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GROUNDWATER IN HARD-ROCK AQUIFERS IN SOUTH INDIA USING INVERSE MODELING.

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Introduction.

- The study focuses on the water quality issues in Nalgonda district in India.
- Particularly fluoride contamination and salinity problems in this region's hard-rock aquifers.
- This area is highly vulnerable to fluoride and salinity issues due to various geochemical processes.

Fluoride contamination and Salinity

- The dissolution of fluoride minerals like fluorite and apatite increases fluoride concentrations, particularly under high pH and temperature conditions.
- The weathering of minerals such as silicates, carbonates, and evaporites releases salts and other ions, further enhancing salinity.
- These geochemical processes, combined with human activities like irrigation and fertilizer use, make the groundwater highly vulnerable to fluoride and salinity contamination, impacting water quality and public health.

Introduction Cont.

- Previous studies have identified factors influencing groundwater chemistry

- Few have focused on quantitative modeling.

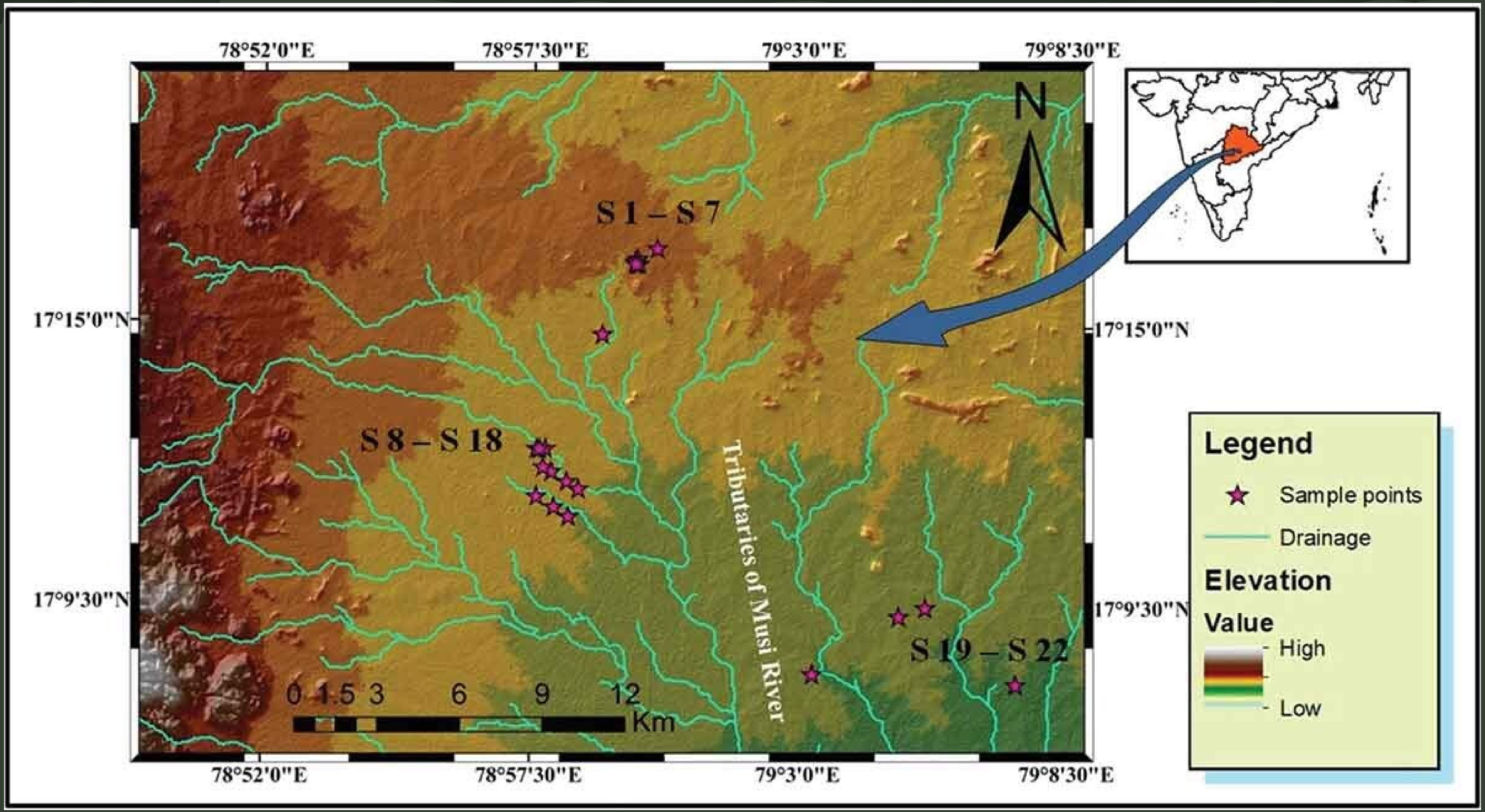
- This study adopts a quantitative approach using PHREEQC inverse modeling.

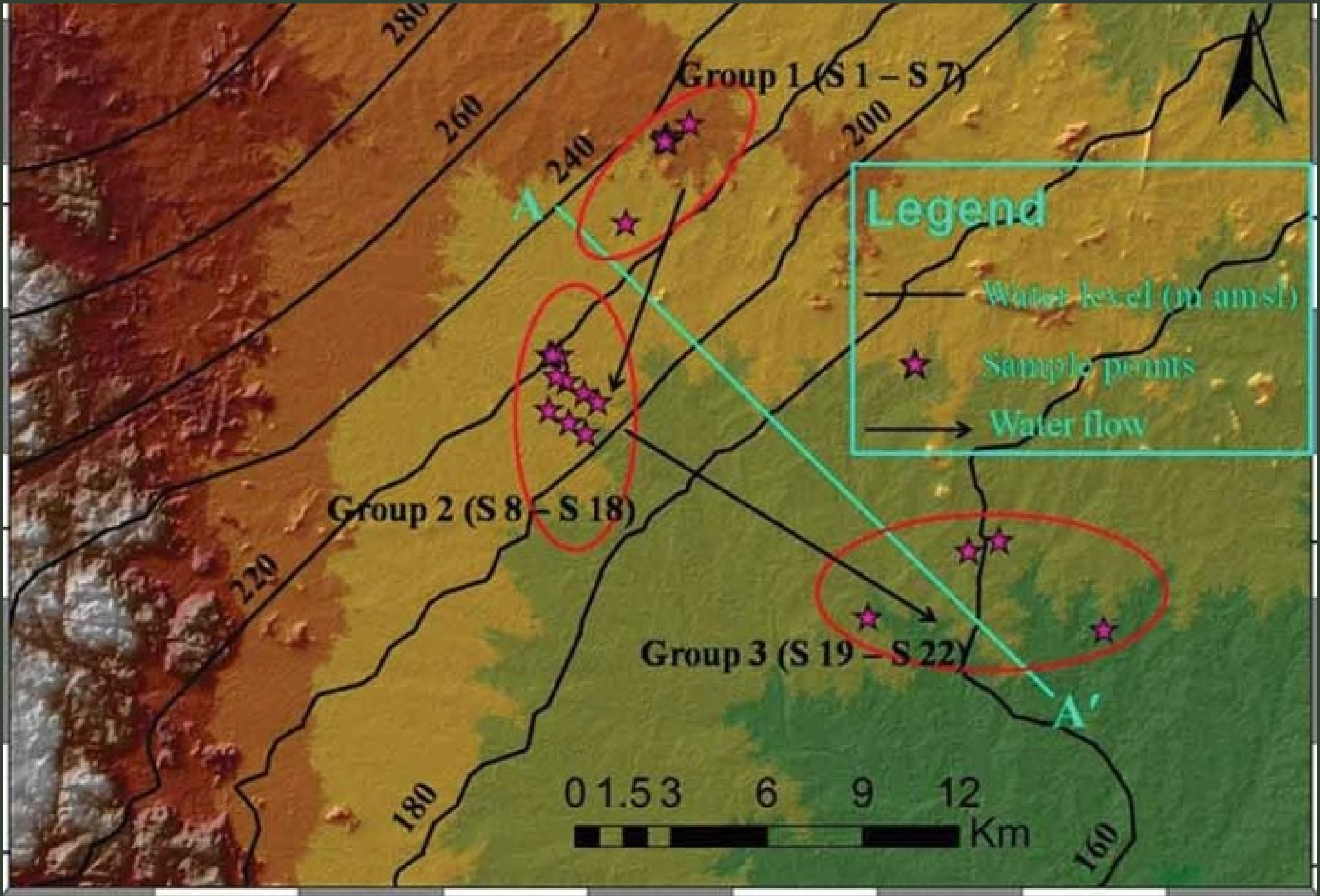
What is inverse modeling?

- **Inverse modeling** refers to a technique used to interpret and predict the geochemical processes that influence groundwater composition.
- It is employed to understand how the observed groundwater chemistry such as these ions relates to underlying geological processes, such as mineral dissolution, weathering, and water–rock interactions.
    - (e.g., concentrations of ions like Ca^{2+}, Na^{+}, F^{-}, SO_4^{2-}, etc.)

Study Area

- The study area is in Nalgonda district, Telangana, India.
- Region features:
  - Hard-rock terrain with dissected hills and valleys
  - Dendritic to sub dendritic drainage system formed by the River Musi
- The main soil types are red, black, alkaline, and alluvial.


78°52'0"E
78°57'30"E
79°3'0"E
79°8'30"E
17°15'0"N
17°9'30"N
N
S1 – S7
S8 – S18
S19 – S22
Tributaries of Musi River
0 1.5 3 6 9 12
Km
Legend
Sample points
Drainage
Elevation
Value
High
Low


280
260
240
220
200
180
160
Group 1 (S 1 – S 7)
Group 2 (S 8 – S 18)
Group 3 (S 19 – S 22)
A
A′
Legend
Water level (m amsl)
Sample points
Water flow
0 1.5 3 6 9 12
Km

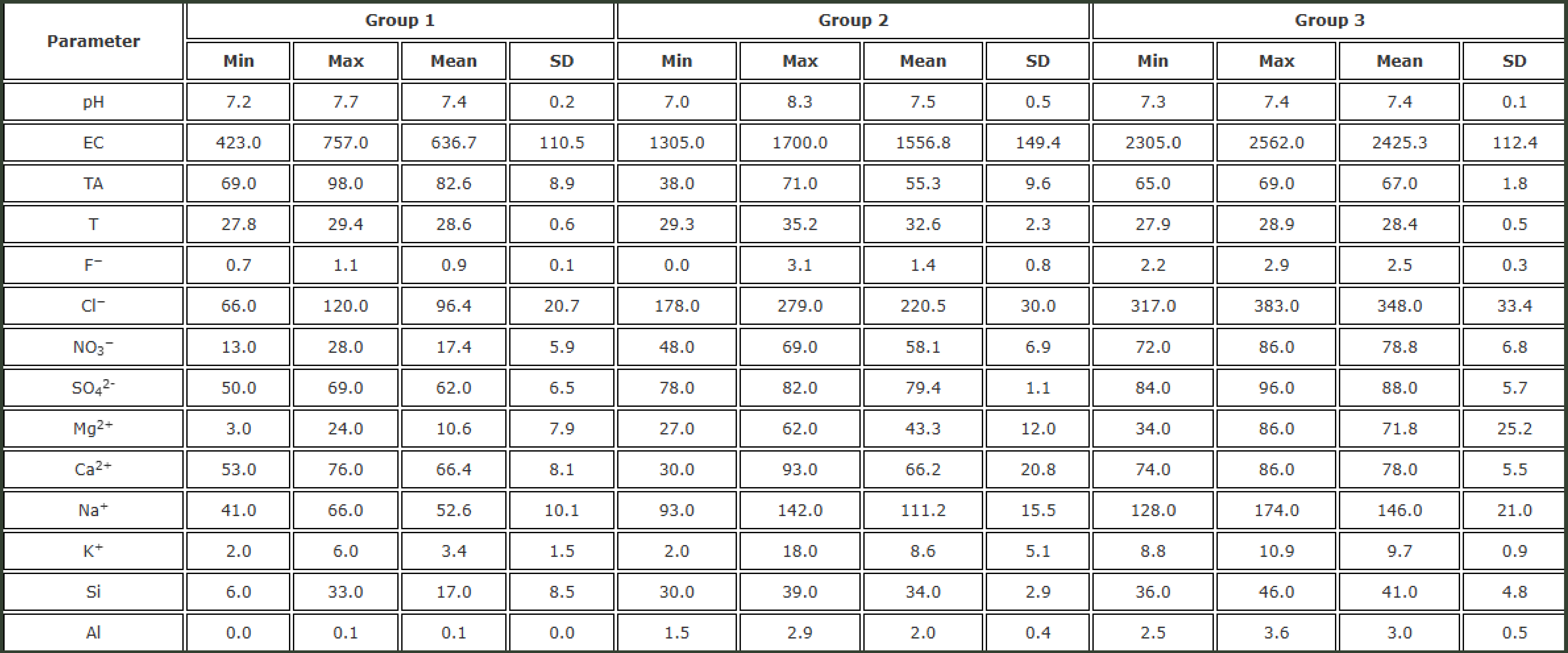
Geology of the study area.

- Predominantly composed of hard-rock formations
- Three main hydrogeological units are identified:
    - **Weathered Zone (up to 30 m):** Overexploited and largely dried out; dug wells are mostly defunct.
    - **Fractured Zone (30–196 m):** Found in granite/gneiss bedrock with quartz veins.
    - **Aquifuge (>200 m):** Massive granite/gneiss bedrock with negligible porosity, making it mostly impermeable.

Sampling and Measurement

- 22 groundwater samples were collected from bore wells and tube wells of varying depths.
- To ensure representative sampling, wells were pumped for 10–15 minutes before collection.
- Samples were filtered, stored in acid-washed polyethylene bottles, and acidified to pH 2 with ultrapure HNO_3 for cation and trace element analysis.
- Field measurements included pH, temperature, and electrical conductivity (EC), using a portable water quality kit.
- Alkalinity was measured by titration.
- Major ions were analyzed via ion chromatography, and trace elements (Si, Al) were measured using ICP-MS.
- Analytical accuracy was confirmed with ion balance errors within 10%.

Results from Source



Parameter	Group 1				Group 2				Group 3			
	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD
pH	7.2	7.7	7.4	0.2	7.0	8.3	7.5	0.5	7.3	7.4	7.4	0.1
EC	423.0	757.0	636.7	110.5	1305.0	1700.0	1556.8	149.4	2305.0	2562.0	2425.3	112.4
TA	69.0	98.0	82.6	8.9	38.0	71.0	55.3	9.6	65.0	69.0	67.0	1.8
T	27.8	29.4	28.6	0.6	29.3	35.2	32.6	2.3	27.9	28.9	28.4	0.5
F^-	0.7	1.1	0.9	0.1	0.0	3.1	1.4	0.8	2.2	2.9	2.5	0.3
Cl^-	66.0	120.0	96.4	20.7	178.0	279.0	220.5	30.0	317.0	383.0	348.0	33.4
NO_3^-	13.0	28.0	17.4	5.9	48.0	69.0	58.1	6.9	72.0	86.0	78.8	6.8
SO_4^{2-}	50.0	69.0	62.0	6.5	78.0	82.0	79.4	1.1	84.0	96.0	88.0	5.7
Mg^{2+}	3.0	24.0	10.6	7.9	27.0	62.0	43.3	12.0	34.0	86.0	71.8	25.2
Ca^{2+}	53.0	76.0	66.4	8.1	30.0	93.0	66.2	20.8	74.0	86.0	78.0	5.5
Na^+	41.0	66.0	52.6	10.1	93.0	142.0	111.2	15.5	128.0	174.0	146.0	21.0
K^+	2.0	6.0	3.4	1.5	2.0	18.0	8.6	5.1	8.8	10.9	9.7	0.9
Si	6.0	33.0	17.0	8.5	30.0	39.0	34.0	2.9	36.0	46.0	41.0	4.8
Al	0.0	0.1	0.1	0.0	1.5	2.9	2.0	0.4	2.5	3.6	3.0	0.5

Results from Samples.

- Mean Values were used for the input.
- High nitrate (NO_3^-) levels (45 mg/L) indicate pollution from anthropogenic sources like fertilizers and sewage.
- Calcium (Ca^{2+}) and magnesium (Mg^{2+}) originate from the dissolution of limestone and dolomite, while elevated sodium (Na^+) and potassium (K^+) levels are attributed to silicate weathering and evaporite dissolution.
- The lower concentration of K^+ compared to Na^+ is due to the higher resistance and lower solubility of K-silicates.
- Silicate weathering in alkaline conditions also increases aluminum (Al) and silicon (Si) in groundwater, with Si existing as quartz, chalcedony, or amorphous SiO_2.

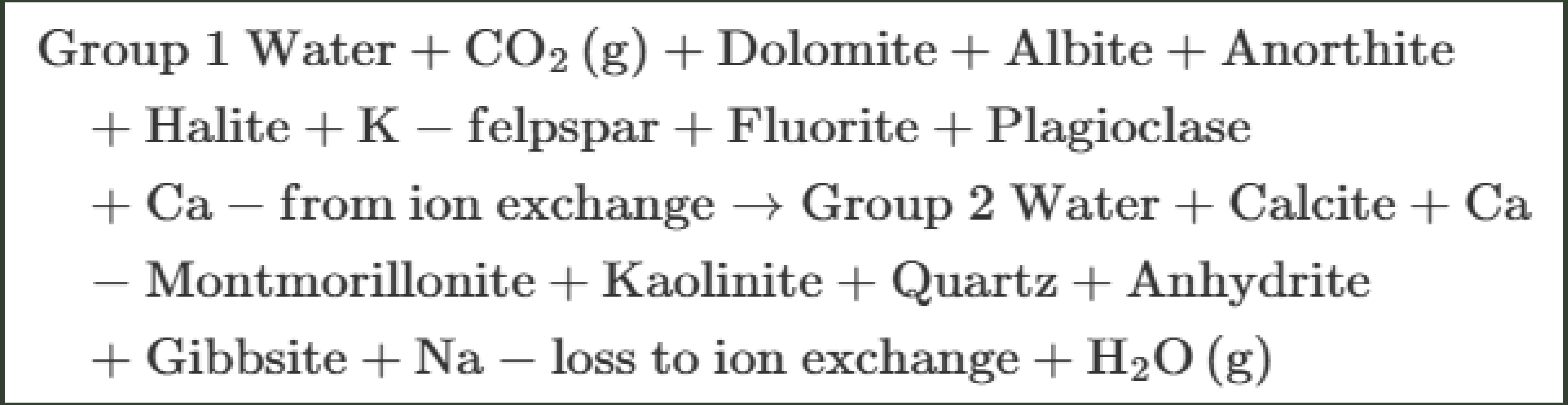
Results from Samples.

- High sulfate (SO_4^{2-}) levels result from gypsum and anhydrite dissolution and sulfide oxidation.
- Bicarbonate (HCO_3^-), the second most dominant anion, contributes to groundwater alkalinity, with total alkalinity ranging from 15 to 98 mg/L
- Sources of HCO_3^- include atmospheric CO_2 dissolution, silicate weathering, and carbonate mineral dissolution.

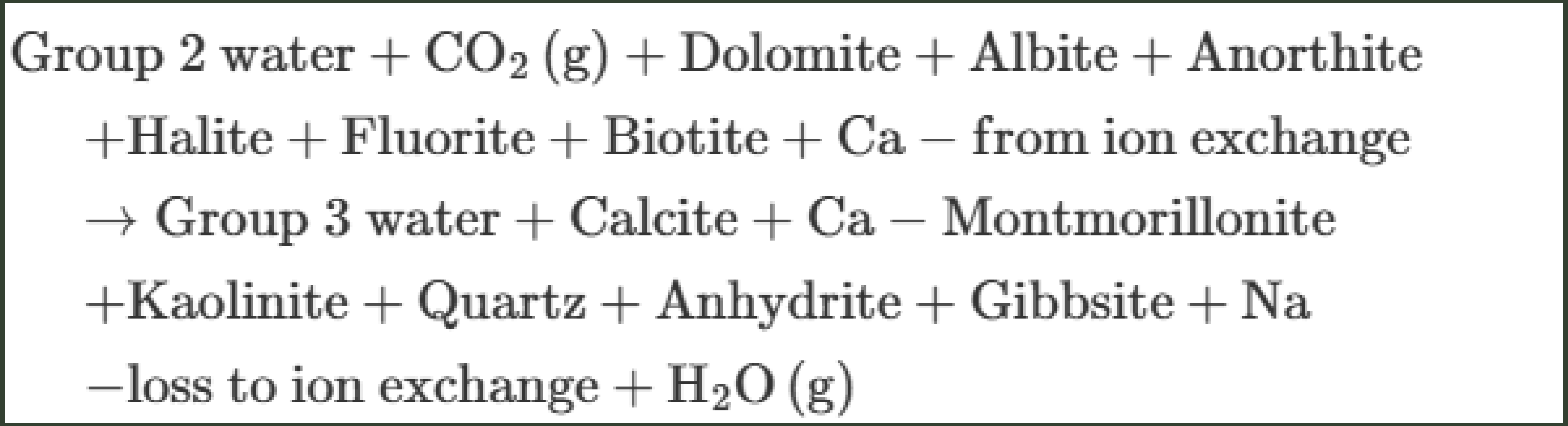
Results from inverse modeling.

- The study involved simulating the geochemical evolution of groundwater along a flow path using PHREEQC.
- Based on chemical analysis, initial and final solution compositions were derived, with the simulations examining transitions between three groups.
- The identified minerals either dissolve or precipitate based on their saturation index values.

Inverse Modeling Flow Paths



$$\begin{aligned}&\text{Group 1 Water} + \mathrm{CO_2}\,(\mathrm{g}) + \text{Dolomite} + \text{Albite} + \text{Anorthite}\\&\quad + \text{Halite} + \text{K} - \text{felpspar} + \text{Fluorite} + \text{Plagioclase}\\&\quad + \text{Ca} - \text{from ion exchange} \rightarrow \text{Group 2 Water} + \text{Calcite} + \text{Ca}\\&\quad - \text{Montmorillonite} + \text{Kaolinite} + \text{Quartz} + \text{Anhydrite}\\&\quad + \text{Gibbsite} + \text{Na} - \text{loss to ion exchange} + \mathrm{H_2O}\,(\mathrm{g})\end{aligned}$$



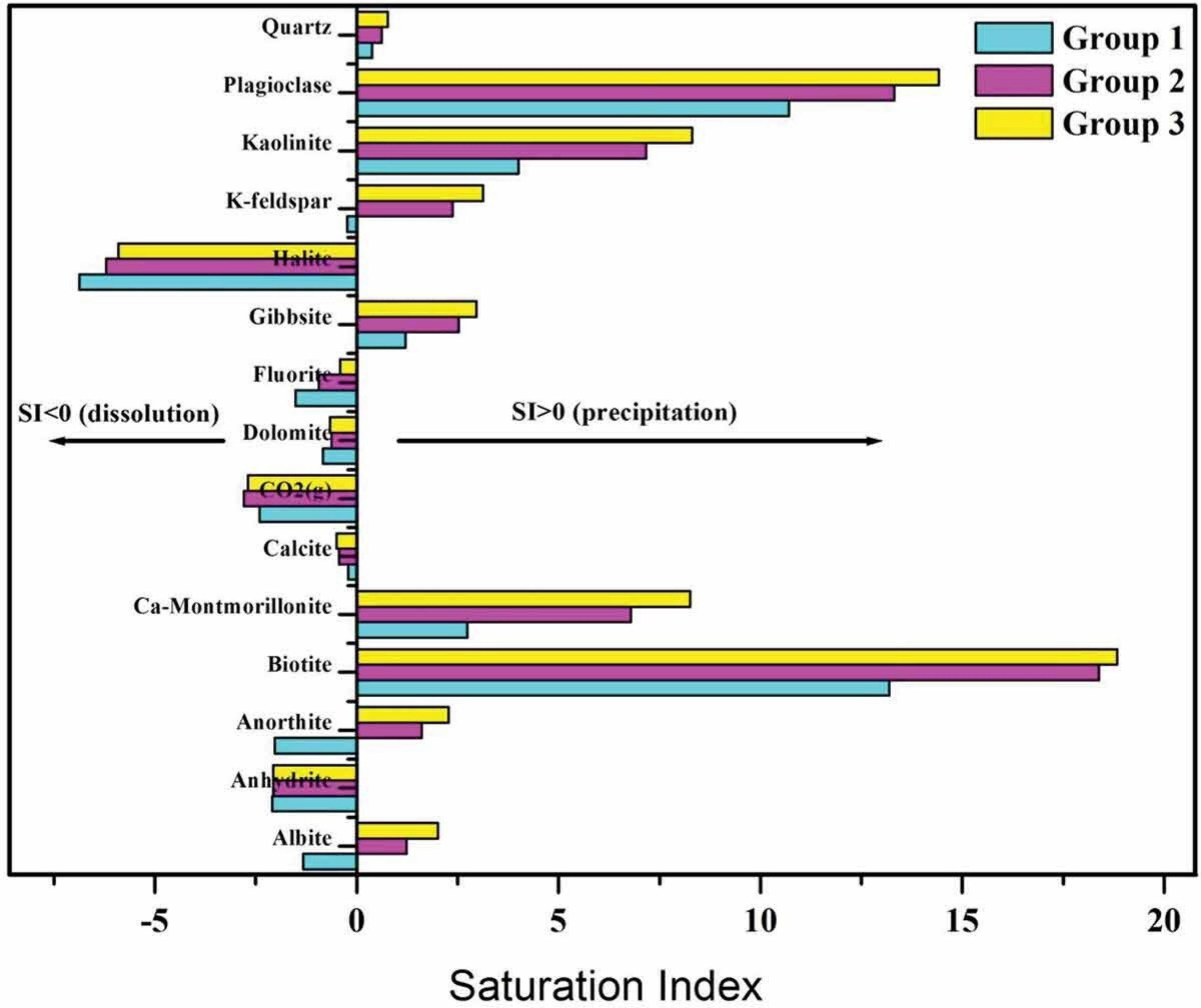
$$\begin{aligned}&\text{Group 2 water} + \mathrm{CO_2}\,(\mathrm{g}) + \text{Dolomite} + \text{Albite} + \text{Anorthite}\\&\quad + \text{Halite} + \text{Fluorite} + \text{Biotite} + \text{Ca} - \text{from ion exchange}\\&\quad \rightarrow \text{Group 3 water} + \text{Calcite} + \text{Ca} - \text{Montmorillonite}\\&\quad + \text{Kaolinite} + \text{Quartz} + \text{Anhydrite} + \text{Gibbsite} + \text{Na}\\&\quad - \text{loss to ion exchange} + \mathrm{H_2O}\,(\mathrm{g})\end{aligned}$$

Results from inverse modeling.

- **Dissolution**: Minerals like dolomite, halite, albite, and K-feldspar dissolved along the flow path, contributing to changes in groundwater chemistry.
- **Precipitation**: Secondary minerals such as kaolinite, quartz, gibbsite, Ca-montmorillonite, calcite, and anhydrite precipitated.
- **Reverse Ion Exchange**: Indicated by hydro chemical inferences and played a significant role in the geochemical evolution of groundwater in this area.

Results from inverse modeling

- **Group 1 to Group 2**: Groundwater showed a dominance of Ca^{2+} over Na^{+} and Cl^{-} over other anions in Group 1.
  - As the groundwater moved to Group 2, Na^{+} became more dominant.
  - This transition involved the dissolution of halite and other minerals, as well as the evaporation of water, which increased the electrical conductivity.
  - The decrease in Ca^{2+}/Mg^{2+} ratio was attributed to dedolomitization, with dolomite dissolving and calcite precipitating.
- **Group 2 to Group 3**: The concentrations of major ions increased, indicating further water-rock interactions.

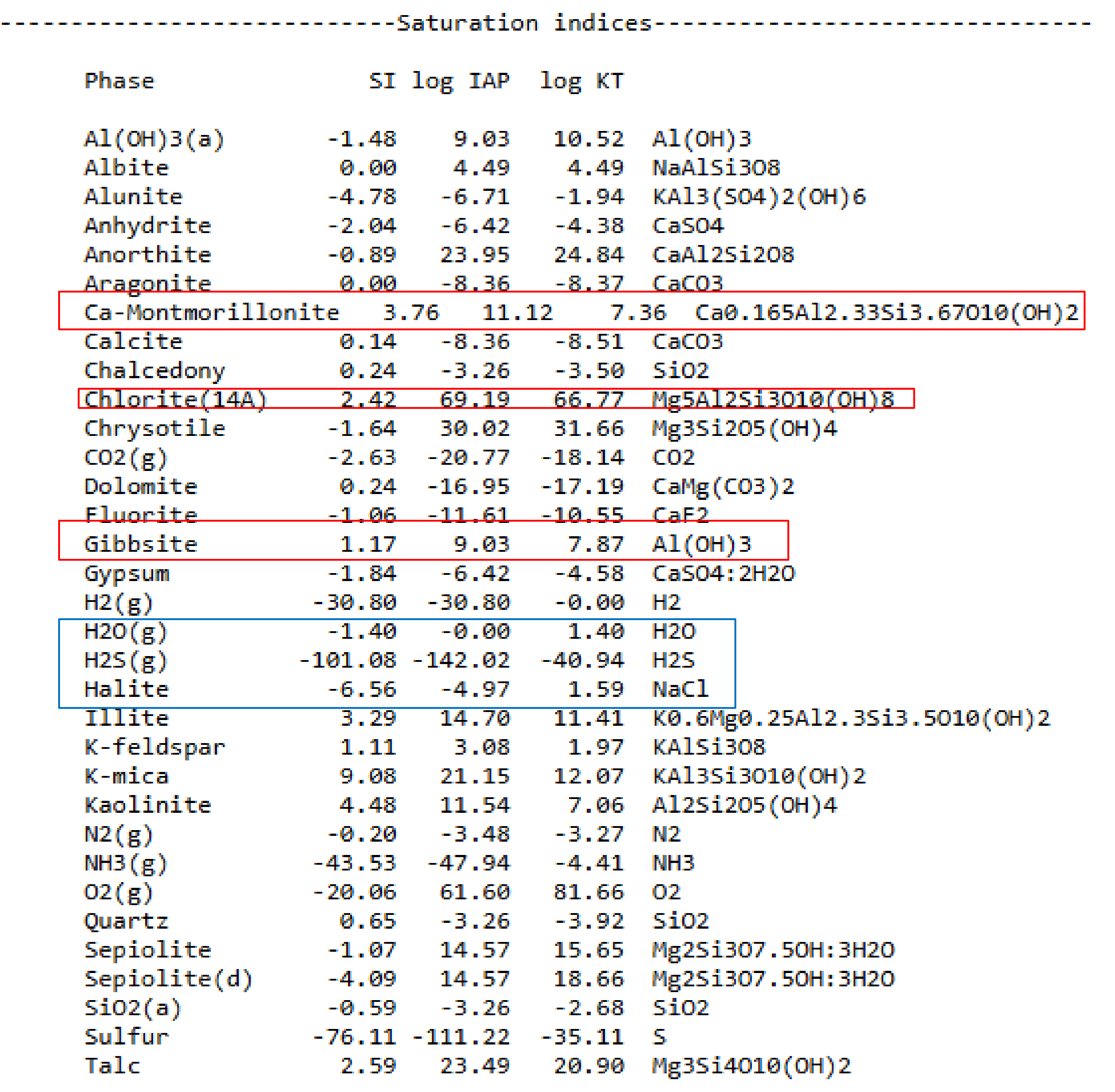

Group 1
Group 2
Group 3
Quartz
Plagioclase
Kaolinite
K-feldspar
Halite
Gibbsite
Fluorite
SI<0 (dissolution)
Dolomite
SI>0 (precipitation)
CO2(g)
Calcite
Ca-Montmorillonite
Biotite
Anorthite
Anhydrite
Albite
-5
0
5
10
15
20
Saturation Index

What if the opposite happened?

- **Meaning:**
  - What if in group 1 Na^+ was more abundant then Ca^{2+}? What would the water-rock interactions be?
  - I Used the max values from group #1 but had Na^+ (90 mg/L) value increased and Ca^{2+} 67 (mg/L) decreased.

Result

- Phases like Gibbsite, Chlorite(14A), Ca-Montmorillonite are most likely to precipitate under the given conditions.
- H2S, CO2(g), Halite, H2O(g), among others, are in undersaturated states and will likely dissolve in the system.
- The equilibrium states for phases like Albite, Aragonite show a balance between dissolution and precipitation under the conditions provided.



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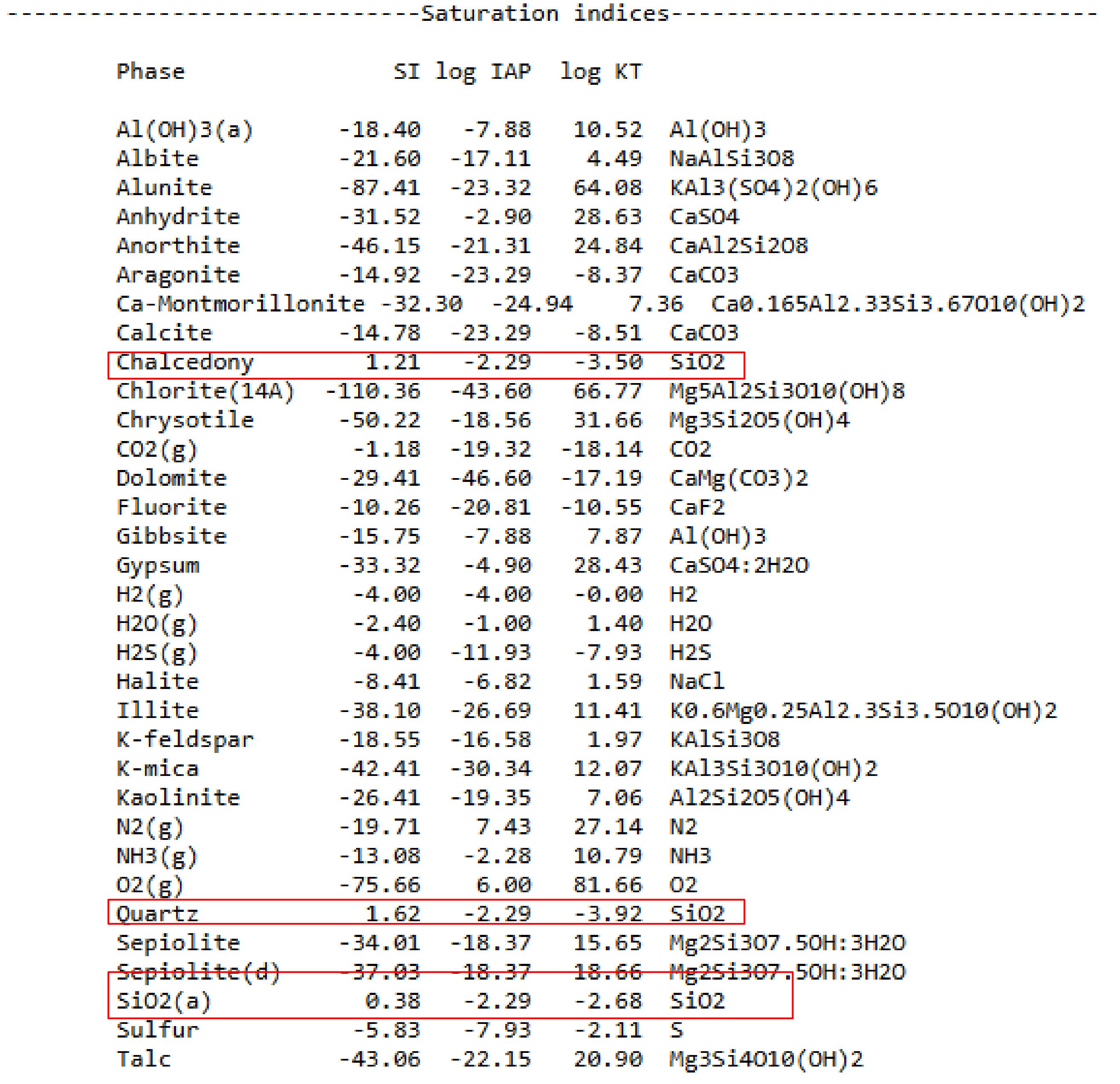
---------------------------Saturation indices------------------------------

      Phase               SI log IAP  log KT

      Al(OH)3(a)       -1.48    9.03   10.52  Al(OH)3
      Albite            0.00    4.49    4.49  NaAlSi3O8
      Alunite          -4.78   -6.71   -1.94  KAl3(SO4)2(OH)6
      Anhydrite        -2.04   -6.42   -4.38  CaSO4
      Anorthite        -0.89   23.95   24.84  CaAl2Si2O8
      Aragonite         0.00   -8.36   -8.37  CaCO3
      Ca-Montmorillonite    3.76   11.12    7.36  Ca0.165Al2.33Si3.67O10(OH)2
      Calcite           0.14   -8.36   -8.51  CaCO3
      Chalcedony        0.24   -3.26   -3.50  SiO2
      Chlorite(14A)     2.42   69.19   66.77  Mg5Al2Si3O10(OH)8
      Chrysotile       -1.64   30.02   31.66  Mg3Si2O5(OH)4
      CO2(g)           -2.63  -20.77  -18.14  CO2
      Dolomite          0.24  -16.95  -17.19  CaMg(CO3)2
      Fluorite         -1.06  -11.61  -10.55  CaF2
      Gibbsite          1.17    9.03    7.87  Al(OH)3
      Gypsum           -1.84   -6.42   -4.58  CaSO4:2H2O
      H2(g)           -30.80  -30.80   -0.00  H2
      H2O(g)           -1.40   -0.00    1.40  H2O
      H2S(g)         -101.08 -142.02  -40.94  H2S
      Halite           -6.56   -4.97    1.59  NaCl
      Illite            3.29   14.70   11.41  K0.6Mg0.25Al2.3Si3.5O10(OH)2
      K-feldspar        1.11    3.08    1.97  KAlSi3O8
      K-mica            9.08   21.15   12.07  KAl3Si3O10(OH)2
      Kaolinite         4.48   11.54    7.06  Al2Si2O5(OH)4
      N2(g)            -0.20   -3.48   -3.27  N2
      NH3(g)          -43.53  -47.94   -4.41  NH3
      O2(g)           -20.06   61.60   81.66  O2
      Quartz            0.65   -3.26   -3.92  SiO2
      Sepiolite        -1.07   14.57   15.65  Mg2Si3O7.5OH:3H2O
      Sepiolite(d)     -4.09   14.57   18.66  Mg2Si3O7.5OH:3H2O
      SiO2(a)          -0.59   -3.26   -2.68  SiO2
      Sulfur          -76.11 -111.22  -35.11  S
      Talc              2.59   23.49   20.90  Mg3Si4O10(OH)2
```

Question #2.

- What if the same concentrations of the ions were in the water but the pH turned basic (pH = 10) and there was too much fertilizer contamination? What are the water-rock interactions?
- **Result:**
  - **Precipitates:** Chalcedony, Quartz, and amorphous SiO_2
  - **Dissolves:** Everything Else
  - Near-equilibrium Phases: $H_2(g)$ and $O_2(g)$ are relatively close to equilibrium.



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------------------------------Saturation indices-------------------------------

        Phase               SI  log IAP  log KT

        Al(OH)3(a)      -18.40   -7.88   10.52  Al(OH)3
        Albite          -21.60  -17.11    4.49  NaAlSi3O8
        Alunite         -87.41  -23.32   64.08  KAl3(SO4)2(OH)6
        Anhydrite       -31.52   -2.90   28.63  CaSO4
        Anorthite       -46.15  -21.31   24.84  CaAl2Si2O8
        Aragonite       -14.92  -23.29   -8.37  CaCO3
        Ca-Montmorillonite -32.30  -24.94    7.36  Ca0.165Al2.33Si3.67O10(OH)2
        Calcite         -14.78  -23.29   -8.51  CaCO3
        Chalcedony        1.21   -2.29   -3.50  SiO2
        Chlorite(14A)  -110.36  -43.60   66.77  Mg5Al2Si3O10(OH)8
        Chrysotile      -50.22  -18.56   31.66  Mg3Si2O5(OH)4
        CO2(g)           -1.18  -19.32  -18.14  CO2
        Dolomite        -29.41  -46.60  -17.19  CaMg(CO3)2
        Fluorite        -10.26  -20.81  -10.55  CaF2
        Gibbsite        -15.75   -7.88    7.87  Al(OH)3
        Gypsum          -33.32   -4.90   28.43  CaSO4:2H2O
        H2(g)            -4.00   -4.00   -0.00  H2
        H2O(g)           -2.40   -1.00    1.40  H2O
        H2S(g)           -4.00  -11.93   -7.93  H2S
        Halite           -8.41   -6.82    1.59  NaCl
        Illite          -38.10  -26.69   11.41  K0.6Mg0.25Al2.3Si3.5O10(OH)2
        K-feldspar      -18.55  -16.58    1.97  KAlSi3O8
        K-mica          -42.41  -30.34   12.07  KAl3Si3O10(OH)2
        Kaolinite       -26.41  -19.35    7.06  Al2Si2O5(OH)4
        N2(g)           -19.71    7.43   27.14  N2
        NH3(g)          -13.08   -2.28   10.79  NH3
        O2(g)           -75.66    6.00   81.66  O2
        Quartz            1.62   -2.29   -3.92  SiO2
        Sepiolite       -34.01  -18.37   15.65  Mg2Si3O7.5OH:3H2O
        Sepiolite(d)    -37.03  -18.37   18.66  Mg2Si3O7.5OH:3H2O
        SiO2(a)           0.38   -2.29   -2.68  SiO2
        Sulfur           -5.83   -7.93   -2.11  S
        Talc            -43.06  -22.15   20.90  Mg3Si4O10(OH)2
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