

Overview of A-ERW & Carbon accounting database

Carbon accounting for ocean sequestration monitored by alkalinity
Kanzaki, et al., PNAS Nexus, 2023, 2, 1-9
<https://doi.org/10.1093/pnasnexus/pgad059>

After application:
Alkalinity 2.40mmol/L
pH=8.05
DIC = 2.12mmol/L
ΔDIC=+0.04mmol/L
→Surface seawater CDR (Residual rate=83.1%)

Project-based net CDR accounting
Σprojects = Potential in Japan
TEA
Dynamic LCA (~2050)

Forested slopes Abandoned mines
Acid neutralization with limestone
Rainwater Surface water
Groundwater
Ore zone
Mine water
Effluent treating
CO₂
River
HCO₃⁻
Ocean alkalization

Keys to success for Japanese ERW:
3 condition-overlapping locations
= **Rocks applicable for ERW** (HRO/AIST database)
× **Existing quarry operators** (List from related associations)
× **Suitable application sites** (Excluding areas: national parks, high population, no forest road)

Evaluation of pretreatment energy customized for type of rocks

Quarry operator
Mining/grinding rocks

Geographic distribution of rock (Hokkaido area)
Mineral composition

Actual measurement value (Basalt dust)
900~1000 kg/h Roller mill
Average rate: 950 kg/h
Average voltage: 205.6 V
Average amperage: 56.65 A
Average power: 20.17 kW
950kg/h, 20.17 kWh=72612 kJ →76.4 kJ/kg
0.010 t-CO₂/t-R (0.48 kg-CO₂/kWh)
40 t-R/ha/y → 1.70 t-CO₂/ha/y
※ Consistent with 0.013 t-CO₂/t-Rock reported in J-LCA CR2 project

Sea←River←Groundwater Literature & macro model evaluation
OAE
Increase in DIC
Marine biological carbon sequestration

Application to farmland Model-based prediction
N₂O/CH₄?
Increase in yield / TEA
CO₂ mineralization & soil carbon balance (QPAC)
Rhizosphere refinement / Certainty improvement
Dynamic change in soil carbon balance
Collaborate with Minamizawa PM as civil science for N₂O reduction

Easiest carbon accounting: Gas-solid contacting house
@Honjo Waseda Campus

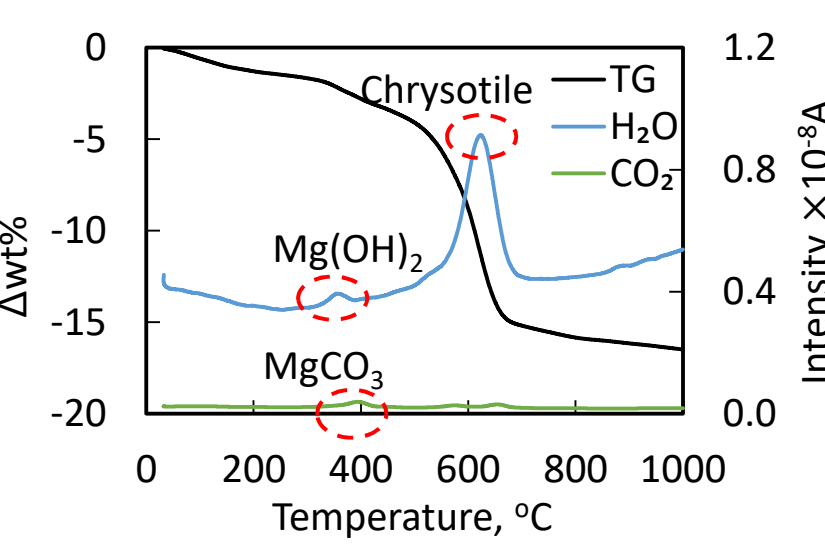
Operation energy data (Courtesy from actual quarry operator in Hokkaido)

Color legend:
Black: Share with Morimoto PM common in two ERW PJ
A-ERW firewall: QJ Science
Blue: A-ERW specific
Light blue: AIST team
Red: Literature-based estimation (Out of scope)

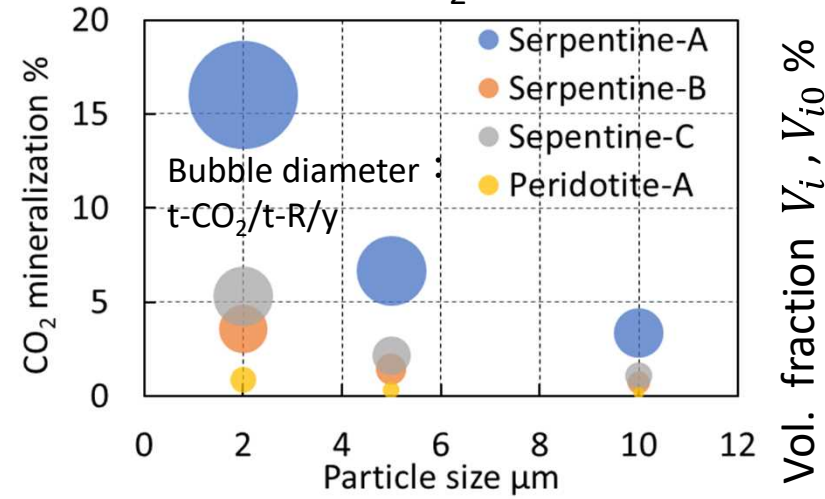
Area-specific annual CDR potential for A-ERW application

	A) Gas-solid contacting house	B)-1 Abandoned mine site	B)-2 Forested slope	C) Farmland
t-CO ₂ /ha/y	6,600~13,200	50 (per site)	0.3	3.0
Area/annual fixation potential	33,000~66,000 t-CO ₂	50 t-CO ₂ /y	37,500 t-CO ₂	20,000 t-CO ₂
Assumptions/Conditions	CO ₂ Mineralization potential =0.5 t-CO ₂ /t-R Reaction extent=44% Required area =0.1ha/site Amount of rock=3,000~6,000 t/y/site Mining depth 2m/y	CO ₂ Mineralization potential =0.0845 t-CO ₂ /t-R Applying 1000 t/y at Shojin river mine site in Hokkaido	CO ₂ Mineralization potential =0.0492 t-CO ₂ /t-rock Applying 20 t-R/ha at Shojin river slope in Hokkaido	150 t-R/ha basalt application on soba farmland in Fukushima (equivalent to 0.59 t-CO ₂ /ha/2.5months)

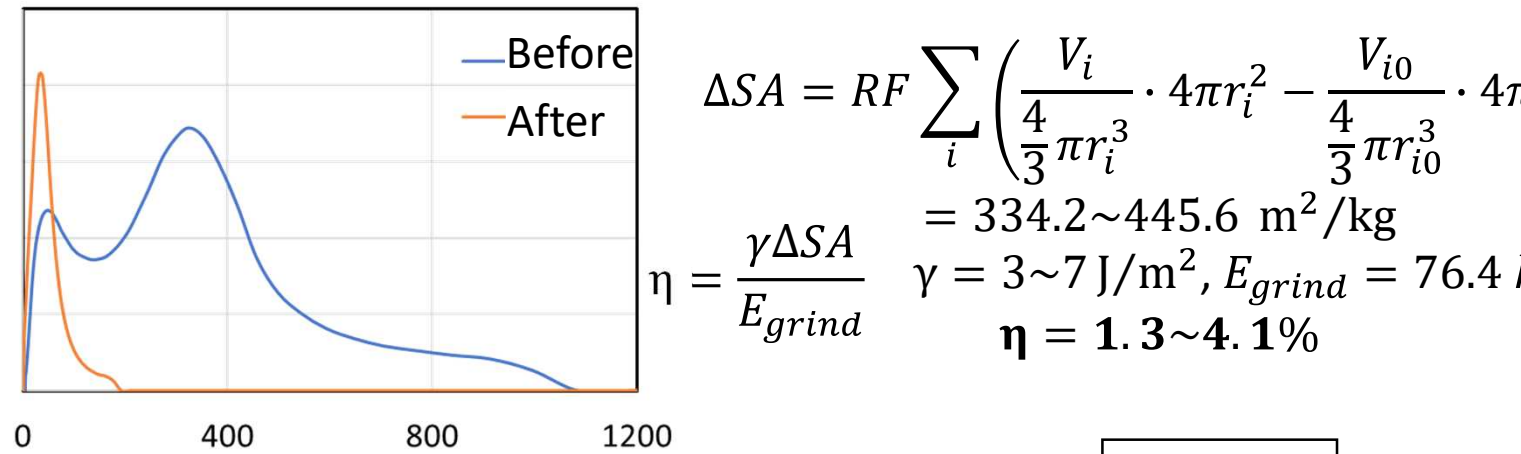
Asbestos analysis based on JIS A 1481 (Serpentine suitable for ERW)



Prediction of CO₂ mineralization



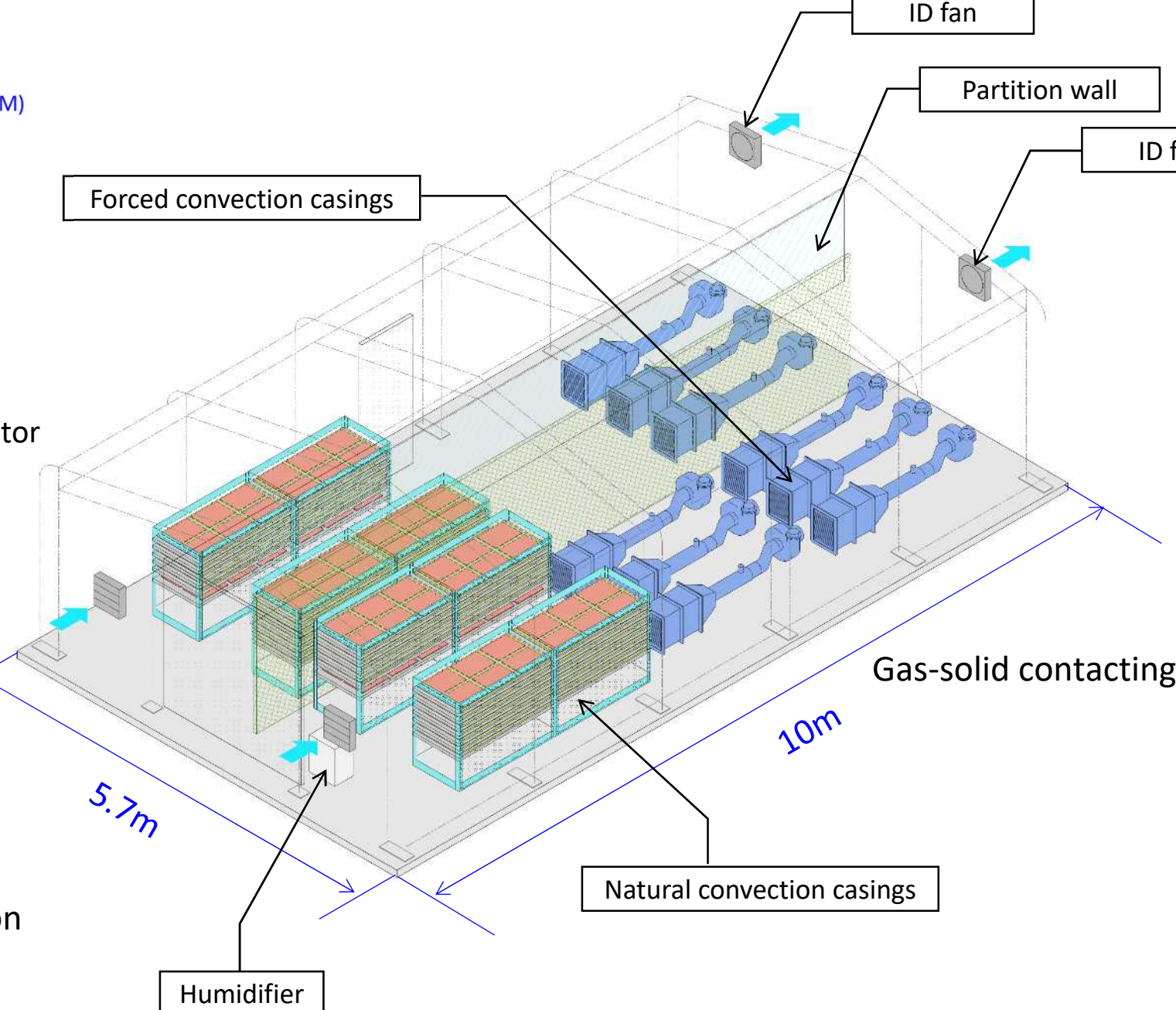
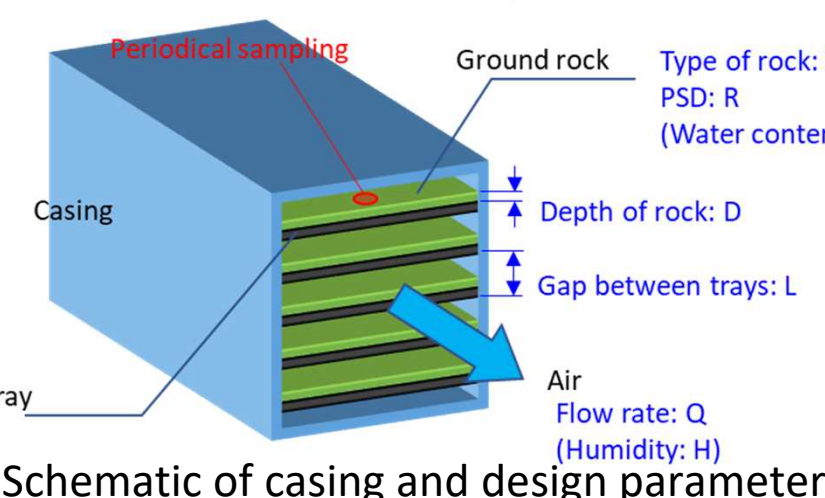
PSD before/after grinding and energy efficiency by Raymond mill



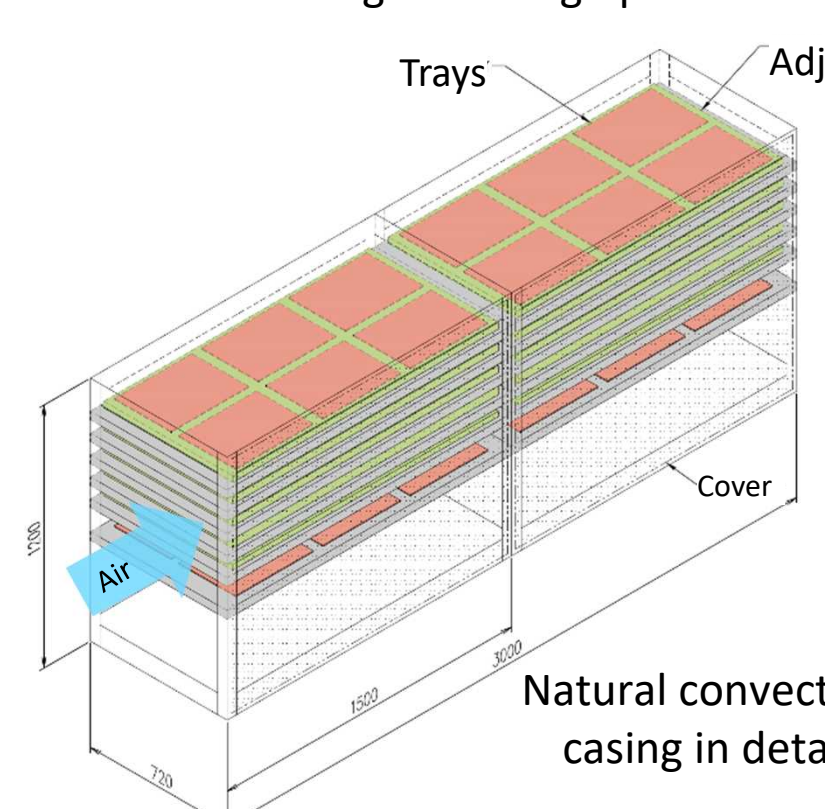
Reference case for benchmarking (trace calculation based on Beerling et al.)

40 t-R/ha/y of 10μm basalt on farmland	Unit	Basaltic type	
		Alkali	Tholeiite
SS: Soil Sequestration	t-CO ₂ /ha/y	1.42	1.55
	t-CO ₂ /t-R/y	0.035	0.039
OS*: Ocean Sequestration	t-CO ₂ /ha/y	6.66	2.70
	t-CO ₂ /t-R/y	0.166	0.068
SS+OS	t-CO ₂ /ha/y	8.08	4.25
	t-CO ₂ /t-R/y	0.202	0.106
Potential	t-CO ₂ /t-R	0.345	0.320
	1 year extent	62.6%	50.9%

SS: Soil Sequestration, OS: Ocean Sequestration
※ Assuming that 83.1% of DIC will remain even after several decades.



- Design and building permission of gas-solid contacting house
- The house will be commissioned by Feb. 2024
- ERW testing from April 2024 to March 2025



How to promote weathering of rocks (minerals)?

General Equation of Mineral Dissolution Rate

$$r = A_s k_+ a_{H^+} \left(1 - \frac{Q}{K} \right)$$

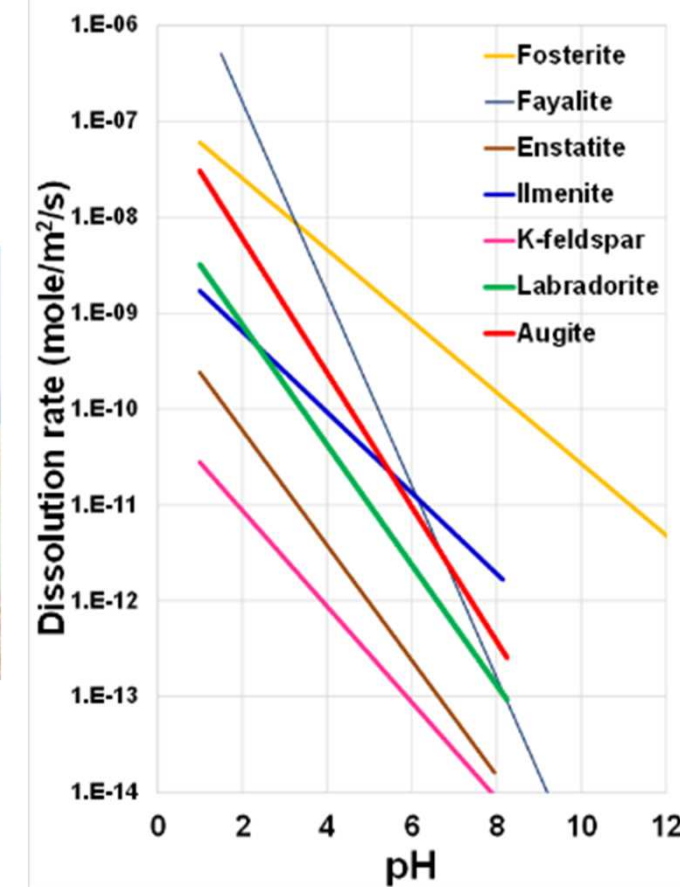
Deviation from equilibrium

- r : dissolution rate
- A_s : reactive surface area
- k_+ : rate constant
- a_{H^+} : H^+ activity (pH)
- Q : ionic activity product
- K : equilibrium constant

Beerling, et al, (2020, Nature)



Spraying basalt powder on farmland



pH dependence of mineral dissolution rate

- (1) Increase the reactive surface area
- (2) At lower pH of the reactive solution
- (3) Maintain a large deviation from equilibrium

Reasons for application to AMD and forested slopes



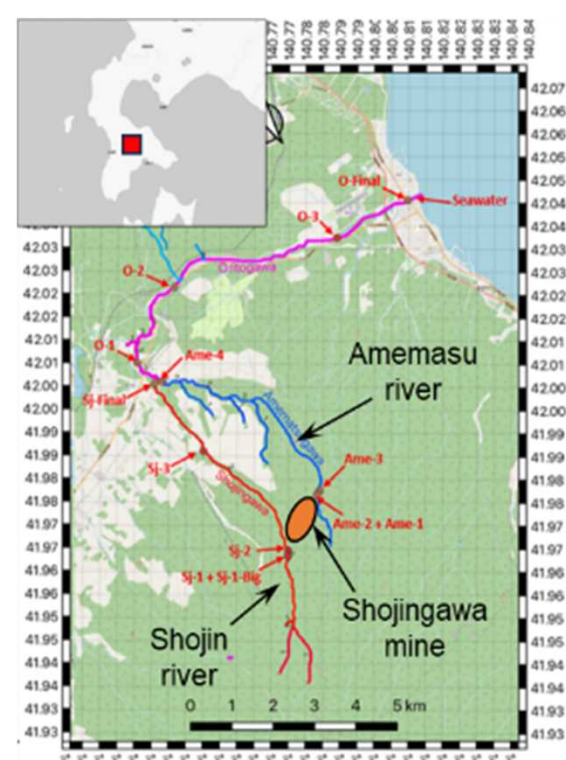
- There are rivers with strongly acidic water.
- There are about 100 abandoned mines that need to be addressed.
- Since the AMD have been monitored for many years, chemistry of the AMD is well known before basalt installation.
- It is relatively easy to get an understanding for basalt installation because of already contaminated.
- Quality of AMD may be improved by basalt.



- There are vast forested areas in Japan (2/3 of the total land area).
- During rainfall, large amounts of rainwater flow over the surface after reaction with basalt.
- Basalt installation could improve quality of forest soils.
- May help prevent landslides.

Field tests at abandoned mine

Details of the field test



Chemistry of AMDs in Amemasu and Shojin rivers

[mg/L]	Amemasu	Shojin
pH	3.04	3.00
Fe	16.22	26.37
SO ₄ ²⁻	549.69	306.31
Ca	15.09	6.78
Mg	2.31	1.87
Na	4.30	3.13
K	2.33	3.35
Si	20.75	11.28
Al	10.42	5.31
Cl	6.04	6.45
As	0.103	0.087
Pb	0.101	0.056

Location and monitoring points of the abandoned mine where field tests were conducted.

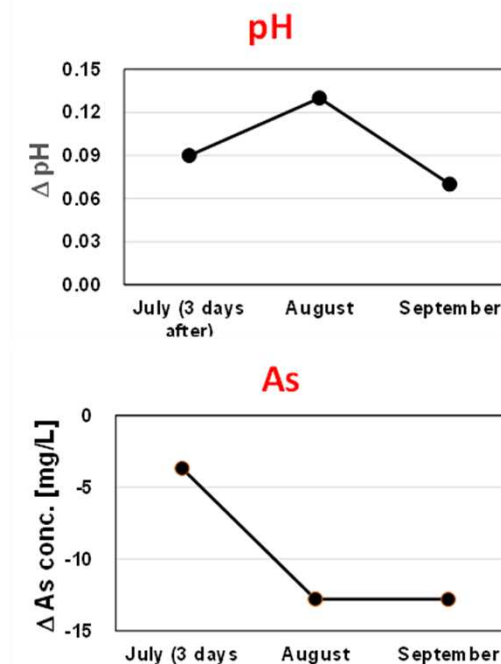
Basalt installed in AMD

TETSUZAN KYOWAGUMI Co.,Ltd., Hakodate (installed into the Shojingawa River)
 YOSHIOKA SAISEKI, Fukushima, Hokkaido (installed into the Amemasu River)
 Use of the dust from the production of crushed stone
 Grain size: 1-2 mm in diameter in polypropylene bags, 5 kg each
 (Bagged for easy removal in the event of problem)

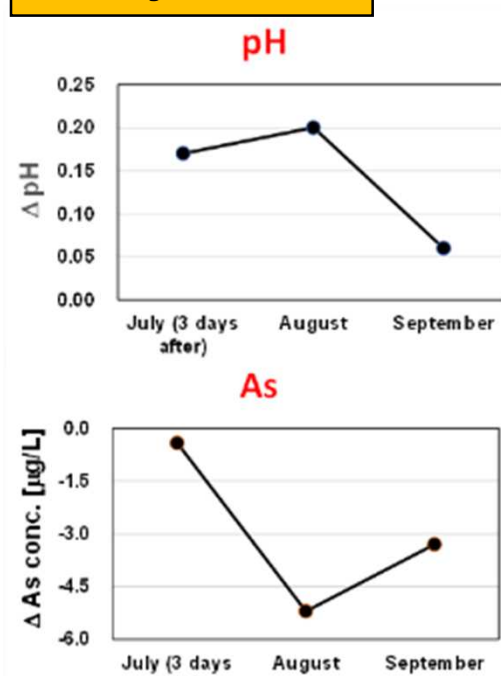


Changes in water quality before and after basalt installation

Amemasu Riv.



Shojin Riv.



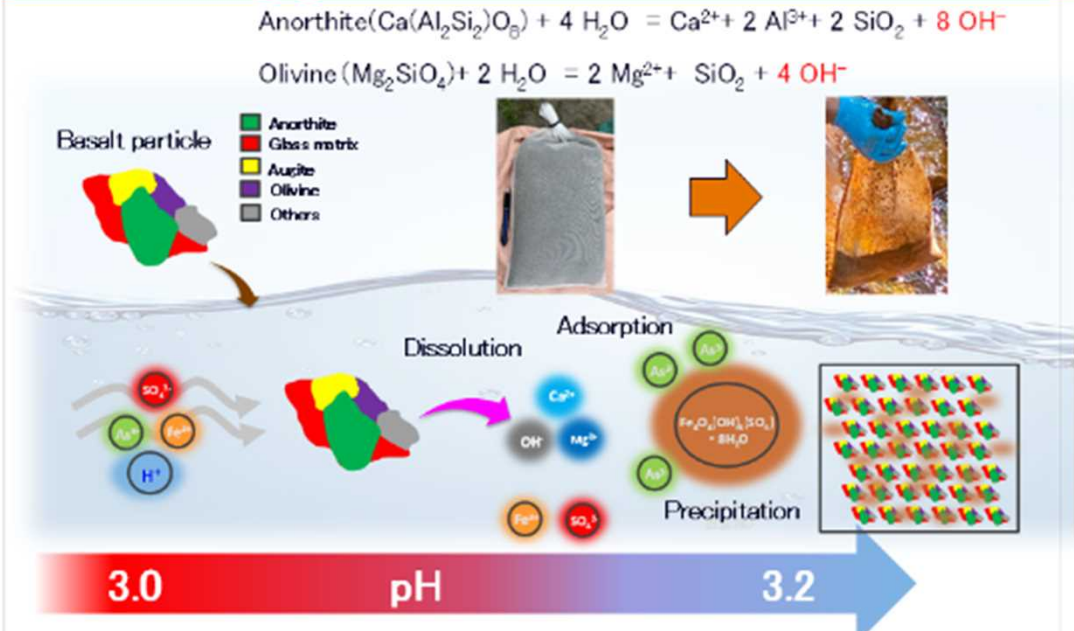
Change in basalt back after 79 days



Some bags were reduced to half their volume.

Huge amount of orange iron mineral was formed in the bags and river.

What's happened after basalt install?

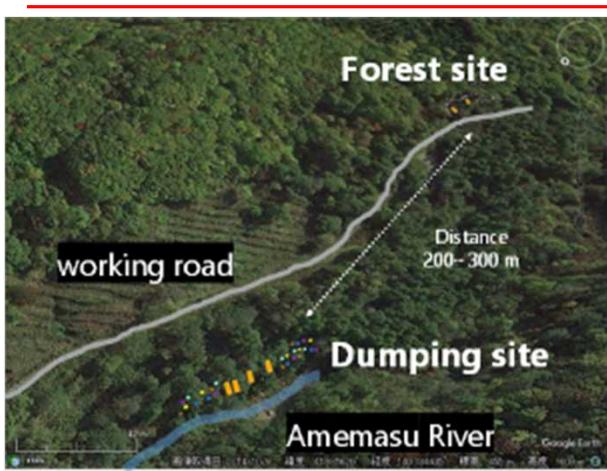


- The pH was elevated.
- Ca and Mg ions were leached from basalt-bearing minerals by their dissolution.
- Arsenic concentration in the AMD was decreased.

Installation of basalt into the AMD accelerated its weathering and reduced As concentration in the AMD

Field tests at forested slopes

Details of the field test



Forested slopes test sites near the Amemasu river

Dumping site (slope: 20°) Sub-plots

Forest site (slope: 30-35°) Mineral bag tests in-situ exposure test

Basalt installed on forested slopes

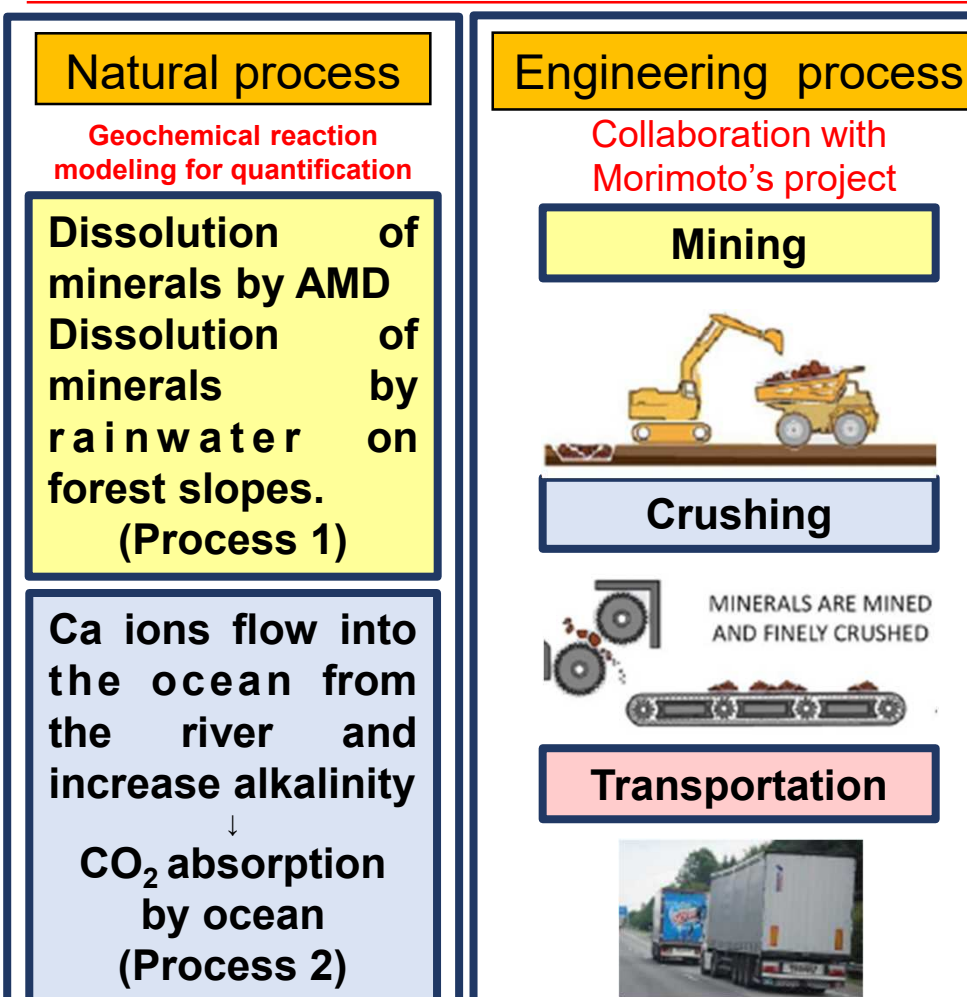
YOSHIOKA SAISEKI, Fukushima, Hokkaido
 Use of the dust from the production of crushed stone
 Powder (150-250μm) and pellets (8mm)
 Amount sprayed: control, 4 and 8 kg/m²



To understand changes in mineral phases and leachate chemistry under different conditions

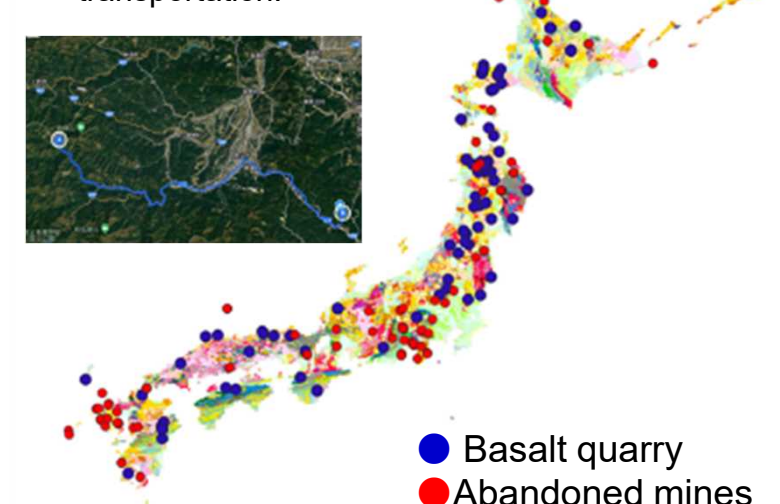
Carbon accounting

CDR of ERW in AMD and forest surface water reacting with basalt



CA trials are underway at all abandoned mines in Japan.

- Calculate the amount of basalt consumed a year at each mine by geochemical reaction modeling.
- Calculate the amount of CO₂ emitted during the mining and crushing of basalt rock.
- Derive the route from the nearest basalt quarry for each abandoned mine
- Calculate the amount of basalt to be transported and the amount of CO₂ emitted during transportation.



00 Project overview

Moonshot Goal 4 states "By 2050, achieve sustainable resource recycling for the regeneration of the global environment" and specifies the development of recycling technologies related to greenhouse gases and the verification of technologies from the perspective of life cycle assessment by 2030. As one of the technologies, the project states "CO₂ carbonation: technology to accelerate weathering by applying rocks, etc." The project aims to achieve this goal by developing technologies to absorb CO₂ by using rocks, and to verify these technologies from the perspective of life cycle assessment. In response to this goal, this project will develop technologies to accelerate weathering using rocks, especially technologies to accelerate CO₂ mineralization in weathering promotion using Japanese agricultural land.

The Agricultural Group is mainly in charge of Survey of potential sites & A-ERW technology in agricultural fields (O1), Development of in situ monitoring methods in agricultural fields (O2), Carbon accounting including natural carbon cycle & Conceptual design for large scale demonstration (O3). Since the effectiveness of rock application is expected to vary greatly depending on the environmental conditions in which farmland is located and on the type of rock applied, many research institutes (Kyoto Prefectural University, Hokkaido University, National Agricultural Research Institute, University of Tokyo, International Agricultural Research Institute, University of the Ryukyus) are participating in the research, which is being conducted in a wide range of test settings from column scale to field scale.

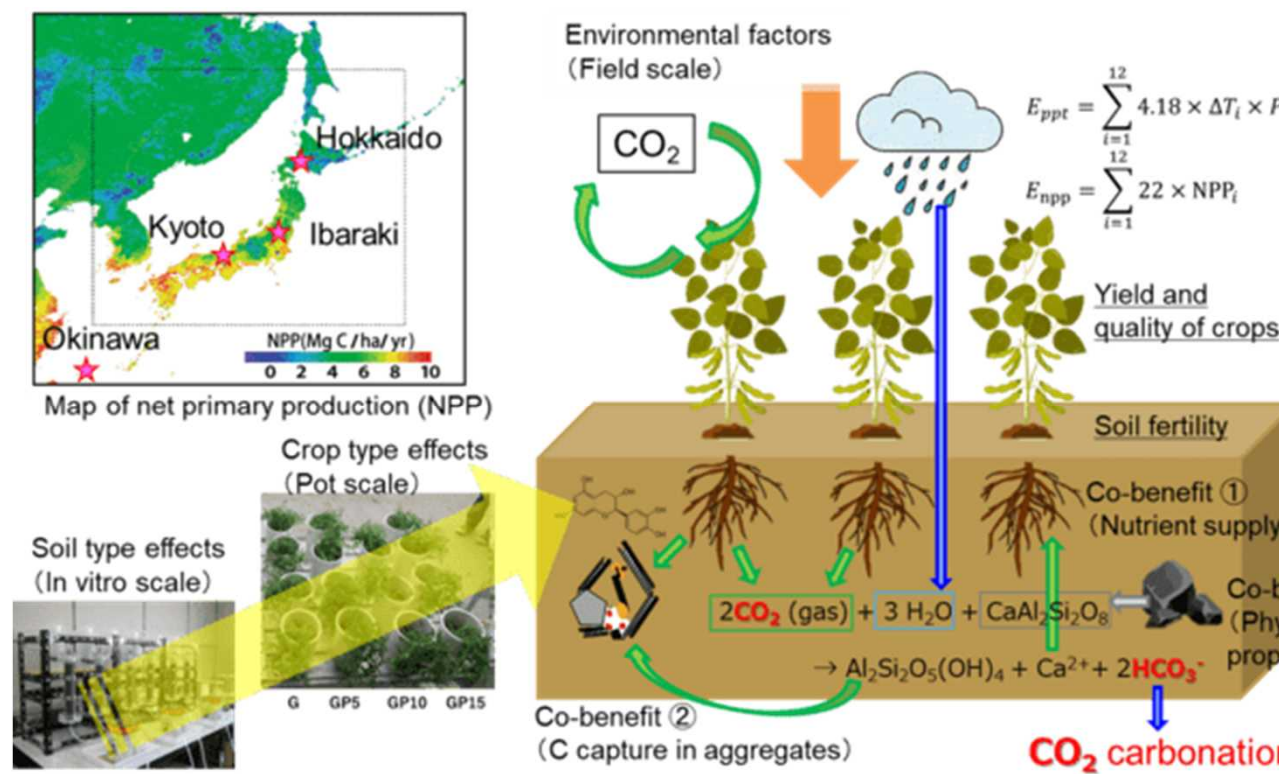


Fig. 00-1. Overview of the ERW research design related to agriculture

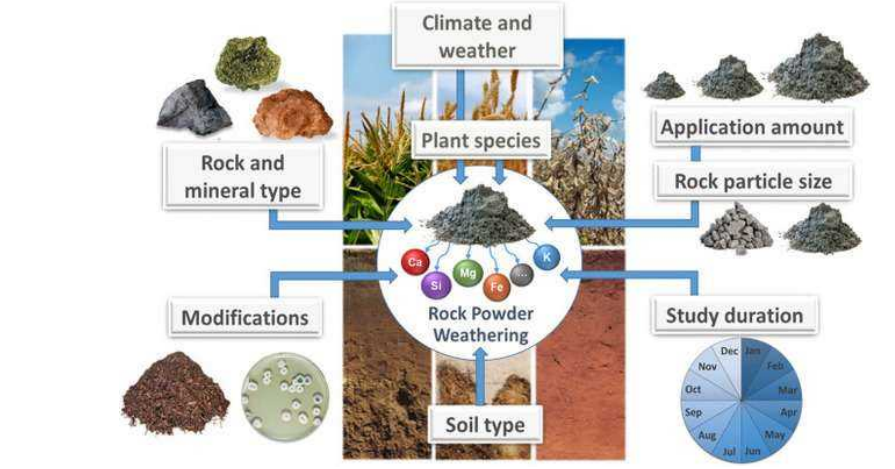


Fig. 00-2. Nutrient supply from rocks (Swoboda et al., 2022)

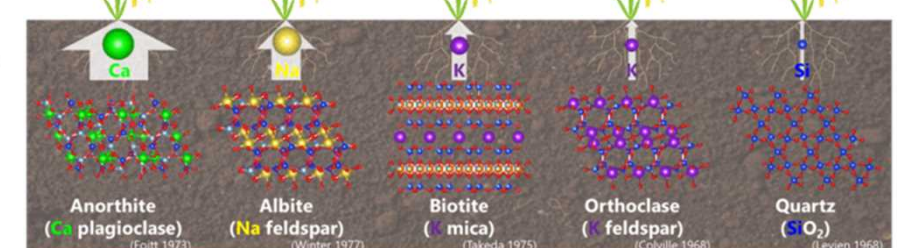


Fig. 00-3. Mineral type and its weatherability

01 Survey of potential sites & A-ERW technology in agricultural fields

Survey of potential sites:

Shorter distance from mining site to agricultural field is recognized as important to reduce the CO₂ emissions caused by rock transportation. However, even if shorter distance, lower weathering effectiveness may occur depending on soil type in agricultural fields. We investigated physical, chemical, and mineralogical properties of soils collected from 178 agricultural fields over Japan. We found that volcanic-ash derived soils contained weatherable primary minerals more than non-volcanic soils (Fig. 01-1), so that basaltic powder weathering rate would be slower in the former soil type.

A-ERW technology in agricultural fields:

First step to develop A-ERW technology is establishing the methods to quantify mineral weathering and CO₂ carbonation in agricultural field. Among our trials to verify optimal quantification methods, we largely improved a powder X-ray diffraction (PXRD) method to quantify mineral composition in agricultural soils by using self-prepared mineral library dataset (Fig. 01-2). Pot experiments to investigate effective cultivation conditions for ERW technologies clarified that crop yields varied largely depending on the combinations of soil and crop types even under the same application rate of basaltic powders (Fig. 01-3).

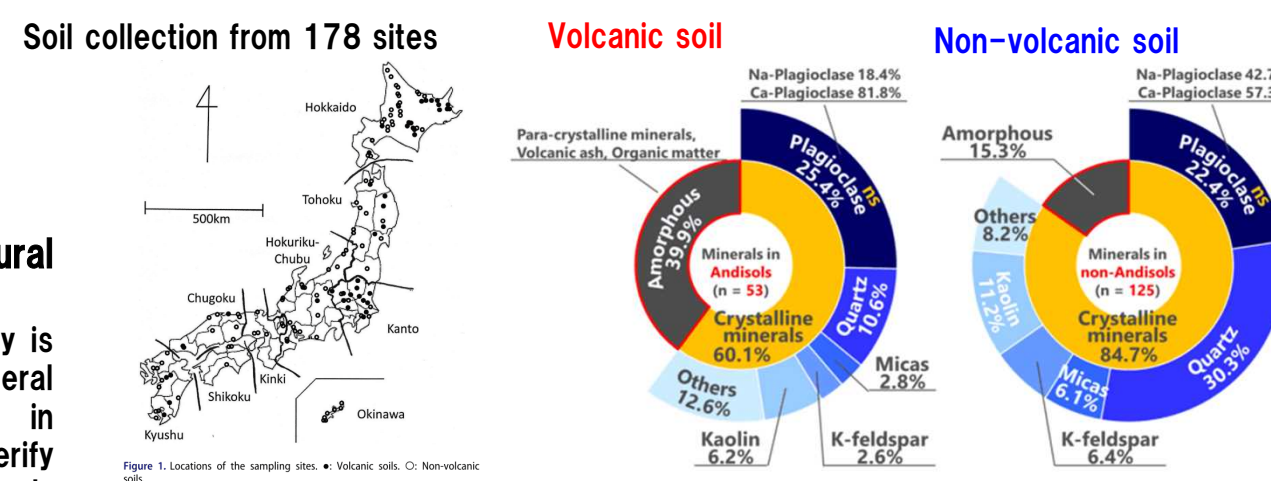


Fig. 01-1. Mineral components in soil before rock application

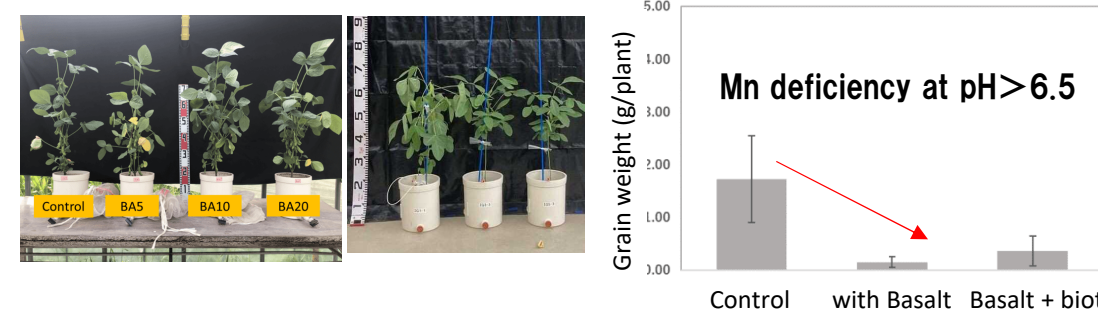


Fig. 01-3. Pot experiments for soybean cultivation by using Hokkaido (left) and Ishigaki soil (right) with or without basalt

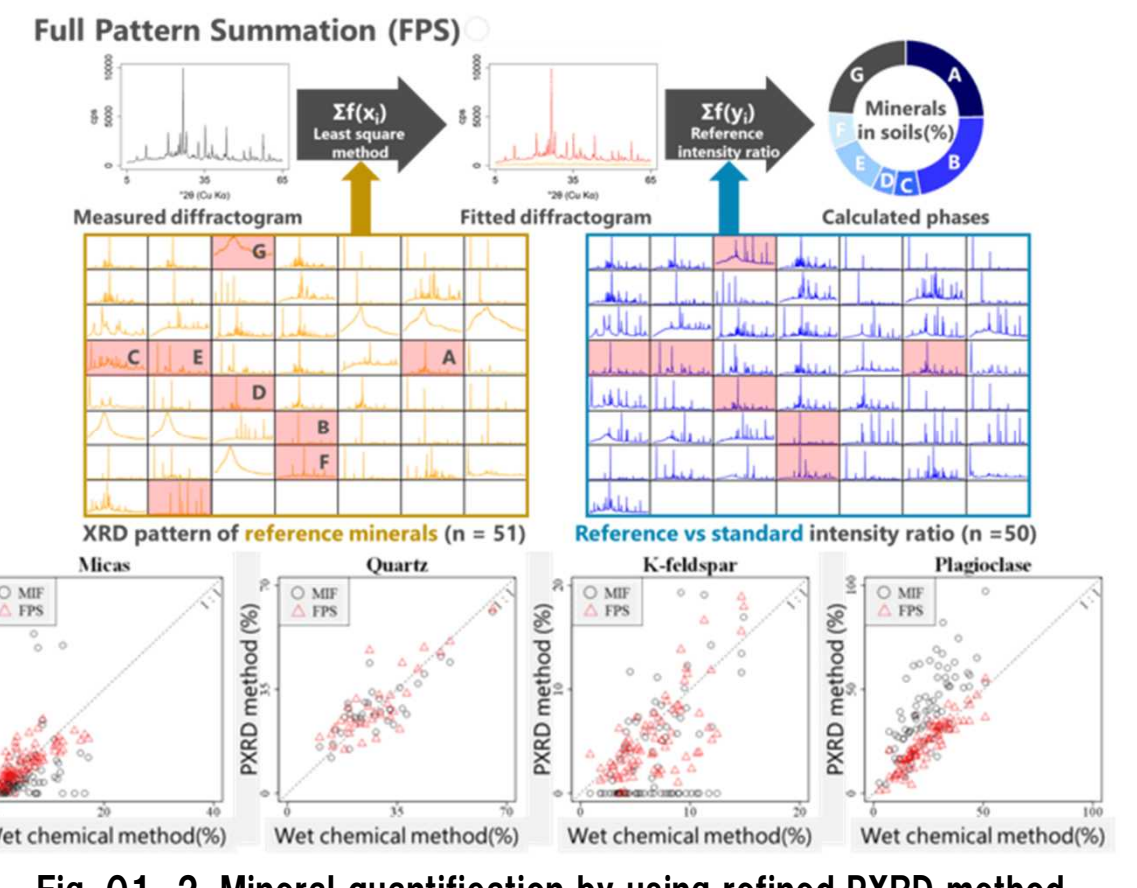


Fig. 01-2. Mineral quantification by using refined PXRD method

02 Development of in situ monitoring methods in agricultural fields

Field experiments for ERW technologies were conducted at four sites (Hokkaido, Ibaraki, Kyoto, and Okinawa) to monitor environmental parameters, to collect leaching water, and to determine crop yields and soil-to-plant transfer of multiple nutrients (Fig. 02-1). Both the Hokkaido and Ibaraki fields were used for investigating co-benefit effects of ERW on soybean cultivation and for estimating annual CO₂ accumulation by ERW (ERWCO₂) based on organic carbon flux monitoring information (Fig. 02-2). We found net increase in ERWCO₂ at Ibaraki field where CO₂ consumption due to mineral weathering may be progressive in summer season (Fig. 02-3).

Three patterns of methods for estimating ERWCO₂ were investigated at the Hokkaido field, which were based on CO₂ flux information obtained by either CO₂ chamber method or CO₂ sensor and physical parameter method. We found that these methods still involve uncertainties derived from different experimental errors, so that further verification is needed to choose an optimal method. Decrease in plagioclase after basaltic powder application through mineral weathering followed by increasing Si supply during rice cultivation was observed at the Kyoto field (Fig. 02-4). Sugarcane cultivation at the Okinawa field is ongoing until the end of February 2024.

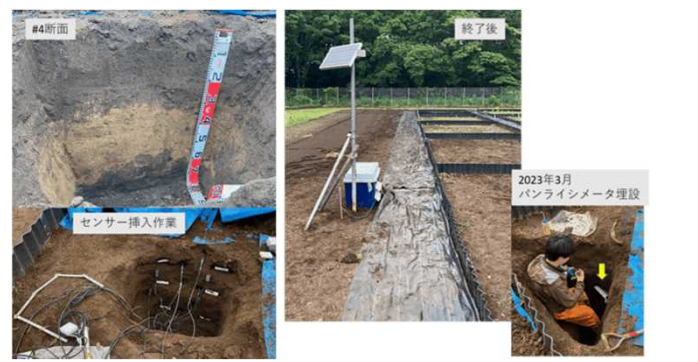


Fig. 02-1. Setting monitoring devices@Ibaraki

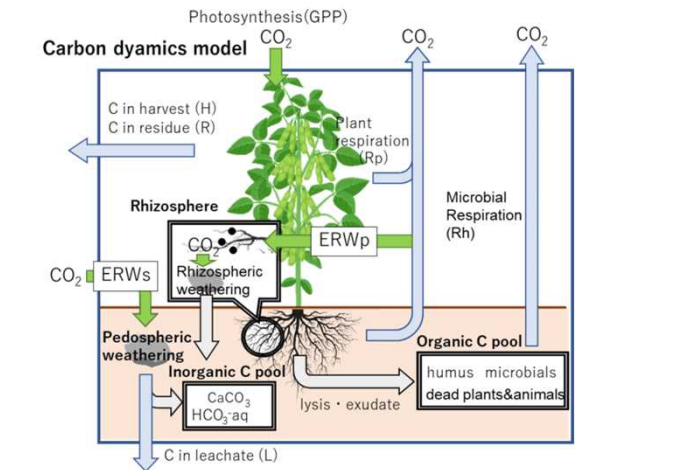


Fig. 02-2. Image of carbon fluxes including ERW-CO₂

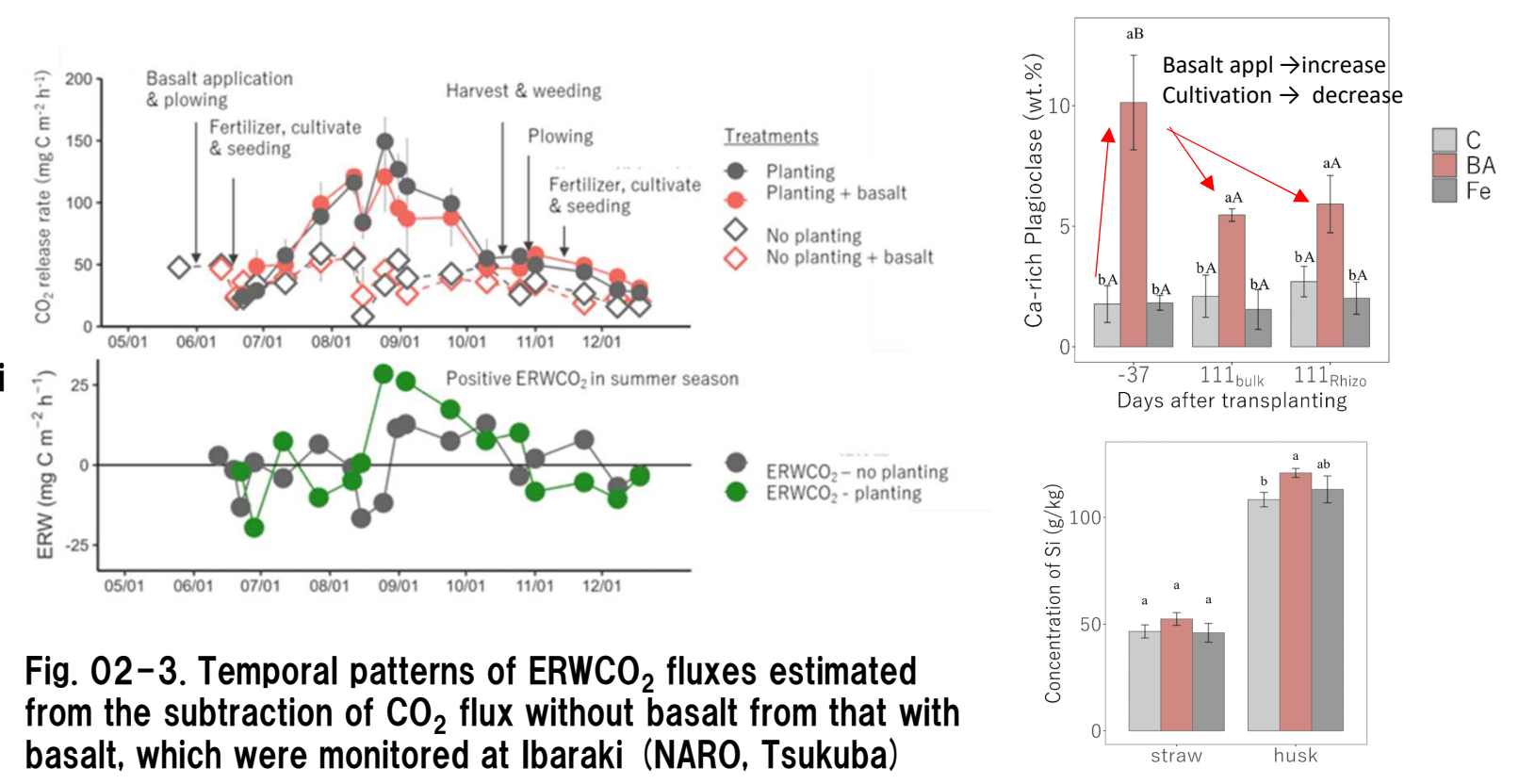


Fig. 02-3. Temporal patterns of ERWCO₂ fluxes estimated from the subtraction of CO₂ flux without basalt from that with basalt, which were monitored at Ibaraki (NARO, Tsukuba)

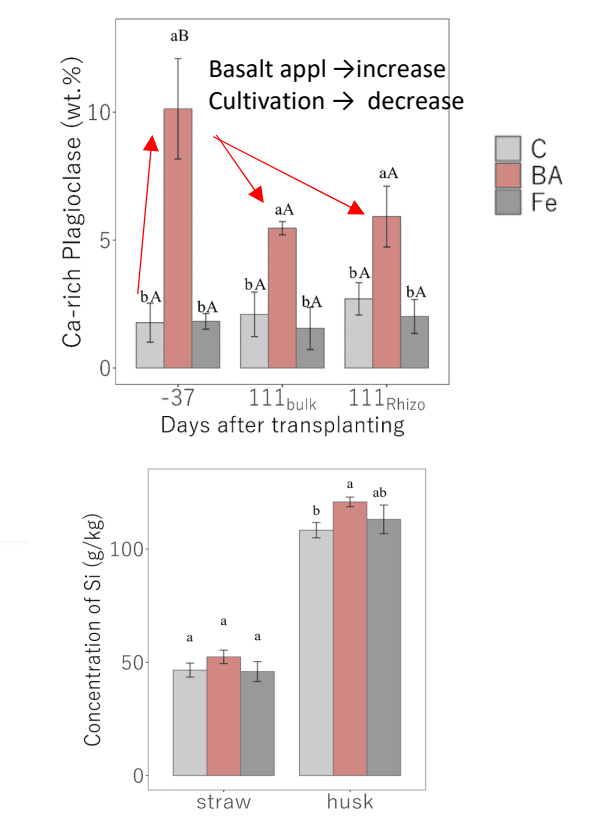


Fig. 02-4. Mineral application and weathering in paddy field (upper), Si uptake by rice (lower)@Kyoto

03 Carbon accounting including natural carbon cycle & Conceptual design for large scale demonstration

Carbon accounting including natural carbon cycle :

Leaching experiment using soil column with inserting multiple sensors (e.g. CO₂ sensor) was conducted to investigate the relationship between inorganic carbon concentration and soil parameters. The relationship was used for developing a monitoring-based model to predict inorganic carbon dynamics in soil (Fig. 03-1). As a result of this experiment, we found that inorganic carbon concentrations in soil solution can be accurately estimated by using CO₂ pressure in soil atmosphere and pH in soil solution (Fig. 03-2).

Conceptual design for large scale demonstration:

We started preparing pilot-scale field experiments at agricultural fields not only experimental fields organized by universities and national institutes, but also those managed by commercial farmers. At the first step, we asked a local farmer in Yosano-town, Kyoto to apply basaltic powder to a paddy field in 2023. As we found that this application increased Si supply to rice with no hazardous impact, the farmer allows us to extend our research area within his farm. Following this result, additional pilot-scale experiments may be allowed (under negotiation) by other commercial farmers in Fukui and Hokkaido in 2024.

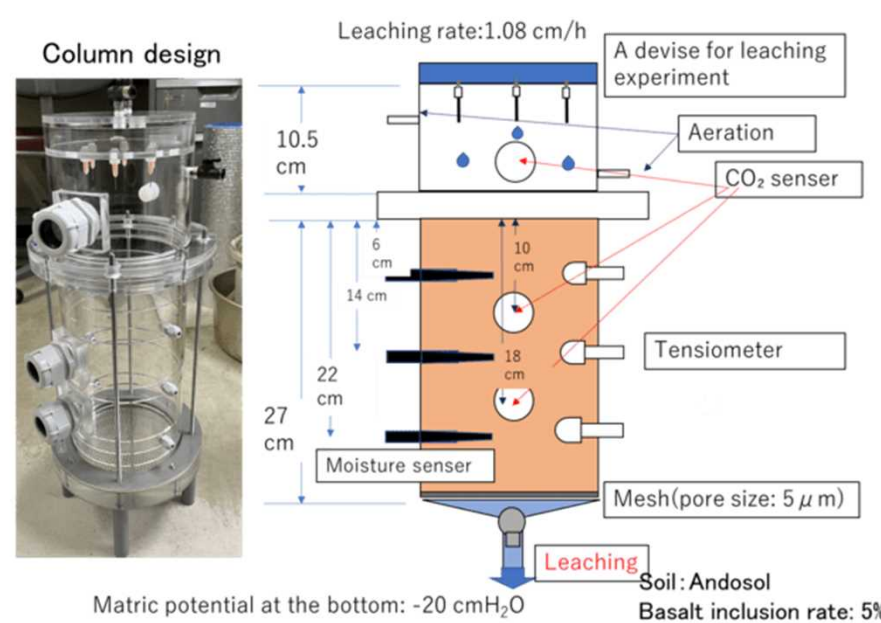


Fig. 03-1. Experimental design for monitoring inorganic C leaching through soil column and changes in soil parameters such as CO₂ pressure and soil moisture content

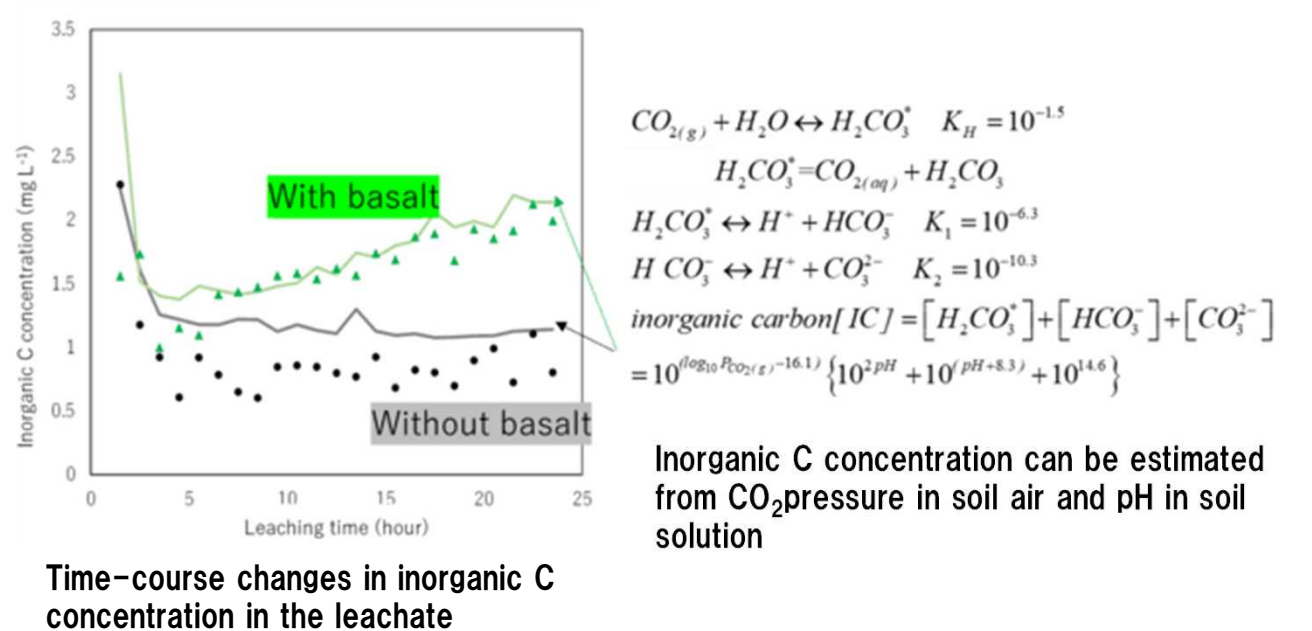


Fig. 03-2. Time-course changes in inorganic C concentration in the leachate. Plots are observation whereas line indicate prediction from modeling using pH and CO₂ pressure

04 Summary & Future perspectives

Summary:

Quantitative PXRD method enables us to survey the potential site containing less amount of weatherable minerals in soil and to investigate the mineral composition changes during crop growing periods. Further investigation is needed to develop better method to quantify inorganic carbon accumulation in soil. Several methods based on field monitoring and simulations are under verification. Pot experiments revealed that basaltic powder application increased Si (Na, Ca, Mg) availability and soil pH in many conditions. Since these changes can increase or decrease crop yields, careful consideration of soil and crop type are very important for effective use of ERW technologies.

Future perspectives:

We will choose better parameters and methods to determine how much CO₂ is accumulated by ERW technologies more precisely and rapidly (Fig. 04-1). An in-house lysimeter experiment is scheduled at Ishigaki (JIRCAS) for better estimation of CO₂ budget in agricultural field (Fig. 04-2). International collaboration research for applying ERW technologies to subtropical region is promoted with National Taiwan University (Fig. 04-3). Long-term survey in many aspects will be conducted after basaltic powder amendment to better understand comprehensive effects of ERW on carbon budget in agricultural fields (Fig. 04-4).

- 1) More accurately, rapidly, and comprehensively
- 2) Challenge into the abroad
- 3) Longer-time monitoring for precise C accounting

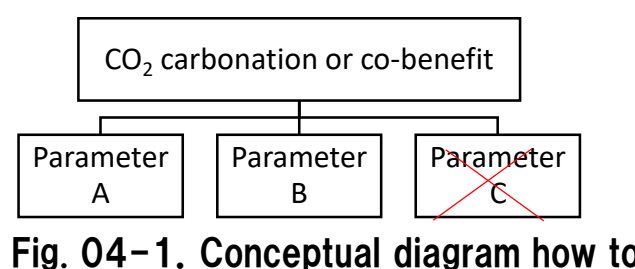


Fig. 04-1. Conceptual diagram how to



Fig. 04-2. In-house lysimeter experiment to quantify carbon budget changes caused by ERW application@Ishigaki

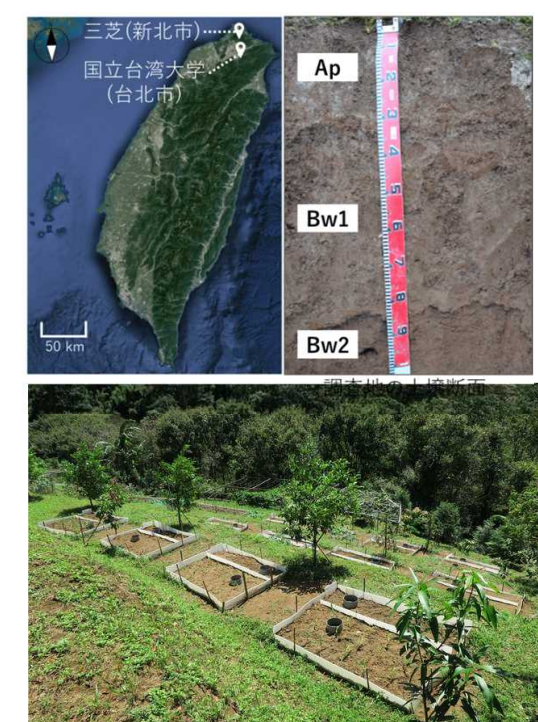


Fig. 04-3. International collaboration research for ERW technology application in subtropical region with National Taiwan University

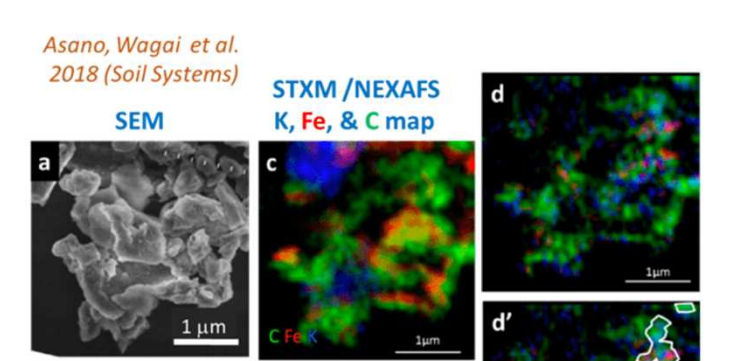


Fig. 04-4. Organo-mineral interactions in micro-aggregate in soil, which would be promoted by long-term application of rock powders

Nano-clays as a byproduct of basalt weathering will contribute to an organic C sequestration.