

2020

## Basalt-CO<sub>2</sub>-brine wettability at storage conditions in basaltic formations

Stefan Iglauer  
*Edith Cowan University*

Ahmed Zarzor Al-Yaseri  
*Edith Cowan University*

Domenik Wolff-Boenisch

Follow this and additional works at: <https://ro.ecu.edu.au/ecuworkspost2013>



Part of the [Engineering Commons](#)

---

[10.1016/j.ijggc.2020.103148](https://doi.org/10.1016/j.ijggc.2020.103148)

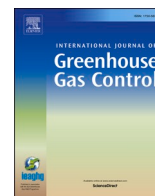
Iglauer, S., Al-Yaseri, A. Z., & Wolff-Boenisch, D. (2020). Basalt-CO<sub>2</sub>-brine wettability at storage conditions in basaltic formations. *International Journal of Greenhouse Gas Control*, 102, article 103148. <https://doi.org/10.1016/j.ijggc.2020.103148>

This Journal Article is posted at Research Online.  
<https://ro.ecu.edu.au/ecuworkspost2013/9020>



Contents lists available at ScienceDirect

## International Journal of Greenhouse Gas Control

journal homepage: [www.elsevier.com/locate/ijggc](http://www.elsevier.com/locate/ijggc)Basalt-CO<sub>2</sub>-brine wettability at storage conditions in basaltic formations

## ARTICLE INFO

## Keywords

CO<sub>2</sub> geo-sequestration  
Basalt  
Storage capacity  
Wettability

## ABSTRACT

CO<sub>2</sub> geo-storage in basaltic formations has recently been demonstrated as a viable solution to rapidly sequester and mineralize CO<sub>2</sub>. In case CO<sub>2</sub> is injected into such basalt reservoirs in supercritical form, a two-phase system (reservoir brine and supercritical CO<sub>2</sub>) is created, and it is of key importance to specify the associated CO<sub>2</sub>-basalt wettability so that fluid distributions and CO<sub>2</sub> flow through the reservoir can be predicted. However, there is a serious lack of data for basalt CO<sub>2</sub>-wettability. We therefore measured water contact angles on basalt substrates in CO<sub>2</sub> atmosphere. The results indicate that at shallow depth (below 500 m) basalt is strongly water-wet. With increasing depth the basalt becomes less hydrophilic, and turns intermediate-wet at a depth of 900 m. We conclude that basalt is more CO<sub>2</sub>-wet than chemically clean minerals (quartz, calcite), especially at depths below 900 m. However, the basalt had a CO<sub>2</sub>-wettability similar to some caprock samples and a gas-reservoir sandstone. The data presented in this paper will thus aid in the prediction and optimization of CO<sub>2</sub> geo-storage in basalt formations.

## 1. Introduction

Carbon Geo-Sequestration (CGS) in basaltic formations is termed an ‘unconventional’ storage mechanism because most CGS attention is turned towards sedimentary formations with large pore volumes and adequate seals. However, igneous lithologies, especially of ultra-mafic and mafic nature, have their merits. Firstly, peridotites and basalts and their mineralogical constituents are far more reactive than sandstones when exposed to acidic CO<sub>2</sub>-charged brine (e.g. Wolff-Boenisch et al., 2011; Gudbrandsson et al., 2011). Secondly, peridotites consist mainly of the mafic minerals olivines and pyroxenes, whereas for basalts Ca-rich plagioclases and interstitial glass are additional major phases. For both rock types, their elemental release contains substantial amounts of divalent cations (Mg, Ca, Fe) that can effectively trap CO<sub>2</sub> in form of solid carbonate minerals (Oelkers et al., 2008). Hence, these rock types promise not only to take CGS to the desired end state of mineral trapping, but also to facilitate mineral trapping in a very short time frame. Indeed, successful *fast* mineralisation of CO<sub>2</sub> in ‘unconventional’ basalt matrices has been demonstrated recently in field studies in Iceland (Carbfix project) and Washington State (Columbia River Basalt Project), respectively (Matter et al., 2016; McGrail et al., 2016).

Furthermore, particularly basalts have been known to occur in staggering expansions and thicknesses rivalling those of sedimentary basins. Large igneous provinces for example spread over hundreds of square km (e.g. Indian Deccan Traps, Siberian Traps, Emeishan Traps) and can reach several km thickness (Ernst, 2014). These localised occurrences are supplemented by other basaltic terrains such as volcanic islands associated with hot spots (e.g. Madeira, Hawaii) and mid-ocean ridges (e.g. Iceland). MORBS (mid ocean ridge basalts) are the most voluminous volcanic rocks on Earth, constituting the top 1–2 km of the oceanic crust and covering nearly two-thirds of the Earth’s surface beneath the oceans (le Roex, 1998). So there is quite a vast playing field for finding a suitable basalt formation in terms of permeability, storage

capacity, and trapping efficiency for supercritical (sc) CO<sub>2</sub> injection, just as for sedimentary deposits (Goldberg et al., 2018).

One key parameter in case of direct (free) CO<sub>2</sub> injection into such basaltic formations is the basalt-water-CO<sub>2</sub> wettability, which determines the spreading and migration of the CO<sub>2</sub> in the basalt’s rock pore network (e.g. Donaldson and Alam, 2008; Blunt, 2017), and consequently basalt wettability also impacts on interfacial areas, mass transfer and mineralization rates (as was for instance shown for deep sandstone aquifers, Al-Khdheawi et al., 2017).

However, there is a serious lack of information on basalt-CO<sub>2</sub> wettability. We thus tested one basalt sample from the Hellisheidi geothermal area in Southwest Iceland (Alfredsson et al., 2013), to provide wettability data for basalt formations and thus enable associated CO<sub>2</sub> flow and storage predictions.

## 2. Experimental procedure

## 2.1. Basalt samples

Basalt samples from the CarbFix injection (Gislason et al., 2010; Aradottir et al., 2012; Snæbjörnsdóttir et al., 2017, 2018) site in Iceland were collected from borehole KB-01 at 535 m depth. This grey fine-grained crystalline basalt had an olivine tholeiitic composition with smectite and calcite as secondary alterations and was between 300,000 to 500,000 years old (Alfredsson et al., 2013). The basalt samples were further characterized via X-ray diffraction [XRD], scanning electron microscopy, quantitative total organic content [TOC] and surface roughness measurements. TOC was 700 ppm, and the basalt was very tight (porosity < 1%).

## 2.2. Experimental tests

For the CO<sub>2</sub>-wettability experiments, cuboid basalt samples were cut

<https://doi.org/10.1016/j.ijggc.2020.103148>

Received 30 April 2020

Available online 1 October 2020

1750-5836/© 2021 The Authors.

Published by Elsevier Ltd.

This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

with a high speed diamond blade (to  $\sim 0.5\text{cm} \times 1\text{cm} \times 1\text{cm}$ ) and each sample was exposed to air plasma for 1 min to remove organic surface contaminants (Love et al., 2005; Iglauer et al., 2014). Although plasma cleaning removes the uppermost molecular organic layers of material (Alam et al., 2014), the basalt contained much more organic matter so that these naturally occurring organics were removed to only an insignificant extent.

Subsequently the advancing ( $\theta_a$ ) and receding ( $\theta_r$ ) water contact angles were measured using the tilted plate method (Lander et al., 1993) for typical storage pressures (4.48–17.23 MPa) and two temperatures (308.15 K and 333.15 K) using synthetic reservoir brine (4 wt % NaCl, 4 wt % CaCl<sub>2</sub>, 1 wt % MgCl<sub>2</sub>, and 1 wt % KCl dissolved in deionized water = 2.2 M ionic strength).

As surface roughness of a substrate can significantly influence measured contact angles (Marmur, 2006), this quantity was measured via atomic force microscopy (using a DSE 95–200 instrument). The root mean square surface roughness measured amounted to 210 nm, and thus had an insignificant influence on the CO<sub>2</sub>-brine-basalt contact angles (Al-Yaseri et al., 2016; Alnili et al., 2018).

The average standard deviation of the contact angle measurements was determined as  $\pm 3^\circ$  based on replicate measurements.

### 3. Results and discussion

The brine contact angles drastically increased with pressure, Fig. 1. This is consistent with most literature published for mineral or rock surfaces (compare Broseta et al., 2012 or Arif et al., 2018; Iglauer et al., 2015a; Hobeika et al., 2017 for an overview). This effect is caused by the increase in intermolecular interactions between CO<sub>2</sub> and basalt with increasing pressure (as shown for quartz surfaces; e.g. Iglauer et al., 2012; Chen et al., 2015; Abramov et al., 2019). Consequently, the basalt turned intermediate-wet ( $\theta > 70^\circ$ ) at pressures above  $\sim 9$  MPa (this corresponds approximately to a depth of 900 m; note that the hydrostatic gradient in the subsurface is circa 10 MPa/km, Duke, 1978). Significantly more rapid CO<sub>2</sub> upwards movement is predicted for intermediate-wet systems (Al-Khdheawi et al., 2017), with resulting reductions in storage capacities and particularly containment security. Furthermore, the pore occupancy of CO<sub>2</sub> changes in an intermediate-wet rock, with significant fractions of the CO<sub>2</sub> now also contacting the basalt surface (precisely this depends on the exact pore morphology and capillary pressure, Blunt, 2017). This changes the basalt-acidic brine interfacial areas (note that at high partial CO<sub>2</sub> pressures brine is acidified considerably by the CO<sub>2</sub> (Peng et al., 2013)) and thus also basalt-brine reaction and mineralization rates. Moreover, a transition from strongly water-wet to weakly water-wet ( $\theta > 50^\circ$ ) behaviour was

observed at  $\sim 7$  MPa, which has similar but less dramatic effects as outlined above. Temperature only had a slight influence, and higher temperature led to slightly elevated contact angles.

The basalt samples showed a wettability response similar to sedimentary caprock samples of a proposed CO<sub>2</sub> storage site (Iglauer et al., 2015b), despite differences in mineralogical composition. This is probably due to a) the somewhat similar elemental composition of the basalt (the caprocks mainly consisted of quartz and clay, illite/chlorite; 72–82 wt% clay + quartz content); and, more importantly, b) the similar TOC content (700 ppm in the basalt versus 510–4400 ppm in the caprocks). Note that surface organic groups strongly enhance the CO<sub>2</sub>-rock wettability (Ali et al., 2019a, 2019b, 2020; Abramov et al., 2019). Again a similar wettability response was observed in a Warro sandstone sample (Perth Basin), despite a different mineral composition (the Warro sandstone consisted of 90 wt% quartz, 3.3 wt% kaolinite, 6.7 wt% feldspar, Alnili et al., 2018). However, TOC was similar in the Warro sample (1600 ppm). We conclude that the main driver for the wettability response in such subsurface samples is the organic content.

Based on these results it is likely that the CO<sub>2</sub> mineralization reaction is strongly affected by this wettability change as the CO<sub>2</sub>-basalt and brine-basalt interfacial areas are expected to be quite different in an intermediate-wet rock (as opposed to a strongly or weakly water-wet rock), Blunt (2017). As higher CO<sub>2</sub>-rock wettability dewets the rock, comparatively lower degrees of dissolution-precipitation reactions are expected in intermediate-wet rock, where brine-basalt interfacial areas would be reduced. However, if wet scCO<sub>2</sub> dominates the fluid-rock interactions and concomitant mineralisation (as hypothesized by Loring et al., 2011; McGrail et al., 2009; Schaefer et al., 2013; Shao et al., 2011), mineral trapping would be accelerated. As a consequence, a mineralisation rate gradient versus depth is expected.

### 4. Conclusions and implications

A basalt wettability shift at 9–10 MPa ( $\sim 0.9$  km depth) from weakly water-wet to intermediate-wet has been identified experimentally. It is concluded that CO<sub>2</sub> is significantly more wetting below 1 km depth, and flows upwards more quickly due to this wettability shift, as predicted for sandstone aquifers (Al-Khdheawi et al., 2017, 2018). Overall, this study was conducted to elucidate basalt CO<sub>2</sub>-wettability, and thus improve the understanding of basalt-scCO<sub>2</sub>-brine systems, which will aid in the optimization of CO<sub>2</sub> storage in basalt formations.

### Declaration of Competing Interest

The authors report no conflict of interest.

### Acknowledgements

The authors wish to acknowledge the Carbfix consortium, especially Sandra Snæbjörnsdóttir, for providing the basalt cores.

### References

- Abramov, A., Keshavarz, A., Iglauer, S., 2019. Wettability of fully hydroxylated and alkylated (001)  $\alpha$ -quartz surface in carbon dioxide atmosphere. *J. Phys. Chem. C* 123 (14), 9027–9040.
- Alam, A.U., Howlader, M.M.R., Deen, M.J., 2014. The effects of oxygen plasma and humidity on surface roughness, water contact angle and hardness of silicon, silicon dioxide and glass. *J. Micromechanics Microengineering* 24, 035010. <https://doi.org/10.1088/0960-1317/24/3/035010>.
- Alfredsson, H.A., Oelkers, E.H., Hardarsson, B.S., Franzson, H., Gunnlaugsson, E., Gislason, S.R., 2013. The geology and water chemistry of the Hellisheide, SW-Iceland carbon storage site. *Int. J. Greenh. Gas Control* 12, 399–418.
- Ali, M., Al-Ansari, S., Arif, M., Barifciani, A., Sarmadivaleh, M., Stalker, L., Lebedev, M., Iglauer, S., 2019a. Organic acid concentration thresholds for ageing of carbonate minerals: implications for CO<sub>2</sub> trapping/storage. *J. Colloid Interface Sci.* 534, 88–94.
- Ali, M., Arif, M., Sahito, M.F., Al-Ansari, S., Keshavarz, A., Barifciani, A., Stalker, L., Sarmadivaleh, M., Iglauer, S., 2019b. CO<sub>2</sub>-wettability of sandstones exposed to traces of organic acids: implications for CO<sub>2</sub> geo-storage. *Int. J. Greenh. Gas Control* 83, 61–68.

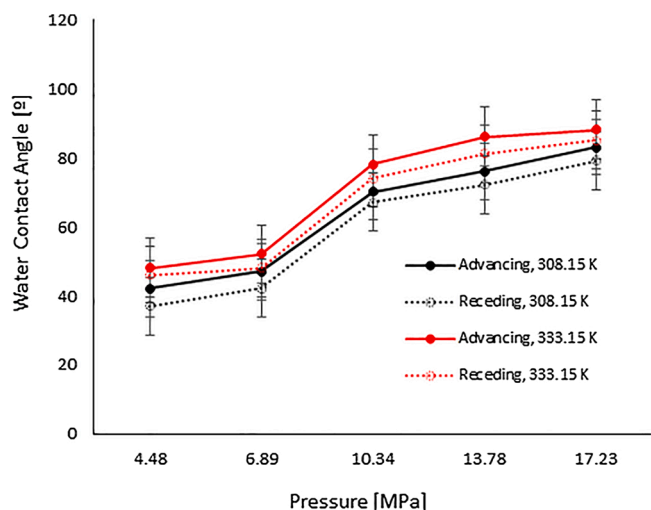


Fig. 1. Water contact angles measured on the basalt sample in CO<sub>2</sub> atmosphere.

- Ali, M., Aftab, A., Arain, Z.U.A., Al-Yaseri, A., Roshan, H., Saeedi, A., Iglauer, S., Sarmadivaleh, M., 2020. Influence of organic acid concentration on wettability alteration of caprock: implications for CO<sub>2</sub> trapping/storage. *ACS Appl. Mater. Interfaces* 12 (35), 39850–39858.
- Al-Khdeewi, E., Vialle, S., Barifcani, A., Sarmadivaleh, M., Iglauer, S., 2017. Impact of reservoir wettability and heterogeneity on CO<sub>2</sub>-plume migration and trapping capacity. *Int. J. Greenh. Gas Control* 58, 142–158.
- Alnili, F., Al-Yaseri, A.Z., Roshan, H., Rahman, T., Verall, M., Lebedev, M., Sarmadivaleh, M., Iglauer, S., Barifcani, A., 2018. Carbon dioxide/brine wettability of porous sandstone versus quartz: an experimental and theoretical investigation. *J. Colloid Interface Sci.* 524, 188–194.
- Al-Yaseri, A.Z., Lebedev, M., Barifcani, A., Iglauer, S., 2016. Receding and advancing (CO<sub>2</sub> + brine + quartz) contact angles as a function of pressure, temperature, surface roughness, salt type and salinity. *J. Chem. Thermodyn.* 93, 416–423.
- Aradottir, E.S.P., Sonnenthal, E.L., Bjornsson, G., Jonsson, H., 2012. Multidimensional reactive transport modelling of CO<sub>2</sub> mineral sequestration in basalts at the Hellisheidi geothermal field, Iceland. *Int. J. Greenh. Gas Control* 12, 399–418.
- Arif, M., Abu-Khamsin, Iglauer, S., 2018. Wettability of rock/CO<sub>2</sub>/brine and rock/oil/CO<sub>2</sub>-enriched-brine systems: critical parametric analysis and future outlook. *Adv. Colloid Interface Sci.* 268, 91–113.
- Blunt, M.J., 2017. *Multiphase Flow in Permeable Media*. Cambridge University Press, Cambridge.
- Brosseta, D., Tonnet, N., Shah, V., 2012. Are rocks still water-wet in the presence of dense CO<sub>2</sub> or H<sub>2</sub>S? *Geofluids* 12, 280–294.
- Chen, C., Zhang, N., Li, W., Song, Y., 2015. Water contact angle dependence with hydroxyl functional groups on silica surfaces under CO<sub>2</sub> sequestration conditions. *Environ. Sci. Technol.* 49 (24), 14680–14687.
- Dake, L.P., 1978. *Fundamentals of Reservoir Engineering*. Elsevier, Amsterdam.
- Donaldson, E.C., Alam, W., 2008. *Wettability*. Gulf Publishing Company, Houston.
- Ernst, R.E., 2014. *Large Igneous Provinces*. Cambridge University Press, Cambridge.
- Gislason, S.R., Wolff-Boenisch, D., Stefansson, A., Oelkers, E.H., Gunnlaugsson, E., Sigurdardottir, H., Sigfusson, B., Broecker, W.S., Matter, J.M., Stute, M., 2010. Mineral sequestration of carbon dioxide in basalt: a pre-injection overview of the CarbFix project. *Int. J. Greenh. Gas Control* 4 (3), 537–545.
- Goldberg, D., Aston, L., Bonneville, A., Demirkanli, I., Evans, C., Fisher, A., Garcia, H., Gerrard, M., Heesemann, M., et al., 2018. Geological storage of CO<sub>2</sub> in sub-seafloor basalt: the CarbonSAFE pre-feasibility study offshore Washington State and British Columbia. *Energy Procedia* 146, 158–165.
- Gudbrandsson, S., Wolff-Boenisch, D., Gislason, S.R., Oelkers, E.H., 2011. An experimental study of crystalline basalt dissolution from 2 ≤ pH ≤ 11 and temperatures from 5 to 75 °C. *Geochim. Cosmochim. Acta* 75, 5496–5509.
- Hobeika, N., Bouriat, P., Touil, A., Brosseta, D., Brown, R., Dubessy, J., 2017. Help from a hindrance: using astigmatism in round capillaries to study contact angles and wetting layers. *Langmuir* 33 (21), 5179–5187.
- Iglauer, S., Mathew, M., Bresme, F., 2012. Molecular dynamics computations of brine-CO<sub>2</sub> interfacial tensions and brine-CO<sub>2</sub>-quartz contact angles and their effects on structural and residual trapping mechanisms in carbon geo-sequestration". *J. Colloid Interface Sci.* 386, 405–414.
- Iglauer, S., Hassan, A., Sarmadivaleh, M., Liu, K., Pham, C., 2014. Contamination of silica surfaces: impact on water-CO<sub>2</sub>-quartz and glass contact angle measurements. *Int. J. Greenh. Gas Control* 22, 325–328.
- Iglauer, S., Pentland, C.H., Busch, A., 2015a. "CO<sub>2</sub> wettability of storage and seal rock and implications for carbon geo-storage". *Water Resour. Res.* 51 (1), 729–774. WR015553.
- Iglauer, S., Al-Yaseri, A.Z., Rezaee, R., Lebedev, M., 2015b. CO<sub>2</sub> wettability of caprocks: implications for storage capacity and containment security. *Geophys. Res. Lett.* 42, 9279–9284.
- Lander, L.M., Siewierski, L.M., Brittain, W.J., Vogler, E.A., 1993. A systematic comparison of contact angle methods. *Langmuir* 9, 2237–2239. <https://doi.org/10.1021/la00032a055>.
- le Roex, A.P., 1998. Mid-ocean ridge basalt (MORB). *Geochemistry. Encyclopedia of Earth Science*. Springer, Dordrecht.
- Loring, J.S., Thompson, C.J., Wang, Z., Joly, A.G., Sklarew, D.S., Schaefer, H.T., Ilton, E.S., Rosso, K.M., Felmy, A.R., 2011. In situ infrared spectroscopic study of forsterite carbonation in wet supercritical CO<sub>2</sub>. *Environ. Sci. Technol.* 45, 6204–6210.
- Love, J.C., Estroff, L.A., Kriebel, J.K., Nuzzo, R.G., Whitesides, G.M., 2005. Self-assembled monolayers of thiolates on metals as a form of nanotechnology. *Chem. Rev.* 105, 1103–1169.
- Marmur, A., 2006. *Soft contact: measurement and interpretation of contact angles*. *Soft Matter* 2, 12–17. <https://doi.org/10.1039/B514811C>.
- Matter, J.M., Stute, M., Snæbjörnsdóttir, S., Oelkers, E.H., Gislason, S.R., Aradottir, E.S., Sigfusson, B., Gunnarsson, I., Sigurdardottir, H., Gunnlaugsson, E., Axelsson, G., Alfredsson, H., Wolff-Boenisch, D., Mesfin, K., Taya, D., Hall, J., Dideriksen, K., Broecker, W., 2016. Rapid carbon mineralization for permanent disposal of anthropogenic carbon dioxide emissions. *Science* 352 (6291), 1312–1314.
- McGrail, B.P., Schaefer, H.T., Glezakou, V.A., Dang, L.X., Owen, A.T., 2009. Water reactivity in the liquid and supercritical CO<sub>2</sub> phase: has half the story been neglected? *Energy Procedia* 1, 3415–3419.
- McGrail, B.P., Schaefer, H.T., Spane, F.A., Cliff, J.B., Qafoku, O., Horner, J.A., Thompson, C.J., Owen, A.T., Sullivan, C.E., 2016. Field validation of supercritical CO<sub>2</sub> reactivity with basalts. *Environ. Sci. Technol. Lett.* 4, 6–10.
- Oelkers, E.H., Gislason, S.R., Matter, J., 2008. Mineral carbonation of CO<sub>2</sub>. *Elements* 4, 333–337.
- Peng, C., Crawshaw, J.P., Maitland, G.C., Trusler, J.P., Vega-Maza, D., 2013. The pH of CO<sub>2</sub>-saturated water at temperatures between 308 K and 423 K at pressures up to 15 MPa. *J. Supercrit. Fluids* 82, 129–137.
- Schaefer, H.T., McGrail, B.P., Owen, A.T., Arey, B.W., 2013. Mineralization of basalts in the CO<sub>2</sub>-H<sub>2</sub>O-H<sub>2</sub>S system. *Int. J. Greenh. Gas Control* 16, 187–196.
- Shao, H., Ray, J.R., Jun, Y.-S., 2011. Effects of salinity and the extent of water on supercritical CO<sub>2</sub>-induced phlogopite dissolution and secondary mineral formation. *Environ. Sci. Technol.* 45, 1737–1743.
- Snæbjörnsdóttir, S., Oelkers, E.H., Mesfin, K., Aradottir, E.S., Dideriksen, K., Gunnarsson, I., Gunnlaugsson, E., Matter, J.M., Stute, M., Gislason, S.R., 2017. The chemistry and saturation states of subsurface fluids during the in situ mineralisation of CO<sub>2</sub> and H<sub>2</sub>S at the CarbFix site in SW-Iceland. *Int. J. Greenh. Gas Control* 58, 87–102.
- Snæbjörnsdóttir, S., Gislason, S.R., Galeczka, I.M., Oelkers, E.H., 2018. Reaction path modelling of in-situ mineralisation of CO<sub>2</sub> at the CarbFix site at Hellisheidi, SW-Iceland. *Geochim. Cosmochim. Acta* 220, 348–366.
- Wolff-Boenisch, D., Wenaus, S., Gislason, S.R., Oelkers, E.H., 2011. Dissolution of basalts and peridotite in seawater, in the presence of ligands, and CO<sub>2</sub>: implications for mineral sequestration of carbon dioxide. *Geochim. Cosmochim. Acta* 75, 5510–5525.

Stefan Iglauer<sup>a,\*</sup>, Ahmed Zarzor Al-Yaseri<sup>a</sup>, Domenik Wolff-Boenisch<sup>b</sup>

<sup>a</sup> School of Engineering, Edith Cowan University, 270 Joondalup Drive, 6027 Joondalup, Australia

<sup>b</sup> School of Earth and Planetary Sciences, Curtin University, GPO Box U1987, Perth, WA-6845, Australia

\* Corresponding author.

E-mail address: [s.iglauer@ecu.edu.au](mailto:s.iglauer@ecu.edu.au) (S. Iglauer).