

# Geochemical changes in experimental water or HCl reactions of the Cooper Basin REM shales

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## SUMMARY

Production or flow-back water from shale gas stimulation has been reported in the USA to contain high salinity, TDS and variable concentrations of potentially toxic metals such as uranium, barium, or lead. The shales of the Cooper Basin REM sequence have a high prospectively for unconventional gas. Water reactions of shale core samples were performed in mildly oxic conditions and at elevated temperature and pressure to investigate potential for metal mobilisation. A relatively higher concentration of lead, vanadium, chromium, zinc and copper, was measured in the Roseneath shale core, which on water reaction mobilized a higher concentration of dissolved uranium, cadmium, cobalt, chromium, zinc, copper and nickel. Mobilized metal concentrations were however generally <10% of the amount available in the core. Relatively higher concentrations of calcium, magnesium and sodium were mobilized from the Murteree shale. Mobilised uranium and barium however remained low. SEM-EDS indicated that the carbonates were most reactive, with dissolution creating porosity in the Roseneath shale. Fe-rich precipitates were also formed in both cases. We found the presence and type of carbonate and sulphide minerals have a strong control on water chemistry and generated acidity. When reacted with HCl, the Epsilon Formation sample showed strong corrosion of carbonates leaving pits, with no Fe-rich precipitates formed. Experimental fluid-rock interactions can give understanding and insights to the potential chemistry of flow back water which may be different from different shale formations.

**Key words:** shale, unconventional gas, hydraulic fracturing, geochemistry, metal mobilisation.

## INTRODUCTION

Hydraulic fracturing has been extensively used in the USA to increase gas production from low permeability or tight shale formations such as the Marcellus, Bakken or Barnett shales. The use of water volumes (with chemical additives and proppants) in the range of 2 - 5 million gallons per well have been reported, with variable proportions (30-50 % typically) returning to the surface as flow back or produced water (Gregory et al., 2011). This water may then be treated or disposed by reinjection, or stored at surface in holding ponds. This generally varies by play depending on the water quality, available treatment facilities, or suitable formations for reinjection. The produced water commonly is highly saline, and has been reported to contain TDS and high or variable concentrations of regulated metals and metalloids which have raised environmental concerns in the USA (e.g. Phan et al., 2015 and references within).

The Cooper Basin in SW Queensland and NE South Australia has been estimated to have ~ 85 Tcf of technically recoverable shale gas by the US EIA (2011). The Permian Roseneath-Epsilon-Murteree (REM) shale, sand, and shale sequence, especially the Roseneath and Epsilon shales have high prospectively for unconventional gas (Jadoon et al., 2016). Core samples from the formations were characterised and, reacted with water (or acid) at elevated pressure and temperature to determine their potential for, and controls on, mobilisation of metals and metalloids.

## METHOD AND RESULTS

Quarter cores were sampled from several depths of the REM sequence (Figure 1) from the Encounter 1 well core drilled by Beach Energy in 2011 in the Nappamerri trough. A core from each of the Roseneath shale, Epsilon Formation, and Murteree shale was subsampled at 3266m, 3491m, and 3497m respectively (Beach Energy 2011). Core bulk mineralogies were determined by X-ray diffraction (XRD), with trace minerals detected by SEM-EDS surveys in back scatter electron mode. Core acid digestions with analysis by ICP-OES and ICP-MS were also performed to determine metal contents, with similar methods published previously (Pearce et al., 2016). The shales were separately reacted in Parr vessels (Figure 2) with custom built thermoplastic liners to contain fluids and sampling dip-tubes, at a temperature of 75 °C and pressure of 200 bar, the reactors have been described in detail previously (Pearce et al., 2015). Roseneath, and Murteree shale core 1 cm<sup>3</sup> cube samples were separately immersed in 70 ml of DI water at a water –rock ratio of ~ 23 (pH 5). The Epsilon Formation core sample was reacted in a HCl solution of pH 1 to check for dissolution and precipitation features. The reactors were flushed with N<sub>2</sub> gas and pressurised with an ISCO injection pump. The water contained residual dissolved oxygen, giving mildly oxic conditions. Fluid was periodically sampled during the water reactions for 7 days, with pH and conductivity measured immediately. Sampled fluids were filtered (45µm), diluted, and acidified with ultrapure HNO<sub>3</sub> for analysis by ICP-OES and ICP-MS. After reactions, the core samples were recovered and oven dried for SEM-EDS analysis to detect mineral dissolution and precipitation features.

The shales all contain siderite, quartz, illite/muscovite and kaolinite, with organic matter and traces of pyrite or S signature in the organic matter. Siderite in all the cores appeared to contain a proportion of Mg, and the Murteree core had a relatively higher proportion of siderite. Trace amounts of Ti-oxide and apatite were observed in all cores. Roseneath contains relatively higher concentrations of several metals including Ba, and Cr, Zn, V, Pb commonly associated with sulphides (Figure 3). SEM-EDS indicated the sampled Roseneath shale core also contained sphalerite. The Murteree and Epsilon cores contained small amounts of ankerite (Figure 4).

After the water reaction of Roseneath, siderite on the surface of the core was corroded leaving pits in the clay matrix (Figure 3D). Fe-rich (red-brown) precipitates covered the surface. After water reaction of the Murteree, some areas of siderite/ankerite were corroded with Fe-rich (red-brown) precipitates on the surface. Compared to the Roseneath, the Murteree surface appeared less corroded. After HCl reaction the Epsilon core appeared bleached, with strong corrosion of the carbonates leaving pits in the surface, no Fe-rich precipitates were formed (Figure 4).

During water reaction of the Roseneath core, solution pH decreased to 2.4 and subsequently increased to ~ 3 (Figure 5). Dissolved concentrations of several metals including Mg, Mn, Cr, As, Ca, Ni, Na, Fe, Zn increased. Dissolved Fe, Na, Cr, As, Ni concentrations subsequently decreased during the reaction.

During reaction of Murteree core, pH increased slightly to 5.5 and subsequently decreased/ stabilised to ~ 4.2 (Figure 5). Dissolved Mg, Mn, Cr, As, Ca, Ni, increased, Cr, As subsequently decreased or stabilised. Dissolved Na and conductivity were initially high on Murteree reaction (393 mg/kg and 2106  $\mu$ S/cm respectively) indicating dissolution of pore salts or fast ion exchange, and subsequently decreased during reaction.

The concentration of dissolved Ca, Mg, Mn from carbonates was higher from Murteree shale during water reaction relative to the reaction of Roseneath. The mobilised concentrations of Cr, As, Ni, Zn and S were higher from reaction of the Roseneath shale (relative to the Murteree), likely from the sphalerite oxidation dissolution. The concentration of dissolved Ba remained low (below 10  $\mu$ g/kg) during both water reactions even though the Ba content in the cores was high. U also remained low, below 3  $\mu$ g/kg during reactions, and Pb concentration was variable but below 33  $\mu$ g/kg.

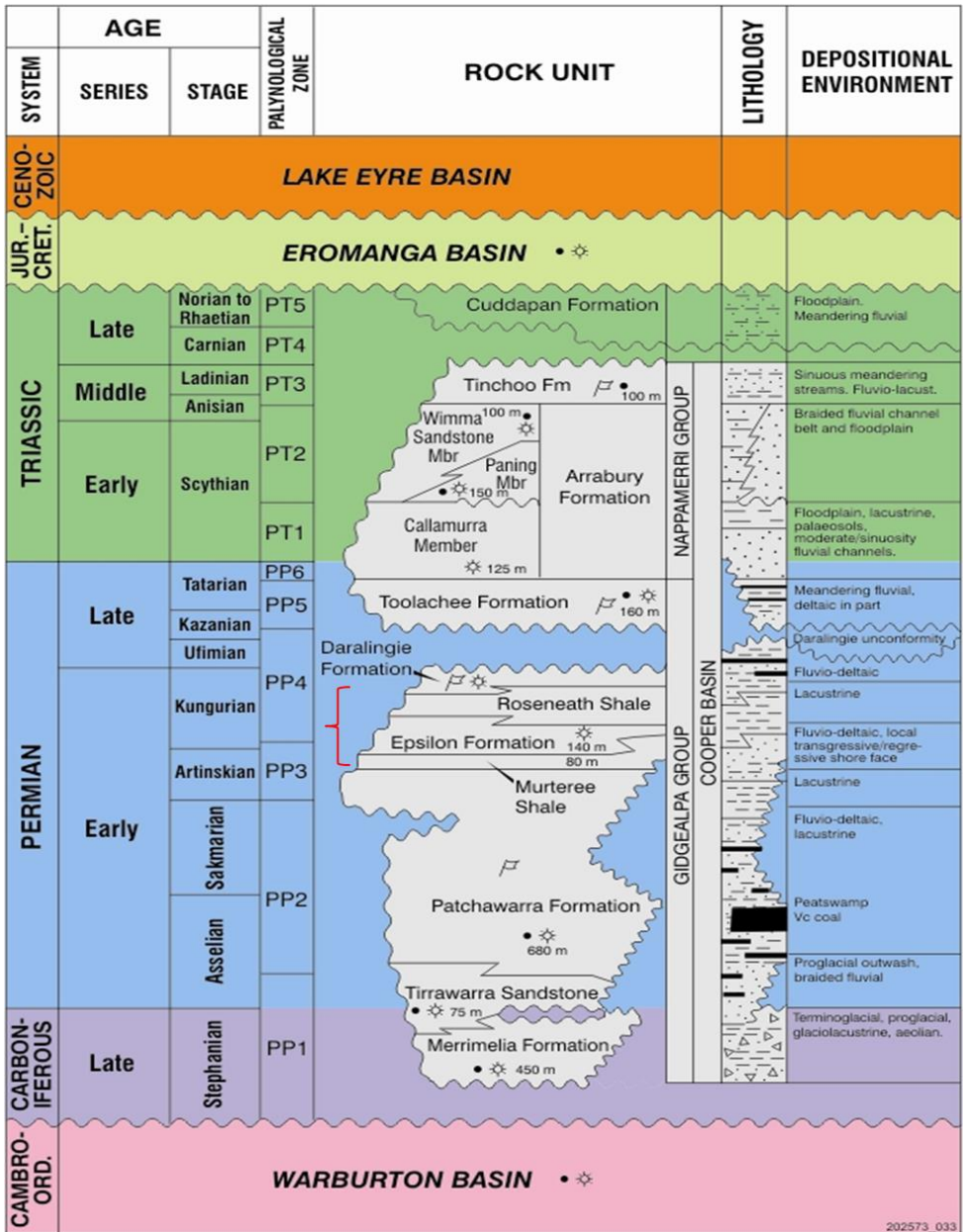


Figure 1: Stratigraphy of the Cooper Basin with the REM sequence group marked by a red bracket. Modified from PIRSA 2007.

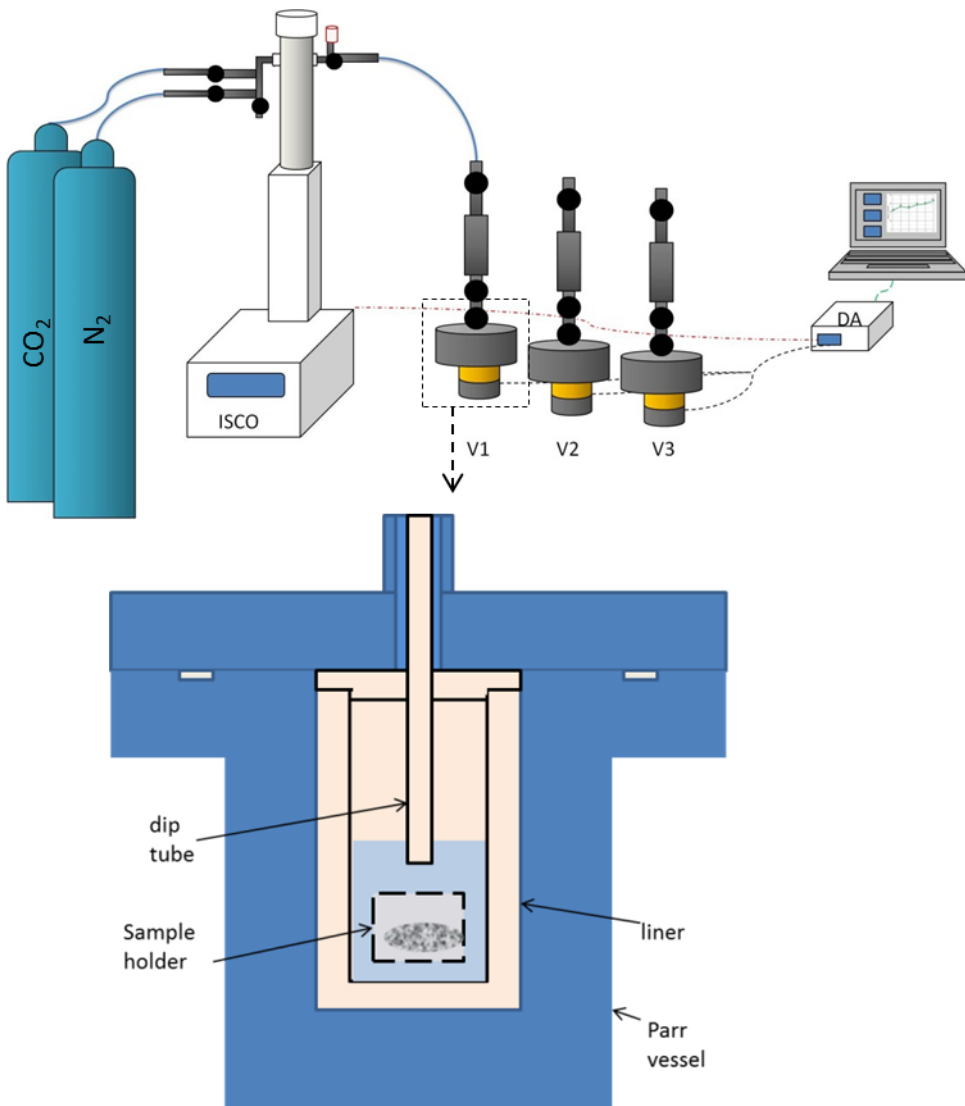


Figure 2: Experimental schematic of the experimental setup and reactor used, where ISCO is the injection pump, V is a vessel, DA is data acquisition.

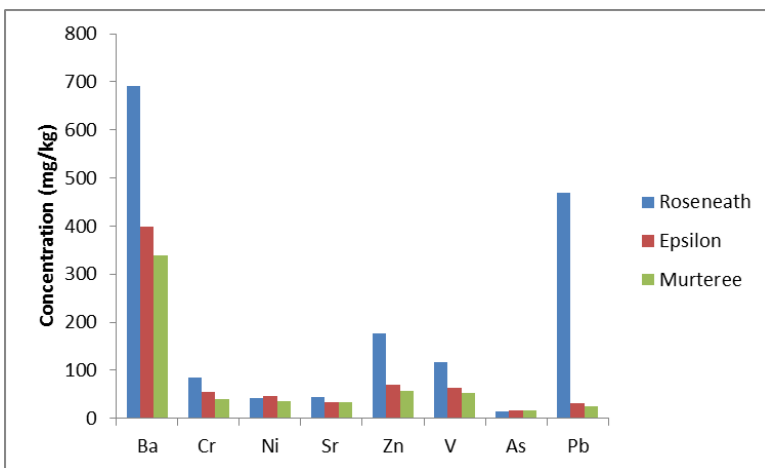
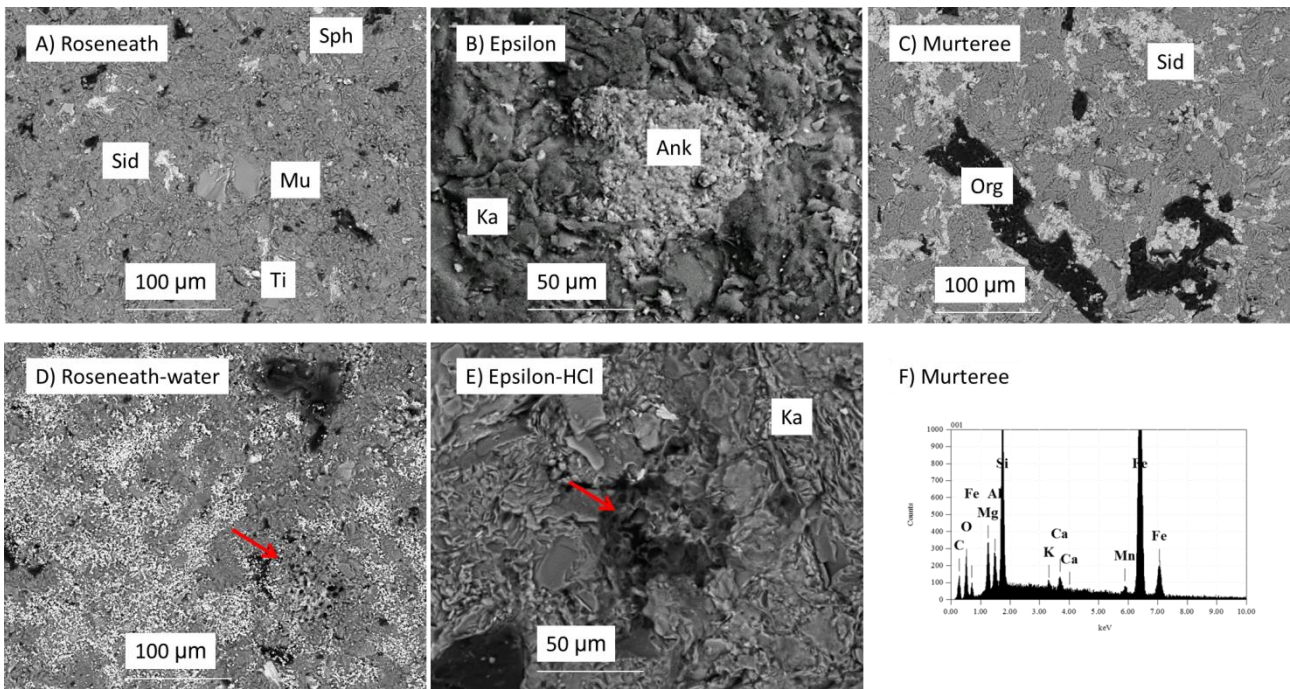
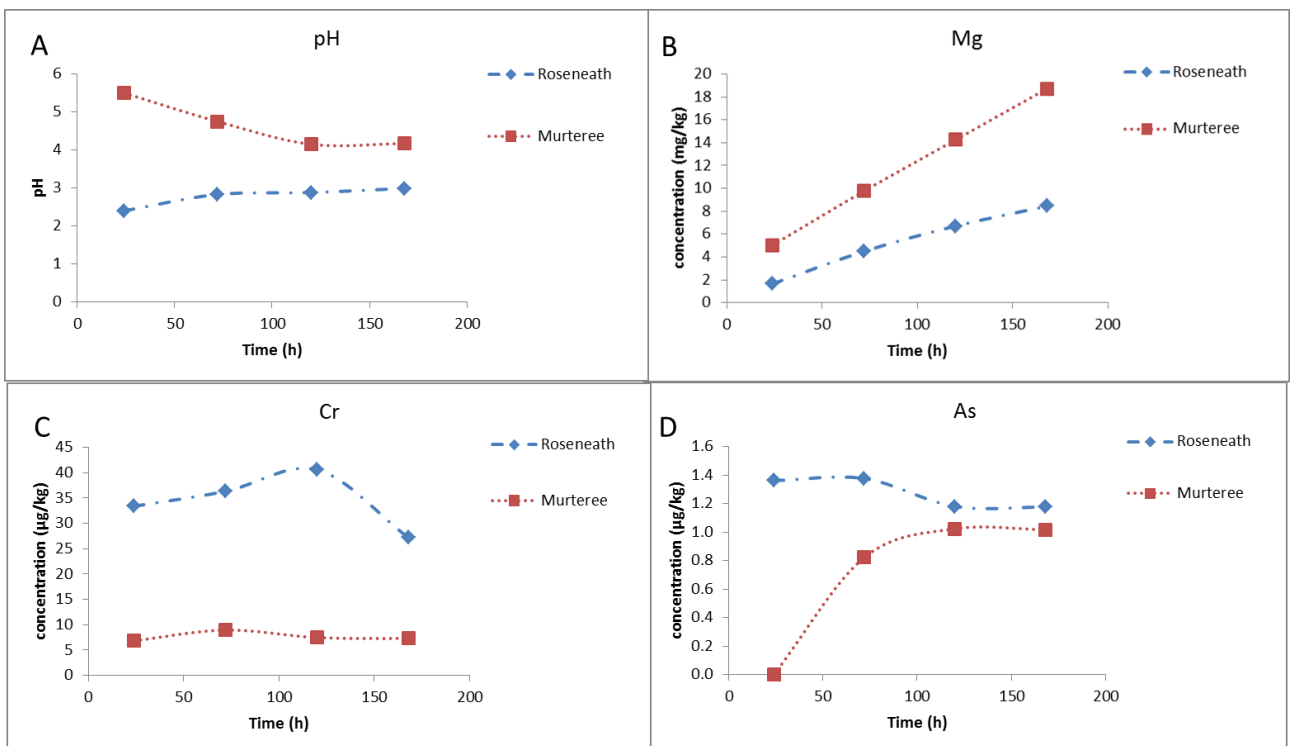


Figure 3: Concentrations of selected metals in the tested Roseneath, Epsilon, and Murteree shale cores from total digestion.



**Figure 4:** SEM-EDS (BSE) images of A – C) Roseneath, Epsilon and Murteree shales where Ti = Ti-oxide, Sid = siderite, Mu = muscovite, Sph= sphalerite, Ka = kaolinite, Ank = ankerite, Org = organic matter. D) Roseneath after reaction with water covered in bright Fe-oxide precipitates, red arrow indicates created pores on the surface. E) Epsilon after reaction with HCl with red arrow indicating a created hole from carbonate dissolution. F) EDS of ankerite (mixed with kaolinite) in the Murteree.

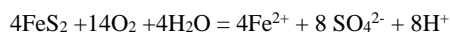


**Figure 5:** Solution pH and concentrations of dissolved metals during water reaction of the Roseneath and Murteree shale cores. A) pH, B) Mg, C) Cr, D) As.

## CONCLUSIONS

Water reactions of Cooper Basin Roseneath and Murteree shales at elevated pressure and temperature and mildly oxic conditions, indicate that the mineralogy of the shale will have a control on the chemistry of the interacting water and potentially the flow back

water. Higher core sulphide contents result in lower generated pH through sulfuric acid generation, with resulting release of metals such as Cr, As, Ni, and subsequent stronger corrosion of other minerals.



Higher carbonate content, especially the presence of ankerite in the Murteree shale core resulted in a more buffered less acidic pH. Subsequent precipitation of Fe-rich phases including Fe-oxides corresponded with a decrease in mobilised metals. Mobilised concentrations of U, Ba, As, Pb remained relatively low.

The geochemical response of shales has been more widely published in the CO<sub>2</sub> storage context as cap-rocks, than reactions of gas bearing shales (e.g. Carroll et al., 2013; Pearce et al., 2015; Pearce et al., 2016; Shao et al., 2014). In the context of gas bearing shale fracture fluid interactions, German Posidonia shales containing 15-73 % carbonate and black Alum shales from Denmark containing pyrite and little to no carbonate were reacted in water experimentally at 100 °C for 24 hours (Wilke et al., 2015). Those authors observed a strong control of solution pH by sulphide or carbonate content, in good agreement with our work. Wilke observed that pH decreased to pH 2-3 in water reactions of Alum shales, with higher concentrations of As, Zn, Cr, Ni, U released from the pyrite rich core. However pH buffered to 7-8 in reactions of calcite rich shales from calcite dissolution. In experiments with a simulated fracture fluid, those authors determined that the resulting pH was independent of the stimulating fluid pH but dependent on the mineral content or buffering capacity of the shale, especially for high carbonate content shales. In similar work on Bakken shale, Eagle Ford shale and Marcellus shale from the USA, generated pH and resulting potentially toxic metal mobilisation from shales was also linked to shale mineral content and oxidant availability (Marcon et al., 2017; Wang et al., 2016). Those studies additionally observed mobilisation of organic components. The addition of acids to fracture fluids has been suggested as a solution to open microfractures too small for proppants in carbonate containing shales (Wu and Sharma 2017 and references within). The use of fluids with high acid content may increase the mineral corrosion and concentrations of mobilised metals.

Flow-back or produced water from shales with high sulphide contents may need more treatment than those from shale with high carbonate contents. Experimental fluid-rock interactions can give understanding and insights to the potential chemistry of flow back water prior to production. Future work with shales of a range of mineral contents and simulated fracture fluids are suggested.

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