Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Supplementary Material 1: General information on

Understanding arsenic mobilization using reactive transport modeling of groundwater hydrochemistry in Datong Basin study plot, China

Harold Wilson Tumwitike Mapoma[1,2]; Xianjun Xie[1*]; Kunfu Pi[1]; Yanxin Wang[1**]; Yaqing Liu[1]; Yapeng Zhu[1]

[1]School of Environmental Studies & State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, 430074 Wuhan, China

[2]Physics and Biochemical Sciences, The Polytechnic, University of Malawi, Private Bag 303, Blantyre 3, Malawi.

Corresponding author:

*Tel: +86-27-67883170; Fax: +86-27-87436235; Email: xjxie@cug.edu.cn

**Tel: +86-27-67883998; Fax: +86-27-87481030; Email: yx.wang@cug.edu.cn

1. General groundwater chemistry

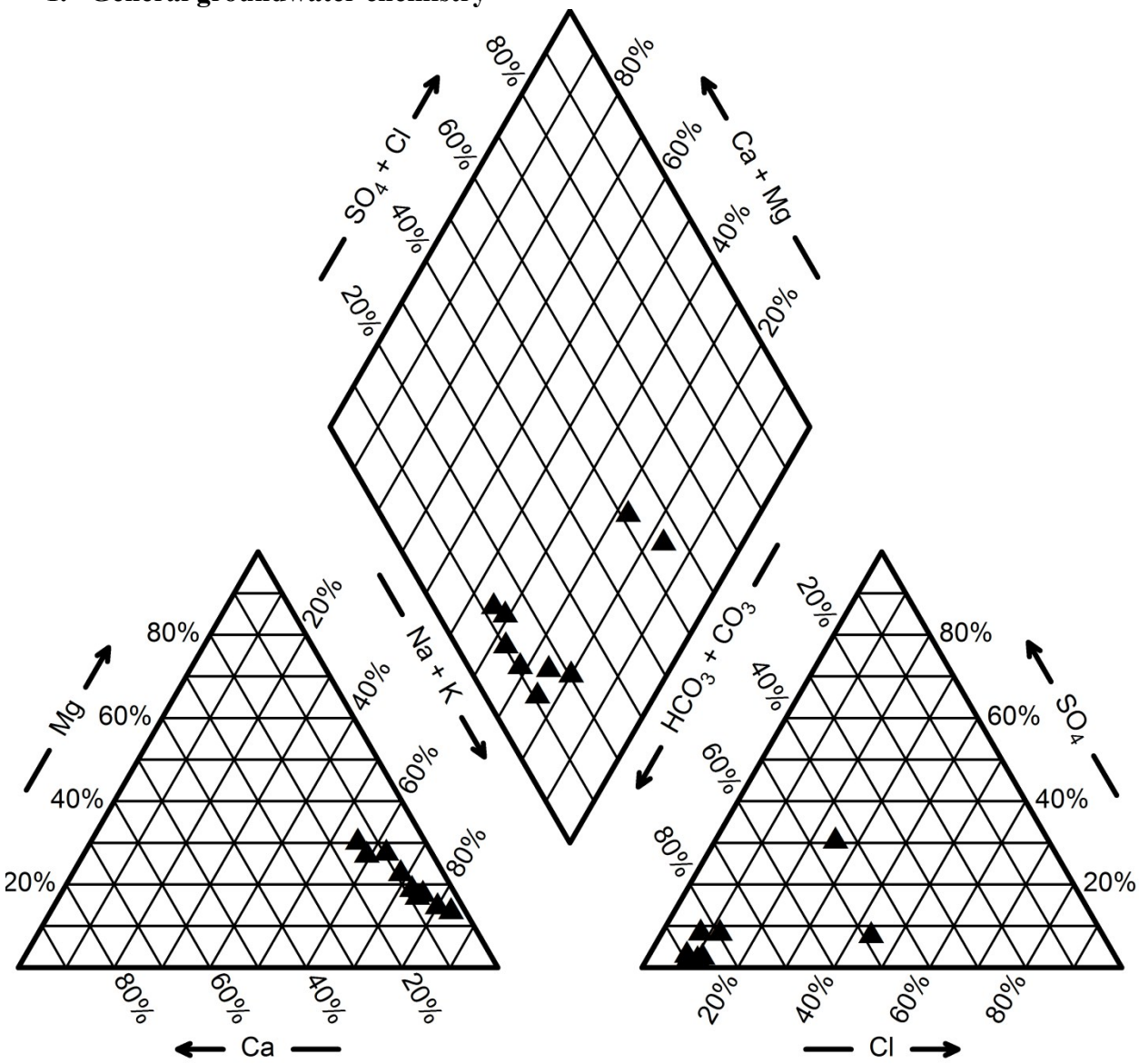

Fig. S1 Piper diagram plotted using field data from the study plot used to identify the main groundwater facies. The diagram identifies Na-HCO_3 is the predominant water type consistent with various observations done in Datong basin.

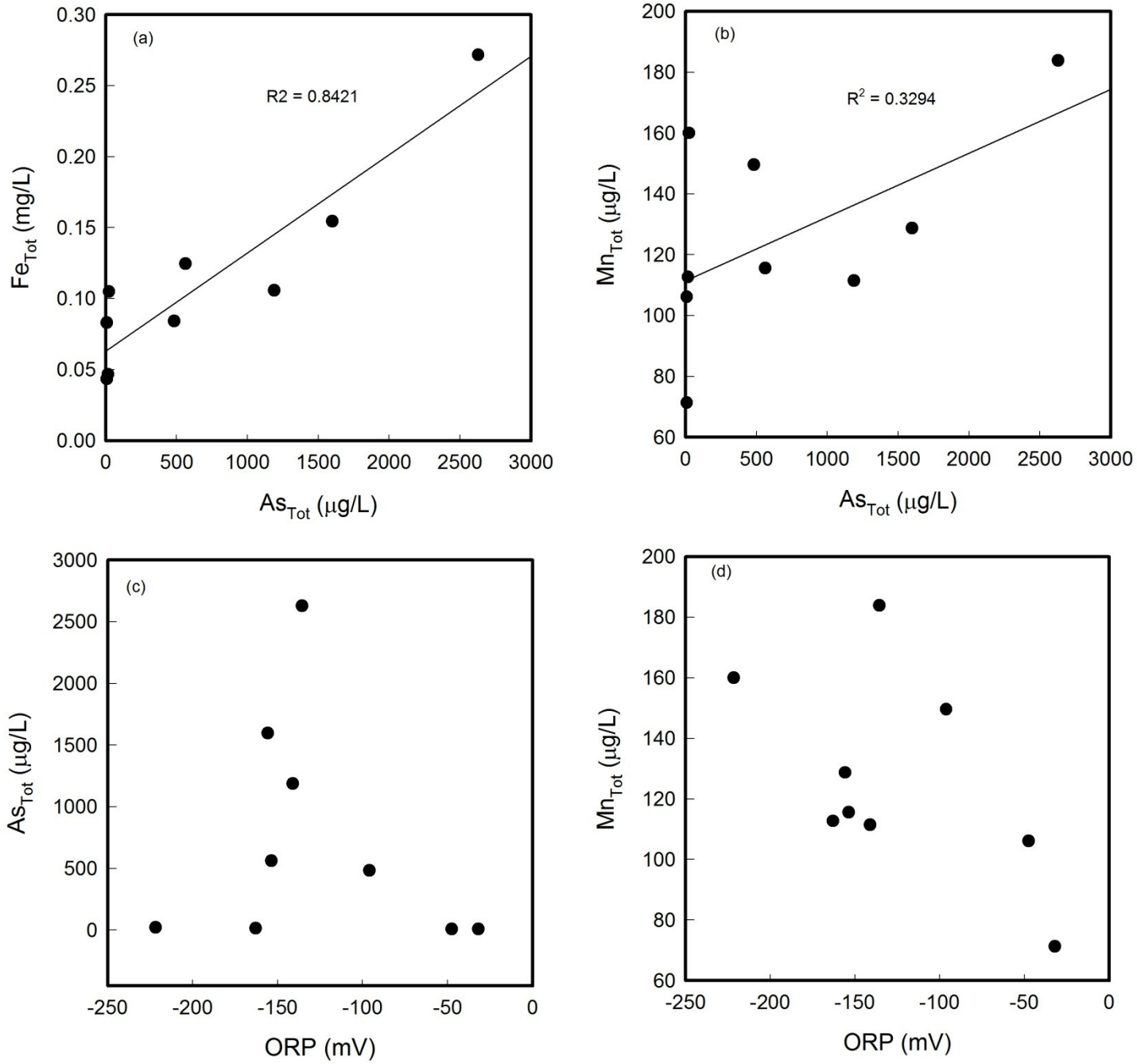

Fig. S2 Relationship between total arsenic and Fe (a), Mn (b) and ORP while total Mn is plotted against ORP (c).

The correlation of As with Fe suggests that Fe is a significant factor contributing to mobilization of As in the study area under reducing conditions. Otherwise poor correlations were observed between As and Mn/ ORP. Yet, Mn inversely correlated with ORP (Figure S3d) and that higher concentration of As is observed under reducing conditions.

2. Raw Data

Table S1 Raw Data in mg/L (unless where indicated) obtained from field data as explained in the main paper.

No	T (^{0}C)	pH	ORP (mV)	EC (µS/cm)	Ca	Mg	Na	K	HCO_3	SO_4	Cl	Si	Fe^{2+}	Fe	S^{2-} (µg/L)	NH_4^+	Mn (µg/L)	Al (µg/L)	AsT (µg/L)	AsIII (µg/L)
A1	9.01	7.97	-47.5	1512	14.06	37.26	440.3	1.05	663.3	348.9	214	4.615	0.04	0.083	4	0.39	106.1	2.13	8.4	1.8
A3	8.40	7.85	-96.1	444	19.18	22.69	93.98	0.52	373.8	7.98	27.9	7.662	0.04	0.084	12	0.32	149.6	6.03	482.4	271.7
A5	8.68	8.03	-153.7	446	19.52	25.21	88.14	0.65	374.8	5.799	26.15	5.394	0.07	0.125	22	0.51	115.6	4.28	562.0	489.0
B2	8.79	8.04	-31.9	511	10.65	16.52	134.8	0.6	438.7	11.06	22.28	5.758	0.01	0.043	1	0.15	71.3	5.49	8.2	0.0
B4	8.67	8.17	-155.9	454	12.5	18.97	109.2	0.44	377.4	5.537	22.11	5.247	0.08	0.155	15	0.20	128.7	1.91	1598.1	1389.0
B5	8.81	8.08	-141	401	11.93	20.78	90.16	0.56	343.9	4.471	19.25	5.282	0.09	0.106	27	0.33	111.4	3.73	1187.4	662.5
C1	8.97	8.02	-75.8	907	11.05	17.75	252.4	0.72	489.9	105.6	83.06	4.838	0.04	0.136	15	0.28	102.1	103.00	13.1	10.9
C5	8.83	7.94	-135.5	695	15.41	18.85	158.4	0.53	479.1	36.07	26.44	5.687	0.24	0.272	30	1.53	183.8	5.85	2627.1	1885.3
D2	8.51	7.69	-221.7	1002	24.64	32.63	239.6	1.11	441.1	51.73	221.6	5.006	0.02	0.105	293	0.91	160.0	5.57	22.4	7.1

3. Mineral Reaction Kinetics and kinetics

Table S2 Minerals and their solubility constants used in reactive transport simulation obtained from field data at Datong Basin

Mineral	Reactions	Solubility constant ($log_{10}K$)	Volume fraction
Albite	$NaAlSi_3O_8 = Na^+ + 3SiO_2(aq) + AlO_2$-	-20.119	0.055
Annite	$KFe_3AlSi_3O_{10}(OH)_2 + 6H^+ = K^+ + 3Fe^{2+} + 3SiO_2(aq) + 4H_2O + AlO_2^-$	6.5860	0.203
Calcite	$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$	1.8490	0.097
Chlorite	$(Mg,Fe^{2+})_5Al_2Si_3O_{10}(OH)_8 + 8H^+ = 3SiO_2(aq) + 2.5Fe^{2+} + 2.5Mg^{2+} + 8H_2O + 2AlO_2^-$	4.2900	0.165
Illite	$K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2 = 1.2H^+ 0.25Mg^{2+} + 0.6K^+ + 3.5SiO_2(aq) + 0.4H_2O + 2.3AlO_2^-$	-47.418	0.205
K-Feldspar	$KAlSi_3O_8 = K^+ + 3SiO_2(aq) + AlO_2^-$	-22.910	0.009
Montmorillonite-Na	$Na_{0.33}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2 = 0.68H^+ + 0.33Mg^{2+} + 0.33Na^+ + 0.66H_2O + 4\ SiO_2(aq) + 1.67AlO_2^-$	-37.158	0.089
Quartz	$SiO_2 = SiO_2(aq)$	-3.7390	0.176
Mackinawite	$FeS + H^+ = Fe^{2+} + HS^-$	-3.6000	
Orpiment	$As_2S_3 + 6H_2O = 2H_2AsO_3^- + 3HS^- + 5H^+$	-79.416	

The reactions and solubility constants are from database used for modeling (see main paper). The volume fraction values are converted from weight percentage obtained from laboratory analysis of aquifer material using XRD analysis.

Table S3. Parameters for calculating kinetic rate constants of minerals obtained from Palandri and Kharaka's open file[1]

Mineral	Acid Mechanism			Neutral Mechanism		Base Mechanism			
	k^{25} (mol/ cm/ s)	E (KJ/ mol)	n(H^+)	k^{25}	E	k^{25}	E	n(H^+)	A
Albite	6.9183×10^{-11}	65.0	0.457	2.7542×10^{-13}	69.8	2.5119×10^{-16}	71	-0.572	9.8
Annite	1.4100×10^{-12}	22.0	0.37	2.8200×10^{-14}	22.0	2.8200×10^{-15}	22	-0.22	9.8
Calcite									
Chlorite	7.7620×10^{-12}	88	0.5	3.0200×10^{-13}	88				151.6
Illite	1.0500×10^{-11}	23.6	0.34	1.6600×10^{-13}	35.0	3.0200×10^{-17}	59	-0.4	151.6
K-feldspar	8.7096×10^{-11}	51.7	0.5	3.8905×10^{-13}	38.0	6.3096×10^{-22}	94	-0.823	9.8
Montmorillonite-Na	1.9498×10^{-13}	48.0	0.22	3.8905×10^{-15}	48.0	3.8905×10^{-15}	48	-0.13	151.6
Quartz				1.0233×10^{-14}	87.7				9.8

NOTE: k^{25} is the rate constant at 25 °C, E is the activation energy, n is a power term (constant) for both acid and base mechanism with respect to H^+ and A is specific surface area. Calcite and chlorite were allowed to react at equilibrium

4. Aqueous Complexes

The list of aqueous complexes used in this study can be obtained from the text file (Chemical.out) accompanying the manuscript.

5. XRD Results

Figure S1 provides evidence of XRD analysis as stated in the manuscript. The methodology behind XRD as used in Datong Basin is available in Gao et al.[2] Explanation of the outcome is beyond the scope of this manuscript.

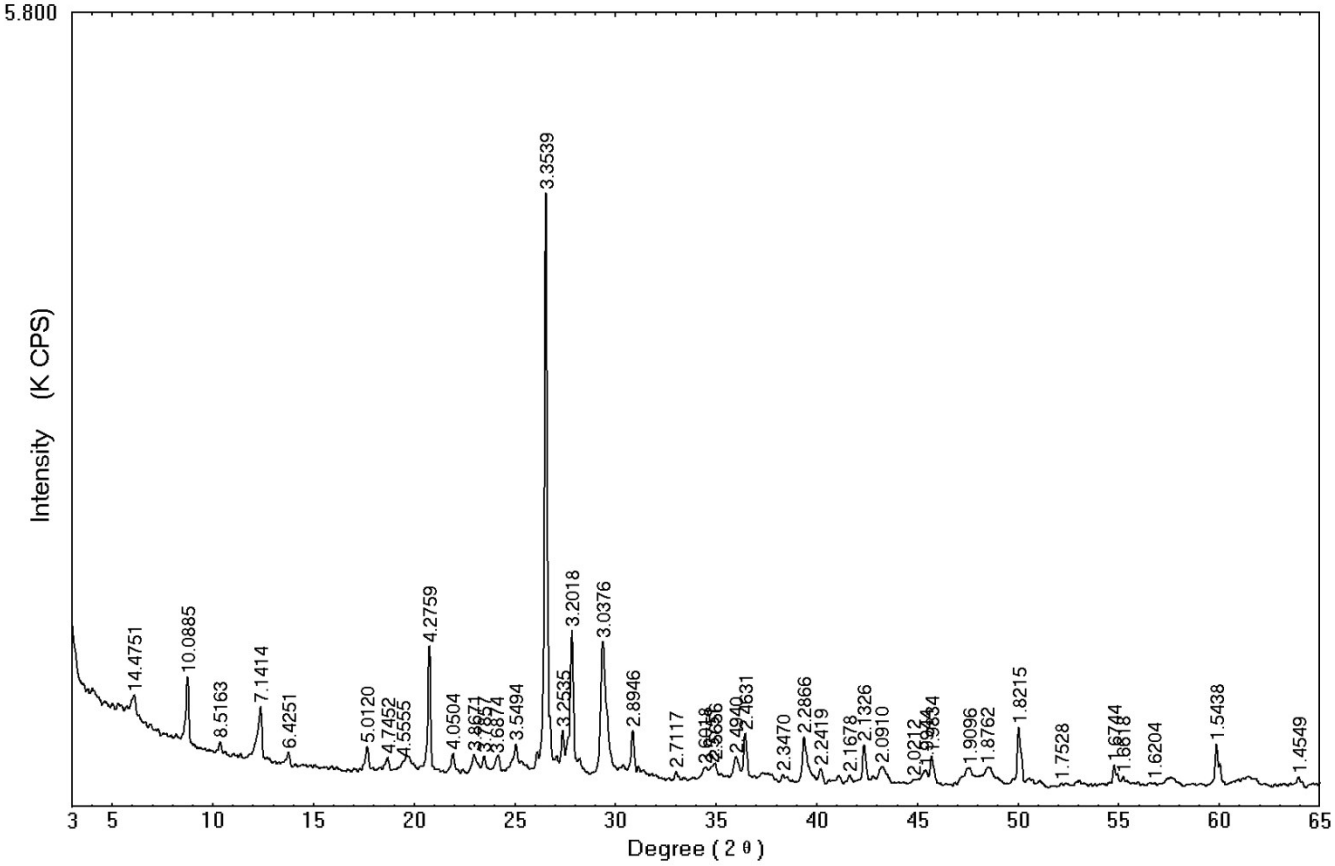

Fig. S3 XRD output used to obtain mineral volume fraction for Datong Basin aquifer sediments. The Minerals (weight perecent) identified from the XRD analysis are albite (6%), annite (17%), calcite (10%), chlorite (16%), illite (22%), K-feldspar (1%), montimorillonite (10%) and quartz (18%).

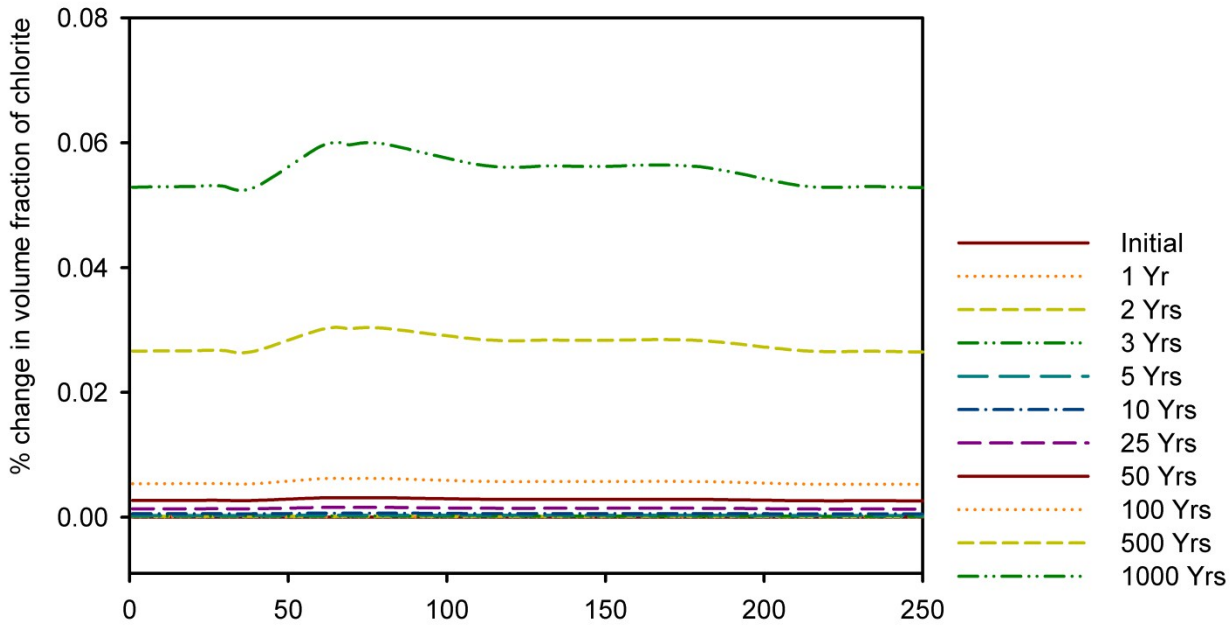

Fig. S4 Percentage change in volume fraction of chlorite which displays incongruent dissolution with annite (main article)

References

1. J. L. Palandri and Y. K. Kharaka, *A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modeling*, DTIC Document, 2004.
2. X. Gao, C. Su, Y. Wang and Q. Hu, *Journal of Geochemical Exploration*, 2013, 135, 93-103.