Carbonation of anthropogenic concrete; Evaluation of carbonation process in concrete with analysis of carbon isotopes (^{14}C, $\delta^{13}C_{PDB}$)

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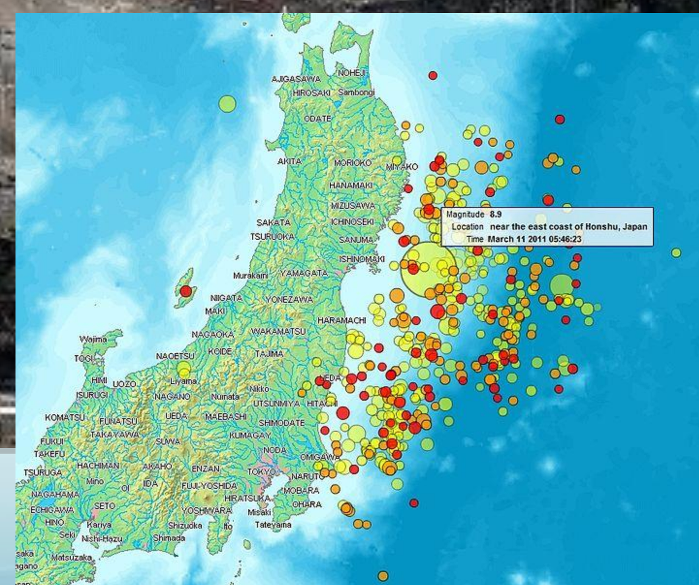
At first…Mega Earthquake attacked Japan



JAEA Tokai

… to fix all damage is ca. 25 billion yen!
(25,000,000,000 yen)

liquefaction

Content

***Background**

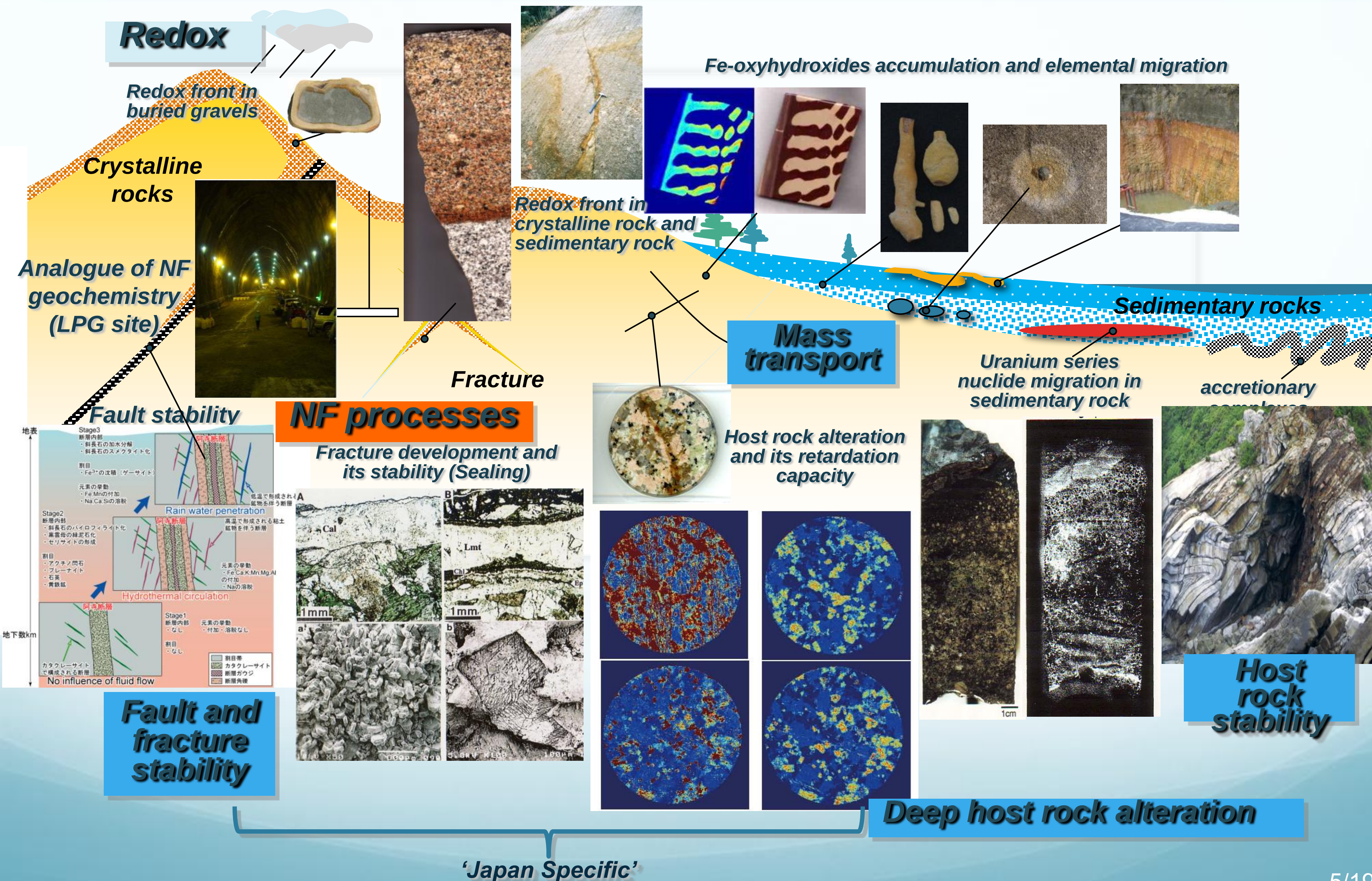
***Concrete carbonation study** **(needs from engineering purposes)**

-To understand the detailed carbonation process
(e.g. microscopic changes, geochemical changes and the progressing rate)

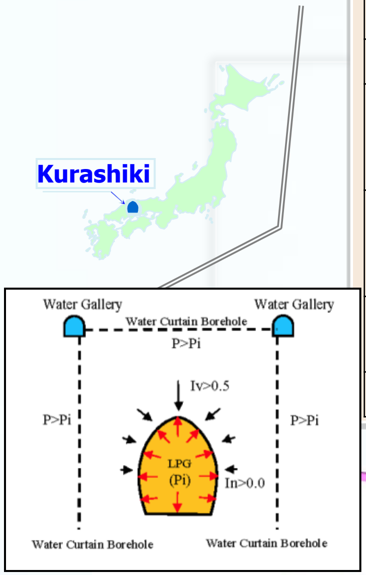
-To develop methodology to estimate quantitative rate
(or age) of carbonation by using isotopic analysis – ^{14}C ***(and*** $\delta^{13}C_{PDB}$***)***

***Concluding remarks (analogous point of view)**

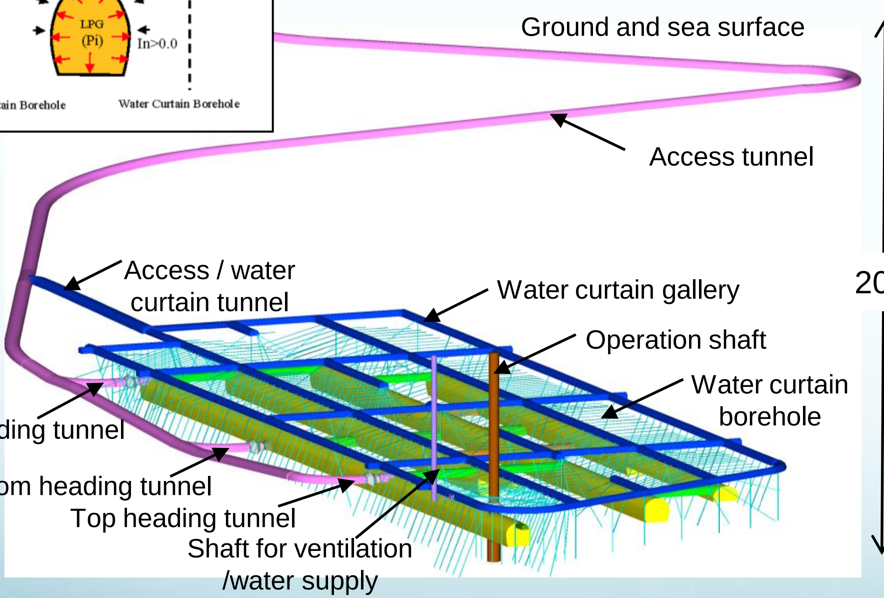
Analogous studies relevant to barrier function and geological stability



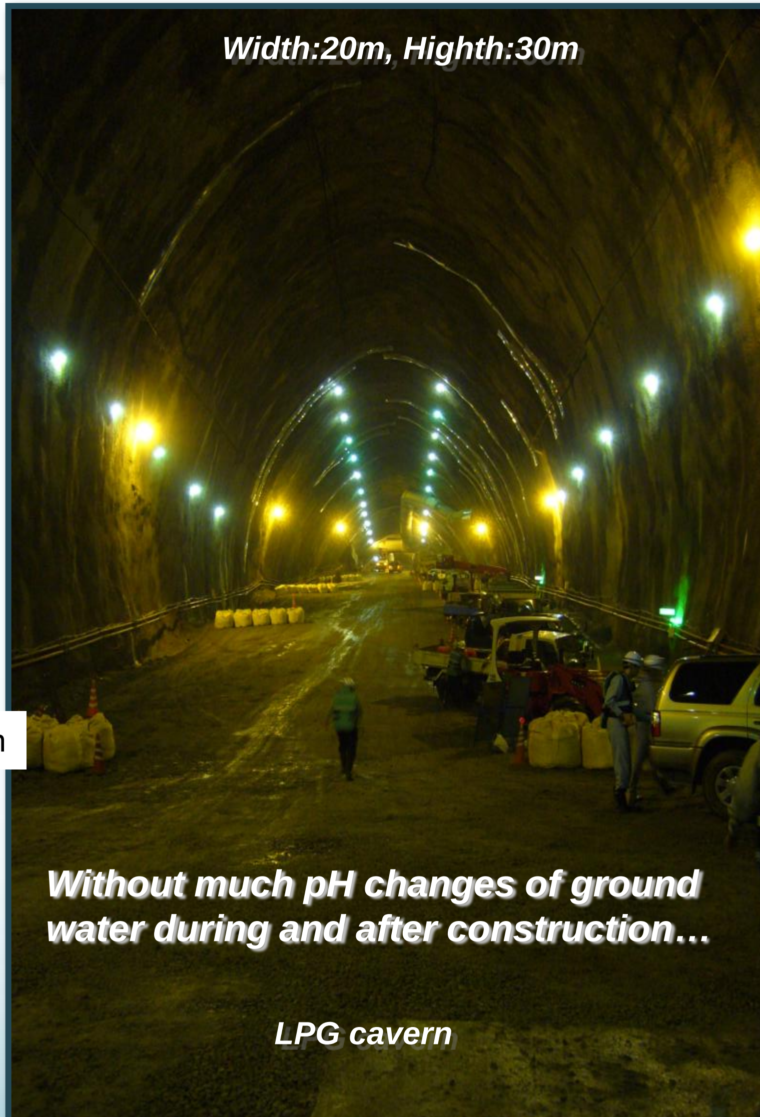
Use of concrete in underground (LPG site under the Seto inner seabed of Japan)



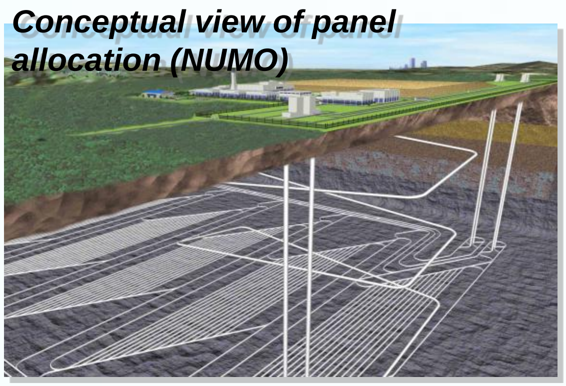
Specification	
Capacity	400,000 tons (Propane)
Dimension of storage cavern	18m(W)×24m(H) cross-sectional area :365m^2 4 caverns (maximum: 640m length)
Dimension of water curtain gallery	6.5m(W)×6m(H) cross-sectional area :34m^2 4.5 galleries
Elevation	Water curtain: -140m (bottom) Storage cavern: -160m (crown)
Design pressure	0.95MPa (Propane)



Specification and schematic view of Kurashiki LPG site



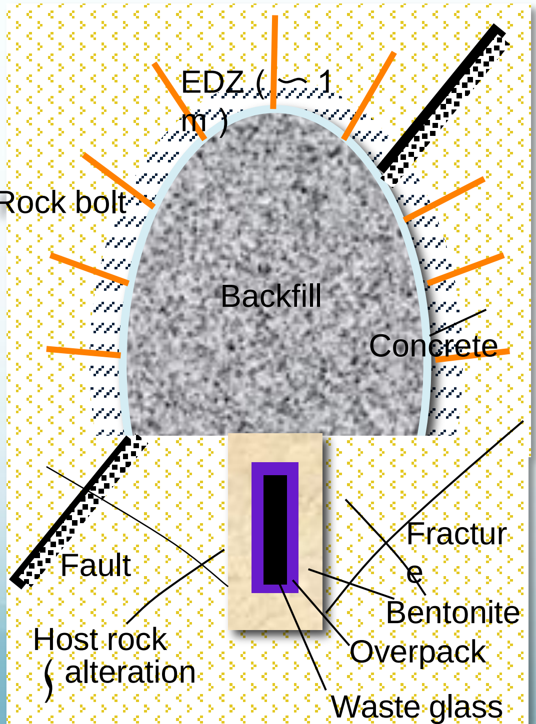
NF processes should be clarified relevant to barrier function



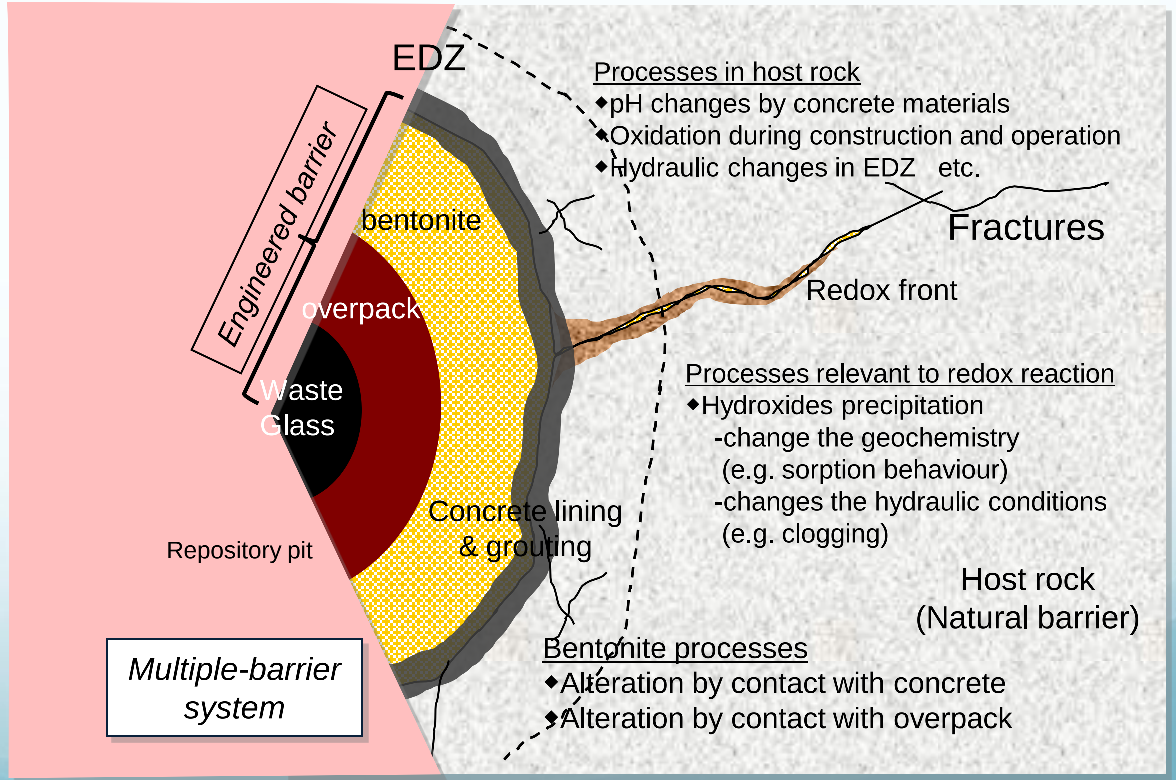
Condition of concrete after long time periods is still ambiguous.
→Try to define with analogous materials and data.

****Analogous aspects…***

-Understand the detailed carbonation processes of concrete
-Estimate the condition of carbonated concrete in post closure
-Development of methodology to estimate quantitative rate of carbonation



Try to define a realistic concept of NF components



Study samples of concrete

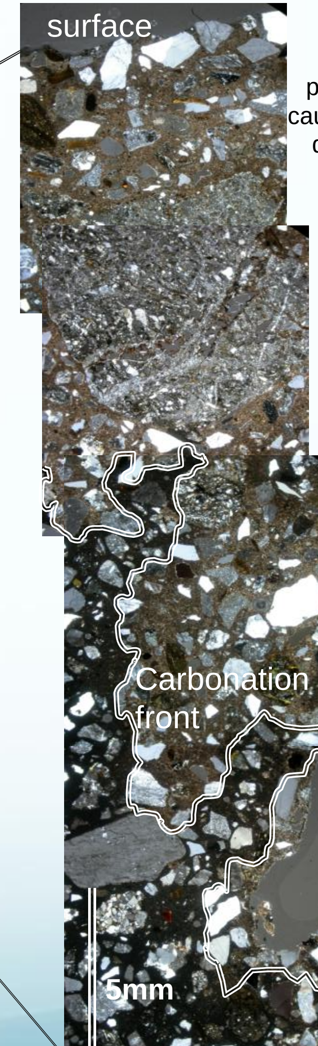
Rebuilt the old building of Nagoya University (built in 1965)

Analysis carried out…

***Thin-sectioned analysis - Optical microscope, SEM**
***X-ray mapping (Macro, Microscopic) - SXAM, EPMA**
***Bulk analysis - XRF, XRD**
***Isotopic analysis - ^{14}C , $\delta^{13}C_{PDB}$**

Carbonated zone visualized by using phenolphthalein (pH 8.3 -10.0)

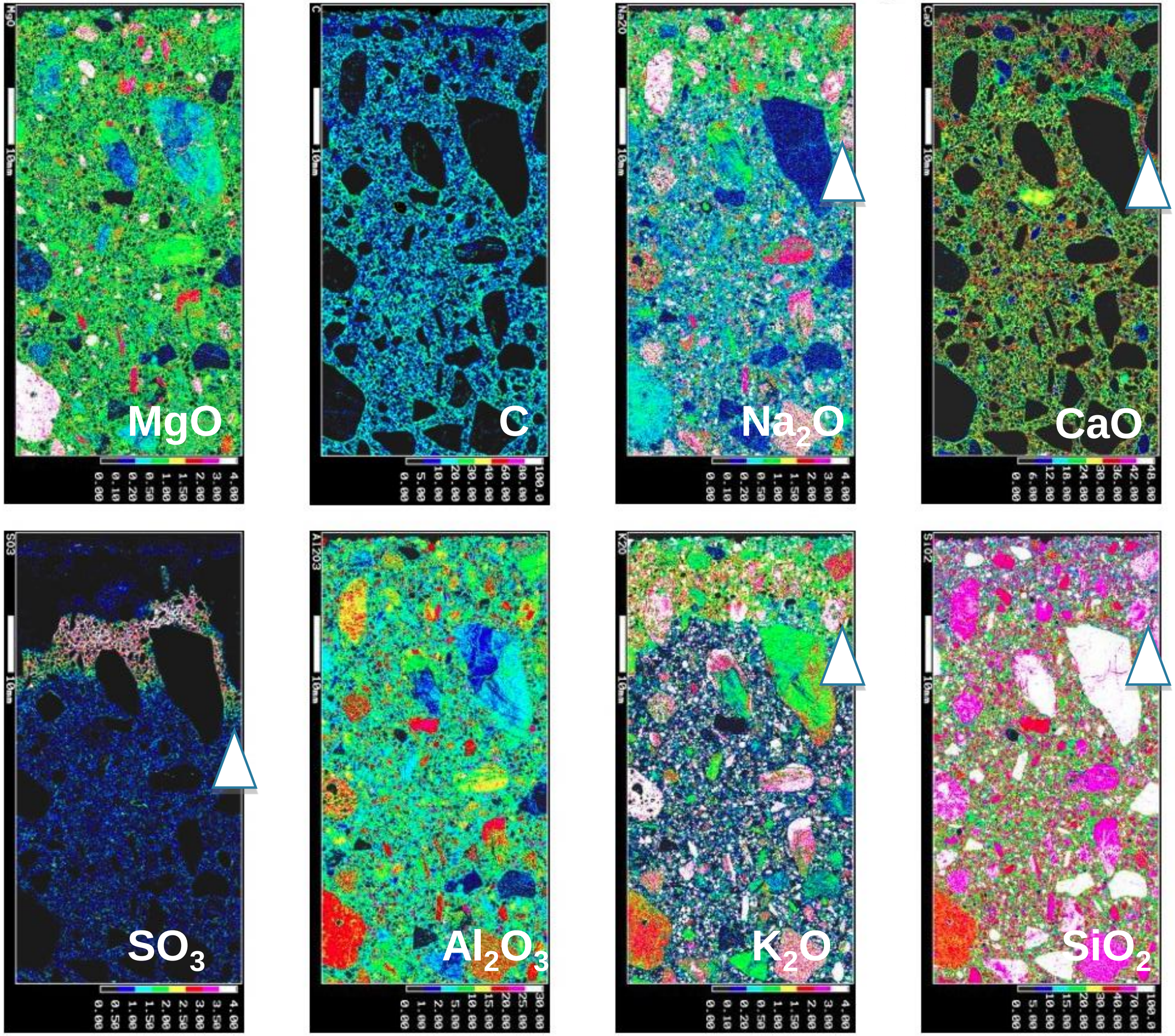
Thin-section micrograph



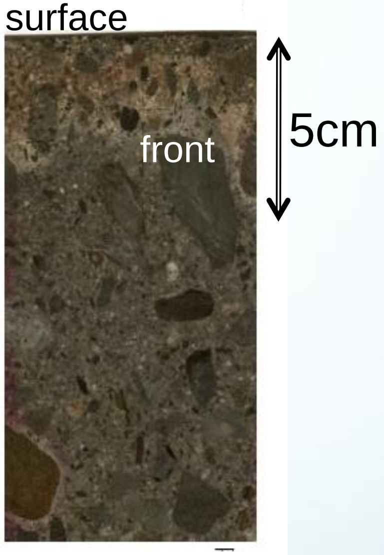
$CaCO_3$ precipitation causes porosity decreasing

C-S-H, $Ca(OH)_2$ (amorphous)

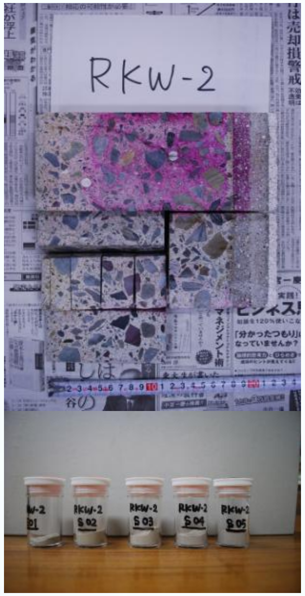
EPMA and SXAM mapping



RSW-2



Isotopic analysis (^{14}C, $\delta^{13}C_{PDB}$)



Analytical Procedure

 # $^{14}C/^{12}C$ ratio

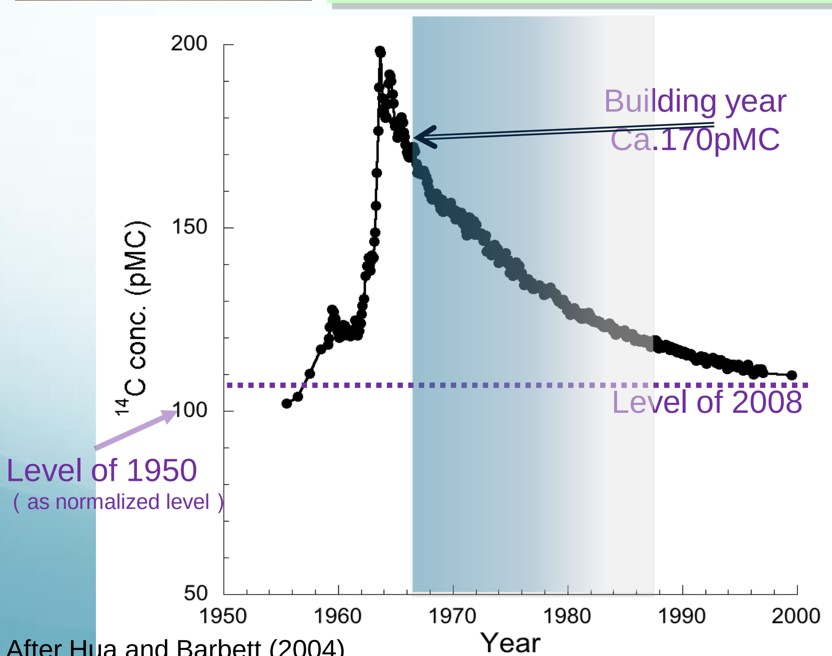
The pulverized sample was treated with H_3PO_4, and extracted CO_2 gas was purified cryogenically in a vacuum line. Then the CO_2 gas was reduced to graphite by hydrogen with an Fe catalyst at 620 °C for 6 hrs.

→Tandetron AMS (HVEE model 4130-AMS) *Center for Chronological Research, Nagoya University (detection limit; 1/1000 of present air CO_2 content)*

 # $\delta^{13}C$ (and $\delta^{18}O$)

The pulverized sample was set in a reaction container, which was put by a septum cap and purged by He gas, and reacted with H_3PO_4 by syringe. The CO_2 gas extracted during the reaction for 24 hrs was carried in He carrier gas to the mass spectrometer.

→IR-MS (Thermo Fisher DELTA V Plus + GasBench) *SI Science, CO., Ltd.*



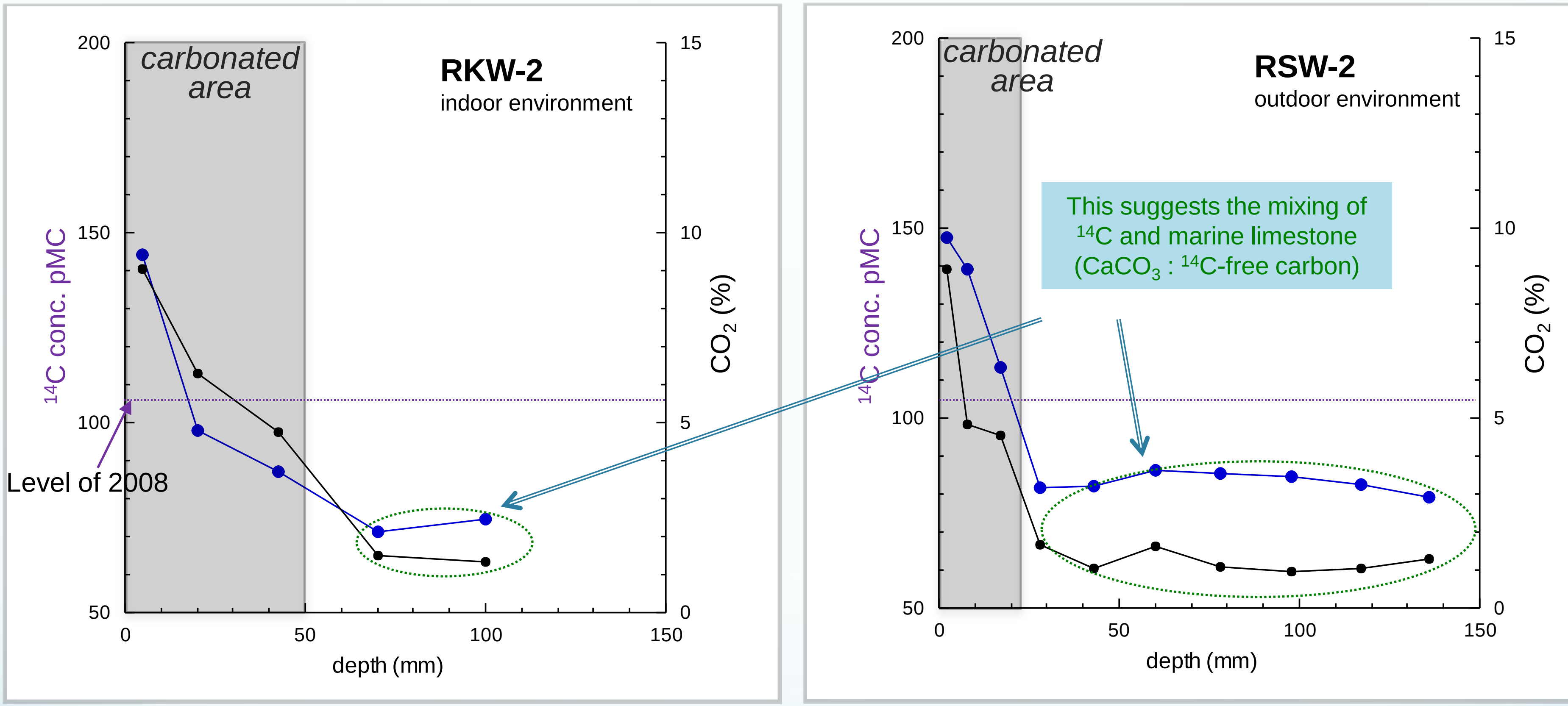
After Hua and Barbett (2004)

< Basic concept >

*Concrete…basically dead carbon material (check the starting compositions)

^{14}C will be increased after concrete placing, therefore the profile can be applied for the estimation of the rate of carbonation.

^{14}C concentration profiles



For the methodology development, it is necessary to confirm;

- ^{14}C is mixed at the beginning in the 'cement', or
- ^{14}C of air has been diffused into beyond the carbonated area for 45 years (?)

Check the source of ^{14}C within concrete

Check the contents of ^{14}C and $\delta^{13}C$ of carbonate in the fresh concrete

Materials used for concrete preparation;

- Cement admixture (air-entraining and high range water-reducing admixture;CHUPOL HP-11)

  C content = 13〜15%, ^{14}C concentration ≒ 0 pMC

  CO_2 content (Leached by H_3PO_4) = 0.003%

  → ^{14}C contribution ≒ 0

- Cement (commercially available 'Portland cement' in Japan)

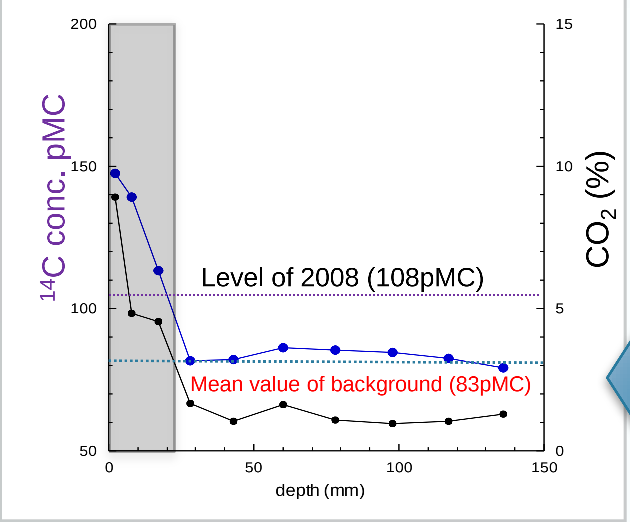
  CO_2 content = 1.3%

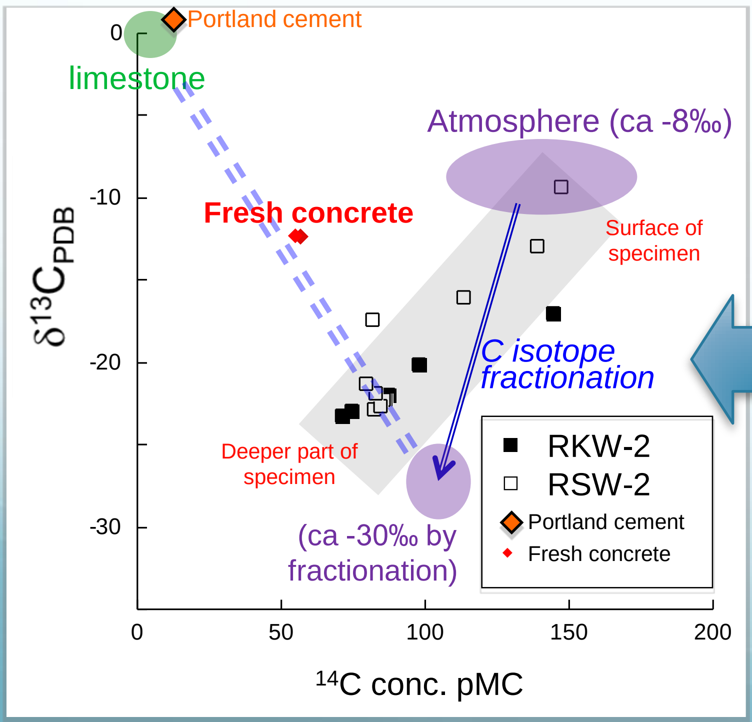
  $\delta^{13}C$ = +1.4‰ , ^{14}C content = 11.8 pMC

  (This shows that ca.10% of MC has been inevitably mixed during the preparation of cement in Japan.)

<u>Fresh concrete used above materials has been analyzed.</u>
Produced in 2008 and preserved in plastic back to use for background analysis.

^{14}C and $\delta^{13}C_{PDB}$ in the fresh concrete





Result of ^{14}C content in fresh concrete = 57 pMC

[^{14}C content of atmospheric CO_2 (2008) ≒ 108 pMC
^{14}C content of marine limestone = 0 pMC]

→Mixture rate between atmospheric CO_2 and marine limestone (^{14}C-free carbon) ≒ 1:1

(Probably it has been inevitably progressed during the construction.)

→If this rate would not change, the rate will be applied to estimate the primary content of ^{14}C of 40 years old concrete.

- ◆Construction time = 1965 (^{14}C =165 pMC known by monitoring)
- ◆Estimated ^{14}C primary content ≒82 pMC

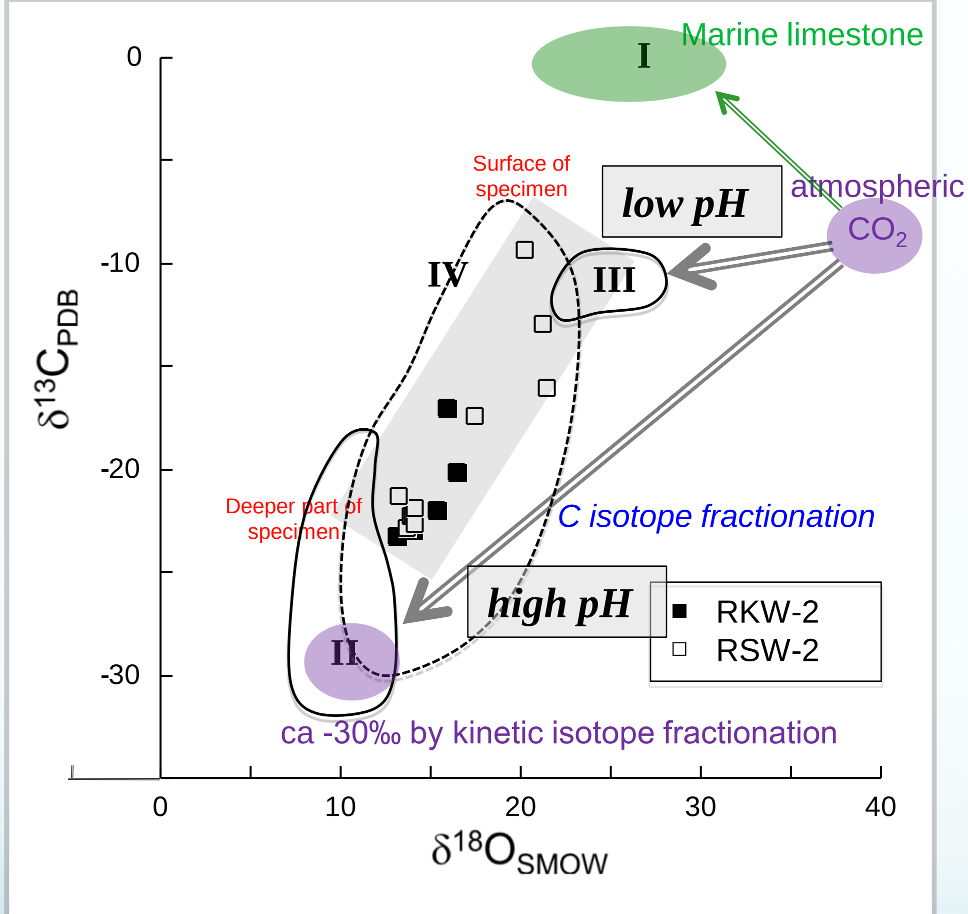
This value is almost coincidence with the mean value of background ^{14}C content. = 83 pMC

Result of $\delta^{13}C$ measurement = -12‰

[$\delta^{13}C$ of atmospheric CO_2≒ –8‰
→known to change up to -30‰ by fractionation
(Kosednar-Legenstein et al.2008(GCA)]

$\delta^{13}C$ of marine limestone ≒ 0‰

C isotope fractionation by carbonation



$$CO_{2(g)} = CO_{2(aq)}$$

$$CO_{2(aq)} + OH^- = HCO_3^-$$

$$HCO_3^- = H^+ + CO_3^{2-}$$

$$H^+ + OH^- = H_2O$$

$$Ca^{2+} + CO_3^{2-} = CaCO_3$$

$$CO_{2(g)} + Ca^{2+} + 2OH^- = CaCO_3 + H_2O$$

Fractionation

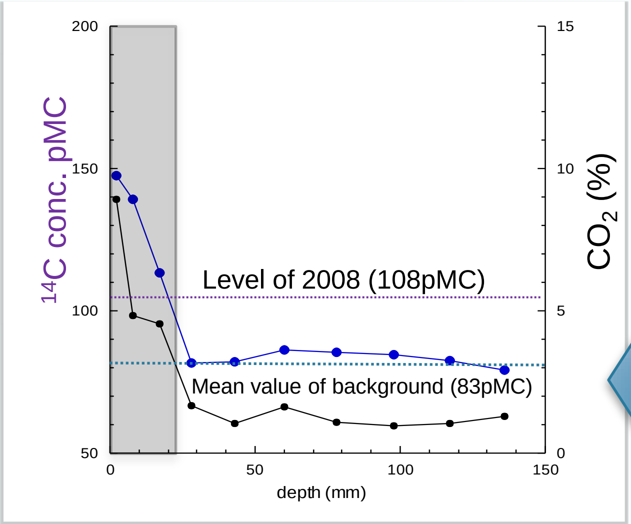
$\delta^{13}C_{PDB}$ and $\delta^{18}O_{SMOW}$ in concrete

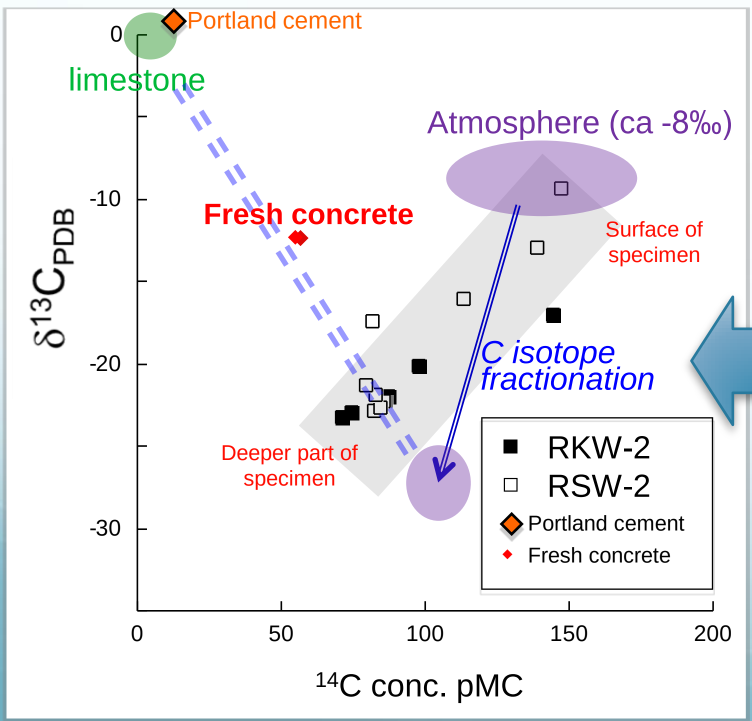
I :limestone of marine origin
II : from CO_2 absorption at high pH
III : from total precipitation of CO_2 dissolved in continental waters
IV : from various modern concretes

(Rafai *et al.*, 1991)

It is known that kinetic isotope fractionation has been progressed during carbonation under high pH condition.

^{14}C and $\delta^{13}C_{PDB}$ in the fresh concrete





Result of measurement; ^{14}C content = 57 pMC

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[$\delta^{13}C$ of atmospheric CO_2≒ –8‰
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$\delta^{13}C$ of marine limestone ≒ 0‰]

◆Value of fresh concrete (-12‰) settles between limestone (0‰) and fractionated lower $\delta^{13}C$ value (-30‰).

◆The fractionation has been progressed due to the pH changes by CO_2 trapping.

◆Concrete samples also showing the same trend.

Summary of carbon isotopes (^{14}C, $\delta^{13}C_{PDB}$) analysis

45 years old concrete and fresh samples (also source materials) have been analyzed and the results show that;

1)Microscopically readily identified carbonation.

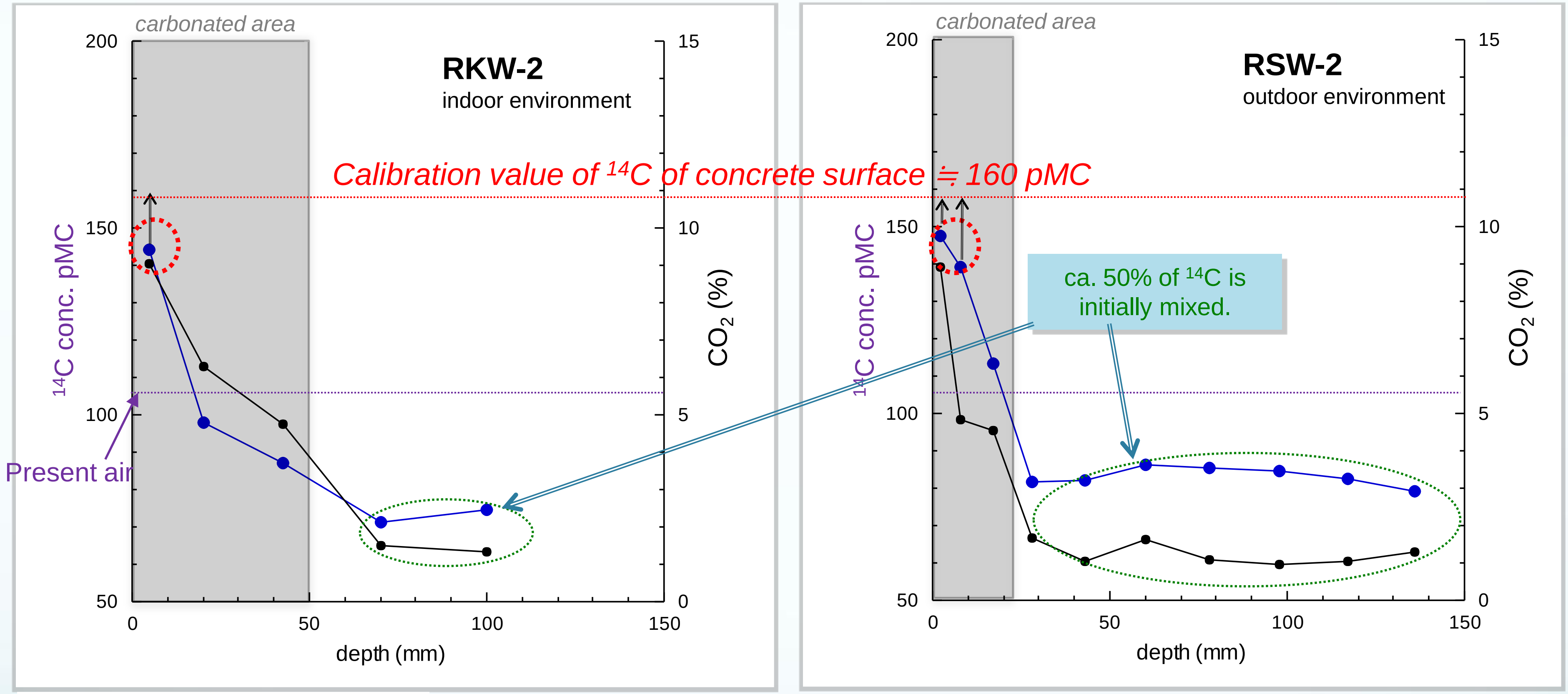
2)Portland cement includes ca.10 pMC.

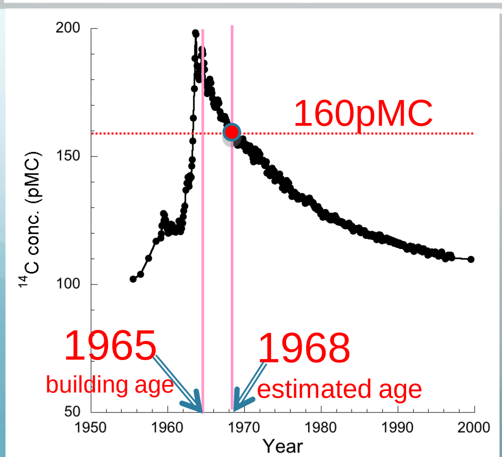
3)Concrete just after mixing inevitably includes ca. 50% of the ^{14}C.

4) ^{14}C dating methodology can be used to estimate by the calibration with initial ^{14}C level.

5) $\delta^{13}C_{PDB}$ data and profile in the concrete can be applied to check the fresh part of concrete.

Calibration of ^{14}C concentration and age estimation





^{14}C concentration of CO_2 absorbed after concrete placement

$$R^{absorbed}_{sample} = \frac{C^{measured}_{sample} \times R^{measured}_{sample} - C_{initial} \times R_{initial}}{C^{measured}_{sample} - C_{initial}}$$

C : CO_2 content (%)
R : ^{14}C concentration of CO_2 (pMC)
initial : C and R of CO_2 at the depth of less carbonation (deeper part of the concrete)

Calibration by using the value of primary mixing of ^{14}C shows 160 pMC at the surface part of concrete (see equation).

→The year estimated from the calibrated value is 1968 (42 years old). This is however the mean value of 1 cm of specimen. This suggests the estimation can be more precise (Tandetron AMS in Nagoya University can be measured ^{14}C from 1~3mg of $CaCO_3$).

Concluding remarks (how to use the results…)

<Carbonation of concrete>

Textural and geochemical changes of carbonation area (a few mm~cm)

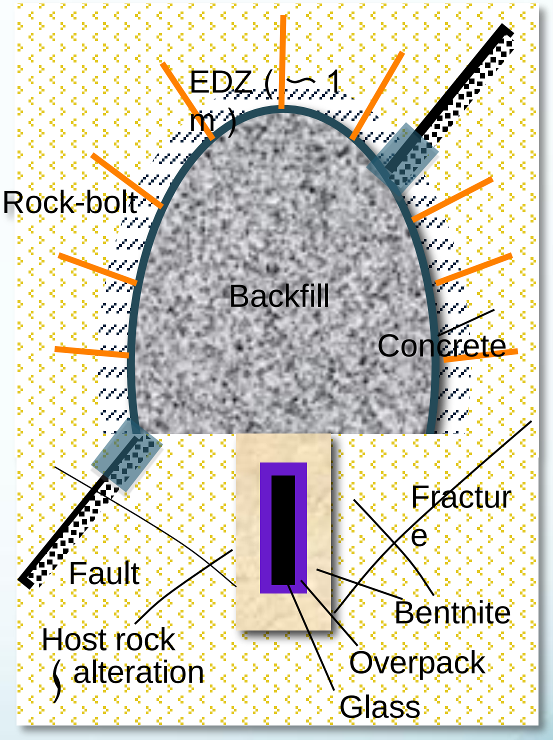
→ e.g. porosity decreasing by $CaCO_3$ precipitation

→ isotopic changes by CO_2 trapping (can be used for age estimation)

Developing the realistic post closure NF concept

→ Influence of carbonation (Hydraulic and geochemical properties)

→ If the carbonation is important, carbonation curing will be considered. (This has been taken into account for LLW repository.)



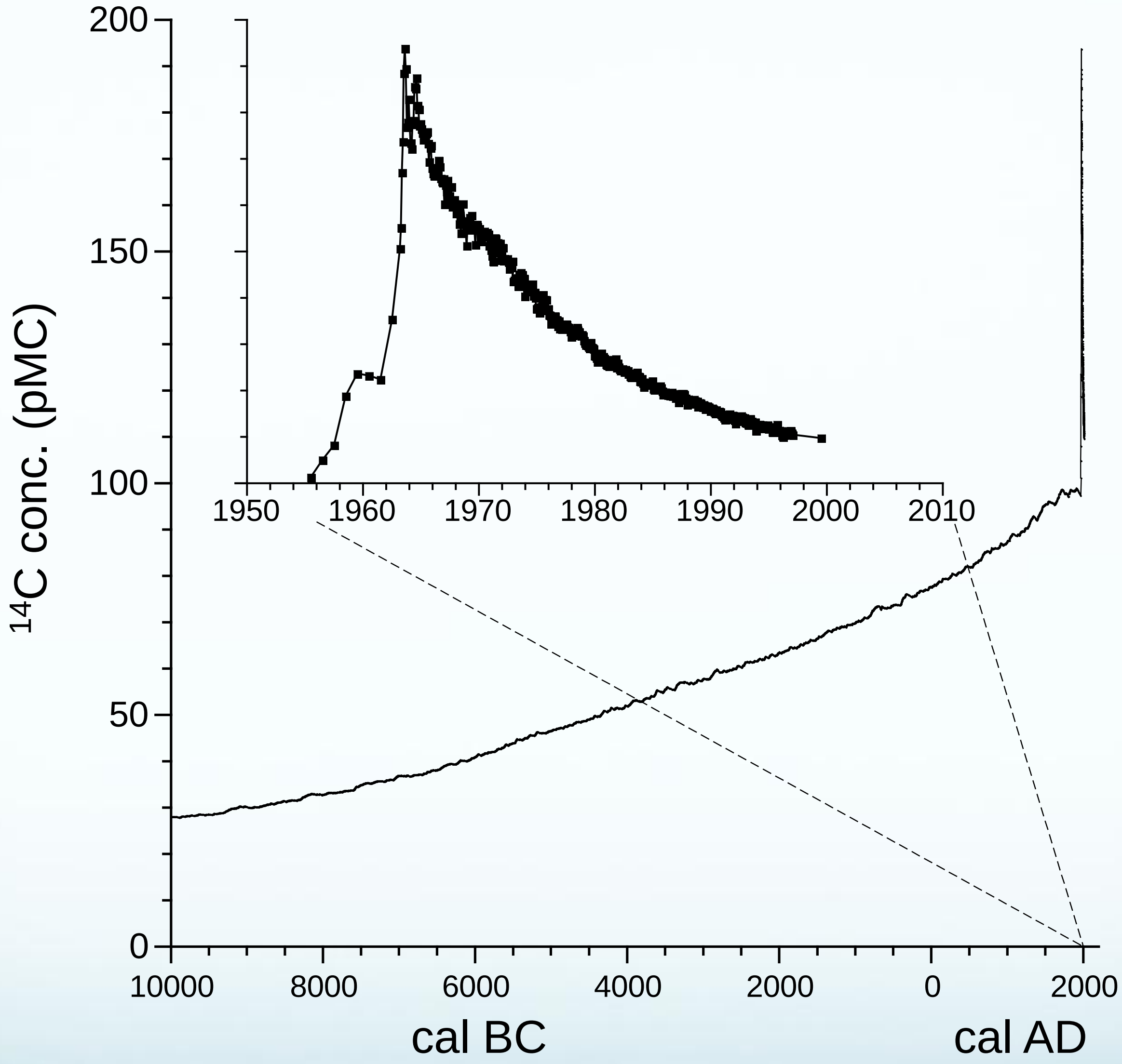
<Use for analogue>

Understanding long-term carbonation process and the rate estimation by the carbon isotope

→ Applicable for detailed analysis of older or ancient concrete

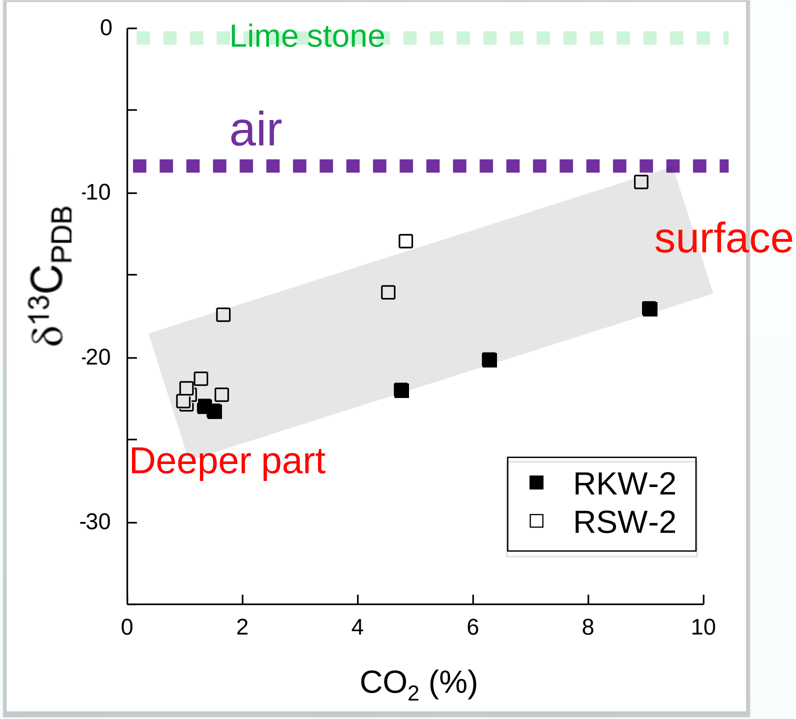
Yifthel concrete
Ca. 10000 yeas old?

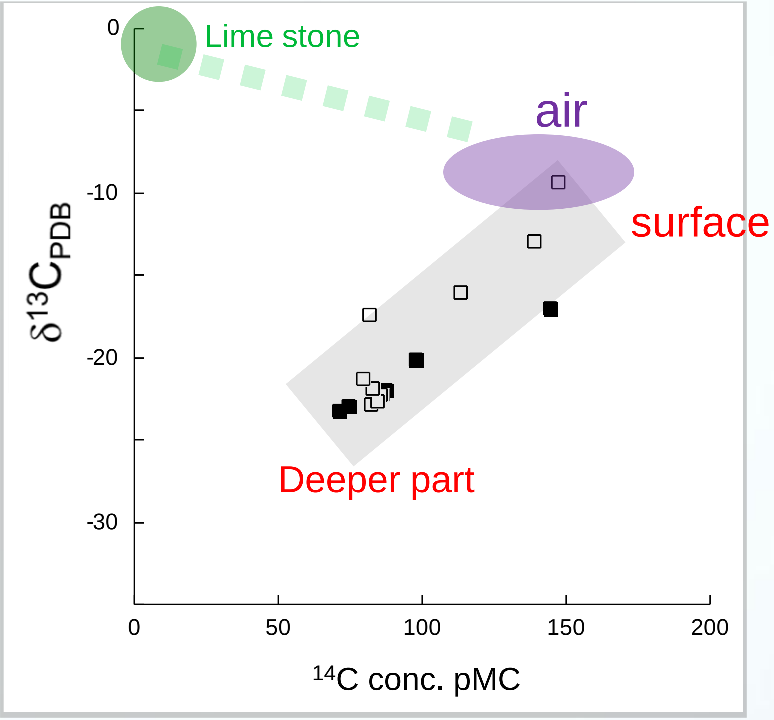
This aerial photo shows the archaeological site at Yifthel. The square excavations are each 16x16 ft., and the 18x40-ft. building footprint with parts of its floor shown is oriented in the direction of the North Star. Mixing and placing concrete to cover the 720 sq. ft. of floor is a major undertaking.



IntCal09 Northern Hemisphere atmospheric ^{14}C calibration curve (Reimer et al., 2009) extended by tropospheric ^{14}C curve during the bomb peak period (Hua and Barbettii, 2004).

Relationship of CO_2, 14C and $\delta^{13}C_{PDB}$





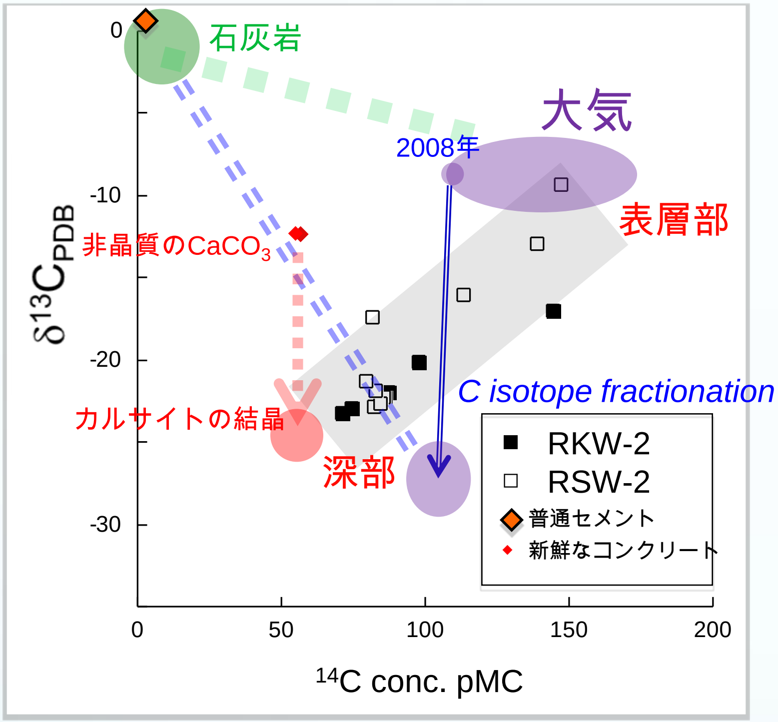
Deeper part of $\delta^{13}C_{PDB}$ is different from the value of air CO_2 and limestone used for concrete sources .

高アルカリ性環境下で大気CO_2から$CaCO_3$が形成される時のkinetic isotope fractionation (e.g. O'Neil and Barnes, 1971)

$$Ca^{2+}(aq) + 2OH^{-}(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$$

(コンクリート中の高pH細孔溶液へのCO_2の拡散，溶解)

^{14}C and $\delta^{13}C_{PDB}$ in the fresh concrete



^{14}C濃度 = 57 pMC

大気CO_2の^{14}C濃度（AD2010）≒ 108 pMC
石灰岩中のCO_2の^{14}C = 0 pMC

→ 大気CO_2と石灰岩中のCO_2が約１：１で混合

理学部E館のコンクリート中のCO_2にも同様に，1967年建築時（^{14}C =165 pMC）に初生的に含まれていたと仮定

→ ^{14}C濃度の初生値 = 82 pMC

↕

深部の^{14}C濃度 = 71〜86 pMC とほぼ一致

$\delta^{13}C$値 = –12

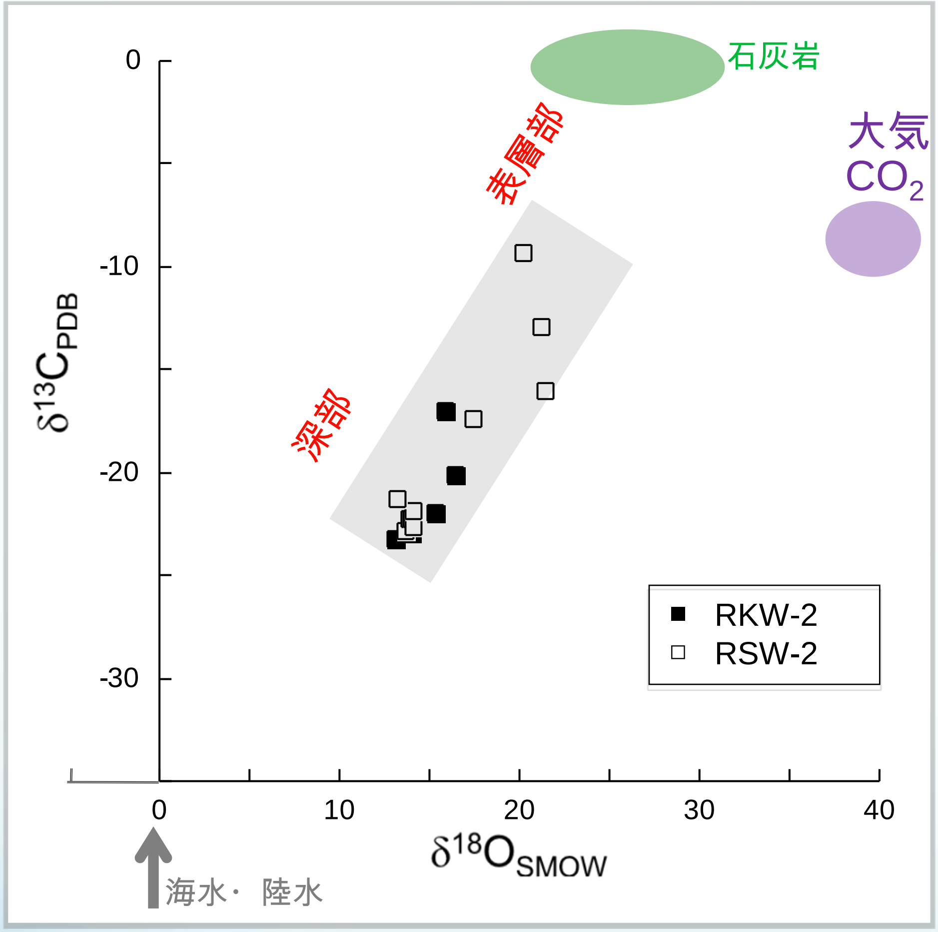
大気CO_2の$\delta^{13}C$ ≒ –8‰
石灰岩中のCO_2の$\delta^{13}C$ ≒ 0‰

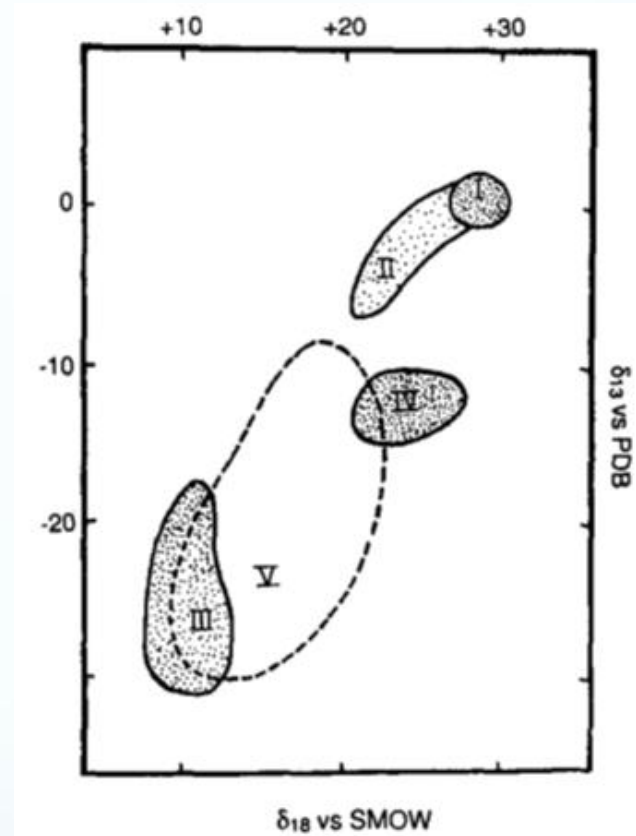
→ 大気CO_2と石灰岩中のCO_2の$\delta^{13}C$値より低い

↓

新鮮なコンクリートに大気CO_2が取り込まれる時に同位体分別が起こっている

$\delta^{13}C_{PDB}$ and $\delta^{18}O_{SMOW}$ in the concrete





炭酸カルシウムの炭素・酸素同位体組成

I :limestone of marine origin

II :limestone of continental origin

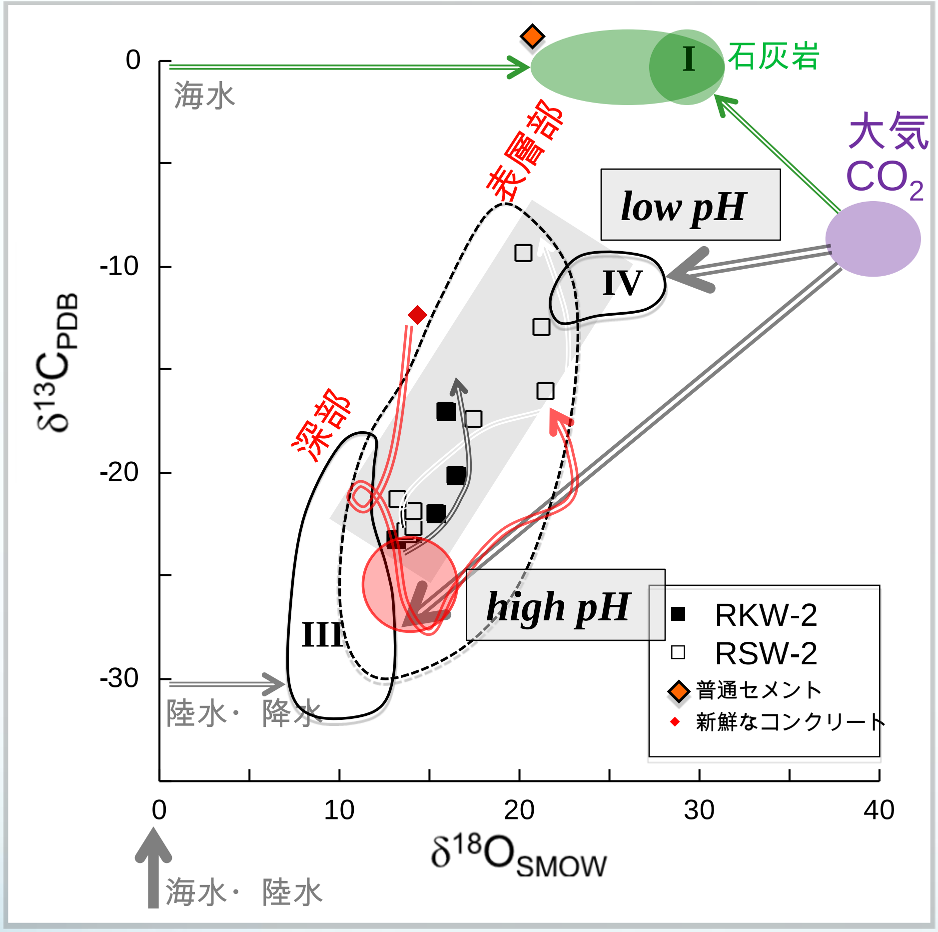
III : from CO_2 absorption at high pH

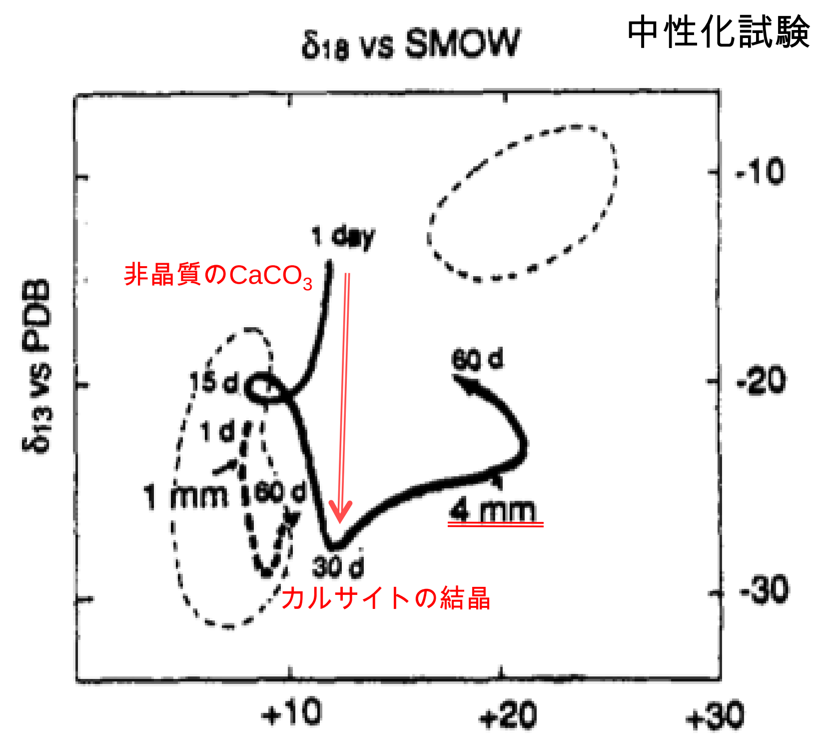
IV : from total precipitation of CO_2 dissolved in continental waters

V : from various modern concretes

(Rafai *et al.*, 1991)

$\delta^{13}C_{PDB}$ and $\delta^{18}O_{SMOW}$ in the concrete





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(Rafai *et al.*, 1991)

コンクリートを作る時に形成された非晶質の$CaCO_3$が，高アルカリ性環境下でカルサイトの結晶に変化しつつ，新たなカルサイトも形成される過程でkinetic C isotope fractionationが起こっている．

→ これが深部のCO_2の起源であろう

コンクリートの中性化試験による
$\delta^{13}C_{PDB}$値と$\delta^{18}O_{SMOW}$値の深度変化

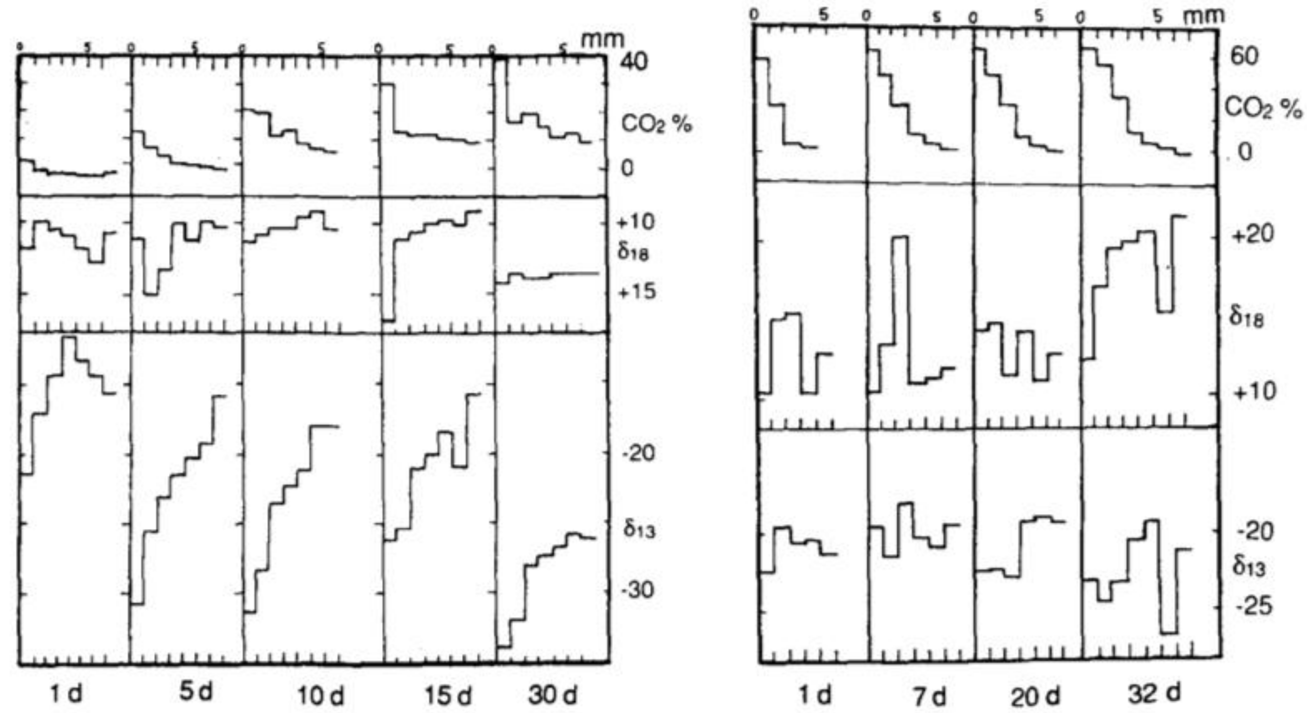

FIG. 2 a

Results of carbonation experiments on C_3S. Abscissae : depth in cement probes in mm ; I : recovered CO_2 (expressed in $CaCO_3$) per cent weight of carbonated cement ; II : δ_{13} ‰ (vs PDB) ; III : δ_{18} ‰ (vs SMOW).
II and III δ_{18} and δ_{13} of extracted CO_2 ; experiments from time of mixing to 30 days.

Fig. 2 b

Same for C_3S further evolution after 30 days hardening.

Rafai *et al.* (1991)

硬化コンクリートの組織構成

セメント (C_3S, C_2S, C_3A, C_4AF) ＋ 骨材 ＋ 水 ＋ 混和剤 (界面活性剤

→ 石灰岩＋粘土質材料を混合･粉砕し、高温で焼成

C : CaO, S : SiO_2, A : Al_2O_3, F : Fe_2O_3, H : H_2O

コンクリートの中性化（炭酸化）

コンクリートの主成分であるセメント水和物は

・ 高アルカリ物質（pH > 13）であり，

・ 大気中の二酸化炭素との化学反応でpHが下がる（中性化）

$$\mathbf{Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O}$$

$$(CaO)_3(SiO_2)_2(H_2O)_3 + 3CO_2 \rightarrow 3CaCO_3 + 2SiO_2 + 3H_2O$$

▼

鉄筋が錆びやすくなる

（酸化鉄の不動態皮膜が破壊されやすくなる）

▼

コンクリート構造物の劣化（“組織，物理強度の変化”）

放射性炭素^{14}C

・セメントの主成分である石灰分は地質時代の石灰岩起源であり，新鮮なセメント中の炭素には^{14}C（半減期5730年）は含まれない（^{14}C-free carbon）．

・新鮮なコンクリートが大気CO_2と反応すれば，時間とともに^{14}C量は増加するはず．

▼

建築時から現在までの中性化の定量的変化の把握

タンデトロン加速器質量分析計

現在の大気CO_2中の^{14}C濃度の**約1/1000**まで測定可能

▼

コンクリート中性化の初期段階の評価
コンクリート深部におけるわずかな中性化の評価