Non-destructive geochemical analyses of shale from outcrop and core using state-of-the-art LA-ICP-MS

Dave Keighley, Chris McFarlane, and Yan Luo

Department of Earth Sciences, University of New Brunswick

Fredericton, NB. E3B 5A3

keig@unb.ca; crmm@unb.ca; yanluo@unb.ca

Introduction

Geochemical analyses of shale commonly has involved preparatory crushing and powdering of a volume of sample (hence destructive of the sample); techniques restricted in their simultaneous measurement of a full suite of major and trace elements; and (or) techniques where small sample size and analytical resolution are problematic. Also, sampling for such analyses results in a thickness of shale being used that is of greater scale than that of the typical lamination present. The crushing mixes together, and the analytical results are an average of, variable numbers of laminae that are likely different in every preparation. Interpretations of such analyses are therefore compromised by the inability to determine whether variations occur sharply at one lamina, gradationally across many laminae, or cyclically where related to the recurrence of a particular compositionally distinct lamination.

However, various non-destructive geochemical analyses of samples with dimensions up to 15 cm x 10 cm x 2 cm are now possible with continued development of Laser Ablation – Inductively-Coupled Plasma – Mass Spectrometry (LA-ICP-MS) equipment. Inherent with the latest equipment is the ability to detect abundances across 9 orders of magnitude for elements other than H, He, N, O, F, Ne, and Ar, including detection limits as low as 20 ppb for heavy elements. This presentation illustrates some of the benefits such advances permit with respect to studies investigating (1) compositional variation in different gas-shale facies of the Albert Fm. (AF), New Brunswick and (2) regional correlation of specific oil-shale beds of the Green River Fm. (GRF), Utah.

Method

Halved core samples <15 cm long and <2 cm thick were flattened and polished to a 1200 grit finish. The polished core was mounted in a 'universal' sample holder supplied with the Resonetics 'Resolution Series' 193nm ArF excimer laser ablation system operated by UNB Dept. of Earth Sciences. The core was loaded together with a series of pre-polished standard blocks (Figure 1). These standards included a pressed pellet of either the USGS SBC-1 Brush Creek Shale or SGR-1 Green River Shale as the calibration standard, as well as NIST610 glass for instrument tuning, and USGS BCR-2G basaltic glass for quality control purposes. The loaded sample holder was scanned on a conventional flatbed scanner. The resulting image was imported into the laser control software as an overlay layer to help guide the position of the ablation targets.

The laser sample cell (Laurin Technic Pty. S-155) was repeatedly evacuated and backfilled with high-purity helium to remove any traces of ambient air in the cell. The laser cell was then connected to the ICP-MS (Agilent 7700x) using a combination of Ar, He, and N2 as the laser aerosol carrier gas. For the initial anaylses, ablation of the polished core slab, calibration standards, and quality-control standards was conducted using a 200 µm diameter crater, a repetition rate of 10 Hz, and a stage scan speed of 80 µm/s. This scan speed enables a 12-15cm length of core to be analyzed in 25 to 30 minutes. The Agilent 7700x was tuned to obtain oxide production (^{248}ThO$^+$/^{232}Th$^+$) < 0.3% and doubly-

charged production ($^{22}M^+/^{44}Ca^{++}$) <0.4% while also minimizing light-element backgrounds (e.g. ^{13}C, ^{44}Ca) as measured by scanning across NIST610 glass. A suite of 50+ elements were analyzed using dwell times between 0.01 sec for high abundance elements (e.g. ^{29}Si, ^{27}Al, ^{44}Ca) and 0.1 sec for low abundance elements (e.g. Zr, Ta, Hf, W). The total sweep time for the element list was 3 to 4 seconds depending on the number of elements of interest. The data for calibration standards, unknowns, and quality control standards were collected in a single file and reduced offline using the Iolite v. 2.2 (Paton et al., 2011) trace element data reduction scheme.

Data reduction was carried out for the AF samples using Si as an internal standard with an estimated value of 22 to 32 wt% Si based on XRD analyses of stratigraphically equivalent surface samples (Keighley 2008). The veracity of the method was checked by analyzing homogeneous glass reference materials (e.g. USGS BCR-2G) using the same analytical conditions, calibration strategy, and data reduction. Similar reduction was undertaken for the GRF material.

Data collected from the progressive ablation of rock along the length of the core can be normalized and tabulated for the entire thickness, or large sections, of the slab. This gives values similar to what would be produced from destructive ICP analyses, where the entire sample, or large chips representing several mm-thick laminae, are crushed and thus mixed together. Alternatively, data collected for individual time components during the analysis may be plotted as various ratios at any or all distances along the slab (equivalent to stratigraphic depths). Statistical analyses followed data transformation to centred log ratios.
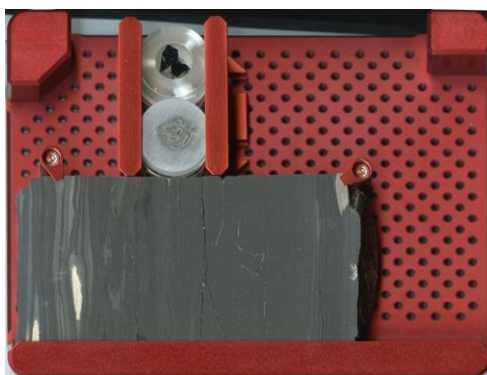

Figure 1: Set-up of the sample holder including an 11.5 cm long by 6 cm wide piece of AF slabbed core (stratigraphic top is to the left) and two standards (round plugs)

Examples

The AF sample illustrated (Figure 1) is from a 3 m-thick deep shale at 2835.5m that interbeds (tight) sandstone in the McCully H-28 well. Such strata are interpreted to be offshore muds interfingering with lower shoreface sands, and are more abundant in core than rooted deltaic mudstone. Figure 2 illustrates some results from beneath the sulfide nodule. The graphs show selected elemental ratios plotted for successive time periods. For example, in Figure 2, the Mg:Ca ratio indicates several relatively Ca-rich intervals (e.g. around -5.0 cm). Since there is no appreciable change in the corresponding values for Mg:C, the simplest interpretation is that the Ca reflects Ca-silicate or Ca-sulfate enrichment, not changes in dolomite-calcite composition. The P:U and Pr:Yb curves generally mimic each other, with anomalous peak U and Yb values at -7.6 cm. Phosphorus peaks tend to coincide with increased Pr, a light rare-earth element (REE), with the notable exception of -5.4 cm.

When the REE data are then displayed as PAAS-normalized (McLennan, 1989) spider plots (Figure 3), three types of profile are notable. Predominant is a gentle hump-back profile with peak enrichment (relative to the PAAS standard) around Gd, such as at -7.8 and - 8.0 cm. Rare is a more pronounced middle REE hump with peak values extending to Dy (e.g., -8.2 and -8.4 cm). Unique is the profile associated with the uranium anomaly at -7.6 cm, where there is a continuous gradual relative enrichment with progressively heavier REEs (hence the Yb:Pr anomaly in Figure 2). The same profile of HREE enrichment also is reported in ICP work on several GRF oil shale (Keighley, in press).
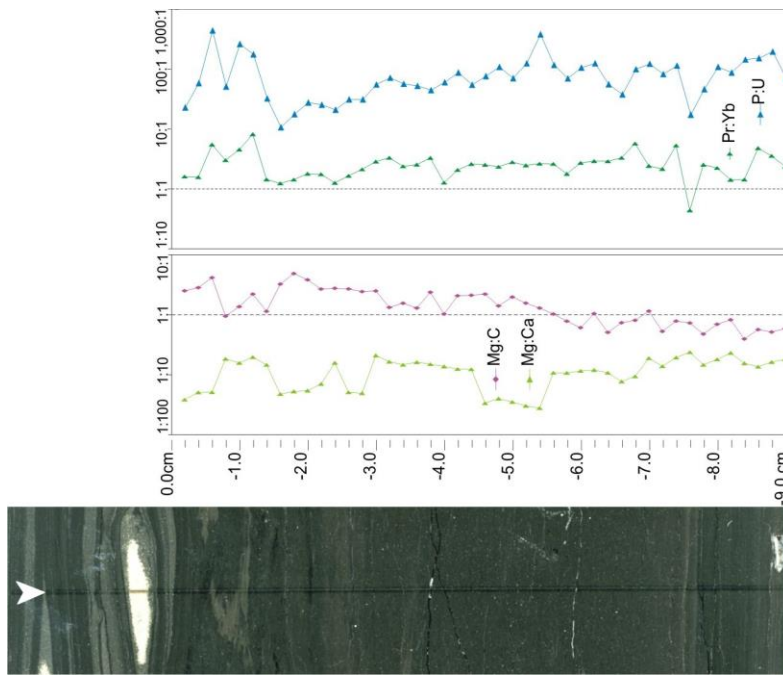
Figure 2: Ratio plots of selected elements showing relative distributions at incremental 2mm depths below the sulfide nodule in the AFsample. Values represent data collected along the laser ablation line (arrowed)
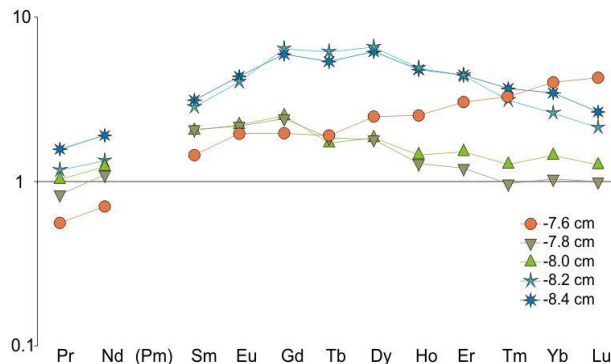

Figure 3: Spider plot of REE distribution for 7.6 to 8.4 cm below the nodule in the AF sample. Values are normalized to PAAS standard

The GRF sample illustrated (Figure 4) is from a 20 cm-thick phosphatic oil shale 128.2 m abMOSZ (above the base of the Mahogany Oil Shale Zone) at Buck Canyon, Utah. Previous work on over 200 shale samples from three sections in the GRF, including the 128.2 shale, has used destructive ICP methods (Keighley, in press). This work identifies a predominance of shale REE profiles that are flat and that approximate to the SGR-1 standard (Figure 5, bottom left); exceptions include samples of several phosphatic oil shale such as the 128.2 example from Buck Canyon. The work also tentatively correlates the 128.2m oil shale with an oil shale 124.8m abMOSZ over 50km away, based on the REE profile.

The ongoing analyses illustrated herein (Figures 4, 5) indicate that use of destructive ICP methods limits the resulting data to that of values averaged across many compositionally distinct laminae, with the average being dependent on the number of laminae, and which laminae are sampled (i.e. the stratigraphic thickness of the sample taken). Significant additional detail and variation is attained by LA-ICP-MS. The HREEs (e.g. Lu in Figure 4) show a highly significant ($\alpha = 0.01$) correlation co-efficient (+0.895) with U; the MREE (e.g. Tb), a highly significant correlation co-efficient (+0.899) with Th. When REE profiles are plotted for individual zones, the gradual enrichment from

LREE progressively to HREE noted by destructive ICP, is revealed to be a function of the data averaging of several distinct and successive REE spider profiles. This provides additional potential for correlation of (oil-) shale beds and permits a more detailed model of the evolution of the shale bed and various diagenetic phases.
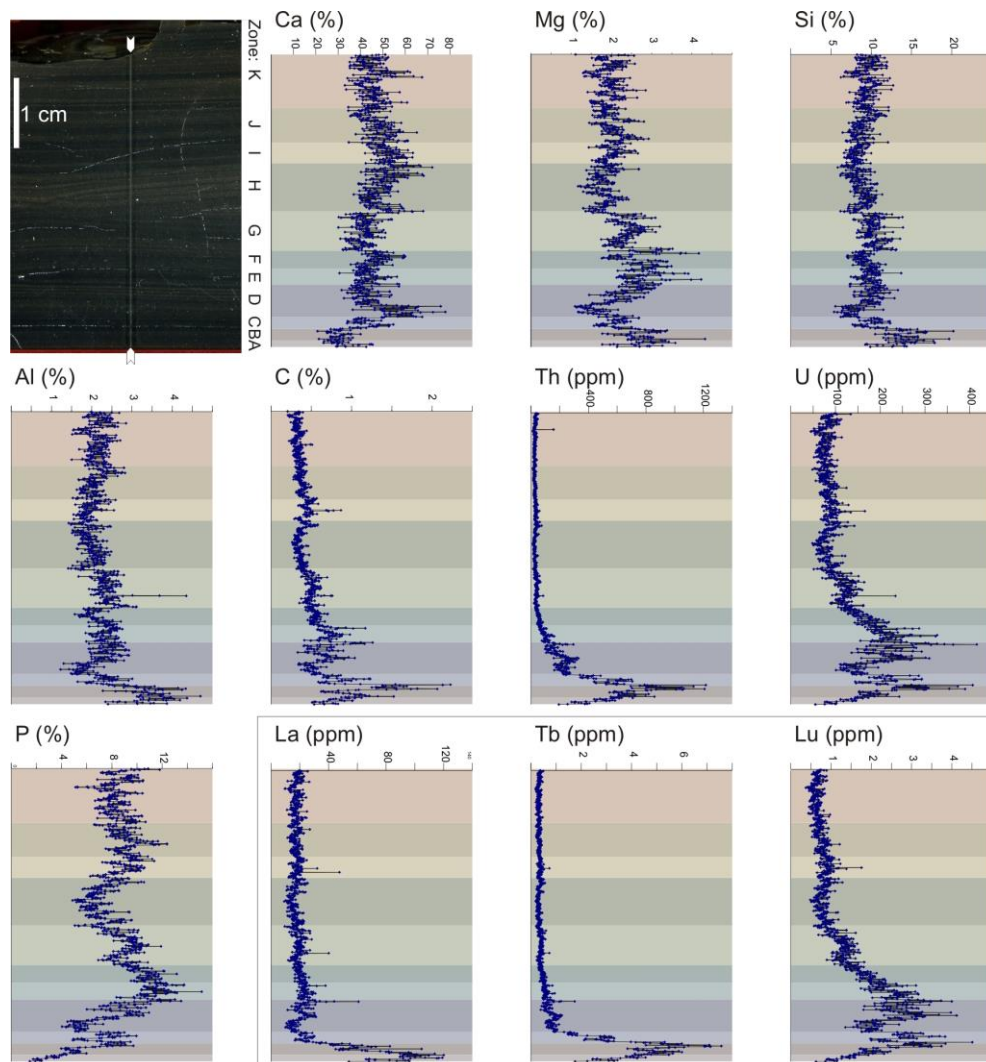

Figure 4: Depth:abundance plots for selected elements in the upper ~5cm of a phosphatic oil shale in the Green River Fm. Analyses are at depth increments of ~40 μm. A plot of C is shown although calibrations currently indicate significant error. Eleven zones are identified from the 1189 datapoints. Note the variation in U, P and the selected REEs in the lower zones.

Conclusions

The LA-ICP-MS approach to the geochemical analysis of core is non-destructive of the material while also providing researchers with information regarding the continuous mm-scale variability of shale or other fine-grained rock for stratal thicknesses of up to 15 cm. Preliminary work indicates a greater number of elements can be analyzed, over a greater abundance range, than by other ICP methods, and that such analyses may be beneficial to the recognition of small-scale mineralogical variations between strata, with beneficial implications for chemostratigraphic-correlation and diagenetic studies.
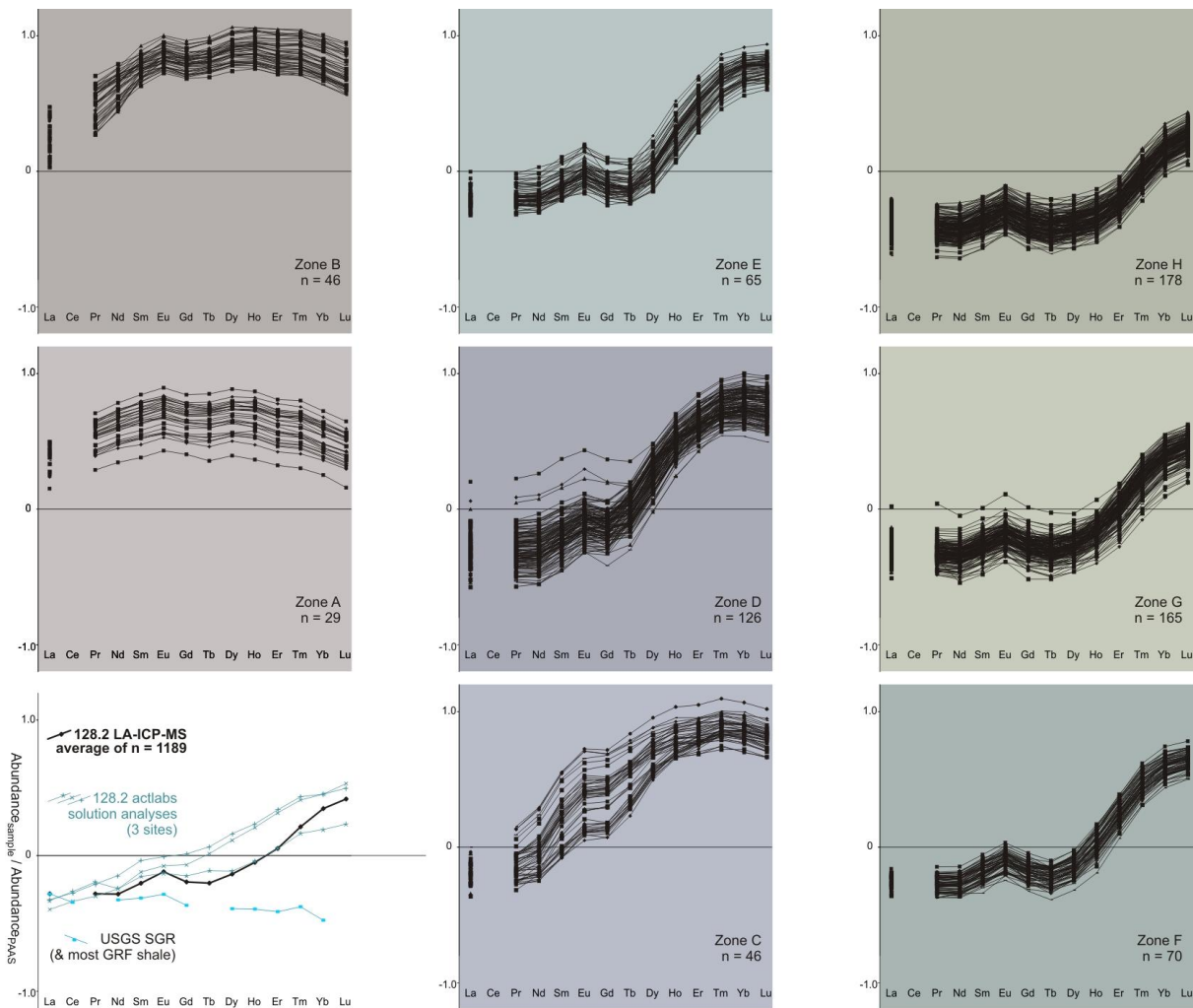
Figure 5: Spider plots of REE abundances in lower zones of the Green River Fm. oil shale ("128.2") normalized to PAAS standards. Data for Ce omitted due to high calibration error. Bottom left: the average of all readings for all zones is plotted against values from other 128.2 outcrop samples analyzed by destructive ICP methods, and the SGR-1 standard.

Acknowledgements

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References

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