



Electrolyte effects on surface chemistry of basaltic glass in the initial stages of dissolution



Stefan Dultz ^{a,*}, Harald Behrens ^a, Gundula Hensch ^b, Joachim Deubener ^b

^a Institute of Mineralogy, Leibniz Universität Hannover, Callinstr. 3, D-30167 Hannover, Germany

^b Institute of Non-Metallic Materials, Clausthal University of Technology, Zehntnerstraße 2a, D-38678 Clausthal-Zellerfeld, Germany

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ABSTRACT

For an understanding of the effect of solution composition on the dissolution rate of basaltic glass detailed knowledge of surface chemistry is important. Here the zeta potential (ζ) as a characteristic parameter of the magnitude of surface charge at the solid–liquid interface was used to determine ionic effects on surface chemistry in initial stages of basaltic glass dissolution. In a systematic approach powdered synthetic basaltic glass was dispersed in solutions of different cations (NO_3^- salts of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Zn^{2+} , and Al^{3+}) and anions (Na^+ salts of F^- , Cl^- , I^- , NO_3^- , SO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$, HPO_4^{2-}), each in concentrations of 0.1, 0.5, 1.0, 2.5, and 5.0 mmol/L. ζ was traced in time sequences up to 12,000 h at ideally circumneutral pH. Ion affinities to glass surfaces were characterized by sorption isotherms. A change of glass chemical composition by the formation of altered layers was determined by depth profiling using secondary neutral mass spectrometry (SNMS). The dissolution of the glass was quantified by the amount of Si released after 4000 h.

A marked decrease of ζ in deionized water within the first 3 h reaction time is assigned to the desorption of alkali and alkaline earth metal cations from the glass surface and formation of negatively charged $\text{Si}-\text{O}^-$ sites. The addition of anions resulted in stronger negative initial ζ values in comparison with the experiment in deionized H_2O indicating marked anion adsorption on surface sites, most obvious for F^- , $\text{C}_2\text{O}_4^{2-}$ and HPO_4^{2-} . The initial ζ was increased upon the addition of divalent cations indicating neutralization of negatively charged surface sites. Over time a striking shift from negative to positive ζ was obtained, most markedly for Ca^{2+} and Zn^{2+} . The addition of trivalent Al^{3+} resulted directly in positive ζ indicating a strong adsorption on glass surfaces. With the progress of the experiment the sign of ζ reversed to negative values again. The reason for charge reversal is not fully understood and might be related with cation adsorption exceeding the negative surface charge and a concentration of Fe oxides at the glass surface. After an ~ 2000 h reaction time ζ adjusted for most electrolyte additions to slightly negative ζ until the end of the experiment, indicating that a final state in the composition of surface sites was reached. The presence of monovalent Na^+ and K^+ in solution suppressed Si release from the glass, whereas it is accelerated by bivalent cations. It appears that the neutralization of deprotonated $\text{Si}-\text{O}^-$ sites by monovalent cations – their preferential binding is also indicated by chemical analysis – favors polymerization resulting in slower Si release. Upon the addition of Al^{3+} it is likely that $\text{Si}-\text{O}-\text{Al}-\text{O}-\text{Si}$ bonds are formed, which can suppress Si release. The presence of F^- , $\text{C}_2\text{O}_4^{2-}$, and HPO_4^{2-} clearly enhances glass dissolution, most probably by increasing the coordination of network forming cations, hereby weakening bonds. The observed generation of positive ζ on basaltic glass surfaces is remarkable, and can improve in natural systems the adsorption capability of the basaltic glass surface for negatively charged compounds from pore solution, anions, dissolved organic matter and also bacterial cell walls.

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1. Introduction

Basaltic glass is formed during rapid cooling of magma by water or air. Due to its isotropic nature and chemical composition it is rated as a ‘fast reacting solid’ in soils or aquatic environments (Schott et al., 2009). Based on the large number of volcanic areas and the susceptibility of basaltic glass to weathering, it plays an important role in local and

global cycling of elements in many ways. During chemical weathering the release of alkali and earth alkaline cations is linked with a buffering of acidification. Released Ca^{2+} , Fe^{2+} and Mg^{2+} can be a trap for CO_2 (Pierrehumbert, 2010). Microbial colonization of basaltic glass surfaces for nutrient acquisition increases the quantity of biomass which is important for carbon storage.

The secondary product formed during the weathering of basaltic glass is called ‘palagonite’, which can be highly variable in chemical, mineralogical, and structural properties depending on the nature of the glass and environmental conditions. More specific the dissolution

* Corresponding author.

E-mail address: dultz@ifbk.uni-hannover.de (S. Dultz).

rate of the glass and the preservation of elements in palagonite depends on a number of factors, such as glass chemistry, specific surface area, composition of the solution, temperature, and coating on glass surfaces (Stronck and Schmincke, 2002). Glasses consisting of compounds with different solubilities have the tendency to dissolve incongruently. Mono- and divalent network modifier cations are released to solution, and a leached glass matrix from network formers and intermediates remains. Formation of a leached layer directly bonded to the glass surface is a widely accepted mechanism of glass alteration (Grambow and Müller, 2001; Techer et al., 2001). However, from experiments in the laboratory (Geisler et al., 2010) and analysis of archeological (Hasdemir et al., 2013) and natural glasses (Hay and Iijima, 1968; Dultz et al., 2014) there are observations on a distinct separation between glass and secondary phases, pointing to a congruent dissolution and reprecipitation mechanism. For an understanding of the principal mode of dissolution and turnover of elements the knowledge of surface chemistry of a dissolving mineral, revealing sorption/desorption reactions and structural changes during dissolution is regarded as a prerequisite (Schott and Berner, 1983). Within the principal changes in the surface chemistry of basaltic glass in contact with aqueous solutions the behavior of structurally bonded ferrous iron can be exceptional due to its susceptibility for oxidation.

Sinks for glass particles deposited with volcanic ash are soils and different aquatic systems, various saline as well as fresh waters being possible with a broad spectrum of solution parameters, which influence element release from the glass. For assessing the effect of solution chemistry on basaltic glass dissolution rate, parameters such as kind and concentration of ions present, pH, and redox potential have to be considered (Schott et al., 2009). Surface adsorbed ions were shown to play an important role for the dissolution rate (Chave et al., 2011; Oelkers and Gislason, 2001; Wolff-Boenisch et al., 2004). Studies on ionic effects on glass dissolution rates considering for example divalent SO_4^{2-} (Flaathen et al., 2010), the organic anion oxalate (Oelkers and Gislason, 2001) and cations such as Ca^{2+} (Chave et al., 2011) clearly indicate that glass surface sites react with dissolved ionic species. Glass dissolution rate appears typically promoted by strongly adsorbing anions such as fluoride and oxalate, whereas addition of certain cations such as Al^{3+} can suppress glass dissolution (Oelkers and Gislason, 2001; Wolff-Boenisch et al., 2004). In studies on pH dependent charge properties of mineral surfaces the monovalent cations and anions Na^+ , K^+ , Cl^- , Br^- , and NO_3^- are assumed to be largely indifferent to solid surfaces and hence used as background electrolytes (Kosmulski, 2014), whereas the interactions of multivalent ions with mineral surfaces can be stronger.

pH dependent protonation and deprotonation of glass surface sites is well known to have a strong impact on the far-from-equilibrium dissolution rate (Oelkers and Gislason, 2001). For simple oxides the dissolution rate is at its minimum at the point of zero charge (*pzc*), where the sum of negatively and positively charged sites is zero. It is at pH 2.5 for SiO_2 , 7.0 for Fe_2O_3 and 8.5 for Al_2O_3 (Kosmulski, 2014). At low and high pH protonation and deprotonation reactions result in charged surface sites, which tend to weaken surface bonds and hereby increase dissolution rate. For basaltic glass with a complex chemical composition the *pzc* does not necessarily represent the point with the lowest dissolution rate, which is due to the presence of surface sites of different acidity. Protonation of oxygen bonds with Si will appear first at pH <3 but for those with Al and Fe at pH <7–8.5 already. Hence the minimum far-from-equilibrium dissolution rate for the complex basaltic glass will be at the pH where the sum of absolute values of charges at different surface sites is at a minimum. Derived from titrations with acid and base the *pzc* of powdered basaltic glass is at pH 6.8 (Schott, 1990), which is only slightly higher than that of experimental observations and modeling (Flaathen et al., 2010). Hence, in dissolution

experiments with a focus on ionic effects adjustment of pH to circumneutral values is a measure to avoid extensive adsorption of H^+ and OH^- which can overlay effects from ions introduced. From curves predicted from measured steady-state basaltic glass dissolution rates at 50 °C minimum values in the far-from-equilibrium dissolution rate are between pH 5.3 and 6.2 (Flaathen et al., 2010), which appear at only slightly lower pH than the *pzc* of basaltic glass determined from titrations. From data compilations on pH-dependent mineral dissolution rates Drever (1994) derived that for most silicate minerals the far-from-equilibrium dissolution rate is typically at a minimum and independent from pH in a relatively broad circumneutral region from pH 4–5 to ~8. As chemical compounds in basaltic glass are similar to those in silicate minerals it appears that in our experiments the broad circumneutral pH region is ideally suited for the determination of ionic effects on the surface chemistry of basaltic glass. The competition between electrolytes and protons/hydroxy ions will be weak and the far-from-equilibrium dissolution rate of basaltic glass at a minimum.

For dissolution studies basaltic glasses are usually milled. Hereby broken bonds are generated at the surfaces, which have a high reactivity in aqueous solution. In natural systems the occurrence of such fresh glass surfaces is limited to initial stages of glass alteration, for example directly after fracturing due to thermal and mechanical stress evolving from rapid cooling of glass in contact with water or air, during tectonics at mid ocean ridges, transport of glasses by water or ice, and strain release. Sites exposed to the solution on fracture surfaces with unsatisfied bonds differ in chemistry and molecular level 3D-structure to those in the glass interior (Zallen, 2004). A range of surface sites with different energies exists given by the complex chemical composition of basaltic glasses and also by site conformation with plane, edge, and kink positions. Edge and kink sites on a fractured surface will be more reactive than plane sites (Lasaga, 2014).

For tracing chemical reactions on glass surfaces such as ion adsorption, element release, precipitation and structural changes we determined ζ (zeta potential), which is a characteristic parameter of the solid–liquid interface in aqueous suspensions (Kirby and Hasselbrink, 2004). Determination of ζ allows the characterization of the solid–liquid interface in situ, whereas other techniques focusing on the molecular level such as spectroscopic methods work best in the dry state implying the risk of artifacts based on the need of prior drying of the sample. The use of spectroscopic methods in the wet state is limited by the fact that signals coming from surface sites are strongly overlain by signals from the bulk glass and the aqueous solution.

Analysis of the electrical state of the interfacial region is a new approach for understanding the complex reactions on glass surfaces in solutions (Snellings, 2015). Here we want to determine the potential of this method to get new insights in surface reactions of basaltic glass based on the characteristics of the diffuse double layer. For this purpose we choose a systematic experimental approach considering seven different cations and seven different anions in five different concentrations. Due to the complexity of sites on the basaltic glass surface the ζ signal is an integral value, which can be affected in our experiments by different also overlapping factors such as ion ad-/desorption, structural changes and shifts in surface chemistry. Hence complementary data were collected to support findings from ζ measurements. For this purpose, sorption isotherms for quantitative estimates on ion transfer were established, depth profiling of glass chemical composition was performed and Si release from the glass was quantified.

2. Theoretical background

Minerals in contact with an aqueous solution establish variable charges on their surfaces. The charged sites establish an electric field,

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