Mineral-Fluid Interaction in the Lungs

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Rationale

- The health effects of asbestiform and other minerals have garnered significant attention in the past several decades.
- How these minerals evolve by reaction in the lung remains poorly understood.
- Possibility of in situ mineral transformation in the lungs have not been addressed exhaustively.
- Most studies of dissolution behaviour or biodurability of minerals in the lungs have dealt with congruent reactions.
- However, most weathering reactions involving silicate minerals in nature are incongruent dissolution reactions.

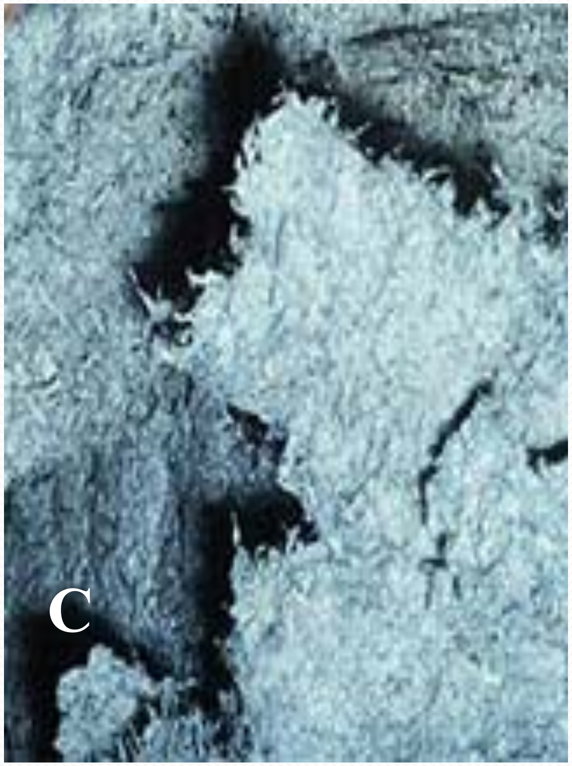
- Mineral transformation is likely to occur in the lung at body temperature within human life spans.
- Churg (1993) reported that for humans exposed to asbestiform minerals over long periods of time, the ratio of tremolite to chrysotile in the lung is significantly higher than the tremolite/ chrysotile ratio in the asbestos material to which they were exposed.
- Geochemical modeling techniques showed that transformations of chrysotile and/or tremolite to other minerals might be feasible.

Minerals associated with lung diseases

Tremolite
$Ca_2Mg_5Si_8O_{22}(OH)_2$

Chrysotile
$Mg_3Si_2O_5(OH)_4$

Crocidolite
(Riebeckite)
$Na_2Fe_3^{2+}Fe_2^{3+}Si_8O_{22}(OH)_2$

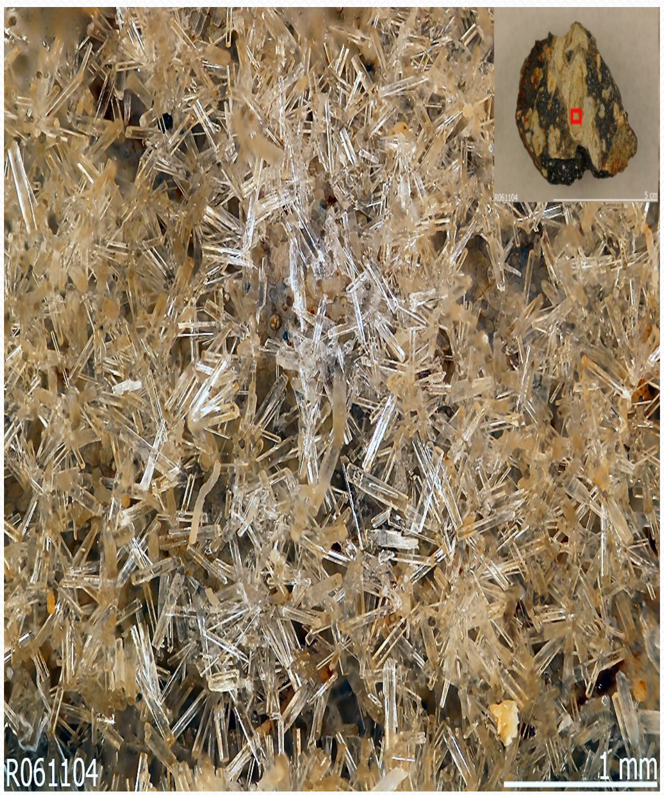


http://www.webminerals.com

Minerals associated with lung diseases

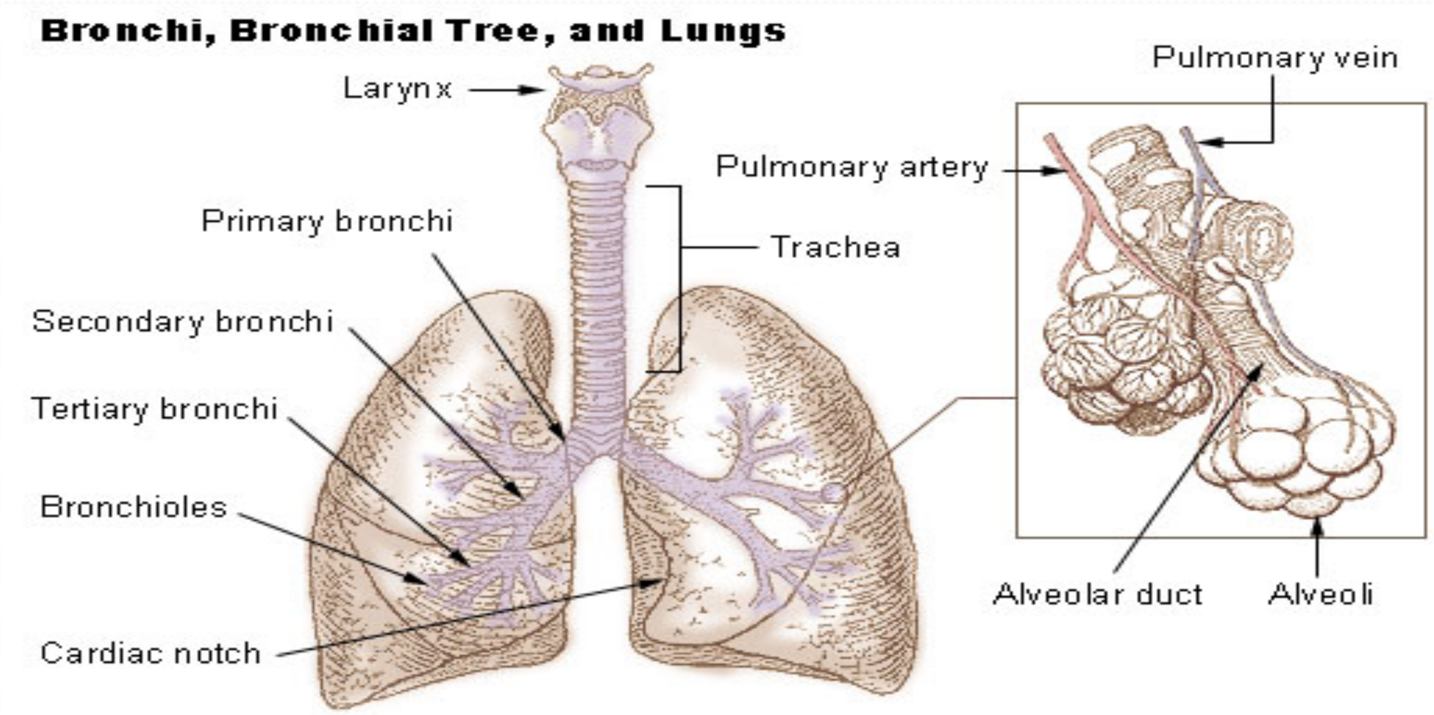
Erionite ($NaK_2MgCa_{1.5}$)
($[Al_8Si_{28}]O_{72}\ 28H_2O$)

Quartz (SiO_2)



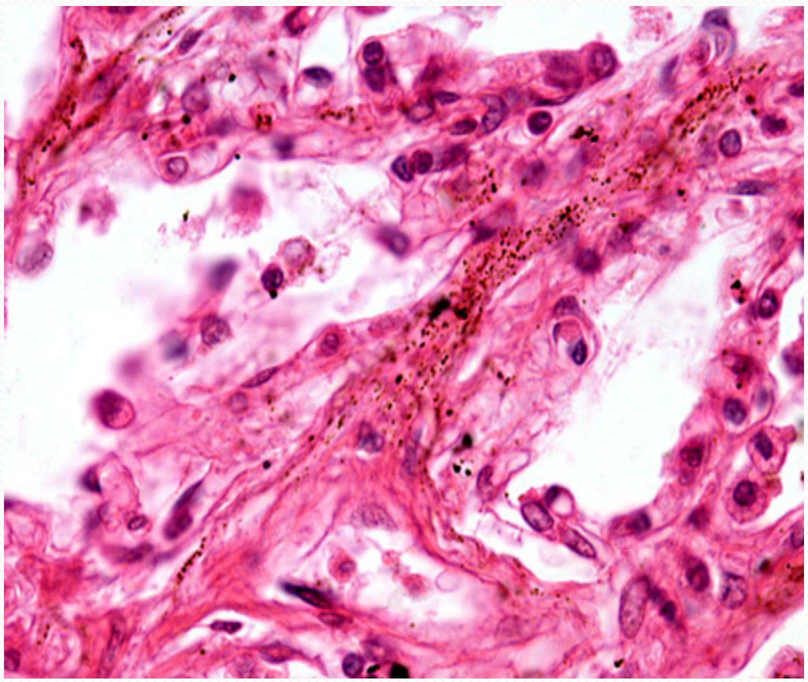
How do lungs function?

- The lungs carry the oxygen we breathe through the trachea, or windpipe, which branches into two main tubes that make up the left and right lung, respectively. These tubes further branch into 100,000 smaller tubes, bronchi and bronchioles, and more than 300 million air sacs, or alveoli.

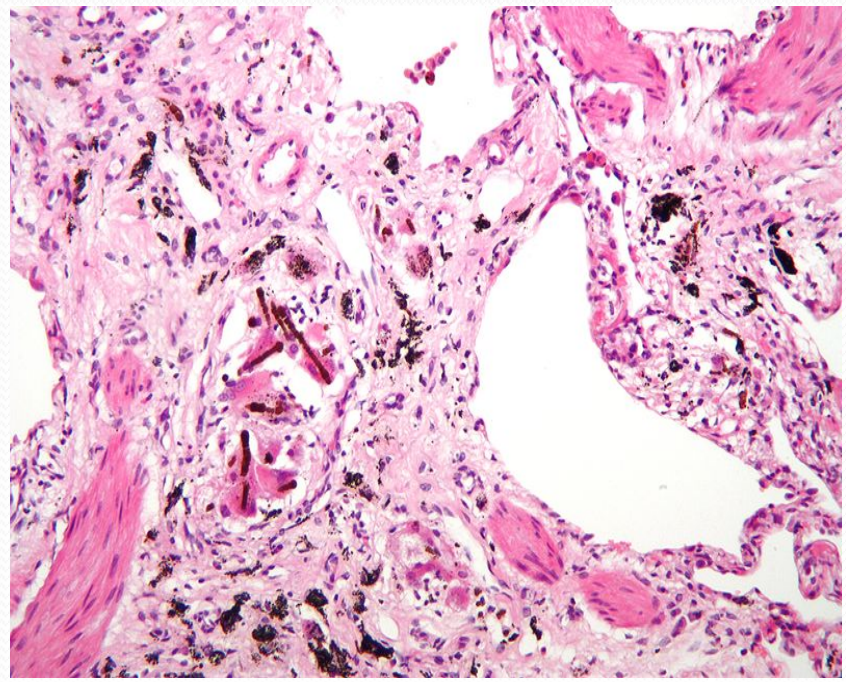


Health threats of minerals

Main diseases
- Silicosis
- Asbestosis
- Lung cancer
- Mesothelioma



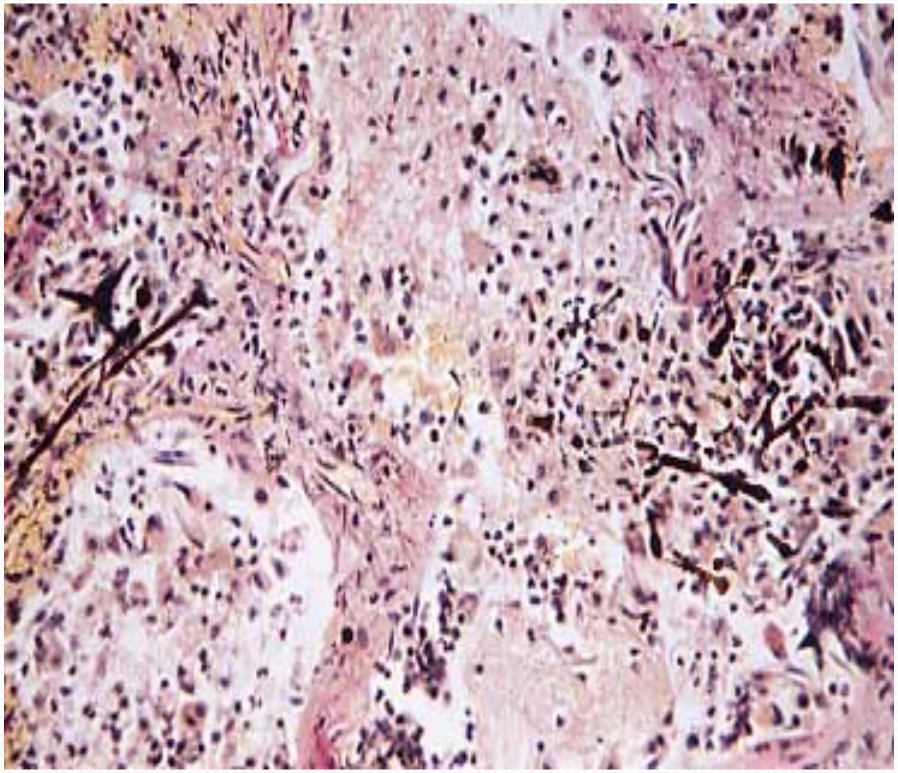
Silicosis

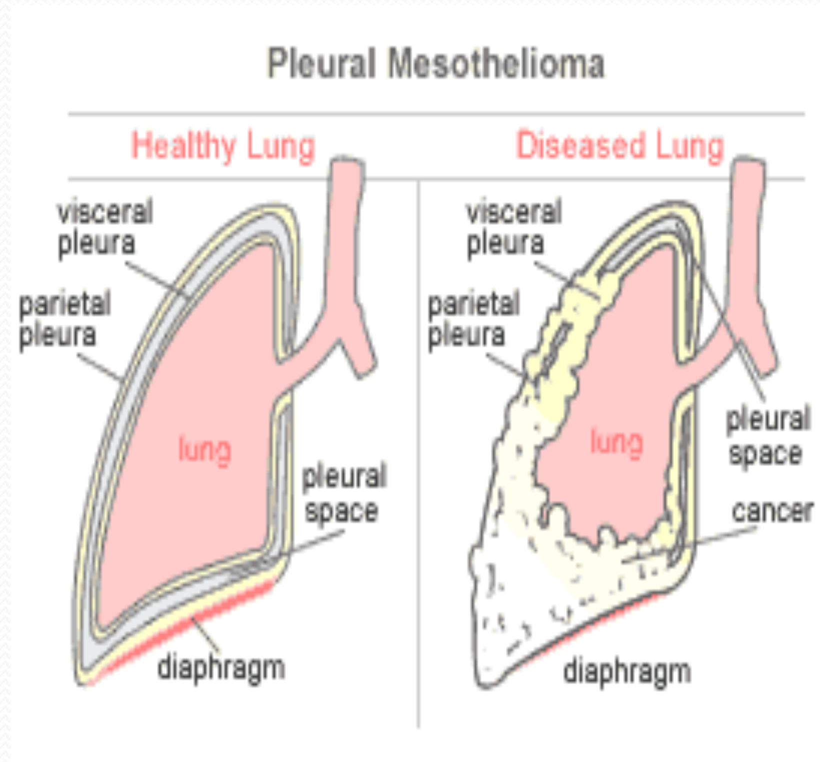


Asbestosis

en.wikipedia.org/wiki/File:Asbestosis_high_mag.jpgmolite

Health threats of minerals





Mesothelioma

•Asbestos fibers are attacked by macrophages and sealed in scar tissue which diminishes lung capacity.

http://www.mesotheliomacenter.org/

The Paper researched

Wood SA, Taunton AE, Normand C, Gunter ME. 2006 Mineral-Fluid interaction in the Lungs: Insights From Reaction-Path Modeling. Inhal Toxicol. 18(12):975-84.

Approach and methodology

- The researchers employed thermodynamic modeling to study the fate of chrysotile and tremolite in the human lung.

- They used geochemical tools, including calculation of saturation indices, activity-ratio diagrams, and reaction-path modeling.

Saturation indices

- Saturation indices (SI) were determined for chrysotile and tremolite in a model lung fluid.

Solubilities of chrysotile and tremolite at 37^{0}C in an open system

Chrysotile

$$Mg_3Si_2O_5(OH)_4 + 6H^+ \leftrightarrow 3Mg^{2+} + 2SiO_2(aq) + 5H_2O$$

pH = 4; SI = -1.37

pH = 7.35; SI = -0.19

Tremolite

$$Ca_2Mg_5Si_8O_{22}(OH)_2 + 14H^+ \leftrightarrow$$
$$2Ca^{2+} + 5Mg^{2+} + 8SiO_2\,(aq) + 8H_2O$$

pH = 4; SI = -1.47

pH = 7.35; SI = -0.23

Activity-Ratio diagrams

- Activity-ratio diagrams show the phase relations among many related minerals as a function of ion activities in aqueous solutions.

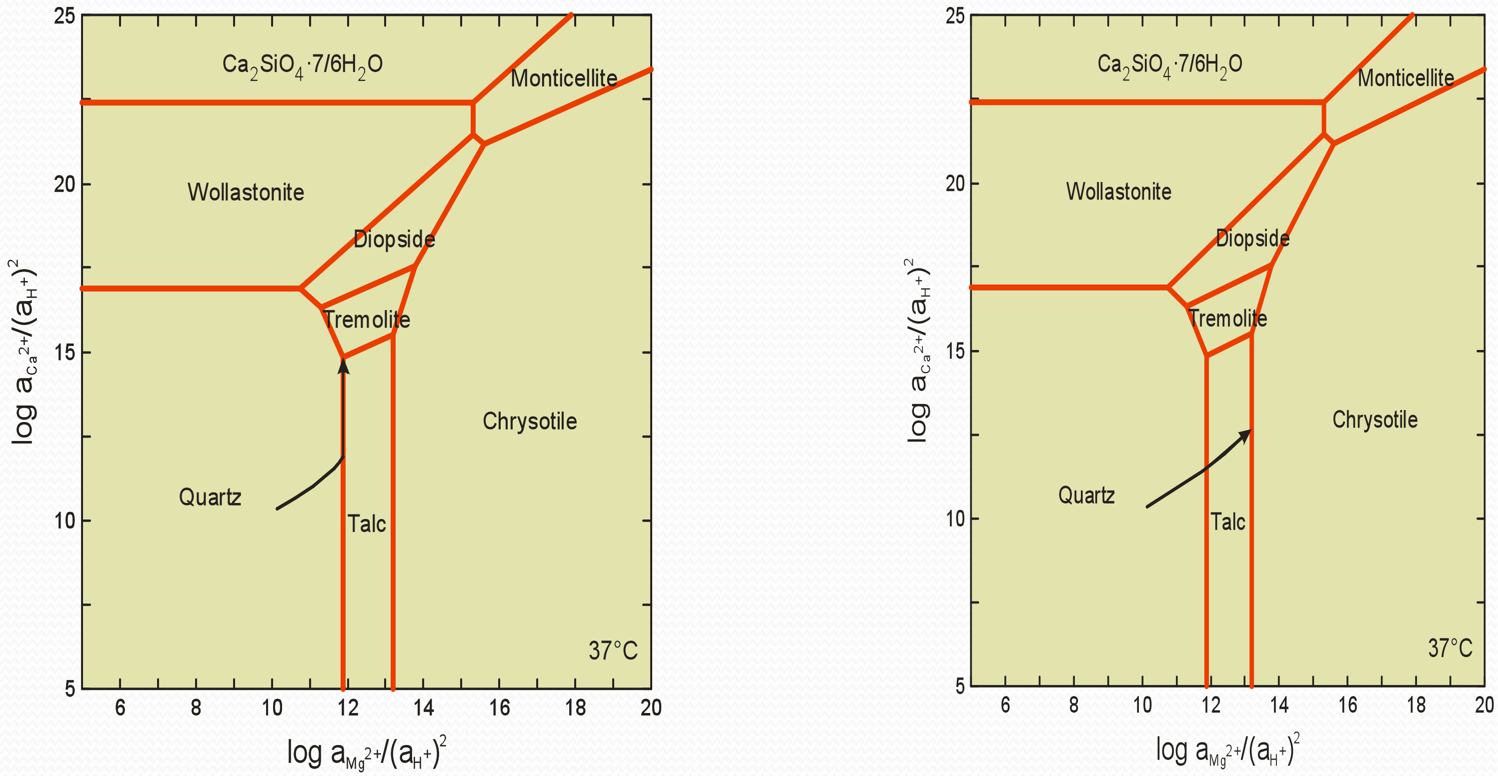


Figure 1. An activity-ratio diagram, that is, a plot of log $aCa^{2+}/(aH^+)2$ versus log $aMg^{2+}/(aH^+)2$ for minerals in the system Ca-Mg-Si-O-H at 37^0C and 1 bar

Reaction-path modeling

- Two different sets of reaction-path calculations were conducted. The first simulated a mostly open and is referred to as a flush model.
- The second set of calculations simulated a completely closed system.
- Calculations for both open and closed models were carried out at 4.5 and 6.8. The lower pH represents conditions within a macrophage, whereas the higher pH value is closer to the pH of blood plasma.

Open system flush with kinetic constraints

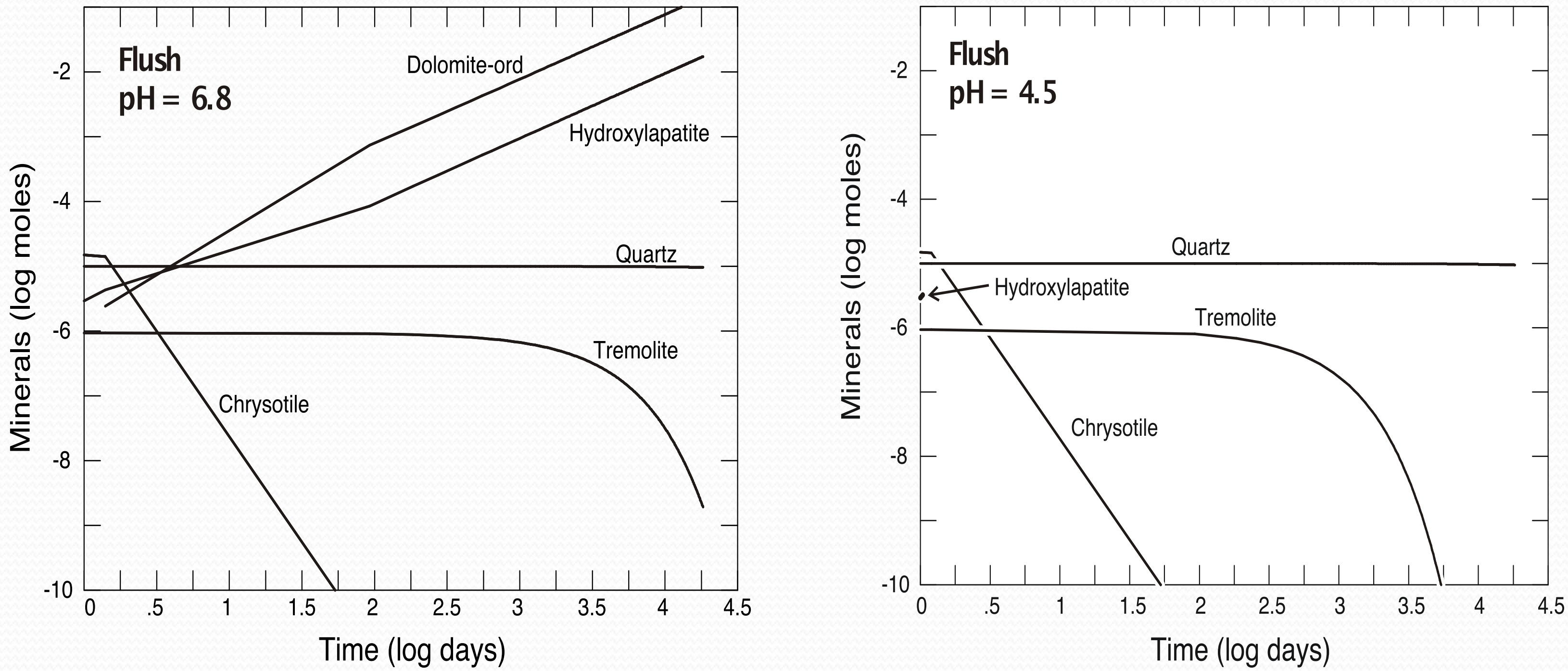


Figure 2. Plot of the mass of minerals (log scale) versus time in an open system (flush) for the reaction of quartz, tremolite, and chrysotile with simulated lung fluid where the fluid was replaced on a daily basis.

Closed system with kinetic constraints

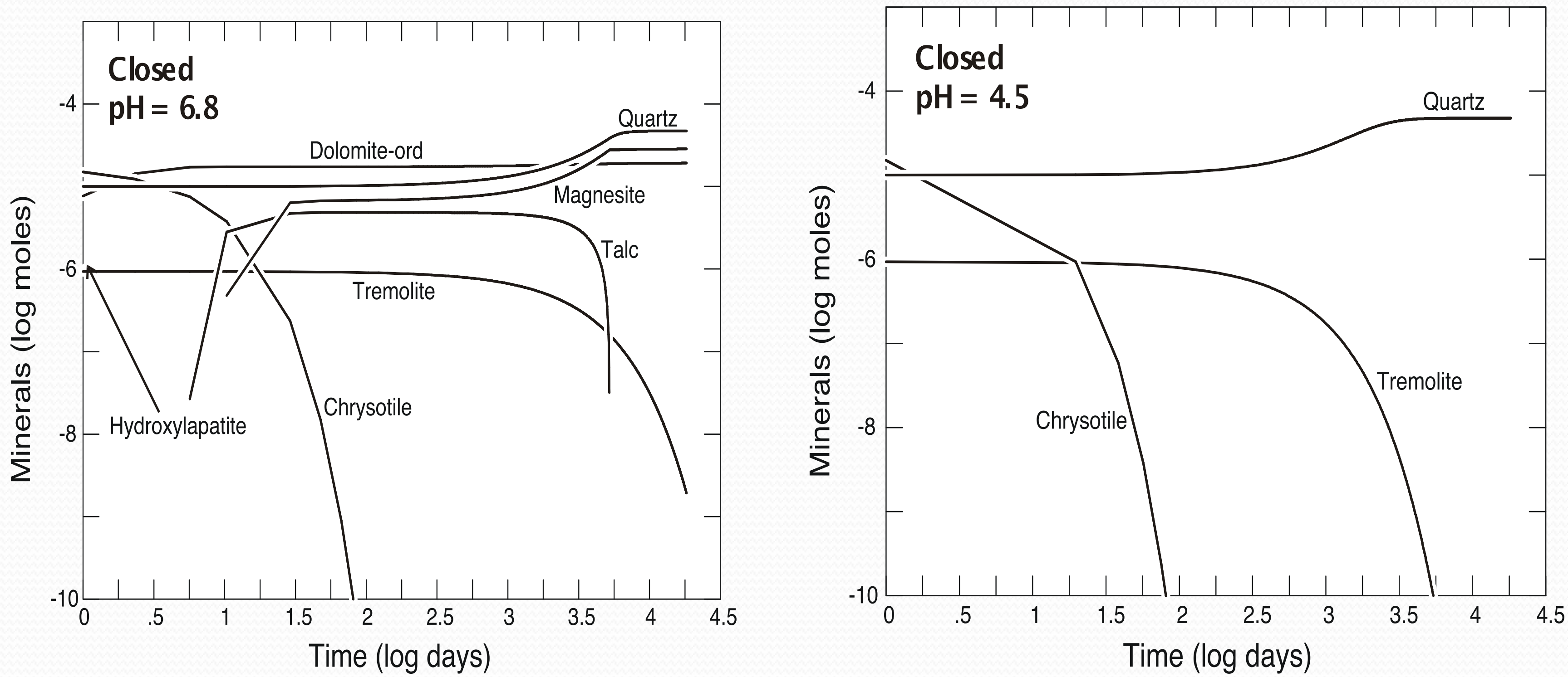


FIG. 3. Plot of the mass of minerals (log scale) versus time in a closed system for the reaction of quartz, tremolite and chrysotile with simulated lung fluid

Simulation with Cadmium

- Cadmium intake from cigarette smoking is about 1 to 3 µg of cadmium per day
- One cigarette contains about 1 - 2 µg of cadmium
- About 10% of the cadmium content is inhaled when the cigarette is smoked
- Biological half life of cadmium is 13.6 and 13.9 years for men and women, respectively. Thus, Cadmium will accumulate in the body of smokers.
- A smoker will breathe in 3*360*14 µg = 15120 µg = 15.12 mg in 14 years.
- An adult human male, who weighs 70 kg, has a blood volume of about 5 liters.
- Thus the concentration of Cd will be 3.024 mg L^{-1} (0.34 mol L^{-1}) in the body of a smoker after 14 years.

Objectives

- The specific objectives of this modeling were:
  1) to determine the speciation of Cd
  2) to see the solubility of Cd-containing minerals
  3) to see the effect of pH on the solubility of minerals

Modeling procedure

- Using PHREEQC model from USGS, the impact of Cd on minerals was investigated in lung fluid.

- Three simulations were run employing the phreeqc database.

  1) Simulation with the model lung fluid based on Gamble's solution, following Jurinski and Rimstidt (2001).

  2) Simulation with the model lung fluid and 0.34 mol L^{-1} Cd at pH 7.4

  3) Simulation with the model lung fluid and 0.34 mol L^{-1} Cd at pH 4.5

Model lung fluid used for modeling

Jurinski and Rimstidt (2001)

Component	Concentration ($mol\ L^{-1}$)
Ca^{2+}	0.001735
Cl^{-}	0.115063
HCO_3^{-}	0.03214
Mg^{2+}	0.001043
Na^{+}	0.144845
HPO_4^{2-}	0.001043
SO_4^{2-}	0.000556
$SiO_2(aq)$	0.00015

Simulation with model lung fluid

---Saturation indices---

Phase	SI	log IAP	log KT	
Anhydrite	-2.75	-7.18	-4.43	CaSO4
Aragonite	0.61	-7.81	-8.42	CaCO3
Calcite	0.75	-7.81	-8.56	CaCO3
Chalcedony	-0.39	-3.80	-3.42	SiO2
Chrysotile	-4.53	26.24	30.77	Mg3Si2O5(OH)4
CO2(g)	-1.15	-2.75	-1.60	CO2
Dolomite	1.54	-15.81	-17.36	CaMg(CO3)2
Gypsum	-2.60	-7.19	-4.59	CaSO4:2H2O
H2(g)	-22.80	-26.00	-3.20	H2
H2O(g)	-1.21	-0.00	1.21	H2O
Halite	-3.64	-2.04	1.61	NaCl
Hydroxyapatite	6.38	1.94	-4.45	Ca5(PO4)3OH
O2(g)	-33.69	-36.66	-2.97	O2
Quartz	0.01	-3.80	-3.81	SiO2
Sepiolite	-4.31	11.15	15.46	Mg2Si3O7.5OH:3H2O
Sepiolite(d)	-7.51	11.15	18.66	Mg2Si3O7.5OH:3H2O
SiO2(a)	-1.19	-3.80	-2.62	SiO2
Talc	-1.45	18.64	20.08	Mg3Si4O10(OH)2

Simulation with the model lung fluid and 0.34 mol L^{-1} Cd at pH 7.4

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

Phase	SI	log IAP	log KT	
Anhydrite	-3.58	-8.01	-4.43	CaSO4
Aragonite	0.04	-8.38	-8.42	CaCO3
Calcite	0.18	-8.38	-8.56	CaCO3
Cd(OH)2	-0.02	13.63	13.65	Cd(OH)2
CdSiO3	1.31	9.90	8.59	CdSiO3
CdSO4	-5.27	-5.79	-0.52	CdSO4
Chalcedony	-0.32	-3.74	-3.42	SiO2
Chrysotile	-4.49	26.28	30.77	Mg3Si2O5(OH)4
CO2(g)	-1.66	-3.26	-1.60	CO2
Dolomite	0.43	-16.93	-17.36	CaMg(CO3)2
Gypsum	-3.43	-8.02	-4.59	CaSO4:2H2O
H2(g)	-22.80	-26.00	-3.20	H2
H2O(g)	-1.22	-0.00	1.21	H2O
Halite	-4.56	-2.95	1.61	NaCl
Hydroxyapatite	5.54	1.09	-4.45	Ca5(PO4)3OH
O2(g)	-33.70	-36.67	-2.97	O2
Otavite	5.94	-6.16	-12.10	CdCO3
Quartz	0.07	-3.74	-3.81	SiO2
Sepiolite	-4.17	11.29	15.46	Mg2Si3O7.5OH:3H2O
Sepiolite(d)	-7.37	11.29	18.66	Mg2Si3O7.5OH:3H2O
SiO2(a)	-1.12	-3.74	-2.62	SiO2
Talc	-1.27	18.82	20.08	Mg3Si4O10(OH)2

Simulation with the model lung fluid and 0.34 mol L^{-1} Cd at pH 4.5

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

Phase	SI	log IAP	log KT	
Anhydrite	-3.57	-8.00	-4.43	CaSO4
Aragonite	-2.81	-11.24	-8.42	CaCO3
Calcite	-2.68	-11.24	-8.56	CaCO3
Cd(OH)2	-5.83	7.82	13.65	Cd(OH)2
CdSiO3	-4.48	4.11	8.59	CdSiO3
CdSO4	-5.27	-5.79	-0.52	CdSO4
Chalcedony	-0.31	-3.73	-3.42	SiO2
Chrysotile	-21.85	8.92	30.77	Mg3Si2O5(OH)4
CO2(g)	1.28	-0.31	-1.60	CO2
Dolomite	-5.27	-22.63	-17.36	CaMg(CO3)2
Gypsum	-3.42	-8.02	-4.59	CaSO4:2H2O
H2(g)	-17.00	-20.20	-3.20	H2
H2O(g)	-1.22	-0.01	1.21	H2O
Halite	-4.56	-2.95	1.61	NaCl
Hydroxyapatite	-11.94	-16.39	-4.45	Ca5(PO4)3OH
O2(g)	-45.30	-48.27	-2.97	O2
Otavite	3.07	-9.03	-12.10	CdCO3
Quartz	0.08	-3.73	-3.81	SiO2
Sepiolite	-15.74	-0.28	15.46	Mg2Si3O7.5OH:3H2O
Sepiolite(d)	-18.94	-0.28	18.66	Mg2Si3O7.5OH:3H2O
SiO2(a)	-1.11	-3.73	-2.62	SiO2
Talc	-18.61	1.47	20.08	Mg3Si4O10(OH)2

Saturation indices at a glance

Phase	Saturation indices		
	Sim. 1	Sim. 2	Sim. 3
Aragonite	0.61	0.04	-2.81
Calcite	0.75	0.18	-2.68
Dolomite	1.54	0.43	-5.27
Hydroxyapatite	6.38	5.54	-11.94
Quartz	0.01	0.07	0.08
$CdSiO_3$	----	1.31	-4.48
Otavite	----	5.94	3.07

Conclusion

- In simulation 1, all the minerals were found undersaturated except aragonite, calcite, dolomite, hydroxyapatite and quartz.
- In simulation 2, the solubility of all the minerals decreased except quartz. $CdSiO_3$ and otavite appeared in the simulated lung fluid and control the solubility of Cd species.
- All the minerals which were supersaturated in simulation 1 become undersaturated in simulation 3. Otavite remains supersaturated.
- So within the macrophage (pH 4.5), otavite will remain saturated and could pose a health hazard for human beings.

Thank You