

Supplementary Material:

Sensitivity to CO₂ partial pressure and additional simulations of the Aquifer 2

Section 1: Injection and final fluid composition from Sr isotopic simulations *AQI*

The injection fluid used in simulations *AQI* is obtained by diluting the composition of Cathedral well by a factor of 8.28, to obtain a Cl content of 3000 mg/kg H₂O. The diluted brine is then reacted with calcite, anhydrite and quartz until equilibrium, considering a partial pressure in CO₂ (P_{CO_2}) of 10 bars. Varying the P_{CO_2} does not affect significantly the composition of the injection fluid (Table S.1). Ca increases from 128 mg/kg H₂O ($P_{CO_2} = 1$ bar) to 153 mg/kg H₂O ($P_{CO_2} = 20$ bar), while HCO₃ does from 18 to 75 mg/kg H₂O. Concentrations in other major elements remain similar. Each of these solutions is then injected within the 1D mesh under the same P_{CO_2} , all other conditions are identical to the base-case *AQI-a* (10 bar) simulation. Final solutions sampled at 1000 m of distance are chemically and isotopically similar (Table S.1). Slight variations in concentrations are observed for example for Na (1930–2226 mg/kg H₂O) and K (204–226 mg/kg H₂O), while final Sr concentrations and isotopic ratios are similar. This sensitivity analysis reveals that Sr isotopic simulations *AQI* are not sensitive to P_{CO_2} within the explored range (1–20 bar).

Table S.1. Results from the sensitivity analysis to the CO₂ partial pressure. Simulations referred as ‘base-case’ are discussed in the manuscript. Concentrations are expressed in mg/kg H₂O. All solutions are read after 2 years of simulation.

Simulation	Sampling distance (m)	T (°C)	P _{CO2} (bar)	pH	SiO ₂	Na	K	Ca	Mg	Al	HCO ₃	Cl	SO ₄	Sr	⁸⁷ Sr/ ⁸⁶ Sr
<i>Sr isotopic simulations</i>															
AQ1-a (1bar)	0	250	1	6.01	371	1823	106	128	30	0.00	18	3000	25	10	0.70750
	1000	250	1	6.50	378	1930	204	15	0.01	0.14	54	2999	13	7	0.70400
AQ1-a (10 bar, base-case)	0	250	10	5.49	370	1820	106	143	30	0.00	54	2995	24	10	0.70750
	1000	250	10	6.43	378	2095	218	3	0.01	0.14	189	2989	18	8	0.70400
AQ1-a (20 bar)	0	250	20	5.33	370	1816	106	153	30	0.00	75	2989	24	10	0.70750
	1000	250	20	6.36	380	2226	226	3	0.02	0.13	849	2978	19	8	0.70400
<i>Reproducing AC-AT spring compositions: cooling and mixing</i>															
AQ1-cool-a (0.1 bar)	1000	50	0.1	6.52	228	1152	133	297	10.92	4.6	274	1736	661	ns	ns
AQ1-cool-a (0.5 bar, base-case)	1000	50	0.5	6.12	228	1152	133	390	10.92	4.6	548	1736	661	ns	ns
AQ1-cool-a (1 bar)	1000	50	1	5.94	228	1152	133	453	10.92	4.6	729	1735	661	ns	ns
<i>Varying mixing location and temperature</i>															
AQ1-cool-a (0.5 bar) - 50m	1000	50	0.5	6.12	228	1152	133	390	10.9	4.61	548	1736	661	ns	ns
AQ1-cool-a (0.5 bar) - 500m	1000	50	0.5	6.17	228	1152	133	285	10.9	4.61	614	1736	357	ns	ns
<i>Varying mixing fluid composition</i>															
AQ1-cool-a (0.5 bar) - mf	1000	50	0.5	6.18	245	1053	115	277	1.07	1.45	614	1496	399	ns	ns

Section 2: Cooling and mixing simulations - Reproducing AC-AT spring compositions

The original cooling and mixing simulation *AQ1-cool-a (0.5 bar, base-case)* is performed considering calcite is reacting mineral under a P_{CO_2} of 0.5 bar in the whole mesh (anhydrite is only able to precipitate). The sensitivity of the solution to P_{CO_2} is tested through 2 additional simulations where P_{CO_2} in the mesh is set to 0.1 bar and 1 bar: *AQ1-cool-a (0.1 bar)*, *AQ1-cool-a (1 bar)* (Table S.1, Figure S.1). By increasing P_{CO_2} from 0.1 to 1 bar, Ca and HCO_3 increase from 297 to 453 mg/kg, and from 274 to 729 mg/kg, respectively. The match between the computed water and AC-AT spring composition is not improved by increasing the P_{CO_2} , as HCO_3 concentrations depart from observed concentrations (Figure S.1).

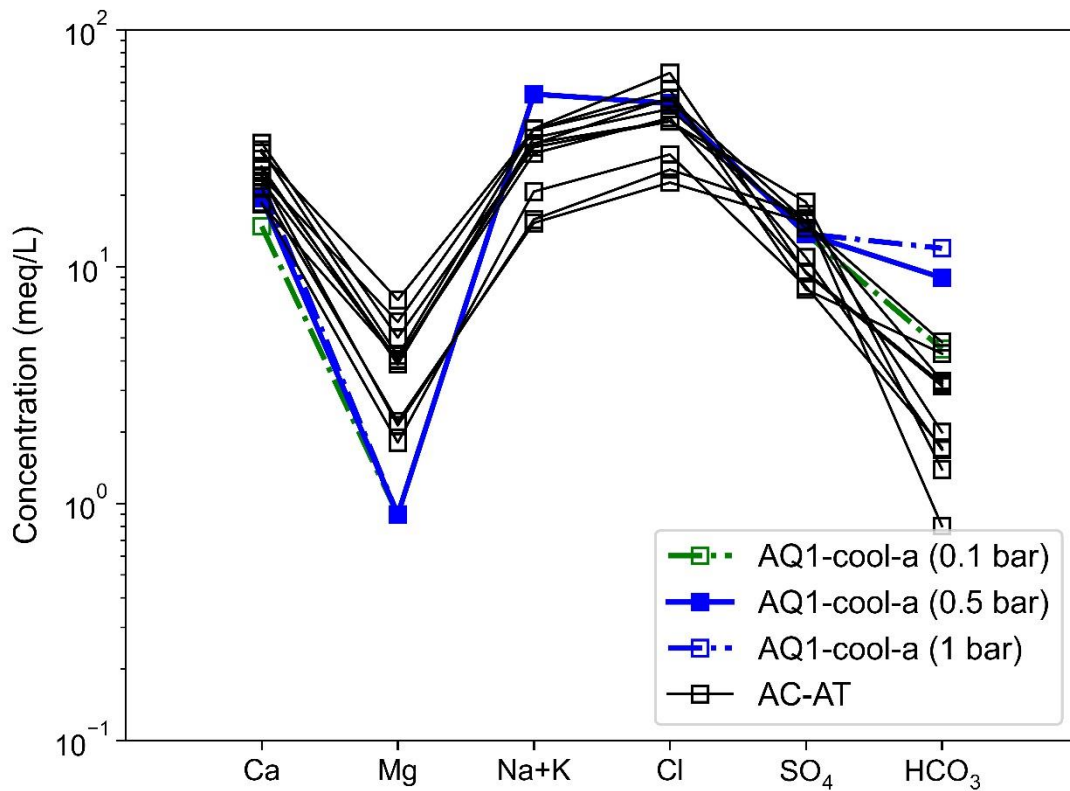


Figure S.1. Schoeller diagram showing AC-AT spring and computed compositions in simulations *AQ1-cool* as a function of P_{CO_2} .

These cooling and mixing simulations are performed considering that the mixing occurs 250 m before reaching the surface, where the temperature is 100 °C. A sensitivity analysis to the mixing location along the mesh and the corresponding mixing temperature is also performed to evaluate if the chemical composition of the fluid produced at the surface varies. The two additional simulations *AQI-cool-a (0.5 bar) - 50m* and *AQI-cool-a (0.5 bar) - 500m* consider that mixing happens 50 m and 500 m before reaching the surface, respectively. Apart from the mixing location, the simulations are run with the same settings as *AQI-cool-a (0.5 bar, base-case)*. The temperature at 50 and 500 m from the surface are 60 °C and 150 °C, respectively.

Results from *AQI-cool-a (0.5 bar) - 50m* are identical to the base-case cooling and mixing simulation, while Ca and SO₄ concentrations (285 mg/kg and 357 mg/kg, respectively) are lower in simulation *AQI-cool-a (0.5 bar) - 500m* (Figure S.2.). When mixing occurs at 150 °C, anhydrite becomes saturated and controls the Ca and SO₄ content together with calcite, which causes a decrease in Ca and SO₄ concentrations in the fluid produced at the surface (Figure S.2.). Apart for Ca and SO₄, the computed elemental concentrations are similar to what observed in simulation *AQI-cool-a (0.5 bar, base-case)*.

Finally, the model response to the chemical composition of the admixed fluid is investigated as well. To do so, in simulation *AQI-cool-a (0.5 bar) - mf* the water composition from AR-Nov09 spring is chosen (Table 1) as an additional composition of the admixed fluid. The modeled chemical composition is less concentrated in Ca and SO₄ (Ca = 277 mg/kg H₂O, SO₄ = 399 mg/kg H₂O), when compared to the original simulation *AQI-cool-a (0.5 bar)* (Figure S.2.). Furthermore, Mg concentration is not matched, likely because Mg-rich clays are not considered in the model.

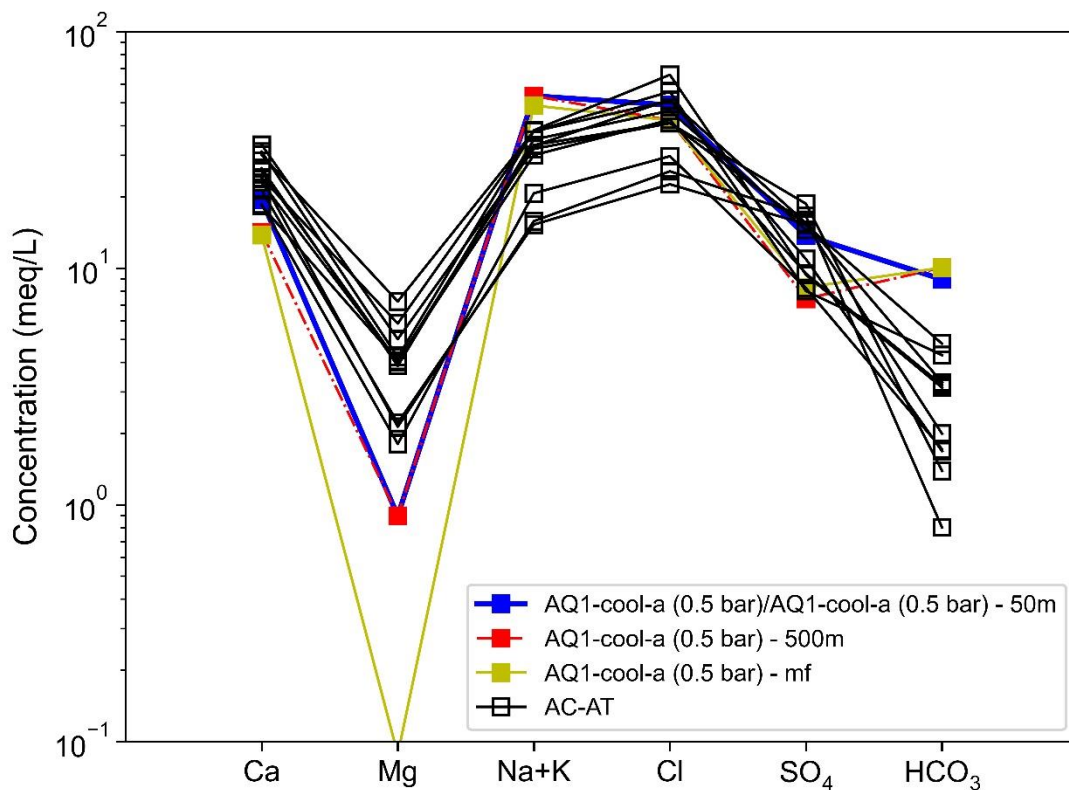


Figure S.2. Schoeller diagram showing AC-AT spring and computed compositions in simulations *AQ1-cool-a (0.5 bar) - 50m*, *AQ1-cool-a (0.5 bar) - 500m* and *AQ1-cool-a (0.5 bar) - mf*.

Section 3: Cooling and mixing simulations - Reproducing ASn spring compositions (Aquifer 2)

S 3.1. Conceptual model and modeling setup

The composition of Cathedral oil-field water with 24,848 mg/kg H₂O Cl is used as the starting fluid for reproducing the composition of Aquifer 2 deep fluid and ASn springs. Close-to-surface mixing with diluted superficial fluids (dilution factor of 2–2.5) is required to lower the Cl content to observed maximum values (10,051–11,978 mg/L) (Peiffer et al., 2015).

The first step of the modeling (simulation AQ2) involves to react the water at 250 °C until reaching equilibrium with the stable secondary mineral assemblage (defined in section 2 of the manuscript),

including clinozoisite and anhydrite. This first step is modeled without flow (0D batch reactor type) as we are only interested in the composition at equilibrium. The presence of clinozoisite is justified by the following reasoning. ASn springs are particularly rich in Ca (up to 1427 mg/L) compared with AC-AT springs, which can be related to two different scenarios. First, Ca enrichment may be a shallow characteristic inherited upon mixing with the superficial fluid. In this case, a low Ca concentration in the deep fluid is required. This is possible when Ca is controlled by calcite under high P_{CO_2} (e.g. 10 bar, Ca <100 mg/kg H₂O), such as modeled in isothermal 1D simulations. However, this scenario is not realistic as the superficial fluid would have to be extremely concentrated in Ca (>3000 mg/L) to enrich the uprising deep fluid in this element upon mixing. Calcite solubility at close-to-surface conditions (low T and P_{CO_2}) is not compatible with such high Ca concentrations. The second scenario assumes (the one simulated) that the deep fluid is rich in Ca and the mixing with superficial fluid dilutes the Ca concentration. This is possible through a solubility control by calcite under low P_{CO_2} . Low P_{CO_2} can be produced through equation 6 (section 2 of the manuscript), i.e. involving a Ca-aluminosilicate such as clinozoisite together with calcite in order to buffer the P_{CO_2} . As ASn springs are the most distant from the crater, low P_{CO_2} conditions in Aquifer 2 are likely. The sensitivity of the results in function of P_{CO_2} is discussed below, where the base-case simulation is declined in several scenarios (Simulations *AQ2-b* to *AQ2-e*, and *AQ2-cool-b* to *AQ2-cool-e*) by varying the P_{CO_2} .

Another characteristic of the ASn springs is their low content in SO₄ (minimum of 65 mg/L). Such characteristics imply that both the deep and the superficial mixing fluids have low SO₄ concentrations.

The second step of the modeling (simulation *AQ2-cool*) involves the upflow of the deep fluid and subsequent mixing with a shallow dilute fluid. It is simulated in the same way as for AC-AT springs using a 1000 m-long mesh with an identical linear temperature gradient from 250 °C to 50 °C. Calcite is the only mineral that may either dissolve or precipitate in the mesh, anhydrite is only able to precipitate. The same injection rate for the deep fluid is used (1.44×10^{-3} kg s⁻¹), while a value of 2.14×10^{-3} kg/s is assigned at 250 m before reaching the surface to induce the mixing with the superficial fluid. Such mixing dilutes the deep fluid by a factor of 2.5. As some additional SO₄ is required to match ASn spring composition, the superficial fluid is simulated as a pure acid-

sulfate water with 200 mg/kg H₂O of SO₄. This accounts for some (limited) H₂S dissolution in the sub-surface. Another way of adding SO₄ would be to leach some magmatic anhydrite. We do not perform this additional simulation as results would be similar. Note that for this 1D cooling simulation, the P_{CO₂} is adjusted to 0.06 atm in the whole mesh to produce a HCO₃ concentration similar to observed values.

S 3.2. Results of the cooling and mixing simulations

The match between simulated water extracted at the mesh outlet of simulation *AQ2-cool* and real spring compositions can be visualized by similar patterns in the Schoeller diagram (Figure S.3; Table S.2). The chemical composition obtained in simulation *AQ2-cool-a* shows a high degree of similarity with the ASn springs, as all simulated concentrations (except Mg) fall in the observed range. This good match is only possible if the Ca concentration of the deep sedimentary fluid is high, which can only be achieved with a low P_{CO₂} (e.g. 0.26 bar) when equilibrating the original sedimentary fluid. The following section demonstrates this point. Near-surface re-equilibration with Mg-rich clays (not simulated) likely causes the discrepancy between modeled and observed Mg concentrations.

These simulations explain why the AS/ASn springs have different Cl/Ca and Cl/Mg ratios compared with AC-AT springs.

S 3.3. Sensitivity analysis to CO₂ partial pressure

The injection fluid used in simulation *AQ2* (base-case, Table S.2) is obtained by reacting the Cathedral well water with the stable secondary mineral assemblage (defined in section 2), including clinozoisite and anhydrite. Equilibrium between the fluid, clinozoisite and calcite buffers the P_{CO₂} to a low value (0.26 bar). Three additional simulations (*AQ2-b* to *AQ2-d*) explores the sensitivity of the injection fluid composition to P_{CO₂} (1–10–20 bars). As HCO₃ concentrations increases upon increasing P_{CO₂}, Ca shows an inverse trend to maintain equilibrium with calcite. A low concentration in Ca of 93 mg/kg H₂O is obtained at 20 bars of P_{CO₂}. On the opposite, SO₄ increases to maintain equilibrium with anhydrite. At 20 bars (*AQ2-d*), the SO₄ concentration required to

reach equilibrium exceeds the original concentration of Cathedral well water (566 mg/kg H₂O). Anhydrite is hence sub-saturated under such condition as this mineral is not included as an initial mineral (only able to precipitate). Simulation *AQ2-e* is a duplicate of *AQ2-d* ($P_{\text{CO}_2} = 20$ bar) in which anhydrite is present as an initial mineral. In this case, the mineral dissolves and SO₄ concentration increases to 772 mg/kg H₂O .

The cooling and mixing simulation *AQ2-cool* is run again with each of the different fluid described above (simulations *AQ2-cool-b* to *AQ2-cool-e*; Table S.2). Ca concentrations of the resulting waters (sampled at 1000 m within the mesh after 2 years) are much lower than in the base-case simulation *AQ2-cool* (93–665 mg/kg H₂O Ca versus 1526 mg/ kg H₂O; Figure S.3), and cannot reproduce the high Ca concentrations observed in ASn springs (up to 1427 mg/L).

Table S.2. Results from ‘cooling and mixing’ simulations aiming in reproducing the ASn springs composition (Aquifer 2). A sensitivity analysis to the CO₂ partial pressure is also performed. Concentrations are expressed in mg/kg H₂O. All solutions are read after 2 years of simulation.

Simulation	Sampling distance (m)	T (°C)	P _{CO2} (bar)	pH	SiO ₂	Na	K	Ca	Mg	Al	HCO ₃	Cl	SO ₄
<i>Reproducing ASn spring compositions: cooling and mixing</i>													
AQ2 (base-case)	0	250	0.26	5.96	372	11458	1011	3557	0.30	0.1	6	24848	21
AQ2-cool (base-case)	1000	50	0.06	6.37	150	4611	407	1526	0.12	0.0	130	10000	128
AQ2-b	0	250	1	5.88	371	13858	1221	1370	0.43	0.1	18	24845	49
AQ2-cool-b	1000	50	0.06	6.55	149	5577	491	665	0.17	0.0	194	10000	139
AQ2-c	0	250	10	5.84	371	15352	1367	174	0.56	0.1	162	24811	392
AQ2-cool-c	1000	50	0.06	6.80	149	6178	550	211	0.23	0.0	346	9985	277
AQ2-d	0	250	20	5.83	371	15561	1394	93	0.61	0.1	322	24771	566
AQ2-cool-d	1000	50	0.06	6.85	149	6263	561	167	0.25	0.0	390	9969	347
AQ2-e (with anhydrite)	0	250	20	5.83	371	15647	1412	94	0.63	0.1	321	24772	772
AQ2-cool-e	1000	50	0.06	6.85	149	6297	568	168	0.25	0.0	391	9970	430

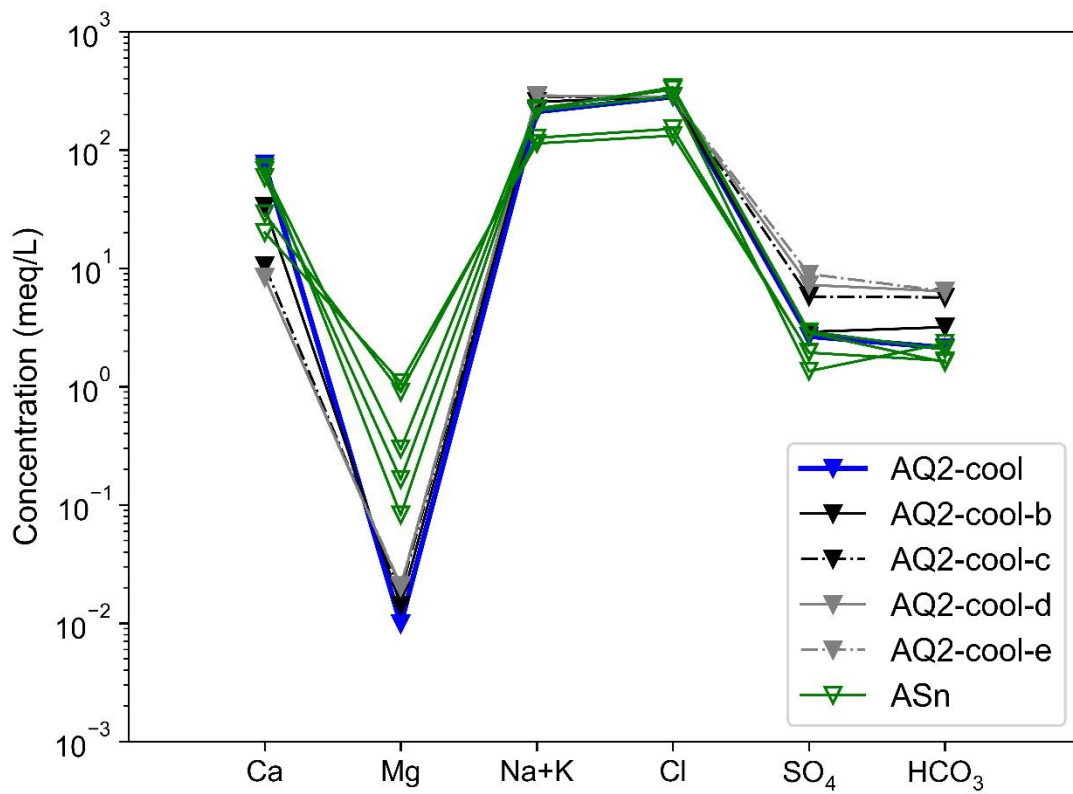


Figure S.3. Schoeller diagram showing ASn spring and computed compositions in simulations *AQ2-cool* as a function of P_{CO_2} .