Is BET surface area proportional to reactive surface area?

M. ODSON

Department of Soil Science, University of Reading, Reading, UK, RG6 6DW

Introduction

It is universally accepted that one of the key variables that governs the amount of mineral dissolution that can take place is the amount of mineral surface area available for dissolution. In recognition of this fact the dissolution rates of minerals, as determined in the laboratory, are almost without exception normalised to mineral surface area, typically the specific surface area as determined by gas adsorption (normally N_2) and application of the BET isotherm. But what if the BET surface area of a mineral is not proportional to the reactive surface area of the mineral?

Previous work

Most workers accept that BET surface area is proportional to reactive surface area. However two studies that oppose this view stand out in the literature. Holdren and Speyer (1985, 1987) famously found that feldspar dissolution rates in batch experiments were not proportional to BET surface area over a BET surface area range of $0.05 – 4.48$ m^2 g^{-1}. Gautier *et al.* (2001) dissolved quartz under far from equilibrium conditions using flow through apparatus and found that mass normalised dissolution rates remained constant whilst BET surface area normalised dissolution rates decreased as BET surface area increased from 0.07 to 0.37 m^2 g^{-1}. The BET surface area increase was attributed to unreactive etch pit walls exposed as etch pits deepened.

Current work

In this study powders of hornblende, anorthite and orthoclase ranging in grain size from $180 – 150$ μm to $10 – 20$ μm and BET surface area from $0.10 – 0.70$ m^2 g^{-1} (hornblende), $0.08 – 0.42$ m^2 g^{-1} (anorthite) and $0.07 – 0.48$ m^2 g^{-1} (orthoclase) were dissolved in pH 3 HCl in continuous flow reactors in order to determine whether the surface area normalised dissolution rates were constant for powders of the same mineralogy but differing BET surface area. No significant differences in dissolution rates were found. All grain sizes gave dissolution rates of c. $1 \ x \ 10^{-12}$ mols m^2 s^{-1} (hornblende), c. $5 \ x \ 10^{-9}$ mols m^2 s^{-1} (anorthite) and c. $1 \ x \ 10^{-12}$ mols m^2 s^{-1} (orthoclase). These results indicate that BET surface area appears to be proportional to reactive surface area for these minerals under far from equilibrium dissolution conditions.

References

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An experimental study of aqueous formic acid decomposition rates as a function of pH and temperature from 175 to 250° C

ERIC H. OELKERS, LIONEL RUHIER, AND ROBERT GOUT

Géochimie, LMTG-UMR CNRS n°5563, Observatoire Midi-Pyrénée - Université Paul-Sabatier 38, rue des 36-Ponts 31400 Toulouse, FRANCE (oelkers@lmtg.ups-tlse.fr)

The overall goal of this work is the improved understanding of rates of reactions among aqueous organic species at elevated temperature. Formic acid decomposition has been studied due to 1) its role as an reaction intermediary of the destruction of other aqueous organic species, such as oxalic acid 2) the overall potential importance of carboxylic acids in geochemical processes, and 3) its simple structure/formula. Aqueous formic acid decomposition rates were quantified through closed system experiments performed by heating initial solution containing HCOOH ± HCl or NaOH in rocking titanium reactors and in sealed quartz tubes. After a brief reaction removing residual oxygen in each reactor, aqueous formic acid was consumed exclusively by the reaction

$$HCOOH \rightarrow CO_2 + H_2 . \qquad (1)$$
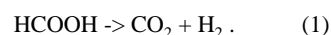
Concentrations of the liquid and gas phases throughout the experiments were verified and quantified using Raman spectroscopy. Preliminary data indicates that the rates of this reaction (r) are first order with respect to aqueous HCOOH^0 concentration ($[HCOOH^0]$) and consistent with

$$r = k \ [HCOOH^0] \qquad (2)$$

where k refers to a rate constant. This rate dependence is consistent with the assumption that reaction (1) is a homogeneous reaction which is not catalysed by the reactor wall surfaces (e.g. Akiya and Savage, 1998). As $[HCOOH^0]$ decreases with increasing pH due to aqueous formic acid dissociation, so to do the rates of reaction (1). Regression of 250° rate data yield a rate constant of 9×10^{-4} s^{-1} which is in rough agreement with formic acid decay rates reported by Small and Manning (1993). This rate suggests a formic acid half life of 2.6 days at pH 7, but less than one hour at pH<3. Preliminary data suggest this rate is strongly temperature dependent; a preliminary rate constant of 1.5×10^{-7} s^{-1} was found for 175° C. Further work aimed at assessing the potential catalytic effect of the presence of mineral surfaces is planned prior to the meeting.

References

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