

The effect of soil solution chemistry on the weathering rate of a Histic Andosol

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Abstract

Histic Andosol in Western Iceland was studied using laboratory based repacked microcosms conjointly with sampling of field soil solution. The main primary phase of the 205 cm thick soil profile was basaltic glass, allophane content ranged from 2 to 22 wt.% and the soil carbon content ranged from 11 to 42 wt.%. At constant temperature, the dissolution rate of the basaltic glass, and probably allophane and imogolite, was dictated by the $a_{\text{H}^+}^3/a_{\text{Al}^{3+}}$ activity ratio only, which in turn is governed by the pH, total dissolved Al and the anions capable of complexing Al^{3+} ; SO_4^{2-} , F^- and organic anions (DOC). Dissolution rate was slowed down by up to 20% by decreasing undersaturation in the field. Dissolution rate of basaltic glass was stable after an initial flushing event at the beginning of microcosm experiments. Predicted dissolution rates increased up to a factor of 7 and 30 by speciating Al^{3+} with oxalate in field and microcosms respectively. Speciation with oxalate generally had more effect in shallow horizons than deep horizons.

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1. Introduction

Andosols, soils derived from volcanic material, cover about 1.9% of the terrestrial surface, store about 4.9% of the Earth's carbon (Eswaran et al., 1993), and host fruitful farmlands in the vicinity of active and/or extinct volcanoes (Kimble et al., 2000). About 30% of the long term fixation of carbon fixed by chemical weathering of silicates in the terrestrial environment of the Earth, takes place on basaltic rocks on the continents and volcanic islands (Milliman and Syvitski,

1992; Dessert et al., 2003). Much of this area is covered by Andosols. Air borne material, often volcanic glass, is the main rock constituent of the soil.

Iceland is the largest part of the ocean ridge system on Earth that is above sea level. The volcanic activity of the island drives soil forming processes, with approximately 54% of Icelandic soils being Andosols. Andosols of Iceland have been classified on the basis of two pedogenic factors, deposition of Aeolian-andic parent materials and drainage (Arnalds, 2004). The Aeolian-andic materials in Iceland are primarily composed of volcanic glass (Jonsson, 1995). The dominating secondary phases of clay size fraction of the soils are allophane and/or imogolite and poorly crystalline ferrihydrite (Wada et al., 1992).

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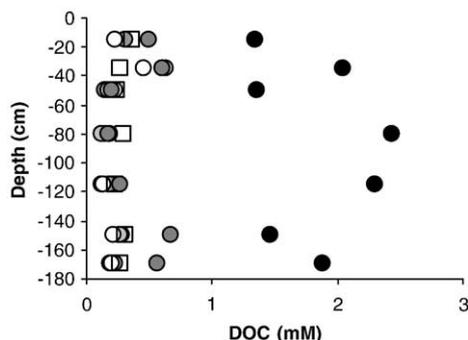


Fig. 1. Depth against total Al in soil solutions. Squares=field samples. Black circles represent first sampling batch and white circles final batch in microcosms.

The dissolution rate of natural Si–Al glasses at far from equilibrium conditions has been shown to be governed by temperature, glass composition and the proton to Al^{3+} activity ratio in the reacting solutions when there is a significant concentration of Al in solution (Oelkers and Gislason, 2001; Gislason and Oelkers, 2003; Wolff-Boenisch et al., 2004a,b).

The objective of this study was to define the effect of soil solution composition on the dissolution rate of basaltic glass under field and experimental conditions.

2. Method

The soil was sampled at Klafastadir in Hvalfjörður, Western Iceland. Soil solutions were sampled with quartz–PTFE suction cups (Prenart) at constant 700 mb suction on three occasions in summer 2002 and treated in an oxygen free environment in the laboratory.

Soil was repacked to field bulk density into 10 cm diameter PVC tubes with a 1 cm layer of prewashed non-absorbent cotton wool between all of the horizons. During the microcosm experiment 74.7 l was leached through each of three replicates simulating 52.8 years of precipitation. Soil solutions (40 ml) were sampled five times during the experimental period. Soil solution samples were taken from the base of each horizon with inert hollow fibre soil moisture samplers (Eijkelkamp).

Dissolved organic carbon (DOC) concentration was analysed in Shimadzu 5000 Total Organic Carbon Analyser and Labtoc® instrument (Pollution Process Monitoring) for field and experimental solutions respectively. Aluminum was analysed in ICP-AES (Thermo Jarrel Ash IRIS) and GFAAS (Perkin Elmer Atomic Absorption Spectrometer 3300) with $\text{Mg}(\text{NO}_3)_2$ as a matrix modifier for field and experimental solutions respectively.

The saturation state, ΔG_r (ΔG_r is equal to zero at equilibrium) and the $a_{\text{H}^+}^3/a_{\text{Al}^{3+}}$ of the soil solutions of this study, were calculated by the PHREEQC speciation program at 25° (Parkhurst and Appelo, 1999).

3. Results

Field DOC concentrations did not change along the soil profile. Microcosm DOC concentrations were characterised by a significant increase from field values at all depths in initial sampling batch but decreased rapidly to concentrations near field values (Fig. 1).

Field aluminum concentrations were 6 μM at 15–35 cm depths but then increased to 50 μM at 50 cm depth (Fig. 2). The concentration increased to 140 μM at 80 cm depth but then decreased significantly to 20 μM at 115 before dropping to 2 μM at 150 to 205 cm depth. In microcosms, aluminum concentrations increased to 20 μM at 15 cm depth at two sampling time points before reaching a steady state around 7 μM . The concentrations increased to 25 μM at 35 cm depth but then reached higher steady state concentrations of 15 μM . Concentrations at 50 to 80 cm depth decreased rapidly from field values to steady state concentrations of 4.5 and 6.4 μM respectively. Concentrations at 115 cm depth increased from 20 μM in field solutions to 2700 μM in first batch of microcosms and then exponentially decreased to concentrations around 100 μM . At 150 and 170 cm microcosm concentrations increased to 1800 and 1560 μM respectively and decreased linearly to concentrations around 100 and 180 μM respectively.

4. Discussion

Calculations show that Basaltic glass was highly undersaturated in microcosm solutions ($\Delta G_r = -14$ to

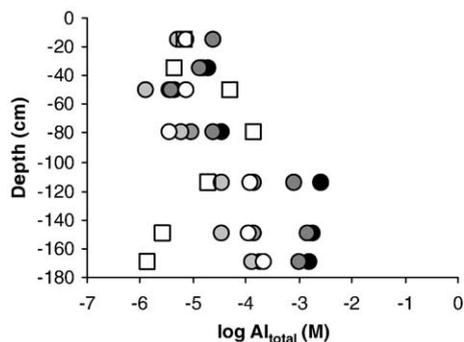


Fig. 2. Depth against DOC in soil solutions. Squares=field samples. Black circles represent first sampling batch and white circles final batch in microcosms.

– 10 kJ mol⁻¹) compared to field solutions (ΔG_r – 8 to – 4 kJ mol⁻¹) (Fig. 3).

There was a significant difference (up to 9 orders of magnitude) in the saturation state of basaltic glass between field and microcosm treatments (Fig. 3). The saturation state changed down the soil profile in field but was always insignificant in microcosms. The dissolution rate of basaltic glass was almost entirely controlled by the $a_{\text{H}^+}^3/a_{\text{Al}^{3+}}$ activity ratio at 15 cm in field solutions (Fig. 3). The dissolution rate was increasingly slowed down by decreased ΔG_r of basaltic glass towards 115 cm. Saturation state decreased dissolution rate by ~20% from 115 cm to 205 cm (Fig. 3). Saturation state decreased dissolution rate by ~4% at 115 cm to ~12% at 205 cm in field solutions when speciation calculations were carried out with oxalate representing all measured DOC. Basaltic glass was highly unsaturated in microcosms at all depths thus the dissolution rate did not slow down due to the saturation state and dissolution rate was altogether controlled by the $a_{\text{H}^+}^3/a_{\text{Al}^{3+}}$ activity ratio.

There was a significant variation in the expected dissolution rate of the basaltic glass, down the profiles, between field and microcosm experiments but less variation with time in the experiments, as shown in Fig. 4. The calculated dissolution rate was faster in the microcosm, the $a_{\text{H}^+}^3/a_{\text{Al}^{3+}}$ ratio was higher, because of less reaction time than in the field. In the field the expected dissolution rate of basaltic glass was fastest at 50 cm depth ($a_{\text{H}^+}^3/a_{\text{Al}^{3+}}$; – 8.8) but slowest at 115 to 205 cm ($a_{\text{H}^+}^3/a_{\text{Al}^{3+}}$; – 10; Fig. 4). This is equivalent to a variation of a 2.5 factor in the basaltic glass dissolution rate with depth in the field. Adding oxalate concentration, equal to the measured total dissolved carbon concentration, to speciate Al³⁺ in the soil solution generally increased the expected dissolution rate (Fig. 5). Expected dissolution rate in-

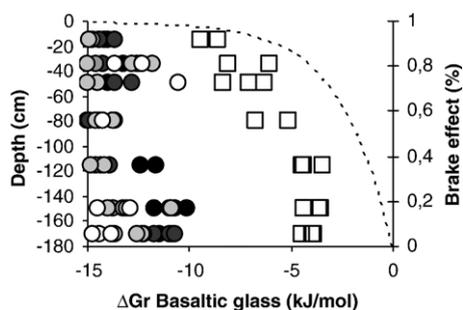


Fig. 3. Depth against ΔG_r for basaltic glass in field (squares) and microcosms (circles) at 25 °C. Brake effect due to decreased undersaturation as dotted line for comparison. Black circles represent first sampling batch and white circles final batch in microcosms.

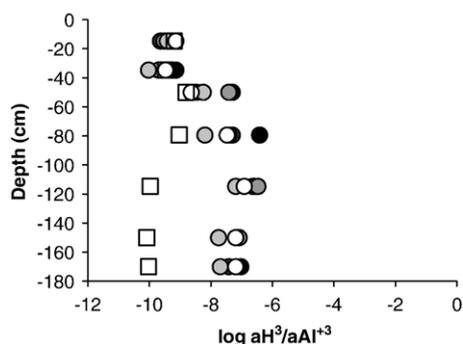


Fig. 4. Depth against $\log a_{\text{H}^+}^3/a_{\text{Al}^{3+}}$ for all treatments with no DOC speciation at 25 °C. This is a minimum value since no DOC was used to speciate the aluminum. Note that a change of 0.2 in pH value varies the value by 0.6. Squares=field samples. Black circles represent first sampling batch and white circles final batch in microcosms.

creased by factor of 7 at 15 cm but this factor was only 1.8 at 205 cm depth in the field. This was because DOC concentrations did not change down the soil profile while combined effects of either increased concentration complexing anions or increased pH lowered the Al³⁺ concentrations in soil solutions. Oxalate effect was notably highest in near surface horizons in experiments from a factor of 37 at 35 cm in the initial sampling batch, when DOC concentrations were high, to a factor of 2 at 115 to 170 cm depth where fluoride and sulphate concentrations were high. Oxalate effect was always highest at 35 cm where DOC concentrations were high compared to at 15 cm before lowering again at 50 cm. Oxalate effect always decreased towards the base of the soil profile in experiments as pH values lowered and fluoride and sulphate concentrations increased. Expected dissolution rate did not change significantly with time in microcosm experiments at 115–150 cm

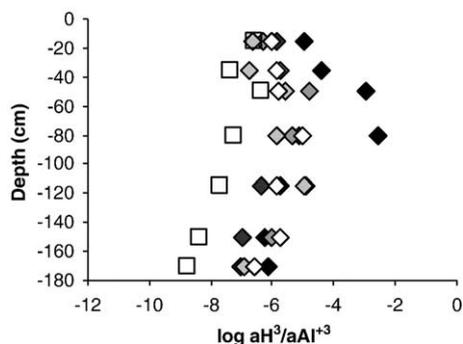


Fig. 5. Depth against $\log a_{\text{H}^+}^3/a_{\text{Al}^{3+}}$ for all treatments with DOC speciation at 25 °C. This is a maximum value since oxalate was used to represent DOC that speciated the aluminum. Field=squares. Squares=field samples. Black circles represent first sampling batch and white circles final batch in microcosms.

(Fig. 5). Expected dissolution rate was higher at 15–80 cm and 170 cm respectively in first sampling batch than in consecutive batches but the rate did not decrease constantly towards end of experiments (Fig. 5). A higher difference in expected dissolution rate with time in experiments when oxalate speciation is taken into account, was due to elevated concentrations of DOC at the beginning of microcosm experiments. The difference with time was significantly lower when no DOC was taken into account (Figs. 4 and 5).

5. Conclusion

At fixed temperature and high undersaturation (ΔG_r), the dissolution rates of the basaltic glass and probably allophane and imogolite, were dictated by the activity ratio; $a_{\text{H}^+}^3/a_{\text{Al}^{3+}}$, of the soil solutions. With decreasing undersaturation of basaltic glass, the rate was slowed down up to 20% in field solutions.

Speciation of Al^{3+} was highly influenced by organic ligands in near surface horizons. Increased pH, fluoride and sulphate concentrations all decreased the effect of organic ligands as $\text{Al}(\text{OH})_x$, AlF_x and $\text{Al}(\text{SO}_4)_x$ species become increasingly abundant. High concentrations of fluoride and sulphate are able to speciate the Al^{3+} that would otherwise be free at the low pH values observed in both field and microcosm experiments.

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References

- Arnalds, O., 2004. Volcanic soils of Iceland. *Catena* 56, 3–20.
- Dessert, C., Dupre, B., Gaillardet, J., Francois, L.M., Allegre, C.J., 2003. Basalt weathering laws and the impact of basalt weathering on the global carbon cycle. *Chem. Geol.* 202, 257–273.
- Eswaran, H., Van Den Berg, E., Reich, P., 1993. Organic carbon in soils of the world. *Soil Sci. Soc. Am. J.* 57, 192–194.
- Gislason, S.R., Oelkers, E.H., 2003. Mechanism, rates, and consequences of basaltic glass dissolution: II. An experimental study of the dissolution rates of basaltic glass as a function of pH and temperature. *Geochim. Cosmochim. Acta* 67, 3817–3832.
- Jonsson, J., 1995. Sandur–Sandar, nokkrar athuganir (Sand—some observations). Research Institute Nedri As Report vol. 53. Hvergerdi, Iceland (in Icelandic).
- Kimble, J.M., Ping, C.L., Sumner, M.E., Wilding, L.P., 2000. Andisols. In: Sumner, M. (Ed.), *Handbook of Soil Science*. CRC Press, Washington D.C., pp. E209–E225.
- Milliman, J.D., Syvitski, J.P.M., 1992. Geomorphic/tectonic control of sediment discharge to the ocean: the importance of small mountainous rivers. *J. Geol.* 100, 525–544.
- Oelkers, E.H., Gislason, S.R., 2001. The mechanism, rates and consequences of basaltic glass dissolution: I. An experimental study of the dissolution rates of basaltic glass as a function of aqueous Al, Si and oxalic acid concentration at 25 degrees C and pH=3 and 11. *Geochim. Cosmochim. Acta* 65, 3671–3681.
- Parkhurst, D.L. and Appelo, C.A.J., 1999. User's guide to PHREEQC (Version 2)—a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. 99–4259, 1–326.
- Wada, K., Arnalds, O., Kakuto, Y., Wilding, L.P., Hallmark, C.T., 1992. Clay minerals of four soils formed in eolian and tephra materials in Iceland. *Geoderma* 52, 351–365.
- Wolff-Boenisch, D., Gislason, S.R., Oelkers, E.H., 2004a. The effect of fluoride on the dissolution rates of natural glasses at pH 4 and 25 °C. *Geochim. Cosmochim. Acta* 68, 4571–4582.
- Wolff-Boenisch, D., Gislason, S.R., Oelkers, E.H., Putnis, C.V., 2004b. The dissolution rates of natural glasses as a function of their composition at pH 4 and 10.6, and temperatures from 25 to 74 °C. *Geochim. Cosmochim. Acta* 68, 4843–4858.