Chlorine Isotopes in Groundwaters

A Unique Diffusion Tracer

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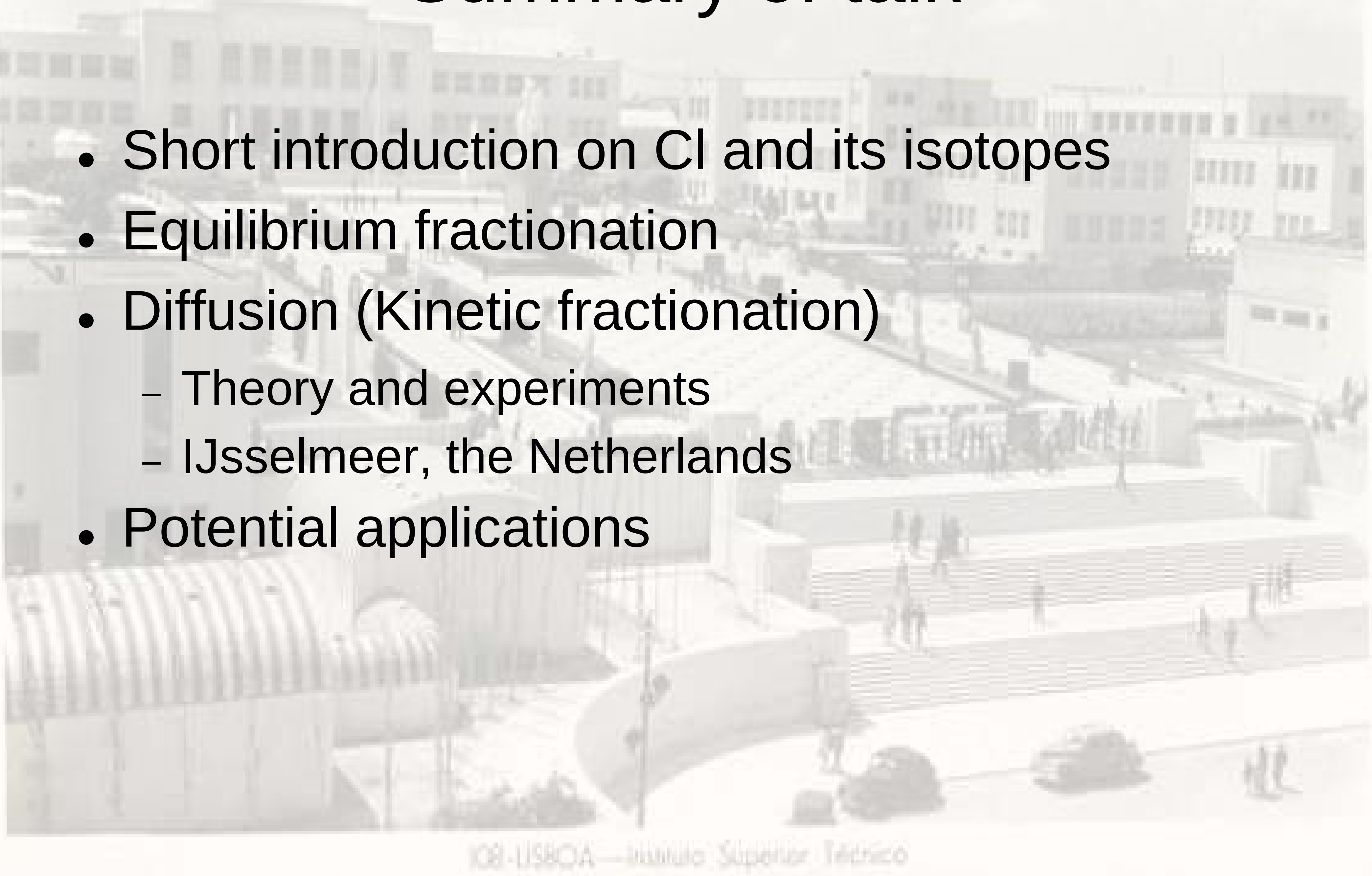
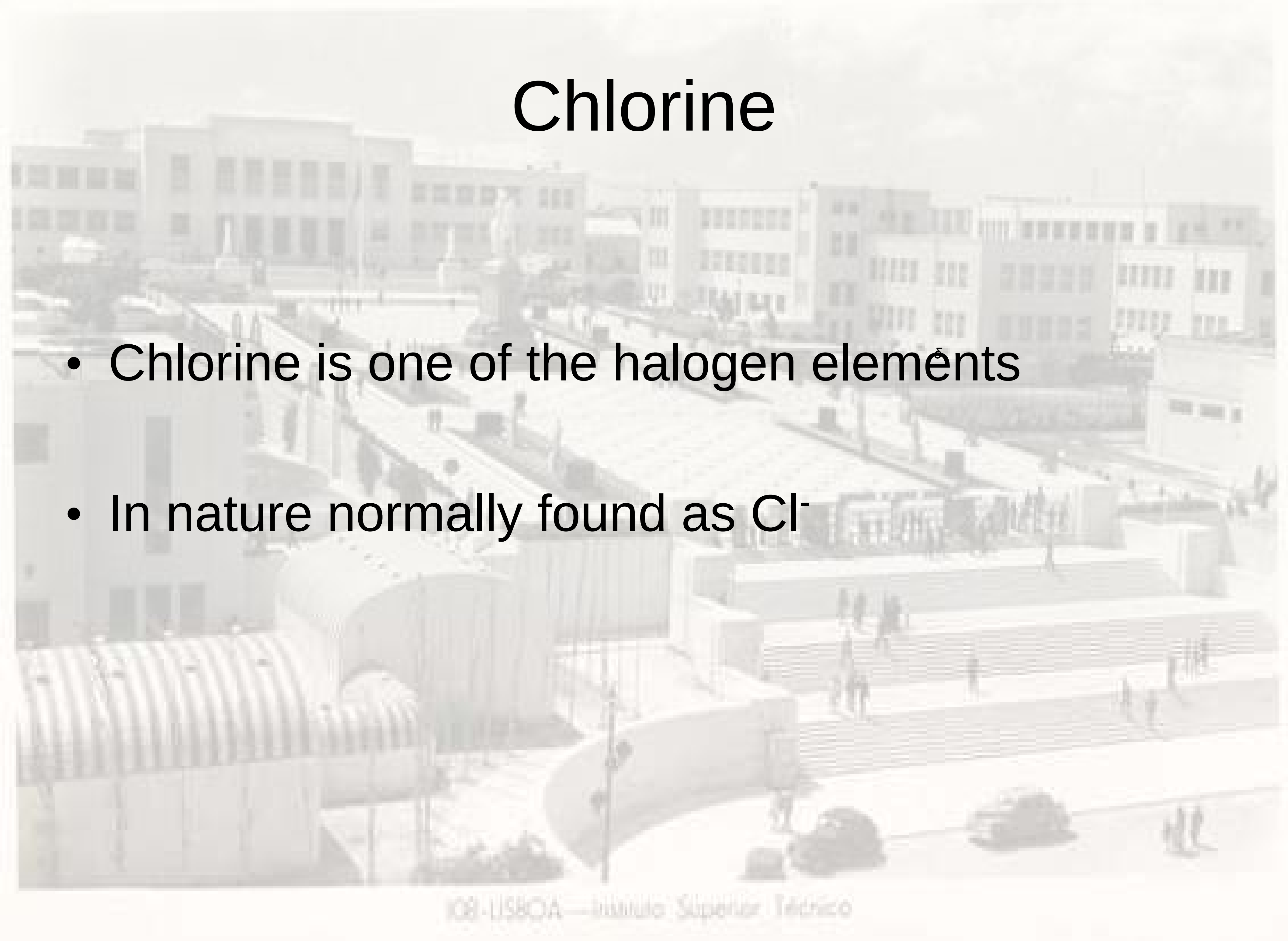
Summary of talk

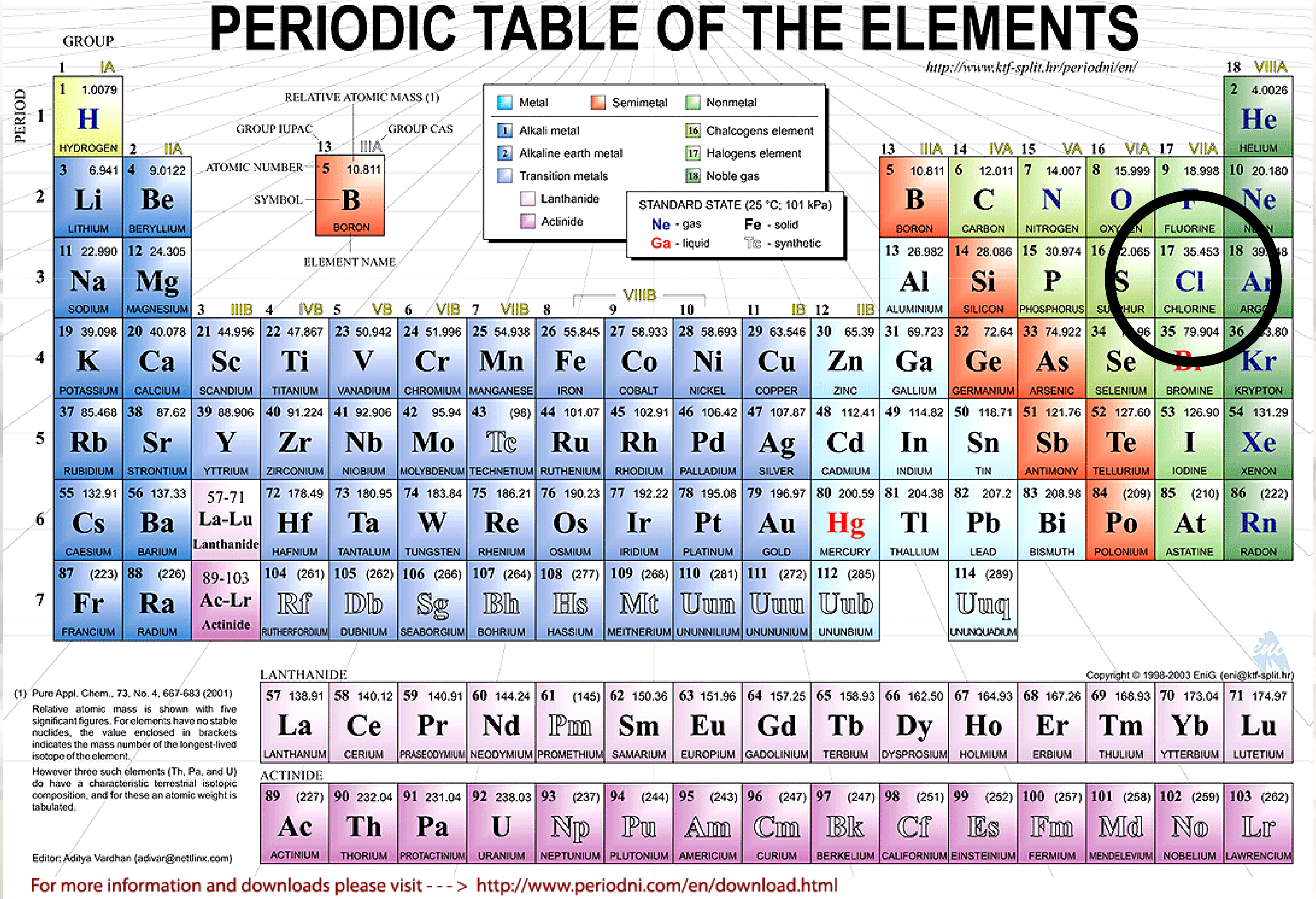


- Short introduction on Cl and its isotopes
- Equilibrium fractionation
- Diffusion (Kinetic fractionation)
  - Theory and experiments
  - IJsselmeer, the Netherlands
- Potential applications

Chlorine



- Chlorine is one of the halogen elements
- In nature normally found as Cl^-



PERIODIC TABLE OF THE ELEMENTS

http://www.ktf-split.hr/periodni/en/

RELATIVE ATOMIC MASS (1)
GROUP IUPAC
GROUP CAS
ATOMIC NUMBER
SYMBOL
ELEMENT NAME

13 IIIA
5 10.811
B
BORON

- 🟦 Metal
- 🟥 Semimetal
- 🟩 Nonmetal
- 1 Alkali metal
- 2 Alkaline earth metal
- Transition metals
- Lanthanide
- Actinide
- 16 Chalcogens element
- 17 Halogens element
- 18 Noble gas

STANDARD STATE (25 °C; 101 kPa)
Ne - gas
Ga - liquid
Fe - solid
Tc - synthetic

PERIOD \ GROUP	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.0079 H HYDROGEN																	2 4.0026 He HELIUM
2	3 6.941 Li LITHIUM	4 9.0122 Be BERYLLIUM											5 10.811 B BORON	6 12.011 C CARBON	7 14.007 N NITROGEN	8 15.999 O OXYGEN	9 18.998 F FLUORINE	10 20.180 Ne NEON
3	11 22.990 Na SODIUM	12 24.305 Mg MAGNESIUM											13 26.982 Al ALUMINIUM	14 28.086 Si SILICON	15 30.974 P PHOSPHORUS	16 32.065 S SULPHUR	17 35.453 Cl CHLORINE	18 39.948 Ar ARGON
4	19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	21 44.956 Sc SCANDIUM	22 47.867 Ti TITANIUM	23 50.942 V VANADIUM	24 51.996 Cr CHROMIUM	25 54.938 Mn MANGANESE	26 55.845 Fe IRON	27 58.933 Co COBALT	28 58.693 Ni NICKEL	29 63.546 Cu COPPER	30 65.39 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.96 Se SELENIUM	35 79.904 Br BROMINE	36 83.80 Kr KRYPTON
5	37 85.468 Rb RUBIDIUM	38 87.62 Sr STRONTIUM	39 88.906 Y YTTRIUM	40 91.224 Zr ZIRCONIUM	41 92.906 Nb NIOBIUM	42 95.94 Mo MOLYBDENUM	43 (98) Tc TECHNETIUM	44 101.07 Ru RUTHENIUM	45 102.91 Rh RHODIUM	46 106.42 Pd PALLADIUM	47 107.87 Ag SILVER	48 112.41 Cd CADMIUM	49 114.82 In INDIUM	50 118.71 Sn TIN	51 121.76 Sb ANTIMONY	52 127.60 Te TELLURIUM	53 126.90 I IODINE	54 131.29 Xe XENON
6	55 132.91 Cs CAESIUM	56 137.33 Ba BARIUM	57-71 La-Lu Lanthanide	72 178.49 Hf HAFNIUM	73 180.95 Ta TANTALUM	74 183.84 W TUNGSTEN	75 186.21 Re RHENIUM	76 190.23 Os OSMIUM	77 192.22 Ir IRIDIUM	78 195.08 Pt PLATINUM	79 196.97 Au GOLD	80 200.59 Hg MERCURY	81 204.38 Tl THALLIUM	82 207.2 Pb LEAD	83 208.98 Bi BISMUTH	84 (209) Po POLONIUM	85 (210) At ASTATINE	86 (222) Rn RADON
7	87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89-103 Ac-Lr Actinide	104 (261) Rf RUTHERFORDIUM	105 (262) Db DUBNIUM	106 (266) Sg SEABORGIUM	107 (264) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (268) Mt MEITNERIUM	110 (281) Uun UNUNNILIUM	111 (272) Uuu UNUNUNIUM	112 (285) Uub UNUNBIUM		114 (289) Uuq UNUNQUADIUM				

LANTHANIDE

57 138.91 La LANTHANUM	58 140.12 Ce CERIUM	59 140.91 Pr PRASEODYMIUM	60 144.24 Nd NEODYMIUM	61 (145) Pm PROMETHIUM	62 150.36 Sm SAMARIUM	63 151.96 Eu EUROPIUM	64 157.25 Gd GADOLINIUM	65 158.93 Tb TERBIUM	66 162.50 Dy DYSPROSIUM	67 164.93 Ho HOLMIUM	68 167.26 Er ERBIUM	69 168.93 Tm THULIUM	70 173.04 Yb YTTERBIUM	71 174.97 Lu LUTETIUM

ACTINIDE

89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMERICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKELIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MENDELEVIUM	102 (259) No NOBELIUM	103 (262) Lr LAWRENCIUM

(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)
Relative atomic mass is shown with five significant figures. For elements have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.

However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

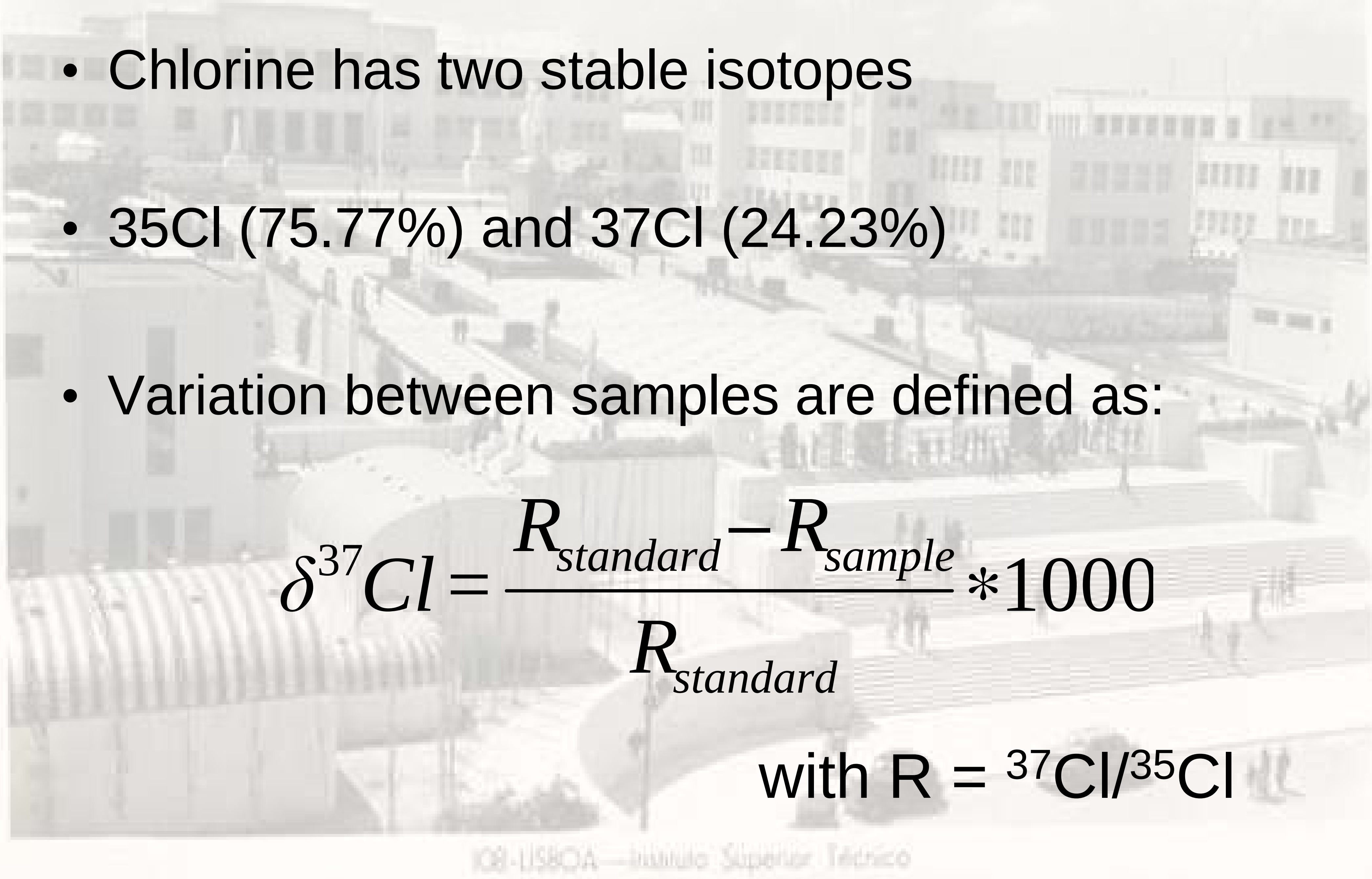
Editor: Aditya Vardhan (adivar@nettlinx.com)

Chlorine isotopes

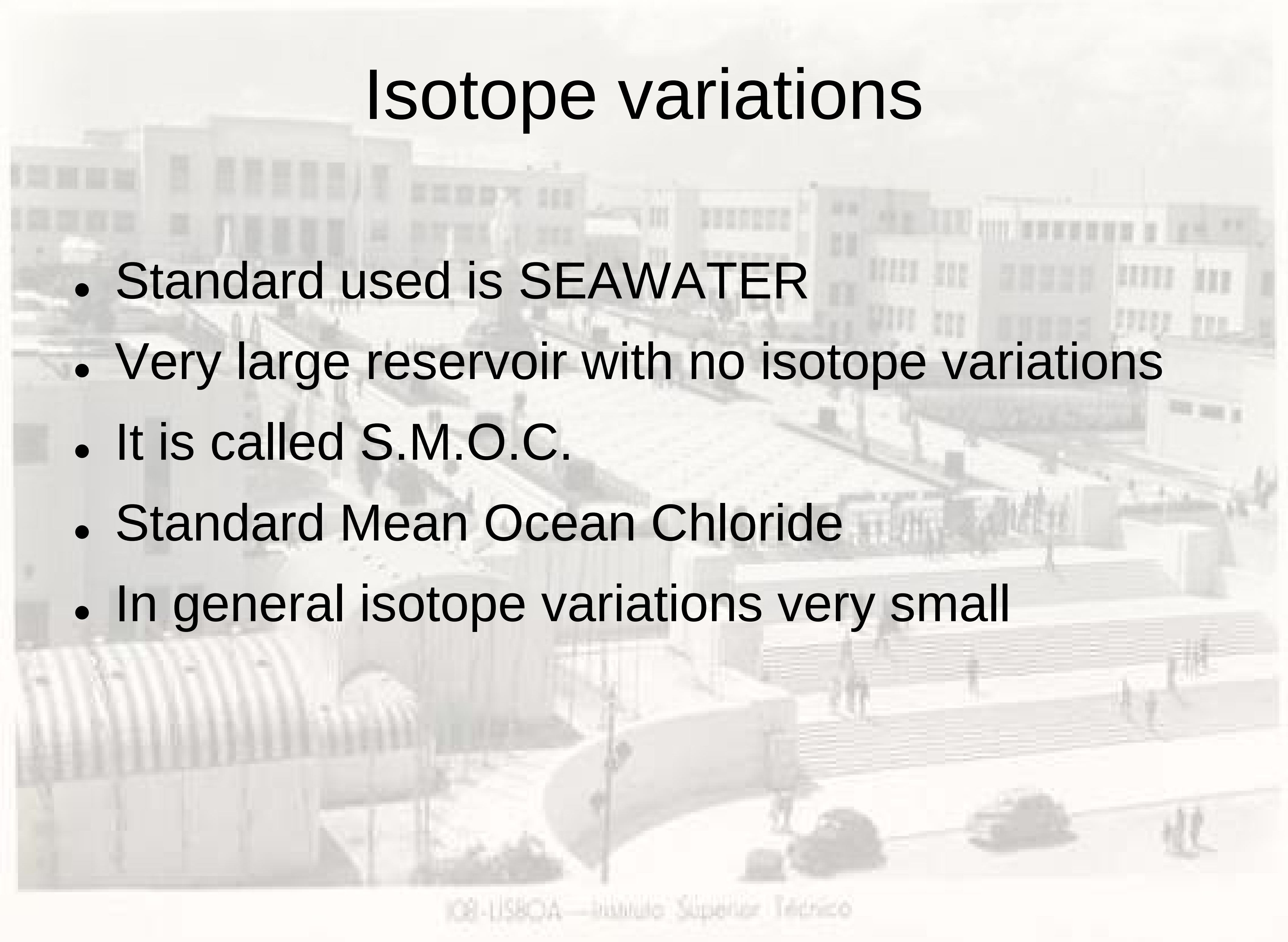
- Chlorine has two stable isotopes
- 35Cl (75.77%) and 37Cl (24.23%)
- Variation between samples are defined as:

$$\delta^{37}Cl = \frac{R_{standard} - R_{sample}}{R_{standard}} * 1000$$

with R = ^{37}Cl/^{35}Cl



Isotope variations



- Standard used is SEAWATER
- Very large reservoir with no isotope variations
- It is called S.M.O.C.
- Standard Mean Ocean Chloride
- In general isotope variations very small

Chlorine in the hydrological cycle

Equilibrium fractionation: Cl in evaporites (theory…)

- Small but significant fractionation in evaporites
- NaCl +0.26‰
- KCl: -0.09‰
- MgCl2: -0.06‰

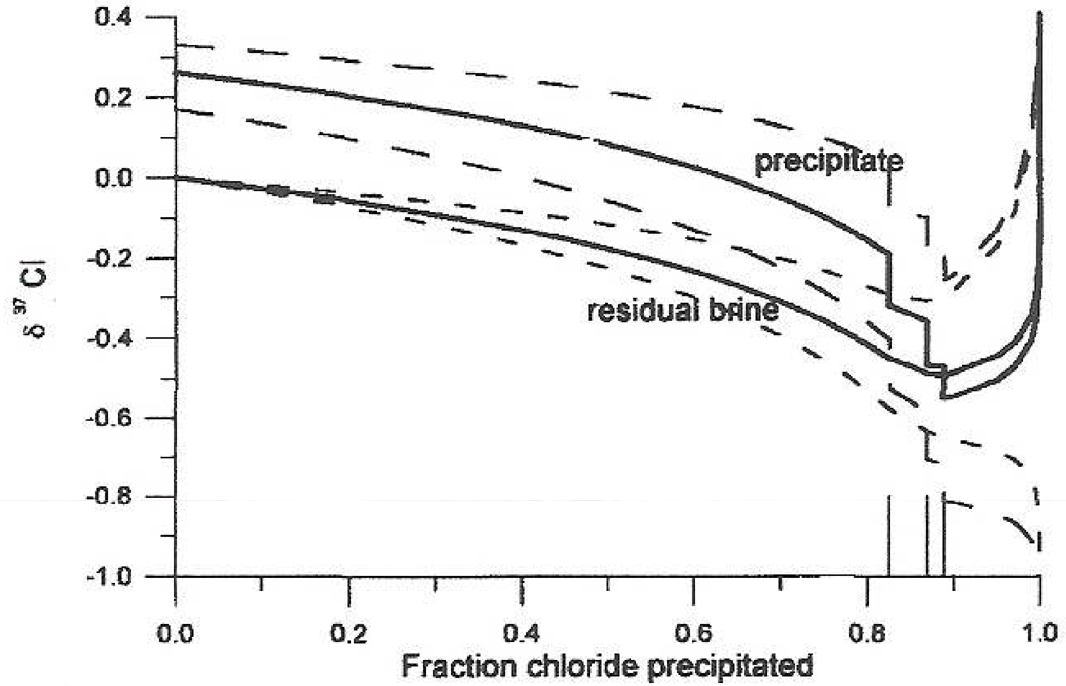


FIG. 1. Calculated δ^{37}Cl values of the precipitate and the remaining brine. The bold lines indicate the average values. The area between the short-dashed lines indicates the error for the residual brines and the area between the long-dashed lines indicates the error for the precipitates. Note the discontinuities in the curves for the precipitates.

(…and observed)

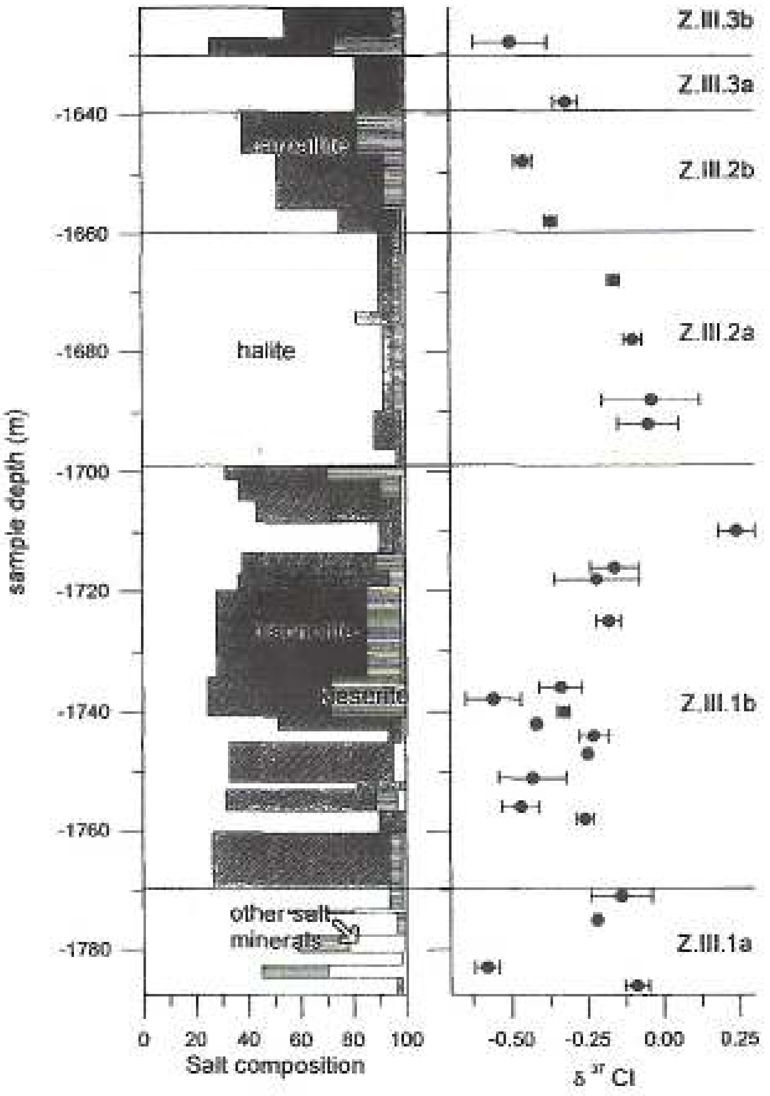
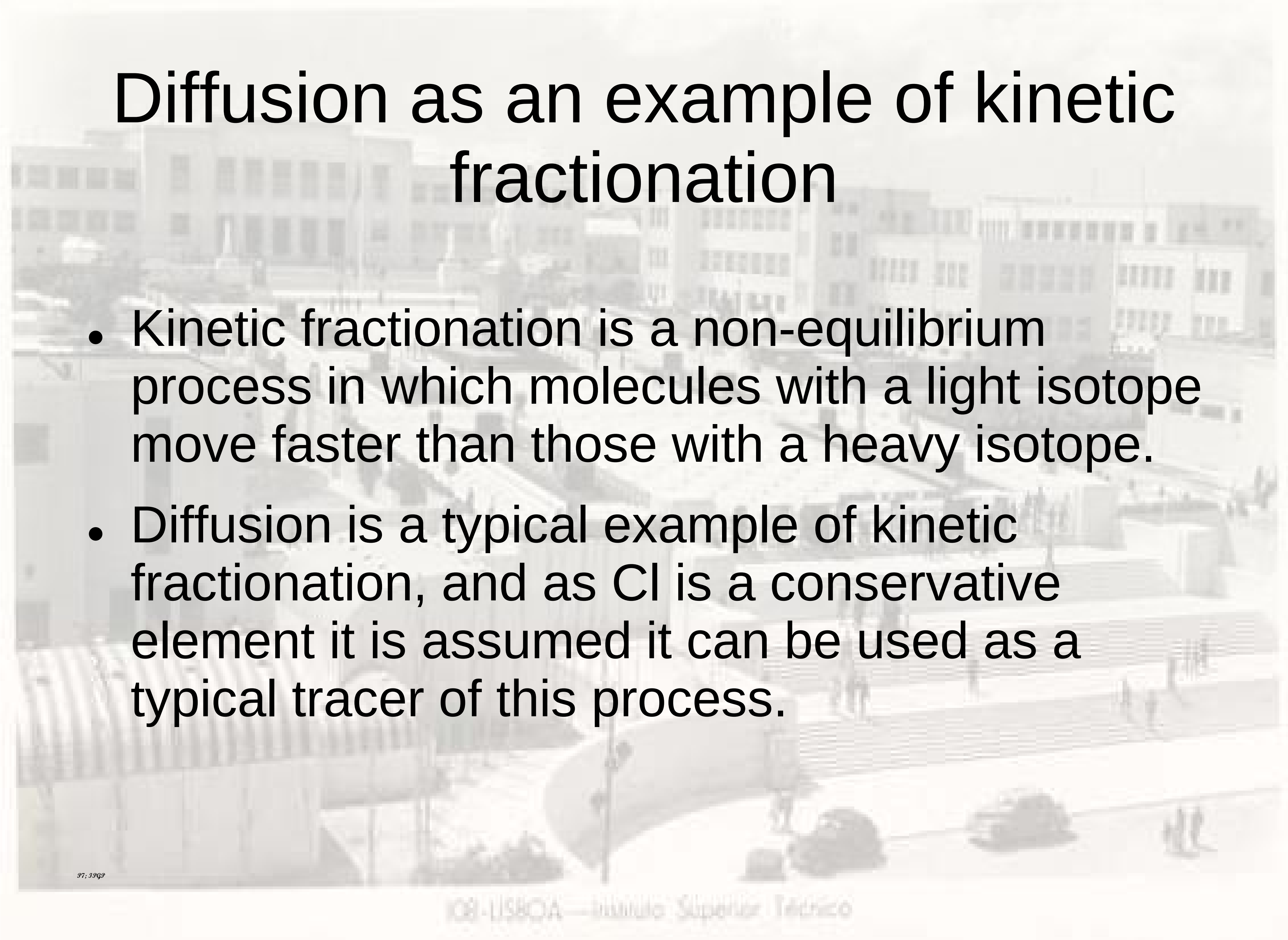


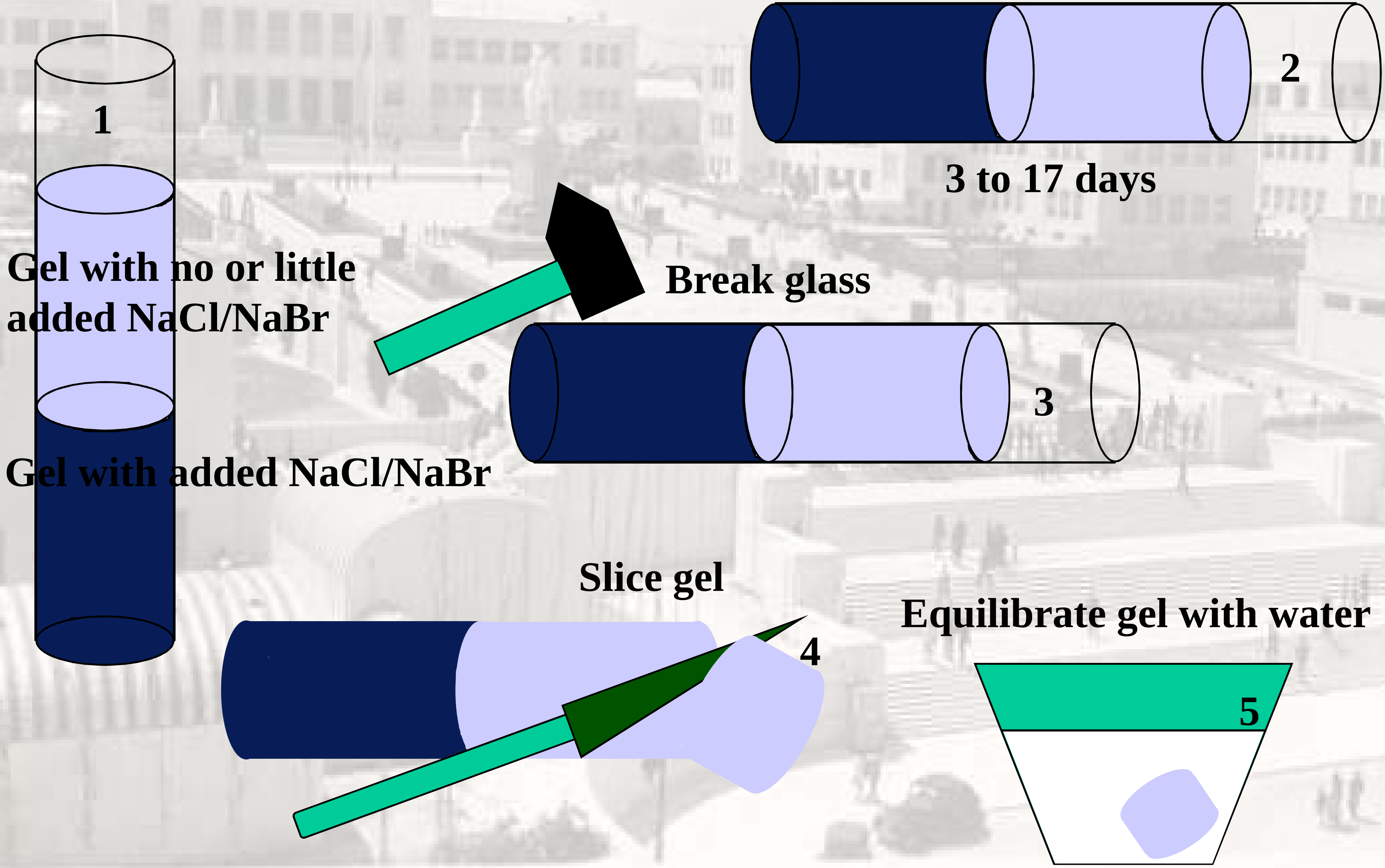
FIG. 3. Left, stratigraphic column of drillhole TR-2 indicating the average mineral composition of the salt minerals per interval. Right, measured δ^{37}Cl values of samples taken from the indicated depths. As can be seen δ^{37}Cl values in halite rich layers are generally higher than δ^{37}Cl values in carnallite and bischofite layers. Other salt minerals indicate mainly sylvite and langbeinite.

Diffusion as an example of kinetic fractionation



- Kinetic fractionation is a non-equilibrium process in which molecules with a light isotope move faster than those with a heavy isotope.
- Diffusion is a typical example of kinetic fractionation, and as Cl is a conservative element it is assumed it can be used as a typical tracer of this process.

Diffusion experiments



1

Gel with no or little added NaCl/NaBr

Gel with added NaCl/NaBr

2

3 to 17 days

Break glass

3

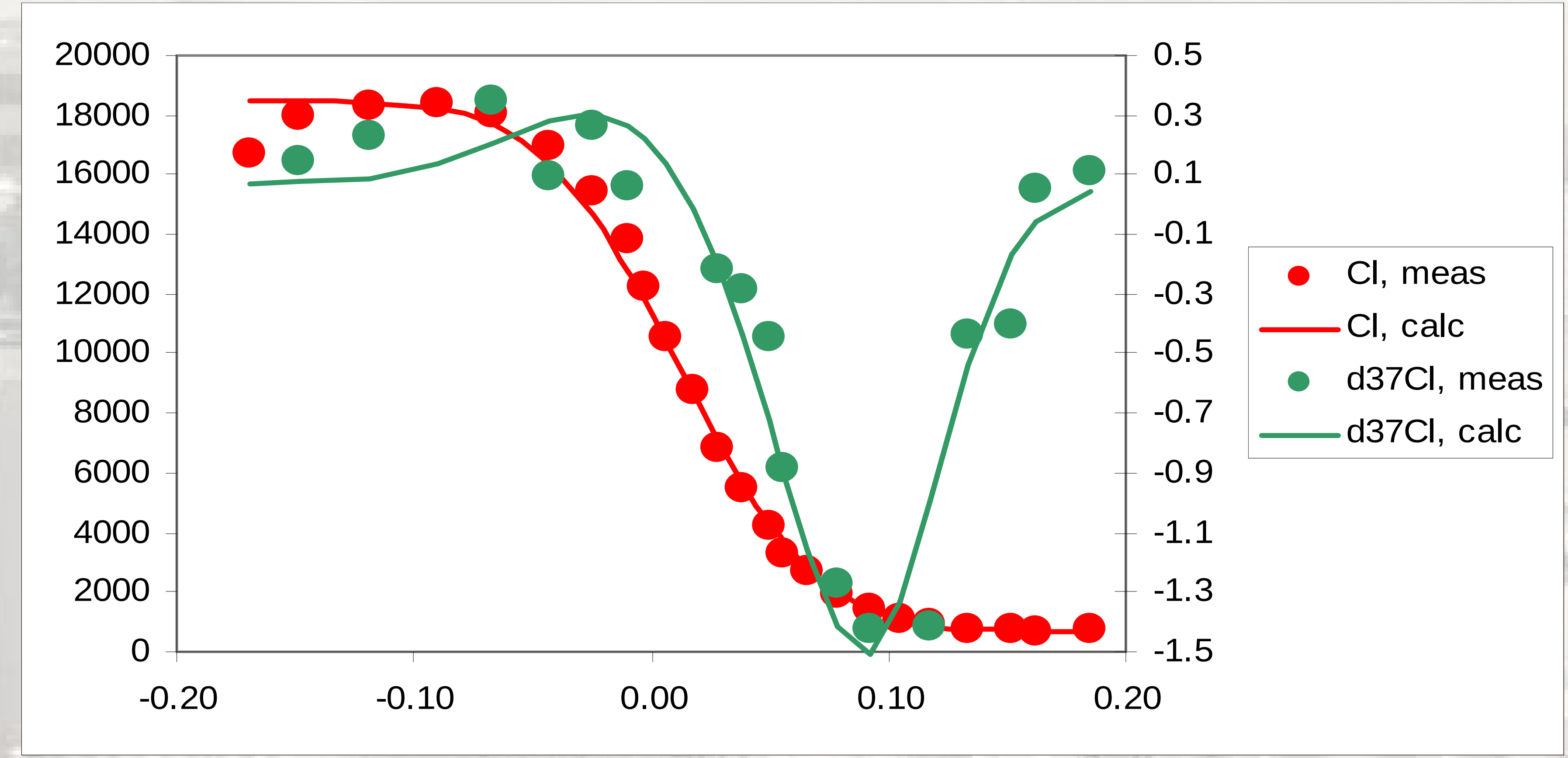
Slice gel

4

Equilibrate gel with water

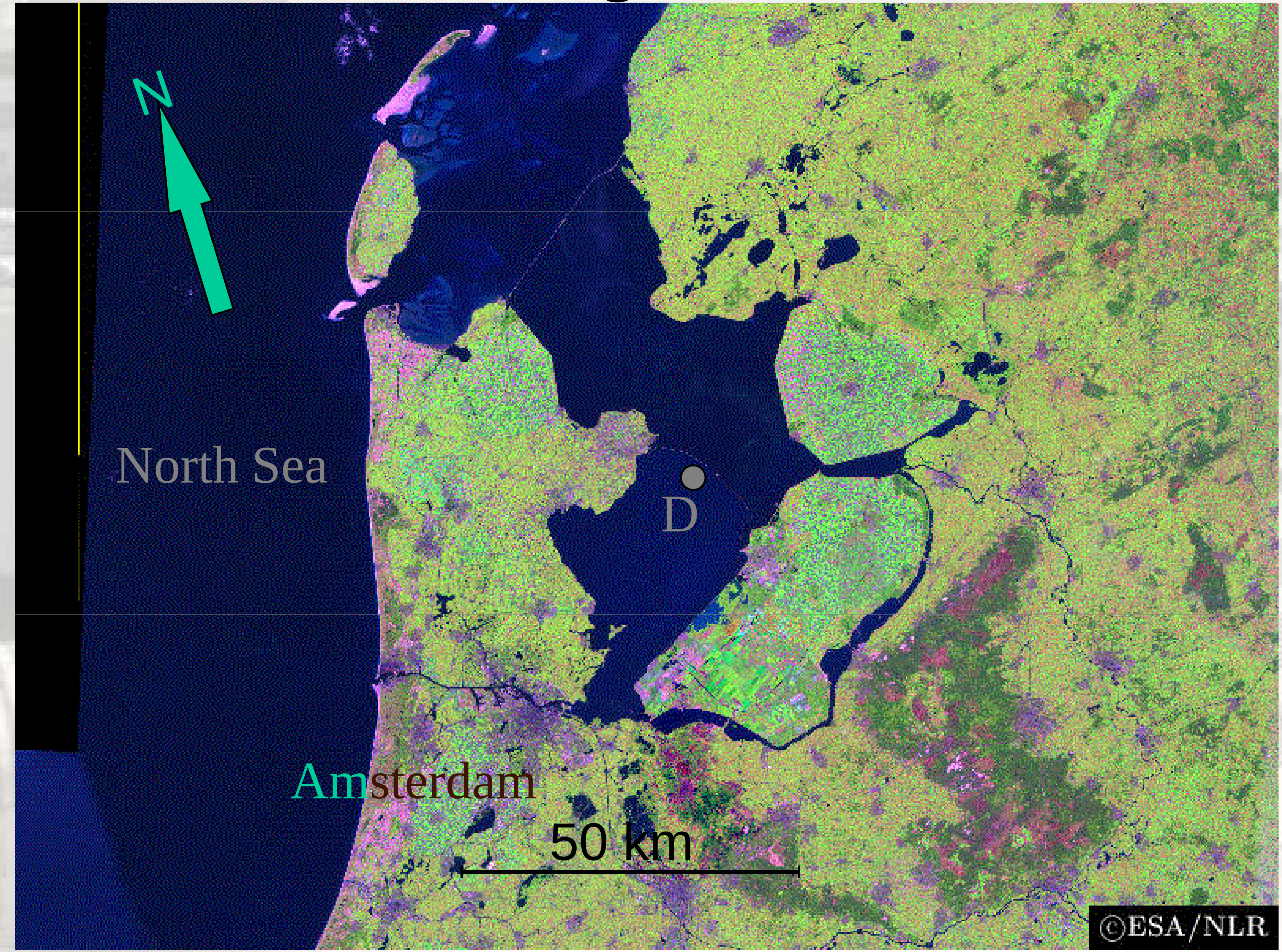
5

Experimental

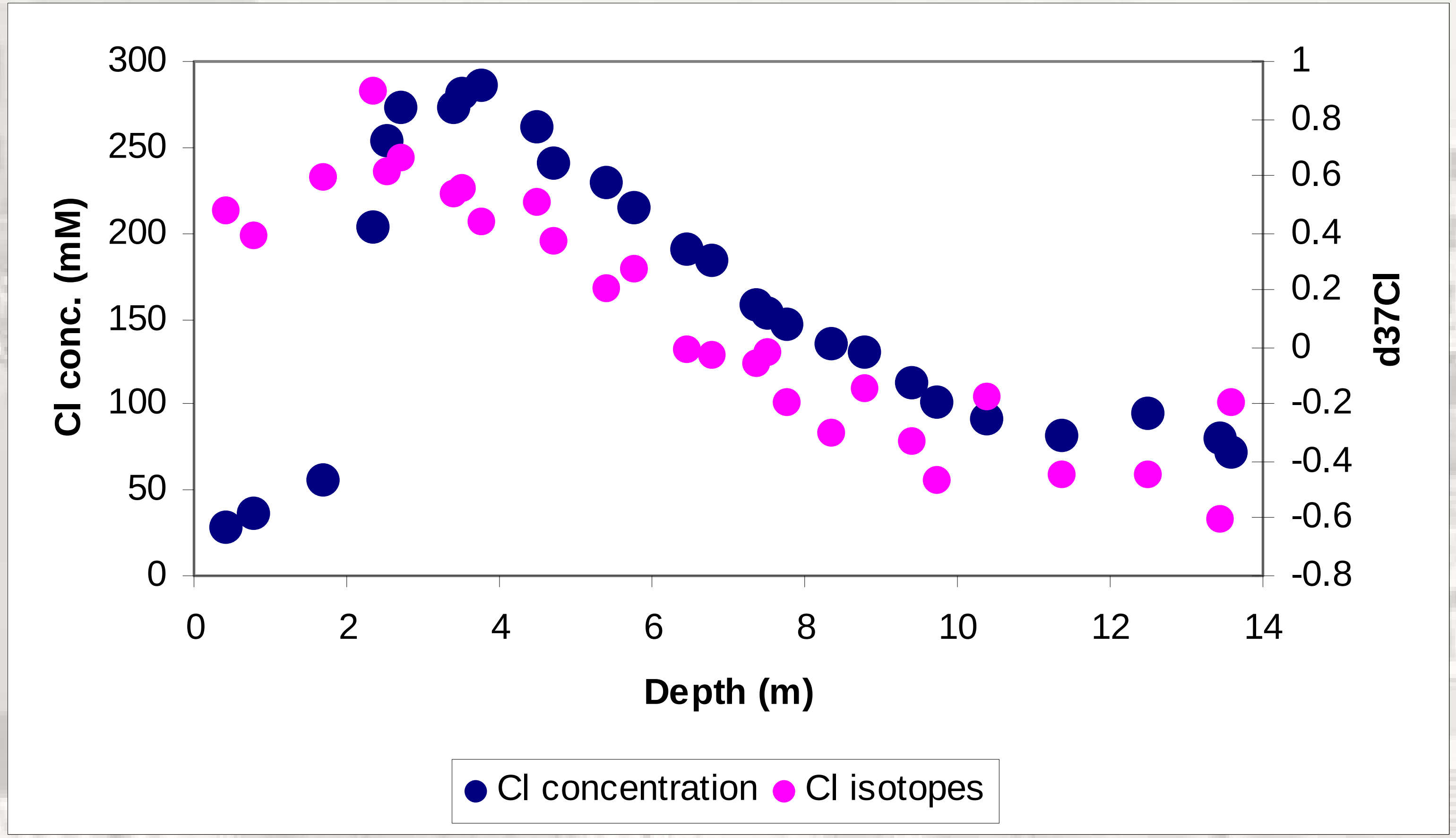


- Experimental relationship between Cl isotopes and concentration
- $C=C_0{*}\mathrm{erfc}(x/2\sqrt{Dt})$

Satellite image Netherlands



Relationship between Cl and δ^{37}Cl



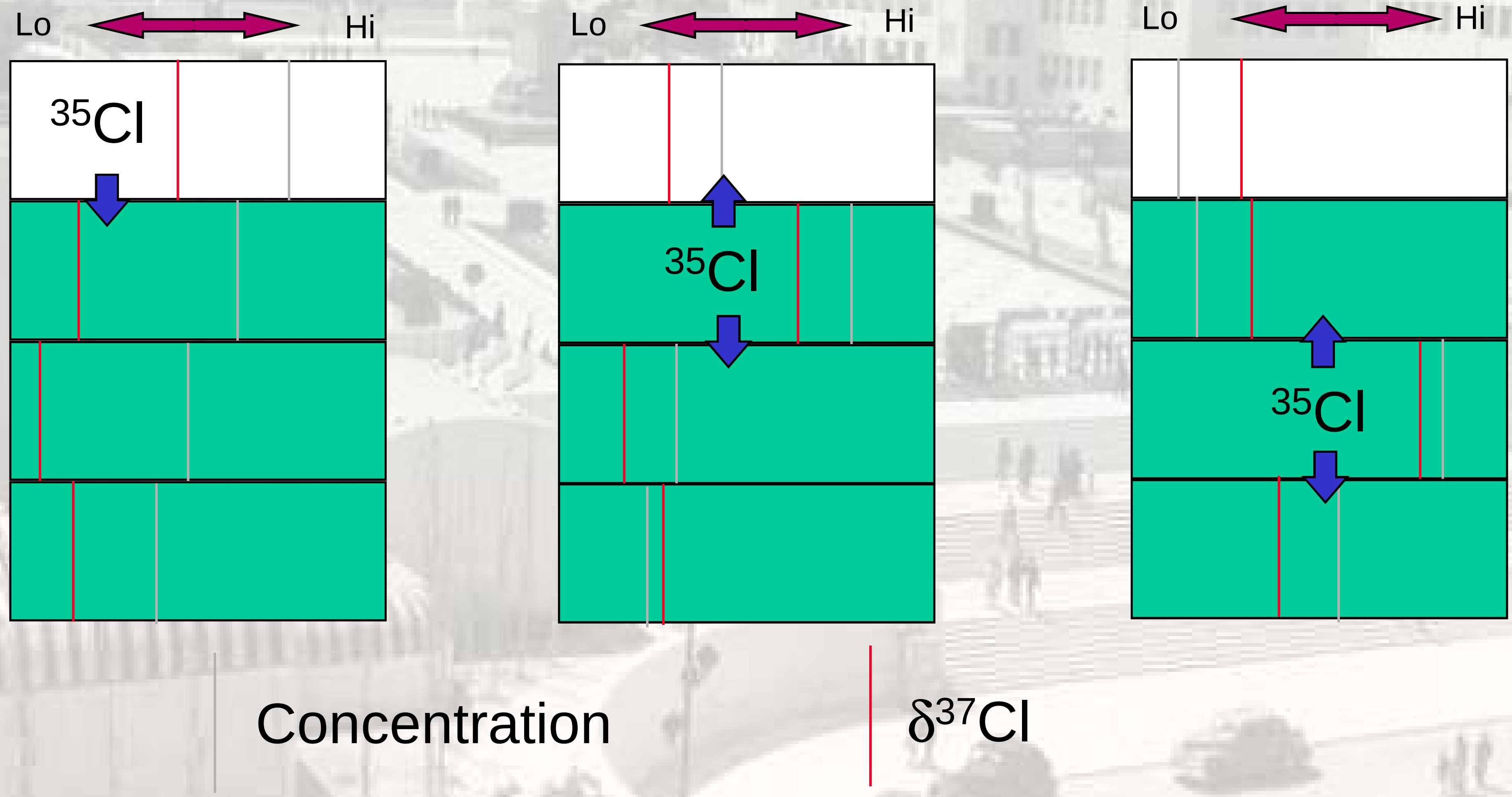
- Natural observation; IJsselmeer, the Netherlands
- Sedimentation and changing salinity

Development of model

sedimentation/ increasing salinity

storm/after which refreshening

recent refreshening



Lo Hi

^{35}Cl

Lo Hi

^{35}Cl

Lo Hi

^{35}Cl

Concentration

$\delta^{37}Cl$

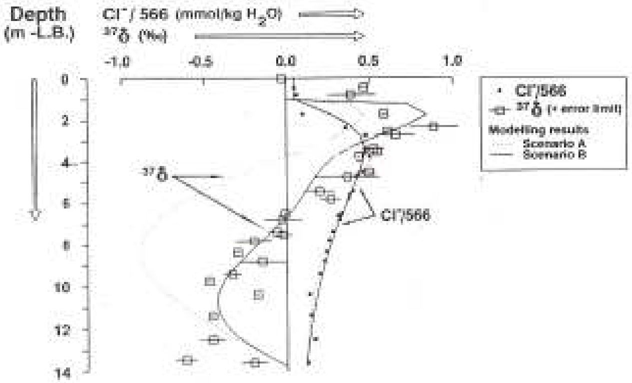


Figure 4.16
Best fits between calculated and observed Cl⁻ and $^{37}\delta$ at site D for scenarios A (diffusion from a fixed boundary plane) and B (diffusion including sedimentation).

Figure 4.17
Evolution of Cl⁻ and $^{37}\delta$ profiles for scenario B with constant diffusion coefficient (τ=0.30). The calculated profiles represent the ends of (calm) diffusion periods.

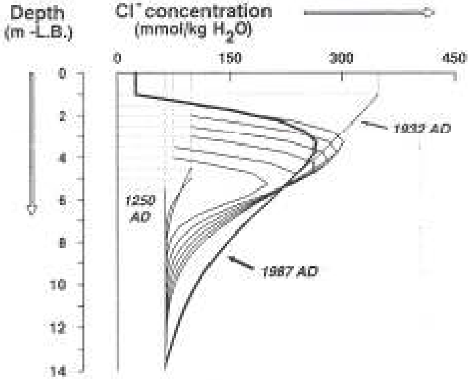


Figure 4.17a Evolution of Cl⁻.

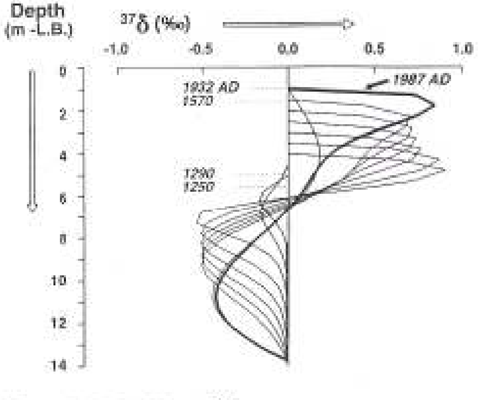
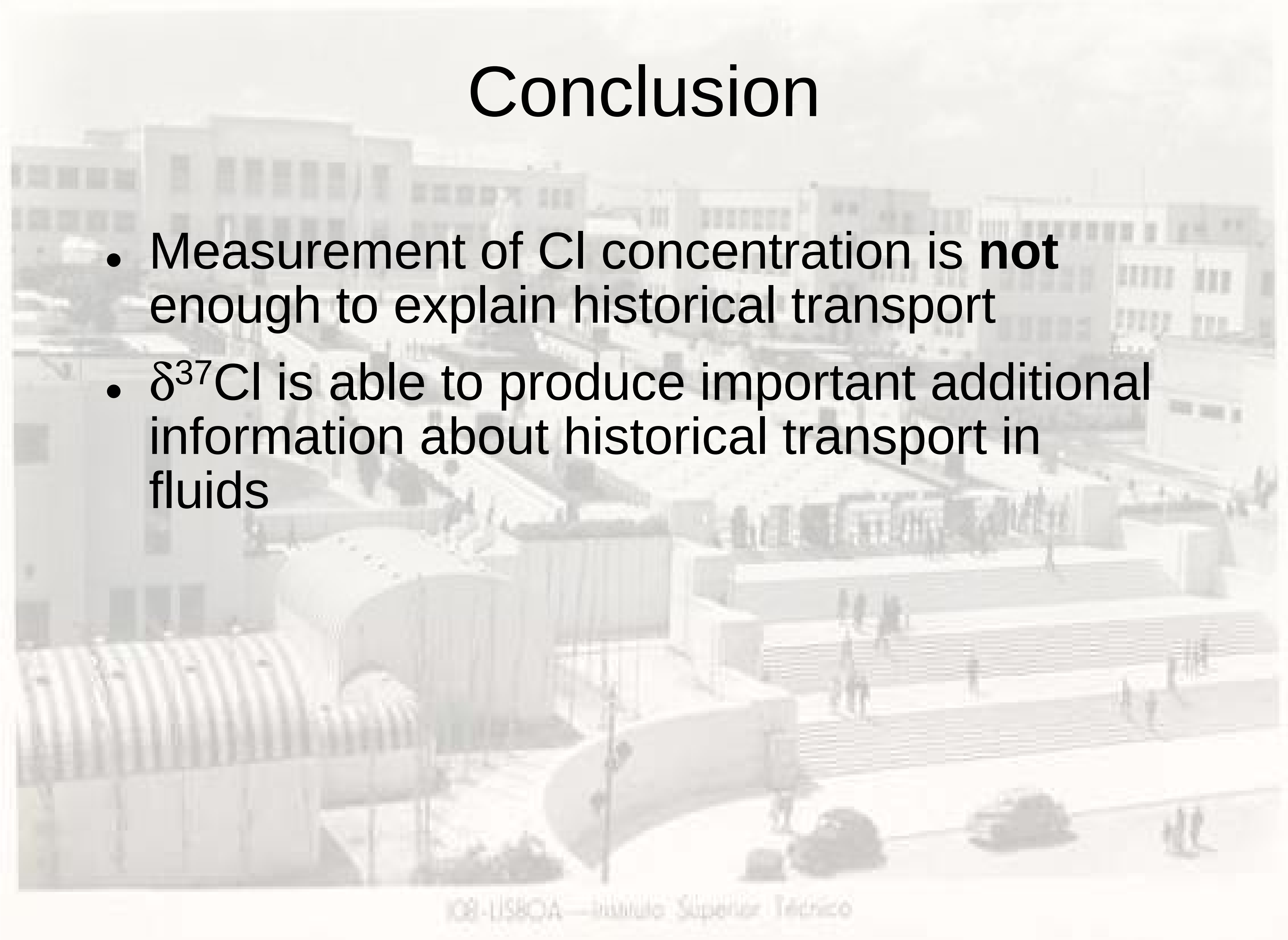


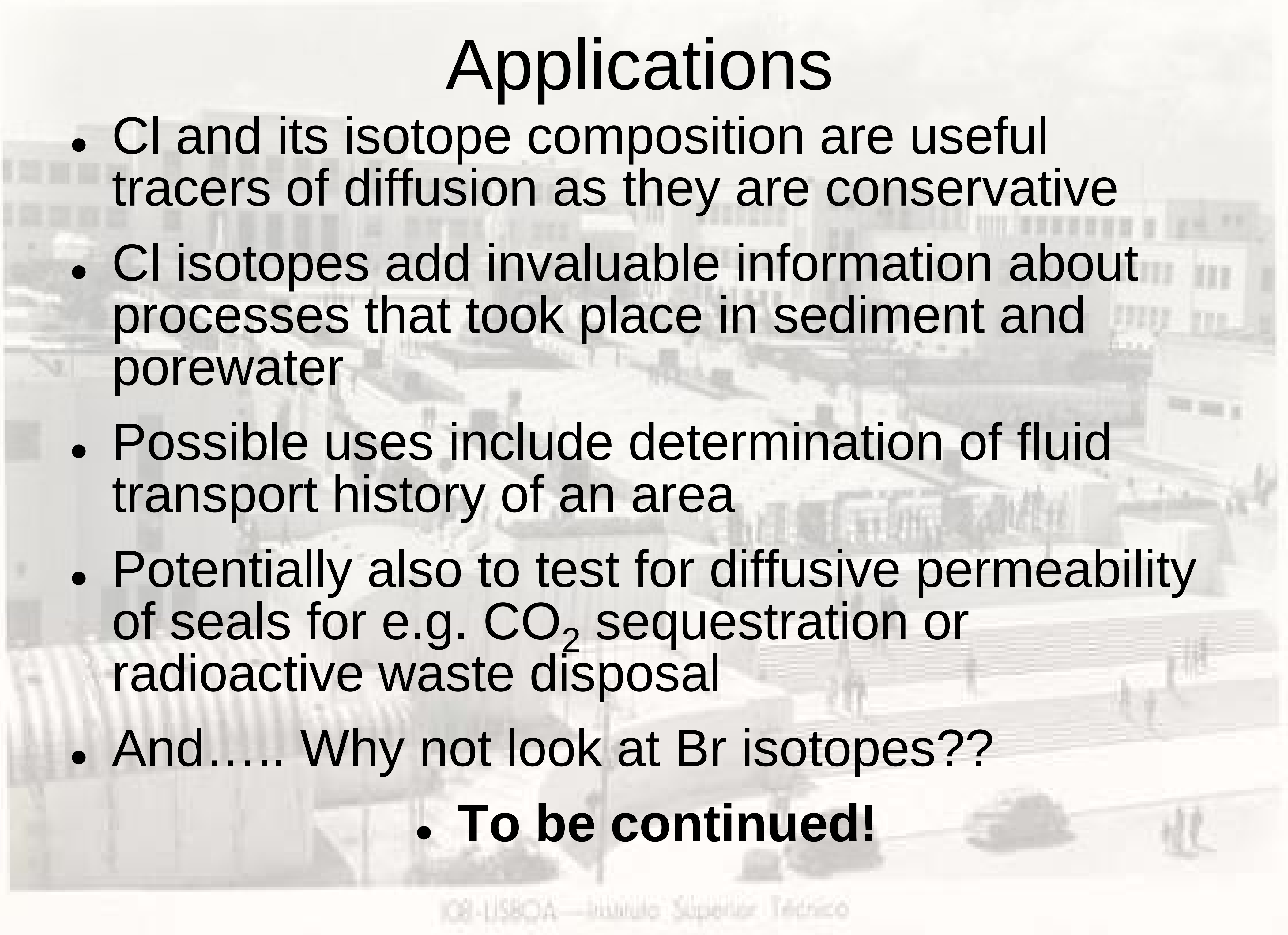
Figure 4.17b Evolution of $^{37}\delta$.

Conclusion



- Measurement of Cl concentration is **not** enough to explain historical transport
- δ^{37}Cl is able to produce important additional information about historical transport in fluids

Applications



- Cl and its isotope composition are useful tracers of diffusion as they are conservative
- Cl isotopes add invaluable information about processes that took place in sediment and porewater
- Possible uses include determination of fluid transport history of an area
- Potentially also to test for diffusive permeability of seals for e.g. CO_2 sequestration or radioactive waste disposal
- And….. Why not look at Br isotopes??
  - **To be continued!**

Thank you for your attention!

- This presentation was not possible without the invaluable help of my teachers:
- **Max Coleman**
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- **Tony Appelo**
- **Rob Kreulen**
- **Guus Koster van Groos**
- **Olaf Schuiling**

CENTRO DE PETROLOGIA E GEOQUÍMICA

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