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An experimental and analogue study of iron release from red sandstones

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Abstract

The Jurassic Entrada sandstone at Salt Wash Graben, Utah, USA, a red sandstone contains significant rock bleaching. The cause of the bleaching has been thought to be associated with the modern day CO_2-rich fluids in the area which present on the surface by utalising the local fractures, some of which are filled with calcite and iron rich minerals (e.g. Jarosite). An experimental study was conducted to determine the cause of the bleaching. CO_2 was found not to cause sandstone bleaching. However, the CO_2 was found to mobilize significant amounts of iron from the fracture minerals suggesting that this is a possible source of the iron in the modern pore fluids.

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Keywords:

1. Introduction

An experimental study has been conducted to better understand the features of a CO_2 natural analogue at Salt Wash Graben, Utah. The site is located in south east Utah, USA and is a large Jurassic sandstone outcrop which includes the Entrada formation. The formation is cut through with local faults that are associated with CO_2 rich springs, leaving numerous fractures filled with secondary minerals such as calcite, goethite and jarosite. A key feature of the red Entrada sandstone formation at the site is the presence of significant rock bleaching (iron reduction/ mobilisation) that often occurs parallel to bedding and adjacent to fracture zones [1]. The bleached sandstone contains slightly less total iron than the red sandstone It has been suggested that the bleaching may be

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associated with the presence of modern day CO_2 in the area [2]. For reservoirs that contain relatively low concentrations of alkaline earth metals (e.g. Ca^{2+}, Mg^{2+}) but have been identified as potential CO_2 storage reservoirs for carbon capture and storage then the release of Fe^{2+} may be a desirable to enhance mineral trapping of the CO_2[3]. A series of experimental tests were subsequently designed to better understand iron release processes from the red sandstone in this natural CO_2 analogue.

2. Experimental method

A series of laboratory experiments was set up to investigate the effects of CO_2 on two different aspects of the Entrada formation:

- The bulk rock (red sandstone)
- The fracture mineralization

2.1. Experimental set-up

Cores of red sandstone (1.6cm diameter x 3cm length) pre-saturated under vacuum with experimental fluid (to remove air from the pore space) were weighed and placed inside batch vessels. For the fracture fill material monoliths were cut instead of cores as the material was delicate. These were more irregularly-shaped than the small cores, but were of similar weight. Sample dimensions were measured using veneer calipers and recorded to determine a surface area.

The batch vessel, a PTFE-lined stainless steel fixed volume reactor was assembled as shown in Figure 1 with a fluid:rock ratio of 10:1. Starting experimental fluids were synthetic versions of a brine and a more dilute near-surface water from the Green River area (Table 1) [4]. The batch vessels were placed in an oven, heated to 40°C and pressurised to a constant 50 bar with CO_2 or nitrogen (N_2) using an ISCO syringe pump. N_2 was used to pressurise some experiments, acting as a non reactive case for comparison with the CO_2 experiments. A small magnetic stirrer bead in the base of the vessel allowed for periodic agitation of the fluids (2 minutes every 4 hours). Given the relatively long duration of the experiments and their relatively frequent stirring, the aqueous fluids were effectively gas saturated[5]. Experiments were run for approximately six months duration.

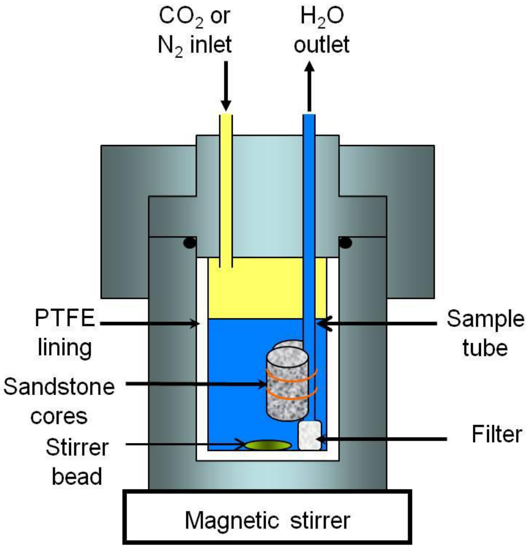

Fig. 1. Schematic diagram of an assembled batch reactor.

1.2 Sample preparation

Fluid samples were extracted via a titanium dip tube whilst the reactor was still under run conditions with the pressure being maintained using the ISCO pump. Periodic sampling of both the CO_2 and N_2-pressurised experiments was done in an identical manner. This involved degassing approx 12ml of sample into a sterile polythene syringe connected to a valve at the end of the dip tube. Pre-flushing the sample line with an initial 1 ml of solution ensured that a non-contaminated fluid sample was taken.

The sampled fluid was split into several sub-samples for chemical analysis:

- 1 ml was taken for immediate analysis of pH (at room temperature and pressure)
- 2 ml was taken for immediate analysis of alkalinity
- 2.7 ml was immediately added to 0.3 2,2-dipyridyl solution for subsequent analysis of Fe^{2+}
- 8 ml was filtered using a 0.2 µm nylon syringe filter, placed into a polystyrene tube and acidified with 1% v/v of concentrated nitric acid. This was analysed subsequently for major and trace cations by inductively coupled plasma – mass spectrometry (ICP-MS)
- 1 ml aliquot was filtered using a 0.2 µm nylon syringe filter, placed into a polyethylene tube for analysis of anions by ion chromatography (IC). This sample was diluted (typically to 25% concentration) to minimise the potential for carbonate mineral precipitation prior to analysis

At the end of the experiments all of the remaining experimental fluid (approximately 100-150 ml) was withdrawn. The pressure vessel was slowly depressurised to minimise damage to the sandstone samples. On removal, the solids were placed on absorbent filter paper and gently washed with 1-2ml of deionised water to remove excess salt. The filter paper was dried and stored as it potentially contained reaction products that may have been displaced during the washing.

Table 1. Chemical composition of paradox basin formation brine and dilute green river spring used as starting fluids for laboratory experiments[4].

Fluid name	**pH (field)**	**Al (µmol/l)**	**Ba (µmol/l)**	**Ca (mmol/l)**	**Fe (µmol/l)**	**K (mmol/l)**	**Mg (mmol/l)**	**Mn (µmol/l)**
Ismay Brine	6.8	-	1.28	192.13	25.07	28.13	65.83	9.28
Big bubbling spring	6.3	**5.10**	**0.10**	**21.55**	**2.66**	**9.36**	**8.55**	**7.23**
Fluid name		**Na (mmol/l)**	**Si (mmol/l)**	**Sr (mmol/l)**	**Cl (mmol/l)**	**SO_4 (mmol/l)**	**Alkalinity (mEq/l)**	**TDIC (mmol/l)**
Ismay Brine		2261.85	0.18	2282.58	3102.7	11.45	1.23	1.31
Big bubbling spring		212.87	0.14	157.44	178.29	32.17	66.04	116.33

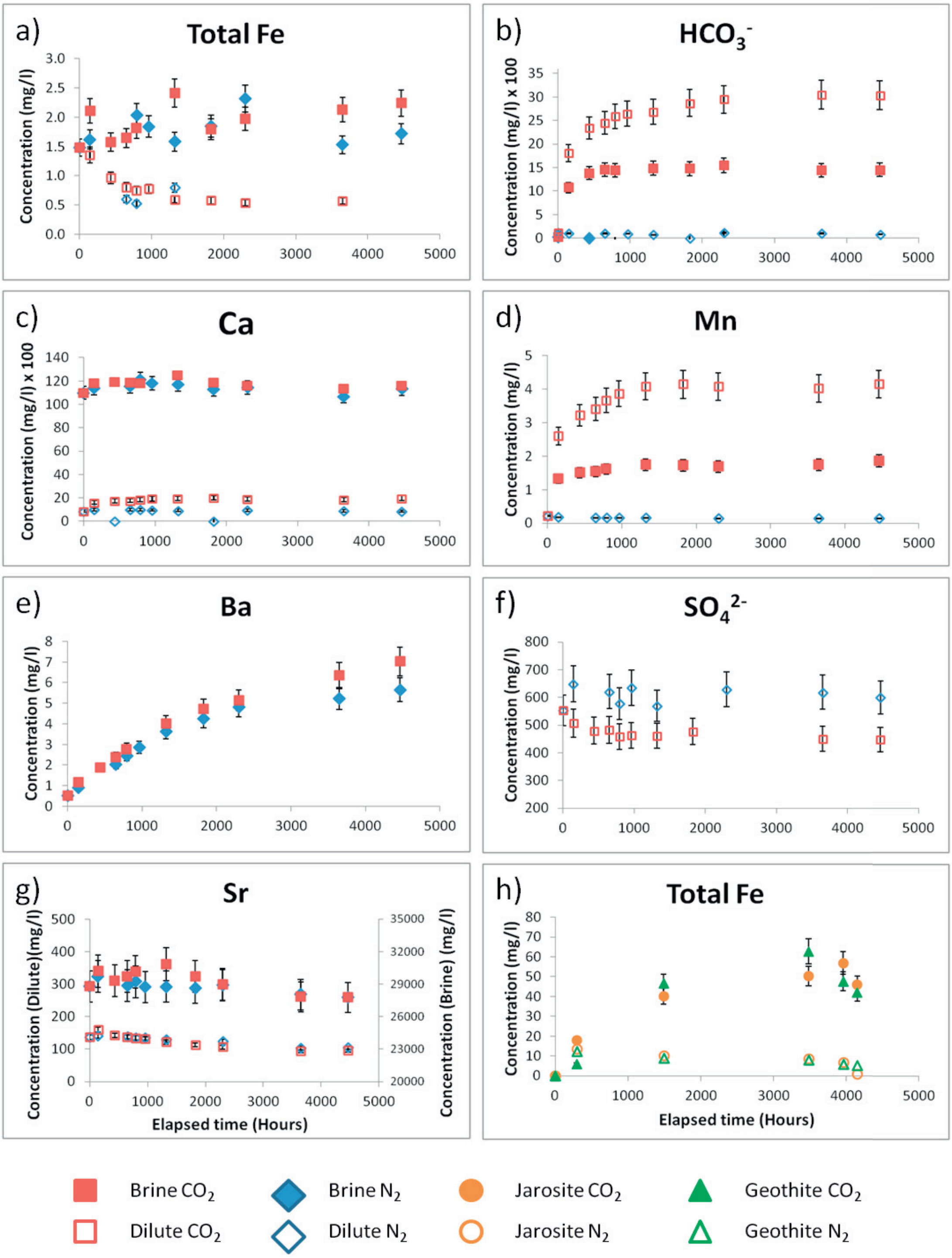

Fig. 2. Graphs showing the evolution of key elements and species over the duration of both the CO_2 and N_2 pressurised batch experiments using red Entrada sandstone cores (a-g) and Fracture fill monoliths (h). Note that figures b and c are represented as 1% of their actual value for ease of plotting the figure.

3. Results

3.1 Can CO_2 be responsible for the bleaching of the Entrada?

On removal of the red Entrada sandstone cores from the batch vessels which had been pressurised with CO_2 for 6 months there was no visible colour change. Fluid chemistry taken over the course of the experiment also showed a very limited amount of iron was released from the sandstone on exposure to CO_2 (Figure 2a). The release of iron in the CO_2 pressurised experiments was comparable to that of the N_2 pressurised experiments for both the dilute and brine, although there was a slightly higher concentration found in the brine fluids. These experiments do not provide any evidence to suggest that CO_2 can mobilise iron from the red sandstone and provides strong evidence that the bleaching in the Entrada formation is a result of other processes.

3.2 What is the effect of CO_2 on red Entrada sandstone?

Other reactions did occur as a result of exposing the sandstone to CO_2. There was an increase in bicarbonate ion concentration which reached steady state at around 2500 hours (Figure 2b) suggesting rock buffering of pH generated by the CO_2 saturated fluid. The rate at which bicarbonate ions went into the solution appeared quicker initially and slowed towards steady state. The dilute fluid pressurised with N_2 also showed a very slight increase in bicarbonate concentration. Bicarbonate concentration was overall higher in the dilute fluid relative to the brine, as CO_2 is more soluble in dilute fluids**[5]**. Carbonate dissolution caused an increase in the concentration of calcium (Figure 2c) and manganese (Figure 2d) in both the dilute and brine experiments on exposure to CO_2. The difference in calcium and manganese concentration relative to the N_2 pressurised equivalent was more pronounced with the dilute fluid which is likely to be related to the saturation of calcium carbonate. The presence of barium (Figure 2e) in the brine (pressurised with both N_2 and CO_2) may suggest feldspar dissolution and its absence in the dilute fluid may reflect the presence of sulphate ions (Figure 2f), the low solubility of barium sulphate, and hence its precipitation. Three times the amount of sulphate was added to the dilute starting fluid (Table 1) compared to the brine. The absence of sulphate in the brine experiments suggests precipitation and the reduced concentration of Sr (Figure 2g) suggests this was as strontium sulphate. Mineralogical evidence found the precipitation of strontium sulphate, but also strontium chloride during the course of the experiment.

3.3 What is the effect of CO_2 on the fracture fill material?

The reaction of the monoliths of fracture fill material containing iron bearing minerals (goethite and jarosite) with CO_2 was very significant in terms of iron (II) release. The concentration of iron (II) peaked at approximately 63mg/l with jarosite and 67mg/l with goethite experiments. The solubility of these minerals in CO_2-saturated fluid suggests that they may be the source of iron in the modern day fluids present in the Salt Wash Graben area. An unexpected observation in the later stages of the experiments was that the concentration of iron (II) decreased, which may suggest precipitation of a secondary iron phase. Mineralogical assessment of the cores post experiment did not produce any strong evidence for this, however the amount of precipitate that would have been formed need only be small, making it difficult to detect.

4. Discussion

Experimental evidence shows that the cause of the bleaching in the Entrada formation is probably not related to CO_2 alone. The presence of a reducing agent in the formation fluid is more likely to give a better explanation for the bleached zones. It has been suggested that a reducing agent such as CH_4 along with CO_2 may dissolve hematite in the grain coatings[5] and other rocks in the area show evidence for bleaching by CH_4 and H_2S[6]. Ongoing experiments are being conducted using the same method over a 6 month period using the red Entrada sandstone and reducing agents. The reducing agents were methane (5%) and thioacetamide, a compound that breaks down on the addition to water releasing reduced sulphur. Thioacetamide has previously been used in experimental systems as a source of H_2S gas or HS^- generated in low concentrations at low temperatures[7],[8]. The concentration of thioacetamide used was 1mg/l, equivalent to the amount of H_2S needed to reduce all the iron (III) in the core sample to iron (II). Initial results from these experiments support the theory that the bleaching event was driven by a reducing agent (H_2S mobilized 15mg/l iron (II) during the experiments in comparison to 5% CH_4 which only mobilized 3mg/l at most from the red sandstone (Figure 3)).

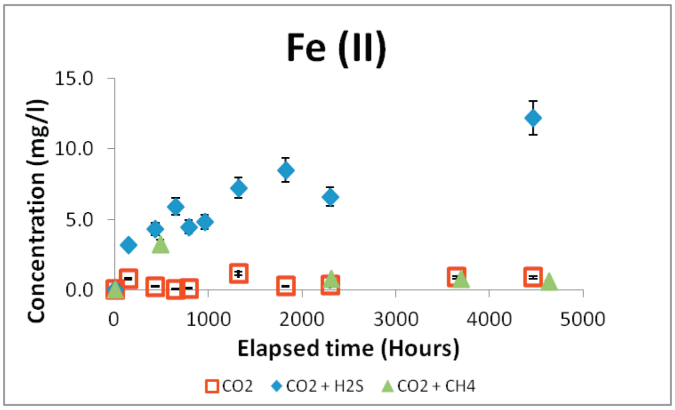

Fig. 3. Graph to show the effect of impurities in CO_2 on the mobilization of iron (II).

Ongoing examination of fracture fill material from Salt Wash Graben (from the centre of a bleached zone) shows evidence of residual pyrite and pyrite pseudomorphs. This is consistent with a model of reducing sulphur-rich fluids migrating up fractures, mobilising iron from the rock and depositing it as sulphide minerals in the fractures[9]. Also found in the fracture fill are jarosite and goethite which indicate subsequent (and probably relatively recent) oxidation of sulphide minerals in the fracture[9].

The potential for having H_2S in this natural system, mirrors current modelling studies showing that it can help mobilise M^{2+} ions such as iron[3]. Large releases of iron (II) into solution due to the presence of gas impurities in the CO_2 stream may assist in locking up the dissolved CO_2 in the reservoir as iron carbonate enhancing storage[10]. This effectively demonstrates how gas composition can be used to drive dissolution and precipitation of desirable minerals. H_2S-CO_2 gas mixtures have already been injected at industrial test sites in western Canada[11]. This could result in a cost benefit for CCS, potentially reducing the overall cost to the separation of CO_2. In the experiments there was no evidence of siderite ($FeCO_3$) formation based on mineralogical investigations, but ongoing modeling work of the same batch system did indicate that strontinite, $SrCO_3$, was predicted to form in preference to $FeCO_3$. The brine composition selected for the batch experiments was based on local formation brine (Ismay brine) which is naturally over saturated with strontium. This is a clear example of how the final mineralisation of the CO_2 is likely to be heavily dependent upon reservoir composition.

5. Conclusions

Study of natural systems are at times complicated and caution must be made when interpreting evidence as it may represent a series of overprinted events which can make it difficult to establish cause and effect. Lab experiments can help to explain individual processes. This study showed that the mobilization of iron from minerals such as goethite and jarosite is possible with CO_2 but not from the hematite responsible for the red colouration of the Entrada sandstone. It is clear from laboratory experiments and mineralogical evidence from Saltwash Graben that the bleaching in the Entrada formation is not due to CO_2 but more likely to the presence of reducing agents (possibly H_2S). Very little reaction occurred with the sandstone when exposed to CO_2, a favourable outcome for CO_2 storage as the rock structure is maintained. The potential addition of reducing gases e.g. H_2S to the CO_2 stream is likely to enhance the dissolution of hematite and increase the concentration of iron (II) in the reservoir and thus the potential for mineral trapping of the CO_2.

Acknowledgements

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