Post-metamorphic gold–quartz veins from N.W. Italy: the composition and origin of the ore fluid

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Abstract

Multi-element crush-leach analysis of H_2O–CO_2 inclusion fluids from a suite of six vein samples from gold–quartz veins in the Brusson district demonstrates that their solute chemistry (c. 5 wt.% NaCl equivalent) is dominated by sodium chloride with lesser amounts of calcium bicarbonate, potassium chloride and sodium bicarbonate. The samples have been analysed both for gas species (CO_2, H_2O, N_2 and H_2S) and for Na, K, Li, Rb, Ca, Mg, Sr, Ba, Fe, Mn, Zn, Pb, Cu, Al, As, B, SO_4^{2-}, F, Cl, Br and I. The fluids contain appreciable H_2S ($>10^{-3}$ molal), which correlates with the contents of As, CO_2 and B. Concentrations of many cations remain similar irrespective of wall rock, but there is evidence of leaching of Li, and possibly I, from some wall rocks. Large variations in the K-content of the fluid may result from precipitation of sericite. The bicarbonate concentrations in the fluids, estimated from charge imbalance, are substantially less than their total CO_2 content when trapped as single phase fluids, indicating a low pH. Sulphate:sulphide ratios suggest relatively reducing conditions, which is consistent with Fe concentrations significantly greater than Mn.

The gold–quartz veins formed as H_2O–CO_2 fluids of modest salinity and very uniform composition ascended from depth. Halogen ratios of the fluids are consistent with an ultimate origin for these fluids from deep-penetrating surface or connate waters although such a model requires extremely low fluid:rock ratios, to account for the hydrogen isotope composition of many similar deposits. There is as yet insufficient reference data to use halogen ratios as a rigorous test for the alternative model of an origin for the fluid by metamorphic devolatilisation.

KEYWORDS: gold, quartz, fluid chemistry, fluid inclusions, Italy.

Introduction

MANY orogenic belts exhibit mesothermal gold mineralisation in the form of quartz–gold veins which formed after the peak of regional metamorphism. Phanerozoic examples occur in both the western and eastern Alps, the Caledonides (e.g. Wales), S. Australia, New Zealand, Alaska, California and the Canadian Cordillera. They appear to be similar to some Archaean deposits. Certain characteristics of this class of deposit are remarkably uniform, irrespective of age or location. Temperatures of formation are in the range 250 to 400 °C at pressures between 0.7 and 2.0 kbar. Fluid inclusions indicate that the ore fluid was composed predominantly of H_2O with c. 10 mol.% CO_2 and a few equivalent wt.% NaCl. Evidence for fluid immiscibility in the form of minor CO_2-rich fluid inclusions is commonly present. Despite the fact that the general characteristics of the deposits are so well defined, their origin remains controversial. The most widely accepted hypothesis at present is that the ore fluids are of metamorphic origin (Kerrich and Fyfe, 1981, and many subsequent authors), either derived from continuing high-grade metamorphism at depth, or trapped at deeper crustal levels at the metamorphic peak and only released subsequently (Goldfarb et al., 1991b). Alternatively, a surface origin from deeply penetrating groundwaters has been proposed for the ore fluid in examples from the Canadian Cordillera

(Nesbitt *et al.*, 1989), while other workers have proposed an igneous origin for the hydrothermal fluids (e.g. Rock and Groves, 1988).

The Monte Rosa gold district

This paper describes in detail the chemistry of fluid inclusions in quartz from the mesothermal gold–quartz veins of the Monte Rosa district in the northwestern Alps of Italy. The gold–quartz veins of this region, and their fluid inclusions, have recently been described by Diamond (1986, 1990), Curti (1987), Lattanzi (1990) and Lattanzi *et al.* (1989). They are of late Alpine age (Diamond and Wiedenbeck, 1986), and thus 5–10 Ma younger than the peak of Alpine metamorphism. Quartz is the dominant vein mineral, often forming well-developed prismatic crystals several centimetres in length. Gold is principally associated with sulphides which are dominantly pyrite and arsenopyrite; minor carbonates and sericite are also present. Total historic gold production from the region is estimated at 20 tons (Lattanzi, 1990).

The samples studied in detail here all come from Val d'Ayas, in the vicinity of Brusson, where individual veins crosscut a wide range of lithologies (Diamond, 1990). Gold mineralisation is not restricted to any one host, but in the case of the Fenilia vein, a major vein cutting varied lithologies, gold is found where the host is metagranite or siliceous metasediment, but not where it is carbonate or ultramafic rock

(Diamond, 1990). Similar associations are known from comparable ore bodies elsewhere, notably from the work of Bohlke (1989) at Alleghany. The results of microthermometric and laser-Raman studies of fluid inclusions in the same, or closely related, samples as those studied here have been presented by Diamond (1990), and some of his results for gas compositions of individual inclusions are included in Table 1. Most inclusions are water-dominated H_2O-CO_2 inclusions. They are three-phase at room temperature (H_2O liquid, CO_2 liquid and CO_2 vapour) with about 5 wt.% equivalent NaCl dissolved in the aqueous phase. A few CO_2-dominated inclusions occur also. We have analysed the inclusion fluids from 6 samples of vein quartz, sampled from 4 veins in a variety of host rocks (Table 1); sample numbers are from the study of Diamond (1986). Diamond (1990) concluded that mineralisation occurred during uplift over the range of conditions 300 °C, 1300 bars to 230 °C, 600 bars. Much gold precipitation occurred in the earlier, higher temperature stages of this evolution, whereas unequivocal evidence for fluid immiscibility (CO_2-dominated inclusions) is present only at the final stages.

The composition of the ore fluid

The presence of only a single compositional type of fluid inclusion, demonstrated by Diamond (1990) and outlined above, makes these samples ideally suited for analyses by bulk methods which,

TABLE 1: Fluid Inclusion gas analyses from the Brusson district

a) Raw Bulk Gas Analyses, this study (mole % total gases)

Sample	LD659	LD671	LD872	LD886	LD888B	LD910
H2O	95.42	95.87	90.76	92.07	92.41	95.9
CO2	4.3	3.91	9.01	7.82	7.39	3.78
N2	0.26	0.21	0.2	0.19	0.18	0.32
H2S	0.02	0.007	0.035	0.019	0.014	0.007
Vein	Orbeill.	Gaebian.	Fenilia	Fenilia	Fenilia	Bechaz
Host Rock	Meta-basalt	Granite-gneiss	Graphite mica-schist	Granite-gneiss	Mica-schist	Granite-gneiss

b) Individual water-rich inclusions, computed from laser-Raman Analyses
(mole % total gases, from Diamond, 1990)

Sample	LD888	LD888	LD888	LD927	LD927	LD928	LD928
Generatn.	3	4	4	2	3	1	4
H2O	94.4	95.1	94.8	93.5	94.3	93.2	94.6
CO2	5.5	4.7	5	6.3	5.6	6.6	5.2
N2	0.11	0.12	0.13	0.2	0.11	0.16	0.14
CH4	0.003	<0.002	0.003	0.002	<0.002	<0.002	<0.002

Notes: LD888, Fenilia (see part a); LD927, Bechaz; LD 928, Orbeillaz.
Fluid Inclusion Generations: 1, Primary; 2, Late Primary
3, Early Pseudosecondary; 4, Late Pseudosecondary

while suffering from the drawback that only an average fluid composition is obtained, permit much more detailed investigation of the fluid chemistry than is possible by microthermometry and laser-Raman analysis alone. We have therefore investigated the chemistry of the bulk fluid released by crushing or decrepitation, determining both the gas species (which permits direct comparison with laser-Raman analysis of single inclusions), and the dissolved electrolytes.

Sample preparation

The samples consisted of clusters of prismatic quartz crystals from individual veins, and were included in the study of Diamond (1986). Data on some of the specimens used here are given in Diamond (1990). All the bulk analyses have been carried out on crushed quartz which was selected for its purity and subsequently picked by hand under the binocular microscope to remove any grains containing visible mineral impurities. These samples presented an unusual problem because of the large size of some of the inclusions (>100 μm). Fine grained quartz separates gave low yields, which we attribute to decrepitation of large inclusions during sample preparation. Crushed quartz was seived to separate the 10–30 mesh and 30–60 mesh fractions. The 60–90 mesh material, which we have normally found suitable for bulk analysis, was too fine to give satisfactory yields. The picked quartz was then cleaned in dilute nitric acid and in electrolytic cells, following the procedure of Bottrell et al. (1988b). The major limitation to the sample purity was the presence of fine solid inclusions of carbonate in some of the quartz crystals. Care was taken to exclude such grains from the material prepared for analysis, but in a few cases material with solid inclusions was almost certainly analysed. These examples are discussed in consideration of the results, below.

Analytical strategy

Many analyses purporting to represent the composition of inclusion fluids which have been published in the past lack any independent verification and do not accord with experimental or theoretical results. There are several reasons why we believe that the results presented here are genuinely of value. (a) After analysis of all major cations and anions, except HCO_3^-, the analyses have a small excess of positive charges which, if assigned to the presence of HCO_3^-, permits calculation of the pH of the fluid (below) from

carbonate speciation, and yields a result which is reasonable for hydrothermal fluids. Brines lacking CO_2 analysed in our laboratory usually give charges balanced to within 5% (e.g. Banks et al., 1991). This is because samples are scrupulously cleaned to avoid any solid contamination and the leaching procedures of Bottrell et al. (1988b) are utilised to suppress adsorbtion of cations on the freshly opened quartz surfaces. (b) Analyses of the major cations in fluid inclusions from Brusson have also been performed by crush-leach analysis at Nancy, and by SIMS analysis of single inclusions (Diamond et al., 1991) and give closely comparable results. (c) Results from our laboratory have been further validated by analysis of a sample of synthetic inclusions (Banks and Yardley, 1992) and by agreement of Na : Ca ratios in analysed brine inclusions with compositions estimated for individual inclusions from freezing behaviour (Banks et al., 1991). Ratios between K, Cl, and Br have also been determined on a sample analysed by us utilising laser ablation rare gas mass spectrometry on individual inclusions (Bohlke and Irwin, 1992) and agree within error.

A variety of analytical techniques has been used in this study, some of which determine the yield (of gas species) per gram of quartz, while others give element concentrations relative to Na. We have utilised the microthermometry results to combine data from all these analyses into a bulk fluid composition. The bulk gas analyses (i.e. H_2O, CO_2 and other gases) are comparable to the gas compositions for individual water-dominated inclusions estimated by Diamond (1990) from laser-Raman analyses and optical measurements. (Table 1, see discussion below). They have therefore been taken as representative of the H_2O-rich inclusions, treating the contribution to the analyses from CO_2-rich inclusions as negligible. Water-dominated fluid inclusions yield equivalent salinities of 4.5 to 5.5 wt.% NaCl in a wide range of samples (Diamond, 1990). We have therefore assumed a value for the total dissolved solids (excluding Si, which is at negligible levels at the conditions of laboratory measurement of salinity) of the aqueous portion of the fluid of 5.0 wt.%. The electrolyte analyses have been recalculated to yield this weight ratio to H_2O. The resulting analysis, representing the composition of the aqueous phase in the inclusions at room temperature, has been combined with the gas analyses to yield the total composition of the homogeneous mixed volatile fluid at the time of trapping. These fluid compositions are tabulated in Tables 3 and 4. For at least part of the history of formation of the quartz veins, this analysed fluid coexisted immiscibly with a CO_2-rich fluid con-

taining a water component of somewhat lower salinity (Diamond, 1990).

Analytical methods

Gas analyses

Gases were released from bulk quartz samples (*c.* 0.3 g) by decrepitation at 600 °C for 15 minutes. Two separate decrepitations were carried out. The major gas species were determined simultaneously by mass spectrometry according to the method of Shepherd and Miller (1988). These analyses were carried out by M. Miller at NIGL, Keyworth, courtesy of Dr T. J. Shepherd. H_2S was also determined as a yield per gram of quartz by the method of Bottrell and Miller (1989). This procedure, carried out in Leeds, uses an identical furnace arrangement to that at Keyworth in order to duplicate the decrepitation of the inclusion population. For H_2S determinations, the gas is released into a stream of N_2 and the H_2S trapped in NaOH. Sulphide is then determined by fluorimetry. Results of the bulk gas analyses have been combined to give a total average fluid composition (Table 1). Also given are representative laser-Raman analyses for the same samples, where available. The H_2S levels are about an order of magnitude lower than the detection limit by laser-Raman, which accords with the fact that it could not be detected by that technique.

Crush-leach analyses of electrolyte composition

The procedures used for crush-leach analyses are based on those of Bottrell *et al.* (1988b), and some preliminary results were included in that paper. However several improvements to this procedure have been introduced. Cleaned quartz was crushed by grinding dry in an agate pestle and mortar, prior to leaching and centrifuging. Two types of leach solution were used: acidified dilute $LaCl_3$ (ALC, Bottrell *et al.*, 1988b) and double distilled water (DDW). The ALC leaches were used for analyses by ICP Atomic Emision Spectroscopy (ICP-AES) or Atomic Absorbtion (AA), including use in flame emission mode, (FES), or with a graphite furnace atomiser (GFAA). DDW leaches were used for determination of anions by Ion Chromatography (IC), but Na and K were also determined on these leaches in order that all elements determined could be expressed as concentration ratios to Na.

For each sample analysed, a number of individual crush-leaches were performed with each leach solution. This was largely necessary because the yields of dissolved electrolytes from crushes of

these samples were very low, Na concentrations seldom exceeding 5 ppm in the leach solution analysed. This led to serious possibilities of contamination and relatively large uncertainties in trace element concentrations. The results from the analysis of each crush-leach experiment were tabulated, and anomalously high concentrations from individual experiments were rejected if they were clearly distinct from the bulk of the analyses. Since the most likely sources of error (below) would all lead to anomalously high concentrations, the tendency was to reject high values where other crushes yielded low values. The procedures used to obtain the average analysis for one sample are illustrated in Table 2, which also indicates the analytical procedures used for each element. The average analyses for all the samples, on a weight basis, are given in Table 3. The weights refer to the proportion of the analysed elements in the total, homogeneous fluid. These analyses have been recalculated as molalities (i.e. moles per kg water), in Table 4.

It is apparent from Table 2 that, although a small number of anomalous values were obtained on individual leaches, the overall chemical characteristics of the fluid are well constrained. Likely sources of uncertainty are:

(1) Analytical errors or contamination in the laboratory;
(2) Contamination of the leach solution by solid impurities in the quartz;
(3) Heterogeneity within individual samples.

Of these, laboratory contamination is minimised by the use of clean facilities, and is also monitored by the analysis of procedural blanks consisting of inclusion-free Brazilian quartz. Typical blank values are tabulated in Table 2, and it can be seen that for some elements the sample levels are sufficiently close to the blank for this to be a serious source of uncertainty; several analyses listed in part *a* of Table 2 are rejected in part *b* for this reason, especially where the blank is rather variable (e.g. Ca).

Contamination by solid inclusions is detected by charge imbalance in the final analysis and by correlations between elements which reflect solid phase compositions. For example, Mn/Fe ratios in the fluid are typically much higher than in coexisting silicates (Bottrell and Yardley, 1991) and some individual crushes yielded anomalously high Fe but normal levels of Mn; these were attributed to solid phase contamination of Fe. The overall data set (Table 3) does still contain some possible evidence for contamination. Higher Ca in LD888B may reflect the presence of trace calcite impurities. The high Al values for

TABLE 2: Detailed analytical results for sample LD659

a) Original Analyses (ppb) for individual crushes (blank corrected)

	1	2	3	4	5	6	7	8	9	10	11	Procedural Blank	Method
Na	3325	2050	5037	4256	3809	4800	5100	1700	1710	1113		32	AA-FES
K	124		205	160	155	232	380	96	108			48	AA-FES
Ca			381	251	232	135	180	9	50			113	ICP
Mg	26		53	39	35	33	39	9	10			7	ICP
Fe	21	9	6.5	3	4							12	ICP
Mn	0.9	0.2	0.8	0.2	0.2							0.5	ICP
Al			71	59	50	224	56	45	151			3	ICP
Li	4	2.4	8	5	4	8	8	5	6			1	ICP
Sr			11	11	11		18	7				4	ICP
Ba			3	2	2	3	11	4	5			3	ICP
Cu	0.5	0.5	1	1	1							<0.5	ICP
Zn	0.5	0.1						6				1.7	ICP
Pb	0.5	0.5	0.5	0.5	0.5							0.6	ICP
As	16.5	9	28.7	25.7	23.5	25	33					<0.5	AA
B			125	109	96	99	115	48	47			8	ICP
SO4										64		14	IC
F										21	149	80+	IC
Cl										1375	6681	163	IC
Br										6.2	35	<1	IC
I										0.004	0.49	<1	IC
Leach	ALC	ALC	ALC	ALC	ALC	ALC	ALC	ALC	ALC	DDW	DDW		

Notes: ALC, acidified lanthanum chloride leach solution   DDW, Double distilled water leach
 + Blank value for F largely due to a baseline signal caused by proximity to the "water dip" in chromatogram
 AA, Atomic Absorbtion; AA-FES, AA in flame emission mode;
 ICP, ICP Atomic Emission Spectroscopy; IC, Ion Chromatography

b) Analyses Normalised to 10000ppb Na

	1	2	3	4	5	6	7	8	9	10	11	Mean	st.dev.
Na	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	0
K	373		407	376	407	483	745	565	632			498	128
Ca			*	590	609	281	353	*	*			458	144
Mg	78		105	92	92	69	76	53	58			73	17
Fe	*	*	12.9	7.0	10.5							10.2	2.4
Mn	2.7	1.0	1.6	0.5	0.5							1.3	0.8
Al			141	139	131	*	110	265	*			157	55
Li	12	12	16	12	11	17	16	29	*			15	6
Sr			22	26	29		35	41				31	7
Ba			6.0	4.7	5.3	6.3	21.6	23.5	29.2			13.8	9.8
Cu	1.5	2.4	2.0	2.3	2.6							2.2	0.4
Zn	1.5	0.5						*				1.0	0.5
Pb	1.5	2.4	1.0	1.2	1.3							1.5	0.5
As	50	44	57	60	62	52	65					56	7
B			248	256	252	206	225	282	275			249	25
SO4										575		575	
F										187	276	232	44
Cl										12354	12354	12354	
Br										56	65	61	4.5
I											*	0.906	0.906

Notes: "*" denotes determinations rejected from the compilation
    Analysis 11 normalised to analysis 10 on basis of Cl

some samples may result from contamination with sericite, although there is little evidence for enhanced K that should accompany such contamination. Levels of H_2S are low (in absolute terms) in all samples and do not correlate with concentrations of chalcophile elements, so it is unlikely that there has been any solid sulphide contamination.

Sample heterogeneity is very difficult to demonstrate, but is a distinct possibility because of the relatively coarse grain size of the quartz crushed. The large number of analyses performed on each sample meant that in some cases the original split prepared for analysis became exhausted and a second split was crushed. There are some differences between early and late analyses that may reflect differences between splits. Early analyses that we performed on

TABLE 3: Reconstructed fluid inclusion compositions on a weight basis

	LD659	LD671	LD872	LD886	LD888B	LD910
wt. %						
H2O	85.85	86.71	77.12	79.29	80.08	86.83
CO2	9.45	8.64	18.71	16.46	15.65	8.36
N2	0.36	0.30	0.26	0.25	0.24	0.45
H2S	0.034	0.012	0.056	0.031	0.023	0.012
ppm						
Na	17314	17163	16077	16752	16740	18675
K	863	2526	89	985	824	1017
Ca	793	955	918	665	917	1459
Mg	135	85	12	129	89	60
Fe	18	66	166	120	62	65
Mn	2.2	4.0	2.8	5.0	8.4	5.9
Al	272	669	1133	348	1036	329
Li	27	81	367	239	218	52
Rb	n.a.	8.4	n.a.	13.4	n.a.	n.a.
Sr	53	b.d.	31	54	44	48
Ba	24	68	31	43	39	18
Cu	3.8	7.5	10.5	25.1	7.5	2.8
Zn	1.7	33.5	100.5	34.3	17.6	18.7
Pb	2.6	b.d.	b.d.	b.d.	15.9	1.5
As	96	29	175	147	116	47
B	432	393	439	560	403	387
SO4	996	154	117	102	275	570
F	401	208	537	242	586	351
Cl	21389	20820	18276	19112	18556	20207
Br	104	87	71	70	85	102
I	1.59	0.16	4.78	0.79	0.77	2.38

Notes: b.d., below detection; n.a., not analysed

sample LD872 gave K/Na ratios almost an order of magnitude higher than the preferred values given here, and also higher Fe and Li. This serious discrepancy may result from the presence of mica

TABLE 4: Reconstructed fluid inclusion compositions as molalities

	LD659	LD671	LD872	LD886	LD888B	LD910
CO2(tot)	2.502	2.265	5.512	4.716	4.440	2.189
N2	0.151	0.122	0.122	0.115	0.108	0.185
H2S	0.012	0.004	0.021	0.011	0.008	0.004
Na	0.879	0.865	0.910	0.925	0.910	0.943
K	0.026	0.075	0.003	0.032	0.026	0.030
Ca	0.023	0.028	0.030	0.021	0.029	0.042
Mg	0.0065	0.0041	0.0006	0.0067	0.0046	0.0029
Fe	0.0004	0.0014	0.0039	0.0027	0.0014	0.0014
Mn	0.00005	0.00009	0.00007	0.00012	0.00019	0.00012
Al	0.012	0.029	0.055	0.016	0.048	0.014
Li	0.005	0.013	0.069	0.044	0.039	0.009
Rb	n.a.	0.0001	n.a.	0.0002	n.a.	n.a.
Sr	0.0007	b.d.	0.0005	0.0008	0.0006	0.0006
Ba	0.0002	0.0006	0.0003	0.0004	0.0004	0.0002
Cu	0.00007	0.00014	0.00021	0.00050	0.00015	0.00005
Zn	0.00003	0.00059	0.00200	0.00067	0.00034	0.00033
Pb	0.00001	b.d.	b.d.	b.d.	0.00010	0.00001
As	0.0015	0.0005	0.0030	0.0025	0.0019	0.0007
B	0.047	0.042	0.053	0.066	0.047	0.042
SO4	0.0121	0.0019	0.0016	0.0014	0.0036	0.0069
F	0.043	0.022	0.064	0.028	0.068	0.037
Cl	0.703	0.677	0.669	0.680	0.654	0.656
Br	0.0015	0.0012	0.0011	0.0011	0.0013	0.0015
I	1.46E-05	1.45E-06	4.89E-05	7.82E-06	7.57E-06	2.16E-05
charges:						
Sum +'ve	1.0045	1.1032	1.2162	1.1087	1.1912	1.1110
Sum -'ve	0.9112	0.8302	0.8953	0.9078	0.8694	0.8326
calculated carbonate speciation						
HCO3-	0.093	0.273	0.321	0.201	0.322	0.278
CO2 aq	2.409	1.992	5.191	4.515	4.118	1.910
HCO3-/CO2	0.039	0.137	0.062	0.044	0.078	0.146

inclusions in the first split of quartz, especially since this sample was noted by Diamond (1986) as likely to have solid impurities. Within-sample heterogeneity is also apparent for As in LD910 in particular, where the concentrations in coarse grain fractions are distinctly different from those of finer grained fractions of the same split.

Overall, the values quoted for most cations and anions are believed to have uncertainties of circa ±20%.

Discussion of the results

All the fluids analysed are remarkably similar in their general characteristics, being CO_2-bearing, mildly saline, aqueous fluids, possibly coexisting with a CO_2-rich fluid which was seldom trapped. The aqueous phase is predominantly an $Na(K,Ca)-Cl(HCO_3^-)$ fluid.

Gas species: All the bulk analyses are superficially similar to laser-Raman analyses of individual H_2O-rich inclusions (Table 1). Despite this broad agreement with the laser-Raman analyses, one important discrepancy exists. Diamond (1990) found very constant $CO_2:N_2$ ratios in a range of samples, with a consistent value near 40 for H_2-rich inclusions, but around 16 for CO_2-dominated ones. The $CO_2:N_2$ ratios from the bulk analyses presented here actually span a wider range than the analyses of individual inclusions, which suggests that the bulk analyses are less precise. Furthermore, CO_2-rich fluids from this study have relatively high $CO_2:N_2$ ratios compared with CO_2-poor ones, the opposite of the effect found by Diamond in his laser-Raman study. This discrepancy could result from larger analytical uncertainties in the present work, especially for N_2, or from contamination by CO_2 from solid inclusions of carbonate. However CO_2 contents from the bulk analyses correlate well with other volatile fluid components (below), and so we believe that the discrepancy is most likely due to uncertainties in the N_2 concentrations from the bulk gas analyses. The N_2 data are therefore not discussed further.

Fig. 1a is a plot of the total CO_2 content of the fluids against H_2S, and shows a positive correlation between these non-polar fluid species.

Arsenic and boron: These elements were analysed following leaching, as ratios to Na, and are therefore determined separately from the gas species. Despite this potentially large source of uncertainty in the reconstructed analyses, both elements appear to be correlated to CO_2 and H_2S (Fig. 1b,c). There is a particularly gratifying correlation between As and H_2S (Fig. 1c), which is of interest because of the common observation that arsenic can act as a pathfinder for gold. These
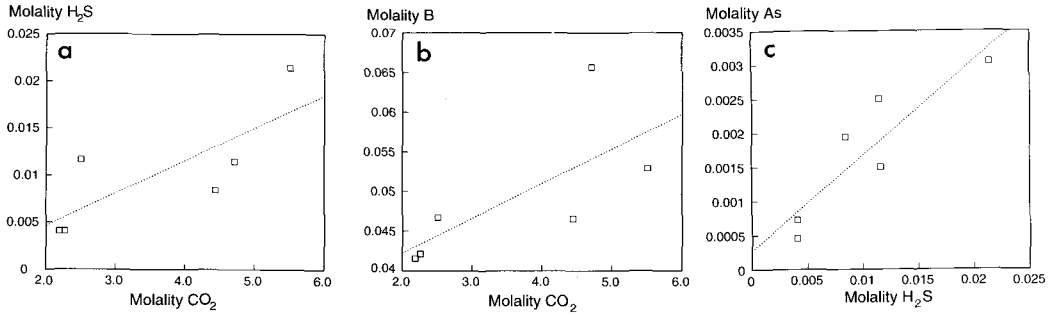
Fig. 1. Plots of volatile species compositions in the reconstructed inclusion fluids. (a) Plot of H_2S against CO_2, demonstrating a poor positive correlation. Much of the scatter is likely to be due to analytical uncertainties. (b) Plot of boron against CO_2, demonstrating a similar correlation to that in a. (c) Plot of As against H_2S, exhibiting a good positive correlation.

data suggest that As is associated with the reduced sulphur content of the ore fluid, not necessarily directly with gold. Although common in parts of the Monte Rosa district, arsenopyrite is generally absent from the veins at Brusson. Heinrich and Eadington (1986) made approximate calculations of arsenopyrite solubility, assuming congruent dissolution. In these fluids, concentrations of Fe, As and S are indeed comparable, and comparison with the plots of Heinrich and Eadington indicates that the analysed fluids are close to arsenopyrite saturation.

Alkali and alkali-earth metals: The sodium content of the fluid phase is constrained to be rather constant throughout the system by the microthermometric data, and Ca is also relatively uniform according to our analyses. A small caveat must be entered here: some much higher Ca determinations for individual crushes of specific samples (e.g. LD888B) were rejected as probably affected by contamination by solid inclusions. In contrast K and Li are highly variable between specimens, but it is notable that Li is a major component of the fluid phase. Potassium concentrations show a weak negative correlation with CO_2 (Fig. 2), although it is difficult to see why this should occur. It is apparent from the triangular diagrams (Fig. 3) that the fluids are all dominated by Na, with rather uniform Na/Ca ratios, low Mg and variable K. The trace components Sr and Ba are present at comparable concentrations to Mg, while Rb, not analysed in all samples, is at very low levels.

Transition metals: Considerable caution is necessary in interpreting the transition metal analyses of these fluids, because the concentrations are so low that there is a serious risk that the results have been affected by contamination. Indeed the most straightforward conclusion is

simply that the concentrations are extremely low. It seems likely that the Mn data are the most reliable, and it is probable that Fe is at significantly higher levels than Mn, as found by Yardley and Bottrell (1991) for fluids from reducing, but not oxidising, environments. Zinc and copper are almost certainly present at higher concentrations than Pb, but large uncertainties exist in this data.

Aluminium: The concentrations of aluminium in all the analysed samples are well above detection levels and are very much higher than values for geothermal fluids at similar temperatures. It is certainly possible that in some samples trace solid inclusions of sericite or clays could have contaminated the leachate with Al, although note that one of the highest Al contents is in LD872, which is very low in K, so leaching of sericite can be ruled out here. The conservative interpretation of the data, given its relatively large uncertainties, is that the higher Al values
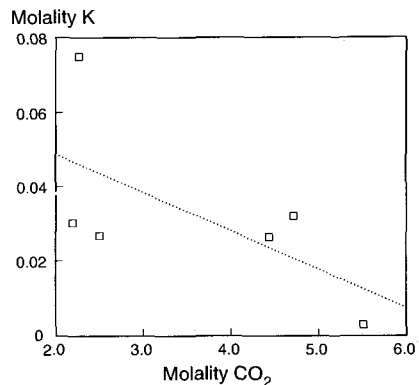

Fig. 2. Plot of K against CO_2 for the reconstructed inclusion fluids, demonstrating a weak negative correlation.
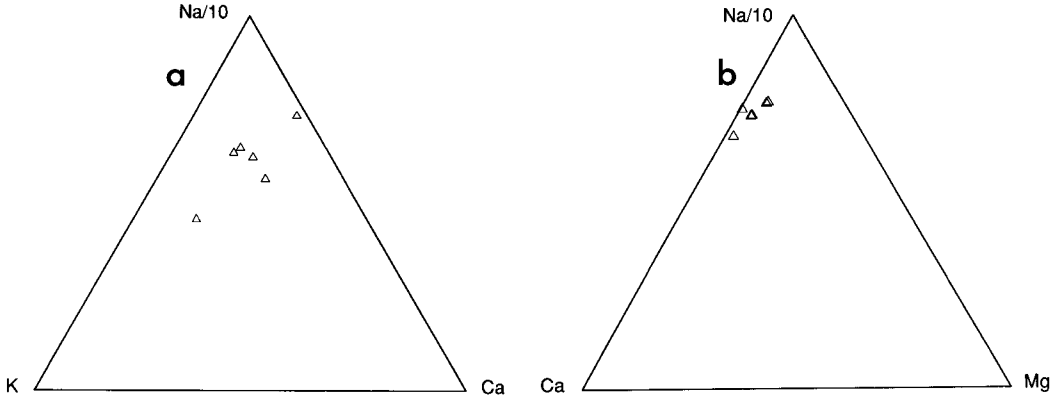
FIG. 3. Triangular plots demonstrating the contents of the major cations in the inclusion fluids. (*a*) Na–Ca–K, (*b*) Na–Ca–Mg. Note the similar concentrations of Na, Ca and Mg in all samples, but variable potassium.

result from some form of solid contamination, while the lower values are more typical of the true fluid composition in all samples. Even at the lowest levels found however (*c*. 0.01 m), the Al concentration is far higher than would be expected from solution in a simple chloride fluid (Pokrovskii and Helgeson, in press), but can be modelled much more closely when formation of AlF_{3aq} complexes is taken into account (below).

Halogens: All anions except I were determined together by ion chromatography on a DDW leach. I was determined with Cl separately, on a 1 ml split of the same leach solution utilising an on-line pre-concentrator to attain the necessary sensitivity. Br and Cl are very similar in all samples, but I is more variable. While this may in

part reflect analytical error, the variation is too large for this to be the sole cause. It is notable that the highest I values are for sample 872, hosted by graphitic schists. I is often associated with organic matter in sediments, and it is therefore likely that there has been some take-up of I from the wall rocks in at least some samples.

Sulphur speciation: Sulphur was determined as both reduced sulphur, as outlined above and quoted here as H_2S, and as sulphate determined by IC on crush-leach runs. There is no apparent correlation between the two forms of sulphur (Fig. 4*a*), and it seems likely that the analyses genuinely determine sulphur in two separate forms, rather than measuring the same sulphur in two different ways. Both analytical techniques are
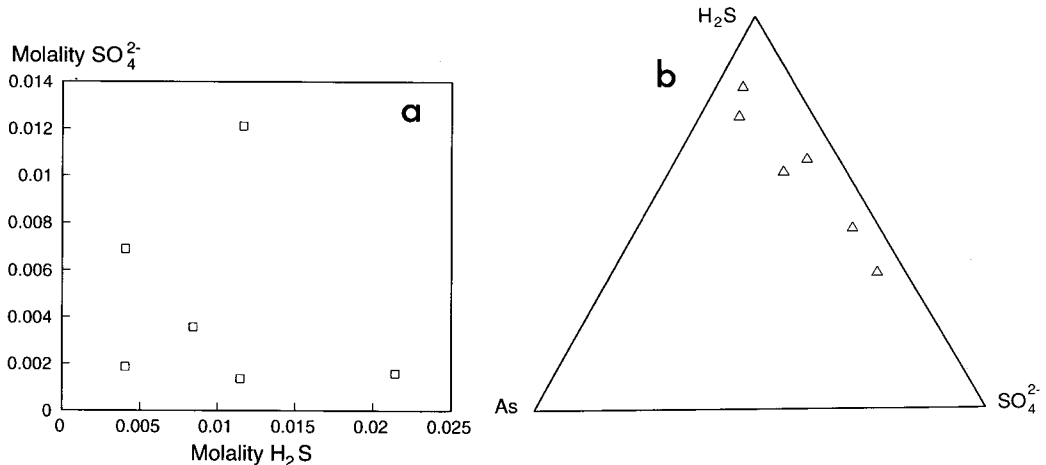

FIG. 4. Plots of sulphur species concentrations in the inclusion fluids. (*a*) Sulphate–sulphide plot to demonstrate the lack of correlation and variable concentrations of both forms of sulphur. (*b*) As–H_2S–SO_4^{2-} diagram demonstrating the uniform H_2S : As ratio, irrespective of sulphate content.

species specific, and while the sulphide procedure offers no opportunity for reduction of sulphate, the dry grinding prior to leaching should result in loss of H_2S from the crushed material prior to leaching and determination of sulphate. We have not been able to demonstrate unequivocally that no sulphide remains and is oxidised to be determined subsequently as sulphate, although the correlations in the data suggest that this is not a serious source of error. Fig. 4b demonstrates the wide range of $H_2S:SO_4^{2-}$ ratios of the samples analysed, suggestive of redox conditions close to the reduced-S–SO_4^{2-} species predominance boundary, and shows that As correlates specifically with reduced S (cf. Fig. 1c).

Charge imbalance: For all analyses there are insufficient negative charges to balance the cation charge. The ratio of negative to positive charges varies between 0.82 and 0.91. It is likely that this imbalance is due to the presence of bicarbonate ions in solution. Taking the charge imbalance as due to bicarbonate it is possible to subtract this amount from the total CO_2 determined and hence estimate the distribution of carbonate species between CO_{2aq} and HCO_3^-. This calculation gives values for HCO_3^-/CO_{2aq} between 0.04 and 0.15 and CO_{2aq} is so predominant that uncertainty in the estimation of its concentration arising from the solubility of CO_2 in the aqueous phase of the inclusions, is negligible.

An interesting point is that on a molar basis (Table 4), Na is less than Cl in all samples. Thus the fluids are sodium (potassium) chloride-calcium bicarbonate dominated with an alkali bicarbonate component.

Interpretation

Geochemical modelling

The general validity of the fluid analyses has been further evaluated by carrying out speciation and mineral saturation state calculations for fluid LD888B at a temperature of 300 °C, using the EQ3NR code (Wolery, 1983), version 3245.1090. A silica content for the fluid (*c.* 500 ppm) was calculated assuming quartz saturation. This modelling is not fully quantitative because the natural pressure lies at higher values than the range over which the code is valid, and the fluids are extremely rich in CO_2. Nevertheless it illustrates a number of points about the fluid chemistry.

The extent to which the fluid appears to be supersaturated with mineral phases is highly dependent on the assumed pH. For relatively high values (*c.* 5.5, see below), a large number of

phases were calculated to be supersaturated, including many chlorite end-members and clays, as well as other Fe–Mg silicates, iron oxides, some sulphides and carbonates. For lower pH values, fewer phases were supersaturated, and for pH 3.8, the main supersaturated phases were pyrite, dolomite, siderite, witherite and baryte (saturation with quartz and muscovite specified). This is close to the observed mineralogy of the veins, apart from the Ba-phases, and indicates that the ore fluids were of relatively low pH, possibly below the optimal value for gold solubility (Seward, 1973), although the numbers from the modelling are not accurate. Another important feature of the speciated analysis is that the bulk of the Ca occurs in solution as a bicarbonate complex, while F is primarily present as AlF_3. This both explains why a fluid with such high levels of Ca and F can avoid precipitating fluorite, and also accounts for the levels of Al determined in the analyses. Calculated Al concentrations assuming the analysed levels of F and saturation with muscovite and quartz are around 150–200 ppm, and thus of the same order of magnitude as analytical values.

Variations in fluid chemistry

The most remarkable feature of the fluid compositions in these veins is their uniformity, rather than their variability. This indicates introduction of fluid from a single remote source. Nevertheless, minor differences are present between samples and these may have arisen for four possible reasons:

(1) Partitioning accompanying phase separation of the primary fluid into CO_2-rich vapour and aqueous liquid.
(2) Precipitation of solids from the fluid independent of wall rocks.
(3) Interactions of fluid with the wall rocks.
(4) Primary variability in the introduced ore fluid.

Partitioning due to phase separation is the likely cause of variations in $N_2:CO_2$ ratios (Diamond, 1990), since they have very different gas distribution coefficients (Giggenbach, 1980). Phase separation may also lead to precipitation of minerals from the aqueous liquid, because it disrupts both the redox and acidity of the fluid. Acid gasses such as CO_2, H_2S and HCl are partitioned into the vapour phase, as is H_2, leaving a liquid that is relatively alkaline and oxidised (cf. Drummond and Ohmoto, 1985). In time, interactions with the wall rock will restore equilibrium rock-buffered values of pH and f_{O_2}, but this process may be slow relative to precipi-

tation of solids from the liquid phase. However precipitation from the fluid without chemical interactions with the wall rocks may also come about through simple cooling and decrease in pressure along the flow path. Probably the best evidence for spontaneous crystallisation is the very low K : Na ratio of the fluid in sample LD872, which is about 1 log unit lower than would be expected from buffering by coexisting muscovite plus albite (Bowers *et al.*, 1984). This value could be explained by precipitation of muscovite, but not albite, from a solution that was initially supersaturated with both, e.g. due to drop in temperature. Further evidence that the fluids were close to saturation with specific phases, which may have been spontaneously precipitating from it, is the uniformly high reduced S contents but low chalcophile element concentrations, consistent with the presence of sulphides in the veins.

Some aspects of the fluid chemistry may also reflect wall-rock interactions, although there is no clear-cut correlation between fluid composition and host rock type. The variability in Li is difficult to explain by processes within the fluid phase alone, since it is not concentrated in any of the phases separated from the initial fluid. High Li values may therefore reflect leaching of specific host rocks. The very variable ratios between reduced and oxidised sulphur (Fig. 4) may also result from partial wall-rock buffering of the redox state of the fluid. It should be noted that all the samples studied here come from veins whose hosts are quartz-bearing metaigneous or metasedimentary rocks. The absence of gold from portions of veins hosted by carbonates or ultramafics (above) clearly demonstrates that wall-rock interactions influenced fluid chemistry, at least where the walls were sufficiently reactive. This is discussed further below.

Environment of ore formation

Two of the most important parameters controlling gold solubility are pH and f_{O_2} (Seward, 1973; Henley, 1984). The information about H_2S/SO_4^{2-} and HCO_3^-/CO_{2aq} ratios, presented above, although imprecise, gives some indication of the values of these parameters, even though it is obtained at room temperature. This is because the concentrations of both carbonate species are much greater than that of hydrogen ions, and the sulphur species concentrations are likewise much greater than that of dissolved oxygen or hydrogen. Hence changes in speciation after trapping, in the absence of any coexisting mineral phase other than quartz, can cause changes in pH or f_{O_2} during cooling, without significantly altering the

concentrations of the analysed or estimated sulphur and carbon species, and hence the calculated original pH or f_{O_2}.

pH: The log of the equilibrium constant for the first dissociation constant of carbonic acid, expressed as:

$$H_2O + CO_2 = HCO_3^- + H^+ \qquad (1)$$

varies from -7.0 at 250 °C to -7.5 at 300 °C, for a pressure of 1 kbar (Fein and Walther, 1987). If we assume ideal behaviour, then the ratio HCO_3^-/CO_{2aq} of 0.036 obtained for sample LD659 (Table 4), yields a value for pH of 5.8 at 270 °C, taking $\log K_1 = -7.2$. Performing a similar calculation for LD888B, which represents the other end of the range of carbonate molalities (Table 4) yields a very similar pH of 5.9. The effect of lower pressures will be to increase this value somewhat, while the non-ideal behaviour noted by Fein and Walther at the X_{CO_2} values relevant to these fluids is likely to compound the non-ideality of the bicarbonate ion and lower the pH value by around 0.75 log units. In view of the large uncertainties in both the estimate of HCO_3^- concentration (by difference) and the calculations, we estimate the pH of the ore fluid as 5.5 ± 0.75, and the results of the modelling (above) suggest that the true value was at the lower end of this range.

log f_{O_2}: At the sort of pH values indicated by the carbonate calculation, above, the predominant reduced S species will be H_2S. The equilibrium constant for the reaction:

$$H_2S + 2O_2 = 2H^+ + SO_4^{2-} \qquad (2)$$
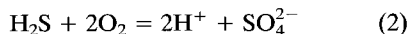
is given by Drummond (1981) for temperatures of 250 °C and 300 °C at pressures on the boiling curve, and has been used here. Assuming ideal behaviour and taking a pH value of 5.5 this data gives $\log f_{O_2} = -37$ at 270 °C. Non-ideality of sulphate is likely to reduce this value by around 1 log unit, and uncertainty in pH introduces further error. We therefore estimate log f_{O_2} as -36 ± 1.5. Most importantly, f_{O_2} was close to the sulphate/sulphide species predominance boundary.

Causes of gold transport and deposition

The importance of sulphide complexes as agents for gold transport at mesothermal temperatures is universally recognised (Seward, 1989). The H_2S concentrations in the Brusson fluids determined here are closely comparable to those reported from the Broadlands geothermal field (Seward, 1989; Table 1), or higher by up to a

factor of 4. Thus, despite the higher chloride content of these fluids, transport as sulphides is assumed to be dominant here also.

For the case of geothermal fluids, boiling has been widely cited as the cause of gold precipitation at ore grade concentrations (Drummond and Ohmoto, 1985; Reed and Spycher, 1985; Seward, 1989), while for many mesothermal deposits, including some gold ores closely comparable to the occurrences at Brusson, analogous processes involving unmixing of an immiscible carbonaceous fluid have been proposed (Roedder, 1971; Lyakhov and Popivnyak, 1978; Bottrell et al., 1988a, among others). At the earliest, highest P, T stage of vein formation at Brusson there were CO_2-bearing fluids present whose compositions were close to the H_2O-rich side of the solvus, and since the solubility of CO_2 in H_2O decreases to lower pressures under upper crustal conditions (Bowers and Helgeson, 1983), such fluids are obvious candidates for unmixing as they rise in the crust. Nevertheless, despite detailed fluid inclusion studies, Diamond (1990) found unequivocal evidence for fluid unmixing only at the final stages of vein formation, after much of the gold had been precipitated. Either, therefore, the fluid inclusion evidence is not telling us the full story about the evolution of fluids in the vein system, or some additional geochemical parameters must be considered that may have caused gold to precipitate.

It is certainly true that, where fluid immiscibility has been reported from fluid inclusion studies, one phase, normally the carbonaceous one, is much less commonly trapped than the water-rich phase. Nevertheless it seems unfortunate that no inclusions of a CO_2-rich phase were trapped during the main stage of vein formation, if such a fluid was present, although the possibility cannot be ruled out.

Of the alternative mechanisms for gold precipitation, Seward (1989) has demonstrated that simple cooling will not precipitate gold in sufficient amounts over a sufficiently narrow temperature interval to cause ore deposits. Two different circumstances apply here however. Firstly, the higher CO_2 content of these fluids relative to geothermal fluids means that changes in pH may have occurred during uplift and cooling that would further influence gold solubility. CO_{2aq} progressively dissociates to lower temperatures according to reaction 1, and by lowering pH this could destabilise $Au(HS)_2$-complexes (Seward, 1973), leading to gold precipitation. The pH estimates for the ore fluid (above) are below optimum values for gold solubility, and may reflect the fluid after gold had precipitated.

Nevertheless, it appears from the compilation of Fein and Walther (1987) that, when the effects of pressure are also considered, it is unlikely that there was a sufficiently large change in carbonate speciation during uprise of fluid.

Secondly, some at least of the drop in fluid pressure as the system evolved may be due to a change in fluid pressure at constant lithostatic pressure, rather than the result of progressive unroofing. If the drop in fluid pressure occurred over a short, structurally controlled, vertical interval, and narrow temperature range, then it could result in more localised precipitation of gold, even without separation of a CO_2-rich phase.

Wall-rock interactions can also lead to changes in fluid chemistry that influence gold precipitation (Bohlke, 1989; Diamond, 1990). This study is limited in so far as we have not investigated veins from the wall rock types which lack gold mineralisation. However the similarity of the fluid chemistry, irrespective of wall-rock, in all the veins studied, makes it unlikely that their fluid composition has been extensively influenced by wall-rock interactions, and accords well with the model for the Alleghany ores of Bohlke (1989). The results of this study contrast markedly with those of Banks et al. (1991) on fluids in low-T veins from Pyrenean thrusts, whose major element chemistry was strongly dependent on the nature of the immediate wall-rock. It is possible that the wall-rock control on gold grades was due to interactions specific to carbonate and ultramafic wall-rocks which served to suppress precipitation of gold in those hosts (Diamond, 1986).

In conclusion, although some evidence is consistent with separation of an immiscible CO_2-rich fluid during uprise as the cause of gold mineralisation, the lack of fluid inclusion evidence for immiscibility during the main stage of mineralisation means that this interpretation remains unproven.

Source of ore fluid: A major reason for the controversy regarding the origin of the ore fluids for mesothermal gold deposits is the difficulty in applying geochemical tracers to determine the origin of fluids derived from rock-dominated systems. The oxygen isotopic composition of the quartz in this type of vein is typically heavier than in epithermal deposits and comparable to values for metamorphic quartz (Kerrich, 1987). For the Monte Rosa district, Curti (1987) found vein quartz $\delta^{18}O$ values ranging from $+11.5$ to $+15.5\%$. Recently Diamond and Sharp (1991) have reported data on quartz from Brusson, obtained by laser fluorination, which indicate a similar range of values but show that the crystals

are not isotopically homogeneous and tend to be zoned to heavier rims.

These values define the vein fluid as 'metamorphic' only in the sense of fluid that has exchanged oxygen with minerals at modestly elevated temperatures, and not necessarily in the sense of fluid that has been liberated from mineral structures during metamorphic reactions. In rock-dominated systems such 'metamorphic' fluid compositions are common, even where the fluid is demonstrably not derived by metamorphic dehydration, as in deep sedimentary basins. Thus although the oxygen in the fluid was almost certainly exchanged with metamorphic rocks, this observation does not demonstrate the origin of the fluid itself. Rather, we can look on crustal fluids in low water : rock ratio settings as saturated solutions of the rocks that host them, continually evolving both chemically and isotopically as they interact with different hosts. An apt analogy is with the human body, individual atoms of which rapidly exchange with the environment while the body itself retains a distinct physical identity. An individual can modify his isotopic composition by moving between extremes of altitude and latitude without changing other aspects of his identity.

If we look on metamorphic fluids as forming discrete packets moving through space and time while exchanging matter with their wall rocks, then it follows that the 'source' of the fluid indicated by different geochemical tracers will depend on the effectiveness with which each tracer exchanges with the host rocks. Elements or isotopes that exchange readily because they are relatively abundant in the host rock will indicate a different source from tracers which are less ready to exchange, but in fact each tracer merely records a different stage along the flow path. It follows that to investigate the 'ultimate' source of the fluid it is necesary to study elements which occur at much higher concentrations in the fluid than in the rock. This is the rationale behind the use of hydrogen isotopes as fluid tracers, although even H can occur at significant concentrations in some minerals (>10 atom % in some phyllosilicates).

Values of δD measured or computed for the ore fluids have been cited in support of both main models for mesothermal gold–quartz veins. For example, Bohlke and Kistler (1986) and Goldfarb *et al.* (1991*a*) report examples with typical metamorphic values, distinct from local precipitation at the time of mineralisation, and cite this in favour of an origin from metamorphic fluid. However Nesbitt *et al.* (1989) reports relatively light δD values, indicative of meteoric input, in the Canadian cordillera (see however Keyser and

Kerrich, 1991). The bulk of the examples that have been described yield a fluid isotopic composition that is neither meteoric nor seawater, but corresponds to what may be termed metamorphic fluid. The compositions are in fact closely comparable to oil field and geothermal waters from the California Coast Range described by White *et al.* (1973), who ascribed them to interaction of fluid with minerals in an effectively closed system.

The ratios of the halogens Cl, Br, I (but not F) provide alternative conservative fluid parameters. Banks *et al.* (1991) showed that fluids of very different cation and isotopic composition from veins related to Alpine thrusting in the Pyrenees all had the similar Cl and Br contents and indistinguishable Br : Cl ratios, indicating a common origin.

Data from the Brusson veins are plotted in Fig. 5, together with results for other fluid provinces from the compilation of Bohlke and Irwin (1992) and our own results. It can be seen that the analyses all have a very similar Br : Cl ratio which is close to seawater and also to bulk Earth. I : Cl ratios are more variable, between seawater and bulk Earth. This pattern of variable I : Cl but uniform Br : Cl is similar to that found in some natural deep groundwaters (Fig. 5), where dissolution or precipitation of halite is not an important factor and tends to support a surface origin for the salinity in the ore fluids. There is however little reference data for halogen ratios in metamorphism, although Boness *et al.* (1991) reported enrichment in rock I with progressive metamorphism.

A magmatic source for the fluid is not supported by the halogen data presented here, which are distinct from the magmatic fluids compiled by Bohlke and Irwin (1992), or shown in Fig. 5 from our own data. In many comparable gold districts, a magmatic origin can be discounted on geological grounds, although in the Monte Rosa district there was some broadly contemporaneous magmatic activity (Diamond and Weidenbeck, 1986).

There are two possible types of metamorphic fluid model. Either metamorphism was continuing at depth and releasing fluid of constant composition (by implication over a prolonged period of time, controlled by the rate of heat supply: Yardley, 1977; Ridley and Thompson, 1985), or fluid was ponded at depth for periods of several million years before being released by tectonic changes (Goldfarb *et al.*, 1991*b*). The first model has been widely assumed in many studies, but has serious drawbacks.There is never any other evidence for the deep metamorphic event; the rate of fluid flow it would produce would be slow and prolonged whereas the veins
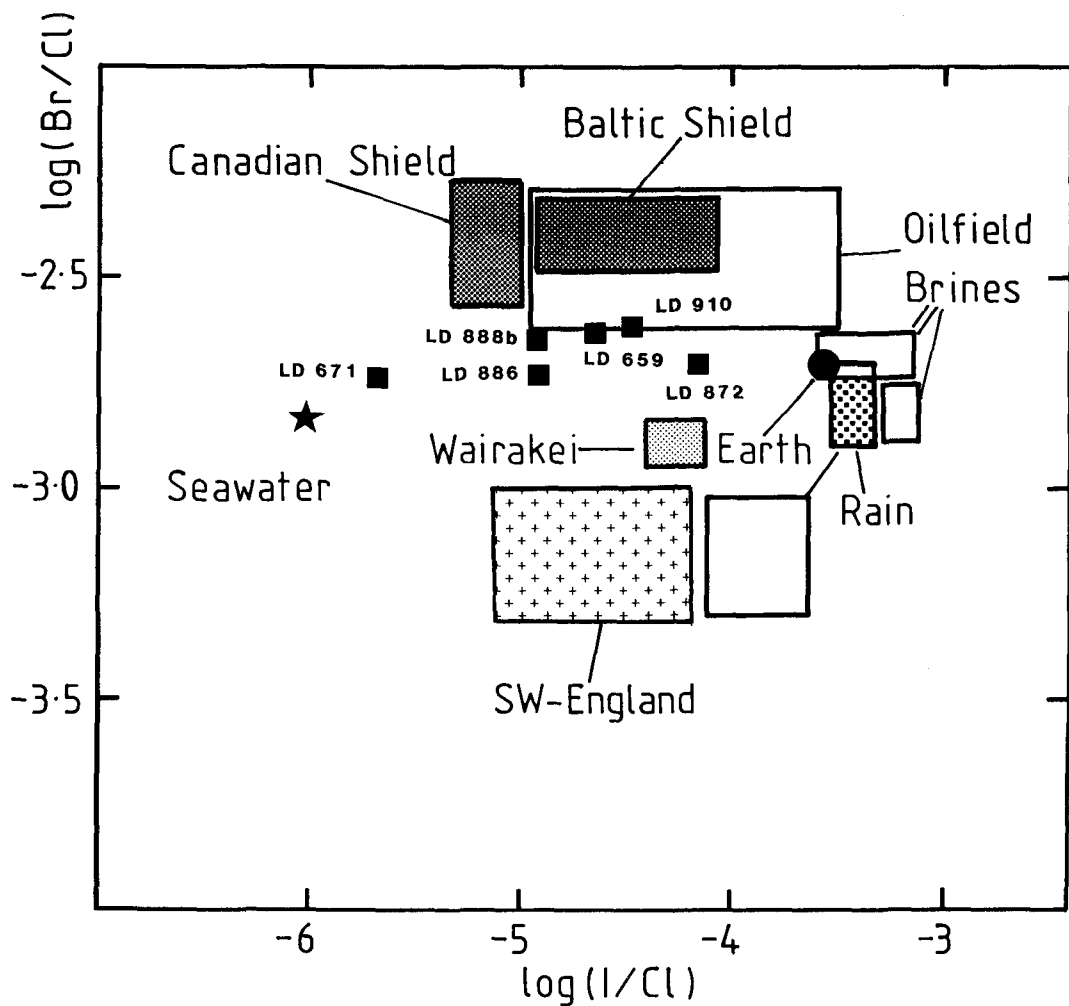
FIG. 5. Plot of halogen analyses for the Brusson fluid inclusions (squares), with halogen data from other crustal fluids for comparison. Seawater and various upper crustal fluids are plotted as fields taken from the compilation of Bohlke and Irwin (1992). The field of SW England fluids comprises unpublished fluid inclusion analyses from our laboratory and is taken as representative of ore fluids with a magmatic salt component. They compare closely with fumarole gas analyses (Bohlke and Irwin, 1992).

appear to form over a short time interval in a single event, something demonstrated quite dramatically for the Juneau veins by Goldfarb *et al.* (1991*b*); finally, a quite specific combination of lithology and P–T conditions would be required to produce fluid of the correct composition, and yet similar fluids are found in post-metamorphic gold–quartz veins from different metamorphic belts with quite different lithological mixes and metamorphic histories. Some, but not all, of these objections are avoided by Goldfarb *et al.*'s (1991*b*) model of deep ponding, but this requires metamorphic rocks to retain far higher levels of

porosity than any textural evidence has suggested, and must also explain why the ponded fluid was not absorbed by retrograde back-reactions (Yardly, 1981), especially since these would be comparable to the reactions that occur rapidly at similar temperatures in geothermal fields. Thus the region of fluid storage must have remained at peak metamorphic temperatures until the episode of veining, and fluid was released over a short time interval, rather than progressively escaping as it was generated.

In so far as the analysed halogen ratios lie close to the array of seawater to rainwater compo-

sitions, deep circulation of surface water or connate water is most obviously consistent with our results. This model requires pumping of such waters along transient cracks into the uprising crust to depths of 6–10 km and temperatures of 350–400 °C, with ore formation during focussed return to the surface (cf. Nesbitt *et al.*, 1989). It is only consistent with hydrogen isotope data available in some other deposits (e.g. Juneau) if the effective fluid : rock ratio of the system was extremely small, in order to permit hydrogen isotope exchange. Goldfarb *et al.* (1991*b*) estimate a water : rock ratio less than 0.01 to achieve the necessary degree of modification of an original meteoric fluid to accord with the ore fluid at Juneau. It is not clear that we have any grounds for deciding what constitutes a 'reasonable' value for fluid : rock ratio in such circumstances, although the results of White *et al.* (1973) demonstrate that it is possible for fluids to attain such an evolved composition.

Thus the present data confirms that the salt component of the fluid likely comes from a single source, and is consistent with an origin from surface waters, but does not preclude or confirm a metamorphic origin for want of a reference data base.

Conclusions

The present results confirm those of Diamond (1990) in emphasising the uniformity of the ore fluid, irrespective of host rock. The ore fluid was a dilute $Na(K,Ca)–Cl(HCO_3{}^-)$ fluid, probably of low pH and mildly reducing. It is clear that this fluid was externally derived, and was rising up through the crust at the time the gold–quartz veins formed. The uniform fluid suggest a single homogeneous source and/or phase equilibrium control. Possible sources are magmatic, surface-derived or metamorphic fluid reservoirs, while the most likely phase control is immiscibility between H_2O and CO_2-rich fluids. If immiscibility at depth controls the composition of the introduced fluid in the ore field, this implies that the immediate source of the fluid is at no very great depth, because the mutual solubility of CO_2 and H_2O is at a maximum at about 2 kbar, decreasing to higher, as well as lower pressures (Sterner and Bodnar, 1991). Thus very deep fluids ascending are unlikely to have compositions that are close to the solvus at the pressures of interest here.

Resolving the question of whether the ultimate origin of the ore fluid was metamorphic or near-surface, depends at present on balancing the improbability of metamorphic fluids being ponded at depth for several millions of years after

metamorphism, ready to be released by later extensional fracturing, against the improbability of deep penetrating surface or connate waters interacting with sufficient rock to change their hydrogen isotopic composition. Halogen data presented here support a surface water origin, but do not unequivocally preclude a metamorphic fluid source because the data base on halogens in metamorphism is inadequate.

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