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Supplementary Information

Quartz solubility Model

Quartz and carbonate solubility were calculated from a combination of the expression for quartz and calcite solubility in pure water (Dolejs and Manning, 2010) with the expression for quartz solubility as a function of salt concentration (Evans, 2007), which replicates observed salting-out and the formation of aqueous Na-silica species. The simplified system is used because mixed salt solutions thermodynamics and the solubility of carbonate minerals other than carbonate are not yet fully determined. Thus, trends are likely to be robust but absolute solubility values are suspect. Fluid density was calculated using the equation of state of Pitzer and Sterner (1994). pH is not accounted for in the calculations because pH is unlikely to be a primary control in the in-equilibrium infiltration scenario, but is discussed in the out-of-equilibrium modeling scenario.

Sources of values in Table DR1

Values, and results are considered robust on the order of magnitude scale.
Decarbonation: reaction [D1]

$$Fe_3O_{4(s)} + CO_{2(aq)} = Fe_2O_{3(s)} + FeCO_{3(s\ or\ ss)}. \text{ [D1]}$$

The initial carbon content of the rock, and the final carbon content of the fluid were taken to be zero. The carbonation reaction was assumed to convert all of the FeO in magnetite, around 140 g kg^{-1} (Thorne et al., 2004), to iron carbonate. The density of the rock was assumed to be 3900 kg m^{-3}, which gives a value for $c_{CO2,rock,final}$ of 7,600 moles m^{-3}. The initial CO_2 content of the fluid is poorly known, so calculations were made for an initial content of 1 mole kg^{-1} and 0.1 mole kg^{-1}, equivalent to 90 to 900 moles m^{-3} for fluid with a density of 900 kg m^{-3}. The chosen water density of 900 kg m^{-3} was used because this is appropriate for hot fluids at moderate pressures; water density is a function of temperature and pressure. CO_2 concentrations were calculated using HCh (Shvarov and Bastrakov, 1999) to simulate batches of evaporitic alkali brines and fluids equilibrated with dolomite, respectively. Calculations were carried out at 200°C and 0.06 — 0.1 GPa. Fluid density was calculated with the Pitzer and Sterner (1994) EOS.

Desilicification: reaction [D2]

$$SiO_{2(s)} = SiO_{2(aq)}\,. \text{ [D2]}$$

The initial SiO_2 content of the rock was taken to be 34 wt%, equivalent to 19,890 moles m^{-3}. The final SiO_2 content of the rock was taken to be 10% of this value. The initial fluid was assumed to be totally devoid of silica, which maximises the progress of the desilicification front. The final fluid was assumed to be saturated in silica at pH values less than 7, where the neutral SiO_2 species dominates. Calculations were

performed with the combined Dolejs Manning / Evans model, as described above, and give an aqueous SiO_2 concentration of 4.35 moles m^{-3}.

Oxidation: reaction [D3]

$$FeO_{(silicate\ or\ carbonate)} + 0.25\ O_{2(aq)} = 0.5\ Fe_2O_{3(s)}\ [D3]$$

The change in the oxygen concentration of the rock was considered to be that required to oxidise the 140 g kg^{-1} of FeO to Fe_2O_3 via reaction [3], a total of 1,900 moles m^{-3}. The initial fluid was assumed to contain oxygen at 10% of present day atmospheric concentrations (0.8 mg $litre^{-1}$, equivalent to 0.023 moles m^{-3}), and the final fluid was assumed to be oxygen-depleted. This assumption produces a maximum value for the progress of the reaction front. Less oxygen in the initial fluid, due to less oxygen in the atmosphere, or significant oxygen remaining in the reacted fluid, would result in retarded reaction front. HCh calculations indicate that the reacted fluid contains less than 10^{-40} moles kg^{-1}, so the assumption of total oxygen depletion is justfied.

Dissociation of water to H_2 and O_2 would not provide significant additional oxidising capacity unless the H_2 could be disposed of, either by reaction, or by preferential release from the reacting volume. The former is unlikely, as there are no suitable electron acceptors present in the rock, and there is no plausible mechanism for the latter.

References

Dolejs, D., and Manning, C.E., 2010, Thermodynamic model for mineral solubility in aqueous fluids: Theory, calibration and application to model fluid-flow systems: Geofluids, v. 10, p. 20–40.

Evans, K., 2007, Quartz solubility in salt-bearing solutions at pressures to 1 GPa and temperatures to 900 degrees C: Geofluids, v. 7, p. 451–467, doi:10.1111/j.1468-8123.2007.00199.x.

Pitzer, K.S., and Sterner, S.M., 1994, Equations of state valid continuously from zero to extreme pressures for H2O and CO2: The Journal of Chemical Physics, v. 101, p. 3111–3116, doi:10.1063/1.467624.

Table DR1: Summary of parameters for chromatographic front calculations

	$c_{i,\mathrm{rock,init}}$	$c_{i,\mathrm{rock,final}}$	$c_{i,\mathrm{fluid,init}}$	$c_{i,\mathrm{fluid,final}}$
	moles m^{-3}			
SiO_2	19,890	1,989	0	4.35
CO_2	0	7,600	90 to 900	0
O_2	*x*	*x* +1,900	0.0225	0