1. Cover Page:

RESEARCH PROJECT REPORT

TITLE OF PROJECT: **Numerical Modelling of Dissolution Kinetics of Common Silicate Minerals**

NAME: **Aditya Ray**

IVR Number: **202100034389**

Application Reference Number: **DST/INSPIRE/02/2021/007899**

Scholarship for Higher Education (SHE) Component under INSPIRE

Format for Project Completion Certificate
(To be filled by the Supervisor of Research Project)

1. IVR Number or Application Ref. No. : 202100034389

2. Name of INSPIRE Scholar: Aditya Ray

3. Name of College where Scholar is studying: Presidency University

4. Name of University to which above College is affiliated: Presidency University

5. Bank Account Number of Scholar: 40955100863

6. IFSC Code: SBIN 0004744

7. Mobile No. and Email Address of Scholar: +91 8293220493 and adityaray2204@gmail.com

8. Title of Project: Numerical Modelling of Dissolution Kinetics of Common Sillicate minerals

9. Broad Subject Area of Research Project: Numerical Modelling

10. Project Duration (in weeks): 7 weeks
    (Minimum 6 to 8 weeks)

11. Date of Start of Research Project: 15.06.2023

12. Date of Completion of Research Project: 03.08.2023

13. Supervisor Name: Dr. Amlan Banerjee

14. Designation of Supervisor: Associate Professor

15. Affiliation of Supervisor
    (a) Department - Geological Studies Unit
    (b) College - Physics & Earth Science Division, Indian Statistical Institute
    (c) University - Indian Statistical Institute
    (d) Address - 203, Barrackpore Trunk Road, Kolkata – 700 108, India
    (e) Mobile no. and Email Address - +91 9330563151 ; amlan@isical.ac.in

16. Major Specialization area of Supervisor: Sedimentary Geochemistry

(Seal & Signature of Supervisor)
AMLAN BANERJEE
Associate Professor
Geological Studies Unit
Physics & Earth Science Division
Indian Statistical Institute
203, Barrackpore Trunk Road
Kolkata - 700 108, INDIA

Date: 04.09.2023

Note: Kindly upload Research Project along with filled and signed Project Completion Certificate

3. Acknowledgements

I would like to express my sincere gratitude to DST INSPIRE for encouraging me to explore research as a career opportunity and providing me this exceptional opportunity. I thank the following individuals who have played instrumental roles in the successful completion of my summer training:

First and foremost, I extend my heartfelt thanks to Prof. Amlan Banerjee for his unwavering support and invaluable guidance throughout my academic pursuits. As my supervisor, his mentorship has been an invaluable asset, and his encouragement and expertise have been pivotal in shaping my work.

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Last but not the least, I am indebted to my parents for their continuous love, encouragement, and unwavering support in all aspects of my life. Their belief in me has been my driving force, and I am forever grateful for their presence in my life.

The unwavering support of these remarkable individuals has been the driving force behind my accomplishments. I am deeply thankful for their contributions, which have had a lasting and profound impact on both my academic pursuits and personal growth. Their belief in my potential and encouragement have inspired me to overcome challenges and strive for excellence. Without them, my journey would not have been as fulfilling and successful. As I embark on the next chapter of my life, I carry with me the lessons and guidance they have bestowed, knowing that their influence will continue to shape my future endeavors.

CONTENTS

4. Title of Research Project:

Numerical Modelling of Dissolution Kinetics of Common Silicate Minerals

5. Aim/Objectives:

1. Develop a numerical model using PHREEQC.

2. Simulate dissolution kinetics of common silicate minerals.

3. Explore complex interactions between dissolved aluminum, pH, base cations, CO2 concentration, and free organic acid radicals and understand their combined influence on the weathering process.

4. Formulate and parameterize equations based on available literature.

5. Utilize developed models for predicting future dissolution trends.

6. Introduction of Research Topic:

Chemical weathering holds paramount importance in comprehending and analyzing numerous critical environmental issues. One such issue is the acidification of soils and waters, which exhibits a strong correlation with the geochemistry of weathering. The weathering process in soils and rocks serves as the sole self-repairing mechanism for acidified ecosystems, offering essential restorative functions. The kinetic dissolution of silicate minerals is of particular importance as it plays a pivotal role in elucidating the underlying drivers of global climatic changes. Additionally, ecological changes are intricately linked to alterations in local chemical and climatic conditions, involving both major and minor elements. The cumulative impact of local weathering effects over extensive geographical areas governs significant geochemical cycles.

Emerging tools rooted in advanced geochemical understanding enable quantitative assessments of ecological changes and facilitate a more thorough evaluation of their causal relationships and consequences. This newfound capability empowers us to address environmental shifts with enhanced precision. Furthermore, the sustainable management of biomass production in forestry and agriculture, water quality assessments, and the safety assessment of atomic waste storage necessitate accurate derivation of weathering rates from geological and mineralogical characteristics of the respective systems.

A comprehensive understanding of chemical weathering processes thus holds intrinsic scientific significance, as it informs our comprehension of various environmental phenomena and underpins informed decision-making for safeguarding ecosystem health and stability.

7. Theoretical Framework of Topic:

7.1. Importance of Geochemical Models:

Geochemical models play a crucial role in research, not merely for generating results, but because they allow us to investigate complex and non-linear systems and interpret data from such systems. Models enable the study of interactions between multiple simultaneous processes within a single experiment. Essentially, all models serve one or both of two purposes:

• Testing the Synthesized Understanding: Models are used to test the synthesized understanding of a system, based on the mathematical representation of its subsystems and the proposed coupling of these subsystems.

• Predicting Future Outcomes: Models help predict future events by explaining how and why things have worked in the past.

When researchers are compelled to formulate equations and parameterize coefficients, their formal understanding of the ecosystem is put to the test. Thus, a model can be seen as the integrated bearer of the modeler's knowledge and comprehension of the system. In modeling, there are no improbabilities as all parameters are assigned quantitative values according to unique and precise rules.

Models can vary in quality, and a good model adheres to the following principles:

• Transparency: A good model is transparent, allowing inspection and understanding of the rules and principles it employs.

• Testability: The model must be testable, functioning on inputs that can be defined and determined, and producing observable outputs.

A model can take the form of a mental understanding of a mechanism, system, pattern, or principle, and it can be substantiated as an equation or a set of equations/rules. In cases where principles and rules are numerous, employing a computer program to manage all connections and accounting is practical.

The goodness or badness of a model is not contingent on the adequacy of the principles within the model. Instead, the quality of a model is determined by our ability to verify or falsify its performance with specific principles incorporated.

Models serve as indispensable tools in scientific inquiry, allowing us to gain insights into intricate systems and make predictions about future outcomes. Emphasizing transparency and testability, good models serve as reliable aids in understanding and exploring the complexities of the natural world.

7.2. Numerical Models:

A numerical model is a computational representation of a real-world system using mathematical equations and algorithms to simulate its behavior. In the context of simulating dissolution kinetics of silicate minerals, a numerical model is designed to describe the dissolution process quantitatively. It considers various factors, such as dissolved aluminum, pH, base cations, CO_2 concentration, and free organic acid radicals, to calculate dissolution rates accurately. By employing numerical models, researchers can investigate the complex and non-linear interactions involved in silicate mineral dissolution. These models play a crucial role in understanding how environmental conditions, chemical compositions, and rates of reaction impact the overall weathering process, aiding in predicting future trends and assessing long-term sustainability in geological and ecological systems.
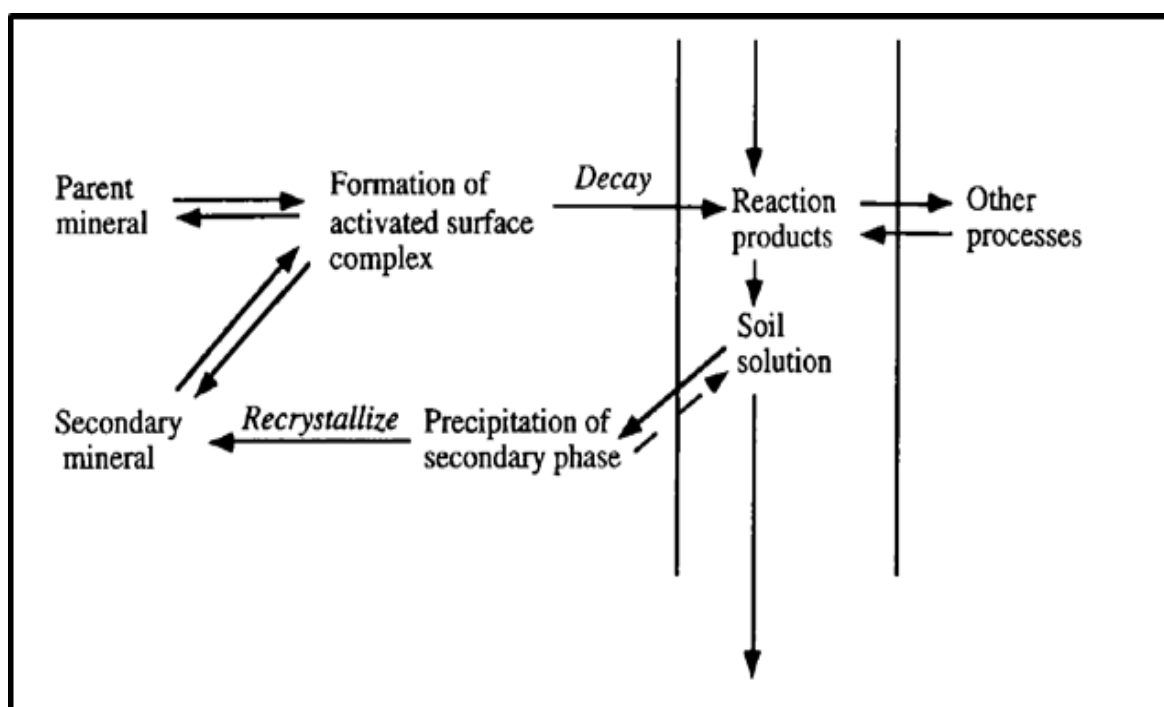

Fig.7.1. *Schematic View of the Weathering Process. Starting with reactants forming an activated unstable surface complex at the mineral surface, the reaction products present in the soil solution affect the complex formation process, which is reversible. The complex subsequently undergoes irreversible decay, proportional to the number of complexes. The presence of reaction products may interfere with the complex formation. Moreover, secondary phases may be formed from the soil solution. Once precipitates have formed irreversibly, they can only dissolve through a kinetic process involving an activated surface complex (Sverdrup and Warfvinge, 1995).*

7.3. PHREEQCC:

PHREEQC Version 3 is a sophisticated computer program developed for simulating chemical reactions and transport processes in natural or polluted water systems, laboratory experiments, and industrial processes. The program is based on the equilibrium chemistry of aqueous solutions interacting with minerals, gases, solid solutions, exchangers, and sorption surfaces, reflecting its original acronym—pH-REdox-EQuilibrium. Over time, PHREEQC has evolved to encompass the modeling of kinetic reactions and 1D transport.

One of the program's significant strengths lies in its user-customizable rate equations, which enable the simulation of kinetic reactions using Basic statements. Additionally, PHREEQC allows for the interconnection of kinetic and equilibrium reactants, facilitating the linkage of surface sites with the consumption or production of kinetic reactants during modeling periods.

The 1D transport algorithm of PHREEQC accounts for dispersion and diffusion phenomena, solute movement in dual porosity media, and multicomponent diffusion with individual, temperature-dependent diffusion coefficients for species while maintaining charge balance during transport.

PHREEQC's versatility extends to its powerful inverse modeling capability, which empowers users to identify reactions that explain observed water compositions over time or along a flowline.

Moreover, the program boasts extensible chemical databases, making it applicable to almost any recognized chemical reaction influencing rainwater, soil-water, groundwater, and surface -water quality.

Originally evolving from the Fortran program PHREEQE, PHREEQC is designed to calculate concentrations of elements, molalities, activities of aqueous species, pH, pe, saturation indices, and mole transfers of phases to attain equilibrium, considering specified reversible and irreversible geochemical reactions.

PHREEQC Version 3 is a comprehensive and powerful tool, providing researchers and professionals with invaluable insights into the intricate dynamics of chemical reactions and transport processes in diverse water systems. Its ability to model kinetic and equilibrium reactions, coupled with its advanced inverse modeling capabilities, has broad applications in environmental research and water quality assessment.

8. Profile of Organization/Research Lab

The Geological Studies Unit (GSU) at the Indian Statistical Institute (ISI) is a testament to interdisciplinary collaboration, reflecting the visionary ideals of its founder, Prof. Prasanta Chandra Mahalanobis. His belief in the symbiotic relationship between statistics and other scientific disciplines, attracting luminaries like Sir Ronald Fisher and Prof. J. B. S. Haldane to the Institute. Established in 1957, GSU has emerged as a dynamic center for cutting-edge earth sceince research and education, spanning diverse fields such as tectonics, sedimentology, geochemistry, geohydrology, palaeo-biodiversity, and biotic evolution. Notably, GSU has made substantial contributions to understanding basin tectonics, ancient sedimentary environments, palaeontology, and Indian stratigraphy.

Beyond its research endeavors, GSU curates a renowned museum housing a remarkable sauropod dinosaur skeleton and a collection of rare exhibits, demonstrating its commitment to public engagement and scientific dissemination. The Institute's groundbreaking discovery of the *Barapasaurus tagorei*, a unique dinosaur species, underscores its unwavering dedication to advancing the frontiers of anthropology and palaeontology. This solidifies ISI's position as a remarkable institution in the realm of interdisciplinary scientific exploration, both within India and on the global stage.

9. Methodology Followed:

9.1. Kinetics of K-Feldspar Dissolution:

The dissolution kinetics of silicate minerals have been extensively studied both in laboratory experiments and in natural settings. In laboratory studies, researchers dissolve mineral grains in solutions with varying compositions, monitoring the rate of dissolution and Si release. This approach allows for the quantification of dissolution kinetics for different minerals and the assessment of crystal size changes during the process. Table 2.1 presents the calculated lifetimes of 1mm crystals at pH 5 for various minerals, indicating a wide range of dissolution rates. For instance, Ca-feldspar (anorthite) dissolves about 700 times faster than K-feldspar.

Remarkably, the lifetimes calculated from laboratory experiments align well with the Goldich weathering sequence (Figure 2.1), which qualitatively describes the order of weathering susceptibility for different minerals. This agreement further strengthens our understanding of silicate mineral dissolution processes and their implications in natural weathering phenomena.

The rate of dissolution largely depends upon the mineralogy as:

In addition to mineralogy, the dissolution rate of silicate minerals can be influenced by various factors, such as solution composition. Equation (2.2) includes different parameters utilized in rate equations proposed by Sverdrup and Warfvinge (1995) to account for these additional influences on the dissolution process.

where

- r is the reaction rate in mol/m2/s.
- ki are rate coefficients for solutes influencing the rate (mol/m2/s).
- [i] represents solute activities of H+, OH-, free organic radicals R2, and pCO2.
- n and o are the apparent reaction orders.
- fi are inhibition factors.
- The first term accounts for the influence of protons (H+) on the rate.
- The second term describes the rate contribution from hydrolysis.
- The third term considers the contribution of hydroxide ions (OH-).
- The fourth term represents the influence of carbon dioxide (CO2).
- The last term explains the effect of organic acids on the dissolution rate.

Mineral	Lifetime (in Years)
Quartz	3,40,00,000
Muscovite	27,00,000
Forsterite	6,00,000
K-feldspar	5,20,000
Albite	80,000
Enstatite	8,800
Diopside	6,800
Nepheline	211
Anorthite	112

Table 9.1. The mean lifetime in years of 1mm crystals of various minerals calculated from laboratory dissolution studies at 25°C and pH 5 (Lasaga, 1984).
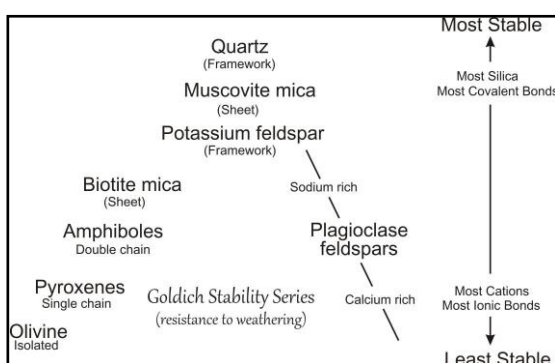

Fig. 9.1. The Goldich weathering sequence based on observations of the sequence of their disappearance in soils (Goldich, 1938).

The inhibition factor fH in Equation (2.2) implies that proton-promoted dissolution is hindered or slowed down by certain solution elements included in the term fH.

$$f_H = \left[1 + \frac{[BC]}{Lim_{BC,H}}\right]^{x_{BC}} \left[1 + \frac{[Al^{3+}]}{Lim_{Al,H}}\right]^{x_{Al}} \qquad (2.2a)$$

$$f_{H_2O} = \left[1 + \frac{[BC]}{Lim_{BC,H_2O}}\right]^{z_{BC}} \left[1 + \frac{[Al^{3+}]}{Lim_{Al,H_2O}}\right]^{z_{Al}} \qquad (2.2b)$$

$$f_{org} = \left[1 + \frac{[R^-]}{Lim_{org}}\right]^{0.5} \qquad (2.2c)$$

$$f_{OH} = f_{CO_2} = 1 \qquad (2.2d)$$

where
- Lim is the limiting activity below which specific solute inhibition becomes negligible. •
[BC] sums up the activities of base cations: Na+, K+, Mg2+, and Ca2+.
- Exponents xi and zi are empirical values used to adjust the dissolution equation.

Thus the rate equation that combines all factors can be considered as:

$$\textbf{Rate = Rm * r * (m/m0)\^0.67} \qquad (2.3)$$

This is the equation which is used for numerical modelling of dissolution of silicate minerals.

Mineral	pk_H	n_H	Lim_{Al}	x_{Al}	Lim_{BC}	x_{BC}	pk_{H_2O}	z_{Al}	z_{BC}	pk_{OH}	o_{OH}
K-feldspar, $K(AlSi_3)O_8$	11.7	0.5	4	0.4	500	0.15	14.5	0.14	0.15	13.1	0.3
Albite, $Na(AlSi_3)O_8$	11.5	0.5	4	0.4	500	0.2	13.7	0.14	0.15	11.8	0.3
Anorthite, $Ca(Al_2Si_2)O_8$	6.9	1.0	4	0.4	500	0.25	13.2	0.14	0.25	12.0	0.25
Muscovite, $KAl_2(AlSi_3)O_{10}(OH)_2$	12.2	0.5	4	0.4	500	0.1	14.5	0.2	0.1	12.7	0.3
Apatite, $Ca_5(PO_4)_3OH$	10.8	0.7			300	0.4	13.8		0.2		

*Table 9.3. The coefficients (ki) for calculating approximate dissolution rates of silicate minerals in soils, used with Equation (2.2), are provided in units of mol/m2/s. They are given as pki * log ki for 8°C. The coefficients (Limi) are given in units of 10e6 (10^6). The Arrhenius factors required to recalculate pki to other temperatures can be found in Table 2.3. Specifically, kCO2 is equal to 10^13 mol/m2/s, korg is equal to 10^12 mol/m2/s, and Limorg is approximately 5 * 10^6.*

$$pk_{i,T} = -\log k_{i,T} = pk_{i,271} + \frac{E_a}{2.303\,R}\left[\frac{1}{T} - \frac{1}{271}\right]$$

	pk_H	pk_{H2O}	pk_{OH}	pk_{CO2}	pk_{org}
$E_a / (2.303\,R)$	3500	2000	2500	2000	3000

Table 9.4. Temperature factors (Ea / (2.303R) in the Arrhenius equation for calculating silicate weathering rates ki at another temperature (T K) than 8°C (271 K)

9.2. Template Model and Explanation:

```
                        # Database set to phreeqc.dat during input
SOLUTION 1              # Define solution code block
temp 10                 # Temp of 10C
pH 4    charge          # pH value of 4; adjusted to charge balance
Cl 0.1                  # Cl conc in mMol/kgw


EQUILIBRIUM_PHASES 1    # Define Eq_phase code block; defined in database file
Gibbsite 0 0            # Gibbsite ppt when supersaturated; Target SI and Amount
# CO2(g) -2.5           # pCO2


KINETICS 1              # Define Kinetic silmulation code block
K-feldspar              # Call defined phase in database file
        -m0 2.16                    # 10% K-fsp, mol/L pore water
        -parms 2.26 0.162           # A0 in m2, V in L
        -steps 4.7e7 in 40          # 1.5 years in seconds; 40 steps
INCREMENTAL_REACTIONS true          # t0->t1 ---> t1->t2 ... ; less cpu usage


RATES                               # Define rate of dissolution
        K-feldspar                  # Call defined phase in database file
        -start                      # start kinetic simulation
                                    # specific rates from Table 8.7 in mol/m2/s
        # parm(1) = A in m2, parm(2) = V in L (recalc's sp. rate to mol/kgw)
        1 A0 = parm(1); 2 V = parm(2)
        # find activities of inhibiting ions from output file
        3 a_Al = act("Al+3")
        4 BC = act("Na+") + act("K+") + act("Mg+2") + act("Ca+2")
        # temp corrected with the Arrhenius eqn
        # the difference in temperature, 271 for 8C, TK gives soln. temp in Kelvin
        10 dif_T = 1/TK - 1/271



    # rate by H+...
        20 pk_H = 11.7 + 3500 * dif_T
        22 rate_H = 10^-pk_H * act("H+")^0.5 / ((1 + a_Al / 4e-6)^0.4 * (1 + BC / 5e-
4)^0.15)
        # rate by hydrolysis...
        30 pk_w = 14.5 + 2000 * dif_T
        32 rate_w = 10^-pk_w / ((1 + a_Al / 4e-6)^0.14 * (1 + BC / 5e-4)^0.15)
        # rate by OH-; fOH- = 1
        40 pk_OH = 13.1 + 2500 * dif_T
        42 rate_OH = 10^-pk_OH
        # rate by CO2; fCO2 = 1
        50 pk_CO2 = 13.0 + 2000 * dif_T
        52 rate_CO2 = 10^-pk_CO2 * (10^SI("CO2(g)"))^0.6
        # Sum the rate contributions
        #General rate eqn for sillicate mineral dissolution
        60 rate = rate_H + rate_w + rate_OH + rate_CO2
        # normalize to mol/kgw, correct for m/m0 and the approach to equilibrium
        # consider rate by saturation state and A0, V; SR = IAP/K
        #Value fetched from output file; Rimstidt and Barnes (1980)
        70 rate = rate * A0 / V * (m/m0)^0.67 * (1 - SR("K-feldspar"))
        # integrate...
        80 moles = rate * time
        90 save moles
        -end            # end rate calculation


    USER_GRAPH                  # Define graph to output
        -head year Si           # Define axis values
        -axis_titles Years "mmol Si/L"      # Define axis titles
        -start              # Start fetching values from output file
        10 graph_x Total_time / (365 * 24 * 3600)   # Time in years
        # Total Si = [H4SiO4] as it is the dissolved phase; in mmol
        20 graph_y tot("Si") * 1e3
        -end                                        # end graphing
    END                                             # end simulation
```

Each line of code can be explained as follows:

1. The code is using the "phreeqc.dat" database for input.
2. The initial solution is defined in a code block labeled SOLUTION 1. It has a temperature of 10°C and a pH of 4, adjusted for charge balance. The concentration of chloride (Cl) in the solution is set to 0.1 mMol/kgw.
3. The code includes an EQUILIBRIUM_PHASES code block, where Gibbsite is introduced as a phase. The starting solution is considered to be supersaturated with respect to Gibbsite (0 0).
4. The code defines a kinetic simulation using the KINETICS 1 code block.
5. The kinetic phase considered is K-feldspar, which is called from the database. The initial moles of K-feldspar (m0) are set to 2.16 mol/L of pore water.
6. Parameters A0 and V are defined as 2.26 m2 and 0.162 L, respectively.
7. The simulation is set to run for 1.5 years (4.7e7 seconds) with 40 steps. Incremental reactions are enabled to optimize CPU usage.
8. The rate of dissolution is calculated using the RATES code block.
9. The specific rates for K-feldspar dissolution are calculated based on various factors, such as the activities of inhibiting ions (Al+3) and base cations (Na+, K+, Mg2+, Ca2+).
10. Temperature corrections are made using the Arrhenius equation from Table 2.3.
11. The rate of dissolution is calculated separately for H+ (protons), hydrolysis, OH- (hydroxide), and CO2, considering their specific factors (fH, fOH, fCO2).
12. The individual rate contributions are summed up to obtain the general rate equation for silicate mineral dissolution, based on Sverdrup and Warfvinge (1995).
13. The rate is normalized to mol/kgw, considering factors such as m/m0 (ratio of initial to current moles) and the approach to equilibrium. The saturation state (SR) for K-feldspar is also considered.
14. The rate is integrated over time to calculate the moles of dissolved K-feldspar.
15. The calculated moles are saved for further analysis.
16. The user graph code block is used to create a graph to output the results.
17. The graph displays the total time in years and the Si concentration in mmol/L.
18. The graph fetches the relevant data from the output file and plots the results.
19. The simulation is concluded with the END keyword.
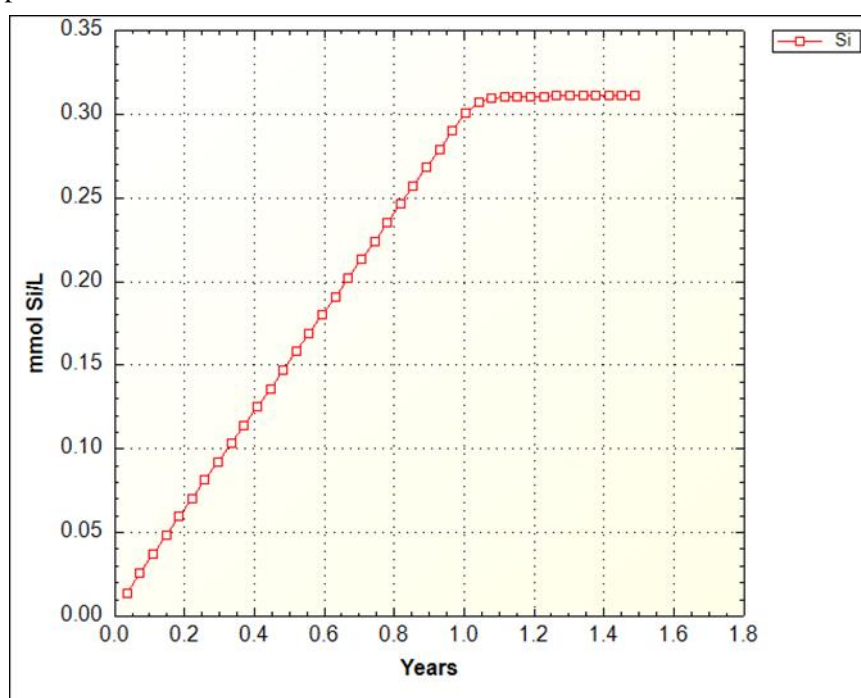
The graph output of the model is as follows:

Fig.9.2. Graph output of template model

9.3.   Modifications in Database File and Debugging:

There is no kinetics model specified for Apatite(Hydroxyapatite) in the database file, Thus, a kinetics model is introduced into a new database file named *"phreeqc_ar.dat"*. It is a modification of the phreeqc.dat database which is the most accurate and updated database used by PHREEQC. The modification was done as follows:

Kinetics Model:
```
###########
#Hydroxyapatite
###########
#
# Sverdrup and Warfvinge, 1995, Estimating field weathering rates
# using laboratory kinetics: Reviews in mineralogy and geochemistry,
# vol. 31, p. 485-541.
#
# As described in:
# Appelo and Postma, 2005, Geochemistry, groundwater
# and pollution, 2nd Edition: A.A. Balkema Publishers,
# p. 162-163 and 395-399.
#
# Assume soil is 10% Hydroxyapatite by mass in 1 mm spheres (radius 0.05 mm)
# Assume density of rock and Hydroxyapatite is 3190 kg/m^3 = 3.19 kg/L
# GFW Kspar 0.504 kg/mol
#
# Moles of Hydroxyapatite per liter pore space calculation:
#   Mass of rock per liter pore space = 0.7*3.19/0.3      = 7.44    kg rock/L pore space
#   Mass of Hydroxyapatite per liter pore space 7.44x0.1        = 0.744    kg Kspar/L
pore space
#   Moles of Hydroxyapatite per liter pore space 0.744/0.504      = 14.76     mol Kspar/L
pore space
#
# Specific area calculation:
#   Volume of sphere 4/3 x pi x r^3                = 5.24e-13 m^3
Hydroxyapatite/sphere
#   Mass of sphere 3190 x 5.24e-13                = 1.67e-09  kg
Hydroxyapatite/sphere
#   Moles of Hydroxyapatite in sphere 1.67e-09/0.504           = 3.31e-09  mol
Hydroxyapatite/sphere
#   Surface area of one sphere 4 x pi x r^2          = 3.14e-8  m^2/sphere
#   Specific area of Hydroxyapatite in sphere 3.14e-8/3.31e-09 = 9.48 m^2/mol
Hydroxyapatite
#
#
# Example of KINETICS data block for Hydroxyapatite rate:
#       KINETICS 1
#       Hydroxyapatite
#              -m0 2.18          # 10% Hydroxyapatite, 0.1 mm cubes
#              -m  2.18          # Moles per L pore space
#              -parms 6.41  0.1   # m^2/mol Hydroxyapatite, fraction adjusts lab rate to
field rate
#              -time 1.5 year in 40
```

The new database file was then used for carrying out the simulations. This resulted in proper convergence of model which was not achieved prior to this debugging.

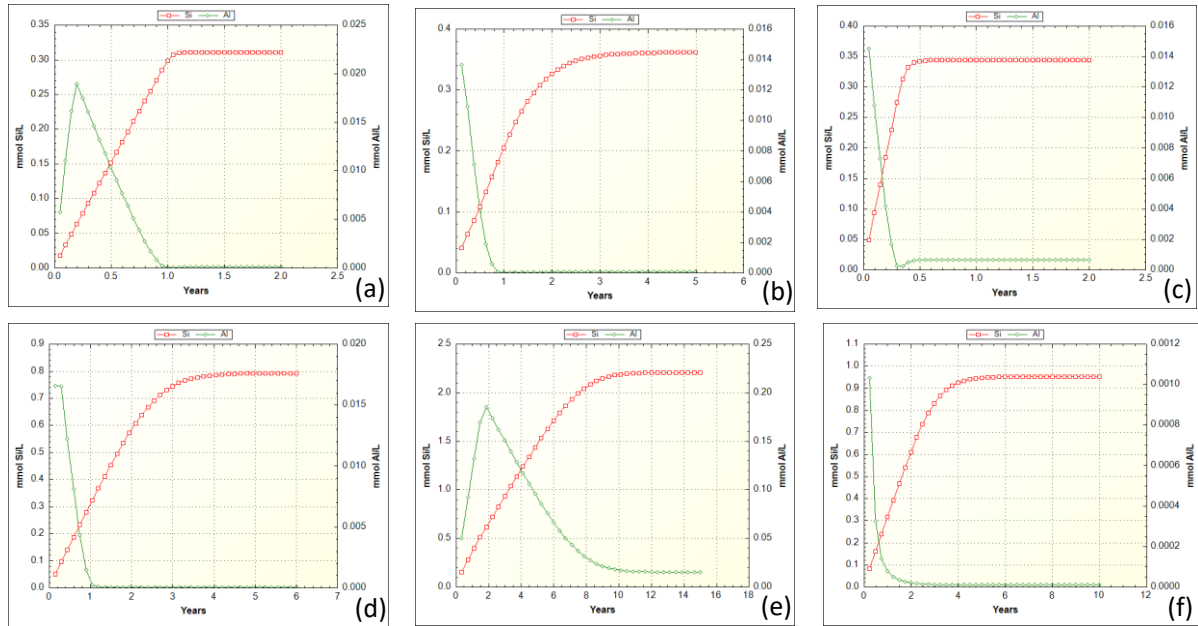# 10. Analysis and Interpretation of Research Project:

Fig.2.3. PHREEQC calculation of K-feldspar dissolution kinetics using Equation (2.2). The conditions are varied as follows: (a) Equilibrium for gibbsite imposed, initial pH of 4 and 10°C. (b) as case (a) but with equilibrium for kaolinite, (c) as case (a) but using a temperature of 25°C, (d) as case (a) but with pCO2 of 10^-2.5 imposed, (e) as case (a) but with 0.8 Cl (f) as case (a) but with 1C

(a) Equilibrium for Gibbsite: K-feldspar dissolved until reaching equilibrium, with some saturation. Al3+ and OH- ions were removed due to gibbsite precipitation.

(b) Equilibrium for Kaolinite: With gibbsite removed, less than half of K-feldspar dissolved to reach saturation. Al3+ and OH- ions remained in solution.

(c) Increased Temperature: At 25°C, K-feldspar dissolution rate more than doubled, indicating the significant temperature impact on weathering rates and higher K-feldspar solubility.

(d) pCO2 of 10^-2.5: Introducing pCO2 increased K-feldspar dissolution rate slightly and facilitated the formation of HCO3- ions, allowing for more extensive dissolution before saturation.

(e) 0.8 Cl Concentration:
In this scenario (case e), the Cl- concentration was set at 0.8. This reduced the dissolution rate but largely increased dissolution before reaching equilibrium.

(f) 1C (No description provided):
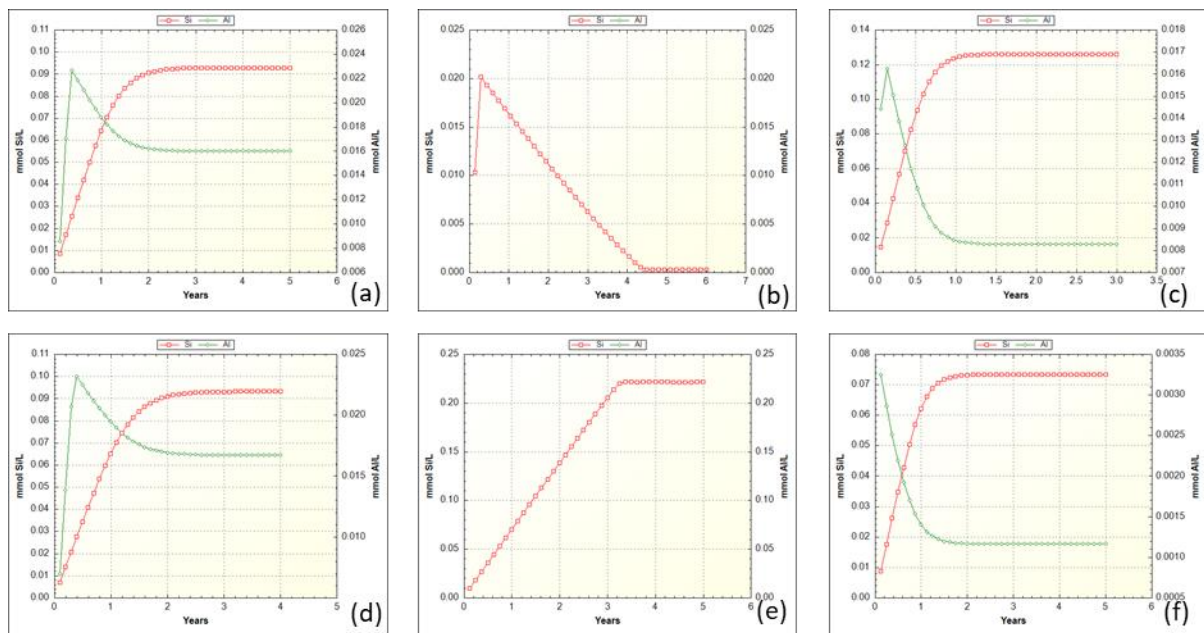*Lastly, case (f) involved a parameter labeled as 0.1C. Effect similar to (case e).*

Fig.10.1. *PHREEQC calculation of Muscovite dissolution kinetics using Equation (2.2). The conditions are varied as follows: (a) Equilibrium for gibbsite imposed, initial pH of 4 and 10°C. (b) as case (a) but with equilibrium for kaolinite, (c) as case (a) but using a temperature of 25°C, (d) as case (a) but with pCO2 of 10^-2.5 imposed, (e) as case (a) but with 0.8 Cl (f) as case (a) but with 1C*

(a) Equilibrium for Gibbsite Imposed, Initial pH of 4, and 10°C:
In the initial scenario (case a) for muscovite, the equilibrium constraint for gibbsite was imposed. Consequently, muscovite dissolution proceeded towards equilibrium, and some fraction dissolved until reaching saturation. The presence of gibbsite led to the removal of nearly all Si produced during the dissolution, resulting in no Si remaining in the solution at equilibrium.

(b) Equilibrium for Kaolinite Imposed:
In this scenario (case b), the equilibrium constraint was switched to kaolinite for muscovite dissolution. Similar to K-feldspar, muscovite also experienced a different outcome. With gibbsite removed from the system, less than half of the muscovite dissolved to reach equilibrium. Unlike K-feldspar, muscovite did not produce any Si in solution at equilibrium due to the presence of kaolinite, which took away all the Si.

(c) Temperature Increased to 25°C:
Increasing the temperature from 10 to 25°C (case c) resulted in a significant increase in the dissolution rate of muscovite, similar to K-feldspar. However, unlike K-feldspar, muscovite dissolution was not influenced by pCO2.

(d) pCO2 of 10^-2.5 Imposed:
In contrast to the effect observed on K-feldspar, imposing a pCO2 of 10^-2.5 atm (case d) did not significantly affect the dissolution rate of muscovite.

(e) 0.8 Cl Concentration:
In this scenario (case e), setting the Cl- concentration to 0.8 resulted in no change in the dissolution rate of muscovite. However, it caused a much larger dissolution of muscovite compared to K-feldspar.

(f) C 1 (HCO3- Concentration):
Lastly, when the parameter C was set to 1 (case f), the dissolution rate of muscovite increased significantly, similar to K-feldspar. However, this increase in the dissolution rate was accompanied by a lesser amount of muscovite dissolution at equilibrium.
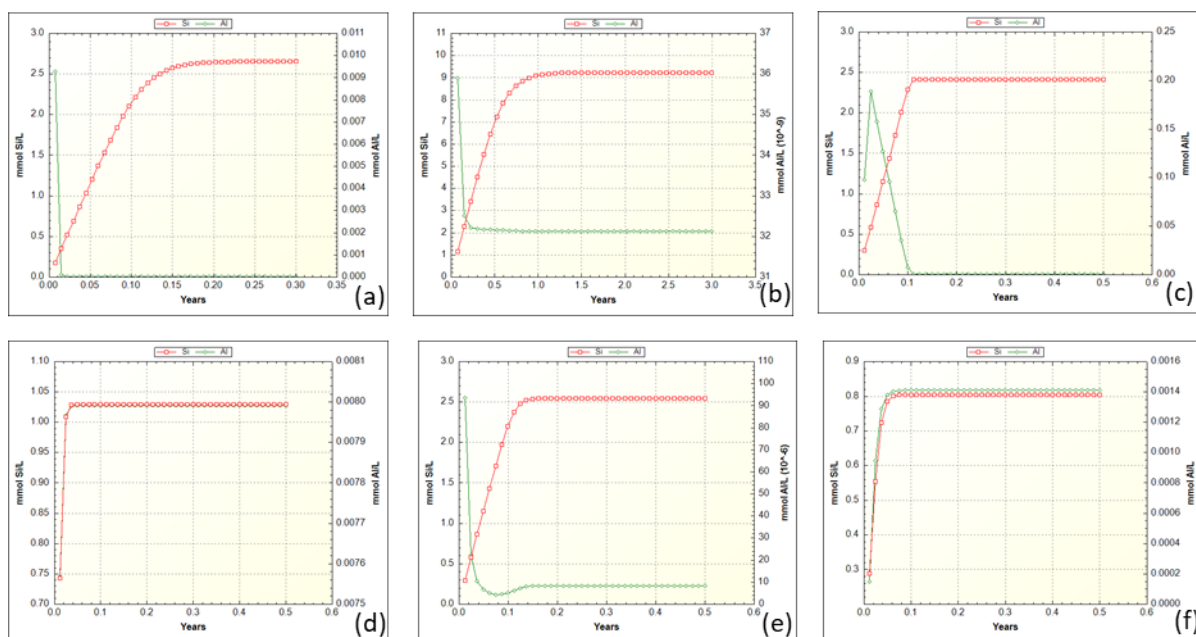
Fig.10.2. *PHREEQC Calculation of Albite Dissolution Kinetics using Equation (2.2). The conditions are varied as follows: (a) Equilibrium for gibbsite imposed, initial pH of 4 and 10°C. (b) as case (a) but with equilibrium for kaolinite, (c) as case (a) but using a temperature of 25°C, (d) as case (a) but with pCO2 of 10^-2.5 imposed, (e) as case (a) but with 0.8 Cl, (f) as case (a) but with 1C.*

(a) Equilibrium for Gibbsite Imposed, Initial pH of 4, and 10°C:
In the starting scenario (case a), the equilibrium constraint for gibbsite was imposed for albite dissolution. The results showed that albite proceeded to reach equilibrium, with some fraction dissolving to saturation. Similar to K-feldspar, the presence of gibbsite caused the removal of Al3+ and OH- ions from solution due to precipitation.

(b) Equilibrium for Kaolinite Imposed: In case (b) with kaolinite as the equilibrium constraint, the dissolution rate of albite significantly increased, more than doubling the amount dissolved compared to the initial scenario. Kaolinite had a remarkable impact on enhancing albite dissolution kinetics, with Al3+ and OH- ions remaining in solution and contributing to the accelerated dissolution rate.

(c) Temperature Increased to 25°C:
Case (c) involved raising the temperature from 10 to 25°C for albite dissolution. As observed with K-feldspar, the dissolution rate of albite also significantly increased, more than doubling the rate observed at the lower temperature. This emphasizes the considerable influence of temperature on weathering rates, resulting in higher solubility of albite.

(d) pCO2 of 10^-2.5 Imposed:
For case (d), a partial pressure of CO2 (pCO2) of 10^-2.5 atm was introduced for albite dissolution. Similar to the effect observed for K-feldspar, the presence of pCO2 considerably increased the dissolution rate of albite. However, due to this increase in dissolution rate, less albite was dissolved before reaching equilibrium.

(e) 0.8 Cl Concentration:
In this scenario (case e), the Cl- concentration was set at 0.8 for albite dissolution. The result indicated that the presence of Cl- slightly increased the dissolution rate of albite, leading to a moderately higher dissolution rate compared to the initial scenario.

(f) 1 HCO3- Concentration:
In case (f) with C = 1, the dissolution rate of albite was greatly increased, leading to a faster attainment of equilibrium compared to the initial scenario. It had a significant effect on enhancing the dissolution kinetics of albite, resulting in a more rapid dissolution process.
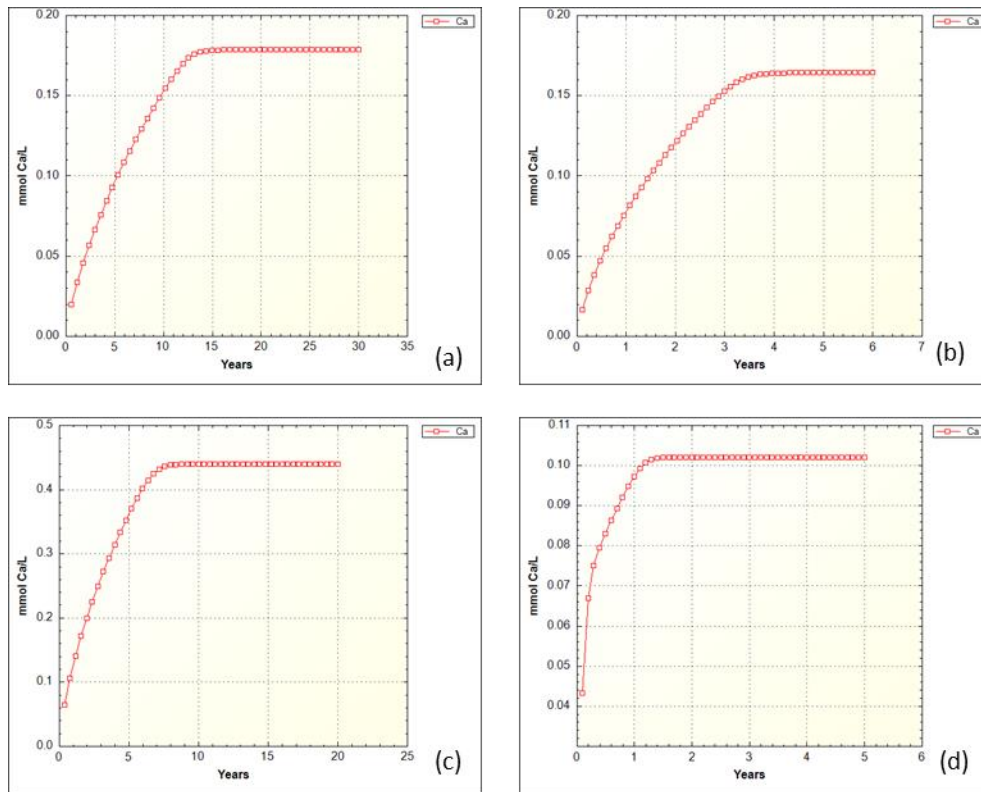
Fig.10.3. *PHREEQC Calculation of Apatite Dissolution Kinetics using Equation (2.2). The conditions are varied as follows: (a) Equilibrium for calcite imposed, initial pH of 4 and 10°C. (b) as case (a) but with 25°C, (c) as case (a) but using C(4) 0.2, (d) as case (a) but with Cl 0.1 and temperature of 25°C.*

(a) Equilibrium for Calcite Imposed, Initial pH of 4, and 10°C:
In the initial scenario (case a), the system is constrained with the equilibrium of calcite. Apatite dissolution occurs at a slow rate due to the specified conditions. The dissolution proceeds until equilibrium is reached, with a relatively small amount of apatite dissolved.

(b) Temperature Increased to 25°C:
For case (b), the temperature is elevated from 10 to 25°C. As expected, the dissolution rate of apatite significantly increases under these conditions. However, it is worth noting that while the rate rises, the overall amount of apatite dissolved is slightly reduced compared to the lower temperature.

(c) C(4) Concentration Set to 0.2:
In this scenario (case c), the concentration of C(4), which is a specific parameter, is set to 0.2. As a result, the dissolution rate of apatite experiences a considerable increase, and a larger amount of apatite dissolves compared to case (a).

(d) Cl Concentration at 0.1 and Temperature of 25°C:
Lastly, case (d) involves setting the Cl concentration to 0.1 and maintaining a temperature of 25°C. These conditions lead to a sharp increase in the dissolution rate of apatite. However, contrary to case (b), the amount of apatite dissolved is reduced under these conditions.
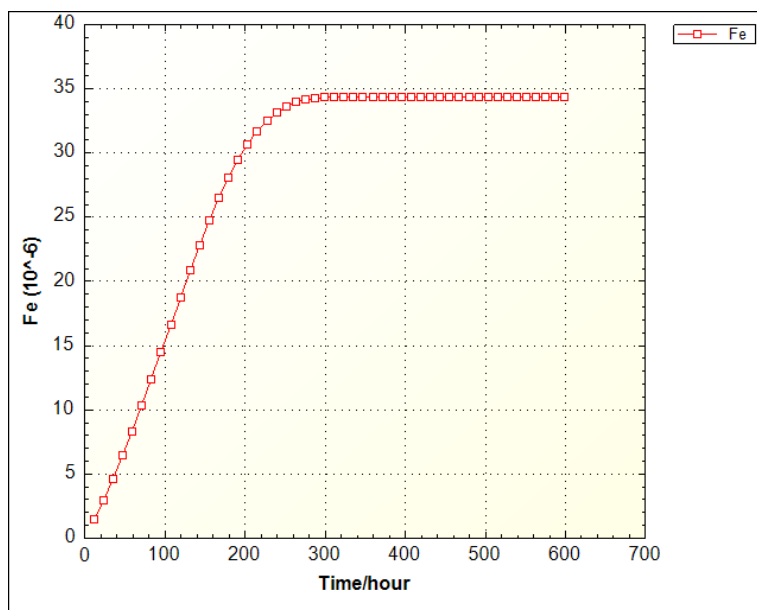
Fig.10.5.(a) PHREEQC Calculation of Pyrite Dissolution Kinetics. The conditions are: Equilibrium for Goethite imposed, initial pH of 4 and 25°C. Dissolution of pyrite is much faster as compared to other minerals. It also dissolves in much more in acidic medium. Equilibrium is also attained at a much faster rate than other minerals.
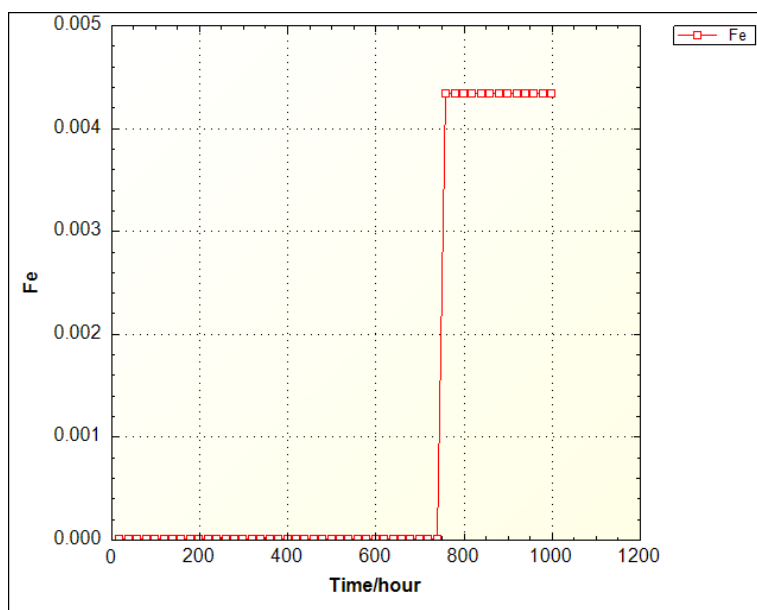

Fig.10.5.(b) PHREEQC Calculation of Pyrite Dissolution Kinetics. The conditions are: Equilibrium for Goethite imposed, initial pH of 7 and 15°C. Amount of Fe in the solution is minimal. At around 750 hours, the amount dissolved suddenly reaches 0.004mmol and attains equilibrium. This states that the dissolution kinetics of Pyrite is unlike other sillicate minerals.
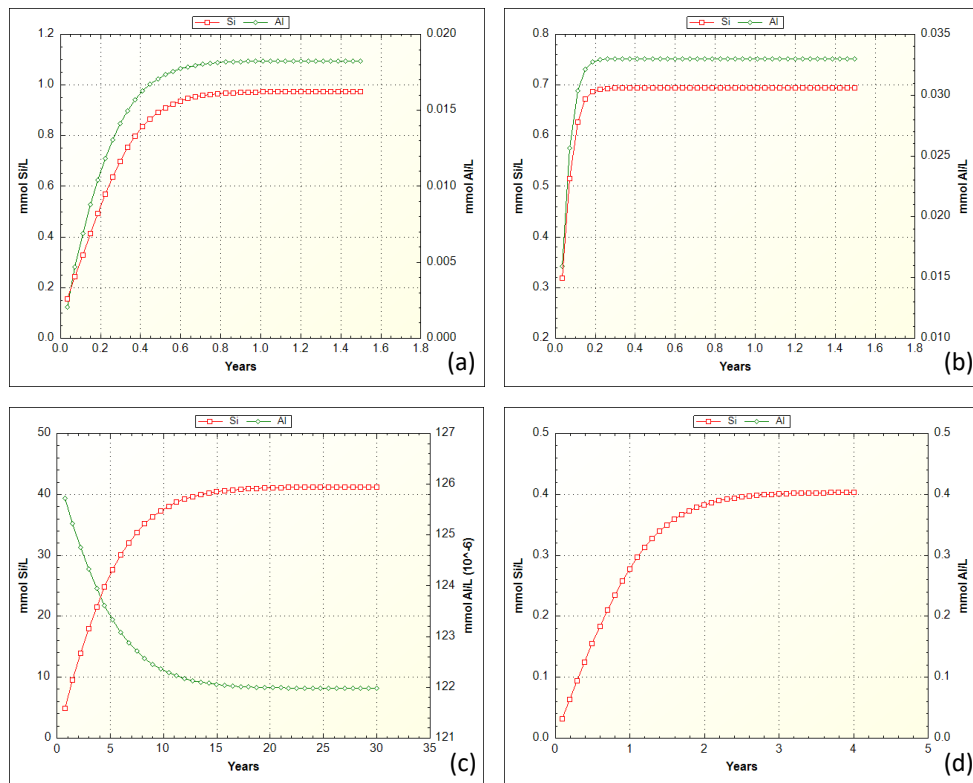
Fig.10.6. *PHREEQC Calculation of Anorthite Dissolution Kinetics using Equation (2.2). The conditions are varied as follows: (a) Equilibrium for Gibbsite and calcite imposed, initial pH of 4 and 10°C. (b) as case (a) but with temperature of 25°C, (c) as case (a) but using C(4) 1 and temperature of 25°C, (d) as case (a) but with equilibrium for kaolinite.*

(a) Equilibrium for Gibbsite and Calcite Imposed, Initial pH of 4, and 10•C:

In the initial scenario (case a), the equilibrium constraint for both gibbsite and calcite was imposed. As a result, the dissolution of Anorthite proceeded towards equilibrium, with a fraction dissolving to saturation. Similar to the K-feldspar case, both Al3+ and OH- ions were removed from solution due to the presence of gibbsite precipitation. Additionally, the co-presence of calcite could have further impacted the dissolution process.

(b) Temperature Increased to 25•C:

For case (b), the temperature was increased from 10 to 25°C. This change significantly increased the dissolution rate of Anorthite, similar to the K-feldspar results. However, interestingly, the total amount of Anorthite dissolved slightly decreased compared to the lower temperature scenario. This indicates that while the rate of dissolution is enhanced, some other factors might be influencing the total dissolved amount.

(c) C(4) Set to 1 and Temperature Increased to 25•C:

In this scenario (case c), a parameter labeled C(4) was set to 1, and the temperature was increased to 25°C. As a result, the dissolution rate of Anorthite was largely increased, and the total dissolved amount also substantially increased compared to the initial case (a). This suggests that the parameter C(4) plays a significant role in governing the dissolution kinetics.

(d) Equilibrium for Kaolinite Imposed:

For case (d), the equilibrium constraint was switched to kaolinite, similar to the K-feldspar study. The presence of kaolinite as an equilibrium phase reduced the dissolution rate of Anorthite, and consequently, the total amount of Anorthite dissolved was also reduced compared to the initial case (a). This further emphasizes the impact of different equilibrium phases on the dissolution kinetics.

11. Conclusion & Suggestion of Research Project

In conclusion, numerical modeling has emerged as the state-of-the-art methodology in geochemical studies, offering unparalleled precision and insight into complex geological processes. Among these, the dissolution of silicate minerals is often highlighted as a critical process, given the significant role of silicate minerals in Earth's crust and their impact on various geological and environmental phenomena.

Understanding silicate mineral dissolution is paramount for a wide range of applications, from assessing groundwater quality to predicting the consequences of mining activities and comprehending landscape evolution over geological time scales. An indispensable tool of choice for this study is PHREEQC, a versatile and robust geochemical modeling software developed by USGS. PHREEQC's ability to simulate complex chemical reactions, account for kinetic and equilibrium reactions, and integrate various environmental factors makes it an invaluable resource for unraveling the complexities of silicate mineral dissolution and its broader geological implications.

Future research avenues in this field could explore the integration of machine learning and artificial intelligence algorithms to enhance the predictive power of geochemical models. Additionally, investigating the influence of climate change on silicate mineral dissolution and its implications for water resources and ecosystems is an emerging area of study.

12. Result(s) Achieved:

The general results observed after modelling the kinetic dissolution of silicate minerals are as follows:

- **pH Dependency:** The concentration of aluminum under natural conditions is strongly pH dependent. This implies that pH plays a crucial role in controlling the dissolution rate. Higher or lower pH levels may lead to varying rates of mineral dissolution based on the geochemistry of the mineral.

- **Effect of Temperature:** Higher temperatures generally lead to an increase in the dissolution rate of minerals. Elevated temperatures provide more thermal energy to the system, which enhances the mobility of reacting species and increases their collision frequency at the mineral surface. As a result, the dissolution reaction proceeds more rapidly at higher temperatures.

- **Role of Base Cations:** The presence of free base cations in solution can slow down the silicate dissolution. Base cations, such as sodium, potassium, calcium and magnesium, may compete with the mineral surface for protons, affecting dissolution kinetics.

- **Influence of Dissolved Aluminum:** Low concentrations of dissolved aluminum inhibit the dissolution rate of al containing minerals. This suggests that the presence of certain dissolved ions can act as inhibitors, impacting the overall dissolution kinetics of minerals.

- **Effect of CO2:** High levels of CO_2 can accelerate the dissolution rate of silicate minerals. CO_2 acts as a provider of protons, contributing to the dissolution process. Moreover, the carbonate ion can directly accelerate silicate weathering, particularly in the near neutral and basic pH range.

- **Organic Radicals:** High content of free organic acid radicals can also accelerate the dissolution rate. These radicals may enhance the proton supply and promote the dissolution of minerals.

- **Numerical Coefficients:** Coefficients obtained from studies like Sverdrup and Warfvinge (1995) and Sverdrup (1990) are used to calculate approximate dissolution rates. These coefficients are essential for accurately modeling the dissolution kinetics of specific minerals and changes in them will affect sensitive analysis.

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14. Declaration by Scholar:

I _____ **Aditya Ray** _____ (Full name) hereby declare that the details/facts mentioned above are true to the best of my knowledge and I solely be held responsible in case of any discrepancies found in the details mentioned above.

Aditya Ray

(Signature of Scholar)

Date: 04.09.2023

Place: Kolkata