Unusual, oil-bearing inclusions in fluorite from Baluchistan, Pakistan

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Abstract

Phenomenally large (up to 2 mm) oil-bearing and associated brine inclusions in fluorite from carbonate-hosted, epigenetic, fluorite–calcite–(baryte) deposits of the Koh-e-Maran area are investigated using a combination of microthermometry, UV-microscopy and FTIR microspectroscopy. The liquid hydro-carbon phase in primary 'oil' inclusions is brown in colour and is dominated by saturated, low molecular weight, aliphatic hydrocarbons.

Two types of mixed aqueous and 'oil' inclusions occur. Aqueous/oil types represent co-eval trapping of immiscible drops of oil and brine during primary growth. In oil/aqueous inclusions the oil appears to 'wet' the aqueous phase resulting in an odd 'dish-shaped' meniscus. The oil or liquid hydrocarbon part of the inclusion is *primary* but the aqueous part is thought to represent a *secondary* infill. The fluid inclusion evidence suggests that fluorite precipitated from a dilute (3.5 wt.% NaCl) brine at temperatures around 110–140 °C in the presence of an immiscible liquid hydrocarbon phase dominated by saturated, light hydrocarbons. This 'oil' was present as an emulsion in the aqueous fluid and the phenomenal size of the inclusions is thought to reflect the large droplet size in the emulsion. Infiltration of a more saline, calcium-enriched brine into pre-existing oil inclusions resulted in complex oil–water inclusions showing a reversal in the nature and shape of the oil-water interface due to the presence of unspecified surfactants in the brine which affected the wetting characteristics of the oil.

The homogenization temperatures and the presence of liquid petroleum inclusions are characteristic of Mississippi Valley-type (MVT) and manto-type fluorite deposits in many other parts of the world.

KEYWORDS: fluorite, oil-bearing inclusions, brine inclusions, Baluchistan, Pakistan.

Introduction

FLUID inclusions containing varying proportions of gaseous, liquid and solid hydrocarbons are a relatively common feature of diagenetic mineral phases in sedimentary environments (see reviews by Roedder, 1976; Burruss, 1981; McLimans, 1987; and Rankin, 1990). The occurrence of co-eval aqueous and liquid hydrocarbon or 'oil' inclusions is a particularly notable feature of fluorite from several Mississippi-Valley Type (MVT) and manto-type deposits worldwide and provides one of the main lines of evidence in support of a com-mon provenance for oil and ore-forming MVT fluids in the sedimentary environment (see reviews by Roedder, 1984 and Sverjensky, 1986). Here we report on the optical, thermometric and geochemical characteristics of some phenomenal oil inclusions in fluorite from Baluchistan. The inclusions are phenomenal in two senses. Firstly, they are exceptionally large (up to 2 mm) and, secondly, they display variable and unusual wet-ting characteristics in relation to the aqueous fluids with which they co-exist (see plate 9 in Roedder, 1972). The controls on the distribution and origin of the various types of fluid inclusions

FIG. 1. Map showing the location of the Koh-e-Maran fluorite deposits within the Axial Belt of Central Pakistan. Hatched area represents the outcrop limit of Mesozoic sediments. Modified from Sillitoe (1978).

are discussed and implications for metallogeneses in the Koh-e-Maran area are proposed in the light of these findings.

Sample location and geological setting of fluorite mineralization

The occurrence of exceptionally well-developed inclusions containing 'liquid bitumen' was first noted in fluorite from the Koh-e-Maran area of the Kalat District, Baluchistan, Pakistan, by Shcheglov (1969), a feature which led Sillitoe (1978) to refer to the mineralization as Mississippi Valley-type despite the absence of any discernible lead and zinc. Comments on, and a photomicrograph illustrating, the wetting characteristics of oil and brine in a mixed oil/brine inclusion in fluorite from Koh-e-Maran are provided in a recent review by Roedder (1984), but to date a detailed description of these inclusions and an interpretation of their geological significance has not been attempted.

The fluorite deposits of Koh-e-Maran (Fig. 1) constitute a small, though potentially significant, mineral resource in the central part of Pakistan. The mineralization is exposed naturally and in numerous small workings, predominantly as a series of stratiform 'manto-type' replacement bodies, pipes/pods and discordant veins at the top of an approximately 1000 m thick sequence of well-bedded limestones of Middle Jurassic age (the Chiltan Limestone). Fluorite and calcite dominate the mineralization throughout the area, while baryte only occurs as a minor constituent generally and base-metal sulphides are notably absent.

Individual replacement deposits rarely exceed a metre or so in thickness and there is a distinct lack of continuity between them. Furthermore, the evidence suggests that pipes and discontinuous veins acted as feeder channels for this stratiform mineralization which is formed along bedding planes at favourable horizons.

The present study was confined to one sample locality where colourless, crystalline fluorite con-

tains especially large and abundant oil inclusions. These are clearly visible to the naked eye or with a hand lens, and a distinctive odour of 'kerosene' is released when the host crystals are crushed or fractured.

Analytical methods

Microthermometry was carried out on thick (1 mm), doubly polished wafers using a Linkam TH600 combined heating/freezing stage calibrated using the known melting points of pure organic compounds. Reported homogenization temperatures (Th) are accurate to within $\pm 1\,°C$ and first and last ice melting temperatures (Tfm and Tlm respectively) and clathrate melting temperatures (Tmc) are accurate to within $\pm 0.5\,°C$.

Ultraviolet fluorescence microscopy was carried out using a Nikon Optiphot microscope system equipped with a mercury-xenon UV light source (excitation wavelength 365 nm) and UV barrier filter at 400 nm. Fourier transform infrared microspectroscopy (FTIR) was carried out on individual inclusions, and on the hydrocarbon component of mixed inclusions. The equipment used was a Bruker IFS45 FTIR spectrometer coupled to optical microscope equipped with reflecting optics and a ×15 objective. Normally, the sample area exposed to the beam is restricted to 80 μm, well below the average size of the inclusions studied. Transmission spectra were recorded in air in absorbance mode with a $4\,cm^{-1}$ spectral resolution using 200 scans and a liquid-nitrogen-cooled, cadmium telluride detector. To account for the possible interference effects of water, CO_2 and host mineral absorbance, blank spectra were subtracted from each sample spectra.

Optical characteristics and classification of fluid inclusions

The inclusions contain varying proportions of liquid and gaseous hydrocarbons, and aqueous fluid. The liquid hydrocarbon ('oil') component is easily ditinguished by its brown to pale yellow colour and characteristic ultraviolet fluorescence.

The darker oils fluoresce yellow, but the paler coloured oils fluoresce pale blue. So far we have not explored the possibility that these represent paragenetically distinct oils. Certainly all of the oil-bearing inclusions are primary and, as we show later, their IR spectra are similar. Occasional solid particles (wax?, bitumen?) are sometimes observed within the oil but daughter minerals are absent from the aqueous phase. Five inclusion types may be distinguished on the basis of their bulk composition and distribution throughout the crystal (Fig. 2). These are referred to as oil, aqueous (I), aqueous (II), aqueous/oil and oil/aqueous types in decreasing order of relative abundance.

Oil inclusions (Fig. 2A) are dominated by liquid hydrocarbons and contain a small, mobile, vapour bubble presumably composed essentially of light hydrocarbon gases. Aqueous fluid is absent. The inclusions range in size up to 2 mm, averaging between 100 and 500 μm, and are characteristically ovoid, oblate, tear-drop, and bottle-shaped with long axes parallel to the growth direction of the crystal.

The inclusions frequently form planar groupings or clusters and are unequivocally primary in origin.

Aqueous (I) inclusions generally range in size from about 20 to 200 μm. They show a similar distribution pattern to, and are often associated with the oil inclusions above, and are therefore also primary in origin. Shapes range from equant, negative crystals to elongate and highly irregular. A small contraction vapour bubble is typically present but necking-down is common resulting, on occasions, in highly variable phase proportions of liquid and vapour.

Aqueous (II) inclusions (Fig. 2F) are again simple two phase (l + v) types but are distinguished from aqueous I inclusions by their smaller size (usually less than 50 μm) and occurrence in random planar groupings which extend to the edge of the crystals. These inclusions are clearly secondary and, as indicated by microthermometric analysis (see below), are compositionally distinct from these earlier fluids.

Aqueous/Oil inclusions (Fig. 2B, C) range in size up to about 400 μm and contain up to about 60% aqueous brine and one or more globules of immiscible oil. A vapour bubble is typically present in the larger oil globule. The inclusions are primary and represent co-eval trapping of aqueous brine and oil during crystal growth.

Oil/Aqueous inclusions (Fig. 2E, F) are similar in size and distribution to oil and aqueous/oil inclusions, but are distinguished from the latter by the dominance of the liquid hydrocarbon ('oil') component and the unusual wetting characteristics of the oil/water interface resulting in an odd 'dish-, or disc-shaped' meniscus. This phenomenon is independent of the colour and fluorescent properties of the oil. Although these inclusions appear primary, as discussed later, part of their infill may be secondary in origin.

Microthermometry

The main results for each inclusion type are summarized in Table 1. The mean homogeniza-
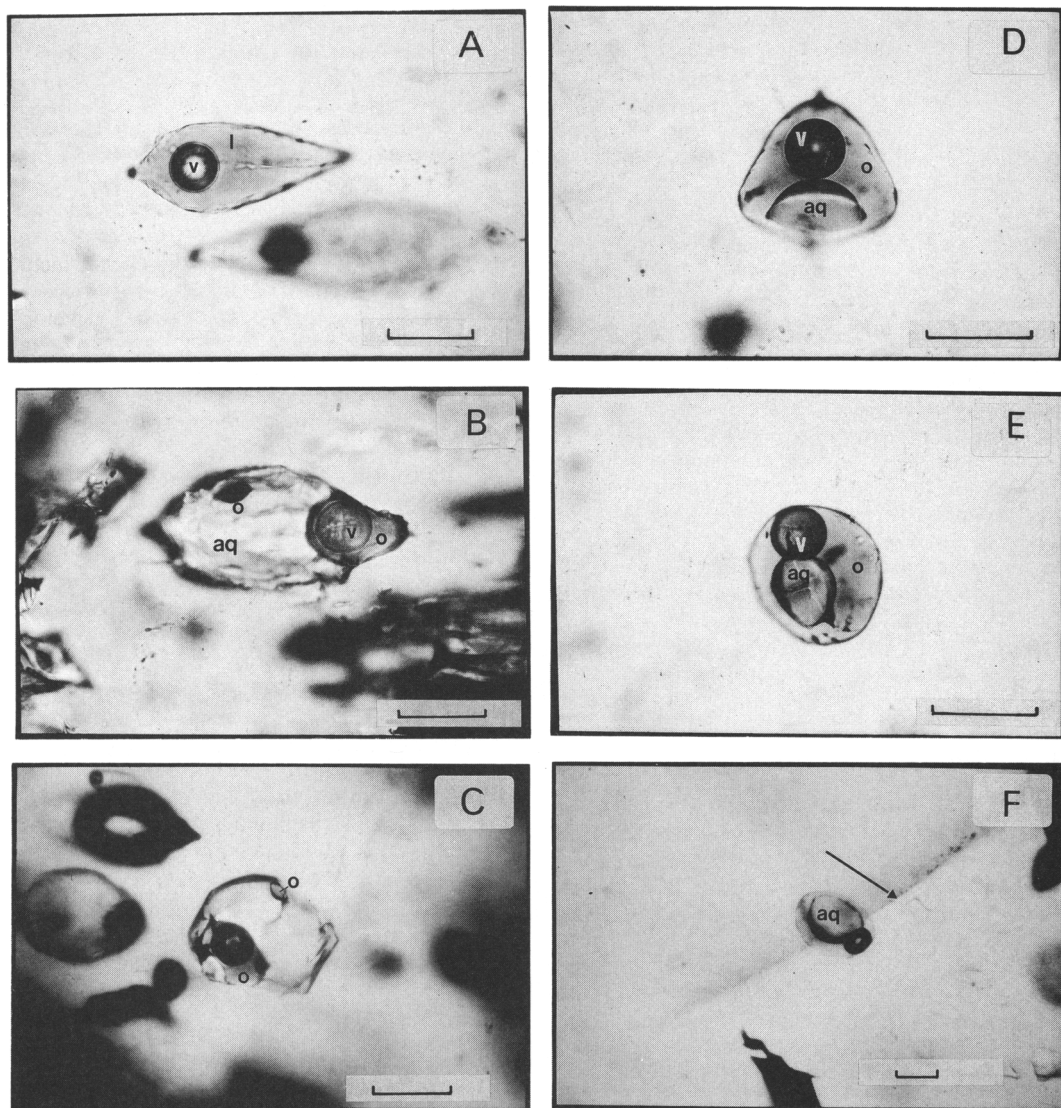
FIG. 2. Photomicrographs of fluid inclusions in fluorite from Koh-e-Maran. Bar = 150 μm in all photographs.
A Two phase (l + v) hydrocarbon inclusions showing typical 'tear-drop' shape. B Aqueous/oil inclusion containing
aqueous fluid (aq) and two immiscible globules of oil (o). The larger globule contains a vapour bubble (v).
C Aqueous/oil inclusion containing two globules of oil (o). The larger globule contains a vapour bubble and
the smaller one shows a saucer-shaped meniscus. D Oil/aqueous inclusion containing oil (o), vapour (v) and
a saucer-shaped aqueous phase (aq) completely enclosed within the oil. E Oil/aqueous inclusion containing oil
(o), vapour (v) and a rounded globule of aqueous fluid (aq). Note the absence of vapour within the aqueous
brine. F Oil/aqueous inclusion containing large aqueous phase (aq). Note the occurrence of the fracture plane
(arrowed) which crosses the inclusion, and itself contains small, secondary aqueous inclusions.

tion temperatures for primary and secondary
aqueous inclusions are identical though the ranges
differ. The wider spread for secondary inclusions
is probably due to necking-down and leakage
which though often manifest, was not always easy
to avoid. The *Tfm* values for primary aqueous
inclusions are close to the eutectics for the system
$NaCl–KCl–H_2O$ at between −20 and −23 °C

TABLE 1 – SUMMARY OF THERMOMETRIC DATA

HOMOGENIZATION TEMPERATURES Th (°C)				
	number of inclusions	min	max	mean
Primary aqueous	36	103	135	112
Secondary aqueous	33	96	143	111
Oil	42	96	108	101

LAST ICE MELTING TEMPERATURE Tlm (°C)				
	number of inclusions	min	max	mean
Primary aqueous	25	-4.5	-0.1	-1.9
Secondary aqueous	35	-7.4	-2.0	-5.4
Oil/aqueous	10	-10.8	-9.2	-10.0 Clathrate present
Aqueous/oil	2	-3.3	-1.0	-2.1

CLATHRATE MELTING TEMPERATURE TMC (°C)				
	number of inclusions	min	max	mean
Oil/aqueous	15	+1.0	+3.5	+2.0 *

* Also, melting at oil/water interface observed at c. 25°C, 37.5°C and ¦56°C in some inclusions.

($n = 20$). However, the Tfm temperatures for secondary inclusions range from about -45 to $-50\,°C$ ($n = 15$), indicating the additional presence of $CaCl_2$ and/or $MgCl_2$ in the fluids. The mean Tlm values for primary and secondary aqueous inclusions correspond to salinities based on the model system $NaCl-H_2O$ (Hall et al., 1988), of 3.5 equiv. wt.% NaCl and 9 equiv. wt.% NaCl respectively.

The Tfm and Tlm data for the aqueous phase in mixed aqueous/oil inclusions and primary aqueous inclusions are closely comparable. For mixed oil/aqueous inclusions, however, Tfm values around $-45\,°C$ ($n = 10$, $+/-2\,°C$) and Tlm values between -11 and $-9\,°C$, are more compatible with the microthermometric data for secondary aqueous inclusions.

Pale green to colourless clathrate phases develop in the aqueous component of mixed oil/aqueous inclusions after freezing. At their maximum extent these account for 5% of the total volume of the aqueous phase. They melt abruptly, without development of a vapour bubble. Clathrate melting temperatures (Tmc) fall mostly in the range $+1.0$ to $2.4\,°C$ and are likely to be due to methane-rich and/or CO_2-rich clathrates. Melting temperatures were also recorded at around 25,

37.5 and 56 °C at the oil–water interface in some inclusions. These also undoubtedly represent clathrates rich in higher order alkanes (Hitchon, 1974). Clathrates incorporate substantial amounts of water into their structure. Consequently, their development may cause an artificial lowering of Tlm values in aqueous inclusions resulting in an overestimate of salinity (Roedder, 1984).

The discrepancy between the Tlm values for the aqueous component of mixed oil/water inclusions and for secondary aqueous inclusions is therefore readily explained by clathrate development and is compatible with the view that the aqueous fluids in both these inclusion types are of the same composition and origin.

The homogenization of the liquid and vapour hydrocarbon phases in all oil-bearing inclusions is always into the liquid phase and confined to a narrow temperature range from 96 to 108 °C (mean = 101 °C). The oil and aqueous components in complex inclusions showed no signs of homogenization even on heating to 250 °C and maintaining this temperature for several hours. In oil/water inclusions, however, the edges of the aqueous phase became dispersed as a myriad of tiny (generally 5 to 30 μm) spherical droplets within the oil. These persisted in a state of constant motion after cooling to ambient temperatures and showed little or no sign of coalescence back to the aqueous fluid.

In oil inclusions the liquid hydrocarbon took on a granular appearance and solids appeared below about $-120\,°C$. Most of these melted between -90 and $-80\,°C$ but a few tiny fragments (waxes or bitumens) remained. In view of the complexity and difficulty in interpreting these changes a fuller presentation and further discussion of results is beyond the scope of the present paper.

FTIR microspectroscopy

Representative spectra for each inclusion type are shown in Fig. 3. The spectrum of the host fluorite shows that the choice of spectral parameters produces a high signal-to-noise ratio and that atmospheric effects have been cancelled. The advantage of examining fluorite-hosted inclusions in the mid-IR region is that above $1000\,cm^{-1}$ fluorite is effectively IR transparent.

1. Primary Aqueous (BAL14003). This spectrum is typical of 'liquid water' and exhibits the fundamental absorptions of molecular H_2O (Aines and Rossman, 1984). The broad band at $3400\,cm^{-1}$ and the peak at about $1650\,cm^{-1}$ arise from the stretching and bending vibrations of the H_2O molecule respectively.

2. Oil (BAL14009). This spectrum, of brown-

coloured oil, is dominated by absorption peaks between 3000 and 2800 cm^{-1} and at 1455 and 1373 cm^{-1}. These are assigned to the stretching and bending vibrations of the saturated C–H bonds in the CH$_3$ and CH$_2$ molecules present, i.e. they indicate the presence of low molecular weight alkanes (Colthup et al., 1975). The shoulders above 3000 cm^{-1} can be assigned to aromatic/olefinic C–H bonding. In other spectra we have identified peaks possibly representing ring stretching (at 1613 cm^{-1}) and carbonyl bonds (at 1697 cm^{-1}). Since the intensity of absorption is proportional to the concentration of the species present, the spectrum shown in Fig. 3 is characteristic of a mixture of aliphatic hydrocarbons with a small proportion of aromatic/olefinic hydrocarbons also present. These would be responsible for the brown colour of the 'oils'. This endorses the results obtained from preliminary GC analysis kindly provided by Dr J. Ferguson (Imperial College). The strong single peak at 2333 cm^{-1} is due to the asymmetrical stretching vibration of the CO$_2$ molecule. It is distinguishable from atmospheric CO$_2$ by its position and shape (Barres et al., 1987).

On comparing this spectrum with that of the aqueous inclusion, there are no peaks present which can be confidently identified as being due to water, unless, as other authors have indicated for similar 'water-free' oil inclusions from other deposits (Roedder, 1984; Guilhaumou et al., 1988, 1990) post-depositional changes have removed or consumed any water originally held within the inclusions. It would seem improbable for a pure oil inclusion to be formed in a mineral grown from an aqueous emulsion without trapping at least some water.

3. Mixed oil and aqueous inclusions (BALI4006/4012/4014). The spectra for aqueous/oil and oil/aqueous inclusions are very similar and appear to be composites of the aqueous and oil spectra. The hydrocarbon peaks are more pronounced in the oil/aqueous spectrum but this is probably due to less water being present. The characters of these peaks are similar and it can be assumed that the oil is similar in both cases. By making use of a smaller aperture it was possible to obtain a spectrum of just the oil phase in an oil/aqueous inclusion and this is also shown in Fig. 3. It is essentially indistinguishable from the 'oil-only' spectrum. It is interesting to note that the CO$_2$ peak occurs in the oil phase of this inclusion, proving that the CO$_2$ is more soluble in the hydrocarbon phase.

Thus, from data obtained from IR analysis, the character of the oil phases in both oil/aqueous and aqueous/oil inclusions is essentially the same.

This oil is virtually indistinguishable from that which occurs in the 'oil-only' inclusions.

The combined microthermometric, FTIR, optical and UV fluorescence data show that the liquid hydrocarbon components in all three oil-bearing inclusion types are indistinguishable and therefore of common origin. The occurrence and distribution of co-eval oil, aqueous and aqueous/oil inclusions further suggests that the oil was present as immiscible globules in the fluids responsible for primary fluorite mineralization.

The Th values for primary aqueous inclusions represent minimum temperatures of formation (mean = 112 °C). A precise estimate of the magnitude of the pressure correction is presently unavailable, but on geological evidence it is unlikely to exceed about 30 °C.

The lower homogenization temperatures for coexisting oil inclusions (mean about 101 °C) are easily reconcilable with conditions of coeval and isothermal trapping because of the much higher compressibility of low atomic weight hydrocarbon mixtures compared to aqueous brines. Once the composition of these oil inclusions can be established with greater confidence it will be possible, at a later date, to use the information to construct appropriate isochores for both fluid phases and to use the 'isochore intersect' method (e.g. Burruss, 1981; McLimans, 1987) to define uniquely the pressure and temperature of trapping.

The origin of oil/aqueous inclusions in which the aqueous phase is completely enclosed within the oil phase is more problematical. These inclusions are indicative of 'oil-wet' as opposed to 'water-wet' conditions during entrapment. Though such conditions appear possible in natural petroleum reservoirs (Archer and Wall, 1986) it is difficult to imagine how primary oil-wet conditions could prevail during fluorite growth without contact of the crystal surface with aqueous brine, unless this oil was precipitating fluorite directly which seems unlikely. A more plausible explanation, compatible with the microthermometric data for secondary aqueous inclusions, is that the oil component of the inclusions is primary but the aqueous part was introduced later via small microfractures which traversed large primary oil inclusions (Fig. 2).

Indeed, microfractures containing trails of secondary aqueous inclusions are common in these fluorites. The cause of the reversal in wetting characteristics with time must therefore be due to surfactants in these later aqueous fluids. According to modern theory, both inorganic and organic compounds may markedly alter the surface properties of natural oils and bring about reversals in the shape of water–oil interfaces
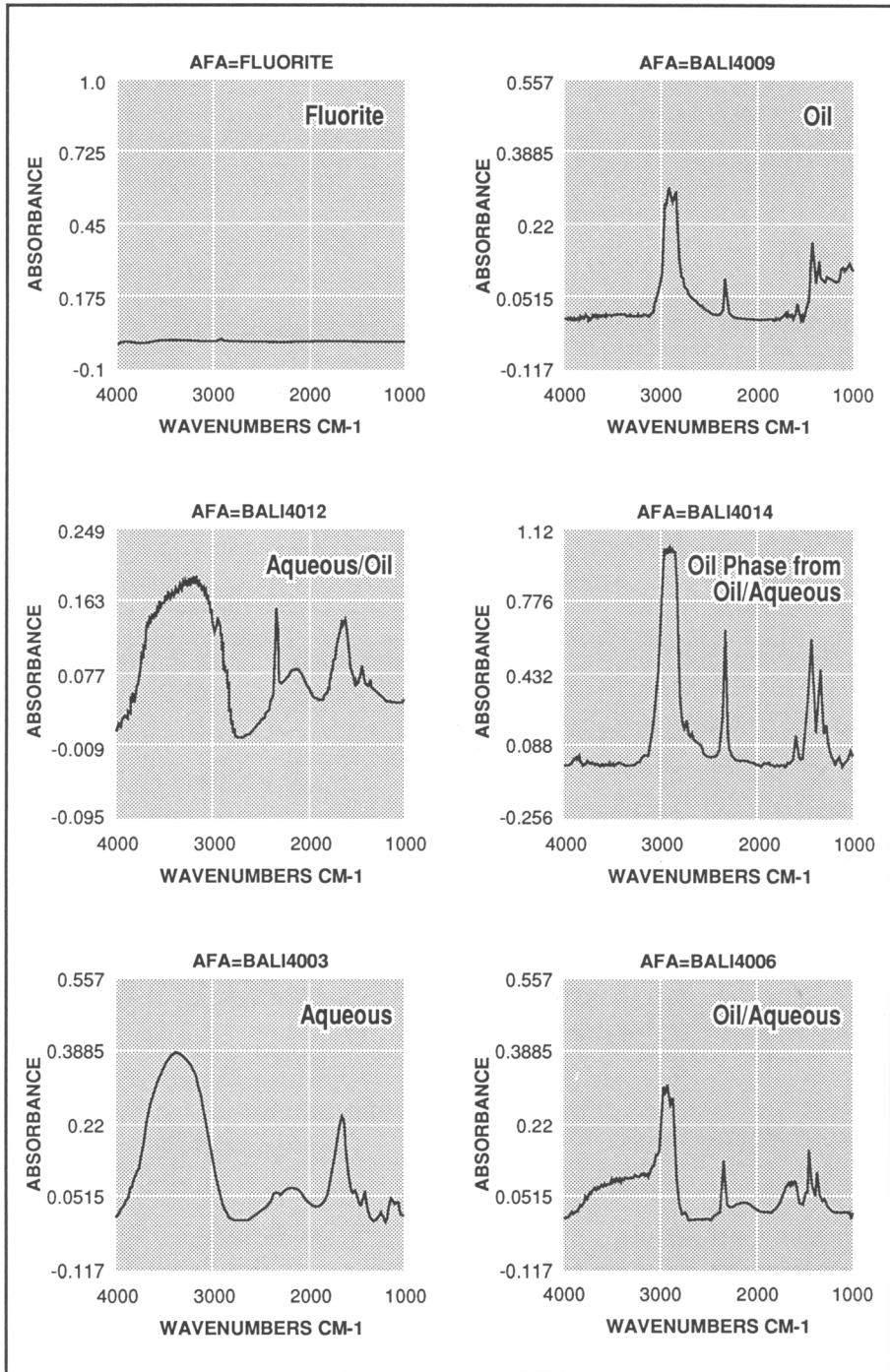
FIG. 3. FTIR spectra of the oil and aqueous phases in primary oil-bearing and aqueous inclusions in fluorite from Koh-e-Maran (see text for explanation).

(Sumner, 1954). So far the only major differences in chemistry between primary and secondary fluids are the increased salinity and elevated calcium and/or magnesium levels in the later fluids. Laboratory experiments (op. cit.) have shown that the addition or absence of inorganic salts can cause a reversal in the wetting characteristics of oil/water mixtures. However, this does not rule out the possibility that indicated traces of organic surfactants in the brine were responsible for this reversal in the inclusions from Koh-e-Maran fluorite.

Conclusions

Fluorite precipitation resulted from a dilute low-calcium–magnesium brine, around 110 °C, in the presence of an immiscible liquid hydrocarbon phase dominated by saturated, low-order aliphatic compounds. This 'oil' was probably present as an emulsion in the aqueous fluid, and the phenomenally large size of the inclusions is thought to reflect the large droplet size in the emulsion. The origin of this oil is, at present uncertain, especially in view of the dearth of aromatic and unsaturated hydrocarbons.

At a later stage the fluorite recrystallized in the presence of a more saline, calcium-enriched, homogeneous brine. Infiltration of this brine into pre-existing oil inclusions resulted in complex oil–water inclusions showing a reversal in the nature and shape of the oil–water interface due to the presence of unspecified, but probably inorganic (Ca^{2+}), surfactants in the brine which affected the wetting characteristics of the oil. To our knowledge this is the first detailed report of fluid inclusions indicative of oil-wet conditions in rocks. The homogenization temperatures and the presence of liquid hydrocarbon inclusions with similar compositions are characteristic of both MVT (Roedder, 1984) and 'manto-type' fluorite (Kesler, 1977) deposits in other parts of the world. However, the low salinities and low calcium contents of the primary fluids are atypical. It is interesting to speculate that the absence of lead and zinc from the Koh-e-Maran area is as much due to the poor metal-carrying potential of chloride-poor brines as availability of metals in the source region.

Acknowledgements

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