# Application of chlorine and bromine stable isotope variations in understanding aqueous fluids in sedimentary basins

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# Summary of talk

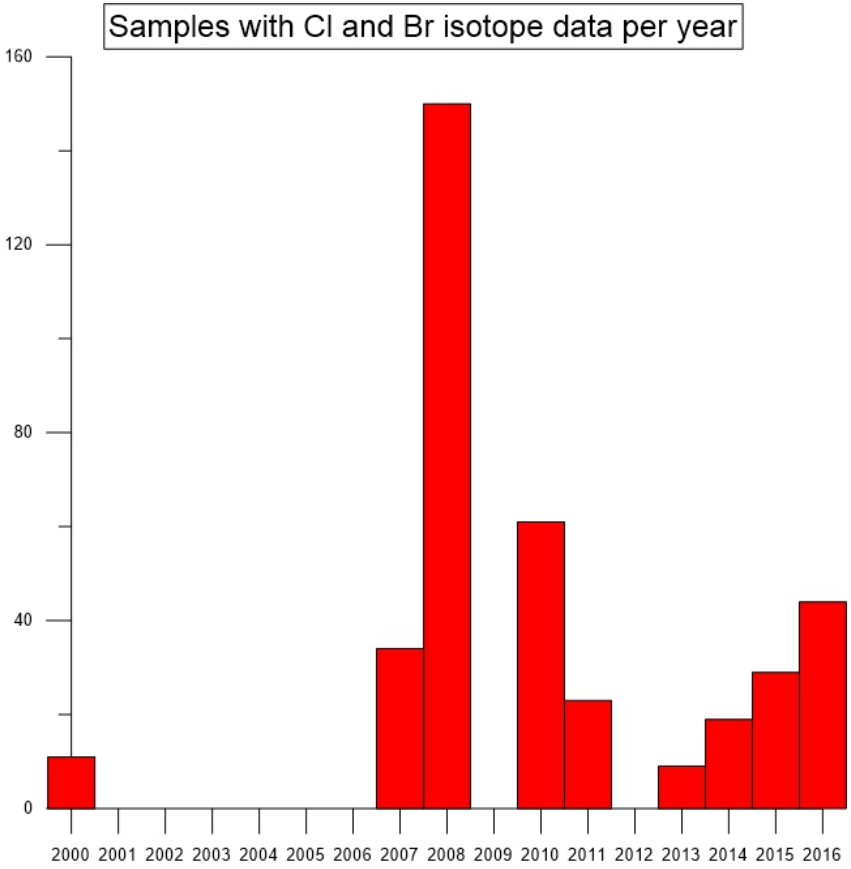
- Short recall of the previous talk
- Overview of research that applied both Br and Cl isotopes
- Indicative results of these studies
- Application of Br and Cl isotopes in two case studies, Oseberg (NO) and Kangan (IR)
- Planning of research on combined Br / Cl isotope geochemistry at the IPGP

# From experiment to observation

- In the previous talk we discussed processes that fractionate Cl and Br isotopes
- In the current talk we present examples of research that applied both Br and Cl isotopes in different water types, mainly in sedimentary basins
- We will see that, even though the origin of the variations is not always well understood, these isotopes can be used for water charactisation

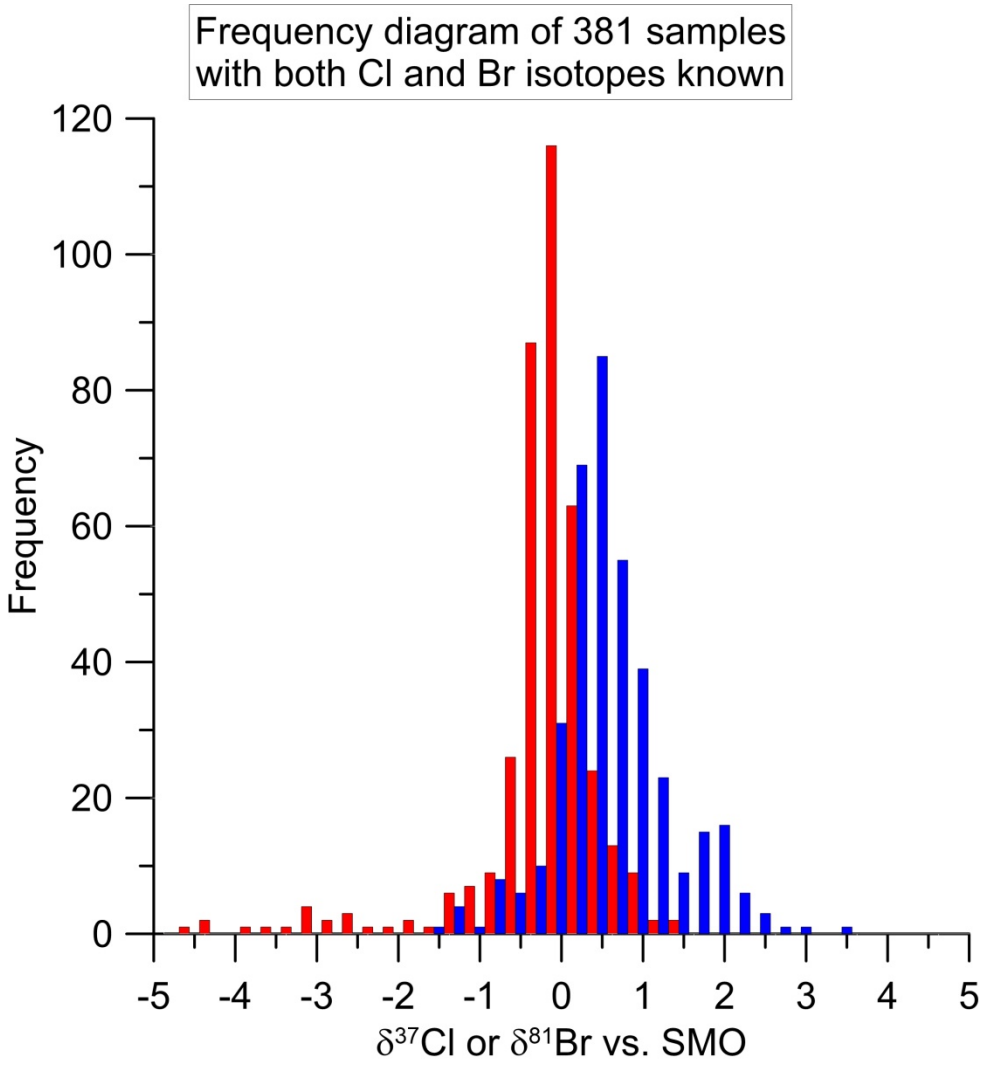
# Isotope studies

- 14 studies are known to us in which both Cl and Br isotope values of the samples were measured
- A total of 381 samples published in these studies have both their Br and Cl isotope compositions measured

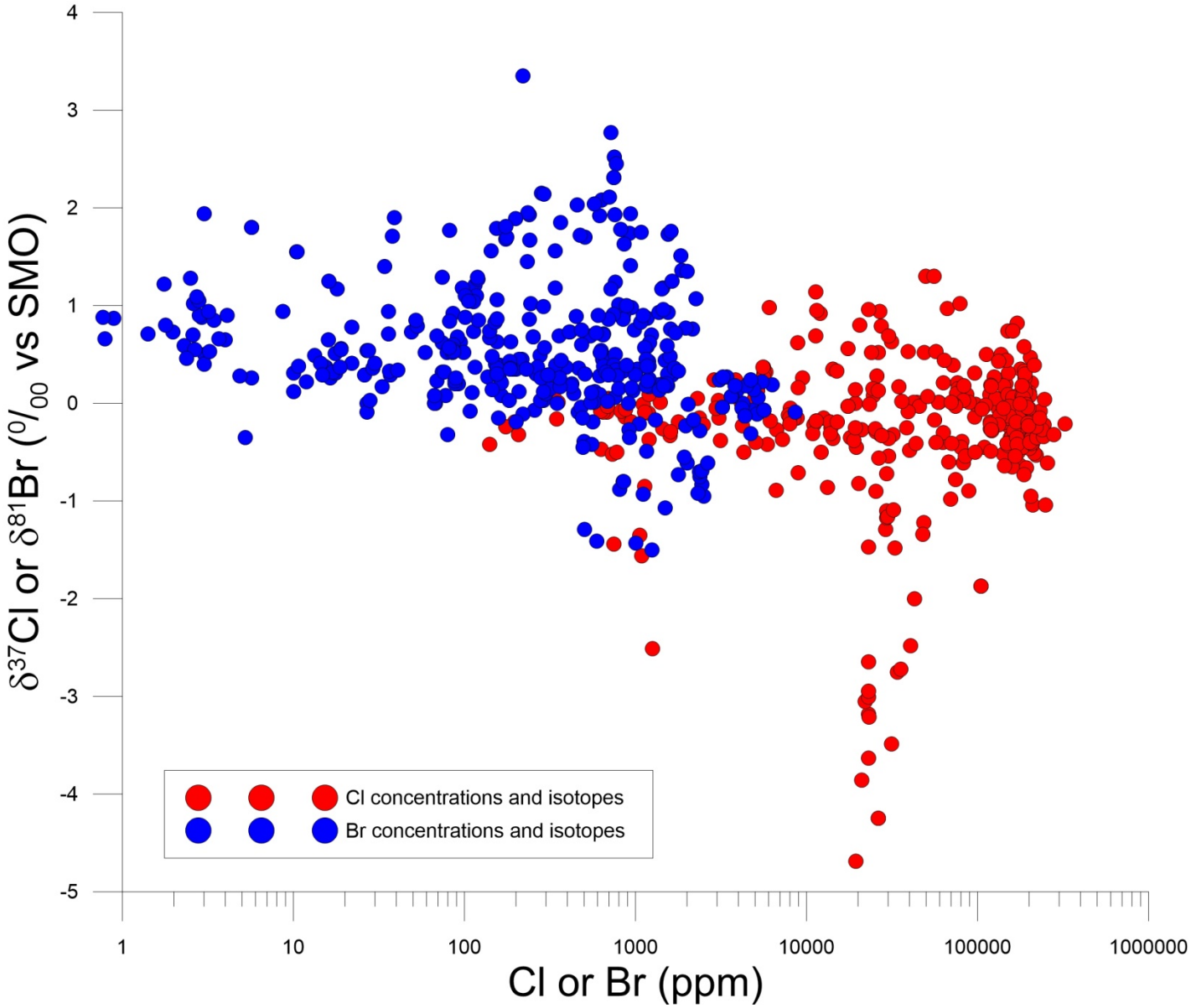


# Isotope distribution

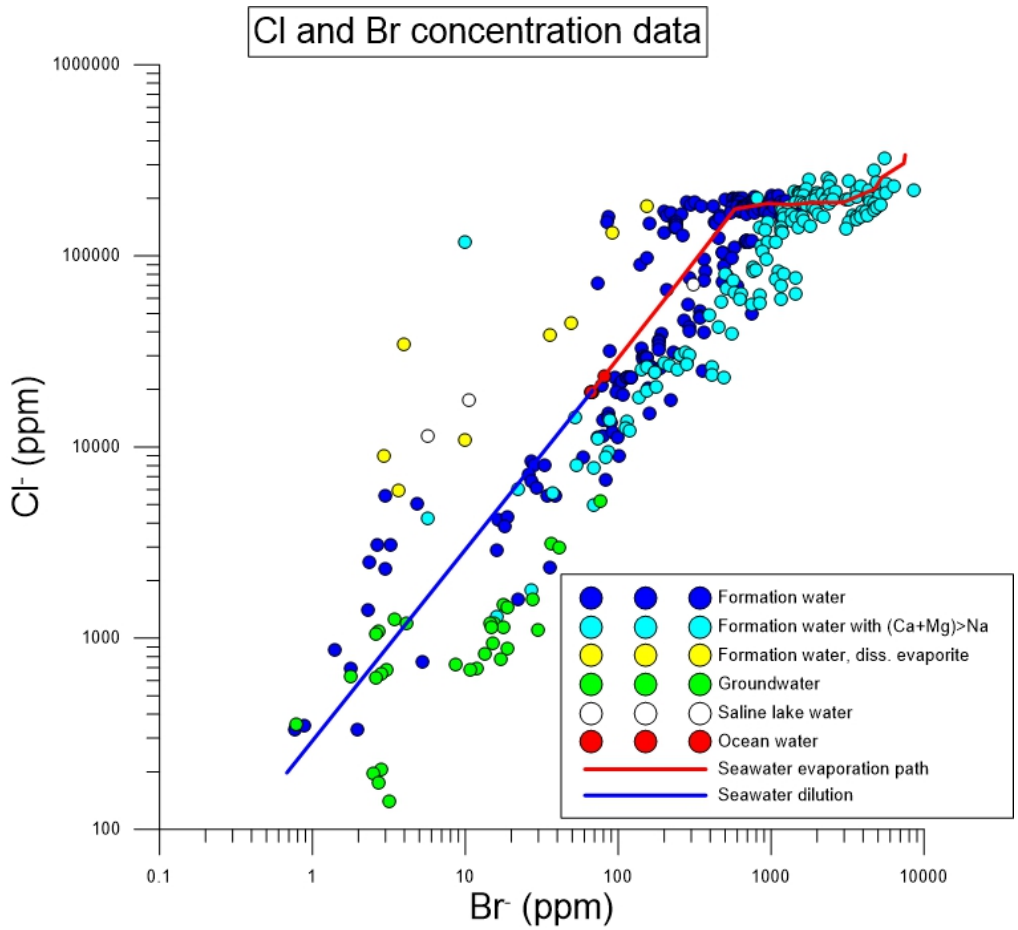
- The oceans are very large and homogeneous reservoirs for both $Cl^-$ and $Br^-$
- That is why they are used as standard with by definition a value of 0‰
- Isotope distributions for Cl and Br are very different

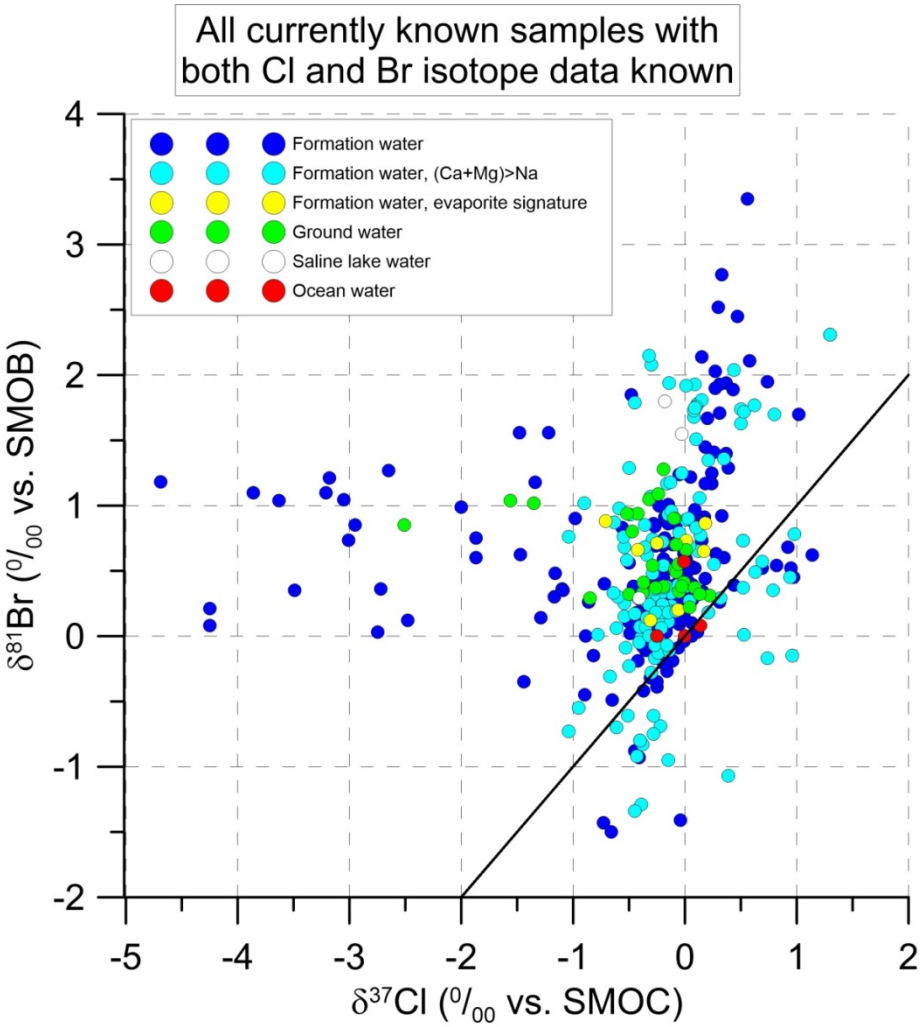


# Combined with isotopes…

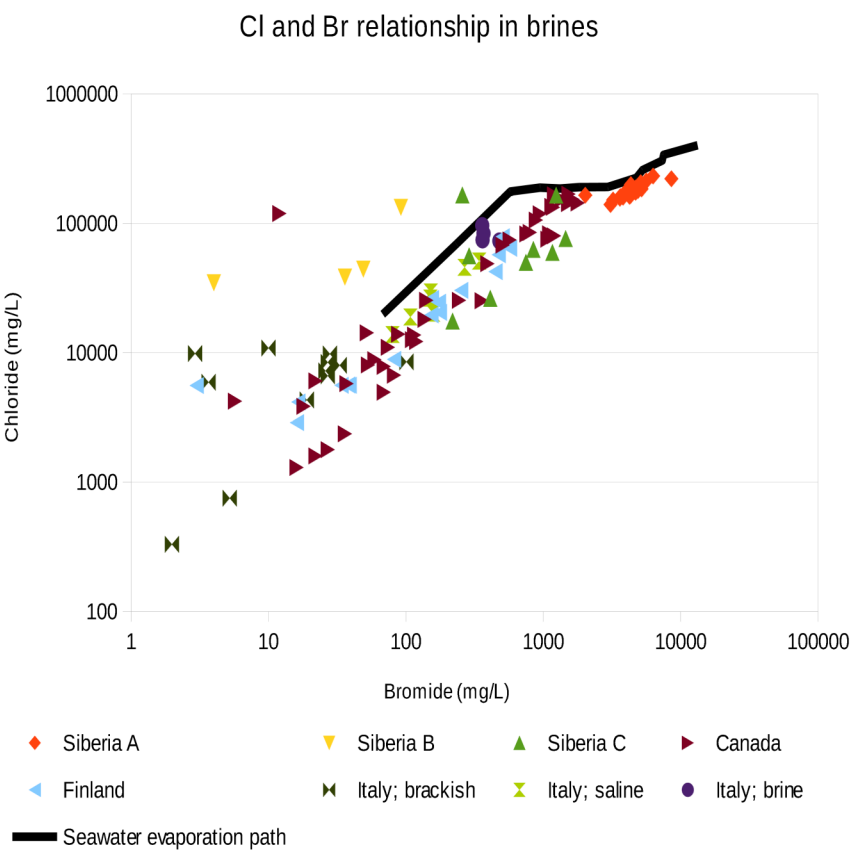


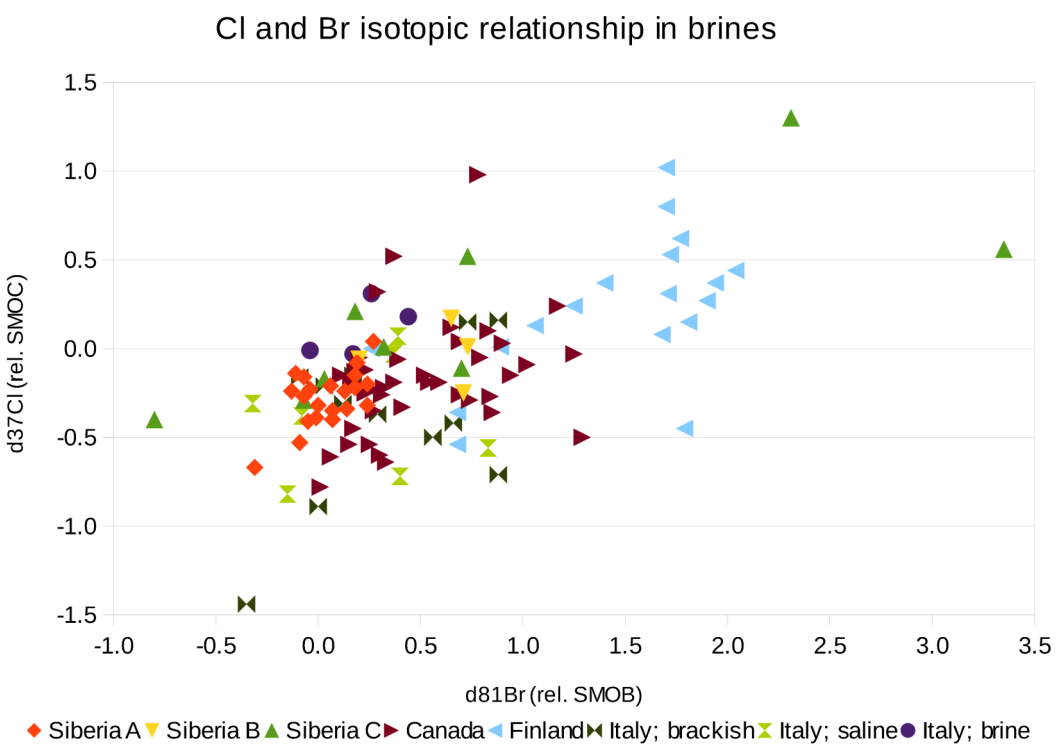
# Behaviour of Cl and Br during evaporation and dilution



# Cl and Br data in different basins



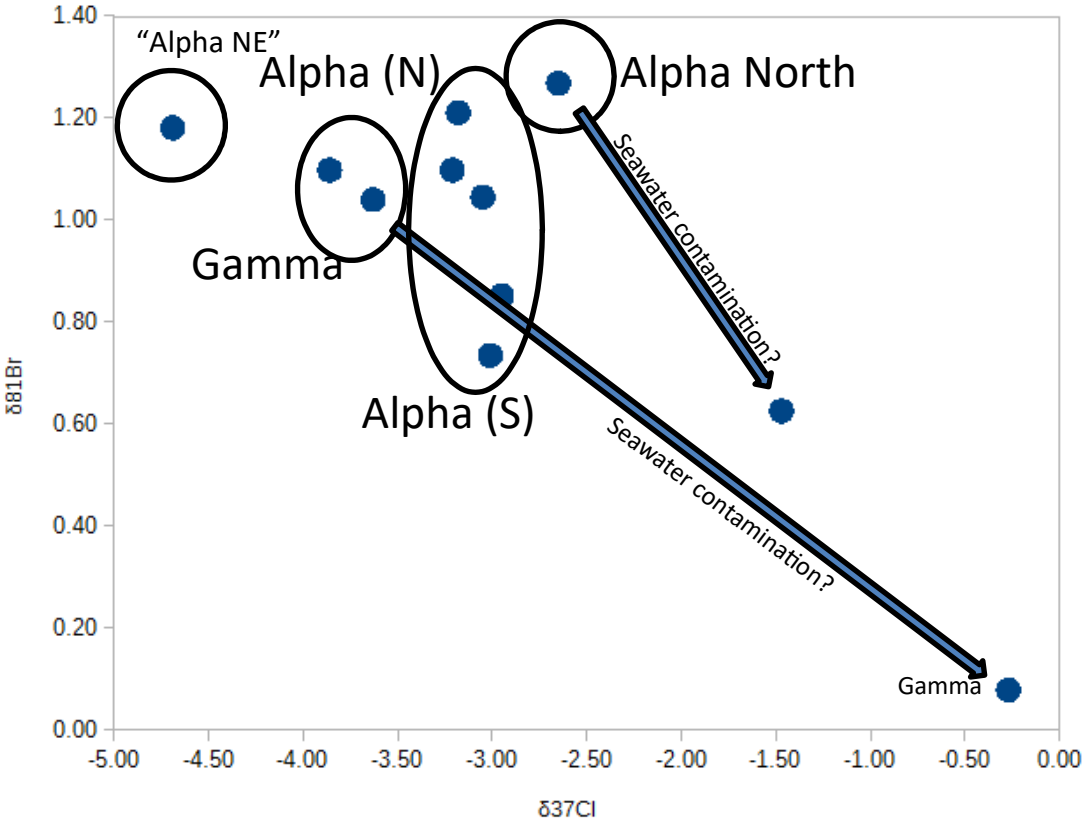



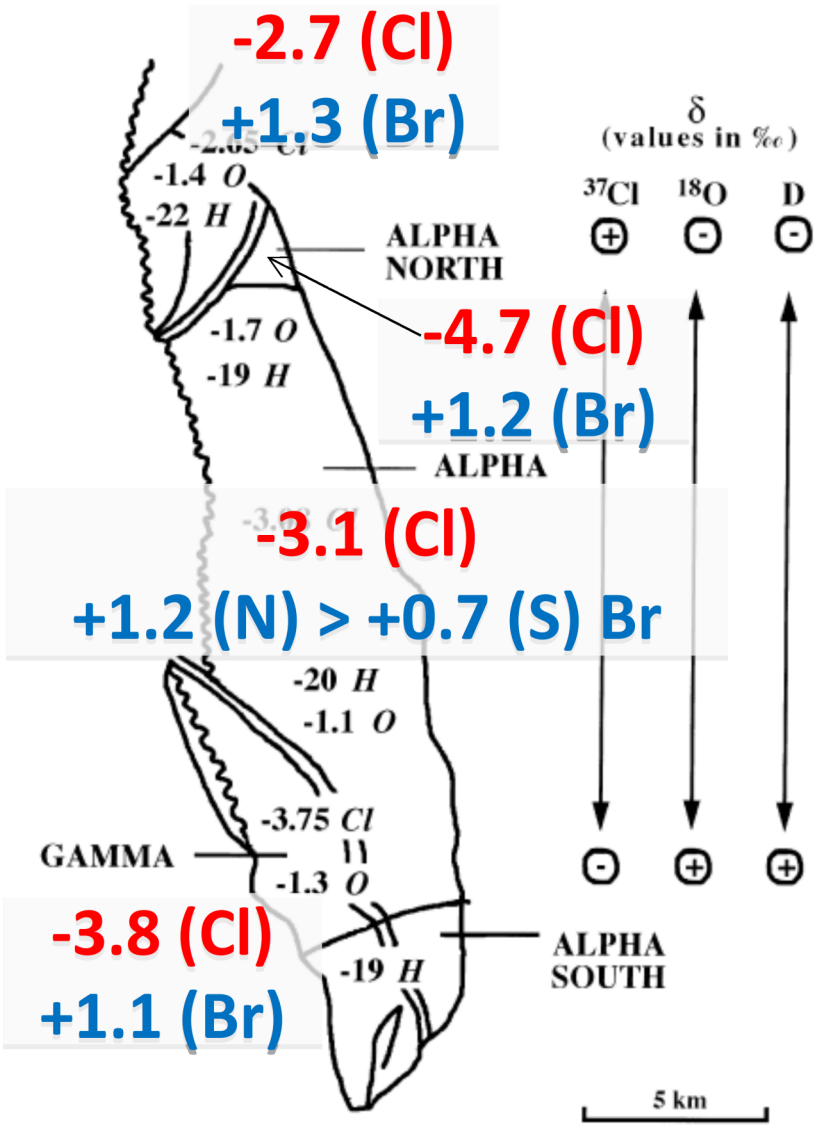
# Case studies

# North sea oil-filed application

- The Oseberg oil field is on the Norwegian Continental Shelf
- Cl and Br isotopes have been used to get information on the aquifer waters in this reservoir
- Clear groups can be recognised in different parts of the field separated by faults
- However, the origin of especially the extreme Cl isotope values remain unexplained

# Cl and Br isotope characterisation

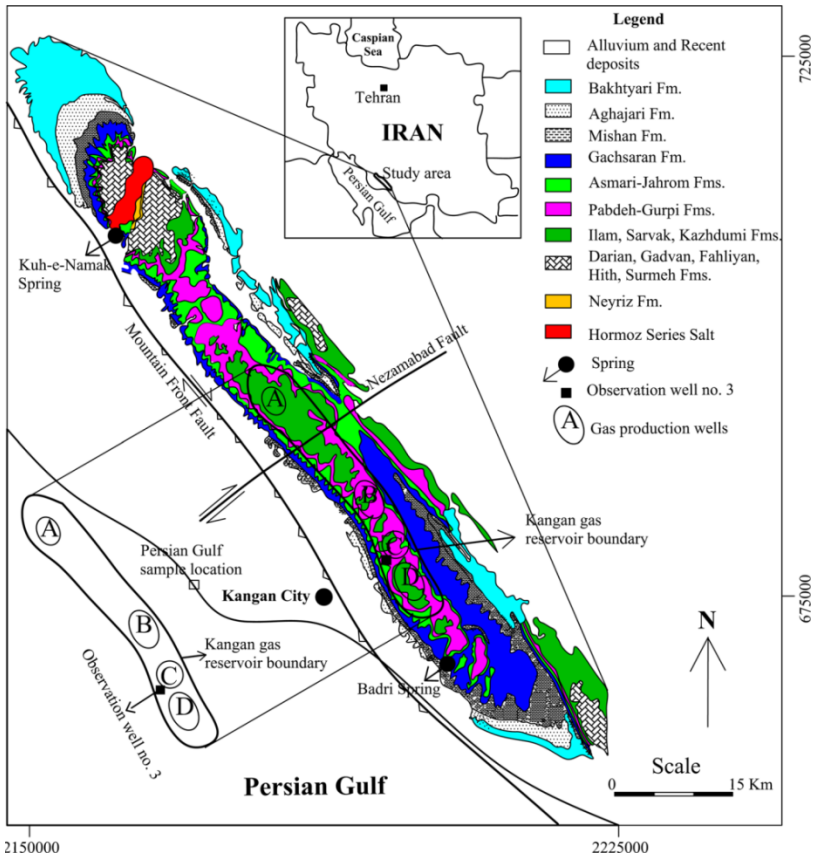


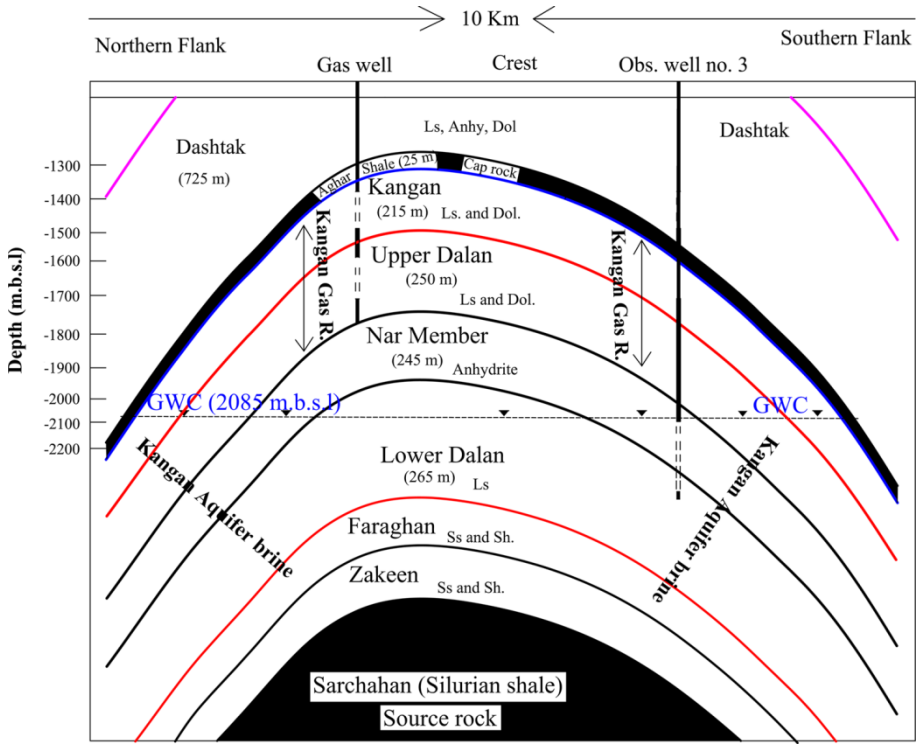



# Application in a carbonate reservoir

- The Kangan gasfield is a large gas producing reservoir in Southern Iran
- It produces natural gas since 1994
- Originally the produced water was fresh in all wells
- Salinity increased gradually in some of the wells, leading to corrosion of pipes and reduced gas yields
- Increased salinity during production may be:
  - Mixing with aquifer water
  - Halite dissolution
  - Evaporation
  - (Ion) filtration

# The Kangan gasfield

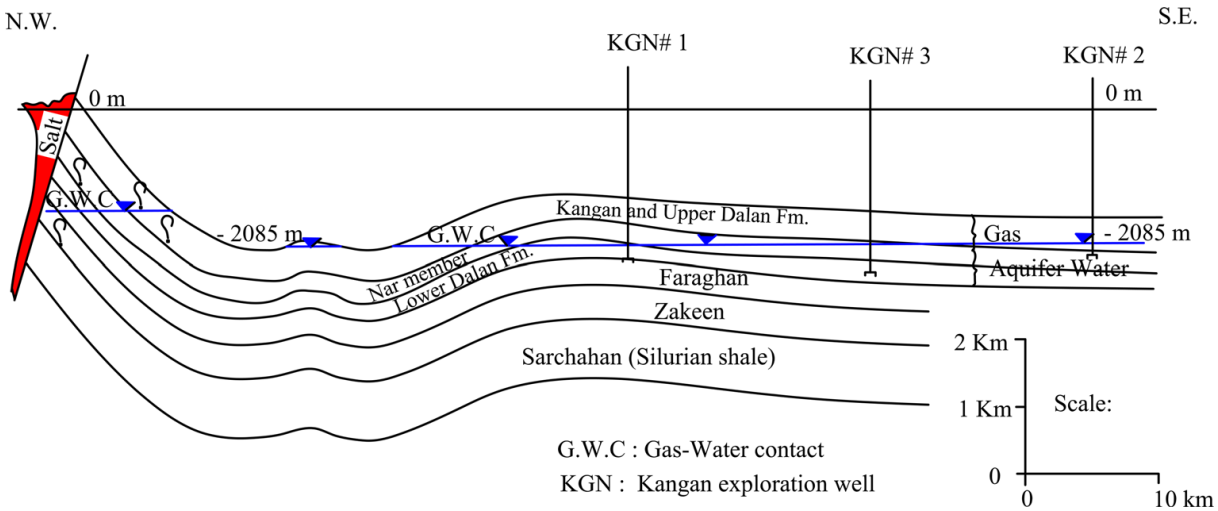


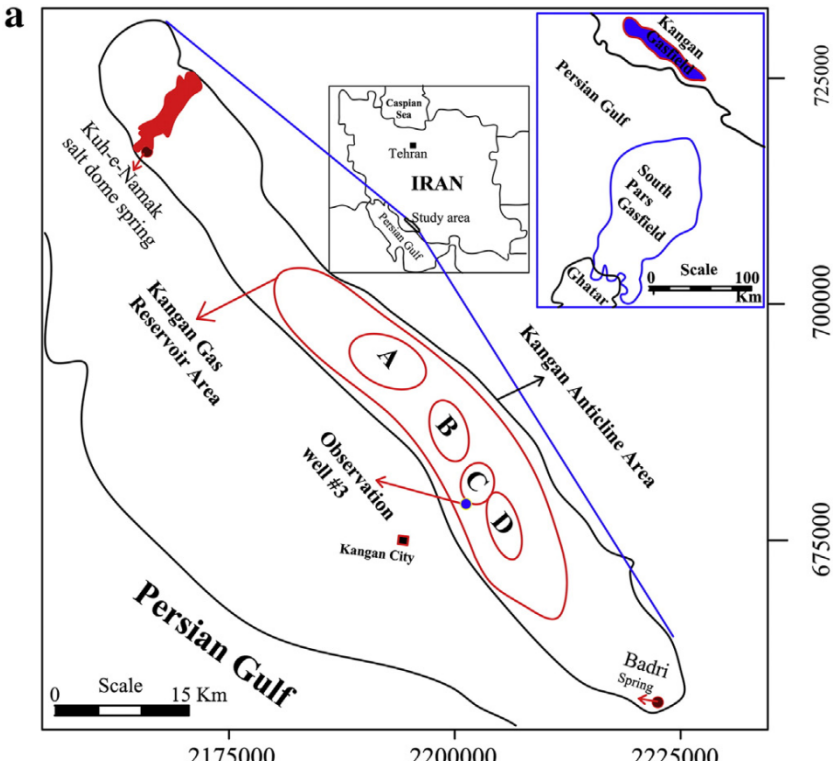




Source is Sarchahan formation
Reservoir in Kangan and
Upper Dalan formations

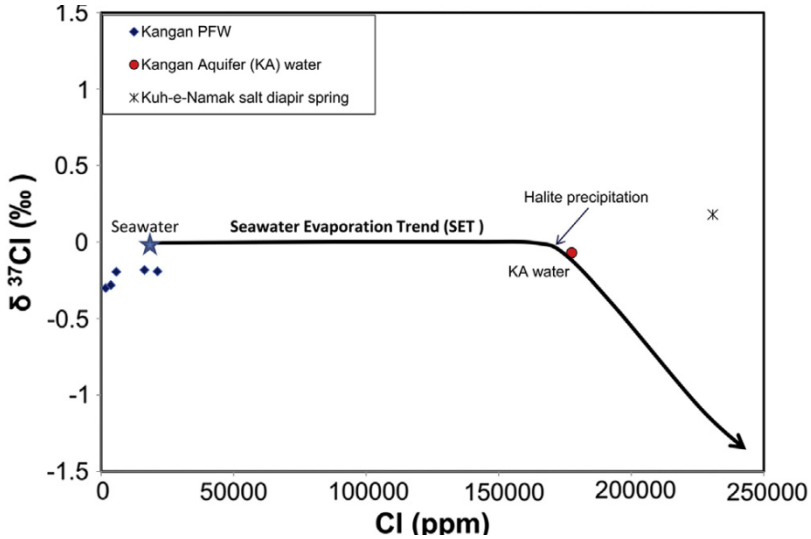
# The suspected salt dome

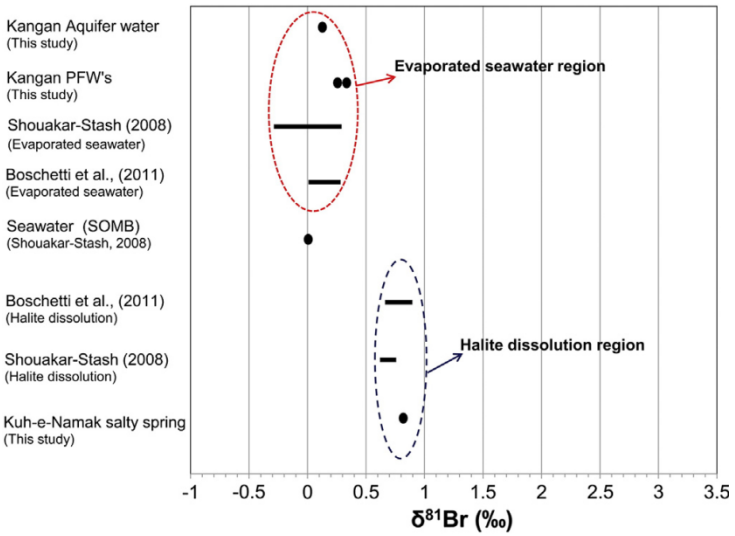
- Possible salt dome is the origin of salinity



# Results of Cl and Br isotopes




- Cl isotopes are close to 0 in the range of seawater, residual evaporation brine and aquifer water, no evidence for effects as ion-filtration, ion exchange or diffusion
- Br isotopes preclude halite dissolution, and have an evaporated seawater composition

# Combination of isotopes with chemistry

- Cl and Br isotopes confirm observations on the water chemistry and other isotopes (O, Sr)
- The chemistry indicates that the origin of the increased salinity is not the aquifer water but Permo-Triassic evaporated seawater after water-rock interaction
- This is confirmed by the Cl and Br isotope data

# Current status on Cl isotopes

- Processes that fractionate Cl isotopes are now reasonably well understood
- Ion / membrane filtration processes are not yet well understood but considered important causes for isotope fractionation in formation waters
- Extremely low $\delta^{37}Cl$ values in (mostly) North Sea formation waters not explained yet
- Data obtained can be used to explain processes between end-members even while the origin of the end-members may not be understood

# Current status on Br isotopes

- Processes that fractionate Br isotopes have hardly been studied, except diffusion and simple salt precipitation
- Most studies done on highly concentrated formation waters
- Methods to analyse small amounts are developed in a few labs the last years, so there is space for a fast development now

# Comparison of Cl with Br

- In natural environments both Cl and Br are present as halide ion (chloride or bromide)
- Both concentrate in aqueous solution
- Both are normally considered “conservative”

There are differences in their isotope effects, mostly because their mass difference en fractionation factors for Cl are 2 to 5 times larger than for Br

# Consequences

- Following this we would expect that:
  - The isotope variation for Br would be (much) smaller than the isotoep variation for Cl
  - This is not the case. Although the total variation may be smaller (-1.5 > +3.5 vs. -4.5 > +1.5), 80% of samples are between -0.1 > +1.5 (Br) or -1.2 > +0.4 (Cl), indicating a comparable variation for both
  - Interestingly, while Cl prefers to be **negative**, Br prefers to be **positive**

# Causes for these differences

- It is suggested here that:
- Because $Br^-$ is considerably easier to oxidise than $Cl^-$
  - It is known that certain plants in salt marsh environments produce $CH_3X$ from $X^-$
  - $CH_3Br$ is produced perhaps 100 times more efficient than $CH_3Cl$ by these plants
- It is possible that the overall fractionation effect is larger than for Cl

# Planned development at IPGP

- The next few years we plan to extend our knowledge on Br isotopes in comparison with Cl isotopes
- This is done through experimental work as well as analyses on natural samples
- All work will be done on both isotope systems to be able to compare the effects on both

# Planned research (1)

- Evaporites
  - Following the successful determination of fractionation factors in single salt solutions we will determine fractionation in seawater of different compositions (taking into account historical variations)
  - Analyse different stages within one salt deposit ($NaCl > KCl > MgCl_2$)
  - Analyse salt deposits from different ages between recent and Neoproterozoic

# Planned research (2)

- Understanding the behaviour of Br and Cl isotopes in ion-filtration processes.
  - To understand processes in deep aquifers
- Br and Cl isotope fractionation during oxidation processes.
  - To understand the isotope fractionation as well as the efficiency of the process. We hope that this may explain why Br isotope data tend to be positive relative to ocean bromide

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