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Reservoir-scale CO₂-fluid rock interactions: Preliminary results from field investigations in the Paradox Basin, Southeast Utah

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Abstract

Despite a long history of detailed study, the extensive Jurassic sandstone outcrops of the Colorado Plateau in Southeast Utah, USA continue to provide opportunities to examine reservoir-scale processes. There are a number of large-scale CO₂ accumulations in these reservoirs and locally also natural and man-induced CO₂-rich springs and geysers, often producing or associated with travertine deposits. These rocks have therefore been exposed to CO₂ and/or CO₂-rich waters over a substantial period of time, and as such may provide information on resulting geochemical and geomechanical processes.

Salt Wash Graben is a WNW-ESE trending structure that cuts across a northerly plunging anticline to the south of Green River, Utah. The Salt Wash Graben lies to the south of the well-studied 'Crystal Geyser', and itself contains several CO₂-rich springs and abundant travertine deposits. Rocks of the Slick Rock and Earthy members of the Jurassic Entrada Sandstone outcrop in the core of the anticline immediately to the north of the graben. These are locally extensively bleached, the bleaching being most pronounced towards the base of the stratigraphically lowest exposed strata, forming a light coloured area in aerial photos.

Field investigations of the nature of this bleaching and its relationship to faults and fractures, travertines and CO₂ springs, have been supported by detailed analysis of aerial photographs and other satellite-based remote sensing data. The remote sensing data provides a geological context that serves to highlight the different structural and stratigraphic controls which were observed between the regionally extensive bleaching and the bleaching in the Salt Wash Graben. Diagenetic analyses have identified the geochemical processes responsible for bleaching (loss of iron-staining) and other fluid-rock interactions, notably increased porosity in bleached sandstones and differences in carbonate cementation. Simple laboratory experiments have also attempted to replicate these processes by reacting samples of unbleached Entrada Sandstone with CO₂-rich formation waters. In this paper, we present a preliminary hypothesis that attempts to link the features described in the Salt Wash Graben, which suggest that CO₂-rich fluids may have produced the observed features. If this hypothesis is proved correct, the Salt Wash Graben offers considerable potential to study in detail the flow-constrained geochemical processes at reservoir scale.

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1. Introduction

The principle objective of CO₂ storage of ‘permanent containment’, as recently defined in European legislation requires that before an operator is permitted to inject CO₂ underground, they must demonstrate that the reservoir is able to contain the fluid over geologically significant periods of time. While the physical retention of CO₂ by reservoir seals is likely to provide the principle method of retaining the buoyant plume in the immediate period after injection, it will also be necessary to demonstrate that the slower geochemical interactions which occur as CO₂ dissolves into in situ reservoir porewater are at least understood and preferably that these interactions increase the likelihood of long term containment. In order to demonstrate the site-specific reactions expected, predictions of geochemical interactions via coupled flow-geochemical modeling will be undertaken. Such calculations rely on thermochemical databases that define the properties and rates of reaction. While in many cases such parameters are very well defined, a better understanding of the rates of reactions, especially at more representative reservoir scale conditions is desired. One way of constraining the behavior of CO₂-rich fluids is to study relevant natural systems in an attempt to obtain indications of both the likely directions and scale of geochemical reactions.

There are a number of large-scale CO₂ accumulations in reservoir rocks of the Colorado Plateau, SW USA [1]. In addition, locally in this region there are also natural and man-induced CO₂-rich springs and geysers, often producing or associated with travertine deposits. These rocks have therefore been exposed to CO₂ and/or CO₂-rich waters over a substantial period of time (though exactly how long has yet to be determined), and as such may provide information on resulting geochemical processes. In Salt Wash Graben there is extensive bleaching of sandstones in the area around these springs and travertines. This paper describes the nature of this bleaching and its relationship to faults and fractures, travertines and CO₂ springs, and presents a preliminary hypothesis that attempts to link these features.

Previous studies of relevance have focussed on either the many CO₂-rich springs in the area [e.g. 1] as analogues for near-surface CO₂-leakage, reservoir processes derived from fluid geochemistry [e.g. 2, 3] or have proposed that extensive regional bleaching is associated with the passage of buoyant hydrocarbon fluids and the existence of large hydrocarbon pools which were lost during uplift and exhumation [e.g. 4]. Bleaching of red sandstones in the northern and central Colorado Plateau region is widespread and commonly attributed to removal of iron resulting from the passage of buoyant hydrocarbon fluids. Field relationships in the Salt Wash Graben suggest that the origin of the bleaching in this area may be different. Our recent studies have addressed the question of whether, in some areas at least, evidence of large-scale reservoir palaeo-fluid movement and geochemical interactions, may be attributable to more recent CO₂-rich fluids [e.g. 5].

Here we describe the nature of relationships between bleached rocks exposed in the Saltwash Valley and features associated with the passage of CO₂ determined by fieldwork undertaken as part of the CRIUS project to determine reaction kinetics relevant to reservoir-scale injection.

2. Geological setting

Rocks in this area form part of the fill of the Paradox Basin which lies within the Colorado Plateau in SE Utah and SW Colorado, and formed along a series of NW-trending basement faults following the late Carboniferous Ouchita orogeny. Sediments are dominated by continental red bed deposits and are thickest along the NE margin where it is bounded by the Uncompahgre fault. Basin fill started with late Carboniferous cyclic carbonates, black shales and thick evaporites. This was followed by up to 2400m of dominantly aeolian and fluvial / alluvial sediments of Permian age. Triassic sediments range from coastal plain deposits of the Moenkopi Formation, through fluvial and lacustrine Chinle Formation sediments to the massive erg deposits of the Wingate Sandstone, and the overlying fluvial sheet flood sandstones of the Kayenta Formation. The thick dune deposits of the Navajo Sandstone span the Triassic-Jurassic boundary and are overlain by the Entrada Sandstone, dominated by dune deposits but with marginal marine and lacustrine influences at the base. The Slick Rock and Earthy Members that are the focus of this paper are combined as a unit in the 10 mile Graben and lie at the top of the Entrada Sandstone. Where mapped as

separate units elsewhere, the Earthy member ranges up to 42m thick and the Slick Rock from 43 – 152m. Approximately 30m is exposed in the core of the gently N dipping anticline and the base is not exposed.

NW-SE trending salt walls are the dominant structural feature in the Paradox Basin, resulting from movement of the Carboniferous evaporites at various times during the Triassic and Jurassic, and probably initiated by movements along controlling basement faults. Uplift of the Colorado Plateau eventually facilitated dissolution of the upper part of these salt walls and resulted in collapse of their crestal portions and the formation of wide and deep valleys. These features are commonly bounded by major NW-SE trending faults at surface, such as the Moab Fault, which are intermittently active to the present day. The Ten Mile Graben and Little Grand Wash fault to the north trend WNW and approximately E-W respectively. They both downfault Jurassic and Cretaceous strata, the youngest strata preserved being of late Cretaceous age.

Paradox Basin sediments are widely exposed throughout this region and are commonly and extensively bleached. This regional scale bleaching has mostly been attributed to the passage of hydrocarbon-bearing fluids [4]. The field relationships of the bleaching in this area however, appear different and may suggest a different origin.

Salt Wash Graben is a WNW-ESE trending structure that cuts across a northerly plunging anticline to the south of Green River, Utah (Figure 1). It lies to the south of the well-studied 'Crystal Geyser', and on its northern margin has several CO₂-rich springs and abundant travertine deposits. Rocks of the Slick Rock and Earthy members of the Jurassic Entrada Sandstone outcrop in the core of the anticline immediately to the north of the graben. These are locally extensively bleached, the bleaching being most pronounced towards the base of the stratigraphically lowest exposed strata, forming a light coloured area in aerial photos.

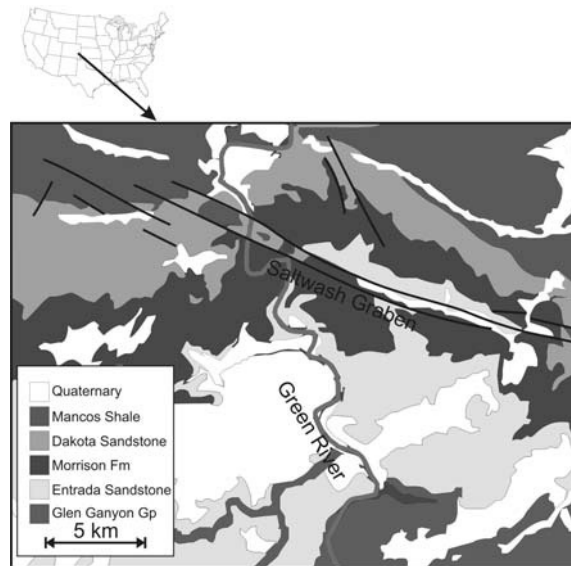


Figure 1: Location map of the study area.

3. Field relationships

As in most other areas of the regional exposure in southeast Utah, outcrops of the Slick Rock and Earthy Members of the Entrada Sandstone exposed in the Saltwash Valley immediately to the north of the fault-bounded Tenmile Graben are typically red in colour. However, analysis of aerial photos, confirmed by subsequent field investigations, indicate that towards the western end of the valley and especially in the valley floor, the Entrada Sandstone has been bleached to a light colour, which varies from light grey to yellow. Although outcropping in stream banks and cliff exposures broadly parallel to the northern bounding fault of the Tenmile Graben over a distance of 8.5 km, the largest continuous area of bleaching is exposed at the western end of the valley. Bleaching is exposed up to 800 metres north of the fault which is well exposed in places along its length in this area. The western bleached outcrops form the valley bottom, and form a completely exposed section from the fault over an area of 800 by 350 metres (Figure 2).

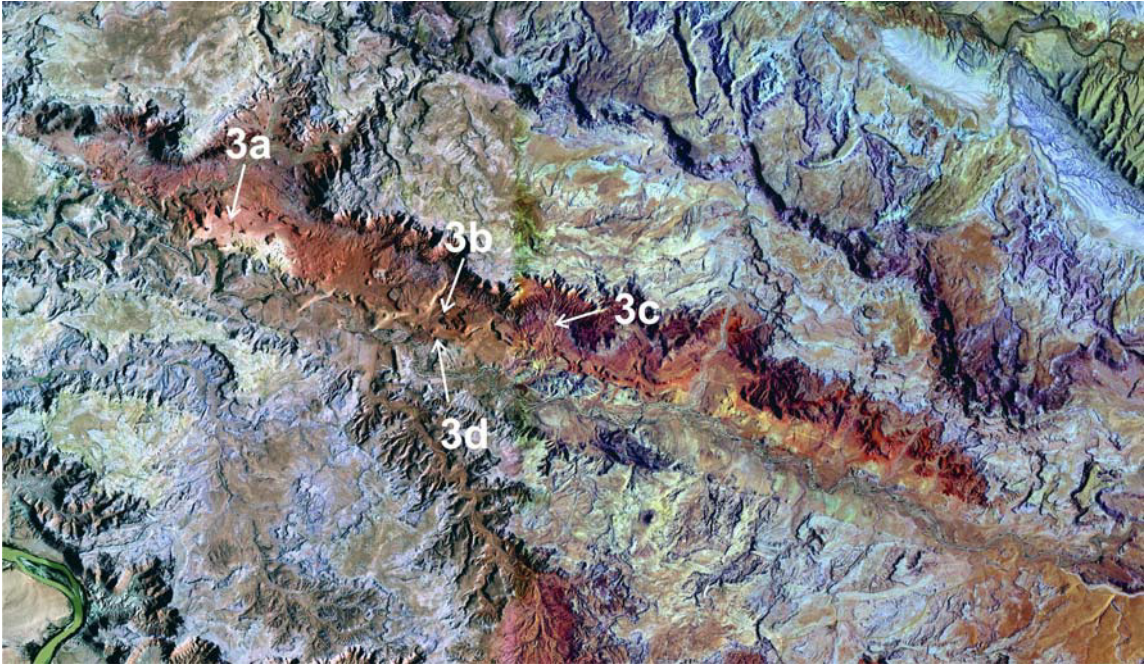


Figure 2: Contrast-enhanced aerial photograph of the Saltwash Graben, draped over a 1m resolution digital elevation model. Areas of bleached Entrada Sandstone are clearly visible in the valley bottom and exposed along the base of the northern valley slope. Locations of photos in figure 3 are indicated by arrows.

The thickest bleached exposure occurs immediately to the north of the fault itself in the core of the anticline where a maximum thickness of approximately 25 metres of bleached sandstone is observed in outcrops. The bleached contact is stratigraphically higher by a few metres here relative to that in the east of the valley. The true base of the bleached horizon is not exposed.

There is a well-defined top to the bleaching. At the regional scale, analysis of aerial images and mapping of the bleached contact indicates that this contact is broadly conformable with the stratigraphic dip. However, at the outcrop-scale, the contact between underlying bleached and overlying unbleached sandstone cuts down within a given unit at a steeper angle than the stratigraphic dip. The contact is sharp with gradation occurring over a maximum 20 mm distance. One of the most striking features of the contact is the metre-scale cusperate nature of this upper contact, which is particularly well developed in outcrops with orientations broadly parallel to the major graben-bounding structural fault (Figure 3a). Detailed examination of these outcrops indicates that there is no apparent lithological control on the vertical position and morphology of this contact, which typically occurs within broadly massive to large-scale dune cross-bedded aeolian sandstone. Outcrops orientated at more acute angles to the fault tend to have generally flatter, bedding-parallel contacts. Although generally subparallel to bedding, the top of the bleaching occasionally changes rapidly over a few metres to a subvertical contact resulting in downward arcing terminations, sometimes within metres of an opposing downward contact. This may suggest that the movement of the fluids responsible for the bleaching occurred in discrete cells.

Conjugate, subplanar fractures, with dominant sets with variable dip up to $\sim 80^\circ\text{N}$, occur at varying densities throughout the valley and cut through the sandstone units. The wallrocks to many of these have been bleached to variable distances up to 50cm, allowing these fractures to be traced over hundreds of metres. In some cases, the bleaching ‘rises’ up along these fractures to form upward protuberances with curved contacts, typically up to 2 metres in height but occasionally forming larger bleached protuberances of several metres wide. The very outer margins of these bleached protruberances are commonly more intensively bleached than the remainder.

Towards the central and eastern areas of bleached sandstone, the bleaching occurs as subhorizontal fingers up to several metres thick with sharp upper and lower boundaries (Figure 3b). This inter-fingering is thought to indicate preferential flow along more permeable zones within the sandstone unit. However, as noted above, these variations

are expected to be subtle as at outcrop no change in lithology can be observed. Ongoing petrographic analyses will provide further information on the subtle controls on fluid movement in these reservoir sandstones.

Outcrops towards the northern limit of the surveyed area contain further examples of vertical migration of the bleaching fluid where subvertical fractures have enabled significant bleaching of adjacent wallrock producing bleaching up to 2 metres across. Higher, presumably more permeable, strata are extensively bleached parallel to the stratigraphy along the entire length of the outcrop, with the junction between fracture and permeable strata above developing a broad funnel-shaped bleached zone (Figure 3c). This outcrop is considered to provide evidence of the bleaching fluid moving vertically along fractures from one broadly stratabound bleached unit to a higher one, several tens of metres above the regional main upper bleached contact.

Travertines cap many of the low hills in the Saltwash Valley, forming extensive aragonite and calcite mineralisation along bedding parallel joints [1]. These are assumed to be form a continuous sequence with modern travertines that form at well-known springs and open wells throughout the Saltwash Valley [e.g. 1, 3] following CO₂ degassing and carbonate precipitation as groundwaters reach the surface. Where exposures permit, it can be seen that these travertines pass downwards into thick anastomosing networks of irregular veinlets of carbonates and iron mineralisation subparallel to the ground surface. Evidence of associated Fe precipitation occurs in the form of variably ochreous staining to wallrock adjacent to some mineralised fractures (Figure 3d) and along permeable bedding surfaces, indicating a further change in redox and precipitation of iron oxide associated with CO₂-rich travertine forming fluids. These in turn are underlain, partially cut and apparently fed by subvertical mineralised fractures with extensive calcite forming thick white, occasionally anastomosing networks. Multiple episodes of aragonite with minor calcite precipitation within a single fracture indicate repeated and sustained mineralisation, with some possible reactivation. Ochreous iron oxyhydroxides coat new aragonite mineralised surfaces indicating iron mobilisation associated with CO₂-rich fluid movement. Occasional voids have enabled development of coarse, euhedral, spar and nailhead calcite development. Some of these fractures pass downwards into the same fractures that occur in the centre and appear to have controlled to vertical protuberances of the top of the bleaching. Where mineralised, these fractures within the upward bleached protuberances appear to have an intensively bleached margin similar to the margins of the protuberances themselves. Bleaching fluids and CO₂ rich fluids have therefore utilised the same fractures and the bleached margins to the mineralised veins may provide circumstantial evidence that the cause of the bleaching may be linked to the migration of CO₂-rich fluids at depth. It may therefore suggests that the evidence of regional fluid migration preserved in these reservoir-like sandstones may be analogous to processes that may occur following CO₂ injection in a geological storage operation.

Although analysis of aerial images indicated bleaching is also developed further south where the same Entrada Sandstone strata are exposed to the north of Ruby Ranch, the bleaching here has some important differences to that observed in the Saltwash Valley. Here, bleaching is thinner, less well-developed with gradational top and bottom contacts which may indicate diffusion from bedding-parallel surfaces, and it only occurs parallel to stratigraphy. Here the bleached rock has a greyish colour relative to the yellow-ish colour of bleached rock in Saltwash. Gradational boundaries and there is no evidence for either dense or buoyant flow.

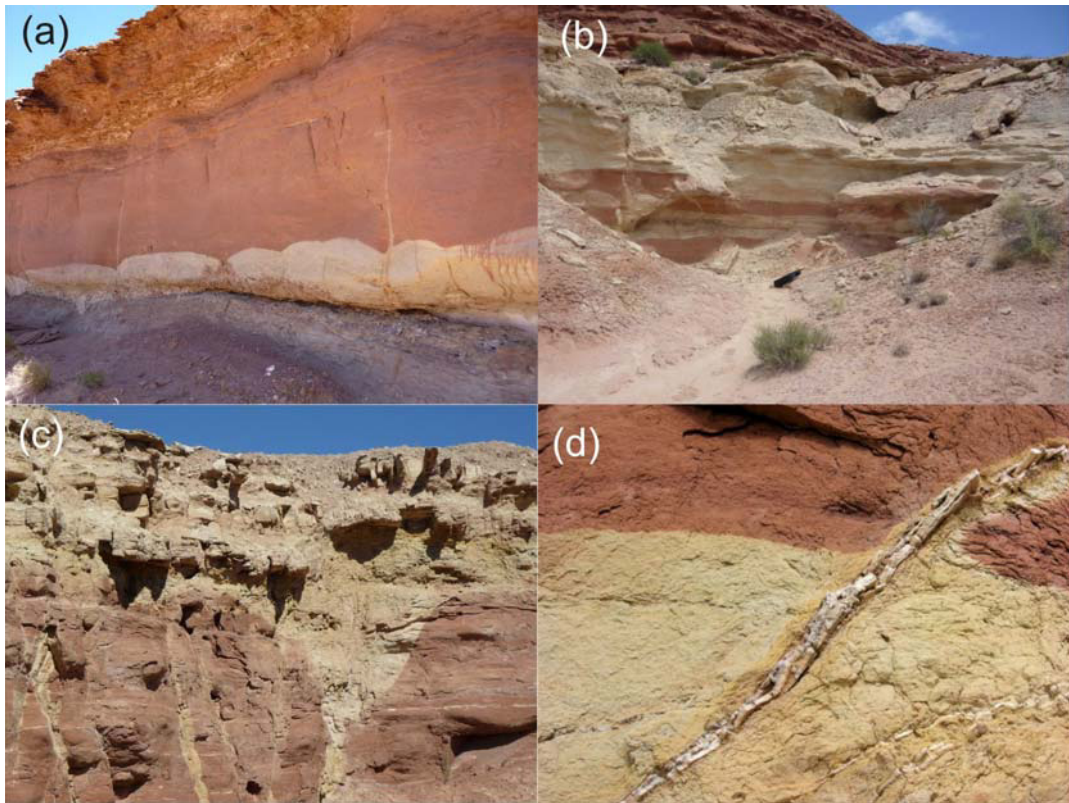


Figure 3a: Cusplate sharp contact between lower bleached and upper unbleached Entrada Sandstone, looking approximately southeast. (b) Interfingering of bleached sandstone reveals subtle changes in permeability. (c) Bleaching developed above main bleached horizon, with bleached margins to subvertical fractures indicating migration of fluid up fractures and along more permeable strata. (d) Close-up of contact between bleached and unbleached sandstone with fracture reactivation leading to travertine mineralisation and wallrock staining by ochreous Fe oxide. See figure 2 for locations.

3.1. Comparisons with regional bleaching

Bleaching of Jurassic red bed continental sandstones have been reported previously for southeast Utah (e.g. in the Navajo, Wingate and Keyenta Sandstones by Beitler et al., 2003) and has been attributed, as for bleached reservoir sandstones elsewhere, due to reduction and subsequent removal of Fe^{3+} to Fe^{2+} by hydrocarbon bearing fluids. Examples of this type of bleaching have been examined for this study and are considered distinct from the bleaching described above in the Saltwash valley. The principle distinction is the distribution of bleached sandstone generally towards the top of a given unit and also occurring towards the top of structural highs, typically anticlinal trap structures and especially within better reservoir quality sandstones in dune cross-strata that concentrate fluid-flow in the upper third of the formation [4]. The style of bleaching described here for the Saltwash Valley differs in that it does not occur in the structurally highest areas and does not display features consistent with migration of buoyant hydrocarbon-rich fluids.

4. Preliminary analytical results

Preliminary petrographic and mineralogical analyses of a few samples are reported here. Four samples of bleached and four samples of unbleached sandstone from several locations within the Saltwash Valley were analysed. Analyses are ongoing on a much larger suite of samples and will be reported elsewhere. In the Saltwash Valley, the Entrada Sandstone comprises a moderately to well sorted, fine to medium grained sandstone. Primary detrital clasts are angular to subangular and quantitative XRD indicates are predominantly quartz (79%), with minor

K-feldspar, relict albite, mica and up to 0.5% pyrite. Detrital grain surfaces are coated in a thin (<5 µm thick) inherited, primary iron-rich clay coating which XRD indicates is predominantly illite with minor illite-smectite. Up to 0.5% hematite is detected by XRD in unbleached sandstones and occasionally observed as euhedral hexagonal micron-scale crystals by BSEM. Variations in the thickness of clay coatings and proportion of interstitial, largely primary, clay matrix across weakly developed laminations controls the proportion of later cements such as later calcite described below. In some areas, dewatering or possible bioturbation(?) has led to the destruction of primary lamination.

Early and sustained compaction reduced much of the primary porosity. However, although variable and patchily distributed, concurrent dissolution of lithic clasts, K-feldspar and albite led to the formation of well-connected secondary porosity, which is occasionally partially filled by euhedral kaolinite books which continued throughout and after maximum compaction. The detrital clasts are partially cemented by trace euhedral quartz overgrowths and minor carbonates. Early dolomite (up to 6%) forms euhedral rhombs with Fe-rich outer zones and minor calcite, most likely associated with formation in subaerial sabkha like environment and, as it infills primary porosity, pre-dating feldspar dissolution. This early dolomite and calcite dominate the cement and is followed by two further generations of calcite being tentatively recognised in petrographic analysis and post-dating the secondary porosity, post-dating maximum compaction. The calcite cement is variably distributed in the few samples examined to date, with secondary voids formed by dissolution of earlier calcites cements subsequently lined by later euhedral calcite spar. The amount of porosity and hence later carbonate cement appears to be controlled by the primary fabric, with laminae containing higher proportions of primary clay matrix having reduced secondary porosity.

The red to orange colour of unbleached sandstones is due to the presence of very fine grained hematite intimately associated with primary clay coatings on detrital grain surfaces, and is the defining feature of continental aeolian sandstones. Loss of this hematite from clay rims is clearly seen in optical petrography, though the small proportion of hematite in unbleached samples, close to limits of detection, makes quantification of the amount lost by XRD difficult. Preliminary petrographic and mineralogical comparisons between the limited number of unbleached and bleached samples indicates that no significant differences are present in the proportion of carbonate minerals. Though a late but minor calcite cement has been identified and could be related to near-surface travertine development, further work is required to determine its exact paragenetic relationship to predominantly aragonite mineralisation within fractures.

5. Proposed fluid migration mechanisms

The distinctive nature of the bleaching and association with CO₂ springs and travertines requires an explanation. We have considered a number of mechanisms, briefly discussed here, that could account for the observed features. While the bleaching along fracture margins and apparent lateral ‘spreading’ of bleaching in permeable zones away from such fractures is consistent with buoyancy-driven flow, the predominant occurrence of bleaching towards the bottom of individual units without other internal lithological control throughout the area would suggest that the fluid responsible for the bleaching was more dense than the in situ porewater. If this is the case then this fluid has been introduced into the sandstone when at depth and under pressure. The steeply dipping fractures are obvious pathways for this fluid driven along a pressure gradient from depth both upwards along fractures and along the base of permeable units encountered along the way. However, though many of these features are consistent with upwards migration of fluids, such migration may be part of a greater fluid circulation pattern with some areas having broadly downwards fluid movement and others corresponding upwards movement [e.g. 6].

Though the spatial proximity and re-use of existing fractures for both bleaching and modern CO₂-rich fluid migration may imply a genetic association, there are some further important considerations that must be taken into account before the extensive bleaching in the Saltwash Valley can be definitively attributed to a CO₂-charged system. Firstly the bleaching has been affected by recent tectonic movement, as it is folded in the central region and faulted in both central and western areas, and hence has predates at least the last movements on the fault. Thicker exposures of bleached Entrada Sandstone occur immediately adjacent to the fault. Although this may simply reflect better exposure in this area, we believe it also suggests that some fault movement predates the bleaching event. Secondly, the reactivation or reuse of fractures to allow current CO₂-fluids to develop travertines may be the latest point in the draining of CO₂-rich fluids from depth. Whilst the relationships of the bleached rocks to the fault do not preclude the fault acting as a barrier to fluid migration from elsewhere in the region, enabling a bleaching fluid to

have been trapped against the fault, the evidence for fluid migration up fractures to higher units indicates the principle source of bleaching-fluid was indeed at depth and that flow was controlled by either pressure-driven movement or buoyancy.

There are several processes whereby Fe could be mobilised from red sandstones, resulting in their bleaching. Most commonly this is seen where organic materials (e.g. oil and gas) act to reduce Fe(III) oxides coating sand grains to form soluble Fe^{2+} , which can then be removed through groundwater movement or diffusion. This can be represented on an Eh-pH diagram by a move in fluid composition to lower Eh values. Though CO_2 will not drive reduction directly, it might act to liberate Fe^{2+} if the acidity associated with dissolved CO_2 caused enhanced dissolution of reduced minerals, which then lowered local Eh. CO_2 might also act to liberate soluble Fe^{2+} through acidification. Finally, the CO_2 may contain small amounts of other gases as impurities (such as CH_4 or H_2S), and it could be these that drive local mobilisation of Fe^{2+} .

6. Conclusions

Red Entrada Sandstones in the Saltwash Valley, Southeastern Utah have been extensively bleached and provide a record of reservoir scale fluid-rock geochemistry. The distribution of the bleached sandstones, largely being confined to the lower portions of apparently lithologically homogenous strata and the greater development of the bleaching close to the northern bounding fault of the Tenmile Graben, suggests that the bleaching was caused by a dense fluid that was migrating via pressure-driven flow from depth. The evidence of bleaching along steeply dipping subvertical cross-cutting fractures indicates that this fluid migration was enabled by fracturing or fracture reactivation, with migration along the fault a likely source.

The proximity of bleached sandstones to recent and modern travertine formation from active CO_2 -rich springs and the reuse/reactivation of fractures with bleached wallrocks to enable CO_2 -rich fluid movement may provide some circumstantial evidence that the bleaching may be attributed to the same CO_2 -rich groundwater. Nevertheless the bleaching has been folded and faulted by at least the most recent fault reactivation indicating that bleaching occurred prior to this latest movement and suggesting that bleaching occurred before modern travertine development.

Diagenetic analyses of a very limited number of samples have not established any systematic differences between bleached and unbleached sandstones, other than the clear loss of iron, mostly in the form of hematite from inherited clay coatings on primary detrital grain surfaces. Work is ongoing with a much larger sample set which aims to determine if any diagenetic modifications to the bleached sandstones, not seen in adjacent unbleached samples, can be attributable to the influx of a CO_2 -rich fluid, either at depth or following uplift.

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