Heat as by-product or sub-product of CO_2 storage in mafic and ultramafic rocks

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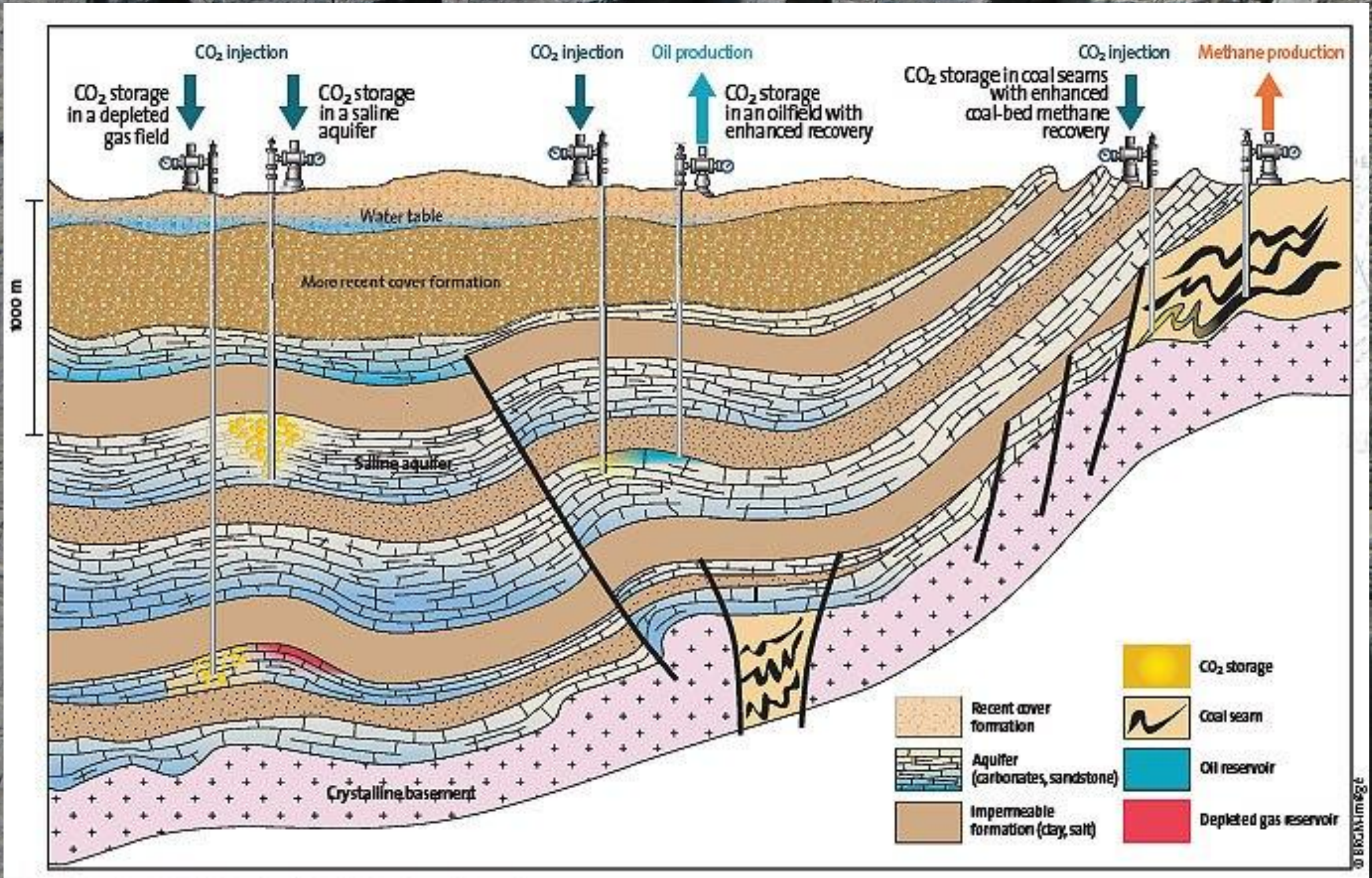
CGE

Presentation Layout:

- CO_2 geological storage solutions;
- Fundamentals of silicate carbonation reactions;
- Heat generation versus confinement:
- Heat released and temperature reached;
- Proposed industrial approach;
- Thermodynamic constraints;
- Expected power plant capacities;
- Conclusions.

CO_2 geological storage solutions:



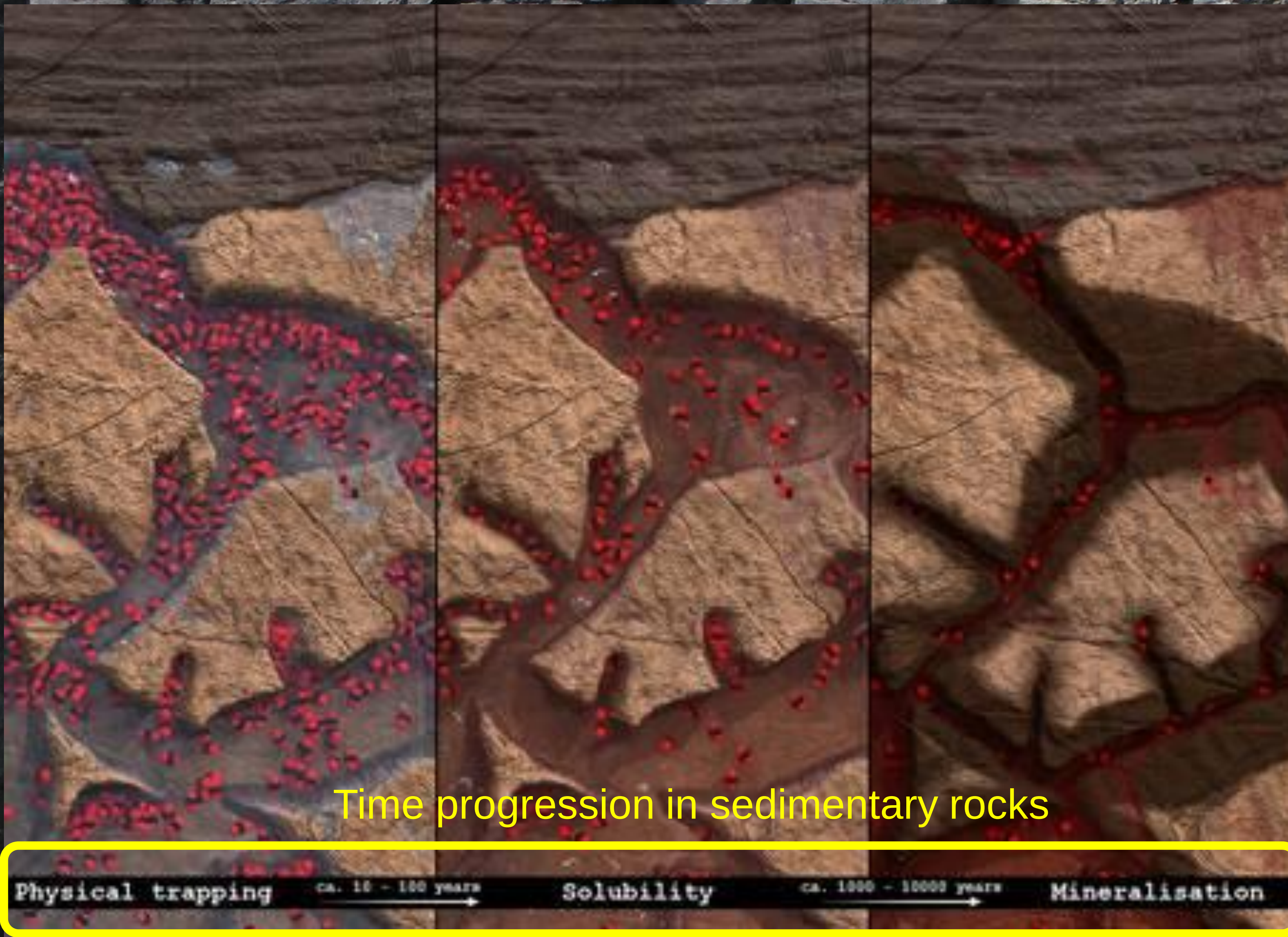
CO_2 geological storage solutions:

In addition to these more frequently mentioned solutions:

- Saline aquifers;
- Depleted hydrocarbon reservoirs;
- Coal seams;

One should also consider:

- Mafic and/or ultramafic rocks:
  - Favourable mineralogy and chemistry;
  - Conversion of CO_2 to carbonate mineral phase;
  - Effectively removing CO_2 permanently from atmosphere;
  - Widespread geographic distribution.



Time progression in sedimentary rocks

Much faster in mafic and ultramafic rocks!

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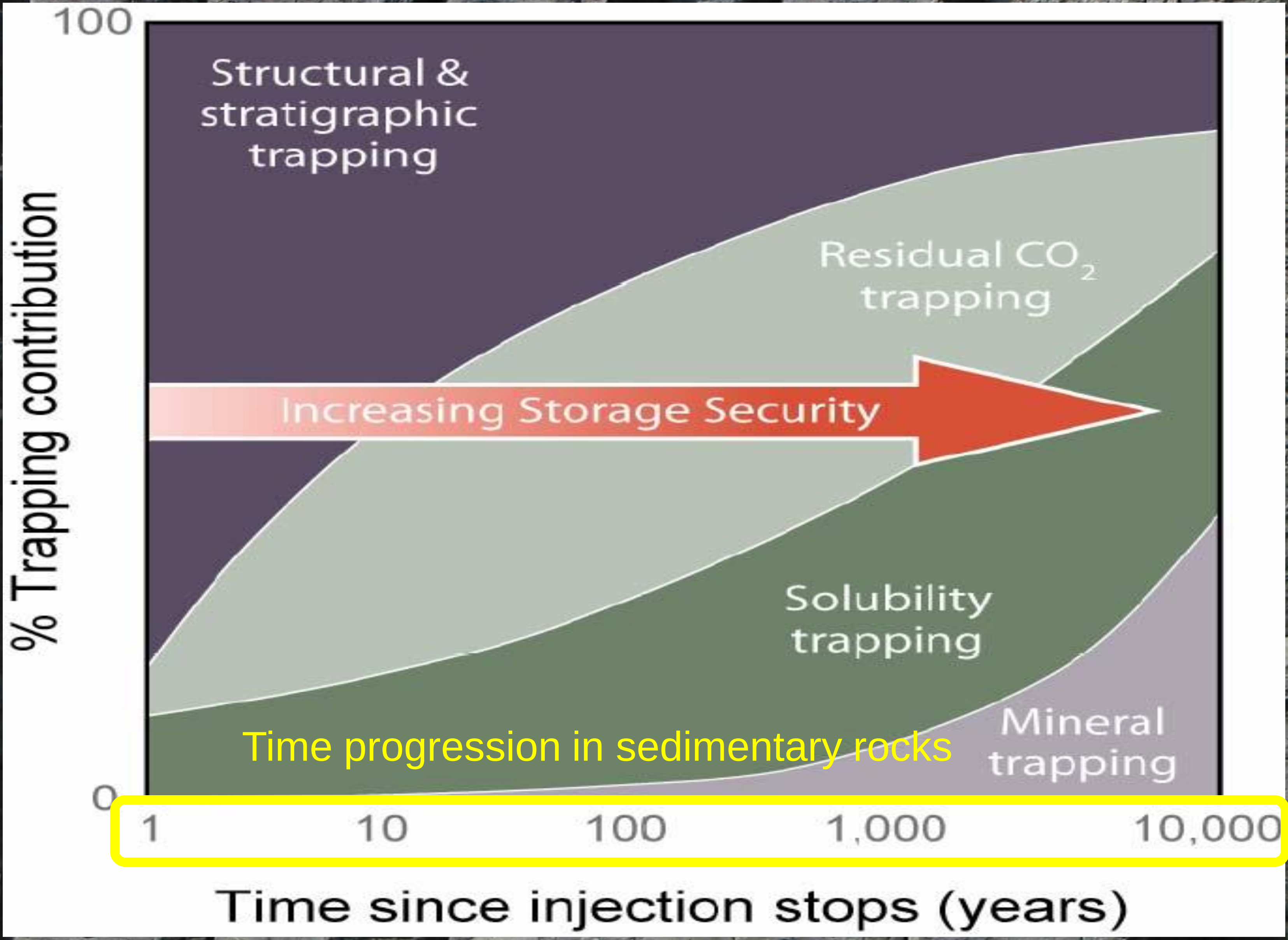

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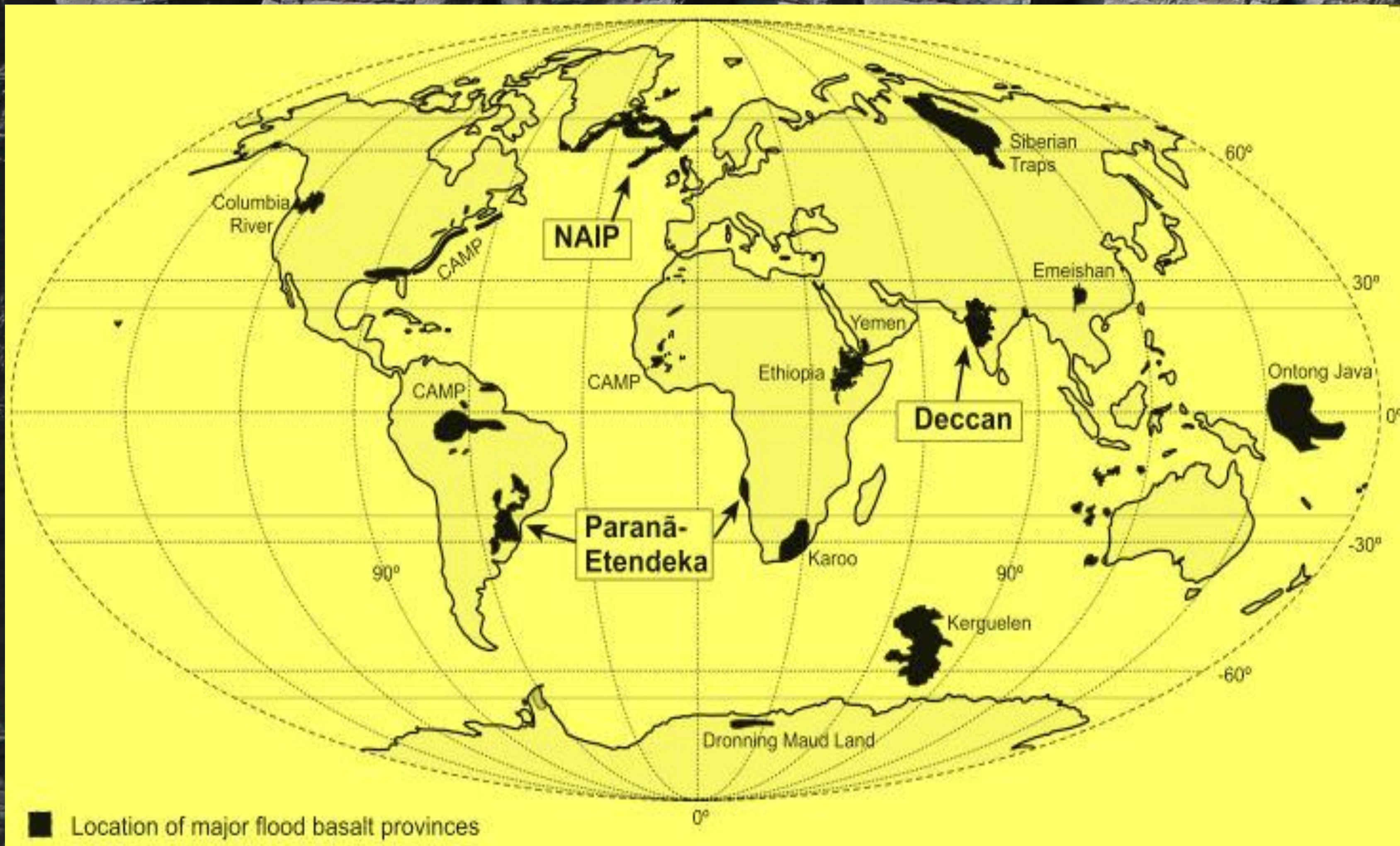
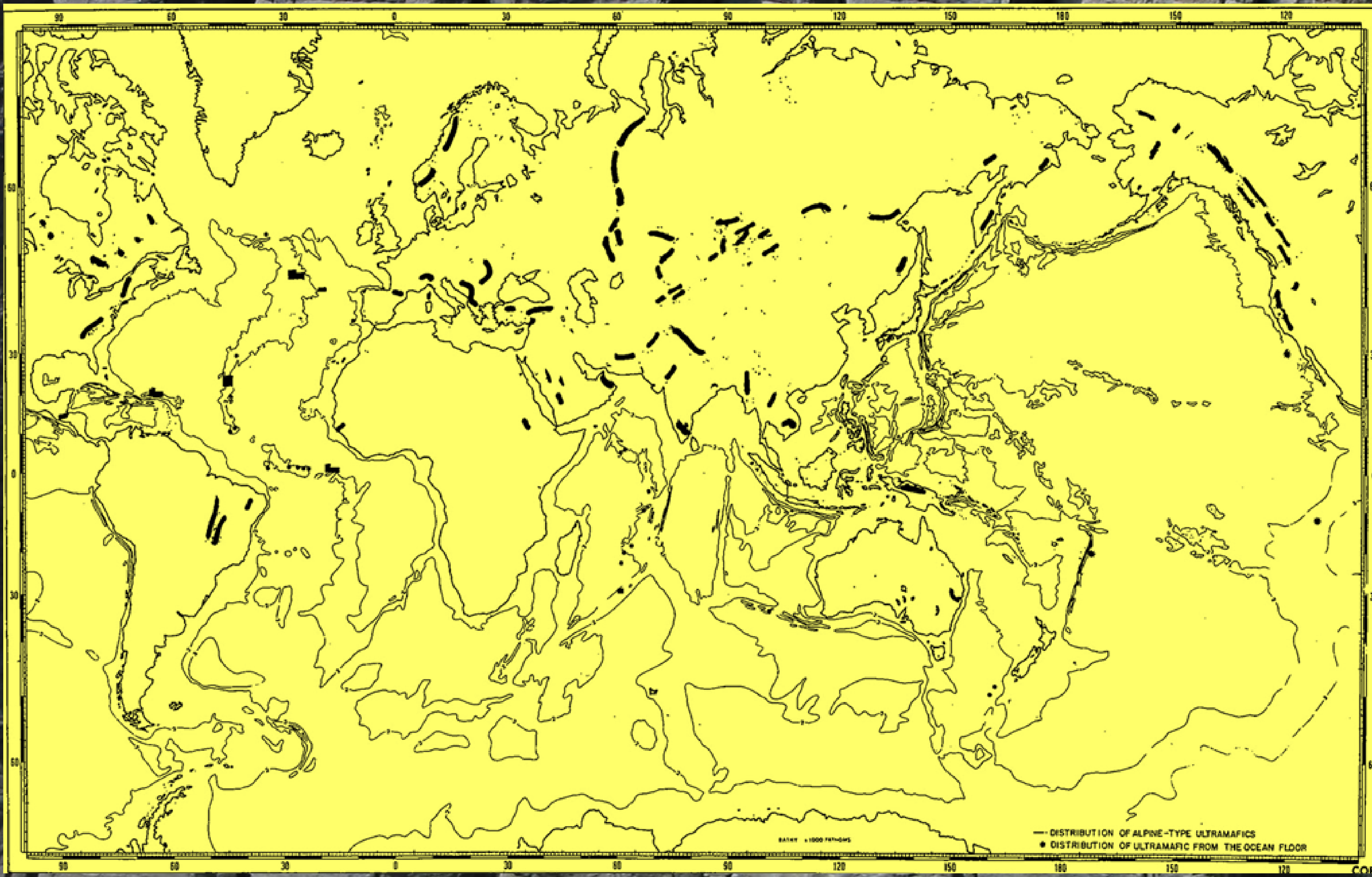


Jerram & Widdowson, 2005



Hekinian (1982)

Fundamentals of carbonation reactions:

Mg,Ca,Fe–Silicate + nCO_2 = Carbonates + Silica

Olivines, Serpentines
(Pyroxenes, Plagioclases)

Constituents of:
Peridotite, serpentinite, basalt and gabbro

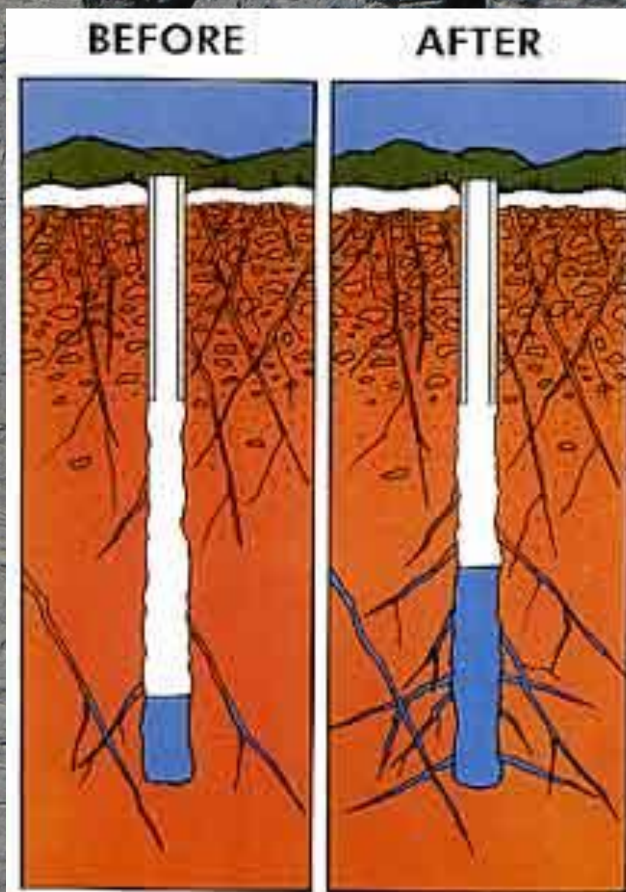
$\Delta G^o < 0$; spontaneously evolve into carbonates and free silica

$\Delta H^o < 0$; releasing thermal energy (heat)

$\Delta S^o < 0$; increase in T or P will stop the reaction

$\Delta V^o > 0$; can lead to obstruction of the fluid flow path

Fundamentals of carbonation reactions:



Hydraulic fracturing or Fracking

Garber & sons Inc

Silicate Carbonation (molar) Properties:

Mineral or Rock Properties	M g/mol	C J/mol.K	ΔGº kJ/mol	ΔHº kJ/mol	ΔSº J/mol.K	ΔVº 10^{-5} m^3/mol
Diopside $CaMgSi_2O_6$	217	168	-63	-162	-333	2.08
Hypersthene $MgFeSi_2O_6$	232	169	- 33	-135		
Enstatite $Mg_2Si_2O_6$	201	115	-64	-170	-348	3.88
Forsterite Mg_2SiO_4	141	118	-71	-175	-352	3.50
Fayalite Fe_2SiO_4	204	135	-65	-169	-348	3.52
Serpentine $Mg_3Si_2O_5(OH)_4$	277		-61	-194		2.24
Anorthite $CaAl_2Si_2O_8$	278	210	-73	-229	-495	3.54
Peridotite	173	125	-68	-172	-350	3.51
Basalt	212	165	-69	-189	-393	3.04

•Heat generation versus confinement:

For:
heat diffusivity (a) ≈ 10^{-6} m^2/s,
reservoir diameter (L) ≈ 10^{3} m,
time (t) ≈ 3.10^{9} s (100 hundred years)

the Fourier number (Fo) = at/L^2 ≈ 0.003 « 1,
which means that generated heat will practically not have diffused out of the reservoir volume within that time frame.

Heat released and temperature reached:

For:
volume $V \approx 1\ km^3$
density $\rho \approx 2.7\ g/cm^3$,

H $= (\rho/M)\,(-\Delta H)\,V \approx 2.5$ EJ (10^{18} J).

This amount of energy, if released along a lifespan of 100 years, would correspond to an average thermal power of nearly 1 GW.

Heat released and temperature reached:

The reaction tends to an equilibrium ($\Delta G = 0$) and the carbonation stops at a temperature lift ΔT (relative to the reference temperature 298 K) given by:

$$\Delta T \approx (-\Delta G^o)/(-\Delta S^o) \approx 219^oC \text{ (peridotite) or } 201^oC \text{ (basalt).}$$

Similarly, the carbonation reaction halts and reverses when the total (lithostatic plus fluid) pressure (relative to the reference pressure 1 bar = 100 kPa) attains and exceeds:

$$\Delta P \approx (-\Delta G^o)/(\Delta V^o) \approx 20 \text{ kbar}$$

Proposed industrial approach:

CO_2 employed a as a feedstock in a two step sequestration and geothermal exploration concept:

First Stage - As a chemical agent, CO_2 is used to promote the generation of heat by carbonation of silicate mineral constituents of mafic and ultramafic rocks. During this stage, lasting up to a decade, CO_2 is basically being sequestered while raising the reservoir's temperature.

Second Stage - While CO_2 is still being sequestered, CO_2 starts to be also used as a heat transfer fluid, to extract the heat being generated to be used either directly or for conversion in an electrical power plant.

Proposed industrial approach:

First Stage:

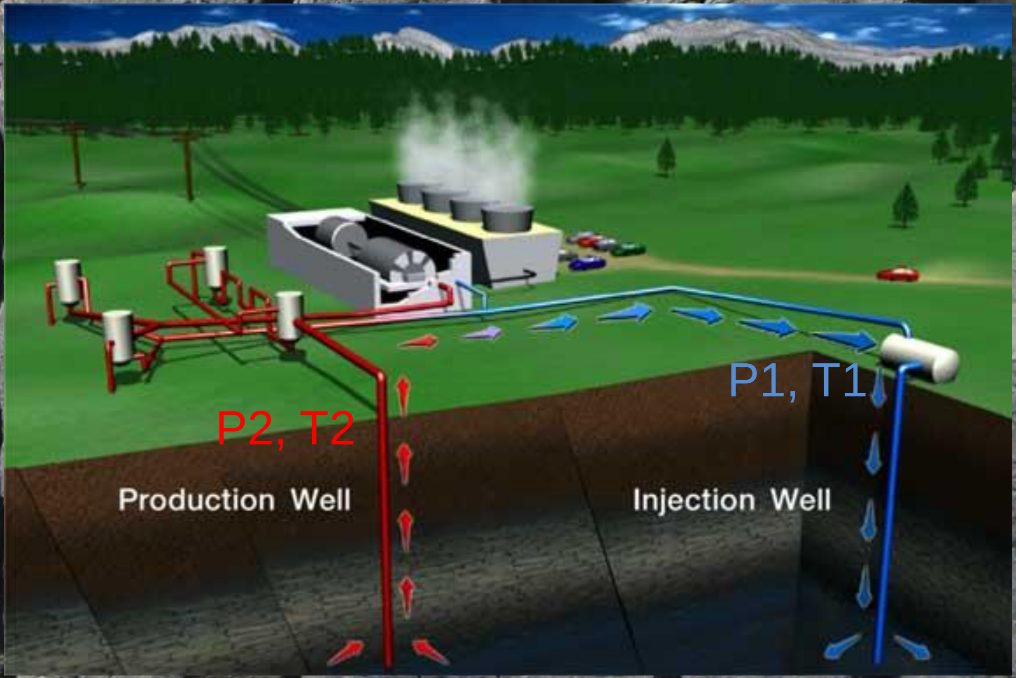
CO_2 in a supercritical state circulates through the rock by means of a set of injection and production wells, implanted in such a way as to drive the fluid to flow and flood the whole reservoir, by convection through the fracture network, and by diffusion into the rock matrix.

The operation of the carbonation reaction can be controlled within limits by regulating the partial pressure and the flow rate of the CO_2 within the reservoir; by adding water steam or other additives; by letting the rock temperature rise; by resorting to fracking.

Proposed industrial approach:

Second stage:

At this stage CO_2 will be made to flow and extract the heat generated, at an acceptable level of power spent in driving the forced circulation. The flow rate should be adjusted to the rate of heat generation, such that the temperature and the collected heat power shall be kept to their long time targets.



Geothermal Education Office

Thermodynamic constraints:

Second stage:

At this stage one should ensure that the power spent in pumping the cooling fluid (supercritical CO_2) is much smaller than the exergy extracted from the wells:

Pumping power: $v\,Q\,(P_1 - P_2)$

Extracted heat power: $c\,Q\,(T_2 - T_1)$

Efficiency of energy conversion:

$\eta = (1 - T_\infty / T_g)$ is the theoretical Carnot efficiency

>>>> Positive heat balance criterion:

$$(P_1 - P_2) \ll (1 - T_\infty / T_g)\,\rho c\,(T_g - T_\infty) = \boldsymbol{\rho c\,(T_g - T_\infty)^2 / T_g}$$

Carnot Efficiency Heat Power extracted by unit volume of fluid

Thermodynamic constraints:

Second stage:

How much power can be extracted? Assuming a Darcy flow through the reservoir :

$$Q = (4\pi k/v)\, \ell\, (P_1 - P_2)$$

The pressure drop being bound by :

$$(P1\text{-}P2) << \rho c\, (T_g - T_\infty)^2/T_g$$

Consequently, the thermal power available will be limited to:

$$d\mathbf{H}/dt = c\, Q\, (T_g - T_\infty) << (4\pi k/v)\, \ell \rho c^{\mathbf{2}}\, (T_g - T_\infty)^3/T_g$$

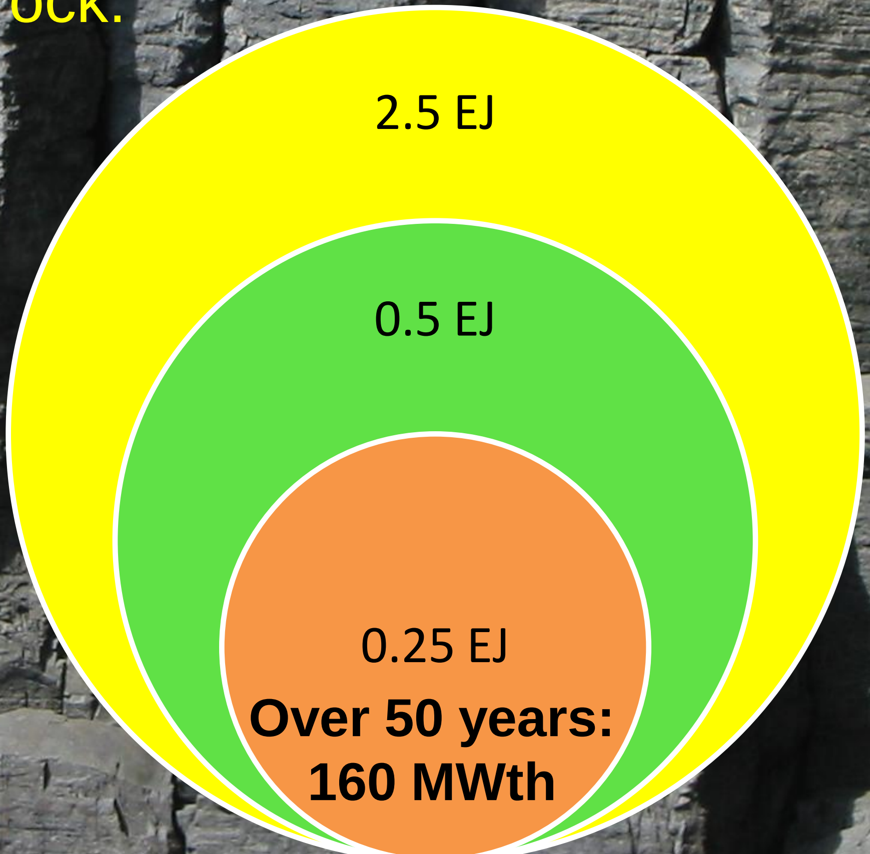
The heat rate available has an upper bound of about 1GW. That is of the order of the thermal power estimated before.

Expected power plant capacities:

In view of thermodynamic constraints, the capacity of a power plant will in practice be considerably less than the theoretical power straightly derived from the heat released by full carbonation of the reservoir rock:

20% carbonation

50% heat released left behind



Expected power plant capacities:

The thermal (conversion) efficiency of the plant depends on the temperature at which the geothermal heat can be delivered, which is expected to attain close to 500 K.
In our case study, the Carnot efficiency will be limited to

$$\eta = (1 - T_{\infty}/T_{g}) \approx 0.4$$

We conclude that the available geothermal power contained in a 1 km^3 reservoir can possibly feed a power plant delivering a steady gross electric power output of up to **W** ≈ 60 MW for 50 years.

Conclusions:

- Carbonation of Fe-Mg silicates, either in-situ or of mined waste-rock is a way of safely disposing of CO_2 and avoid the greenhouse effect from its emission to the atmosphere.
- The carbonation reaction is exothermic, so the heat generated can be employed as a valuable by-product of the CO_2 sequestration.
- Extracting the heat generated and converting it to electrical power, appears feasible at an industrial scale, since the energy and exergy budgets are favourable.
- Geological requirements include favourable fluid trapping structure, sufficient rock permeability (implying fracking procedures in setting up the CO_2 injection/collection wells and in maintaining the fluid flow against carbonate and silica precipitation in the fracture network).
- Our case study suggests the possibility of generating up to about 30 TWh of electrical energy while capturing permanently about 200 Mton CO_2 per 1 km^3 of peridotite or basalt .

Acknowledgements:

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co_2 transport and storage