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PETROLEUM INCLUSIONS IN FLUORITE MVT-DEPOSITS: A REVIEW

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The presence of petroleum inclusions in fluorite of MVT deposits is well known and multiple documented. In this study, petroleum inclusions of the fluorite belt of Mexico are analysed and compared to the data from literature. Different types of inclusions have been observed at La Encantada district (Mexico, Gonzalez-Partida et al., 2002). In transmitted light there are many clear inclusions to observe, some inclusions with a brownish filling and the minority are dark opaque inclusions. These dark inclusions have irregular shapes and indicate decrepitation. Observations under UV light reveals the presence of dark to light blue fluorescent petroleum inclusions. All observed fluorite samples show only one fluorescence colour of the petroleum inclusions, which indicate the presence of one oil type. The aqueous inclusions have no fluorescence colour. Aqueous and petroleum inclusions are frequently associated together in planes and along fractures. The biggest inclusions are petroleum inclusions, which all exhibit a brownish-yellow liquid phase under transmitted light. The liquid oil phase contains numerous solid particles in dark brown to black colour. The inclusions observed are classified in three different types:

1. Two-phase petroleum inclusions, which are separated into a) spherical shaped petroleum inclusions and b) elongated petroleum inclusions; 2. two-phase aqueous inclusions; and 3. three-phase oil+water+gas inclusions (figure 1).

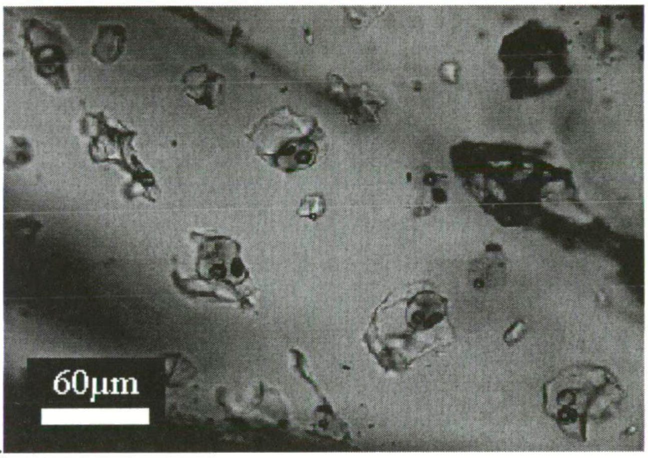

Figure 1. Water-oil-vapour inclusion (3 phases) in fluorite of La Encantada, Mexico.

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The Fv (vapour filling at 20°C), measured by CSLM (Confocal Scanning Laser Microscopy), is constant between 1 to 10%, but some exceptional inclusions have a Fv up to 40%. The group of spherical shaped petroleum inclusions has the largest amount of inclusions compared to the two other petroleum inclusion assemblages. The elongated inclusions are up to 50 μm long and 15 μm large with a mode length of 30 μm. The Fv, measured by CSLM, is constant between 1 to 10%. They appear grouped in trails and crystal planes, in some cases perpendicular to dark crystal cracks. The elongated assemblage has the smallest number of inclusions. The two-phase aqueous inclusions are present as many thousands of inclusions below 1 μm in diameter and in observable sizes of 5 μm, but as well in extreme cases up to 30 μm in diameter. All shape variations - round, negative crystal shape and irregular – are possible within this group. The roughly estimated Fv (<2%) of these inclusions is below the Fv of the petroleum inclusions. The three-phase inclusion group is represented by inclusions with very crazy irregular shapes of 15 μm in diameter as the median value. They are not bigger than 20 μm and not smaller than 3 μm. An inclusion of 15 μm has in the aqueous phase mostly a oil drop of 10 μm with an vapour bubble, whereas the Fv is 3 to 7% (CSLM measured).

The Th of all three types of petroleum inclusions range from 50 to 150°C with a mode located at 100°C. No phase transitions below 20°C have been observed for petroleum inclusions. Only one Tm of three-phase inclusions has been measured at -10.2°C, corresponding to salinity of the aqueous phase of 14.2 wt% NaCl equivalent. While the freezing experiments it was possible to observe that some three-phase inclusions decrepitated and changed their colour to dark opaque inclusions, comparable to other dark inclusions in the samples. The Th histogram of the aqueous inclusions is broad but shows only one mode centred at 120°C. Homogenisation temperatures of aqueous inclusions are generally higher than those of petroleum inclusions. The aqueous inclusions have two groups of different melting temperatures (about -10 and –5°C). The eutectic temperature (Te) of the aqueous inclusions lies between -39°C and –33°C and indicates the presence of different salt types (e.g. NaCl, $CaCl_2$, $MgCl_2$, $FeCl_2$).

Raman measurements of the aqueous inclusions from La Encantada show a dispersion of methane molalities from 0 to 0.1 with a maximum at 0.08 molal. The higher saline aqueous inclusions have various amounts of methane, whereas the less saline aqueous inclusions are rich of methane. No correlation is observed between Th and methane molalities. Raman spectra at Th show the presence of H_2S in significant concentrations. Raman spectroscopy has also been used to confirm the high chlorinity of the aqueous fluid and the presence of hydrohalite up to –25°C, which indicate that NaCl is the main salt type.

The data of the PIT modelled and FT-IR analysed oil composition are given in table 1. Black oils with remarkable CO_2 content, low CH_4 content, high water content dominate the fluids marked by the presence of three-phase (water+oil+gas) inclusions.

Table 1. Composition of petroleum inclusions measured by FT-IR and modelled by PIT compared to literature data.

FT-IR	Inclusion	this study:	a2 (Mexico)	a8 (Mexico)	Pironon et al. (2001):	1 (Illinois)	2 (Tunisia)
	$[CH_4]$mol%		25.0	20.6		26.3	15.1
	$[CO_2]$mol%		5.9	14.5		6.8	11.0
	[Alk]mol%		69.0	64.9		68.4	62.7
	$[CH_2/CH_3]$		7.1	8.0		4.3	6.1
PIT	$[CH_4]$mol%		17.8	18.1		18.0	16.0
	API (°)		14	17		-	-
	Th (°C)		83.9	111.0		112.6	110.1
	Fv %		5.5	9.8		9.0	9.5

Dark solid phases are frequently observed in same proportion in one generation of petroleum inclusions. Post-trapping events are responsible for the inclusion stretching and mark a thermal event probably induced by dolerite intrusion. A careful observation of the data published in other fluorite MVT deposits (e.g. Cave-in-Rock, Illinois and Tunisia in Pironon et al., 2001) shows singular similarities as shown in table 1. The oils are essentially heavy. Black oil is the dominant type with low methane content (<25 mole%). The petroleum inclusions have a characteristically phase behaviour marked by a homogenisation into the liquid phase and sometimes changes of viscosity during the cooling (Grimmer et al., 2003). Many authors observing petroleum inclusion of fluorite MVT deposits describe this behaviour (e.g. Roedder, 1976). CO_2 seems to be ubiquitous with concentrations varying from 1 to 15 mole% (Bouhlel et al., 1988; Guilhaumou et al., 2000; Souissi et al., 1997). Zheng & Liu (2000) show that short-chain carboxylates (-COOH) are common components in hydrothermal ore forming processes and oxidised oils have been recognised in fluorite from Hodna mountains in Algeria (Boutaleb et al., 1999). The presence of CO_2 and oxidised oils could be the results of the brine-oil interaction. This interaction is marked by the presence of brines that are enriched in CO_2, CH_4 and H_2S and of petroleum inclusions that are enriched in water and dark solids. Three-phase water-rich inclusions have been described by several authors (Blasch & Coveney, 1988; Rankin et al., 1990). The conditions of trapping of the oils are located between 160-180 bar and 100-120°C. The highest values of trapping temperature and pressure seem to be due to post-trapping thermal events. Up to now no data are published, where MVT deposits with fluorite mineralisations have volatile oils or gas condensates. This could indicate that transported oils over long distances, like the basinal fluids, are mainly black oils. The literature data and this study indicate that volatile oil or even gas condensates are not preserved, whereas black oils are trapped with aqueous phases. By consequence oils trapped in fluid inclusions from MVT deposits are the result of the migration of an organic basinal fluid on a long distance, which induces the alteration of the oil under oxidising conditions. CO_2 and oxidised organic products are generated and are sometimes associated with H_2S and N_2 (Touray, 1989). The aqueous inclusions seem to be at chemical equilibrium with the oils. The petroleum inclusions associated with aqueous inclusions allow us to precisely determine the P-T conditions of fluorite formation: pressure is around 180 bar and temperature is below 120°C (e.g. Cave-in-Rock, Illinois: 230 bar, 145°C in Guillaume et al., 2003). The post-trapping evolution of the inclusions shows that the MVT fluorite deposits are active systems with an intense hydrothermal activity marked by the presence of numerous magmatic intrusions.

Reference

BLASCH, S. R., COVENEY, R. M. (1988): Geochimica et Cosmochimica Acta, **52**, 1007-1017.

BOUHLEL, S., FORTUNÉ, J. P., GUILHAUMOU, N., TOURAY, J. C. (1988): Mineral. Deposita, **23**, 166-173.

BOUTALEB, A., PIRONON, J., AÏSSA, D. E., TOUAHRI, B. (1999): Terra Nostra 99/6 ECROFI XV Potsdam, abstract, 55-57.

GONZALEZ-PARTIDA, E., CARRILLO-CHAVEZ, A., GRIMMER, J. O. W., PIRONON, J. (2002): International Geological Review, **8**, 755-765.

GRIMMER, J. O. W., PIRONON, J., TEINTURIER, S. & MUTTERER, J. (2003): J. of Geochemical Exploration, accepted.

GUILHAUMOU, N. ELLOUZ, N., JASWAL, T. M., MOUGIN, P. (2000): Marine and Petroleum Geology, **17** (10), 1151-1164.

GUILLAUME, D., TEINTURIER, S., DUBESSY, J., PIRONON, J. (2003): Chemical Geology, **194**, 41-49.

PIRONON, J., THIERY, R., AYT OUGOUDAL, M., TEINTURIER, S., BEAUDOIN, G. & WALGENWITZ, F. (2001): Geofluids, **1**, 2-10.

RANKIN, A. H., HODGE, B. L., MOSER, M. (1990): Mineralogical magazine, **54**, 335-342.

ROEDDER, E. (1976): Handbook on Strata-bound and Stratiform Ore Deposits, Volume **2**, Elsevier, Amsterdam, 67-110.

SOUISSI, F., DANDURAND, J. L., FORTUNÉ, J. P. (1997): Mineralium Deposita, **32**, 257-270.

TOURAY, J.-C. (1989): Chron. rech. min., **495**, 21-30.

ZHENG, Y., LIU, J. (2000): Applied Geochemistry, **15**, 13-25.