## CHLORITE-RICH CLAY ASSOCIATIONS IN INTERBEDDED TUFFS AND MUDSTONES: DIAGENETIC IMPLICATIONS

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The Upper Jurassic of two basins in southern South America and the Antarctic Peninsula is characterized by black shale/mudstone-dominated marine successions with interbedded tuff beds milimetric to decimetric thick. Anoxic environment precluded bioturbation and sediment mixing, and favoured organic matter preservation (TOC 2-8%). Some of these successions may form unconventional oil reserves, such as the VacaMuerta Formation, and therefore the study of clay mineralsis critical for the fracking process. As the clay mineral association developed on tuffs is totally diagenetic it may be regarded as a good tracer for the diagenetic grade. It is also remarkably different from the clay mineral association in the background sediments.

Most tuff beds in our case studies (the Ameghino Formation in the Larsen Basin, northeastern Antarctic Peninsula and the VacaMuerta Formation in the Neuquén Basin, western Argentina) are massively replaced by carbonate, chlorite andillite-smectite interlayers (I/S). In the localities selected for this study both units underwent deep burial in the context of high geothermal gradient basins. Chlorite is more abundant than I/S in the tuffs and the opposite is true for the background shales and mudstones.

XRD studies (bulk rock and fraction <2 microns) show similar composition for clays in carbonatized tuffs (early diagenetic carbonatic concretions developed on tuffs) and argilitized tuffs (white/yellow, soft, plastically deformed thin beds). The main clay mineral in the tuffs of the VacaMuerta Fm is Fe-rich chlorite, with variable contribution of interstratified illite-smectite layers (I/S). The I/S have more smectite layers in the tuffs, that are characterized as R1 I/S, in contrast with the R3 I/S in the mudstones. To Max (498-528 °C) from Rock-Eval Pyrolysis indicate the rocks are overmature and were submitted to temperatures about 150 °C (e.g. Peters, 1986).

The tuffs and carbonatized tuffs in the Ameghino Formation also show abundant Fe-rich chlorite, with variable contribution of I/S classified as R1 I/S in contrast with the R3 I/S in most mudstones. The carbonatized tuffs are slightly richer in smectite interlayers, and vitrinite Ro from 0.72 to 1.23 point to diagenetic temperatures from 100 to 120  $^{\circ}$ C.

The tuffaceous beds in the VacaMuerta and Ameghino Fms. are distal fallout tuffs mostly of siliceous to andesitic composition accumulated in anoxic basins close to a Late Jurassic volcanic arc in the western margin of Gondwana (e.g. Scasso, 2001). Large pumice as well as fine-grained glassy ash, together with the mafic minerals, and sometimes the feldspars and quartz, were replaced by carbonate, clays, pyrite and zeolites. The carbonate precipitated during the early diagenesis forming concretions that precluded later compaction of the beds (e.g. Scasso and Kiessling, 1991). The firstly formed clay mineral phases were probably smectite and a chlorite precursor, coeval with the carbonate precipitation and later transformed into I/S and Fe-rich chlorite during diagenesis. Smectite was transformed to I/S during burial diagenesis and illite interlayers increased substantially.

The clay mineral association in tuffaceous layers is richer in chlorite than the background sediments. The chlorite is entirely diagenetic and may be formed from a metastable precursor (Scasso and Kiessling, 2001) or from smectite transformation during advanced diagenesis (e.g. Foscolos, 1991) favoured by absence of K and limited illitization (Compton, 1991). On the other hand the I/S in the tuffs have more smectite layers than in shales and mudstones, which display poor XRD patterns and may lead to erroneous estimation of the diagenetic grade. A preliminary analysis indicates this may be the result of inherited detritic material in the fraction <2 microns or of the direct precipitation of R3 I/S in shales and mudstones (e.g. Wilson*et al.*, 2016).

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<sup>[4]</sup> Scasso, R.A.(2001). High frequency of explosive volcanic eruptions in a Late Jurassic volcanic arc: the Ameghino Formation on the Antarctic Peninsula. Journal of Sedimentary Research 71(1), p. 101-106.

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