

A New Strategy for identifying shales with high gas retention using noble gas, nitrogen and carbon

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1. INTRODUCTION

"Shale Gas" is stored in shale source rocks as bound gas, adsorbed on or within the matrices of organic matter and rock, and, as free gas in pore spaces or in fractures created either by organic matter decomposition, diagenetic, or tectonic processes, or dissolved in fluid in the pore systems. During shale gas production, the gas recovery is actually impacted by the availability of the free and desorbed gases. Stable isotope and elemental ratios of gases would provide a unique way to quantitatively differentiate the contribution of the two kinds of gases. Variations in carbon and hydrogen isotopic compositions with progressive gas production, as free gas is progressively replaced by desorbed gas from the organic matrix, is known and related to differences in diffusivities and adsorption energies between their different isotopes.

The shales to be studied for carbon, nitrogen and noble gases, following initial petrographic and compositional characterization, are sections representing different depths of a continuous core. The minerals identified and quantified in the samples include quartz (12.7-30.9%), illite+I/S (9.2-32.4%) and calcite (8.5-52.5%) together with plagioclase, K-feldspar, dolomite, siderite, anatase, pyrite, muscovite, kaolinite and chlorite. The less than 2 micron clay fractions are dominated by mixed-layer illite-smectite and illite, but, it is not possible to differentiate illite from illite-smectite. Additionally minor amounts of chlorite are present.

2. NOBLE GASES AND NITROGEN

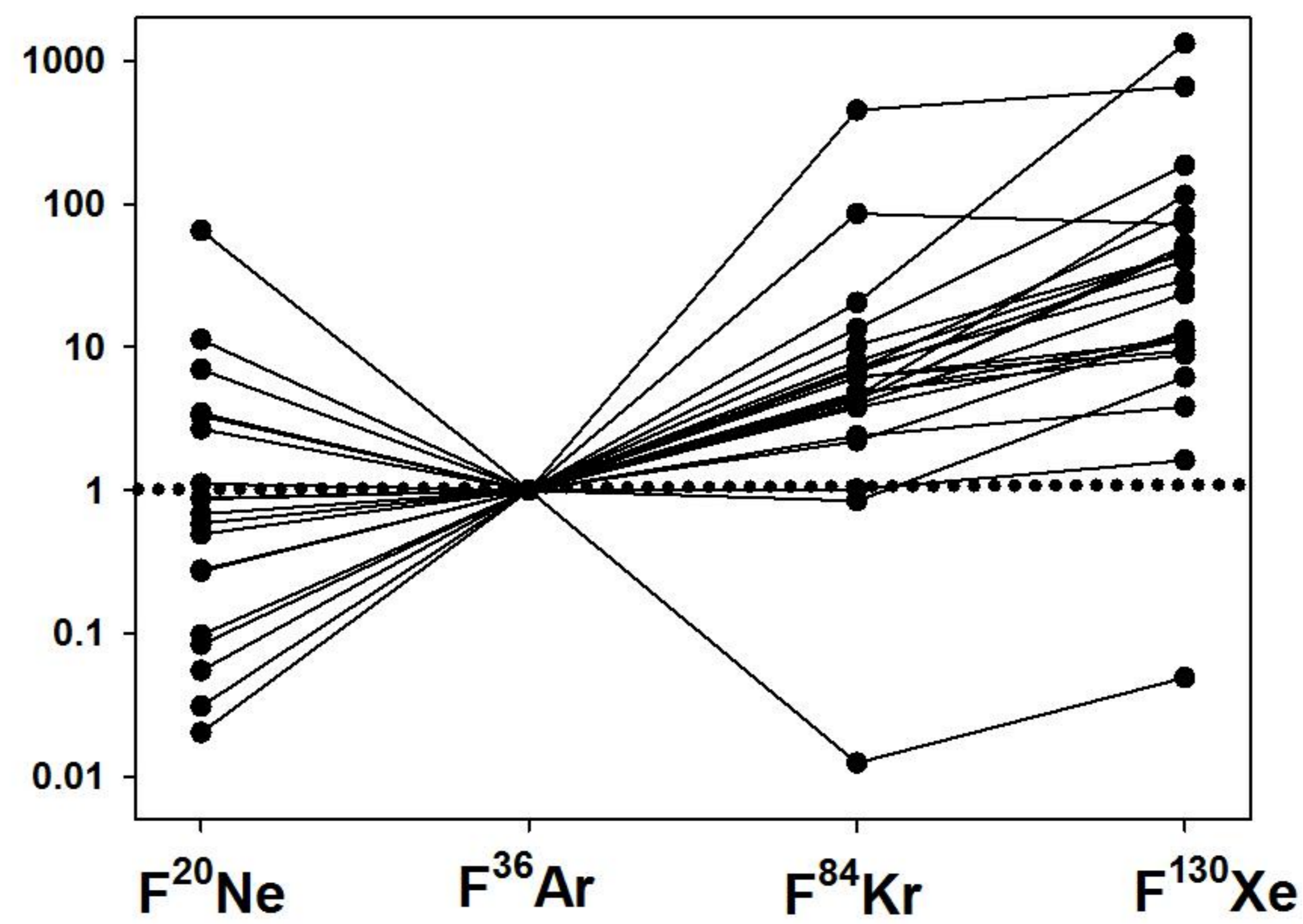


Fig. 1 Noble gas elemental patterns in shales showing enrichment of neon and xenon. [Data sources: Podosek et al., 1980; Bernatowicz et al., 1994]

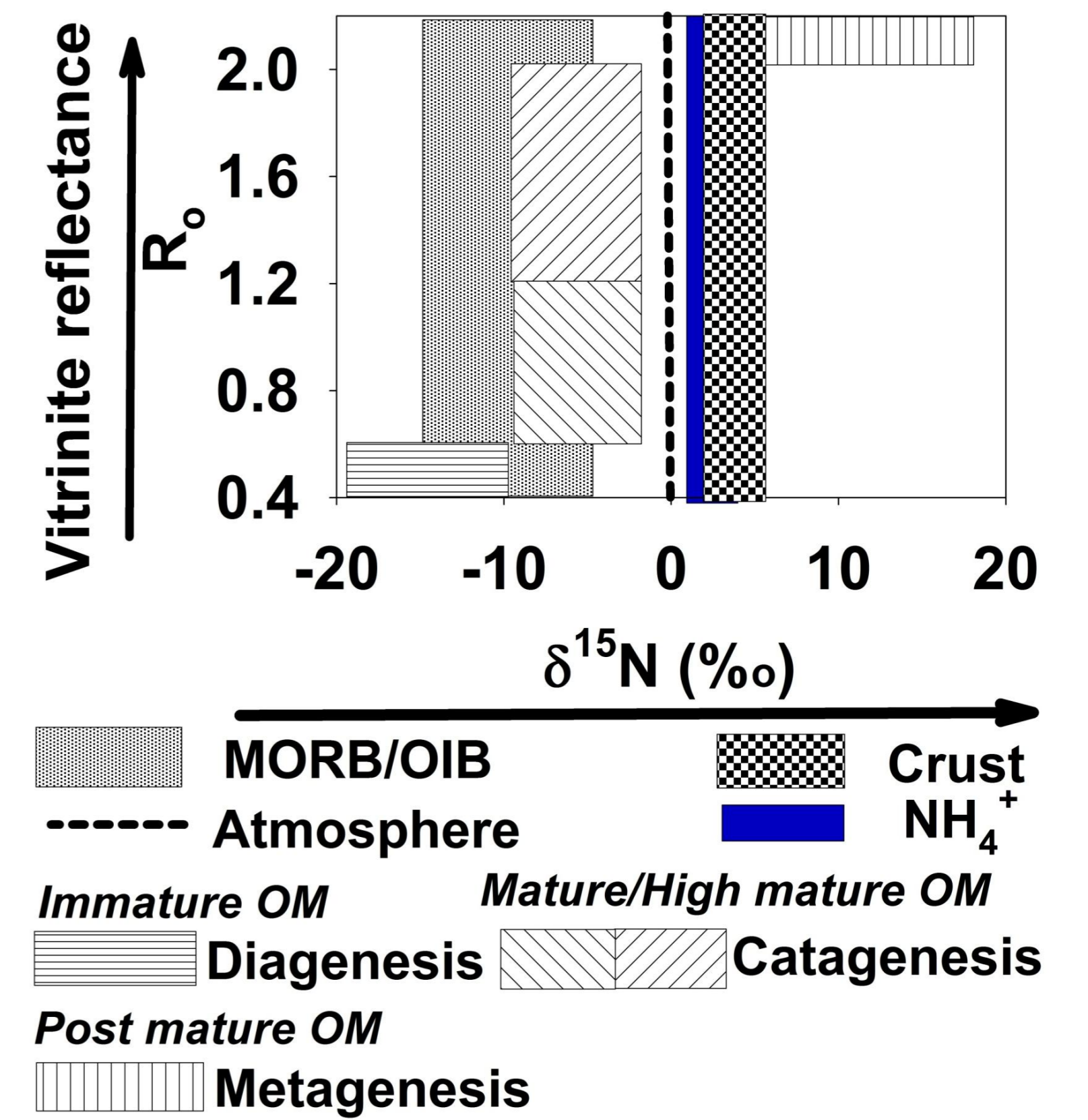


Fig. 2 Increase in the thermal maturity of sediments during diagenesis and catagenesis resulting in enriched $\delta^{15}\text{N}$ values in kerogen as ^{14}N is preferentially released. [Modified after Zhua et al., 2000]

3. MAJOR ELEMENTS

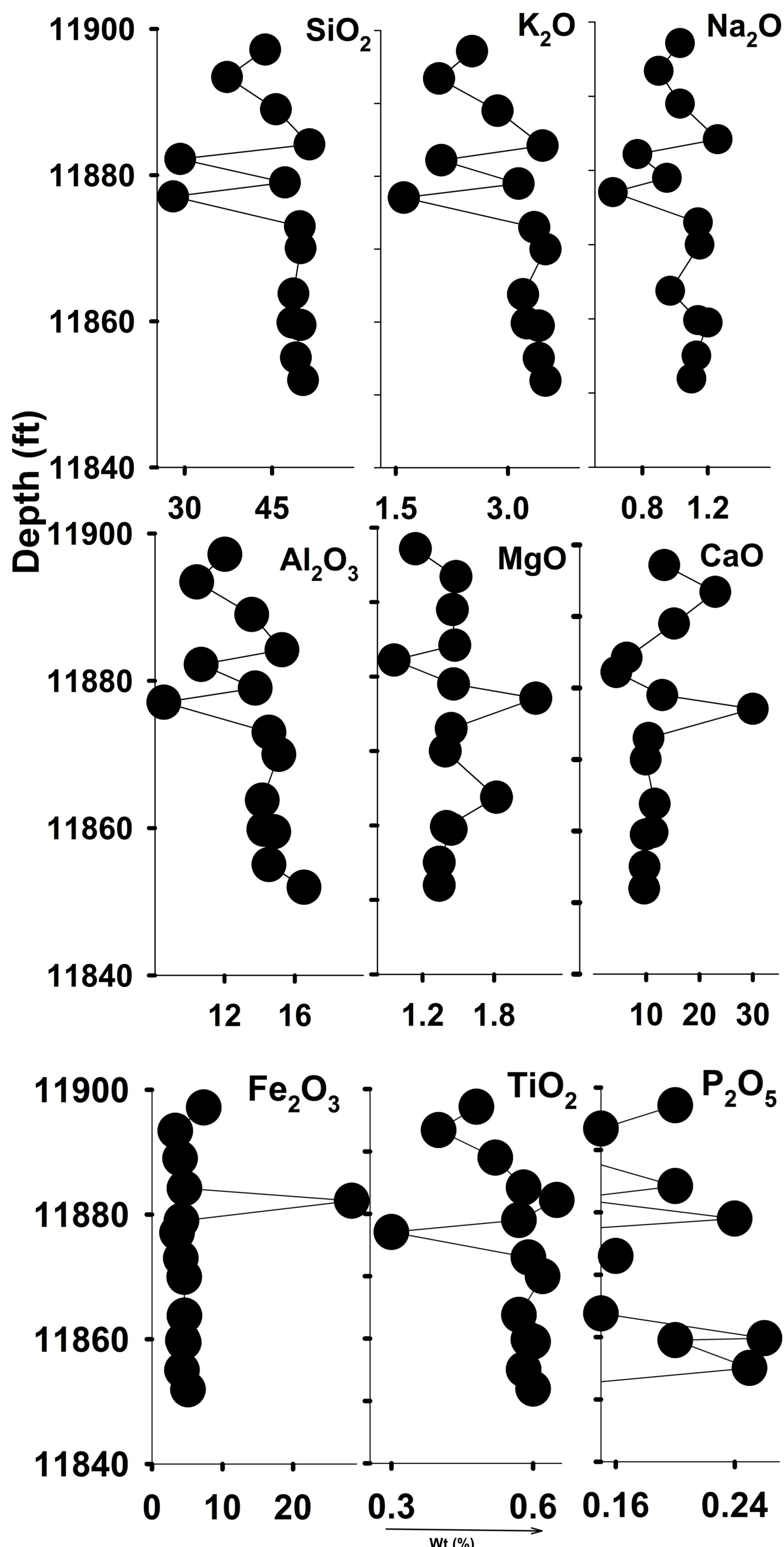
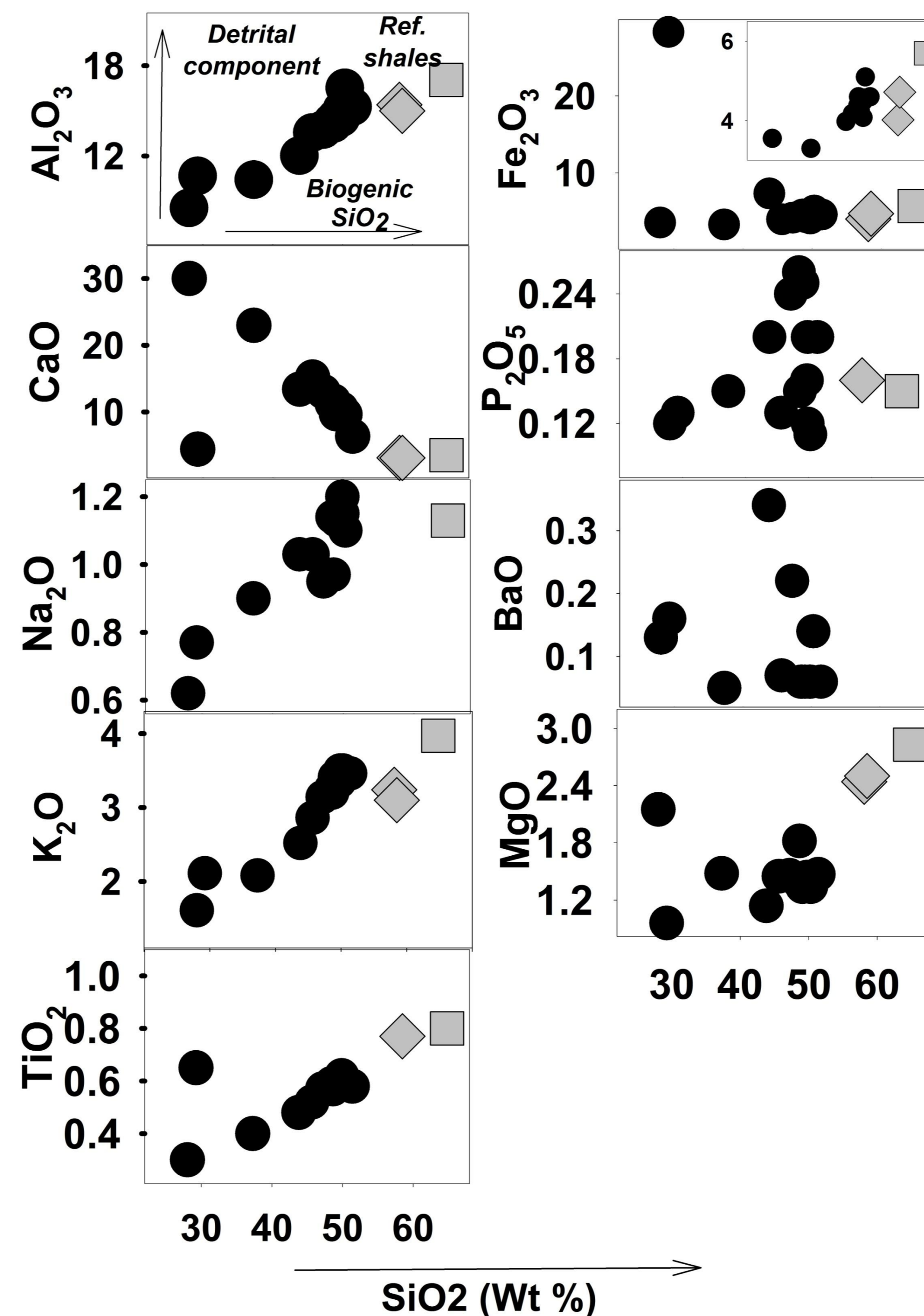


Fig. 3 Major element oxide distribution in core and plots of select oxides vs. SiO_2 . [Data sources for reference shales (symbols in grey): Turekian and Wedepohl, 1961; Pettijohn, 1975; Gromet et al., 1984]



The major element compositions of the shales, determined in powdered bulk rocks, and ~ 2 micron size fraction, by XRPD (x-ray powder diffraction) are shown in Figs 1 and 2. They generally compare closely with published average shale compositions. The absence of any important biogenic SiO_2 contribution is seen from the SiO_2 - Al_2O_3 relationship. The positive correlation of Na_2O , K_2O and TiO_2 , and the negative correlation of CaO , with SiO_2 (and Al_2O_3) is in accordance with the mineralogical composition of predominantly quartz, calcite, plagioclase, K-feldspar, clays and calcite, and indicates the dominantly detrital nature of the sediments. High P_2O_5 , compared to average shale compositions, may reflect presence of phosphatic minerals like apatite or monazite, and/or deposition under a high productivity regime. Fe_2O_3 enrichment is related to either formation under more reducing conditions, or, association of Fe^{3+} with clay-rich layer, very often with Ti. The $\text{Al}_2\text{O}_3 / \text{TiO}_2$ ranges from 16.4 to 28.5, suggesting insignificant mafic contribution. High CIA (chemical index of alteration) and CIW (chemical index of weathering) values suggest intense or prolonged source area weathering. Further, trace elements and REE data will provide better insights to depositional conditions including provenance, paleo-oxygenation conditions and sedimentary history.

The physical properties of noble gases are strong functions of their atomic masses. As a result, due to variations in their individual atomic masses translating into variable diffusion coefficients, many sedimentary rocks including shales show an overall enrichment of the heavy noble gases [where enrichment factor $F(\text{Ng}) = \frac{(\text{Ng}/^{36}\text{Ar})_{\text{sample}}}{(\text{Ng}/^{36}\text{Ar})_{\text{air}}}$ with 'Ng' denoting any noble gas isotope]. Some shales also have dual enrichment of neon (Ne) along with xenon (Xe) (Fig. 1). Although the mechanism of this strong retention is not clearly understood, it remains to be seen if specific enrichment factors as well as pattern can be related to gas retention of the shales. It is noteworthy here that xenon enrichments up to $F(\text{Xe})=650$ have been measured in noble gases co-produced with oil and gas (Togersen and Kennedy, 1990). Nitrogen in its molecular form (N_2) are chemically inert like noble gases. Since the molecular size of N_2 is identical to argon (Ar), the N_2/Ar ratio remains unaltered during various terrestrial processes. N_2/Ar is higher in sediments (bound gas) as compared to air (free gas) by order(s) of magnitude and may prove useful to distinguish the two. The bound nitrogen will occur as NH_4^+ proxying for K^+ with distinct isotopic signatures c. Multiple sources of nitrogen are possible, including contributions from the mantle and crust overlapping with signatures from organic matter (Fig. 3). Magmatic and crustal sources can be identified using a combination of carbon and noble gas isotopic and elemental ratios along with nitrogen.

CONCLUSIONS

An improved understanding of the shale gas formation, integrated with geochemical characteristics including C, N and noble gas compositions is important and essential for better identification of shales with high retention. Such integrated approaches can place constraints on lithologic, mineralogical and geochemical characteristics of shales important for economic production.

References
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