Determination of uranium : carbon ratios in fluid inclusion decrepitates by inductively coupled plasma emission spectroscopy

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ABSTRACT. Uranium has been detected in fluid inclusion decrepitates from quartz of several granites of the British Isles and from vein quartz associated with the Hercynian granites of SW England using ICP. Material, ejected from the inclusions during decrepitation on heating the sample, is transferred into the plasma for qualitative analysis via a stream of argon. Several other elements have been detected in the decrepitate, of which carbon is of particular interest. It shows a strong positive correlation with U and indicates the importance of C (presumably as carbonate complexes) in the transport of U in hydrothermal systems. Approximate order of magnitude estimates of the average U contents of fluid inclusions from the SW England samples, based on the assumption that U in the decrepitates is principally derived from the fluid inclusions, range from less than one to over a thousand ppm. Fluid inclusions may therefore be important in contributing to the levels of U reported in quartz (0.1 to 10 ppm).

INDUCTIVELY coupled plasma emission spectroscopy (ICP) is a powerful and sensitive technique for obtaining multi-element data on the composition of fluid inclusions. A large number of trace and minor elements have been detected in the inclusion fluids using the ICP-linked decrepitation technique outlined in a previous paper (Thompson et al., 1980) and now in regular use for this purpose at Imperial College. These include most of the major ore metals and a number of trace elements previously unreported in conventional fluid inclusion analysis.

In view of the current interest in the distribution of U in British granites (Simpson et al., 1979) we carried out a special study to determine whether

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U could also be detected in fluid inclusions. For this purpose we used an ICP specially equipped with a uranium line at the Applied Research Laboratories Ltd., Luton, UK.

A significant U response was recorded on the instrument for many test samples during decrepitation. The main object of this paper is therefore to show that this response could be attributed to U contained in fluid inclusions. Semiquantitative (order of magnitude) estimates of the U contents of the fluids are given and the positive correlation between U and C in the decrepitates is discussed in the light of current ideas on the transport of U in hydrothermal systems.

We believe that this is the first reported analysis of U in fluid inclusions. The method is rapid and cheap to use and it may have potential in the field of geochemical exploration for U.

Samples studied

Twenty-eight granites from various localities in the British Isles, three uraniferous quartz veins, and three Sn–W–Cu mineralized quartz veins from SW England were studied (Table I). For ICP analysis, pure, graded, quartz concentrates ($\sim$ 0.3 to 0.5 g; 0.5 to 2 mm in size) were carefully hand-picked under a binocular microscope to avoid mixed grains or those containing solid inclusions of feldspar, mica, tourmaline, and other accessory minerals, since even a small amount released into the plasma as fine (less than 10 μm) particles would give spurious results. The quartz concentrates were cleaned with phosphoric acid and allowed to stand overnight in warm concentrated HNO_3 and finally rinsed several times with distilled, deionized water.

Phosphoric acid is a potential source of phosphorus contamination in the decrepitates, but this has proven to be minimal.

Fluid inclusion populations in quartz

Granites. The main fluid inclusion characteristics of each sample are summarized in Table I. A limited number of heating and freezing stage measurements on our samples was carried out. These show a wide range of homogenization temperatures and salinities ($T_H = < 70\,°C$ to $> 560\,°C$, salinity 0 to 50% wt. % equiv. NaCl). CO_2-clathrate has been observed only in two samples from SW England (Goonbarrow, Hemerdon). Insufficient data are available to determine whether CO_2-clathrates are common in granites elsewhere. Several generations of fluid inclusions with differing compositions and thermocryometric properties are usually present in the same sample. It is almost impossible to classify these generations according to origin and establish an unequivocable paragenesis. Instead they are classified into five types according to the volumetric proportions of liquid and vapour and whether they contain halite or CO_2 liquid. The relative proportions of each type are summarized in Table I.

Sn–W–Cu *vein quartz (SW6a, SW13a, D67).* The inclusion populations in the vein quartz samples are less complex than those in the granites (Table I). Two-phase, gas–liquid inclusions dominate, with

TABLE I. Samples studied and summary of their fluid inclusion characteristics

Sample Ref.No.	Locality	Grid Reference	Sample Type	Fluid Inclusion Abundance	Relative Proportions of Different Inclusion Types (%)				
					I	II	III	IV	V
LE1	Penberth Cove	SW403227	GU	M	40	20	15	25	0
LE3	Bostraze Pit	SW384317	GK	H	35	30	15	20	0
LE4	Nr. Morvah	SW412362	GU	H	15	40	5	40	0
LE13	Geevor Mine	SW373347	GU	M	30	25	30	15	0
LE15	Wheal Edward	SW362328	GU	H	20	30	10	40	0
LE17	Wheal Edward	SW362328	GG*	H	35	30	5	30	0
LE18	Wheal Trenwith	SW514400	GU	H	20	40	30	10	0
C1	South Crofty	SW669410	GU	M	10	60	0	30	0
C4	Carn Bren	SW685408	GU	M	5	70	tr	25	0
C5	Carnmenellis	SW696363	GU	M	10	70	tr	20	0
C8	Holmans Quarry	SW656366	GU	M	10	50	0	40	0
SA5	Trelavour Downs	SW960573	GK	H	30	35	10	25	0
SA8	Helman Tor	SX062616	GU	M	30	50	tr	20	0
SA22	Goonbarrow Pit	SX007583	GK	H	40	40	5	15	tr
BM12	Nr. Bolventor	SX178758	GU	L	10	50	0	40	0
D22	Dartmeet	SX672732	GU	H	15	25	30	30	0
SW9	Cligga Head	SW738537	GU	M	5	70	0	25	0
SW10	St. Michael's Mt.	SW515298	GU	M	10	70	5	15	0
SC1	Cairngorm	NH980040	GU	M	25	65	tr	10	0
SC2	Peterhead	Not known	GU	H	60	20	0	10	10
SC3	Ross of Mull	Not known	GU	M	80	10	0	5	5
SC4	Ruthrie	Not known	GU	M	10	65	0	25	tr
SC5	Helmsdale	ND040170	GU	M	40	40	0	10	10
SC6	Nr. Greenburn (R.N.Esk)	Not known	GG	M	25	70	0	5	tr
SC7	Glen Nevis	Not known	GU	M	35	35	0	30	tr
IRL1	Turlough Hill	Not known	GP	M	15	70	0	15	0
LA1	Shap	NY556084	GU	M	20	70	0	10	tr
IM1	Foxdale Quarry	SC285774	GU	H	55	40	0	5	0
SA31	Sth Terras Mine	SW936522	V*	L	100	tr	0	tr	0
SA32	Sth Terras Mine	SW936522	V*	L	100	tr	0	tr	0
LE14	Wheal Edward	SW362328	V*	L	100	tr	0	tr	0
SW6a	Cligga Head	SW738537	V	H	15	75	0	10	0
SW13a	Kit Hill	SX375716	V	H	10	85	tr	5	tr
D67	Hemerden	SX574584	V	H	10	45	tr	45	tr

Locality Abbreviations

LE	=	Lands End
C	=	Carnmenellis
SA	=	St. Austell
BM	=	Bodmin
D	=	Dartmoor
SW	=	SW England
SC	=	Scotland
IRL	=	Ireland
LA	=	Lake District
IM	=	Isle of Man

(tr = trace)

Sample Type Abbreviations

GP	=	Granite, Pegmatite
GU	=	Granite, 'unaltered'
GK	=	Granite, Kaolinised
GG	=	Granite. Greisenised
V	=	Vein, Sn (W–Cu)
*	=	Uranium-bearing

Fluid Inclusion Abundance

H	=	High
M	=	Moderate
L	=	Low

Inclusion Types

I = Low temperature aqueous inclusions. Either monophase or with only a small vapour bubble (less than 10% by volume).

II = Medium to High temperature aqueous inclusions. Vapour occupies between 10% and 60% by volume.

III = Halite-bearing inclusions.

IV = Gas-rich inclusions. Vapour occupies 60% to 100% by volume.

V = CO_2-liquid-bearing inclusions.

a limited salinity range (generally 5 to 15 wt. % NaCl equivs.) but a wider homogenization temperature range (up to a maximum of about 480 °C). Occasional halite-bearing inclusions were recognized in two samples and vapour-rich inclusions in all three (Table I). Detailed fluid inclusion studies at Cligga Head and Hemerdon are described elsewhere (Jackson et al., 1977; Charoy, 1979; Jackson, 1976).

U-*bearing vein quartz (SA31, SA32, LE14)*. There are no previous descriptions of fluid inclusions from uraniferous veins of SW England, and investigations are hampered by the extremely small size of the inclusions (generally less than a few μm). They occur in subparallel planes, often so abundant that the quartz has a striped appearance at high magnification.

In all three samples monophase aqueous inclusions dominate. Some inclusions contain small vapour bubbles which homogenize to liquid at temperatures less than 180 °C (type I in our classification). Rarely, inclusions with a larger proportion of vapour were noted which could be due to leakage of type I inclusions although their precise origin is uncertain.

The small size and irregular shape of the inclusions makes the interpretation of freezing-stage data difficult and often ambiguous. Several indistinct phase changes were commonly observed. Most inclusions showed melting phenomena close to 0 °C. If this is ice it would indicate that the fluids were generally dilute (less than 2 wt.% NaCl equiv.). Additional phase changes were tentatively observed at temperatures between about 0 and +15 °C in a few inclusions. It is possible that this

is the dissocation of small amounts of the CO_2–clathrate (Roedder, 1963). No CO_2 liquid was observed, however, either at room temperature or on cooling, but crushing-stage studies confirmed the presence of gas under pressure in many inclusions. This could be CO_2 or other compressed gases such as low-order hydrocarbons and even H_2 and O_2.

The highest evolution of gas bubbles on crushing was observed in sample LE14 from Wheal Edward mine which contained the highest concentration of pitchblende of all three samples. This result is in accordance with the crushing-stage studies on quartz from U deposits of the Massif Central (Poty et al., 1974a), where a correlation was found between the amount of gas evolved on crushing and the uranium grade in the host rock sampled.

Thus freezing-state data on the composition of these small inclusions are inconclusive and much higher salinities than 2 wt. % NaCl would be indicated if phase changes close to 0 °C are due to NaCl–hydrate dissociation and not ice or gas-clathrate melting.

ICP analysis of decrepitates

In the ICP decrepitation-linked method (Thompson et al., 1980) material is released from the inclusions during sudden decrepitation caused by rapid heating of the sample. The sample is contained within a closed pyrex tube, and heat (up to 600 °C) is supplied to the specimen using a small gas burner (fig. 1). The resulting decrepitates are transferred to the plasma via a stream of argon. Integration is carried out at the onset of visible decrepitation, usually before red-heat, and terminated after 20 seconds, usually before visible decrepitation has ceased. The intensity of decrepitation varied from sample to sample partly as a function of the number of inclusions per unit volume, but also depending on several other variables such as the size, shape, composition, homogenization temperature, and distribution of the inclusions. The most intense visible decrepitation generally occurred in granite quartz from SW England, although one or two samples from elsewhere also showed considerable decrepitation.

The ICP results are not specific to any particular generation of inclusions. Sequential decrepitation caused by carefully controlled ramp-heating was considered but experimental design problems are substantial and there is no guarantee that different generations of inclusions will decrepitate at different temperatures.

The instrument used was an ARL 34000 model capable of simultaneous analysis of up to 42 elements including U. Absolute detection limits
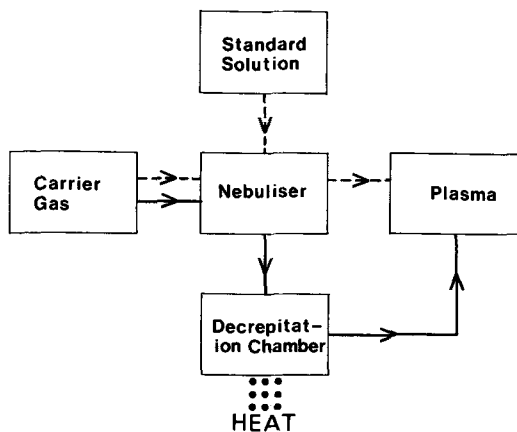

FIG. 1. Flow-chart for ICP-linked decrepitation analysis. Dashed line represents pathway for standard, full line represents pathway for decrepitates.

TABLE II. *Sensitivities determined from conventional nebulization of standard aqueous solutions relative to the least sensitive element, carbon*

Element	C	K	P	U	Si	Na	Al	Ti	Ca	S	Fe	Zr
Sensitivity (increasing)	1	5.6	6.7	10.0	12.8	16.5	32.8	53.0	288.8	298.8	373	414

range from about 5×10^{-13} g to 10^{-9} g. U is amongst the least-sensitive elements (Table II) with an absolute detection limit of about 8×10^{-10} g for its best line used here at 385.96 nm.

In conventional ICP analysis the test solution (standard or sample) is nebulized into the plasma. An effective calibration procedure under conditions simulating decrepitation of inclusions has not yet been achieved, and sensitivity ratios observed in nebulization studies are therefore assumed to apply to decrepitated material (Thompson *et al.*, 1980).

There are several mechanisms whereby material is released into the argon carrier gas and transferred to the plasma during decrepitation. The flow rate of the gas is controlled to restrict the size of particles that can be supported to less than 10 μm. It is presumed (Thompson *et al.*, 1980) that much of the material released during decrepitation is derived from the inclusion fluids.

Inclusion fluid containing dissolved components and any free-moving daughter minerals may be ejected into the gas flowing through the system. This 'spray' will condense to small clots of solute (less than 10 μm) and will be transferred to the plasma. Material can also distil from opened inclusions if the quartz fractures without violent decrepitation. This mechanism is important in transferring the more volatile components of fluid inclusions into the plasma.

Fragments of host mineral less than 10 μm may also be evolved during decrepitation and the relatively high values for Si in the decrepitates (Table III) suggest that this process takes place although it is considered to be of minor importance for other major elements. Assuming that all the Si is from quartz, it is calculated that Si contributes less than 50% to the total mass of decrepitate.

Trace element data for the decrepitates must also be interpreted with care. Even small amounts of metal sulphides, oxides, silicates introduced into the plasma, either as discrete particles or, for volatile materials, by distillation could affect the results significantly. With a few exceptions, however, the results for U indicate that it is mainly derived from fluid inclusions.

General results

Because of the sensitivity of the ICP method a large number of elements (up to 40 in some samples) have been detected in the decrepitates.

Only decrepitate data for U, the major elements (Na, K, Ca, Fe, S, C), and elements indicative of contamination by mineral particles are tabulated here (Table III). Si which is presumed to be derived mostly from the quartz host, and Al which is indicative of the level of contamination by the aluminosilicates, feldspars, micas, and tourmaline are included.

TABLE III. *Relative element concentrations in decrepitates (weight units) evolved from quartz standardized to one gramme*

Sample	Na	K	Ca	Fe	S	Al	P	Ti	C	U	Si
•LE 1	576	136	65	20·7	2·3	16·4	1·1	0·9	1180	0·87	808
LE 3	202	43	4	6·8	1·2	3·5	1·4	•	819	—	119
LE 4	80	39	3	1·5	3·6	1·C	0·9	•	912	0·63	52
LE 13	306	74	26	4·2	63·9	0·9	54·2	•	303	—	72
LE 15	322	66	36	3·5	9·5	2·2	3·8	0·1	728	—	158
LE 17	37	8	3	2·9	36·2	1·8	0·9	0·5	477	—	101
LE 18	252	33	9	2·7	3·1	0·3	1·2	—	624	—	21
C 1	87	17	3	0·8	3·6	1·2	1·2	0·1	1560	2·26	94
C 4	24	2	2	0·3	23·5	0·5	95·8	•	489	—	44
C 5	27	2	117	0·3	5·1	0·7	66·2	•	1075	1·03	31
C 8	160	31	4	0·8	3·7	2·2	1·1	0·1	1294	0·70	97
SA 5	84	19	4	4·8	31·5	8·8	4·1	•	667	0·36	82
SA 8	57	9	3	0·7	6·9	1·9	1·2	•	1576	1·96	75
•SA 22	136	55	37	26·9	14·4	21·8	2·6	0·4	1540	1·86	568
BM 12	87	19	10	5·3	0·7	2·5	0·3	•	668	0·25	123
D 22	84	20	15	13·3	20·4	1·1	3·2	•	1417	1·83	73
SW 9	18	2	1	0·6	4·2	0·9	0·3	—	1437	1·08	38
SW 10	47	10	1	0·2	0·8	0·4	0·4	—	762	0·28	28
SC 1	1	•	•	•	28·7	0·1	23·5	—	512	0·81	4
SC 2	13	2	1	0·4	6·7	0·3	1·9	•	241	—	24
SC 3	27	1	1	•	6·8	—	1·0	—	384	0·42	7
SC 4	10	2	1	•	3·8	0·2	0·7	•	453	0·67	6
•SC 5	56	6	3	1·9	27·9	0·8	2·6	•	1343	1·60	44
SC 6	71	13	1	0·9	3·5	1·8	1·7	0·1	761	4·92	61
SC 7	26	5	•	0·1	3·2	0·1	0·5	—	778	0·54	17
IRL 1	25	5	•	•	16·5	—	1·2	—	420	—	10
LA 1	42	8	1	0·3	2·6	0·6	0·1	0·1	590	—	41
IM 1	99	17	1	0·1	1·9	0·2	—	—	417	—	12
SA 31	458	72	7	10·0	8·9	2·2	1·9	0·1	893	0·64	130
•SA 32	368	360	1	0·2	3·7	0·7	1·3	0·1	131	3·74	4
LE 14	72	13	2	•	3·9	—	1·0	—	1142	1·79	3
SW 6	94	28	37	80·4	10·7	14·0	5·2	0·5	551	1·49	2955
SW 13	36	10	50	33·1	9·3	7·1	3·1	0·3	520	0·76	1053
D 67	48	25	7	13·7	3·5	3·8	2·0	•	410	0·30	528

•   trace   < 0·1
•   Zr detected   < 0·2
—   not detected

Traces of U can occur in such accessory minerals as apatite, monazite, rutile, sphene, ilmenite, and zircon and the indicator elements P, Ti, and Zr are tabulated.

In the majority of decrepitates the most abundant elements are Na, K, Ca, Fe, C, and S. The high Na, K, Ca, and S (presumably as sulphate) are consistent with published data on the major element chemistry of fluid inclusions by analysis of leachates (Roedder, 1972; Poty et al., 1974b). Cl and Mg are also major constituents of fluid inclusion leachates but were not determined during the present study while Fe and C are important constituents in the decrepitates although they are not always reported in conventional leachate studies. In fluid inclusions C can occur either as volatile components (e.g. CO_2, CH_4, and other hydrocarbons) or as carbonates and bicarbonates. The contribution of C could be from more than one of these sources, but the high levels recorded compared to the major cations suggest that it is preferentially transferred to the plasma.

The generally low levels of Al and its lack of correlation with the major cations (Na, K, Ca, Fe) show that these elements are derived mainly from inclusion fluids rather than from admixed contaminants such as feldspar and mica. Apatite could contribute to the Ca values but this appears to be the case only for sample C5 where high Ca and P contents were reported.

Generally high values for major elements were obtained for samples that showed the most marked decrepitation (SW England samples), presumably because more material is released into the plasma. It is apparent from the salinity estimates from freezing-point depressions, however, that the element concentrations in the inclusions also vary. It is difficult to determine which of these two factors is more important in producing high element concentrations in the decrepitates. There appears to be no correlation between the abundance of inclusions (Table I) and the amount of material in the decrepitate.

U levels in the decrepitates. A U signal was detected in twenty-four samples. The relative concentrations were low, but varied by more than an order of magnitude. At such low levels the signal may be due to interference.

In conventional ICP analysis of solutions there are several sources of interference, including spectral line overlap and background changes due to scattered light and other causes. In decrepitation work there are further possibilities; (a) continuum radiation from particles of host mineral (quartz mostly), and (b) momentary changes in base-line radiation due to small shock-waves from decrepitation. The likely effects of all these possible interferences on the results are considered.

There is no known line-overlap of significance on the U line at 385.96 nm but a slight background shift due to C occurs. Fig. 2 shows the raw signals for U and C for all our samples and the maximum levels of interference from C. The magnitude of this shift is insufficient to account for observed U signals when considered in relation to the C response, indicating that the correlation is real.

The possibility of interference from incandescent quartz particles has been studied by introducing large amounts of powdered optical quartz into the plasma carrier-gas. The Si response produced was considerably larger ($\times 10$) than any signal produced by decrepitation although no signal was observed for any other element.

Although the intensity of decrepitation varied between samples there was no correlation with the U response indicating that background changes due to shock-waves do not account for the U response.

The U signal is therefore considered to be due to U introduced into the plasma during decrepitation.

Rogers and Adams (1969) have reviewed published data on U levels in quartz (0.1 to 10 ppm) and its mode of occurrence. It is generally thought to be present in discrete U-bearing mineral phases as solid inclusions, or as coatings on grain boundaries and microfractures. Another possibility cited, although unlikely, is isomorphous substitution in the quartz lattice. Few authors have considered fluid inclusions as a significant source of U in quartz.

Levels of P, Ti, and Zr are low and show no correlation with U, indicating that U-bearing accessory minerals do not make a significant
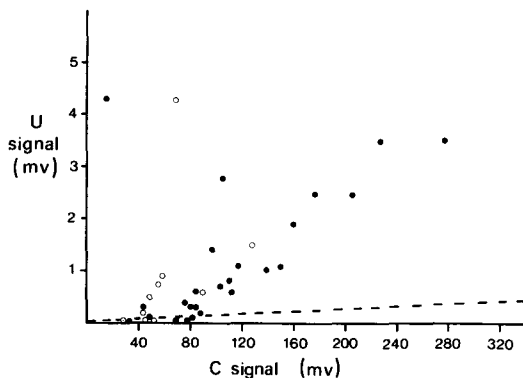

Fig. 2. U and C responses in the decrepitates. Dashed line represents maximum possible interference of U signal by carbon (estimates from a 10% sucrose solution). Full circles, SW England samples; open circles, samples outside SW England.

contribution to the U levels in the decrepitates. Uraninite or pitchblende are more likely contaminants. There are no indicator elements with which to assess this. However, if uraninite admixed with quartz were introduced into the plasma, correlation between U and Si might be expected. The correlation coefficient for all samples is less than 0.1.

The only element to show any significant correlation (at the 95% level) with U is C, with a correlation coefficient of 0.34. This correlation is represented graphically in fig. 2 and suggests that for most samples (except SC6 and SA32) U is principally associated with C in some form. The consistent presence in quartz of admixed rutherfordine (a rare uranium carbonate) and uraninite intimately associated with either carbonaceous matter (Ball and Basham, 1979) or carbonates could account for this correlation, but is considered unlikely. We therefore conclude that, with a few exceptions (discussed below), the U is principally derived from abundant fluid inclusions and that it is associated with C in these fluids.

U *in fluid inclusions*. The magnitude of the U response in the decrepitates, if it is due to fluid inclusions, depends on three main factors: (*a*) the levels of U in the inclusions, (*b*) the number and size of inclusions opened during decrepitation, and (*c*) the efficiency of transfer of U from opened inclusions into the plasma (assumed to be uniform for all samples studied).

The ICP-linked decrepitation method was originally developed as a qualitative technique for fluid inclusion analysis. Element ratios in the decrepitates are unlikely to be identical to those in the inclusions because of possible fractionation or preferential volatilization of certain components. In particular, the U:C ratios in the decrepitates are probably much lower in the decrepitates because of preferential release of gaseous carbon compounds (CO_2, CH_4, etc.) from opened inclusions or pyrolitic decomposition of hydrocarbons and carbonates. For the major cations, Na, K, Ca, and Fe, the relative concentrations in the decrepitates are in general agreement with *expected* element abundances in most fluid inclusions based on our own observations and those in Roedder (1972). The K:Na atomic ratios for all but one of the SW England samples (SA32) are within the range expected for fluids in equilibrium with two feldspar granites at temperatures between 250 and 700 °C (Lagache and Weisbrod, 1977). For samples from elsewhere the average K:Na ratios are lower particularly for those samples where the response for Na and K was low due to poor decrepitation. If it is assumed: (1) that the relative concentrations of U and the major cations in the decrepitates *approximate* to their relative concentrations in the inclusions and (2) that the major cations are present principally as chlorides, an approximate 'order of magnitude' estimate of the average U content of the fluids can be made. The molar proportions of NaCl, KCl, $CaCl_2$, $FeCl_2$, or $FeCl_3$ can be calculated from salinity determinations and element ratios in the decrepitates. This fixes the molar proportion of Na in the fluid. Knowing this, and the U:Na ratio in the decrepitate, the U content of the inclusions can be calculated.

Most samples contain several generations of fluids with differing salinities. An average salinity for these samples is assumed and, taking a figure of 10 wt. % NaCl for all SW England samples, the calculated levels of U in the inclusions range from 0 to about 2000 ppm (mean granites = 350 ppm; mean Sn–W–Cu veins = 223 ppm, mean U-bearing veins = 390 ppm). Assuming the same salinity for samples outside SW England the calculated levels (with the exception of SC1) range from 0 to about 2500 ppm. In the case of SC1, an exceptionally high value was obtained, thought to be due to contamination by a U–P phase.

Three points are emphasized in considering how meaningful these estimates are. Firstly, the calculated levels of U are not specific to any particular generation of fluids in a given sample: they represent only an estimate of the average U content of that portion of the fluid inclusion assemblage which has decrepitated. Secondly, if the assumed salinity estimate is inaccurate by a factor of 2, the calculated concentrations would change by approximately the same amount. Finally, the estimates are only approximate 'order of magnitude' values based on imprecise data and broad assumptions; they were made primarily to test whether U in the decrepitates is principally derived from fluid inclusions.

In spite of the limitations of the method the average 'order of magnitude' estimates for SW England samples may be reasonable. Rich *et al.* (1979) indicate that U-enriched fluids are likely to contain between 0.1 and 500 ppm U. These and the estimates given here are 10^3 to 10^5 times greater than those in average surface and ground waters (op. cit.) but may be attained in high-temperature fluids under the right physico-chemical conditions. Unfortunately, adequate published experimental data on the solubility of U at elevated T and P in fluids of different compositions are lacking.

Attempts to confirm the estimates of high levels in the inclusions by simple autoradiography and ultraviolet fluorescence microscopy have been unsuccessful, but Yeliseyeva (1977), reporting on the occurrence of U in apatite from granite rocks of the USSR, used autoradiography to identify the

abundant fluid inclusions in apatite as an important source of U in this mineral.

Fluid inclusions usually comprise 0.1 to about 1% of the volume of quartz from SW England, these values reaching several per cent in some cases (Sorby, 1858). If the mean U content of fluid inclusions in quartz was approximately 300 ppm, they would contribute on average between 0.1 and a few ppm U to the over-all levels of U in quartz. This is not an unreasonable quantity considering the general levels of U from various sources (0.1 to 10 ppm) previously determined in granitic quartz (summarized by Rogers and Adams, 1969, and Cuney, 1978) and the data reported here, using conventional ICP analysis, of the U content of pure vein quartz from Cligga (3.3 ppm U) and Kit Hill (0.3 ppm).

The U:C correlation. It has been argued that U in fluid inclusions accounts for the U levels in the decrepitates so that the correlation of U with C suggests that the latter is also derived from the fluids. Calculations show that the C levels in the decrepitates are up to $80 \times$ higher than Na and such high levels are unlikely in the fluid inclusions because of the absence of significant quantities of compressed gases, such as CO_2 and CH_4, and identifiable carbonate daughter minerals. Preferential release of volatile carbon species from fluid inclusions provides one possible explanation for the enhanced levels of C. This could be achieved if many inclusions are gently ruptured rather than violently exploded on heating; it is not known how closely the U:C ratios in the decrepitates reflect their true ratios in the fluids.

The common occurrence of CO_2-bearing inclusions in minerals from hydrothermal U deposits, together with published experimental studies on the solubility of U in carbonate solutions at high temperatures, has led many authors to suggest that U is transported in hydrothermal systems mainly as carbonate complexes (Naumov, 1959; Poty *et al.*, 1974a; Rich *et al.*, 1977; Cuney, 1978; Leroy, 1978; Ypma and Fuzikawa, 1980). The U:C correlation supports this view.

Na is the dominant cation in most fluid inclusions. The average salinity of the inclusions may vary but the levels of Na provide a rough measure of the quantity of fluid released during decrepitation (assuming little or no contamination from admixed feldspars). Ratioing to Na will therefore remove the effects of variable decrepitation. For SW England samples a more marked correlation than that for U:C is observed if U/Na is plotted against C/Na (fig. 3). The correlation coefficient increases from 0.36 to 0.87 providing additional evidence that U and C are primarily derived from, and in some way associated in, the fluid. This is not so apparent for samples from elsewhere.

Consider one generation of fluid inclusions, present in all SW England samples, with a fixed U:C:Na ratio; as decrepitation rates vary so would levels of U, C, and Na in the decrepitates. A plot of U against C would give a good correlation but U and C, ratioed against Na, would plot as a single point or cluster of points. This is not the case. It is more reasonable to suppose that a number of different generations of fluid inclusions (with varying salinities) would contribute to the decrepitates. The only way to account for the good correlation between U/Na and C/Na is, therefore, to invoke a more or less fixed U:C ratio for the different fluids.

Granites other than those of SW England are represented by single samples from widely varying geographical areas and geological environments and cannot be treated as a single group. Individual samples fall on the SW England plot (fig. 3) which may be significant, but it is not possible to assess whether similar trends to those of SW England apply in these areas.

Conclusions

Levels of U in quartz decrepitates primarily reflect U in fluid inclusions. An estimate of the average U content of the fluids (about 200–300 ppm) is based on several broad assumptions and should be regarded only as a preliminary 'order of magnitude' value. Calculations show that such levels of U in fluids would make a substantial contribution to the over-all U content of quartz although contribution from such additional sources of U as solid inclusions of uranium-bearing phases cannot be ruled out.
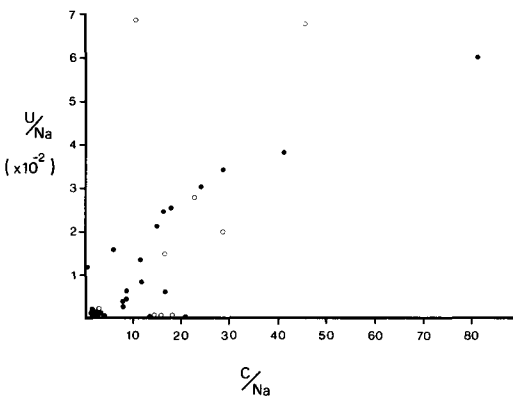

FIG. 3. U/Na against C/Na plot for decrepitates (SC1 plots off scale, indicative of contamination). Full circles, SW England samples: open circles, samples outside SW England.

The correlation between U and C in the decrepitates can be accounted for by an association between these two elements in the fluid inclusions, probably indicating the importance of uranium-carbonate complexes in the transport of U in hydrothermal systems.

The ICP-linked decrepitation method has potential as a method for analysing U in fluid inclusions. It is rapid and sensitive and, if results reported here can be confirmed, it may eventually provide a routine method of geochemical exploration for U since fluid inclusions provide the most direct sampling medium for assessing whether metal-rich and therefore potentially ore-forming fluids have been active in and around a granite intrusion.

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