3 + 7H^+$

  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

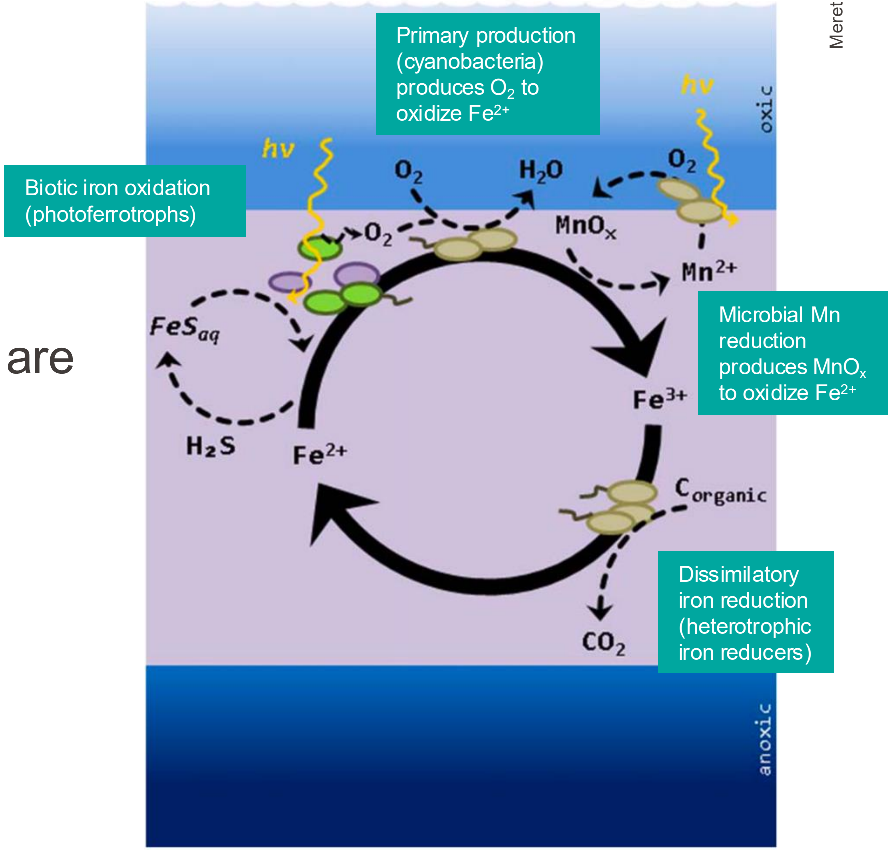
  $C_2H_3O_2^- + 8Fe^{3+} + 4H_2O = 2HCO_3^- + 2Fe^{2+} + 2H^+$

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

  Heterotrophic iron-reducing bacteria

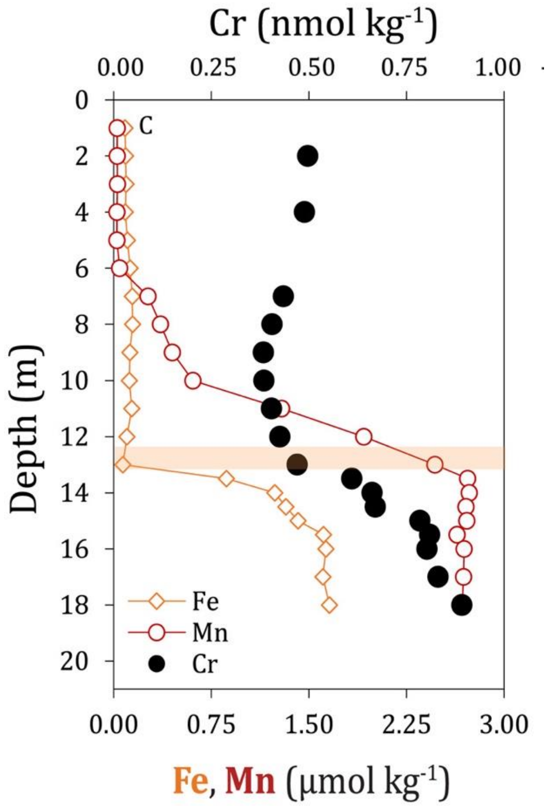
Iron cycling at the chemocline

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



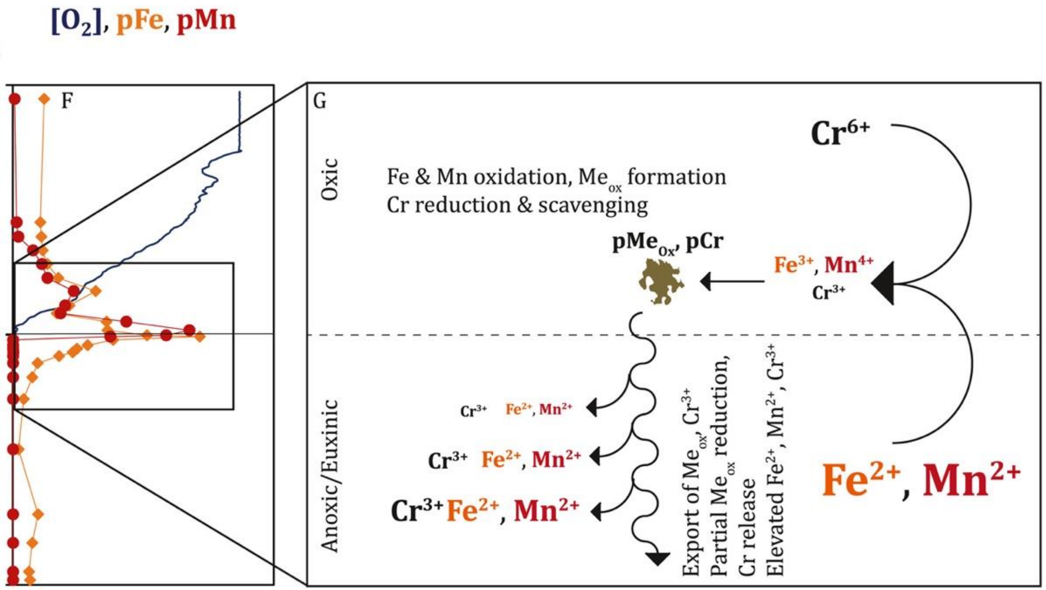
We can explain the Fe and Mn trends with the redox profile. But what about Cr?

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.

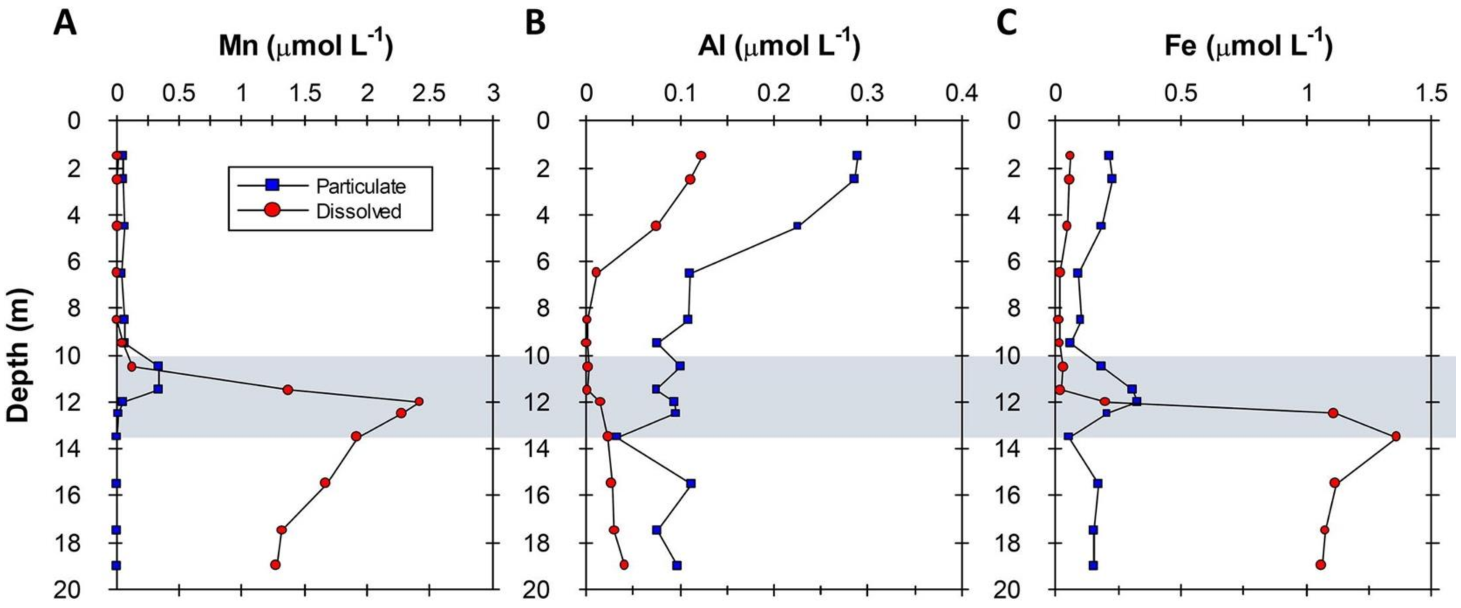
Redox processes at the chemocline



- 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.*

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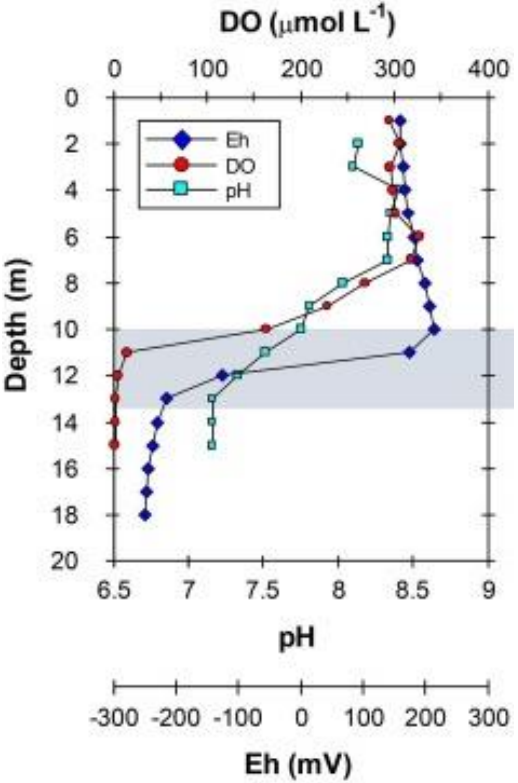
Iron redox processes

- 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?
- Which phases are precipitating?



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

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 used geochemical modeling to make sense of some of the water column data for Lake Cadagno reported in the literature.