The release of trace elements and volatiles from crinoidal limestone during thermal decrepitation

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Abstract

A suite of coarsely crystalline samples of crinoidal limestone adjacent to a PbS–CaF_2–$CaCO_3$ vein in the North Pennine orefield (Greenhow Rake) was analysed by three independent methods [Inductively Coupled Plasma emission spectroscopy (ICP), Mass Spectrometry (MS) and Gas Chromatography (GC)], in order to determine the nature and origin of trace elements and volatiles released on heating and thermal decrepitation, to establish whether fluid inclusions from the host limestone differed in composition from those within the vein, and to assess the value of the results obtained for mineral exploration. The ICP method gave reproducible results for Ca, Na and K, and significant values for Pb and Zn. Na and K correlate with H_2O levels determined by MS/volumetric analysis, suggesting their coexistence within fluid inclusions. No such correlation was found for Pb and Zn, suggesting that these elements were derived by volatilisation, perhaps from traces of galena and sphalerite. Methane showed no correlation with H_2O and a source other than aqueous fluid inclusions is thought probable for this volatile.

The vein calcite showed much lower K/Na fluid ratios (0.05 cf 0.1–0.2), than the limestones. The limestone-hosted fluids occur predominantly in crinoid ossicles and are believed to represent early pre-mineralisation fluids, unrelated to those associated with veining. Combined ICP and MS techniques may be of value in investigating samples where fluid inclusions are too small for microthermometric and optical analysis.

KEYWORDS: limestone, crinodal, thermal decrepitation, inductively coupled plasma emission spectroscopy, mass spectrometry, gas chromatography.

Introduction

A vast amount of fluid inclusion data now exists for the mineral veins of the North Pennine orefield (Sawkins, 1966; Greenwood and Smith, 1977; Rogers, 1978; Small, 1978). Homogenisation temperatures typically cluster around 100–150 °C with salinities varying between about 16 and 24 weight percent NaCl equivalents. In the light of these data Dunham and Wilson (1985) favour a basinal brine model for the development and evolution of mineralizing fluids in the district, noting particularly the similarity between oilfield brines and inclusion fluids. Fluid inclusion evidence on the nature and composition of ancient diagenetic fluids in and around the North Pennine orefield is notably lacking. This is not altogether surprising in view of the extremely small size and poor development of fluid inclusions in sedimentary carbonate rocks (Burruss, 1981), conventio-

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nal thermometric and optical examination usually being out of the question.

In this paper we investigate the possibility of applying three modern instrumental methods to the analysis of microscopic and submicroscopic fluid inclusions in a suite of coarse crinoidal limestones adjacent to one of the major PbS–CaF_2–$CaCO_3$–$BaSO_4$ veins in the southern part of the orefield (Greenhow Rake). All three methods involve release of volatile and trace components from the rock on heating. Inductively-coupled plasma emission spectroscopy (ICP) is particularly appropriate with its multielement capability and high sensitivity for analysing minor and trace metals in inclusion fluids. The so-called ICP-decrepitation linked technique (Thompson *et al.*, 1980; Alderton *et al.*, 1982) has already been applied to the analysis of fluid inclusions in hydrothermal veins and igneous rocks (Rankin *et al.*, 1982) but this is the first time it has been applied to sediments. Mass spectrometry combined with volumetric analysis (MS) and gas chromatography are well-tried and tested techniques (Shepherd *et al.*, 1985) for fluid inclusion analysis. They have been used here to determine the volatile components, H_2O, CH_4, and CO_2 released from the samples on heating.

Analyses were also carried out on vein calcite to test whether fluid inclusions trapped in the host limestone are compositionally distinct from those trapped in the vein and whether any of the components analysed displayed a distinctive pattern away from the vein that may prove useful in mineral exploration.

Sample location and descriptions

Greenhow Rake is one of the major fluorite–galena–calcite veins within the Greenhow Hill Mining district in the southern part of the North Pennine orefield (Dunham and Stubblefield, 1944). The vein can be traced for at least 1 km up to the summit of Greenhow Hill, where it splits into three branches. These are exposed in a small quarry located a few hundred metres southeast of the summit, where sampling was carried out (Duck Street Quarry, SE 411464). Sampling was restricted to the southern split of the vein and to a layer of coarsely crystalline crinoidal limestone at the top of the lower limestone unit (Fig. 1). Studies on poorly crystalline limestone elsewhere in the quarry were unsuccessful. The exact location of Greenhow Rake in relation to Greenhow Hill and further details on the geology of the area are summarised by Dunham and Wilson (1985). As exposed in the quarry the vein is about 1 metre wide and typically contains about 70% calcite and 20–30% fluorite with only minor amounts of galena and barytes. The sampled limestone is most appropriately classified as a crinoidal sparite. It is made up of abundant crinoid ossicles, a few bivalve shell fragments and intraclasts set within a uniform coarse-grained calcite cement (Fig. 2). Minor micritisation of shell fragments is apparent. The petrography of this limestone is essentially uniform over the 25 metre interval sampled.

Microscopically the calcite cement is remarkably clear and contains few visible fluid inclusions. In contrast crinoid and shell fragments are so crowded with inclusions that they take on a speckled appearance (Fig. 2). The inclusions are extremely small (less than a few μm) and it is very difficult to see whether they are monophase or multiphase. Many appear monophase (either liquid or vapour) but two-phase vapour/liquid inclusions have sometimes been observed. Unfortunately, in the absence of a suitable U.V. microscope (Burruss, 1981) it has not been possible to tell optically whether these liquids are aqueous or hydrocarbon-rich. Thermometric analysis was not possible owing to the extremely small size and irregular nature of the inclusions.

Inclusions in vein calcite are typical of those throughout the orefield, being monophase liquid and two phase vapour–liquid aqueous types. Thermometric results for Greenhow Rake samples as determined by Rogers (1978) show a mean salinity of 16.5 equiv. wt. % NaCl and a mean homogenisation temperataure of 152 °C.

Experimental

ICP analysis. The ICP-linked decrepitation technique (Alderton *et al.*, 1982) was used to analyse Ca, Na, K, Pb and Zn evolved on heating the sample contained in a small pyrex test-tube connected directly to the plasma with silicone rubber tubing. Analyses were carried out in duplicate on 0.25 g of material at a standard grain size of between 1 and 2 mm using an ARL 3400 spectrometer.

A small electric furnace held at 600 °C was used to heat the sample for 15 seconds prior to analysis over a 45 second integration time. Audible decrepitation took place well within this time interval at an estimated temperature of between 200 and 450 °C.

The raw data from the photomultiplier tube, less background, are expressed as millivolts (mV). For each element the ICP millivolt response is proportional to concentration in the decrepitates. However, because the relative sensitivities for each element varies it is necessary to convert the

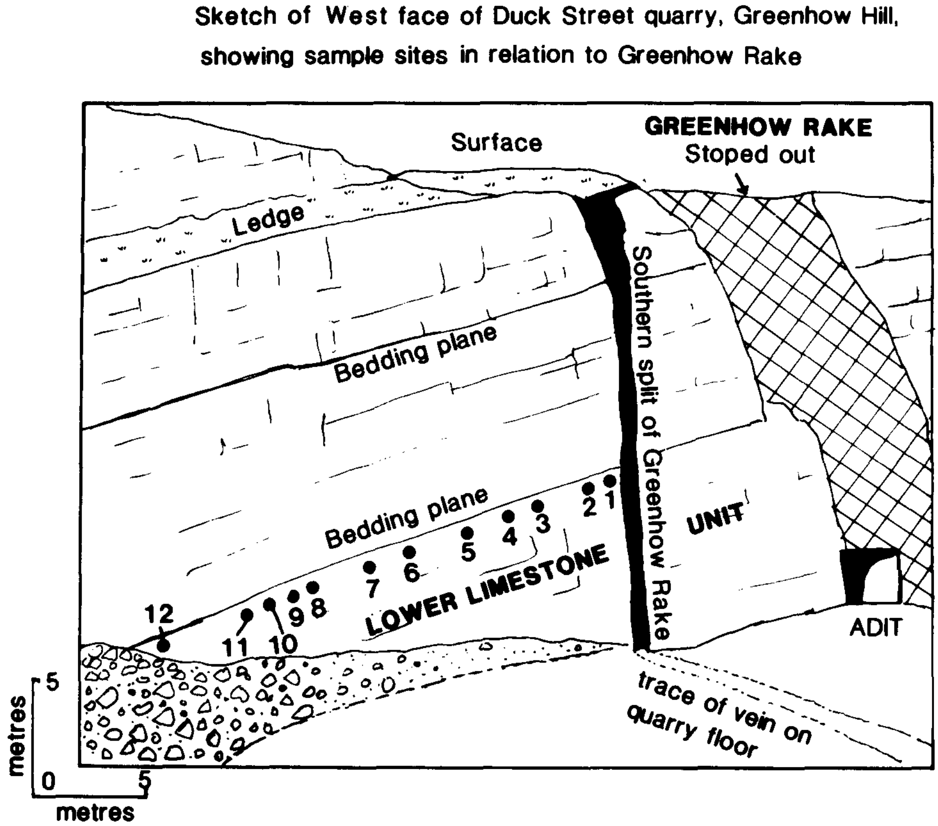
Sketch of West face of Duck Street quarry, Greenhow Hill, showing sample sites in relation to Greenhow Rake

FIG. 1. Sample localities within a coarse crinoidal limestone layer next to Greenhow Rake, N. Pennine Orefield.

raw data to meaningful concentration units. In conventional ICP analysis and calibration the test solution is nebulized into the plasma. An effective calibration procedure under conditions simulating decrepitation of inclusions has yet to be achieved and sensitivity ratios determined in nebulization studies are therefore assumed to apply to decrepitated material (Thompson *et al.*, 1980). Absolute concentrations in decrepitates are only of limited value. Mostly they reflect the total amount of material released into the plasma rather than concentrations in inclusions. Element ratios are preferred (using Na as the standard) as this trends to smooth out the effects of variable decrepitation (Rankin *et al.*, 1982).

Mass spectrometry/volumetric analysis. A small 0.25 g sample contained within a silica tube was heated in vacuo for 60 seconds in the same furnace and with the same temperature setting used for D-ICP analysis (at about 600 °C). The tube is connected to a purpose-built, all-metal gas extraction line heated to about 80 °C to maintain transfer of water. Cryogenic separation using liquid nitrogen and acetone/dry ice traps isolates three distinct fractions; water (after conversion to H_2 using zinc metal held at 400 °C), CO_2 and non-condensable gases. The partial pressures of these three phases are measured using capacitance manometers and the composition of the non-condensable gases (CH_4, N_2, H_2 etc.) is determined using a small quadrupole mass spectrometer (VG supavac instrument). From the data generated, the mole fraction and amount of each gas released from a unit weight of sample can be determined. The technique is further described by Shepherd *et al.* (1985).

Gas chromatography. GC analysis was carried out using a thermal evolution techniques for analysing light hydrocarbon gases developed for mineral exploration purposes (Carter and Cazalet, 1984). A 5 g sample of graded (1 to 4 mm) crushed limestone was heated at 210 °C for 2.5 hours in a glass bottle with an airtight silicone rubber seal. Evolved gases were removed from the

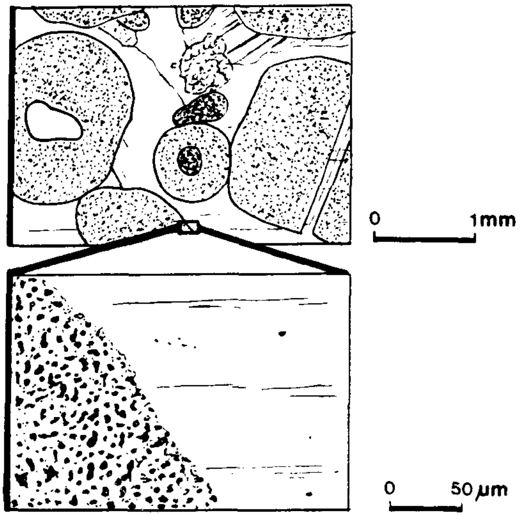

FIG. 2. Typical microscope fields of view of crinoidal limestone at high and low magnification showing the very high abundance of inclusions in crinoid ossicles compared with their scarcity in the calcite cement.

headspace with a needle and syringe and analysed using a Pye-Unicam PU 4500 Gas Chromatograph, fitted with flame ionization detectors and Poropax Q columns. Using this system up to 13 different component gases can be measured. Many have been identified by comparing the chromatograms with those produced by gas mixtures, but here we are only concerned with the major hydrocarbon species, methane. Results are expressed in weight units as ppb methane.

Results

Although the ICP technique has multielement capability only the results of major species normally present in fluid inclusions (Ca, Na and K) and the main ore metals in the region (Pb and Zn) are presented. When considering the raw mV values it must be remembered that, due to variations in the relative sensitivities for each element, the mV values for different elements are not directly comparable. The raw mV values for limestones, after correction for interference effects due to high levels of calcium, are presented in Fig. 3. This diagram also illustrates the good reproducibility of results for all five elements. The corresponding X:Na atomic ratios are shown in Table 1.

Results for H_2O and CH_4 determined by mass spectrometry and for CH_4 by gas chromatography are shown in Table 2 and Fig. 4. Substantial amounts of CO_2 (up to 7.1 mole percent) were also recorded. The principal sources of this gas is almost certainly thermal decomposition of calcium carbonate. For this reason CO_2 results are excluded from further discussion.

Discussion

Source of components evolved on heating and thermal decrepitation. The transfer mechanisms for volatiles and trace elements into the plasma during heating and decrepitation (Thompson *et al.*, 1980; Chryssoulis, 1983) include explosive release of fluid inclusion contents, the accompanying introduction of solid particles of host mineral, and the volatilisation or sublimation of components from the host minearal or impurities within it.

The extraordinary high levels of calcium compared to sodium and potassium are primarily due to solid particles of carbonate introduced into the plasma during decrepitation. Thus the Ca:Na ratio bears little resemblance to its ratio in the original inclusion fluids. The strong positive correlation between the response for calcium and the amount of water liberated over the same temperature interval (Fig. 4) is most readily explained by slight variations in the decrepitation activity of different samples containing the same size population of inclusions. Na and K correlate well with Ca and H_2O as depicted graphically in Figs. 3 and 4. There is little doubt, therefore, that variations in Na and K levels are similarly related to variations in decrepitation activity. The correlation between Ca and Na is particularly marked (Fig. 5). As a check on the possibility that Na and K responses might be due to interference effects from high calcium levels in the decrepitates, solid particles of calcium carbonate and finely ground particles of limestone were introduced directly into the plasma. The effects were found to be negligible. A fluid inclusion source is therefore favoured. Based on previous comparative studies using crush-leach and decrepitate analysis on vein and granite quartz (Chryssoulis, 1983; Rankin and Alderton, 1985) we contend that the K:Na ratio in the decrepitates considered here closely correspond to their ratios in the original inclusion fluids.

The present study is a first attempt at combining data from decrepitate analysis of both water and alkalis determined *under identical operating conditions* as a measure of element concentrations and hence salinity in the inclusion fluids. Estimates of sodium concentrations based on a simple NaCl-brine for vein and limestone samples are shown in Fig. 6. Whilst the values for limestone

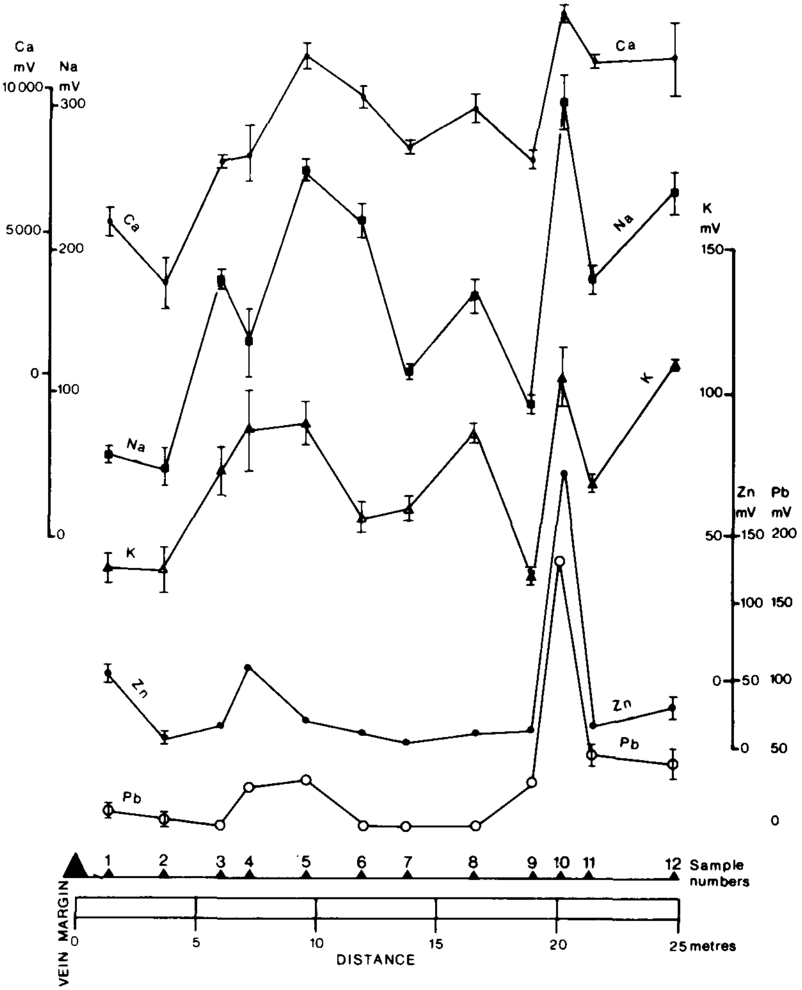

FIG. 3. ICP decrepitate response (mV) less background values for limestones at different sample sites (1 to 12) away from the vein. Symbols represent means of duplicate analysis shown as bars.

TABLE 1. SUMMARY AND COMPARISON OF ICP DECREPITATE DATA FROM LIMESTONE AND VEIN CALCITE.

X:Na atomic	Limestone (n = 24)			Vein Duplicate values
	Min.	Max.	Mean	
Ca	241	612	360	26, 32
K	0.06	0.24	0.14	0.03, 0.05
Pb	10^{-4}	10^{-2}	n.a.	10^{-2}
Zn	10^{-3}	10^{-1}	n.a.	3×10^{-1}, 1.5×10^{-1}

Atomic ratios for Pb and Zn are very approximate due to low mV responses and uncertainties in the measurements. A mean value is not appropriate (n.a.)

TABLE 2. SUMMARY AND COMPARISON OF DATA FOR CH_4 AND H_2O FROM LIMESTONE AND VEIN CALCITE.

Volatile Species	Analytical Method	Units	Limestone (n = 12)			Vein (n = 2)
			Min.	Max.	Mean	
H_2O	MS	10^{-3} g/g	1.32	3.62	2.9	1.71
CH_4	MS	10^{-6} g/g	1.32	3.10	2.1	n.d.
CH_4	GC	10^{-7} g/g	0.63	2.5	1.4	2.9

n.d. = not detected

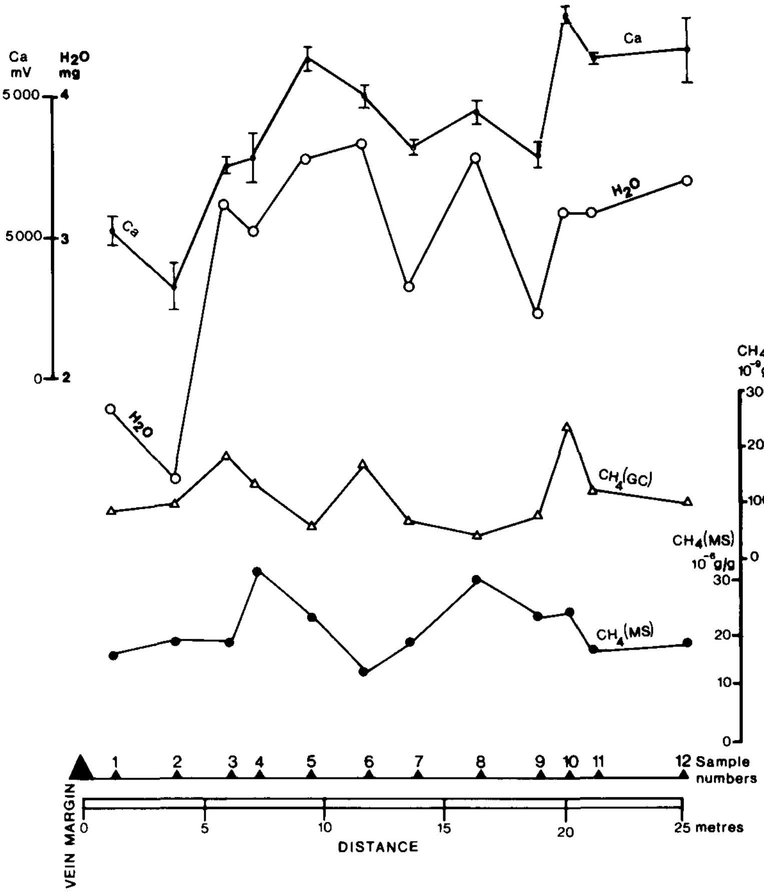

FIG. 4. Comparison of Ca levels (mV), H_2O and CH_4 levels determined by decrepitation of 12 limestone samples collected at intervals away from the vein.

fluids, at between 5 and 15 wt. % sodium (corresponding to salinities of the order of 30 wt. %) may seem reasonable, the inferred values for vein samples, where sodium exceeds water by several orders of magnitude are clearly absurdly high, bearing in mind previously published salinity data (Rogers, 1978). Further work is therefore needed before metal : H_2O ratios can be used to estimate element concentrations in the fluid. For the present we prefer not to report ICP data relative to water but as element ratios relative to sodium which is more conventional in ICP analysis (Rankin *et al.*, 1982).

The metal to sodium ratios for Pb and Zn in the decrepitates are much greater for the vein sample than for limestones samples. There are two major sources of Pb and Zn in decrepitate analysis; from inclusion fluids and volatisation from, or direct introduction into the plasma of, trace amounts of galena, sphalerite and associated Pb- and Zn-bearing mineral phases.

In the case of the two vein samples, because the determined Pb : Na and Zn : Na ratios are inordinately high for even the most potent ore-forming of fluids, they are unlikely to represent their true levels in the inclusion fluids. The levels of Pb and Zn in the limestone decrepitates are lower by two or three orders of magnitude than for the vein. However, the lack of correlation between these two metals and those components dominant in inclusion fluids (Na, K, H_2O) for *all* samples is more suggestive of a major contribution from alternative sources rather than fluid inclusions themselves.

The amount of water released from the limestone samples compared to vein samples reflects the very much greater abundance of inclusions in the limestones. There can be little doubt that

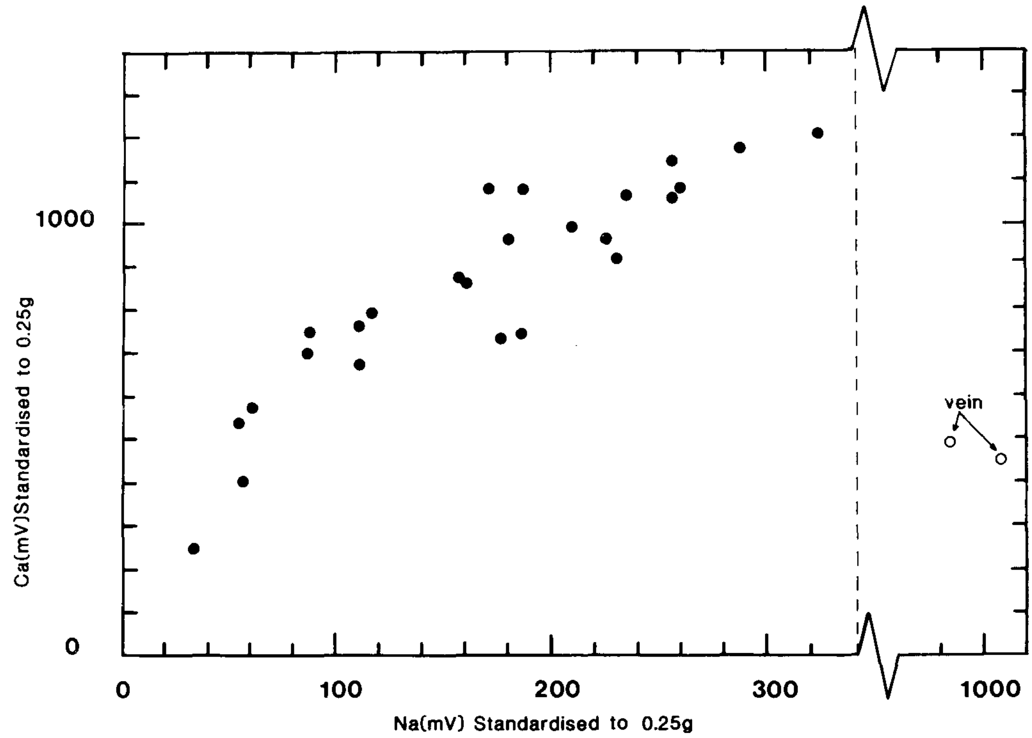

FIG. 5. D–ICP response for Ca plotted against ICP response for Na showing major differences between limestone and vein samples.

the water is derived from a fluid inclusion source in both materials. The source of methane in the mass spectrometric analysis of limestone samples is more problematic. The lack of correlation with H_2O and also with Na, K, Ca suggests a source other than brine inclusions. These sources might include pyrolitic decomposition of admixed carbonaceous matter, chemisorption on crystal surfaces or interstitial (gas pockets) sites along grain boundaries. Although an aqueous fluid inclusion source is not favoured, we cannot rule out the possibility that this gas is derived from separate (co-existing?) methane-rich inclusions in the samples. There is a marked discrepancy in the level of methane determined by gas chromatography and by mass spectrometry. A further discrepancy is revealed when limestone and vein samples are compared; methane determined by MS is very much lower in the vein sample but the reverse is true when the GC results are considered (Table 2). These differences are best explained by the different heating periods and temperatures of the two techniques. It is to be expected that more methane would be released at the higher temperatures used for MS analysis (550 °C compared to 210 °C for GC analysis) whatever the source of methane in the limestone samples. However, the discrepancy between limestones and vein samples cannot be explained.

Variations in results for limestones away from the vein. Carter and Cazalet (1984) recently highlighted the use of hydrocarbon gases as pathfinders in mineral exploration. On a regional scale a distinct methane anomaly has been reported in limestones across the whole of the North Pennine orefield compared to much lower values recorded in 'unmineralized' limestones elsewhere in the north of England (op. cit.). The present study shows that such anomalies are *not* reflected on a local scale.

Recent studies by Chryssoulis (1983) and Jones (1986) have revealed marked variations in the fluid inclusion populations in the immediate vicinity of hydrothermal vein deposits in granites thus confirming the earlier reports of Yermakov (1967) and Roedder (1977) that fluid inclusions may be valuable tools in mineral exploration. The cause of these variations is thought to be infiltration

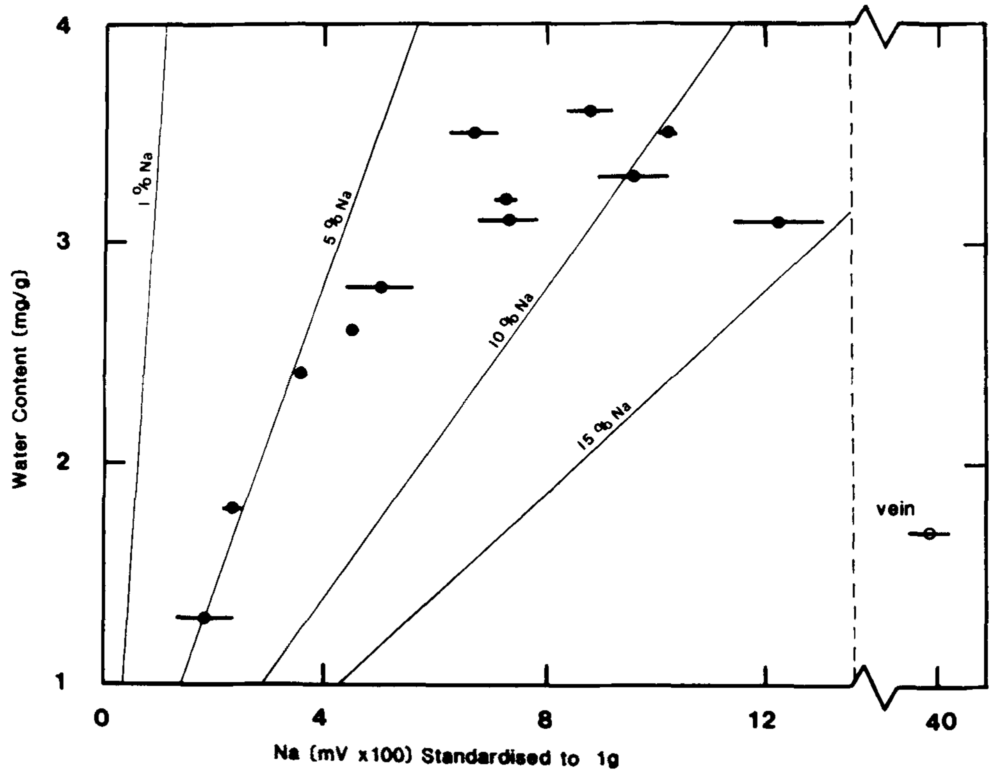

FIG. 6. Plot of water content evolved on heating against ICP response for Na showing difference between vein and limestone samples. Circles, filled for limestone, represent mean of two analysis for Na. Lines marked 1% Na to 15% Na show theoretical yields, assuming the Na : H_2O mass ratio in the fluids is same as in the decrepitates.

of hydrothermal vein fluids into the rock with the concomitant addition of secondary inclusions. Any measurable fluid inclusion parameter such as abundance, composition and distribution can reflect these variations. To the best of our knowledge this is the first time the concept has been applied to a limestone-hosted vein deposit. Unfortunately, the results (Fig. 3) are somewhat disappointing. There is only a slight negative anomaly in the levels of Na, K, Ca, and H_2O very close to the vein, probably reflecting minor recrystallisation of the limestone with the concomitant *loss* rather than *gain* of inclusions. There is a more noticeable positive anomaly, also reflected in the ICP response for Pb and Zn for sample 10. A likely cause is a small joint some 20 cm away filled-with barren calcite. However, these rather indistinct anomalies would seem to occur on too small a scale (centimetres not metres) to warrant their application to local scale exploration in the area.

K : Na ratios. The atomic ratios for vein samples (0.03 and 0.05) compare moderately well with the value of 0.07 determined by Rogers (1978) using the crush-leach method. Much higher values are recorded for the limestone samples (Fig. 3 and Table 1), suggesting that limestone and vein fluids are geochemically distinct and therefore of different origin. Petrographically (Fig. 2), fluid inclusions are overwhelmingly more abundant in crinoid ossicles and fragments than in later calcite cement. Thus the K:Na ratios simply reflect the earliest fluids preserved in the limestone samples. Whether these represent original 'crinoid juice' (Roedder, 1984, p. 329) or very early diagenetic fluids is difficult to determine. It is important, however, to note that they are on average 4 to 5 times enriched in potassium compared to present-day seawater; a fact that is difficult to explain whatever their origin.

Based on the K:Na analyses alone, there appears to be little or no relationship between these early limestone fluids and those responsible for vein formation. However, it would be stretching the results too far to comment further on current ideas for ore genesis in the North Pennine orefield (Dunham and Wilson, 1985).

Summary and conclusions

The present study has highlighted the value and limitations of applying ICP and MS decrepitate analysis to limestone samples. It has shown that fluids trapped in crinoid ossicles are dominantly aqueous and reports for the first time on the K : Na ratios in these fluids. There is no evidence to suggest that methane is held within *aqueous* fluid inclusions and an alternative source for the evolution of this gas on heating must be sought. The order of magnitude difference between the levels of methane determined by the MS and by the GC method reflects the different conditions under which the analysis was carried out (up to 600 and 210 °C respectively).

Except for Na : K ratios the ICP and MS decrepitate data have been of limited value here in determining the composition of minute submicroscopic fluid inclusions in limestones. However, the results do at least reflect major differences between vein fluids and wall rock fluids. From an exploration viewpoint none of the parameters considered have the necessary variations in magnitude and vector qualities to warrant their application to mineral exploration in this region on a very local scale.

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