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APPLICATION OF ABLATIVE LASER DEPTH-PROFILING (ICP-MS) TO PROBE DIAGENETIC INFORMATION LINKED TO SECONDARY MINERAL DEPOSITION IN CARBONATE RESERVOIR ROCK – PART 2

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ABSTRACT

Laser depth-profiling is a valuable tool for unraveling the complexities of subterranean diagenetic processes and post-depositional change associated with carbonate reservoirs. Core fragments were subjected to high-performance ICP-MS laser irradiation (213nm) at several ablation points to depths of 50µm at 10µm intervals. The method is convenient and adequately competent to study diagenetic phenomena of carbonates. It is capable of estimating the dimensions of pore spaces and grain-size distribution in carbonate reservoir rock and shedding light on sedimentary dolomitic-limestone trends within the matrix. Spectral evidence of secondary deposition and co-habitation of strontium and iron due to secondary fluid inclusions was observed at matrix grain boundaries. The application was successful in exploring the internal microstructure of carbonate cores and providing clues linked to certain aspects of pore sizes. The study is of relevance to geologists, reservoir engineers and petro-physicists and can be useful in geostatistical modeling and simulation.

Keywords: Diagenesis, laser ablation, ICP-MS, mineral-deposition, carbonate-rock.

INTRODUCTION

Carbonate oil fields can be generally classified into sedimentary limestone [calcium carbonate/calcite, $CaCO_3$] and dolomite [calcium-magnesium carbonate, $CaMg(CO_3)_2$] reservoirs. Limestone that is partially replaced by dolomite is referred to as dolomitic limestone or magnesian limestone. Carbonate sediments are mostly biological in origin and their features (grain size and sorting) depend largely on the population of the subsisting organism. Intense primeval chemical reactivity of carbonates led to early diagenesis, dissolution and cementation under the influence of meteoric water, pressure and temperature which jointly resulted in complexities in pore type and structure (Pedersen, 1993; Stewart *et al*., 2000; Wilkinson and Haszeldine, 1998). Unraveling and interpreting such complexities is remarkably challenging and forms the basis of understanding fluid flow through porous media (Pedersen and Bjorlykke, 1994; Mclimans, 1987; Haszeldine *et al*., 2000). The pore fluid itself comprises multiple chemical components which intermittently precipitate and re-dissolve under certain conditions of temperature and pressure. The analysis of embedded elements linked to minerals and salts in host rock matrices gives useful information on the diagenetic characteristics of oil-bearing reservoir rocks and also provides significant details on the conditions of mineral growth. Some chemical compounds such as strontium and iron bearing salts enter the calcite matrix through secondary fluid inclusions. Therefore, a detailed knowledge of fluid inclusion chemistry would be helpful to develop sustainable petrophysical models for inveterate rock deposits (Pedersen and Bjorlykke, 1994; Haszeldine *et al*., 2000). Often inclusions are filled with aqueous fluids and brine laden with low-solubility minerals and salts (containing metals such as Mg, Sr, Fe, Ba) that deposit as secondary sediments under favorable physical and chemical conditions deep within the rock itself (Pedersen, 1993). Of significance is that the diagenesis process in carbonate systems tend to occur mainly in two major realms: shallow water and normal marine diagenetic environments (Stewart *et al*., 2000; Wilkinson and Haszeldine, 1998). Generally, meteoric water is strongly acidic and understaurated with $CaCO_3$, and thus has the capacity to dissolve carbonates and cause precipitation elsewhere. This sediment-water reaction also leads to precipitation of metal impregnated salts which provide important clues to diagenetic phenomena linked to meteoric water environments (Touret, 2001).

Depth profiling of reservoir cores by laser ablation ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) is fast emerging as a useful contemporary tool for extracting valuable information on diagenetic phenomena and internal elemental profiles (Sunderlin, 2009). The application uses a micro-beam to ablate samples in a special sample chamber. The fine ablated material is

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rapidly transported to hot plasma by a carrier gas (argon). The extremely high temperature of the plasma (about 10,000K) separates the sample into individual atoms, which are ionized ($M \rightarrow M^+ + e$-) and detected by the mass spectrometer. The technique is highly sensitive and can attain a limit of detection in the parts per trillion range (10^{-6} mg/kg) for most elements. Due to its superior sensitivity, LA-ICP-MS has gained popularity in mineralogical and ore analysis and has been reported to be faster and more accurate than most other techniques. The aim of our work, therefore, was to explore the potential of ablative laser technology to rapidly track specific elemental profiles (magnesium, iron and strontium) within carbonate core sections and examine diagenetic phenomena and post-depositional trends linked to these elements.

MATERIALS AND METHODS

Instrumentation / Sample handling

Samples were investigated with a Perkin Elmer SCIEX DRC-e ICP-MS fitted with a New Wave UP-213 laser ablation system. Core fragments (Fig. 1) were subjected to 213-nm laser irradiation at random points on each sample. The level of the beam energy was 30%, with a fluence of approximately 3 J/cm^2 and beam diameter of 100µm. The laser was programmed to ablate a depth of 10µm at each point and repeatedly scanned the surface, recording measurements after each ablation to a total depth of 50µm. The study was largely semi-quantitative in the absence of standardization, and for comparative purposes all measurements were conducted under identical experimental conditions. Prior to each run the instrument underwent appropriate calibration (certification) and correction for background (Jarvis *et al*., 1992; Robinson *et al*., 2005). Depth-profiling spectra were recorded for each measurement. It is necessary to underscore that in the absence of matching-matrix standards our method was based on evaluating relative intensities (counts/sec) for purposes of comparison. Further details of sampling and instrumentation are reported elsewhere (Pillay *et al*., 2010).

RESULTS AND DISCUSSION

Diagenesis and reservoir rock

Diagenesis of sedimentary rock is a series of post-depositional processes involving marked physical and chemical transformation of sedimentary rock over a period of time (Pedersen, 1993; Wilkinson and Haszeldine, 1998). Compacted sediments formed from primeval precipitation (deposition) from subterranean streams and salty water can undergo post-depositional change (or diagenesis) resulting in the blockage of pores and pore throats. Figure 2 represents a cross-section of a typical sedimentary rock fragment showing the fundamental components and features within the structure (Petr, 2009). Such rock must be both permeable and porous to permit passage of the fluids. It comprises outlying cementitious areas (where chemicals form), sedimentary clays, compacted fossils and pore spaces usually filled with brine (fluid inclusions). Diagenesis linked to reservoir rock is of significance because it tends to decrease the porosity of the rock and reduces the volume of hydrocarbons that it can hold (Mclimans, 1987; Wilkinson and Haszeldine, 1998). A good example is the precipitation of magnesite ($MgCO_3$) from underground brine and subsurface fluid that blocks the pores, thus restricting the flow of petroleum through the rock. A diagenetic change like this also leads to entrapment of magnesium inside the calcite lattice through fluid incursions. In addition, certain compounds originating from Paleolithic fossils could be incorporated as part of the calcite deposition, creating agglomerates that gradually fill the porous regions (Saigal *et al*., 1992). Petrologists study the permeability of source rock and are concerned with physical and chemical changes in the rock environment that produce irregular dissolution and deposition processes that limit permeability. Laser depth profiling of subsurface cores provides valuable evidence of diagenetic changes of this nature, which could be ultimately linked to petroleum production.

Pore spaces, grain boundaries and secondary deposition

Depth profiling is capable of estimating the dimensions of ensconced pore spaces and providing an insight into secondary deposition processes. Typical depth-profiling plots of several core fragments depicting significant features of the study appear in figures 3 to 6 Each figure represents Mg, Sr and Fe spectra superimposed on a Ca spectrum (to identify their position on the matrix structure) taken from a common ablation point on the same core-section. The blue spectra in each figure represent the Ca substrate ($CaCO_3$) and the red spectra correspond to Mg, Sr and Fe intensities (originating from relevant deposits). The penetration of the laser 50 µm from the irradiated surface into the core produced fluctuating elemental intensities that are clearly visible in figures 3 to 6. The recorded spectra portray strong, medium and weak peaks of the metals of interest interspersed by significant breaks or gaps in between the lines corresponding roughly to depths of 5µm in most cases. Prominent Ca lines suggest the impact of the laser into the heart of a calcite grain, whereas diminished Ca lines could reflect grain boundaries (Haszeldine *et al*., 2000). These features are clearly seen in figures 3A to 6A where the general trend depicts a pattern of strong and intermediate Ca lines at a depth of 5µm from the irradiated surface or at the surface itself. Subsequent Ca peaks appear at recurring depths of about 3-10µm representing calcite grains followed by spectral voids of roughly 5µm reflecting inter-granular pore spaces (primary porosity – Fig. 2) (Chaika, 2000). These spectral voids corresponding to diminished Ca intensities seem to be fairly uniform indicating homogeneous pore size distribution (especially prominent in Figs. 4A and 5A). Spectral voids < 5µm could be ascribed to minor intra-granular pore spaces (secondary porosity – Fig. 2). The intrinsic variation of the spectral features is expected and is due to irregularity of grain size generally encountered in limestone rock. It could also be due to the possibility of the laser beam passing through the edge of some of the grains (see Fig. 2). Superimposition of Mg spectra on Ca spectra (Figs. 3A to 6A) delineate concomitant occurrence of Mg and Ca distinctly suggesting the presence of Mg within the calcite grain. This phenomenon further suggests that during the diagenetic process sedimentary dolomitic limestones possibly originated during magnesian calcite dissolution, followed by calcite and dolomite precipitation reactions (Wilkinson and Haszeldine, 1998). Alternatively, these dolomitic limestones could have resulted from the dissolution and subsequent deposition of calcium carbonate precursors in the presence of magnesium ions. Peaks representing Mg at the origin of the relevant spectra (corresponding to 0-5µm depth in figures 3A to 6A) were identified as part of the Ca grain boundary; while other Mg peaks appearing in the spaces where Ca was almost absent were ascribed to entrapment in the calcite lattice (Saigal, 1992). These

Fig. 1. Fragments of core plugs used in investigation.

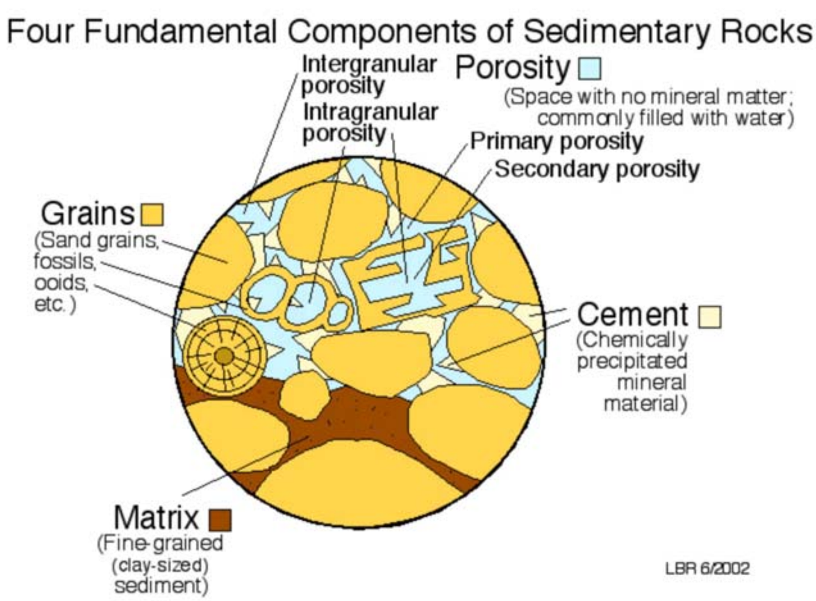

Fig. 2. The fundamental micro-features of a rock fragment.

deposits could be attributed to potential secondary deposition processes in the presence of fluid inclusions and incursions.

Fluid inclusions and co-deposition

One form of diagenetic change arises when the calcite matrix is overlaid with Sr and Fe deposits originating from fossils and fluid inclusions rich in aquifer brine containing these elements. In subterranean environments it is well known that certain physical and chemical conditions exist within reservoir rock that lead to precipitation of metal salts with low solubilities (such as $SrSO_4$ and $Fe(OH)_3$), and formation of post-depositional layers on the primeval calcite matrix (Wilkinson and Haszeldine, 1998). More than one metal salt can co-precipitate this way and a study of our experimental data revealed evidence of co-deposition. Typical depth-profiling spectra of Sr and Fe, (Figs. 3B, 4B, 6B & 3C, 4C, 6C) clearly show that Sr deposits tend to be more prolific in the pore area where Ca is virtually absent. It is reasonable to assume that this phenomenon is related to post-depositional growths from fluid inclusions rich in Sr

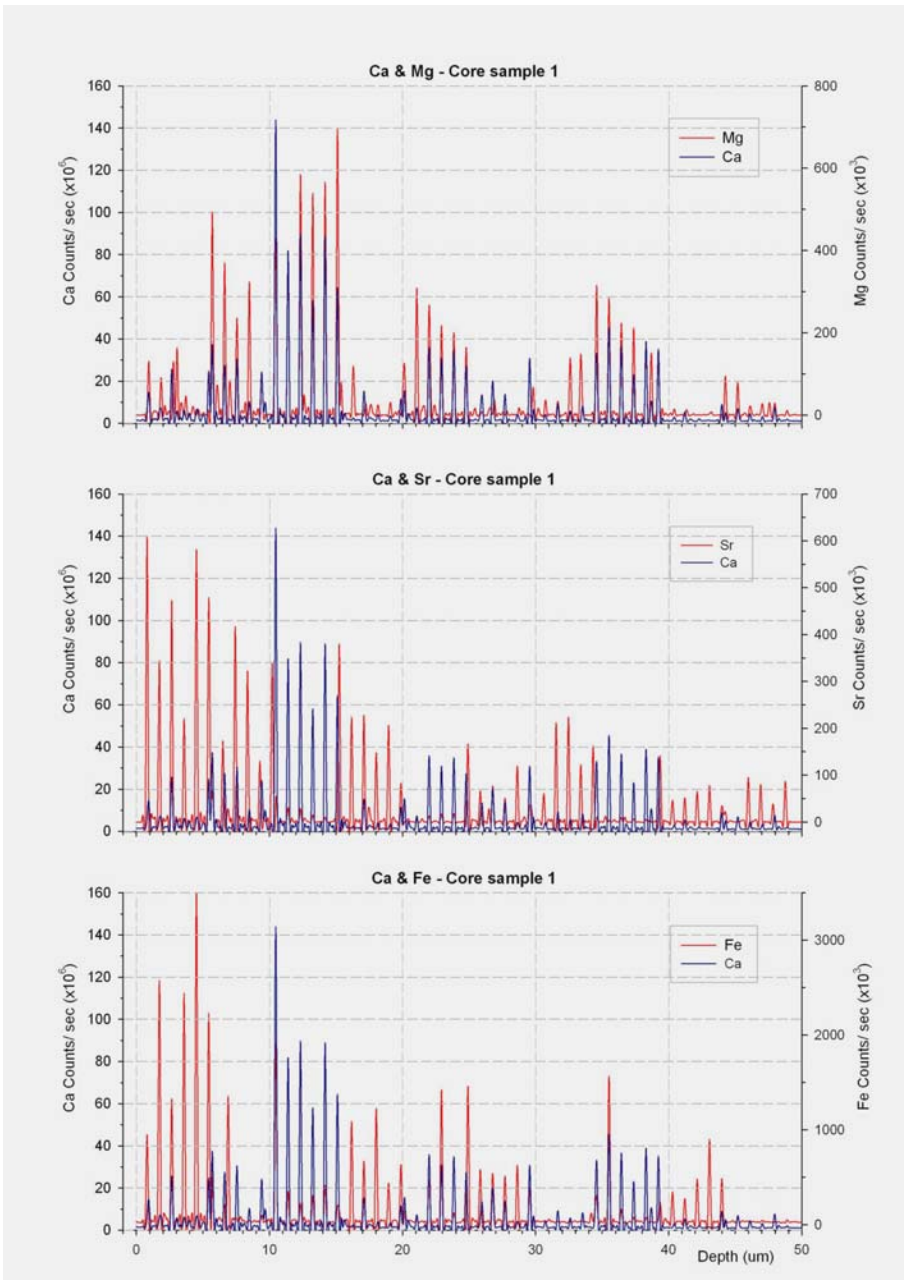

Fig. 3. LA-ICP-MS depth-profiling of Mg, Sr and Fe superimposed on Ca (core-fragment #1).

and Fe because their presence is pronounced at the grain boundaries bordering pore spaces (Bjorlykke, 1993; Kvenvolden and Roedder, 1971). However, at points where the pore fluid made inroads into the matrix itself ingrained deposits of Sr and Fe appear. This particular feature is strongly corroborated in figures 5B and 5C where Sr and Fe peaks are barely separable from Ca peaks, indicating potential co-habitation in the calcite matrix. A point to note is that the experimental data indirectly revealed that for diagenetic change and post-depositional formation of this nature to have transpired favorable conditions must have existed deep within the rock structure (Stewart, 2000).

Impact of our findings

The diagenetic features of reservoir rock are a record of its geological (and paleontological) histories and are inextricably linked to reservoir quality (Stewart, 2000). The diagenetic history of source rock usually determines the formation and migration of petroleum and availability of pore space during oil emplacement (Saigal, 1992). Of significance is that the diagenesis pattern can vary from one limestone to another both laterally and vertically within the same structure and depends largely on pore-fluid chemistry, subterranean temperature/pressure, pore flow rates, mineral and biogenic composition (Pedersen, 1993). During such processes the major events that form

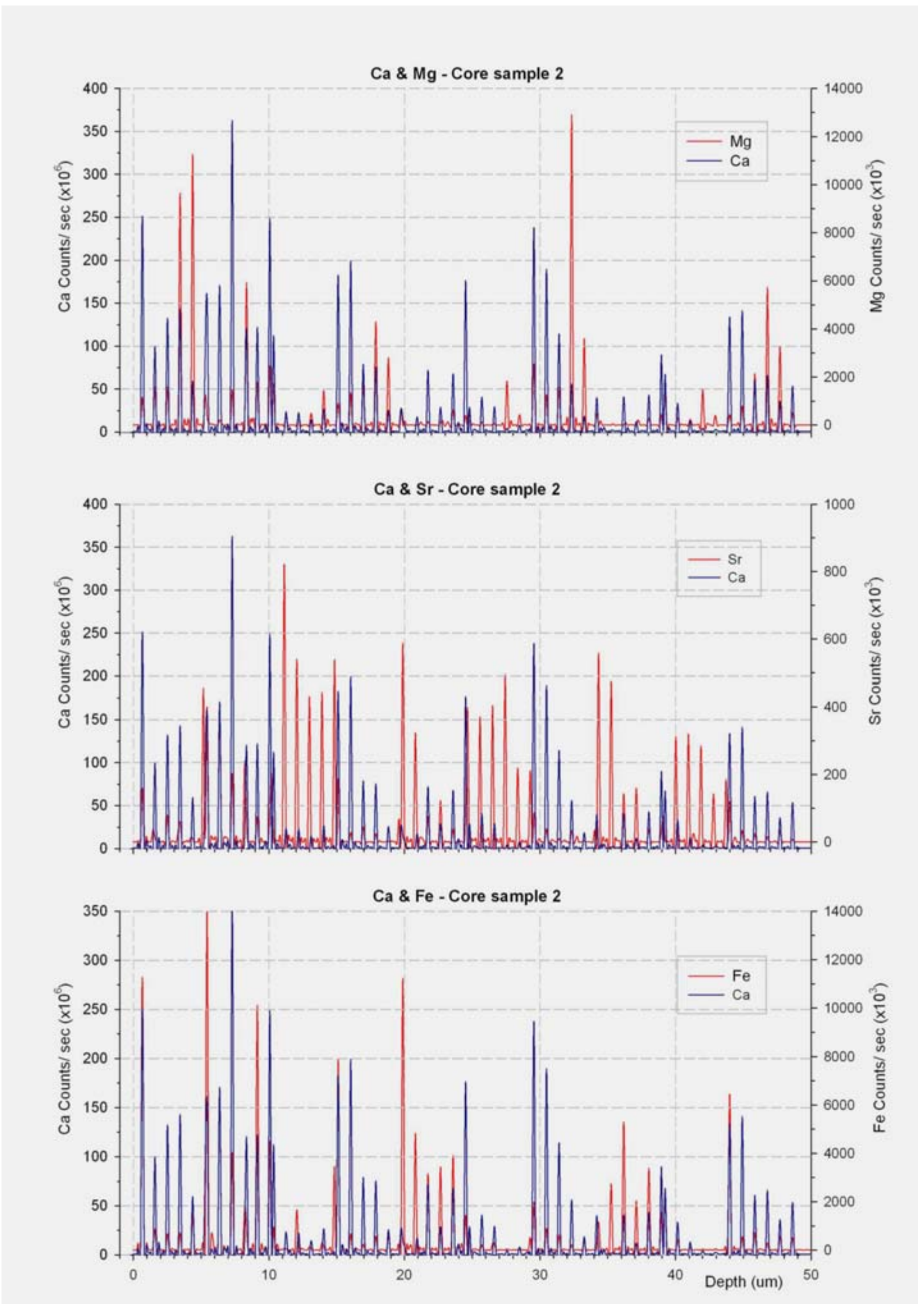

Fig. 4. LA-ICP-MS depth-profiling of Mg, Sr and Fe superimposed on Ca (core-fragment #2).

the rock are cementation of loose sediment to solid rock, dissolution of minerals leading to formation of pores and re-crystallization of various rock components (Fig. 2). In figures 3A and 6A, for example, the phenomenon of cementation was clearly visible in the first 5 µm where the intensities of Mg outweighed the Ca intensities suggesting cementation of loosely bound Mg deposits on the edge of the calcite matrix abutting pore spaces (Wilkinson and Haszeldine, 1998). On the other hand the precipitous trend of Sr peaks (Figs. 3B, 4B and 6B) in the 'pore spaces' reflecting sharp fluctuations in intensities tend to suggest intermittent dissolution and re-crystallization processes. Similar trends were observed for Fe (Figs. 3C, 4C, 6C). Furthermore, figure 5 (A, B, C) is a good example of ingrained deposits, where Mg, Sr and Fe peaks occur concomitantly with Ca in the core sample between 10-40µm, delineating the porous nature of the matrix that permits fluid infiltration and crystal growth. Such growths and deposits could contribute to reduction of porosity and permeability of an oil reservoir (Chaika, 2000).

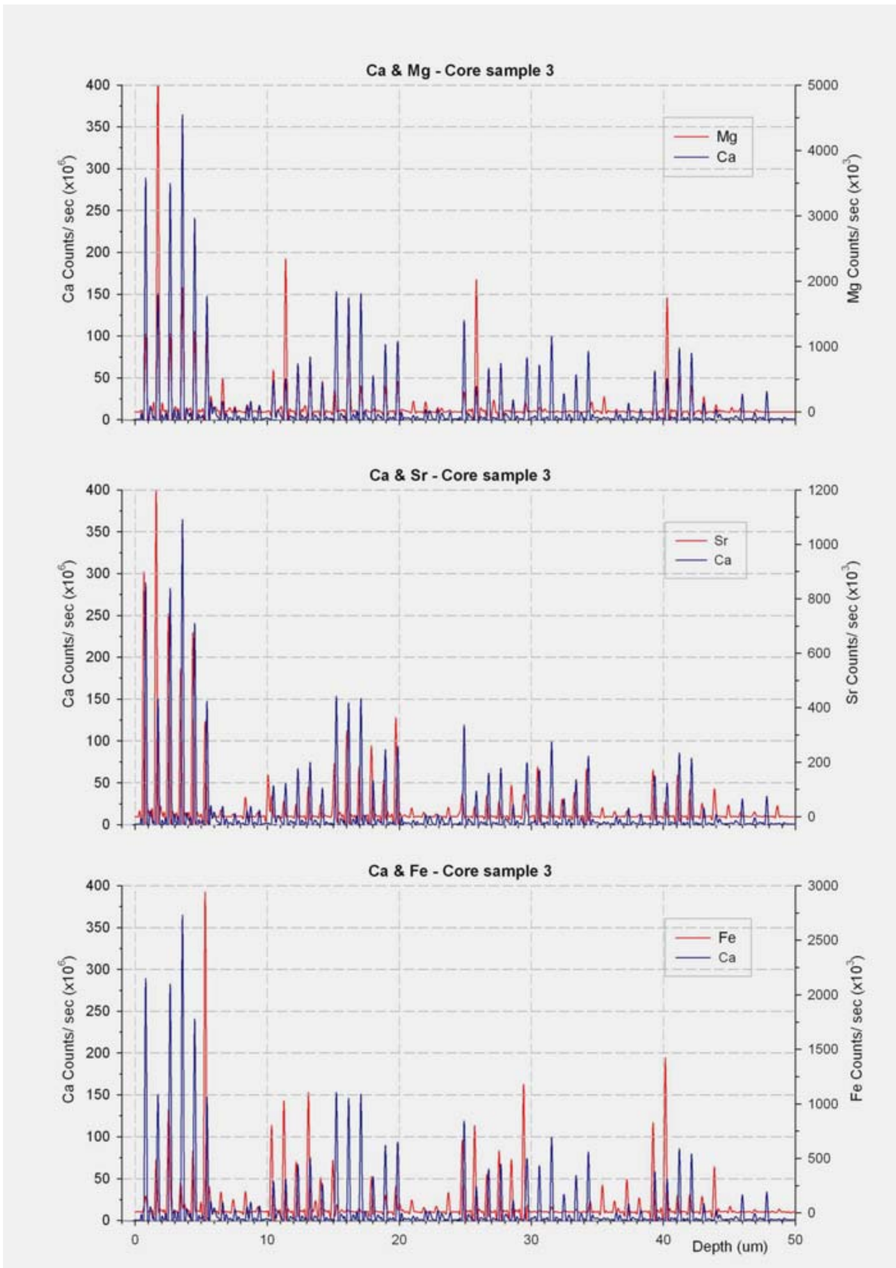

Fig. 5. LA-ICP-MS depth-profiling of Mg, Sr and Fe superimposed on Ca (core-fragment #3).

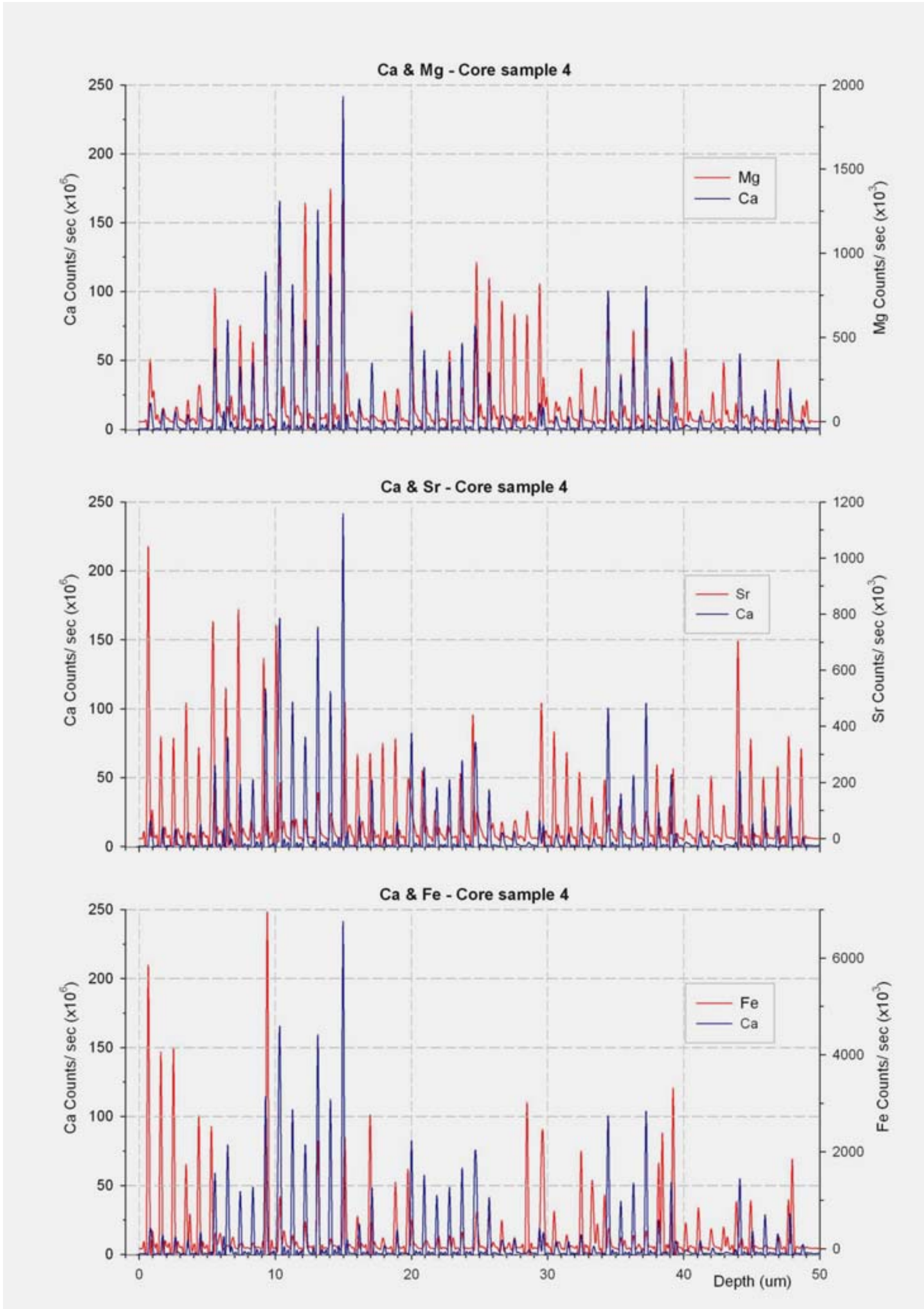

Fig. 6. LA-ICP-MS depth-profiling of Mg, Sr and Fe superimposed on Ca (core-fragment #4).

CONCLUSIONS

The laser technique has the unique capability of creating 'micro-channels' through the matrix of reservoir rock and unearthing hidden information of geological importance. Such information is difficult to extract from other contemporary methods such as SEM and XRD and highlights the pre-eminent nature of depth profiling. Our research has provided an insight into diagenetic processes in carbonate reservoir cores and a suitable extension of this study would be to apply the data in modeling and simulation studies associated with geosciences and petrophysics.

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