Empirical relations to estimate kinetic constants of silicates dissolution from crystallographic and energetic parameters

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Recent works on kinetics of chemical reactions between rock-forming minerals and aqueous solutions have produced data for dissolution rates of minerals. A new geochemical code appears based on thermodynamic potential and kinetic laws. To use these models, the knowledge of kinetic parameters of minerals is necessary. From crystallographic (Si–O length, polarisability...) and energetic parameters (bonding energies, S^0/V^0 ratio...), some kinetic constants of minerals dissolution can be estimated.

Introduction

Recent studies of the weathering processes, involving interactions of water and atmosphere with oxide and silicate minerals, have cleary demonstrated that the rates of these reactions are strongly dependent on the surface structure of the mineral and that the kinetic mechanism is mainly controlled by the formation of surface complexes (Stumm, 1990). The rate of dissolution of many rock-forming minerals is controlled by the hydrolysis of the bridging silicate bonds at the mineral surface. The works with ab initio approach shows that quantum-mechanical calculations on molecular clusters are capable of predicting the crystal structure and the equations of state of many silicates (Lasaga and Gibbs, 1990). The ab initio molecular orbital theory permit to characterize the bonding of water to the siloxane (Si–O–Si) and silanol (Si–OH) molecular groups, and the hydrolysis reaction which creates silanol groups from the bridging bond.

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Previous works

Walther and Wood (1986) find a correlation between the kinetic constant of minerals dissolution and relative entropies per unit volume or gram atom of oxygen. Minerals with high entropy/unit volume ratio (S^0/V^0) dissolve more rapidly at low temperatures than do those with low entropy per unit volume.

Brady and Walther (1989) show that dissolution rates of most silicates can be related to a simple function of mean oxygen site potential. The minerals with low dissolution rates have the higher mean oxygen site potential.

Sverjensky (1992) show that a linear free energy equation, developed for the prediction of the standard Gibbs free energies of formation of isostructural families of crystalline solids, can also be used for predicting the dissolution rates of solids.

Empirical correlations

(1) An empirical relation is observed between the kinetic constant of mineral dissolution at pH = 5 and the polarisability/number of Si in mineral ratio. Thus, more this ratio is small, more the kinetic constant is low (from quartz to olivine; Fig. 1).

(2) An estimation of kinetic constant of mineral dissolution can be carried out from data of the length T–O bonds in silicates minerals (Table 1 & Fig. 1). The smaller Si–O length in minerals correspond to smaller kinetic constants of mineral dissolution (from quartz to nepheline; Fig.2). Moreover, the percentage of aluminium atom in the tetrahedron influences the length Si–O and Al–O bonds (Smith and Bailey, 1963). More Al/Si substitution is fre quent in the tetrahedron, more Si–O distance is important and more the kinetic constant estimated is large.

(3) The oxygen quantity in silicate minerals influences the kinetic constant of dissolution: the higher Si/O ratio the lower the kinetic constant (Madé, 1991).

TABLE. 1. Kinetic constant of mineral dissolution at pH = 5; polarisability of mineral, length of Si-O tetrahedral bond and bonding energies of minerals.

Mineral	k_{dm} (a)	Polar. (b)	Si-O Å(c)	bonding energies (d)
Quartz	−6.30	2.851	1.607	37.320
Albite	−4.85	12.293	1.646	34.335
Anorthite	−4.10	13.342	1.681	31.935
Microcline	−4.30	13.121	1.642	34.266
Nephine	−1.06	6.797	1.687	31.860
Kaolinite	−5.05	–	1.626	–
Muscovite	−5.20	–	1.654	32.494
Diopside	−2.16	9.865	1.636	32.052
Enstatite	−2.50	4.618	1.650	32.344
Augite	−3.10	10.121	–	30.728
Olivine	−2.20	6.327	1.638	29.796

(a) review in Madé (1991), kinetic constant [mol/m²/ yr];
(b) Polar. = Polarisability in Vieillard (1982);
(c) Smith (1954); Smith \& Bailey (1963); (d) Keller (1954))
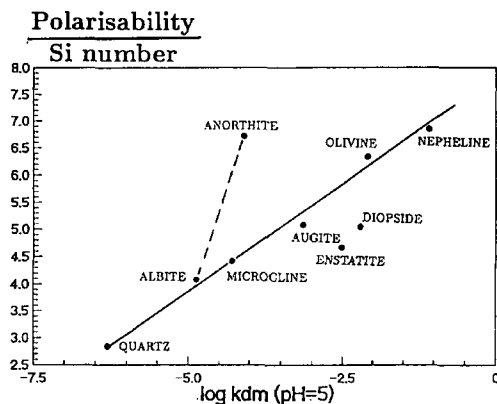
Polarisability
Si number

FIG. 1. Relation between kinetic constants of mineral dissolution (pH = 5) and polarisability/number of Si in mineral ratio.

(4) A correlation appear between the bonding energies of silicate minerals ajusted to 24 oxygens (Keller, 1954) and kinetic constants of dissolution. More the bonding energies is high, more the kinetic constant of dissolution is small for a given mineral (Fig. 3).

References

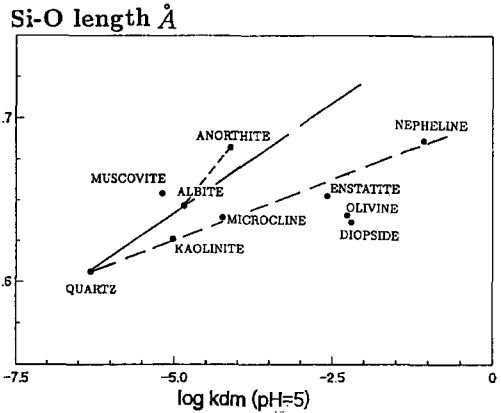Brady P.V. and Walther J.V. (1989) *Geochim. Cosmochim. Acta*, **53**, 2823–30.

Si-O length Å

FIG. 2. Relation between kinetic constants of mineral dissolution (pH = 5) and the length Si-O bond in mineral.
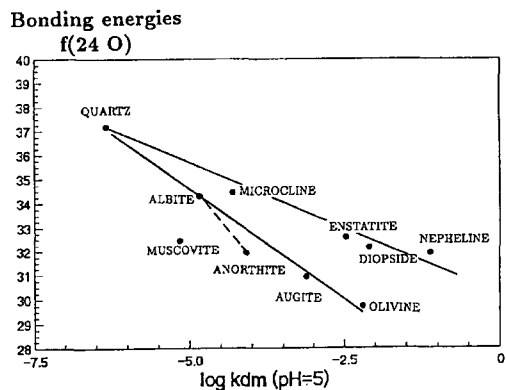
Bonding energies
f(24 O)

FIG. 3. Relation between kinetic constants of mineral dissolution (pH = 5) t and the bonding energies of minerals adjusted to 24 oxygens.

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