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Dynamic Geochemical Tension (DGT) in Multi-Mineral-Water Systems - Origin, Characterization, and Role in Fractal 1-over-f Slopes in Minesite-Drainage Chemistry

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Abstract

Monomineralic abrasion pH shows that each mineral creates a particular pH and aqueous chemistry in surrounding water. This still allows minerals to be gathered into near-neutral, acidic, and alkaline groups. The near-neutral abrasion-pH group contains the most minerals and is consistent with near-neutral pH being most common in natural waters.

Upon blasting or other disturbance of earthen materials, mineral grains can be liberated, fresh mineral surfaces exposed, reaction rates accelerated, and minerals of various abrasion-pH groups mixed or placed repetitively along the same flowpaths. This causes significant increases in "dynamic geochemical tension" (DGT) which has profound effects on full-scale drainage chemistry.

DGT is illustrated here as a "pH pendulum" that is free to swing between acidic and alkaline pH. However, each abrasion-pH group has a "spring" attached to, and pulling on, the pendulum. If one abrasion-pH group is consumed or weakened, then the pH pendulum shifts towards the group with the greatest remaining tension. The pendulum movement is not smooth, but occurs in distinct steps.

One effect that DGT can generate in aqueous geochemistry is $1/f^{\alpha}$ slopes in spectral analysis of time series. One explanation of $1/f^{\alpha}$ slopes, Self-Organized Criticality (SOC), is consistent with DGT. However, other potential explanations exist.

1. INTRODUCTION

Over a half century ago, the concept of abrasion pH was developed by Stevens and Carron (1948), who presented "A simple field test . . . for distinguishing minerals by estimating the pH of suspensions made by grinding them in water." The minerals not only created distinct abrasion pH values, but also released cations and anions to the water. However, pH was easily measured, as opposed to laboratory analyses for the cations and anions, and pH was thus a simple field indicator.

Monomineralic abrasion pH was refined and expanded over the years (e.g., Grant, 1969). Variations on this technique include multi-mineralic paste pH and rinse pH (Sobek et al., 1978; Price, 2009; Morin and Hutt, 1997 and 2001).

Stevens and Carron (1948) listed the abrasion pHs of 280 minerals (some are shown in Table 1). Some important observations from their study are:

- Abrasion pH ranged from 1 to 12 for the 280 minerals.
- Identical or similar minerals from different localities could yield values of abrasion pH differing by up to three pH units. For example, various samples of siderite yielded abrasion pH of 5, 6, and 7 (see also Morin and Cherry, 1986; Morin and Hutt, 2000).
- Minerals with similar abrasion pH were often found together in nature.
- Minerals with abrasion pH at 6 formed the largest rank (Figure 1), followed by pH 7 and pH 8 (collectively called "near-neutral minerals" here). Alkaline minerals (abrasion pH $\geq$ 9) were the second largest group, and acidic minerals (abrasion pH $\leq$ 5) were smallest.

2. ORIGIN OF DYNAMIC GEOCHEMICAL TENSION

When earthen materials like rock and soil are blasted or otherwise disturbed, dynamic geochemical tension (DGT) can arise due to the following processes.

1) Upon blasting or other disturbance, mineral grains can be liberated and/or fresh mineral surfaces exposed.

2) Additional blasting, excavation, hauling, dumping, and/or dozer-grading can enhance the percentages of finer particles, the cumulative surface area of minerals, and the reaction rates of many minerals.

3) Coarser disturbed particles can continue to break apart, exposing new mineral surfaces for long periods of time.

4) Finally, the subsequent placement or disposal of earthen materials can mix minerals of the various abrasion-pH groups together, or place them repetitively along the same flowpaths of surface or subsurface waters.

These processes have a profound effect on the aqueous geochemistry of those flowpaths, by raising DGT.

3. CHARACTERIZATION OF DYNAMIC GEOCHEMICAL TENSION

Due to the mixing and/or repetitive sequential occurrences of abrasion-pH mineral groups upon disturbance, a competitive "tension" develops in the aqueous chemistry of flowing water. This is called here, "dynamic geochemical tension" or DGT. This can be portrayed conceptually as a "pH pendulum" that can swing freely to any pH value and typically points to the most reactive abrasion-pH group (Figure 2). A geochemical "spring" connects each abrasion-pH group to the pendulum, and provides tension pulling the pendulum towards itself.

Table 1. Abrasion pH for some minerals (From Stevens and Carron, 1948)

	Composition		*Abrasion pH*											
			Acidic						Neutral	Alkaline				
Mineral	Formula	Type[1]	1	2	3	4	5	6	7	8	9	10	11	12
Coquimbite	$Fe_2(SO_4)_3 \cdot 9H_2O$	b A	■											
Alunogen	$Al_2(SO_4)_3 \cdot 16H_2O$	b A		■										
Pickeringite	$MgAl_2(SO_4)_4 \cdot 22H_2O$	B b A			■									
Potash Alum	$KAl(SO_4)_2 \cdot 12H_2O$	B b A			■									
Aluminite	$Al_2SO_4 \cdot 9H_2O$	b A				■								
Scorodite	$FeAsO_4 \cdot 2H_2O$	b A					■							
Sessolite	H_3BO_3	a					■							
Jarosite	$K_2Fe_6(OH)_{12}(SO_4)_4$	b a					■	■						
Siderite	$FeCO_3$	b a					■	■	■					
Gypsum	$CaSO_4 \cdot 2H_2O$	B a						■						
Pyrophyillite	$Al_2Si_4O_{10}(OH)_2$	b a						■						
Quartz	SiO_2	a						■	■					
Gibbsite	$Al(OH)_3$	b						■	■					
Andalusite	Al_2SiO_5	b a							■					
Muscovite	$KAl_3Si_3O_{10}(OH)_2$	B b a							■	■				
Calcite	$CaCO_3$	B a								■				
Anorthite	$CaAl_2Si_2O_8$	B b a								■				
Microcline	$KAlSi_3O_8$	B b a								■	■			
Talc	$Mg_3Si_4O_{10}(OH)_2$	B a									■			
Albite	$NaAlSi_3O_8$	B b a									■	■		
Dolomite	$CaMg(CO_3)_2$	B B a									■	■		
Borax	$Na_2B_4O_7 \cdot 10H_2O$	B a										■		
Phlogopite	$KMg_3AlSi_3O_{10}(OH)_2$	B B b a										■	■	
Magnesite	$MgCO_3$	B a										■	■	
Brucite	$Mg(OH)_2$	B											■	
Merwinite	$Ca_3Mg(SiO_4)_2$	B B a											■	
Shertite	$Na_2Ca_2(CO_3)_3$	B B a												■

[1] A = strong acid B = strong base a = weak acid b = weak base

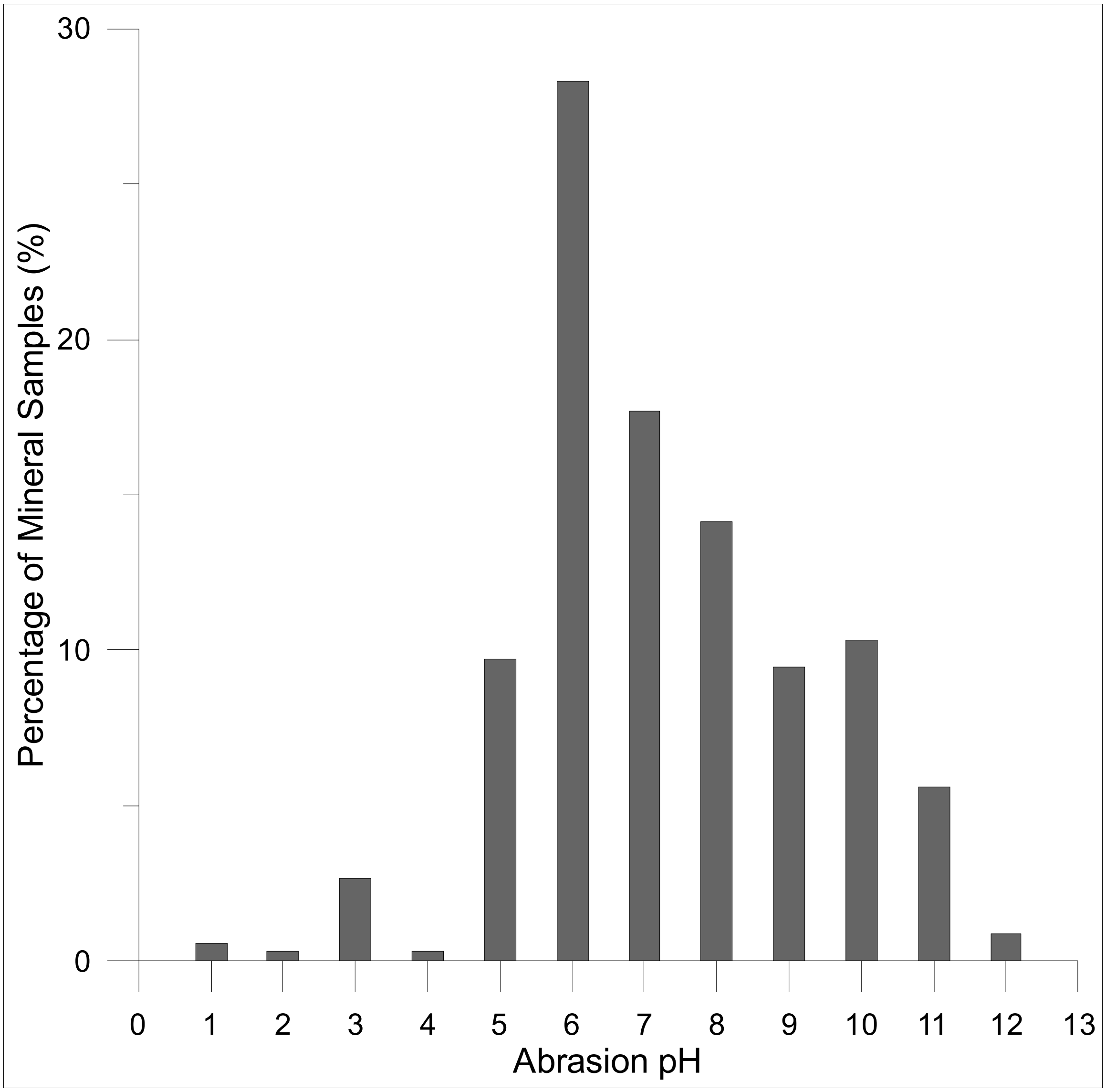

Figure 1. Histogram of abrasion pH values for several minerals (from Stevens and Carron, 1948).

In undisturbed earthen materials, mineral grains have been exposed and weathered for long periods. As a result, they do not provide much tension (Figure 2), and the preference for near-neutral pH (e.g., Figure 1) often pulls the pendulum to the bottom.

However, upon blasting or disturbance described in Section 2, the newly exposed and more reactive mineral surfaces increase their tensions on the springs (Figure 3). This increase in tension can span orders of magnitude upon blasting, excavation, hauling, dumping, and grading.

Eventually, one abrasion-pH group is exhausted or weakens, and the pH pendulum is pulled to one side. Figure 4 shows the acidity-generating minerals dominating, resulting in acid rock drainage (ARD) and, at minesites, acid mine drainage (AMD). Nevertheless, alkaline rock drainage (LRD) can also arise and has been documented at some minesites like diamond mines (Morin and Hutt, 1997 and 2001).

Interestingly, the reactivity of some minerals and their DGT can increase substantially when the pH pendulum is pulled into their range. This pulls the pendulum even farther into their range (Figure 5).

Laboratory-scale and full-scale studies have shown that movement of the pH pendulum is not smooth, but occurs as episodic "steps" reflecting geochemical "sub-regions". This is discussed in detail in Morin (2015a), based on work dating back to the early 1980's (e.g., Morin et al., 1982). In effect, these stepwise shifts in pH represent geochemical "phase transitions" or "shocks".

4. ROLE OF DYNAMIC GEOCHEMICAL TENSION IN FRACTAL 1-OVER-f SLOPES IN MINESITE-DRAINAGE CHEMISTRY

Dynamic geochemical tension (DGT) has major effects on minesite-drainage chemistry above the emergent "scale transition" (Morin and Hutt, 2007). Above this scale transition, not usually tested or characterized well at minesites (Morin 2015a, 2015b, and 2016), DGT can lead to well-buffered aqueous chemistry that is still subject to significant variability and geochemical phase transitions.

One sign of well-buffered but variable aqueous chemistry is fractal $1/f^{\alpha}$ slopes in power spectra of temporal trends of minesite-drainage chemistry. In one study (Morin 2016), these slopes were around $\alpha = 1.0$. For some elements and parameters, the slopes more generally ranged from $\alpha = 0.6$ to 1.3, with extreme values of zero to >2.0. An obvious question is: why were these 1/f slopes so common in that study?

Temporal trends with 1/f slopes (also called pink or flicker noise) have been noted in "an extraordinarily diverse number of physical and biological systems [and] some researchers describe it as being ubiquitous" and "There are many theories of the origin of pink noise. . . . Universal theories of pink noise remain a matter of current research interest." (Wikipedia, 2016).

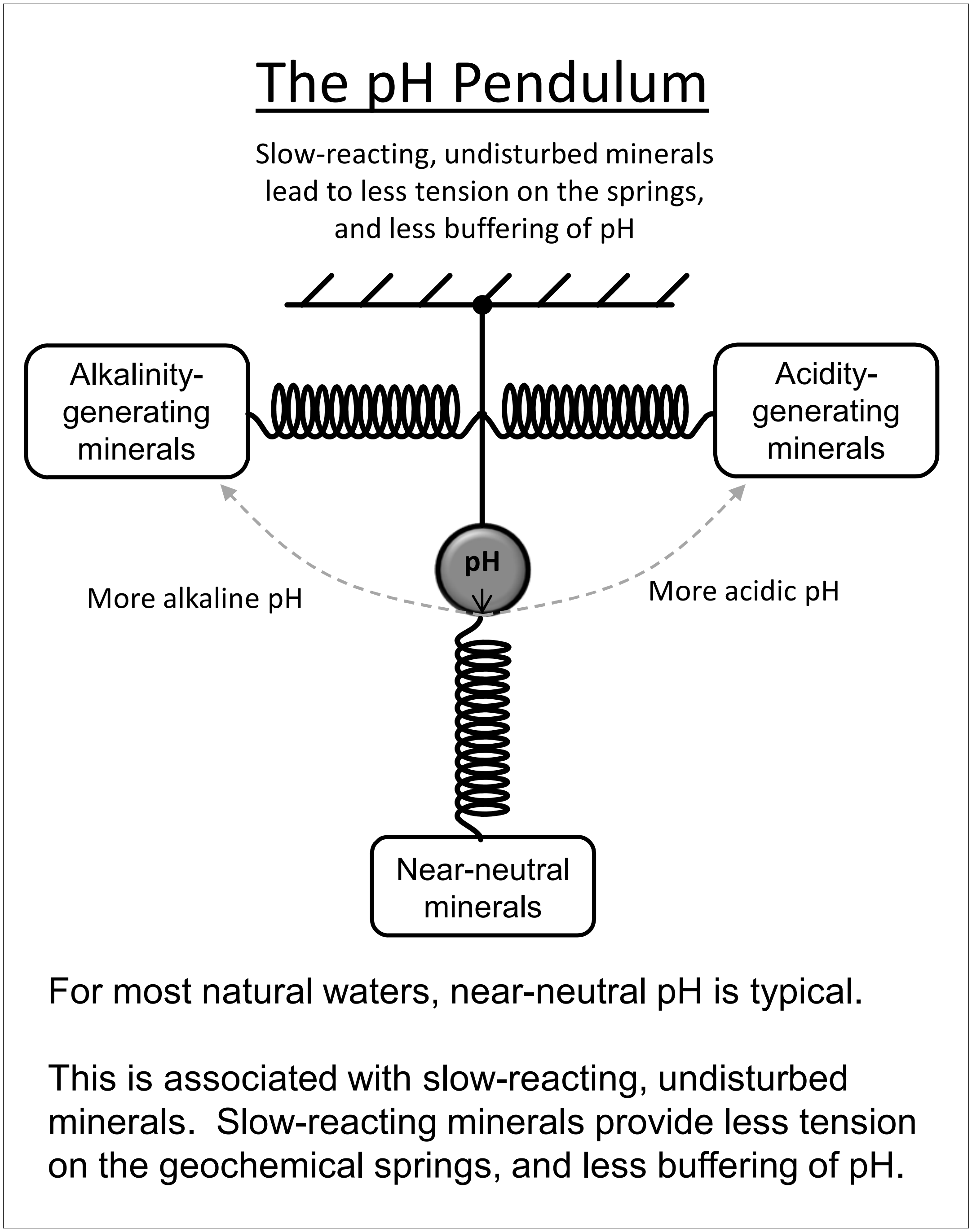

Figure 2. The conceptual model of Dynamic Geochemical Tension shown as a pH pendulum with geochemical springs creating tension where attached to differing abrasion-pH groups. In this figure, only older, well-weathered minerals are exposed, leading to minimal tension on the pendulum.

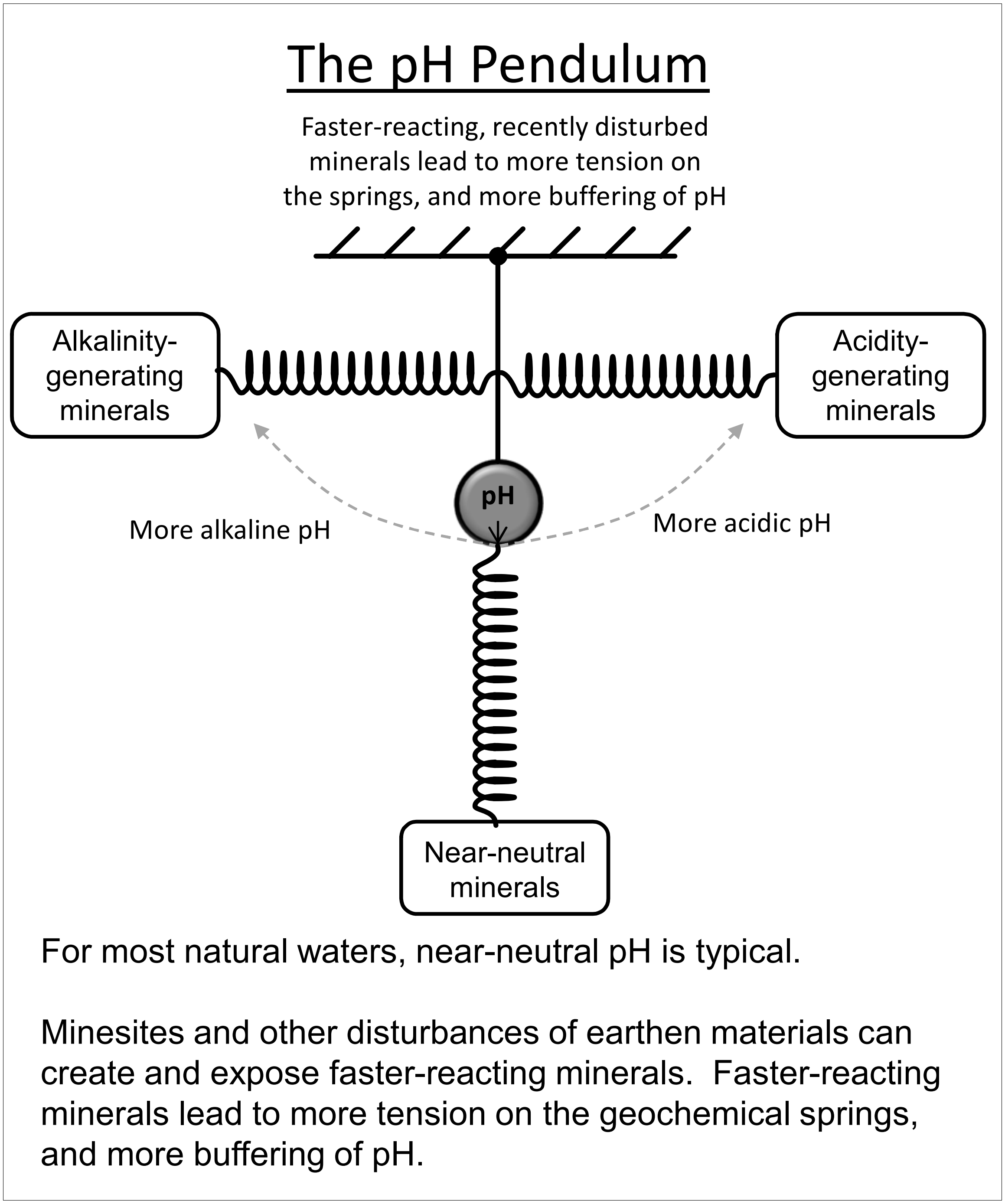

Figure 3. The conceptual model of Dynamic Geochemical Tension shown as a pH pendulum with geochemical springs creating tension where attached to differing abrasion-pH groups. In this figure, mining and other disturbances of earthen materials lead to the exposure of fresh mineral surfaces, leading to greater tension on the springs and pendulum, but near-neutral pH is maintained.

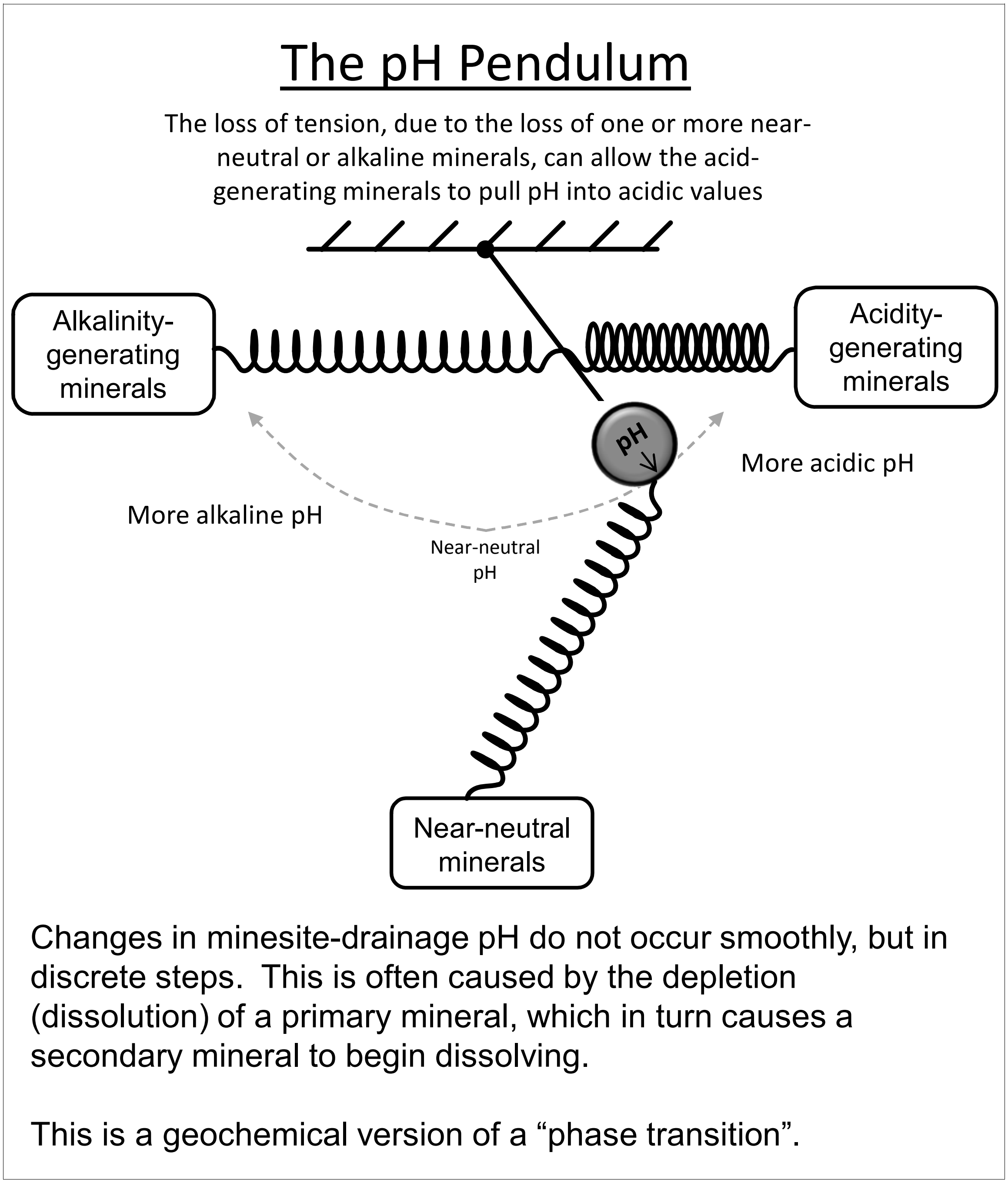

Figure 4. The conceptual model of Dynamic Geochemical Tension shown as a pH pendulum with geochemical springs creating tension where attached to differing abrasion-pH groups. In this figure, the eventual dissolution of a dominant near-neutral or alkaline mineral weakens the tension on this spring, allowing the pH to decrease stepwise to acidic values. This can be viewed as a geochemical "phase transition" or "shock".

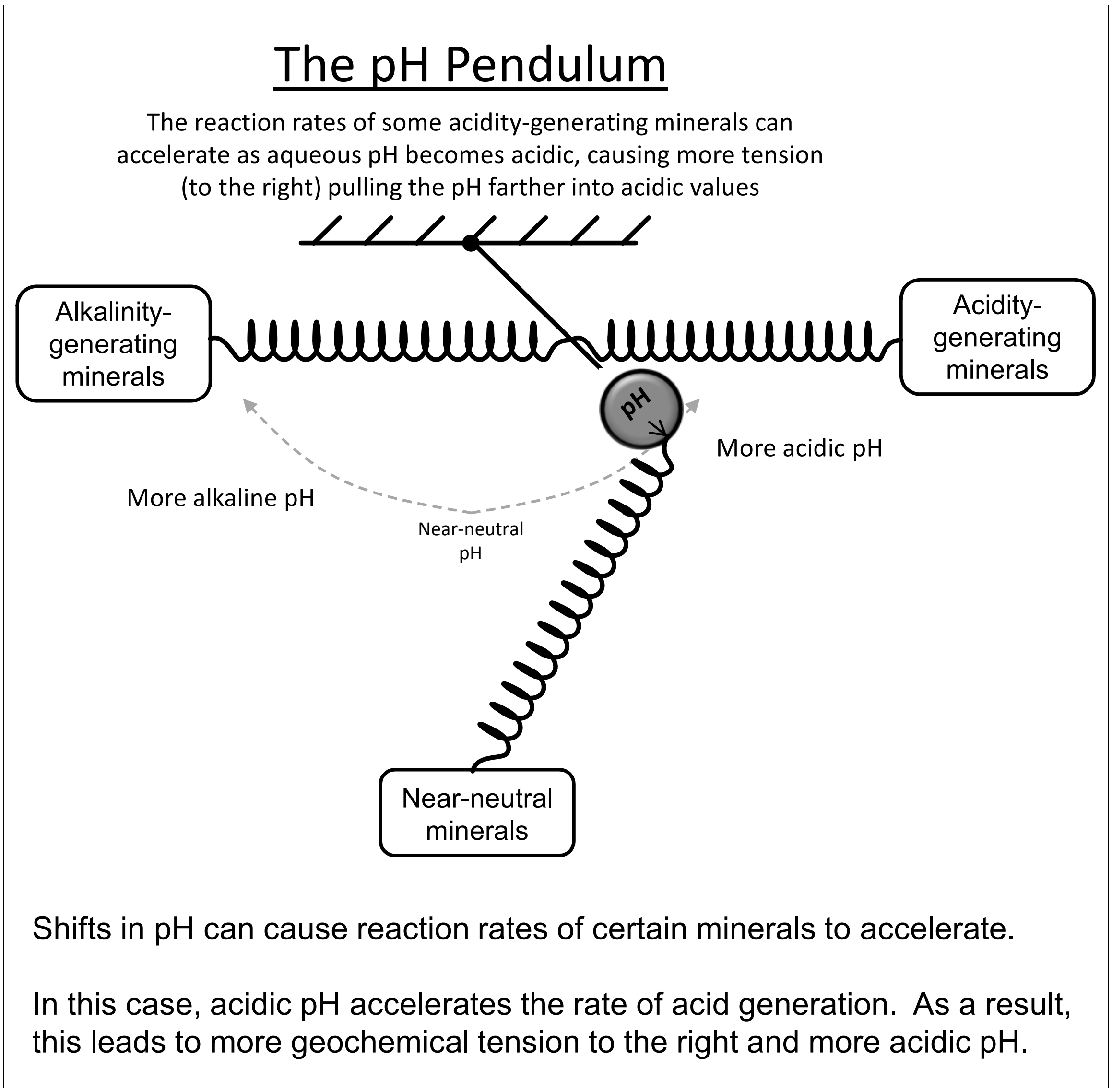

Figure 5. The conceptual model of Dynamic Geochemical Tension shown as a pH pendulum with geochemical springs creating tension where attached to differing abrasion-pH groups. In this figure, the stepwise decrease in pH causes the rates of some acidity-generating minerals to increase, leading to further stepwise decreases in pH.

Systems displaying 1/f and the more general $1/f^{\alpha}$ slopes include: fluctuations in tide and river heights, quasar light emissions, heart beat rhythms, firings of single neurons, resistivity in solid state devices, meteorological data, electromagnetic radiation from quasars, the statistics of DNA sequences, mental states in psychology, average seasonal temperature, annual rainfall, highway traffic, voltage across nerve membranes, rate of insulin uptake by diabetics, economic data, and loudness and pitch of music, paint application of automotive metallic colours, and cavitation in pumps.

One origin of 1/fα slopes was explained by Bak (1996) as "self-organized criticality" or SOC.

> "Self-organized criticality is a new way of viewing nature. The basic picture is one where nature is perpetually out of balance, but organized in a poised state – the critical state – where anything can happen within well-defined statistical laws. . . . Most of the changes take place through catastrophic events rather than by following a smooth gradual path. . . . The state is established solely because of the dynamical interactions among individual elements of the system: the critical state is self-organized. Self-organized criticality is so far the only known general mechanism to generate complexity. . . . In general, systems in balance do not exhibit any of the interesting behavior discussed above, such as large catastrophes, 1/f noise, and fractals. . . . [Additionally,] chaos signals have a white noise spectrum [α = 0], not 1/f. One could say that chaotic systems are nothing but sophisticated random noise generators . . . In short, chaos cannot explain complexity".

Upon comparing the previous quotation with Section 3 of this MDAG case study (Figures 2 to 5), common themes can be seen. These include "organized in a poised state", "catastrophic events rather than by following a smooth gradual path", and "dynamical interactions among individual elements of the system".

Therefore, Dynamic Geochemical Tension (DGT) combined with Self-Organized Criticality (SOC) is one explanation for 1/f slopes in minesite-drainage chemistry. This is not proof that SOC is the only explanation. Other potential explanations include superimposed relaxation processes of differing temporal cycles, the Tweedie hypothesis, and superimposed flowpaths of varying lengths with high dispersivities. These other potential explanations will be discussed elsewhere.

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