Statistical Correlation of Rare Earth Minerals of the Salina Group

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ABSTRACT

The Silurian Salina Group is an extensive evaporite series consisting of interbedded halite, anhydrite, dolomites, and shale that extends from Michigan into Ohio and through New York. Current interests in evaporitic bodies have shifted towards the search for Rare Earth Elements (REEs). These minerals are imperative for the development of batteries, generators, solar panels, and more. Even at low concentrations, these elements could have commercial value.

REEs may help constrain timing across the basin and amongst sub-basins, creating "correlation" lines of deposition. Little data has been published on the concentrations and mechanisms of REEs concentrations in evaporitic bodies. This study proposes to use a combination of core analysis, x–ray fluorescence (XRF), x–ray diffraction (XRD), and scanning electron microscopy (SEM) on rock core consisting of the Silurian Salina Group to produce data sets. These datasets are extensive, typically consisting of 40+ elemental compositions for hundreds of data points, resulting in 8,000+ data points.

This project will provide data for "proof of concept" by showcasing the usefulness and applicability of principal component analysis (PCA), a statistical technique, for analyzing elemental composition datasets. PCA can decouple complex geochemical datasets enabling further research that REEs are abundant in salt bodies and that shales coupled with salt bodies can provide detailed depositional and diagenetic histories.

INTRODUCTION

Little data have been published on the concentrations and mechanism of trace elemental concentrations in evaporitic bodies. The mechanisms and timing of integrating certain elements, such as rare earth elements (REEs), into these bodies are poorly understood. This proof-of-concept project will try to determine vertical variability within the Silurian Salina Group in Ohio of bulk and trace elements, particularly focusing on REEs. Correlations will be made between elements and mineralogy to determine associations of specific elements (i.e., U, V, rare earth elements) with specific minerals (i.e., clay minerals, carbonates, halite). X–ray fluorescence (XRF), x–ray diffraction (XRD), and scanning electron microscopy (SEM) will determine elemental composition, bulk mineralogy, and clay mineralogy, respectively, on core samples from Lake County, Ohio. If REE concentrations are high enough, this could provide evidence for further research specifically focusing on the halite beds and REE concentration as a potential source for these critical minerals. Halite bodies have the potential to prove a valuable resource for trace elements such as Sr, Fe, Mn, Nd Pr, Ce, La, and others (Fig. 1). If found within high enough concentrations, these salt bodies, could prove to be economically useful in our current search for "critical minerals."

However, because of tectonically driven fluid flow during subsequent orogenic events in the Appalachians, the depositional insight provided by the trace element chemistry of halite beds within the Silurian Salina should be considered carefully; the evaporite beds have been recrystallized potentially several times during the past 300 m.y. The interbedded shales, however, record conditions during the time of deposition and are seldom affected by basin flushing events, lending insights into palaeoceanographic chemistry, oxygen levels, and productivity (Algeo and Liu, 2020). Coupled with core analysis, trace elemental analysis on both shales and halite beds can provide a better depositional and diagenetic history of a basin. (Fig. 2)

In this study, we provide evidence to test the usefulness and applicability of principal component analysis (PCA), a statistical technique, for analyzing elemental composition datasets. These data sets are extensive, typically consisting of 40+ elemental compositions for hundreds
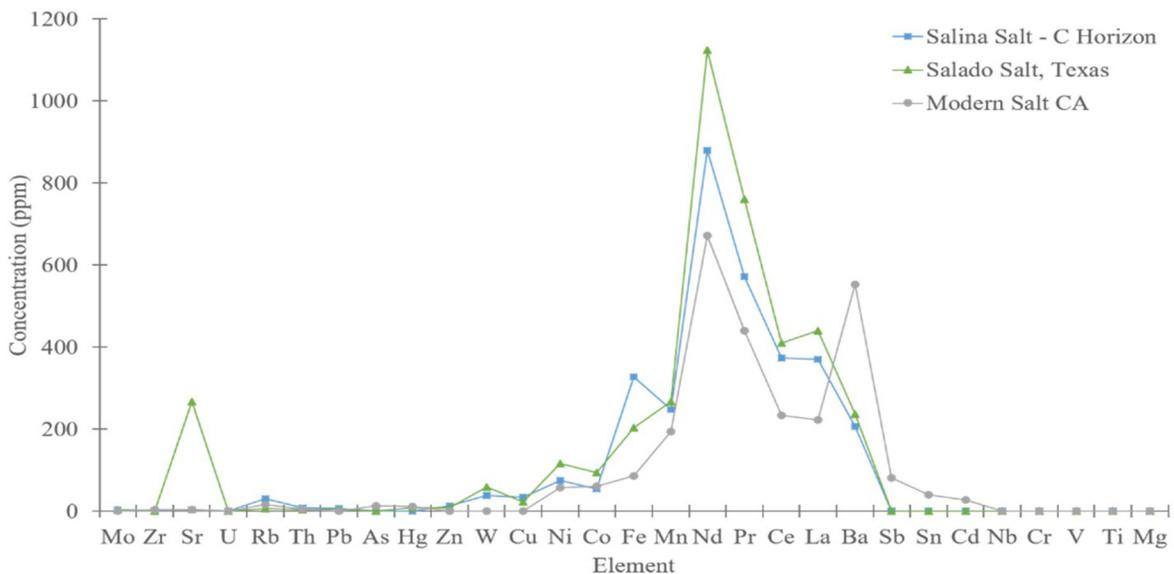
Figure 1. Preliminary elemental concentrations of the Silurian Salina Salt, Permian Salado Salt, and modern salt from California, showing enrichment on REE and other critical elements.
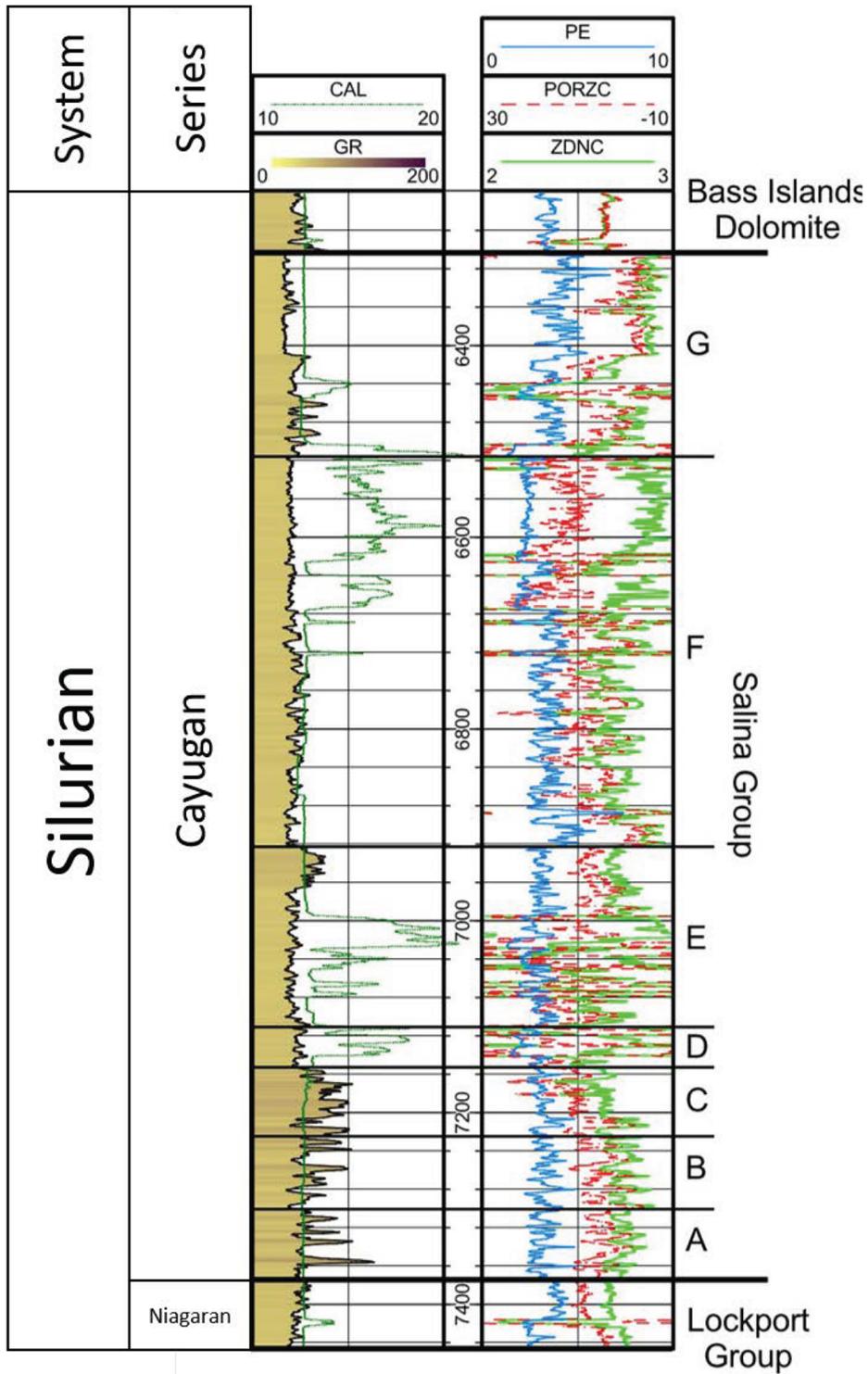
Figure 2. Well log of the multiple salt bed interbedded with dolostone, anhydrite, and shale/siltstone in the Silurian Salina Group. Evaporate sequence was deposited during restriction of the basin.

of data points down a core, resulting in thousands of data points. Furthermore, we provide an updated depositional environment interpretation based upon geochemical and core data from the Silurian Salina Group, Ohio.

METHODS

A combination of XRF, XRD, and SEM was performed on Core 3563 from Lake County, Ohio, archived at the Ohio Geological Survey. A total of 182 samples were taken approximately every 30 cm. Each sample is approximately 2–5 cm in length (Fig. 3). Descriptions of samples were conducted to determine facies, sedimentary structures, and interpret depositional settings.

Approximately 10 g of each sample was hand crushed and sieved to 250 μm grain size, placed into an XRF sample holder, and an x-ray film secured on top of the holder. Each sample was measured with a Thermo Scientific Niton XL3t GOLDD+ XRF analyzer for elemental composition for a total of 300 sec on the TestAllGeo mode by placing the sample in the sample holder and the instrument directly on the sample holder.

Figure 3. Image of samples taken from core of the Silurian Salina Group, Core No. 3563, of (A) micritic dolostone, (B) halite with dendritic shale, (C) pure halite, and (D) halite with shale and organic inclusions. Ruler is for scale, with inches on top and cm on bottom.

To complement elemental analysis, bulk mineralogy was determined using XRD on a Bruker D8 Advanced on approximately 10 samples. The samples were hand-crushed, then passed through a 250 μm sieve. The samples were side-packed into side-loading XRD holders. The samples were run on the Bruker D8 from 5 to 65°2φ with 0.02° step for 2 sec per step with Cu K–alpha radiation. Mineralogy was determined using RockJock from the U.S. Geological Survey. Bulk mineralogy was used to determine elements associated with mineralogy (i.e., S+Ca with anhydrite, Mg with dolostone, etc.).

Finally, SEM was conducted on approximately 10 samples of various lithologies on the JOEL–JSM–6100. Mechanically cleaved or fractured cross sections were prepared and mounted on an Al SEM stub. Samples were coated with a 500 nm Au/Pd layer using a Denton Desk I Sputter coater. The SEM determined clay mineralogy and origin, observed halite crystal micro-structures, and determined grain sizes.

Once datasets were generated and reviewed, they were entered into JMP software for PCA with Varimax rotation using the following elements: Nd, Pr, La, Ce, Ca S, Mn, Sr, Th, Mg, Te, Sn, Sb, Cs, Cd, Ag, Ba, Cr, Sc, W, P, K, Si, Al, Zr, Fe, Rb, Ti, V, Cu Ni, Zn, Co, Pb, and Cl. This included the bulk elements representing mineralogy and critical elements of interest.

RESULTS

The Salina Group in Core 3563 contains interbedded anhydrite, shale, dolostone, and halite (Fig. 3). The dolostone is buff to grey, and generally micritic in texture and laminated (Fig. 3A), suggesting a depositional system just below the wave base. Some of the dolostone also con-tains anhydrite growths, algal laminations and mud cracks. There are also pyrite inclusions in particular locations, and some sections with algal laminations are also partially dolotomized. These suggest shallow water, intertidal environment, and only partial diagenetic dolotomization. The halite beds varied from clear to light yellow to pink in color, sometimes "pure" (ie., no shale inclusions), while other sections contained dendritic shales and organic material (Figs. 3B–3D). Furthermore, SEM images of these show sometimes chevrons, suggesting primary texture (no recrystallization) while others contain mosaics of crstyals (recrystallization). Overall, there ap-pears to be layers of halite that have been recrystallized, while others appear to have no been recrystallized by secondary fluid flushing of basin.

The XRD, XRF, and SEM methods for analysis showed interbedded halite, anhydrite, dolo-mite and shales. The primary elements that represented the anhydrites were S+Ca; shale was Si; dolomite was Mg; halite was Cl. Secondary correlations in concentrations occurred with Sr+S; Zr enrichment in shales with positive correlation with Si. Furthermore, there were zones where Ca correlated well with Mg, indicating zones where dolomitization was not complete. REEs are found throughout all the lithologies, particularly concentrated in the anhydrites and halites.

When PCA was run on just the bulk elements (S, Cl, Ca, K, Fe, Si, Mn, and Mg), there are clear correlations that correspond to the major facies (Fig. 4A). There were 3 factors that were ex-tracted, representing 95% of the total variation. There is a clear grouping of S+Ca (anhydrite), Cl (halite), Mg (dolostone), and Fe, K, Al, and Si (shale). PCA was able to extract four components that represented 78% of the total variance (Fig. 4B). Factor 1 includes positive correlations with Nd, Pr, La, Ce, Ca, S, and Mn, and a negative correlation with Cl. This component represents the anhydrite component, and shows enrichment in Nd, Pr, La and Ce. Component 2 has positive correlations with Te, Sn, Sb, Cs, Cd, Ag, and Ba, and no positive correlations with bulk elements. Component 3 contains positive correlations with K, Si, Al, Zr, Fe, and Rb, representing the shale component, and shows enrichment in Zr, Fe, and Rb. Finally, component 4 has positive correla-tions with Cu, Ni, Zn, Co, and Pb, with no correlations with bulk elements. The PCA shows that there is no direct correlation with halite and an enrichment in trace critical elements or REEs. Also, when analyzing the data using linear correlations, there are also weak correlations with halite and trace elements, and other lithologies with most of the trace elements. Rather, clusters form, and showcase enrichment of critical elements and REEs in both the anhydrites and halite bodies, even more so with the anhydrite bodies. There is some enrichment in the dolostones
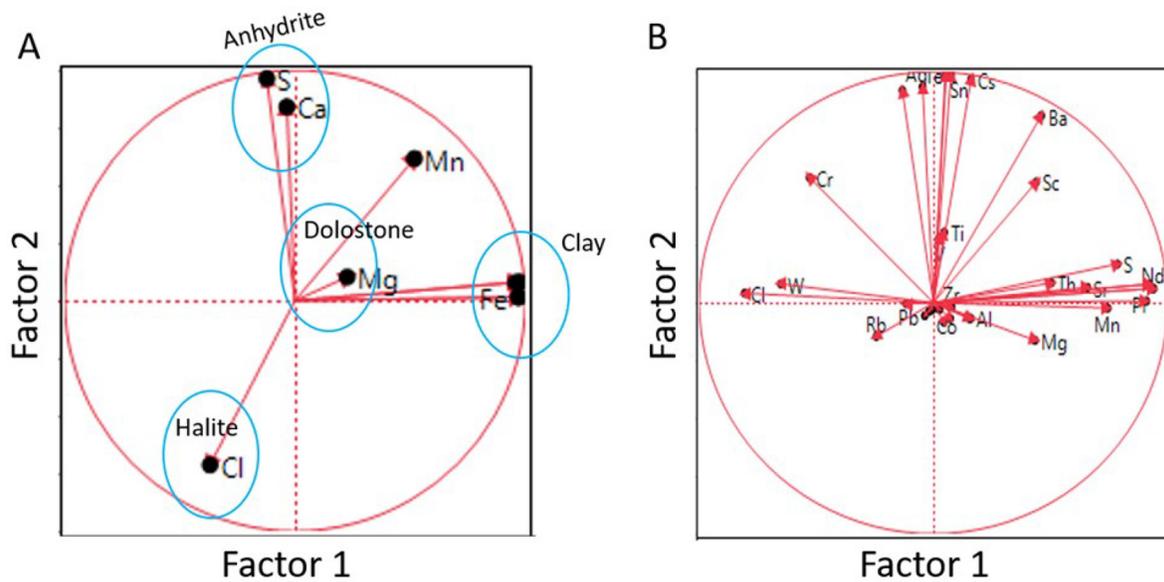
Figure 4. Results of the PCA performed on (A) just the bulk elements, showing grouping by mineral type. Only grouping in lithologies. (B) PCA with the addition of trace elements. There are some correlations with bulk mineralogy and some of the trace elements, although there is no clear correlation or pattern with all the facies, particularlly halite.

and shales, although to a lesser extent. Further work is needed to determine the enrichment mechanisms in these formations.

SUMMARY AND CONCLUSIONS

This current effort with PCA has not provided the hoped-for link to the thousands of data points within the datasets. There was too much variability of trace elements in the datasets. A second proof-of-concept will be considered and adjusting some of the parameters. Perhaps next time use it on a single lithology vs. the entire core. The progress will continue with the XRD, XRF, SEM and enrichment mechanism analysis as we look for a way to help identify the patterns of the REEs in the salt layers.

REFERENCE CITED

Algeo, T. J., and J. Liu, 2020, A re-assessment of elemental proxies for paleoredox analysis: Chemical Geology, v. 540, Paper 119549.