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Carbon-14 speciation during anoxic corrosion of activated steel in a repository environment

C14AST

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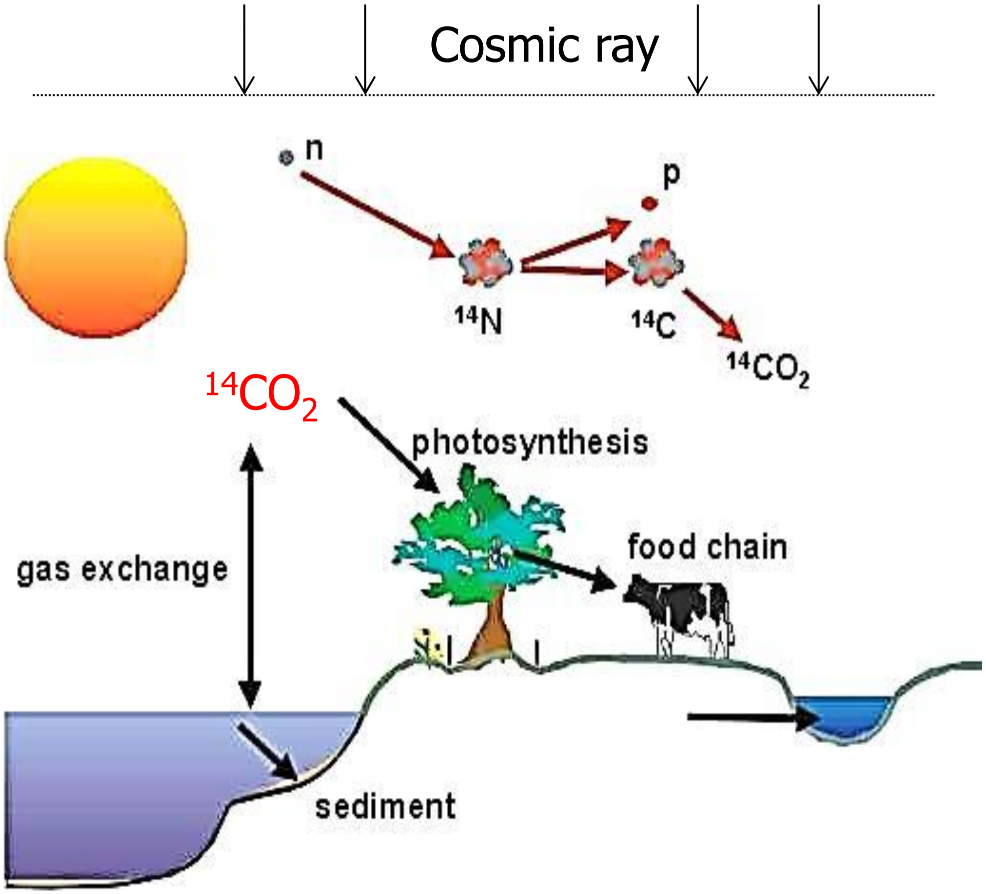
Layout

- Introduction
  - ^{14}C in L/ILW – a dose-determining radionuclide
  - Organic compounds produced during anoxic iron corrosion
- Set-up of corrosion experiment with activated steel
  - Analytical challenge
  - Set-up of the reactor system
  - Characterization of material
  - Development of compound-specific ^{14}C AMS analytical technique
- First results from corrosion experiment with activated steel
- Open issues
- Summary and Conclusions

Carbon-14 a natural isotope



Upper atmosphere

$^{14}N(n,p)^{14}C$

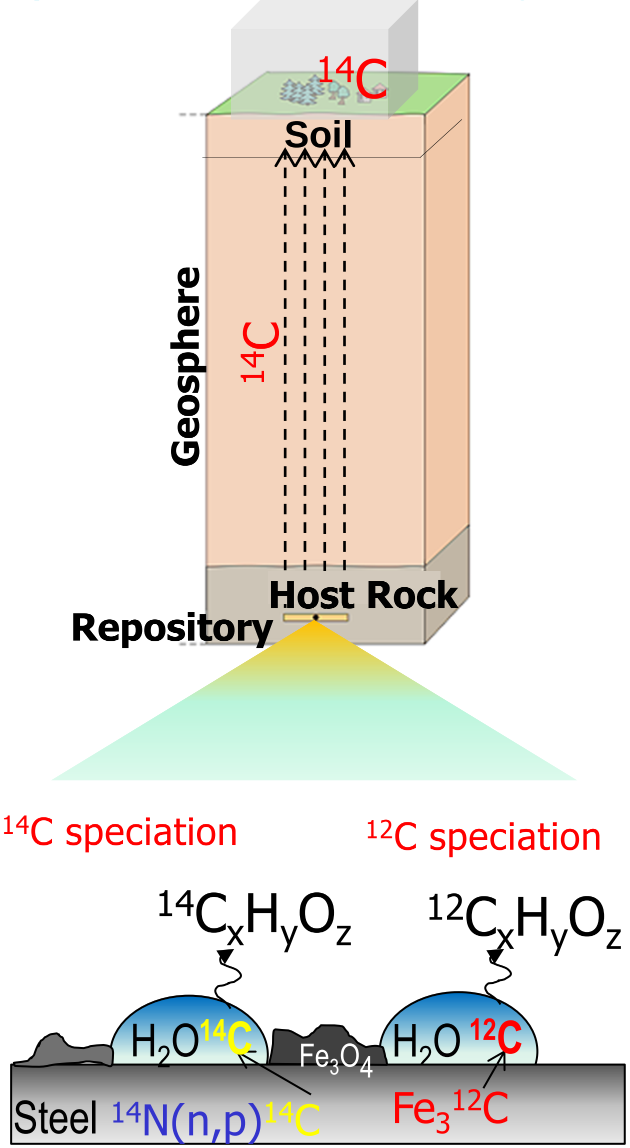
Terrestrial biosphere

Ocean

(http://www.uni-kiel.de/leibniz/Leibniz-web_deutsch/radiokarbonmethode/radiokarbonmethode.htm)

- ❑ Carbon-14 is a natural radioisotope generated due to reaction of neutrons with nitrogen-14 in the earth’s atmosphere
- ❑ Carbon-14 is important because it relates to the human population dose from radiocarbon

Importance of knowledge on chemical speciation for SA



Questions

- What kind of ^{14}C-containing compounds are formed during corrosion of activated metals?
- What is their fate in the repository environment (near and far field)?
- Ratio of gaseous/volatile to dissolved carbons compounds; e.g. $^{14}CH_4$ versus $H^{14}COOH$?
- Amount of inorganic carbon produced, e.g. $^{14}CO_3^{2-}$

Knowledge of ^{14}C speciation is important for SA
Speciation determines migration (pathway etc.)

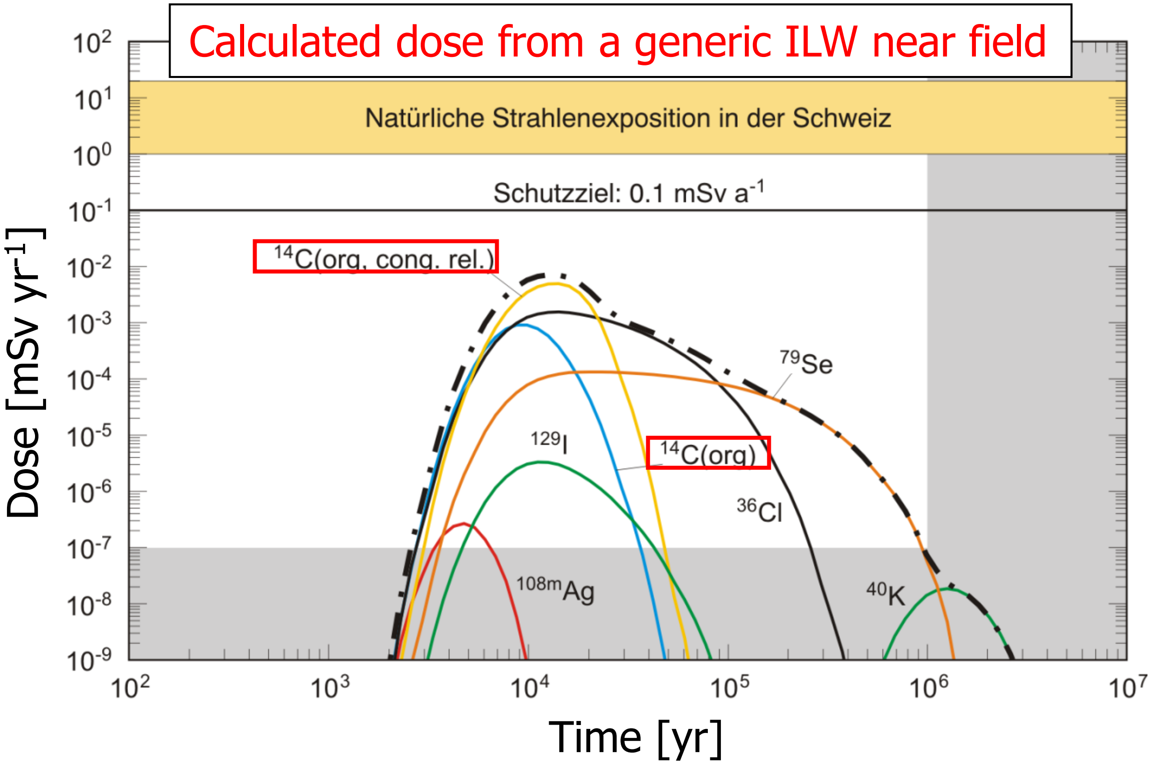
Material inventory in repository

Cement ~ 15 wt% Metals ~ 26 wt%
Aggregate~ 54 wt% Organics ~ 5 wt%

Geochemical conditions of the near field

- alkaline: Reference pH = 12.5 (pH 11.5 – 13.3)
- reducing: Reference E_h = - 230 mV (- 750 mV to - 230 mV)
- Presence of H_2

Swiss L/ILW repository: Safety assessment (SA)



Clay-rich host rock,

Hypothetical hydraulic conductivity 10^{-10} m/s

Nagra Technical Report NTB 08-05

- ❑ ^{14}C is one of the dose dominating radionuclides in PA

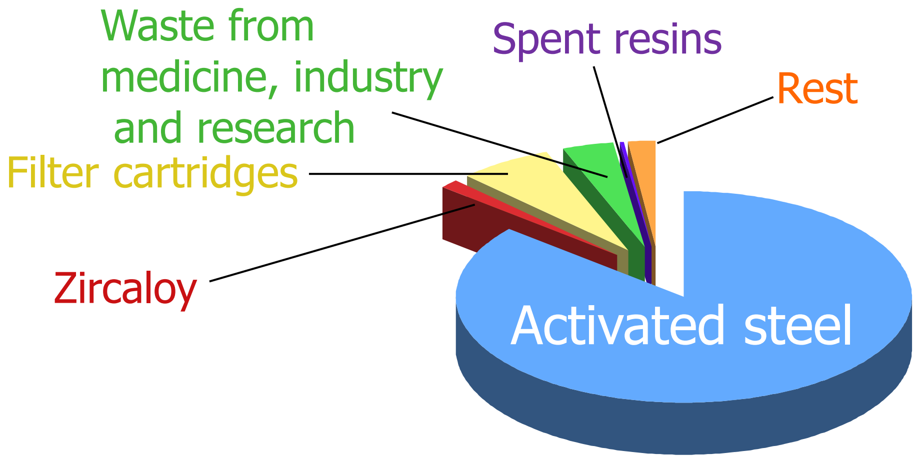
^{14}C instant release:
- $^{14}C_{inorg}$ ($^{14}CO_3^{2-}$ very low dose contribution)
- $^{14}C_{org}$ (spent ion exchange resins etc.)

^{14}C fractional release (10^{-4} yr^{-1}):
- $^{14}C_{org,\ congruent\ release}$ (activated metals)

Key question: What is the chemical speciation determining the $^{14}C_{org}$ and $^{14}C_{org,\ congruent\ release}$ sum parameters?

Carbon-14 waste forms in Switzerland

- ☐ Carbon-14 inventory in deep geological L/ILW repository



- ☐ Activation of steel in nuclear power plants by thermal neutrons

Carbon:	alloying constituent in steels (stainless steel ≤ 0.8 % C in carbide form)
Nitrogen:	nitrogen atmospheres used for cooling, stirring, and protecting metal from oxidation during steel production (stainless steel ≤ 0.09 % N_2)

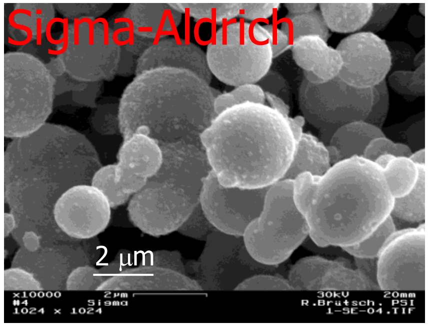
Isotope	**Natural abundance (%)**	**Cross section for thermal neutron capture (barns)**	**Reaction**
^{14}N	99.634	1.81	$^{14}N(n,p)^{14}C$
^{13}C	1.103	0.0009	$^{13}C(n,g)^{14}C$
^{17}O	0.0383	0.235	$^{17}O(n,a)^{14}C$

Organics produced during iron corrosion

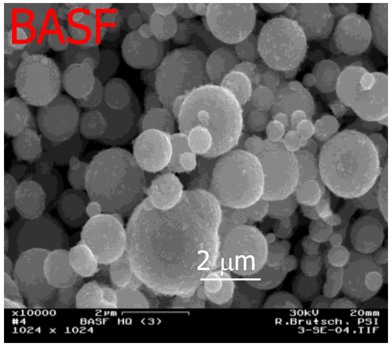
Cvetković et al., 2017

❑ Non-activated iron powders

- untreated and pre-washed with 1N HCl and Milli-Q water rinsed *(Deng et al., 1997)*



d(90) ~ 9 µm
Surface area
$= 0.47\ m^2\ g^{-1}$
Fe content
> 97 %
C content
= 0.83 %

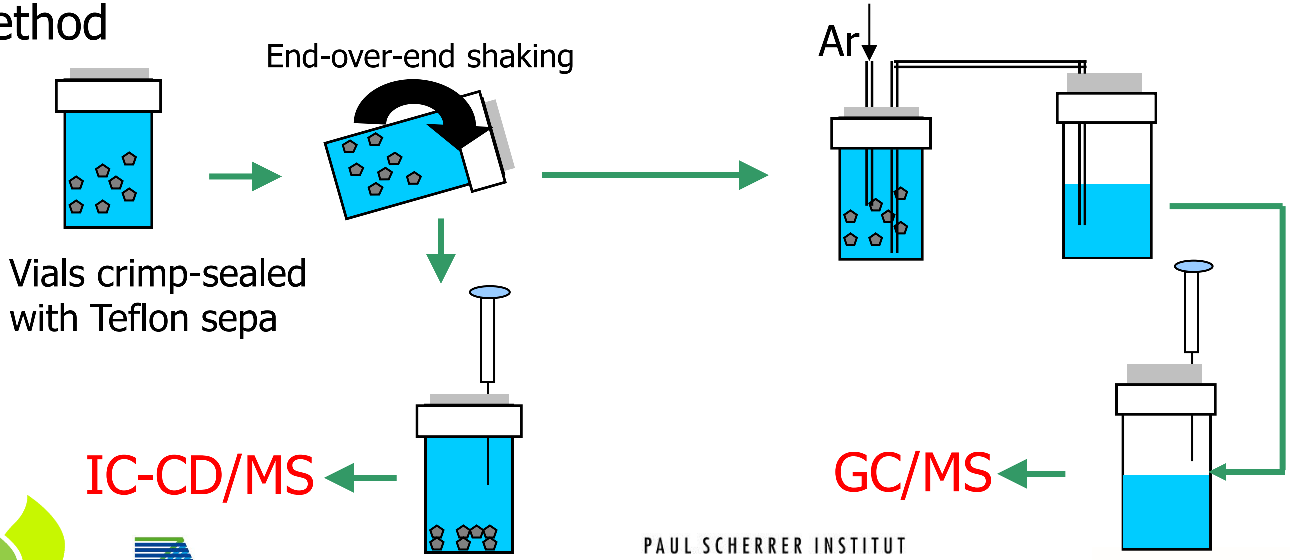


d(90) = 2.2 µm
Surface area
$= 1.088\ m^2\ g^{-1}$
Fe content
> 97.5 %
C content
= 0.9 %

❑ Solutions

- Portlandite-saturated solution (pH = 12.5)
- Ca-Si solution in equilibrium with a C-S-H phase (Ca/Si ratio ~0.8) (pH ~ 11.5)

❑ Method



End-over-end shaking

Vials crimp-sealed
with Teflon sepa

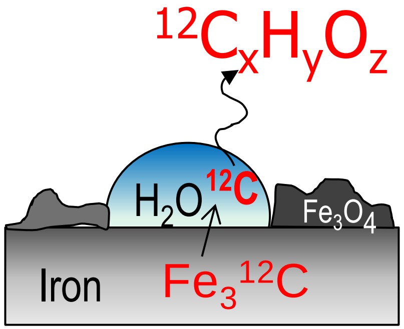
IC-CD/MS

GC/MS

-addition of internal
standard
-vortexed
-headspace injection

Organics produced during iron corrosion

Cvetković et al., 2017



Batch-type experiments with non-activated iron:

- Literature review suggests 19 species at maximum (all table entries except lactate)
- In this study 15 species out of the 19 species + lactate have been identified (all table entries in bold)
- Both oxidized and reduced hydrocarbons are present in corroding iron-water systems
- Small molecules with $C \le 5$ have been identified above the detection limit during the corrosion of iron/steel in cement-type pore solutions

Hydrocarbons	**Alcohols/aldehydes**	**Carboxylate ions**
Methane (CH_4)	**Methanol** (CH_3OH)	**Formate** ($HCOO^-$)
Ethane (C_2H_6)	**Ethanol** (C_2H_5OH)	**Acetate** (CH_3COO^-)
Ethene (C_2H_4)	**Formaldehyde** (CH_2O)	Propanoate ($C_2H_5COO^-$)
Propane (C_3H_8)	**Acetaldehyde** (C_2H_4O)	Butanoate ($C_3H_7COO^-$)
Propene (C_3H_6)	**Propionaldehyde** (C_3H_6O)	**Malonate** ($CH_2(COO^-)_2$)
Butane (C_4H_{10})		**Oxalate** ($C_2O_4^{2-}$)
Butylene (C_4H_8)		***Lactate*** *($CH_3CHOHCOO^-$)*
Pentene (C_5H_{10})		

Corrosion experiment with activated steel – a major challenge

Challenge - Very low concentrations of ^{14}C-bearing compounds expected

- Use of small activated steel samples due to high dose rate (no hotcell available)
  → high dose rate (^{60}Co), low ^{14}C inventory
- Low ^{14}C content in activated steel (~0.1 µg ^{14}C/g)
- Very low corrosion rates under alkaline conditions (≤ 50 nm/year)

Scoping calculations for an experimental set-up (1 g material, moderate surface area of 1cm^2/g, 300 mL reactor volume, 1 day reaction time) result in a ^{14}C concentration of

Total ^{14}C: $\sim 2.8\cdot10^{-15}$ mol ^{14}C/L$\cdot$d = $3.9\cdot10^{-14}$ g ^{14}C/L $\cdot$d = 0.64 µBq ^{14}C/L $\cdot$d

Analytics: small volumes, chromatographic separation causes additional dilution

- Detection limits of standard techniques:

GC or IC coupled to MS/CD: *~ 10^{-8} - 10^{-7} g C/L*

Liquid scintillation counting *(^{14}C detection): ~ 10^{-11} - 10^{-10} g ^{14}C/L*

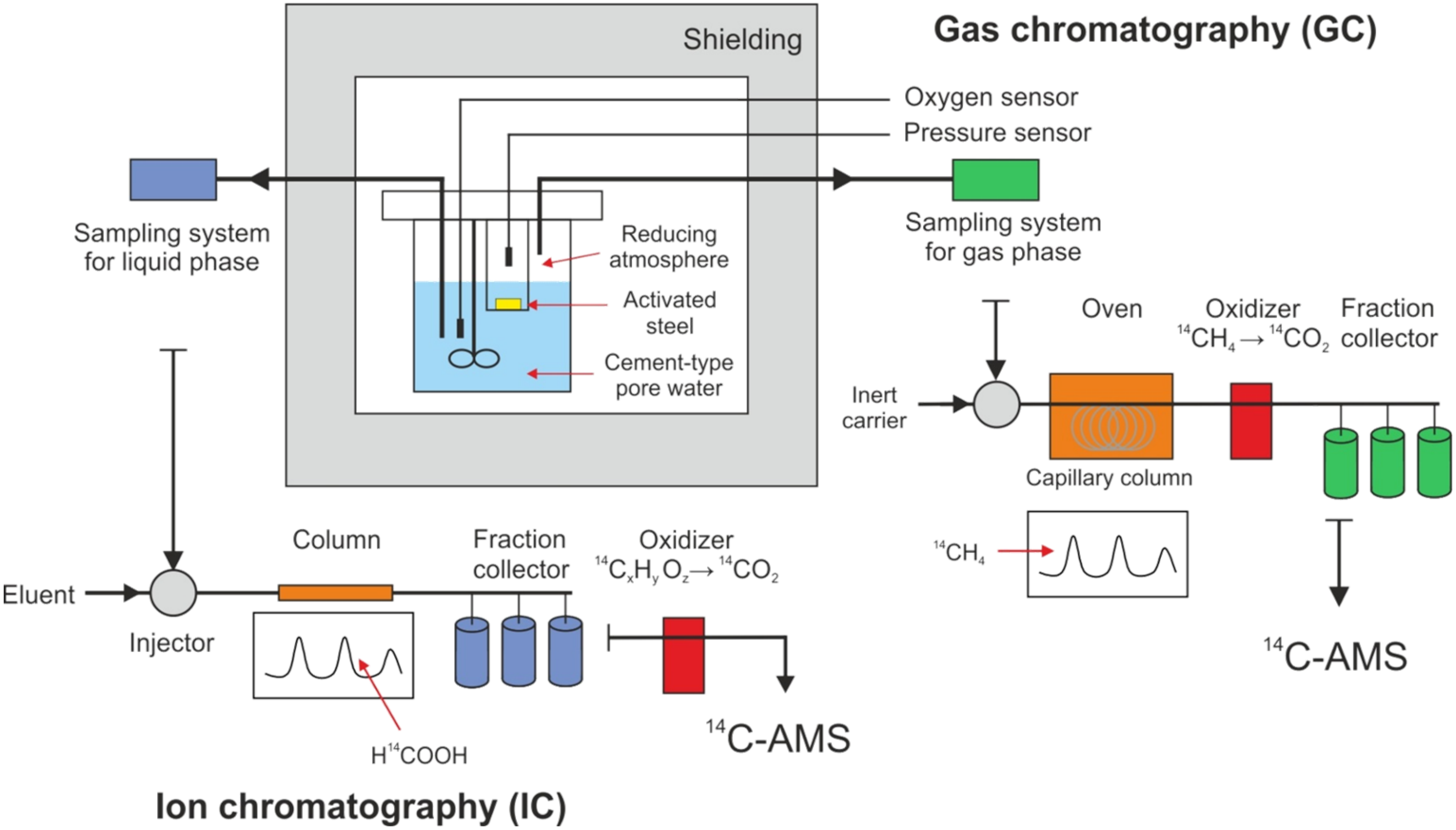
^{14}C accelerator mass spectrometry (AMS): *~ 10^{-18} g ^{14}C (= 20'000 atoms)*

(20 µg total ^{12,13}C carbon, ^{14}C/^{12,13}C isotopic ratio)

→ ^{14}C concentration is below the detection limits of standard analytical techniques

- Development of compound-specific ^{14}C analysis as a combination of chromatographic separation of organics and ^{14}C AMS detection

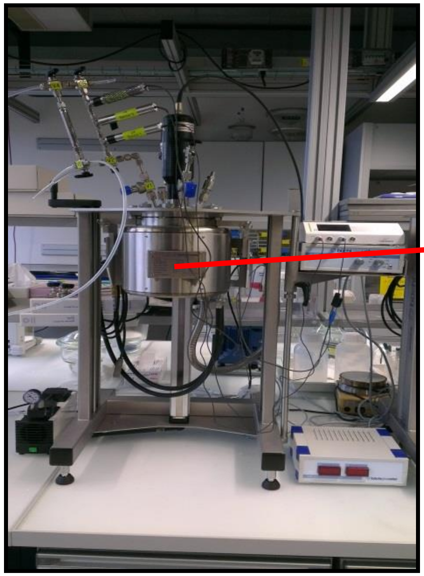
Set-up of the corrosion experiment with activated steel



- ❑ Chromatographic separation and sample preparation using ion chromatography (IC) and gas chromatography (GC)
- ❑ Quantification of the carbon-14 activity by ^{14}C accelerator mass spectrometry (AMS) in both liquid and gas samples (= compound-specific ^{14}C AMS)

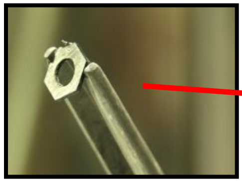
Corrosion reactor

Gas-tight reactor (pressure autoclave) for planned corrosion experiments with specimen prepared from activated steel nut



Top view

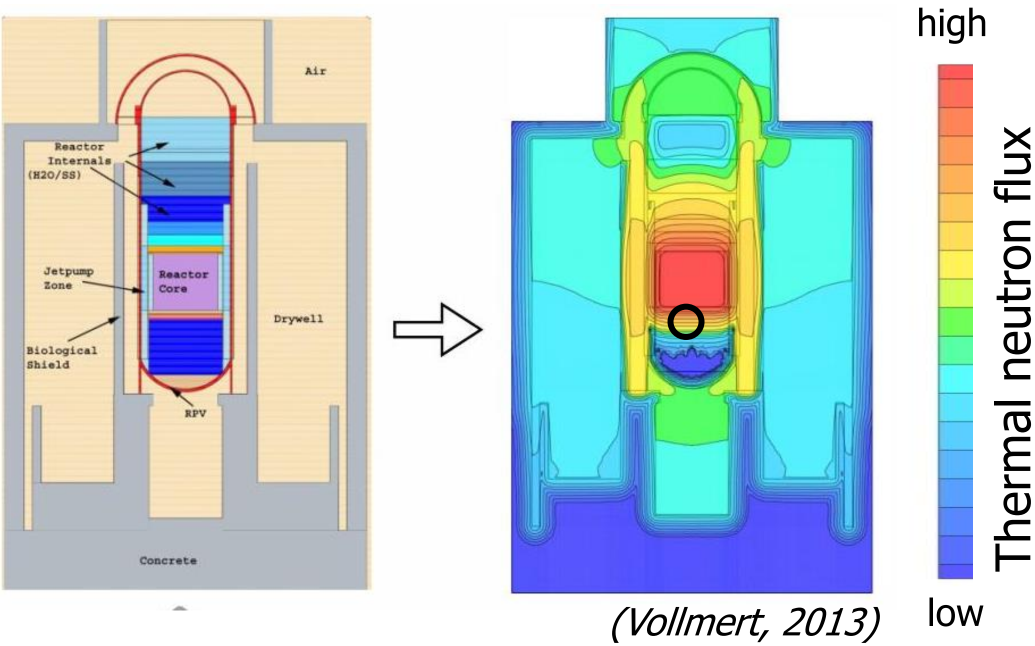
Inside view



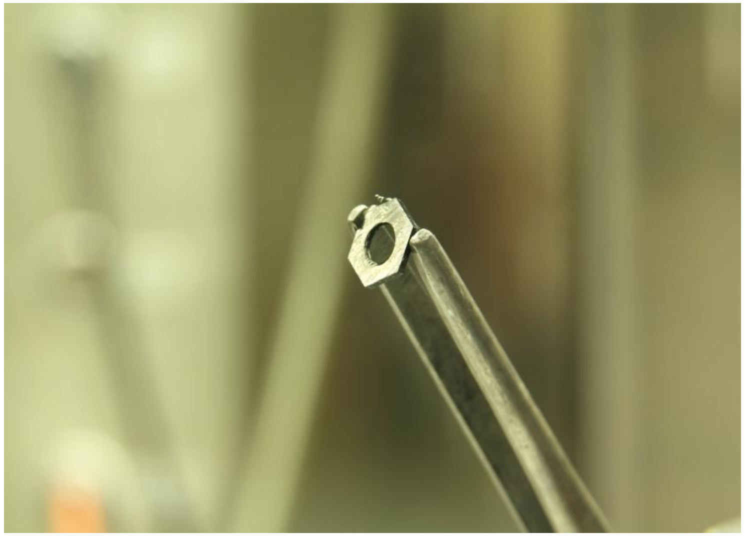
- ☐ Combined stirring and sample container for steel nut (PEEK liner)
- ☐ Sampling of liquid and gas phase and replacement of liquid and gas phase without opening the reactor
- ☐ Sensors for pressure and temperature control and detection of O_2 in aqueous phase

Characterisation of activated steel from NPP Gösgen (Switzerland)

- ❑ Fuel assembly guide tube nut: Nuts used to mount confinement tubes of fuel rods in the reactor core («Brennelement-Führungsrohrmuttern»)



(Vollmert, 2013)



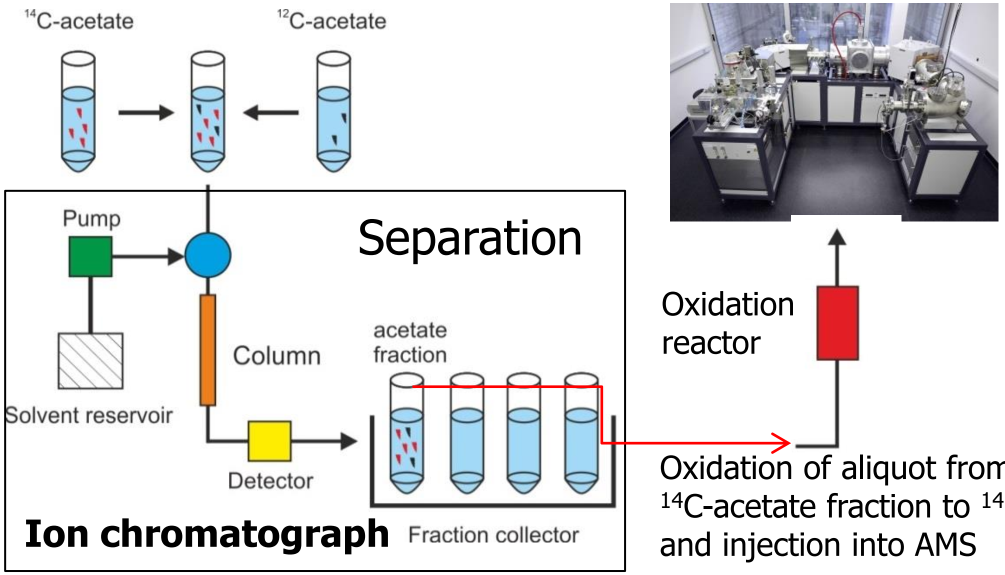
Stainless steel nut

- ❑ Weight: 5 g
- ❑ Dimensions: diameter = 1.1 cm, height = 1 cm
- ❑ Dose rate: ~ 150 mSv/h (contact) due to presence of ^{60}Co, ^{55}Fe, ^{54}Mn and ^{63}Ni
- ❑ Activation: ~ 2 years at neutron flux ~ $8 \cdot 10^{12}$ n cm^{2} s^{-1}
- ❑ C-14 inventory: 17’800 Bq/g

Schumann et al., 2014

Compound-specific ^{14}C AMS for dissolved species

Cvetković et al., 2017



Oxidation of aliquot from ^{14}C-acetate fraction to $^{14}CO_2$ and injection into AMS

❑ Status

Compound-specific ^{14}C AMS

- ❑ Background of ^{14}C: ~0.06 F^{14}C
- ❑ Linear range: ~0.06 - ~50 F^{14}C
- ❑ Measurements are reproducible
- ❑ No cross contamination

$$1\ F^{14}C = {}^{14}C/({}^{12}C \times 1.18 \cdot 10^{-12})$$

❑ Ion chromatography

Dionex IC-MS system:
- Conductivity detection (CD)
- Electrochemical eluent generation
- Gradient and isocratic elution
- Fraction collector

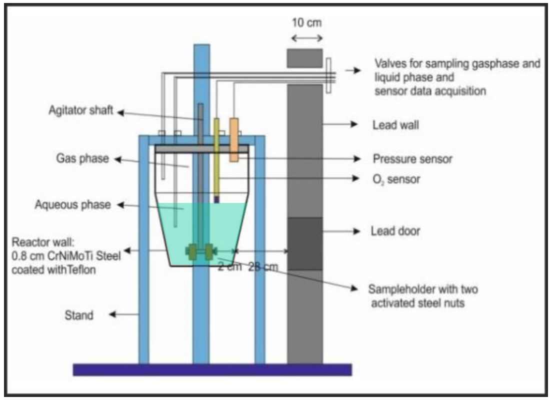
❑ Recovery

AA: ^{14}C-acetic acid
FA: ^{14}C-formic acid

Expected [F^{14}C]	Expected [Bq/L]	Measured [Bq/L]	Recovery [%] AA	Recovery [%] AA + FA
0.21	*0.09*	*0.06*	*64*	*69*
0.47	0.24	0.21	87	96
0.95	0.48	0.39	82	88
2.67	1.23	1.29	105	114
4.39	*2.24*	*2.00*	89	97
11.16	4.81	4.42	92	98
24.61	11.44	10.50	92	99
49.12	22.83	20.49	90	97
		Average:	**91 ± 7**	**99 ± 7**

First results from corrosion experiment

- ❑ Start of corrosion experiment with activated steel: May 2016



Activated steel samples

Mass: 2 x 1 g
Mass-^{12}C: ~ 2 mg
Mass-^{14}C: ~ 0.2 µg
Dose rate (^{60}Co): 60 mSv/h
Activity (^{14}C): 35.6 kBq

Analysis

- ^{60}Co activity
- TO^{12}C and ^{12}C dissolved and gaseous compounds
- TO^{14}C and ^{14}C-bearing aqueous organic compounds by compound-specific ^{14}C AMS

Time	O_2	Pressure	TO^{14}C by AMS		TO^{12}C	^{12}C Hydrocarbons [µM]			^{12}C Carboxylate ions [µM]					^{60}Co
[d]	[ppb]	[bar]	[F^{14}C]	[Bq/L]	[ppm]	Methane	Ethane	Ethene	Formate	Acetate	Oxalate	Glycolate	Lactate	[Bq/mL]
Blank	*58.8*	*5.03*	*0.59*	*0.27*	*n.d.*	*< LOD*	*< LOD*	*< LOD*	*≤ 5*	*< LOD*	*≤ 0.1*	*≤ 0.5*	*< LOD*	-
1	43.2	5.15	0.10	0.04	n.d	*< LOD*	*< LOD*	*< LOD*	2	< 5	0.2	*< LOD*	<0.5.	-
15	38.9	5.02	0.99	0.45	2.33	< 0.06	*< LOD*	*< LOD*	3	*< LOD*	0.4	0.8	1.6	-
29	37.5	5.04	1.56	0.70	2.41	0.07	*< LOD*	*< LOD*	2	*< LOD*	0.4	0.9	1.2	5.2
93	43.2	5.06	3.53	1.60	4.23	0.42	*< LOD*	*< 0.03*	8	< 5	0.6	1.2	2.8	5.2
286	59.7	5.19	2.94	1.33	5.59	0.55	*< LOD*	*0.08*	44	21	0.2	1.1	2.5	4.4
412	69.5	5.02	1.46	0.66	5.92	0.99	*< LOD*	*0.06*	15	10	0.9	1.8	4.1	3.3

^{14}C-AMS **$^{12+14}$C TOC** **^{12}C GC-MS** **^{12}C IC-MS** γ-counting

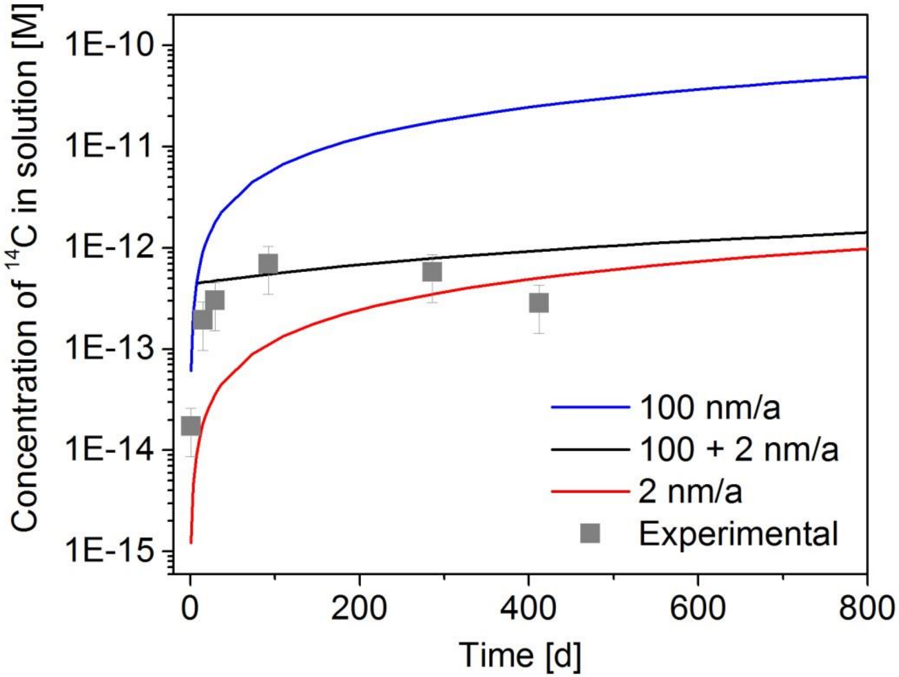
- ❑ Total organic ^{14}C carbon (TO^{14}C) (= total concentration of ^{14}C-containing carboxylate ions) increases with time – individual organic compounds detectable at 412 days sampling
- ❑ Total organic carbon (TOC = dissolved ^{12}C-containing compounds) increases with time – presence of methane and carboxylates indicated

First results from corrosion experiment

- ❑ ^{14}C-containing acetate, formate and lactate determined by AMS after 412 days reaction time and applying a pre-concentration step.

Fraction	**Dilution & background corrected concentration**	
	F^{14}C	Error
^{14}C-lactate (LA)	0.44	0.10
^{14}C-formate (FA)	0.68	0.07
^{14}C-acetate (AA)	0.52	0.17
LA + FA + AA = TO^{14}C [F^{14}C]	1.64	0.34
TO^{14}C [F^{14}C]	1.46	0.28

- ❑ Modelling increase in TO^{14}C with time based on ^{14}C inventory and corrosion rates and on the assumption that the entire ^{14}C inventory of steel is converted into TO^{14}C



- ❑ TO^{14}C corresponds to the concentration of ^{14}C-containing lactate, formate and acetate – carboxylates are important organic compounds formed during corrosion of activated steel
- ❑ Increase in TO^{14}C corresponds to fast corrosion (100 nm/a) during 100 days and subsequent very slow corrosion (2 nm/a)

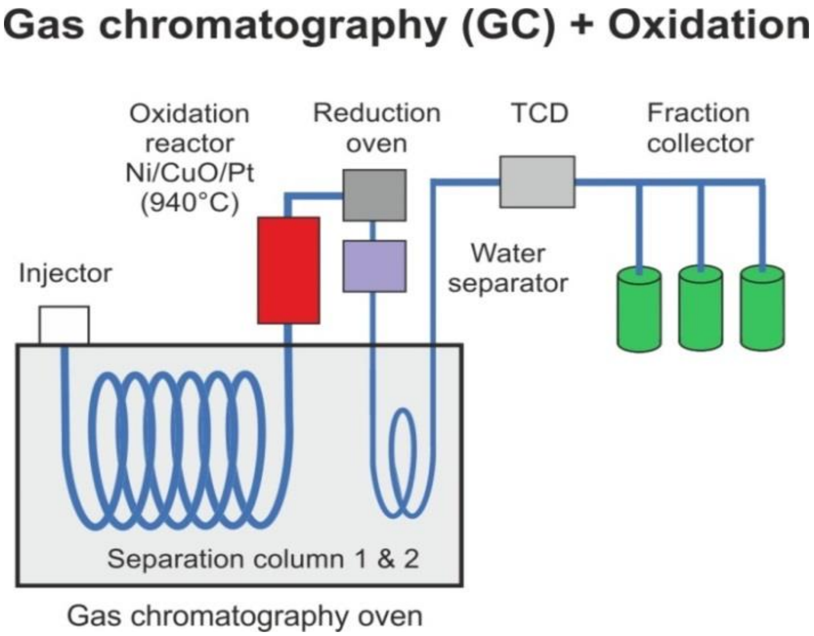
Open issues

- Quantification of inorganic carbon-14 (pH = 12.5): ${}^{14}CO_3^{2-}$ = $T^{14}C$ - $TO^{14}C$

  An analytical method for the determination of $T^{14}C$ is currently being developed

- Ratio of gaseous and volatile ${}^{14}C$ species to dissolved ${}^{14}C$ species:

  A compound-specific ${}^{14}C$ AMS-based techniques for the identification and quantification of gaseous ${}^{14}C$-bearing compounds is under development



Summary and Conclusions

- The chemical speciation of ^{14}C-bearing organic compounds formed in the course of the anoxic corrosion of activated steel in a repository for radioactive waste is still poorly known; specific consideration of the ^{14}C speciation is not possible in safety assessments to date;
- The current project addresses this gap in our knowledge and allows a worldwide unique experiment on the corrosion of ^{14}C-bearing activated steel and the identification of the ^{14}C-bearing organic compounds to be undertaken;
- The concentrations of ^{14}C-bearing organic compounds are expected to be very low in the planned corrosion experiment, in particular below the detection limits of standard ^{14}C radioassay techniques, which requires the development of a very sensitive, compound-specific ^{14}C AMS-based analytical technique;
- First results from leach and corrosion experiments with activated steel show that the identification and quantification of the ^{14}C-bearing organic compounds is feasible using compound-specific ^{14}C AMS.

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Thank you for your attention

^{14}CAST

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Speciation of carbon in iron-water systems - Previous studies

Japanese studies (RWMC studies)

- Carbon steel, Fe_3C, activated steel
- Batch-type experiments, reactor
- Synthetic solutions: pH 8 and 12.5
- Samples stored under N_2
- TOC, HPLC, GC (few samples)
- No pretreatment

Observations

- No volatile hydrocarbons (~ 0.01 %)
- Organic carbon (55 - 85 %)
- Inorganic carbon (15 - 45 %)
- Oxygenated organic compounds:
  - formic and acetic acid, minor portions of aldehydes and alcohols
  - decompose with time in alkaline solution

Deng et al., ES&T 1997

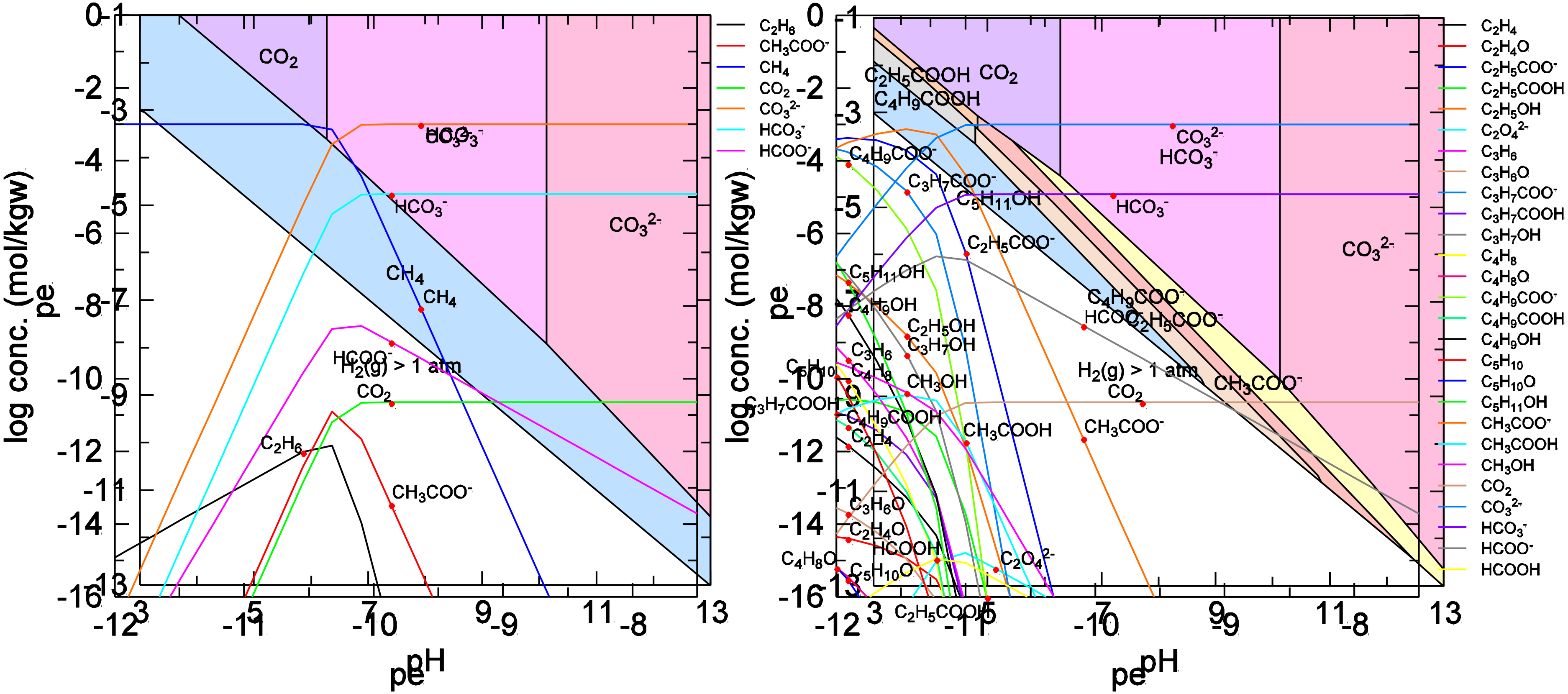
- Fe_3C, various iron powders
- Batch-type zero headspace systems
- Milli-Q water (low and high CO_2)
- Sealed samples in air, or 1 atm CO_2
- GC/FID
- Acid pretreatment of iron powders

Observations

- Volatile hydrocarbons
  - alkanes and alkenes ($C_n \leq 5$)
- Almost complete conversion of carbide carbon into hydrocarbons (dissolution in HCl, mass balance)
- Graphite carbon in iron not converted into hydrocarbons

Thermodynamic modelling of C-H-O systems

Wieland and Hummel, 2015



Comparison of complete (left) and partial (right) thermodynamic equilibrium.

Conclusion

The major uncertainties in modelling the C-H-O system are NOT the uncertainties associated with the thermodynamic data BUT the model uncertainties, i.e. the question of metastability.