Some simple models of chemical alteration caused by the movement of metamorphic fluids in the deeper parts of the crust

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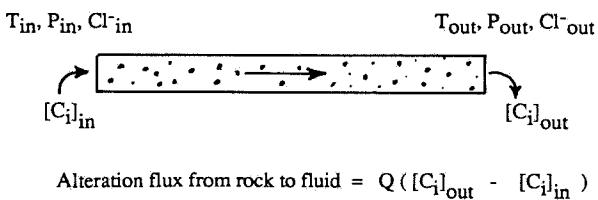
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EXTENDED ABSTRACT

Pore fluids in the crust are generally in chemical equilibrium with the common inorganic rock minerals they contact. The chemistry of the "rock-buffered" pore fluid is not very sensitive to the particular aluminosilicate minerals contacted. For this reason the temperature at which the fluid equilibrated can be inferred from analyses of fluid composition alone through the application of various geothermometers (e.g., Na–K–Ca, SiO_2 and various gas geothermometers; Henley et al., 1984). Pore fluids may equilibrate at temperatures as low as 50°C under common crustal conditions.

If pore fluids are equilibrated with their host rock minerals in the deeper parts of the crust as the above discussion indicates must be the case under reasonably quiescent conditions, rock alteration will occur only when pore fluids move with respect to physical fields that affect their equilibrium chemistry. The most important physical fields are temperature, pressure, and chlorinity (Cl^- being a non-reactive and therefore unbuffered fluid component that controls fluid pH through charge balance). When pore fluids move through such physical gradients, the chemical flux from the rock minerals to the fluid is easily defined:

T$_{in}$, P$_{in}$, Cl$^-_{in}$ T$_{out}$, P$_{out}$, Cl$^-_{out}$

$[C_i]_{in}$ $[C_i]_{out}$

Alteration flux from rock to fluid $= Q([C_i]_{out} - [C_i]_{in})$

Q is the total fluid mass moved through each unit area perpendicular to the flow direction. The equilibrium chemistry, $[C_i]$, can be calculated for a particular mineral buffer assemblage using thermochemical data. A modified version of the EQ3 data base is used here (see Cathles, 1985). Changes in mineralogy follow from the alteration flux through multiplication of the inverted transpose of the mineral buffer stoichiometry matrix.

For a specific example, suppose pressure and salinity are constant, and the fluid moves slowly upward through a normal geothermal gradient of $25°C\,km^{-1}$. For the rock mineral buffer in the table below the temperature derivative at 300°C of the total solution CO_2 is > 20 times that of any other solution component for pore fluids of seawater salinity and > 200 times greater for pore fluids where $Cl^- = 1000$ ppm. In other words at temperatures of ~ 300°C or greater, fluids moving down a temperature gradient through crustal rocks lose essentially only CO_2; changes in all other solution components are comparatively very small.

The transfer of CO_2 from the fluid to the rock as the fluid cools in its upward migration causes precipitation of carbonate *and* a cascade of other mineralogical changes that, on a weight percent basis, are usually larger than the carbonate precipitation. Carbonate precipitation has "mineralogical leverage" because the Ca^{2+}, Mg^{2+} or Fe^{2+} required to make the carbonate must be drawn from other (usually aluminosilicate) rock minerals, and the Al^{3+}, SiO_2 etc. from these phases must also find mineralogical homes. The musical

TABLE 1

Mineralogical changes caused by upward migration of water from 300° to 275°C at a water–rock ratio of 1 g cm^{-3}. For a temperature gradient of 25°C km^{-1}, 100 kg of water would pass through each cm^2 perpendicular to flow

Buffer mineral	30 000 ppm Cl$^-$		1000 ppm Cl$^-$	
	Wt.% alteration	% of new products	Wt.% alteration	% of new products
Muscovite	7.04	3.4	7.08	53.6
Quartz	4.12	31.6	4.26	32.3
Calcite	1.78	13.5	1.79	13.5
Albite	0.17	1.3	0.05	0.4
14A-Daphnite	0.02		0.01	
Pyrite	0.003		0.002	
Magnetite	−0.009		−0.008	
K-feldspar	−4.72		−4.93	
Wairakite	−7.99		−7.78	

chairs mineralogic reshuffling caused by CO$_2$ import from an upwardly migrating fluid phase is shown, for a particular set of mineral buffers, in Table 1. In this table the water–rock ratio is fixed at 1 g water per cm^3 rock.

Notice that the alteration in Table 1 is quite intense even at what is normally considered to be a rather low water–rock ratio. Alteration type is dependent only on the entry and exit temperature; alteration intensity only on Q. Thus, for constant fluid throughout, the alteration will be more intense but of

the same character where the geothermal gradient steepens. (Of course the alteration above assumes no buffer mineral phase is depleted, which may not be the case). If the fluid movement was down rather than up, the signs of the alteration would be reversed. Downward fluid movement will produce a wairakite-K-feldspar-magnetite alteration rather than a muscovite-quartz-calcite-albite alteration.

Interesting changes to this simple picture result if the effects of movement through a

TABLE 2

Alteration produced by the upward passage through a cold water hydrostatic pressure gradient of 100 kg cm^{-2} of liquid and vapor water initially at 300°C

Depth range	T_{in}	T_{out}	Ep%	Ksp%			Ab%	Bio%	Wt.% total alteration	ΔV Rxn
3736–3731	300	297.5	62.4	37.4			0.1		40	−
3731–3051	297.5	295	62.6	37.2			0.2		36	−
3051–2518	295	290	62.8	36.9			0.2		27	−
2518–2097	290	285	62.9	36.4			0.4	0.2	17	−
2097–1761	285	280	60.9	34.2			1.2	3.6	6	−
			Mu%	Cc%	Q%	Hm%				
1761–1266	280	270	45.1	23.1	20.1	7.7	0.8	3.1	11	+
1266– 929	270	260	45.9	23.2	20.6	8.7	0.3	1.1	36	+
929– 693	260	250	46.1	23.2	20.7	9.0	0.2	0.6	61	+
693– 348	250	225	46.2	23.3	20.8	9.1	0.2	0.3	103	+
348– 181	225	200	46.2	23.3	20.8	9.2	0.2	0.2	153	+
181– 48	200	150	46.2	23.2	20.8	9.2	0.2	0.2	160	+
48– 9.8	150	100	46.0	23.3	20.7	9.1	0.4	0.4	98	+

hydrostatic pressure gradient are considered in addition to movement through a temperature gradient. A simple case is the upward migration of 300°C pore fluids in a geothermal area. Pressure is not a significant variable until the fluid has reached close enough to the surface that a separate vapor phase is produced (the fluid starts to "boil"). At this point chemical transport occurs through the vapor as well as the liquid phase. In particular the vapor phase removes CO_2 (and some CH_4) from areas where phase separation first takes place and transfers these components to shallower depths where they enhance carbonate alteration. The result is an epidote-kspar alteration at depth overlain by muscovite-quartz-calcite alteration.

The mineralogical alteration indicated in Table 2 is similar in some respects to alteration seen in geothermal systems such as the Salton Sea and Cyprus, where epidote underlies muscovite-quartz-calcite alteration. Details of the mineralogic alteration depend critically on the identity of the buffer mineral phases and their stoichiometry. These must be carefully matched to the particular geological case addressed. This care has not been taken in the above calculations which are intended to illustrate only the general approach.

Finally, it is interesting that easily available thermodynamic data suggest rock-buffered partial pressures of CO_2 and CH_4 can be *very high* at temperatures above 350°C. For example for the mineral buffer in Table 2, the total pressure at 325°C calcualted from extrapolated thermodynamic data is 1.2 kbar ($P_{CO_2} = 1.1$ kbar, $P_{CH_4} = 34$ bar); at 350°C the calculated total pressure is 9.5 kbar (P_{CO_2} = 6.7 kbar, $P_{CH_4} = 2.6$ bar). Pressures of 9.5 kbar would be more than sufficient to fracture rock at 30 km depth. Sediments in the Gulf Coast lying at 10 to 14 km depth could have attained such temperatures, and therefore could have produced gases at pressures sufficiently high to hydrofracture the rock and escape. If these pressures are real, and not the artifact of improperly extrapolated thermodynamic data, rock hydrofracture and gas escape may be a very important mechanism for rock alteration in the lower crust. These deep gases could also cause significant alteration in the upper parts of the crust as they escape in a fashion analogous to the geothermal case above. Escape of CO_2 would cause epidote alteration as discussed above. Escape of CH_4 would oxidize the rock dramatically, possibly causing intense magnetite alteration.

SHORT LIST OF ESPECIALLY IMPORTANT REFERENCES

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