

## ABLATIVE LASER DEPTH-PROFILING (ICP-MS) OF RESERVOIR CORES TO EVALUATE HOMOGENEITY OF STRONTIUM AND BARIUM DISTRIBUTIONS LINKED TO SCALE DEPOSITION – PART 1

\*AE Pillay<sup>1</sup>, B Ghosh<sup>2</sup>, B Senthilmurugan<sup>2</sup>, S Stephen<sup>1</sup> and A Abd-Elhameed<sup>1</sup>

<sup>1</sup> Department of Chemistry, <sup>2</sup> Department of Petroleum Engineering,  
The Petroleum Institute, PO Box 2533, Abu Dhabi, UAE

### ABSTRACT

The thrust of this work demonstrates the unique capability of laser depth-profiling to ‘peer’ within reservoir cores and reveal anomalies and irregularities associated with sulphate scale deposition. The intrinsic behavior of scale deposition within the pore space of near wellbore formation rock is relatively unexplored, and the essence of this paper concerns the application of an ablative laser technique to study the uniformity of strontium and barium distributions in suitable oil producing reservoir core sections. Information on the spatial and depth distributions of these metal components in side-well core slivers could provide an insight into the location of relevant scale deposits, particularly barium and strontium sulphates. Nucleation and growth on the surface could indicate potentially favorable conditions for precipitation. On the other hand, sporadic ingrained deposits would signal abrupt changes in compositional or physical conditions within the specimen. The investigation was divided into two parts: (i) continuous ‘drilling’ by the laser at random points to uncover metal distribution at successive depths; and (ii) iterative surface scans at randomly selected areas to evaluate compositional consistency. The laser was attached to a high resolution ICP-MS instrument, and irradiations were conducted with a 213-nm beam of 30% total energy and 100 μm diameter. Following iterative surface scanning, the laser ablated a total depth of 50 μm at 10 μm-intervals at each point. The study was largely semi-quantitative in the absence of standardization. Characteristic intensities originating from the metals of interest were measured. The experimental results showed distinct inhomogeneity in the distribution of Sr and Ba – declining sharply to negligible levels in some cases, and occurring sporadically at specific depths. Some data revealed that these deposits were markedly absent from some points in the core fragments, distinctly suggesting that specific conditions in the rock matrix are necessary to influence scale formation. The exact mechanism for this irregular behavior is not clear at this stage, and has considerable scope for extended research, including modeling studies. This work is of definite interest to geophysicists and petroleum scientists.

**Keywords:** Strontium, barium, scale-formation, laser ablation, ICP-MS.

### INTRODUCTION

Barium and strontium sulphate scale deposition is a common problem in hydrocarbon producing wells/reservoirs. Seawater (relatively abundant in sulphates) is injected into these reservoirs for pressure maintenance, and co-mingles with formation brines that contain appreciable levels of barium and strontium. Scale formation near wellbore locations is accelerated because of significant and favorable changes of pressure and temperature at these locations (Bamidele *et al.*, 2009; Jamailahmadi and Muller-Steinhagen, 2008; Merdah and Yassin, 2007; Ohen *et al.*, 2004; Shen and Crosby, 1983; Vetter *et al.*, 1982). Progressive and undesirable congestion by scale deposits tend to reduce the production of oil and gas. The distribution of these deposits in the pore space and pore throats of reservoir rock could provide valuable clues to the mechanism of scale formation and the conditions that exist (Ohen *et al.*, 2004). Our group has developed an ultrasensitive

technique for assessing the distribution of minor metals in reservoir rock samples (that are linked to scale deposits); and pinpointing areas on the surfaces of such rock cores to study spatial dispersion of these metals. Laser ablation depth-profiling (ICP-MS) has the capability of ‘drilling’ through a core-plug and obtaining relevant information on the distribution of scale deposits. The laser itself is linked to a high-performance ICP-MS instrument. The technique is semi-quantitative and capable of high-resolution detection over a wide range of elemental levels (Jamailahmadi and Muller-Steinhagen, 2008; Jarvis *et al.*, 1992; Ohen *et al.*, 2004; Robinson *et al.*, 2005; Skelley-Frame *et al.*, 1998; Ward, 2000). Very few contemporary instrumental methods have the capability to study metal intensity with depth. X-ray methods are useful, but lack the ability to control depth penetration. Nuclear particle irradiation, SEM, SIMS and XPS are equally useful, but such techniques tend to be limited to only a few microns below the surface (Robinson *et al.*, 2005). The competence, therefore, of the laser approach to delve to discreet depths below the surface of a sample is attractive for homogeneity studies in bulk materials.

\*Corresponding author email: apillay@pi.ac.ae

The aim of this work was to explore the potential of ablative laser technology to rapidly track the profiles of barium and strontium in side-well core sections to examine the uniformity of (sulphate) deposits linked to these elements.

## MATERIALS AND METHODS

### Instrumentation / Sample handling

Laser ablation technology (coupled to ICP-MS) uses a micro-beam to ablate samples in a special sample chamber (Fig. 1) (Li and Anderson, 2006; Robinson *et al.*, 2005; Skelley-Frame *et al.*, 1998). The fine ablated material is transported to a hot plasma where it is atomized and converted to ions (characteristic of the elements of the sample), which are subsequently carried to a mass spectrometer for detection. The technique is highly sensitive and can attain a limit of detection of  $10^{-6}$  mg/kg (parts per trillion) for most elements (Skelley-Frame *et al.*, 1998; Ward, 2000). Laser ablation technology is capable of depth and surface analysis, displays the elemental intensities in proportion to their levels, and produces an elemental profile.

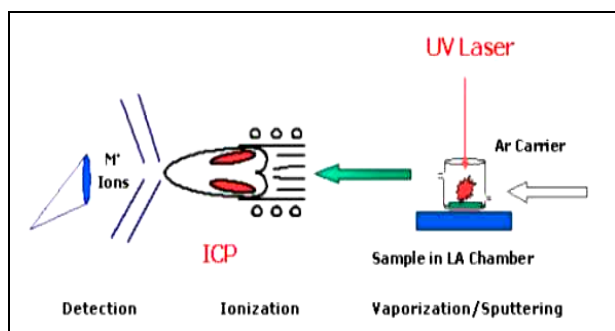


Fig. 1. A schematic of the laser ablation (LA) technique (taken from reference Li and Anderson, 2006).

A side-well core plug (from side-wall coring) containing embedded scale deposits, and collected from a limestone reservoir in the Arabian Gulf region, was slivered with a diamond cutter to produce sections and fragments that were adequate for irradiation (Fig. 2). Specimens were suitably labeled and random points on the top and bottom surfaces were examined with the laser. No serious sample treatment was necessary prior to irradiation. Samples were investigated with a Perkin Elmer SCIEX DRC-e ICP-MS fitted with a New Wave UP-213 laser ablation system. The core-sections were placed in a special sample holder with dimensions 5cm x 5cm. Samples were subjected to 213-nm laser irradiation; the level of the beam energy was 30%, with a beam diameter of 100 $\mu$ m. The laser gas flow was 0.80 L/min. It was programmed to continuously ablate successive depths of 10 $\mu$ m at each point and 'drilled' through the sample to a depth of 50 $\mu$ m. Depth-profiling spectra were recorded for each measurement.



Fig. 2. Cross-sections of core plugs used in this investigation.

### Spectral analysis

Characteristic intensities originating from the metals of interest were measured; and valid considerations were given to potential interferences and matrix effects. Prior to each run, the instrument underwent appropriate calibration and correction for background (Robinson *et al.*, 2005; Jarvis *et al.*, 1992). The study was largely semi-quantitative in the absence of standardization, and for the purposes of comparison, all measurements were conducted under identical experimental conditions. Signal intensities were compared with surface metals and those occurring in the bulk of the sample; and appropriate spectra were produced to observe fluctuations in characteristic metal intensity spatially and with penetration depth. Spatial studies can reveal irregularities by measuring the elemental composition at different points on the surface. Depth profiling has the potential of providing information on the homogeneity of distributions below the surface. Thus detailed analysis of different spots on the sample could provide a valuable insight into the mechanism of scale formation (Ohen *et al.*, 2004).

### Validation of the technique

Solid standards of matching matrix are generally not available, and the only recourse to validating the analytical performance of the laser technique was to examine an available certified standard, which in our case was a glass bead (NIST, Certificate 613). Repeatability studies with the laser could be affected by accumulation of debris in the crater formed by the laser. This effect is not particularly marked, but its extent has not been established and wider studies are needed to determine exactly how pronounced it is. In addition, imperfect beam spots due to slight perturbations in focusing could lead to significant scatter in the results (Robinson *et al.*, 2005). We originally examined the typical analytical performance of the instrument for different isotopes by

Table 1. Typical analytical performance of the ICP-MS as shown by reproducibility measurements (counts/sec) in a NIST 613 glass standard.

Measurement	<sup>59</sup> Co	<sup>85</sup> Rb	<sup>88</sup> Sr	<sup>138</sup> Ba	<sup>140</sup> Ce	<sup>238</sup> U
1	503	718	3688	1618	1023	1805
2	511	736	3672	1624	1141	1814
3	491	735	3587	1620	1036	1792
Mean + RSD	502 ± 1.6%	730 ± 1.1%	3649 ± 1.2%	1621 ± 0.15%	1067 ± 4.95%	1804 ± 0.50%

taking replicate measurements (n = 3) for equivalent counting times at random points on the glass standard. Relative standard deviations of less than 5% were attained (Table 1) indicating that the characteristic performance of the facility was acceptable.

## RESULTS AND DISCUSSION

### Depth profiling

Laser depth-penetration studies of several core-fragments (core-sections) were undertaken, and typical depth-profiling plots to illustrate the salient features of the investigation appear in figures 3-6. Typical Ba spectra of a suitable fragment appear in figure 3. Each spectrum represents a random point on the same core-section. The laser 'drilled' from the surface into the core. Clearly, the general trend shows that in each spectrum a similar pattern emerges where strong barium peaks occur roughly at a depth of 10µm followed by no deposits up to a depth of about 40µm; and then between 40 and 50µm, deposits are again present. This formation is irregular and could be attributed to general conditions within the core matrix and pore distribution pattern. The data seem to suggest that suitable conditions prevail at certain points (possibly pore spaces) to induce Ba precipitation. This indicates that at significant locations in the interior of the core-section conditions for formation of Ba deposits appear favorable; supporting the view that sporadic distribution of pore spaces could be largely responsible for this. Obviously, such scale formation is invariably linked to chemical composition and temperature oscillations (Bamidele *et al.*, 2009; Shen and Crosby, 1983; Vetter *et al.*, 1982), and clearly precipitation will occur if conditions support a shift in chemical equilibrium towards solid formation - which seems to be prevalent at particular sites in the core-section.

In the case of Sr, typical depth-profiling spectra of the same core fragment (Fig. 4) clearly show that Sr deposits tend to be more prolific (than Ba), when compared to the barium plot in figure 3. Here again, each spectrum represents a random point on the core-section. The experimental results (Fig. 4) indicate that Sr scales precipitate intermittently, and such formations tend to fade and re-occur at different points in the interior. The experimental data suggest that favorable conditions are

replicated at different depths within the core. This finding is interesting from the perspective that if particular conditions of temperature and concentrations fluctuate randomly, the conditions at the low points in the spectra could possibly be mimicked to minimize Sr scale deposition (Bamidele *et al.*, 2009). Undoubtedly, replication of the conditions linked to the gaps in the spectra in figure 4 would represent circumstances where Sr deposits are reluctant to form. If the physical (and possibly chemical) conditions of the low points in the spectra could be simulated on a lab-scale, a deeper insight into inhibiting Sr scale formation could be gained (Ohen *et al.*, 2004; Shen and Crosby, 1983; Vetter *et al.*, 1982).

### Deposition trends

It was of interest to know how the elemental profiles would change with the examination of different core fragments. Laser study of another fragment (Fig. 5) delineated a trend which tends to corroborate the view that particular conditions exist intermittently in the core that favor Ba scale formation. The data in the spectrum support the view that circumstances at specific locations induce Ba scale deposition. Inspection of figure 5 shows that Ba is prominent initially in the first 10µm, then fades and re-appears around a depth of 40µm. This trend could provide clues to establish the mechanism of Ba scale formation in reservoir rock. The results imply that certain physical conditions, such as temperature (Bamidele *et al.*, 2009), within the core could be favorable for preventing deposition of Ba scales. This is evident from the gaps in the spectrum (which resemble the gaps in figure 3). An extended study would be to simulate these conditions by flooding virgin cores in a lab study with scale-forming solutions to examine deposition trends.

As regards Sr, the experimental evidence indicates that conditions for scale-formation in the core samples are more favorable than those for Ba, but are irregular and tend to vary. Figure 6 represents laser penetration of a third core fragment, at two randomly selected points (shown in the figure as two independent spectra). The intensities of the Sr peaks in the first 10 µm of the depth-profiling spectra (Fig. 6) are not as pronounced as we progress with depth. The trends in both spectra are somewhat consistent (but differ from those in Fig. 4), suggesting that Sr deposits fluctuate in accordance with

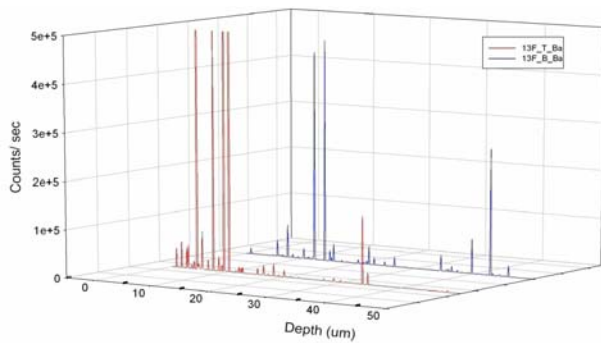


Fig. 3. Depth-profiling plots of Ba (core-fragment #1). Each spectrum represents a random point.

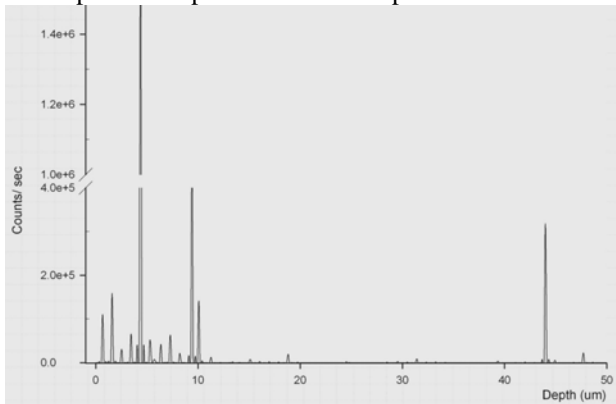


Fig. 5. Interior profile of Ba (core-fragment #2).

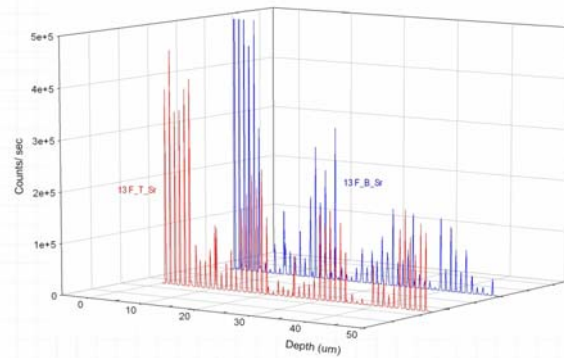


Fig. 4. Depth-profiling plots of Sr (core-fragment #1). Each spectrum represents a random point.

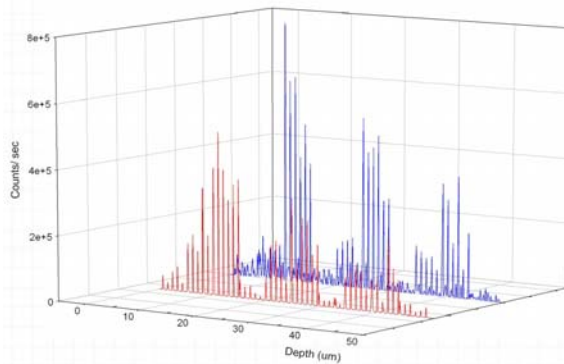


Fig. 6. Interior profile of Sr (core-fragment #3).

circumstances in the core. Unlike Ba, no big gaps appear in the Sr spectra, which proclaim that conditions for Ba and Sr scale deposition differ (as expected). It should be underscored that oscillating conditions in the interior of reservoir rocks are linked to fluctuations in compositional and temperature conditions, which in turn could be affected by permeability, mineral composition and fractures within the matrix structure. Our research represents an indirect method of gaining some insight into changes in physical conditions within the core. These are evident from the abrupt changes in the spectra.

### Impact of our findings

The data in figures 3-6 delineate significant 'gaps' in the spectra which suggest that at these points Ba and Sr deposits were absent. Clearly, these gaps further purport that the conditions for Ba/Sr scale formations at such points in the specimen were not favorable and that either (or both) the concentrations of the scale-forming ions were not adequately elevated to exceed the solubility product (and thus precipitate) or the temperature at these points were not conducive to scale formation (Bamidele *et al.*, 2009). Clearly two of the most significant factors that would encourage deposition are favorable compositional and temperature conditions; and as stated above these factors are linked to features of the core itself. For example, the dramatic appearance of peaks following a

lengthy hiatus in some of the Ba depth-profiling spectra in figures 3 and 5 proclaim that either the laser struck a random crystal of barium, or conditions abruptly changed in the pore spaces and were suddenly favorable for deposition to occur. This further suggests that the interior of the core is possibly prone to sudden cooling and heating (Vetter *et al.*, 1982). What brings about these perturbations in temperature is not clear, but it is feasible that voids or the intrinsic characteristic of minerals in the core itself could contribute to such perturbations (Vetter *et al.*, 1982). On the other hand, 'bottlenecks' inside the core could affect permeability and create the opportunity for scale-forming ions to 'conglomerate' thus exceeding their solubility properties. Based on this study a robust invasive treatment of core plugs could be devised to unblock the pore spaces, and the samples re-examined with the laser.

Our observations revealed that the frequency of gaps in the Ba spectra are more pronounced than in the Sr spectra, indicating that strontium salts are more 'prone' to scale-formation, which would partially account for the more 'prolific' nature of the Sr spectra. A point to note is that the bulk of the core is comprised of calcite as the matrix material with 'voidages' or pore spaces dispersed sporadically (Ohen *et al.*, 2004). Ostensibly, the gaps in the Ba spectra (Figs. 3 and 5) suggest that most of the Ba

precipitation occurred in these sporadic pore spaces – whose dimensions seem difficult to quantify from the spectra themselves - whereas deposition of Sr occurred along with the bulk material (calcite). This observation purports that strontium deposition could be linked to a primary deposition process together with the bulk calcite, whilst Ba deposition is related to a secondary process, largely influenced by conditions in the pore throats and composition of the fluid flow through the porous media. It is also possible that Sr compounds being less bulky than equivalent Ba salts have the advantage of leaching through the calcite matrix - deduced by the abundance of peaks in the Sr spectra (Figs. 4 and 6). Ba deposits, on the other hand, tend to be ensconced in the pore space and less prone to leaching. Accumulated data could be useful for modeling studies (Ohen *et al.*, 2004).

## CONCLUSIONS

High resolution laser technology has the capability of delineating surface and depth distributions of Ba and Sr in core matrices. It appears that such distributions would depend on several variables such as temperature and chemical concentrations; as well as features such as permeability and mineral composition of the cores. It is not clear at this stage whether these distributions could be treated mathematically and modeled. In the case of all distributions we observed varying trends, indicating that applying modeling statistics to these distributions would be complex. In some cases depth-distributions revealed lack of Ba and Sr scale, whereas in other cases the opposite was observed. It would definitely be useful to implement laser technology more widely for modeling purposes and this particular aspect could be a suitable extension to our study.

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