The ligand chemistry of crustal fluids

B.W.D. Yardley   *Dept. of Earth Sciences, University of Leeds, Leeds LS2 9JT,*

D.A. Banks   *UK.*

Introduction

A knowledge of element fractionation between aqueous fluids and minerals or melts is essential for the understanding of many geochemical processes. However the dissolved load of an aqueous fluid is primarily dependent on ligand concentrations, and hence fluid–mineral and fluid–melt fractionation factors will in general also depend on the ligand content of the specific fluid of interest. Unfortunately, this cannot be deduced *ab initio* from the chemistry of the solid rock or mineral end product, although good indications of total 'equivalent salinity' can be obtained from fluid inclusion microthermometry.

The key to the dissolved load of most crustal fluids is the chloride concentration. For fluids equilibrated with a given plagioclase feldspar, the Ca/Na ratio of the fluid depends on its salinity (Orville, 1972), with more saline fluids having higher proportions of Ca. Many other potentially important ligands form minerals with Ca (e.g. fluorite, apatite, calcite and gypsum or anhydrite), and saturation with these minerals at a given Ca concentration provides an upper limit to the relevant ligand's concentration. Hence they will tend to be less abundant, both absolutely and relative to Cl, in more saline fluids. Amounts of other potentially important ligands, including BO_3, H_2S and Br, are not so readily constrained.

Methodology

Despite its pivotal role in controlling fluid chemistry, chloride concentration can generally not be obtained from mineral analyses with adequate reliability, because its substitution for OH is more dependent on pH than on total chloride concentration. As a result, other aspects of the fluid chemistry cannot be estimated from the solid rock alone.

We have therefore set about the empirical investigation of crustal fluid chemistries, utilising crush-leach methods to extract inclusion fluid for analysis from small ($< 1g$) samples of vein quartz with single inclusion populations (Bottrell *et al.*, 1988; Banks and Yardley, 1991). Anions have been analysed by Ion Chromatography except for BO_3^{3-}, determined as B by ICP-AES, H_2S, determined by fluorimetry and HCO_3^-, which can

only be estimated approximately from charge imbalance (Yardley *et al.*, 1993). Total Cl concentrations have been estimated from the depression of freezing point of individual inclusions.

Results

Table 1 summarises the anion and major cation chemistry of 7 different fluid inclusion samples, each representative of a larger data set. In all cases, Cl^- is the major anion, although the fluids range from an H_2O-CO_2 fluid from a Au-quartz vein which is of a type popularly referred to as 'low salinity' (not untypically, it is actually more saline than sea water) to a hypersaline magmatic fluid which might equally be described as a hydrous salt melt. Only the lowest salinity fluid inclusions contain observable CO_2, and the analyses of these yield an anion deficiency that can reasonably be ascribed to the presence of HCO_3^-. While this association of high bicarbonate with low Ca is in accord with the theory outlined above, we find relatively high sulphate and fluoride in the Ca-rich hypersaline magmatic fluid. This may reflect very different speciation in such a concentrated and high-T fluid. The two examples of thrust fault fluids from the Pyrenees do show a reciprocal relationship between Ca and sulphate.

Conclusions

Despite the predominance of chloride, there are also significant levels of borate, sulphate and fluoride in most fluids, and reduced S and Br may also be significant. Of these, borate and fluoride are likely to be of particular significance because they may complex metals that are not strongly complexed by Cl: for example this may account for the much higher mobility of Al observed in natural vein systems than can readily be accounted for by the solubility of Al in chloride fluids alone (Baumgartner and Eugster, 1988; Yardley *et al.*, 1993). The potential importance of reduced S species for Au transport is well known (Seward, 1973), and the highest values that we have found in inclusion fluids are comparable to those of geothermal waters.

TABLE 1. Chemical composition of crustal fluids: examples of ancient fluids preserved as fluid inclusions in quartz

Element	Reconstructed fluid analyses in ppm						
	1	2	3	4	5	6	7
Na	17314	57484	29135	23604	39520	16700	182438
K	863	5219	1218	2604	13960	1144	61409
Ca	793	16687	39004	4877	9620	618	30723
B	432	144	140	81	3975	665	438
SO_4	996	6540	3023	71	6075	2628	24210
H_2S	340						
CO_2	94500						
F	401	< 50	203	177	817	< 50	1770
Cl	21389	130639	124875	35533	106360	20378	398940
Br	104	721	800	227	150	145	146
I	1.59	18	11	2.49	4.8	0.08	0.91

1. H_2O-CO_2 Ore fluid, Au-quartz vein, Brusson, N. Italy, T = c. 270°C (Yardley et al., 1993, sample LD659)

2,3 Low grade fluids from Alpine thrust faults, Pyrenees, Spain, T = c. 300°C (Banks et al., 1991, samples 50176, 50177)

4. Post-metamorphic quartz vein with albite, in gabbro, Modum, Norway (Munz et al., in prep.)

5. Granite-derived tourmaline-topaz-quartz rock, Cornwall, U.K., T = c. 600°C (Bottrell and Yardley, 1988)

6. Quartz vein associated with low-T, granite-related Au-mineralisation, Vila Pouca de Aguiar, Portugal

7. Granite-derived hypersaline brine, quartz-fluorite vein, Capitan pluton, New Mexico, U.S.A.., T = c. 650°C (Banks et al., 1994, sample CPU-2, with additional analyses.

We conclude that the concentrations of the great majority of metals in aqueous fluids depend primarily on the available complexing ligands. Until much more is known about the ligand chemistry of crustal fluids, attempts to investigate element partitioning between fluids and minerals or melts are likely to be difficult to apply meaningfully to natural systems

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