LA-ICP-MS analysis of trace metals in hydrocarbon fluid inclusions associated with ore deposits.

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The characteristics of low temperature MVT style mineralization are well established. The nature and source of the fluids and more recently the metal carrying capacity have been determined using LA-ICP-MS. As well as the high salinity metal carrying brines, found in these and similar types of sedimentary deposits, there is frequently an association with hydrocarbons. Hydrocarbon fluid inclusions are often described associated with ore deposits but few data are available and usually only concern the homogenization temperature, gas content and composition of the organic components (Gonzales-Partida et al., 2003).

The aim of this work is to develop LA-ICP-MS analysis of hydrocarbon fluid inclusions from different ore deposits and to determine their metal content. Organic matter may play an important role in the deposition of metals by acting as a reductant and in metal transport by forming organo-metallic complexes (Parnell, 1988). The initial tests were carried out on synthetic oil standards where the metal content is known, in order to determine the analytical conditions for the instrumentation and the reproducibility of the procedure. Subsequently, natural production oils were analysed in capillaries to validate the method and to compare with the data obtained from conventional methods of oil analysis in the literature. Finally, hydrocarbon fluid inclusions (Fig.1) and organic matter from different low temperature and MVT ore deposits have been studied.

The samples come from different locations [Asturias (Spain), Bou Jaber and Hammam Zriba (Tunisia), Encantada-Buenavista (Mexico), Jbel Tirremi and El Hammam (Morocco), North German basin, Annabel Lee mine, Tri-state MVT district (USA)] where fluorite or lead-zinc occurrences are recognized as vein and stratabound bodies. These deposits all have an association with oil or gas fields. In each, fluid inclusion studies reveals aqueous and hydrocarbon inclusions with low- homogenization temperatures (around 150°C), high salinities (>15 eq mass% NaCl) and with the general characteristics of MVT deposits as reported by Roedder (1984) and Leach and al. (2005).

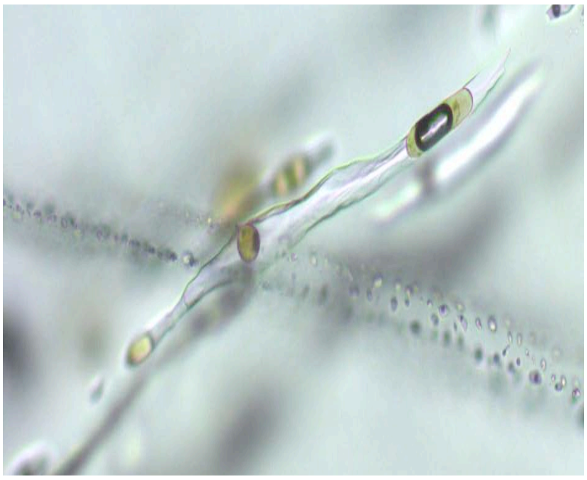

Fig. 1: Fluid inclusions with oil droplets in fluorite from Mexico.

The LA-ICP-MS system used at the University of Leeds and Nancy consists of a GeoLas Pro ArF pulsed 193 nm excimer laser system coupled with an Agilent 7500c series quadrupole mass spectrometer. For the calibration, synthetic oils (CONOSTAN 100 and 500) sealed in capillaries were used. These have been doped with the twenty-two elements chosen for the analysis, ^{11}B, ^{12}C, ^{13}C, ^{23}Na, ^{27}Al, ^{29}Si, ^{31}P, ^{34}S, ^{47}Ti, ^{51}V, ^{53}Cr, ^{55}Mn, ^{57}Fe, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{95}Mo, ^{107}Ag, ^{111}Cd, ^{118}Sn, ^{208}Pb, ^{238}U, at concentrations of 100 and 500 ppm.

The natural crude oils have metal concentrations varying from a few ppm to several hundred ppm depending on element and the origin of the oil. Two elements Ni and V tend to dominate with concentrations similar to those described in the literature for oil from the same regions of the world e.g. several hundreds of ppm for V and Ni and less than twenty ppm for other trace metals (Tissot and Welte, 1984; Royston, 1994). In addition the metal concentration shows a good positive correlation with the sulphur concentration. Finally, for multiple analyses of each sample the V/Ni oil ratio is constant but as might be expected, distinctly different between the different oils from different locations.

The hydrocarbon inclusions from ore deposits contain higher metal concentrations (for all metals) than those measured in the crude natural oils, where there is no associated ore mineralization (Fig.2). However, the sulphur concentration shows no real difference between the two sets of oils (Fig.3). Nickel and Vanadium are no longer the dominant metals in the inclusions, Instead the metals with the highest concentrations are iron, zinc, copper, lead (up to several hundreds of ppm).

Some of the hydrocarbon inclusions from ore deposits show some unusual and interesting results. Hydrocarbon inclusions from the North German Basin have silver concentrations ranging from 100 to 800 ppm with a mean value around 300 ppm which is distinctly different to the other deposits. However in this region there are well known silver deposits and it would appear hydrocarbons have played a part in the mineralization.

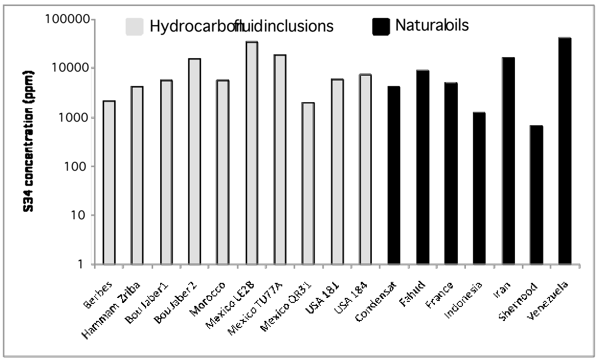

Fig. 2: Average concentrations of ^{34}S obtained from hydrocarbon inclusions from different ore deposits and from crude oils, by LA-ICP-MS.

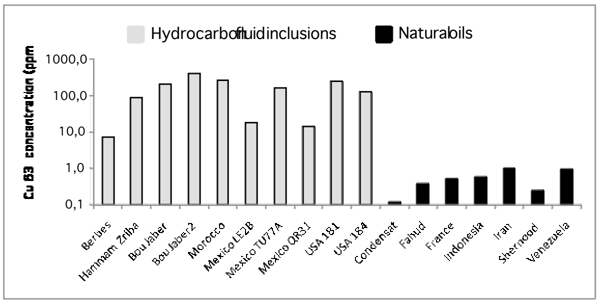

Fig. 3: Mean concentrations in ^{63}Cu obtained on hydrocarbon inclusions from the different deposits and from crude oils, by LA-ICP-MS.

This study shows how the use of LA-ICP-MS for the analysis of hydrocarbon inclusions especially the quantification of S and the metal content for MVT ore deposits can produce valid and reproducible data. The study reveals some interesting implications of the presence of organic components in the formations of low temperature ore deposits. We have shown there to be differences in the metal concentration of oil from production reservoirs and oil associated with mineralization. Our analyses oils from petroleum basins conforms to the expected concentrations for each region, but the metal concentrations in ore-related oils is up to twenty times higher.

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