

## Testing competing hypotheses for soil magnetic susceptibility using a new chemical kinetic model

### Magnetic susceptibility measurements

All samples in Blundell et al. (2009) were measured at 470 Hz on 10 ml samples using a Bartington Instruments dual frequency MS2B sensor, expressed as mass specific low-frequency  $\chi_{lf}$ .

### Reaction included in the model

Figure 1 outlines the reactions included in the model, the data used to develop kinetic expressions, and the empirical parameterisations used to allow for temperature and pH controls.

### Reactions and minerals omitted from calculations

Lepidocrocite, which transforms to maghemite only through dehydration during heating by fire is ignored. Oxidative transformation of magnetite to maghemite, and dissolution of magnetite in persistently anoxic conditions are both neglected. It is well known that pedogenic magnetite can oxidise to maghemite, but there are no suitable reaction rate data from which to establish a kinetic model. Fortunately, the magnetic properties of pedogenic magnetite and maghemite are similar, so disregarding this little alters the predicted  $\chi_{lf}$  enhancement. Dissolution of secondary magnetite occurs in the presence of sulphide by depressing the  $Fe^{2+}$  activity; we assume such dissolution is otherwise negligible, restricting application of our model to sulphide-free environments.

### ALLOGEN model

ALLOGEN is a process model of soil mineral chemical weathering. It is constructed around a generalised version of the mineral-weathering submodel of PROFILE, which exploits a practical implementation by Sverdrup and Warfvinge (1988) of transition state theory, but is modified to minimise the need for site-specific data and to optimise performance for long-term change. Comparison with observed weathering rate data (river flux studies, chronosequences and lake sediment chemical stratigraphy: Boyle, 2007) suggests that soil mineral depletion can be reliably simulated. This being the case, and given representative mineral compositions, the release rates of specific elements should also be reliably simulated. However, demonstrating directly this by comparison with either experimental data or field observations is difficult owing to questions of comparability. What can be done is to show that there is broad compatibility. For example, the data of White (2007) yields a chlorite contribution to total Fe export for the Hauver Branch, Catoctin Mountains, of  $6.2E-12$  moles/litre/second (that is, per litre of soil), if we assume a contributing soil thickness of 25 cm (White, 2007, quotes this only as lying between 0 and 50 cm). In comparison, using the regolith mineralogy data of White (2007), ALLOGEN predicts the Fe flux from chlorite to be  $9.2E-12$ .

### **Conversion of SFM concentration to magnetic susceptibility ( $\chi_{lf}$ ).**

This assumes production of nanoscale magnetite grains lying in superparamagnetic and stable single domain regions (10-30 nm) with a mean  $\chi_{lf}$  value of  $1000 \times 10^{-6}$  m<sup>3</sup>/kg (Maher, 1988; Heider et al., 1996; Dearing et al., 1997).

### **Mineral concentrations in Santa Cruz marine terraces and Chinese loess**

Mineral concentration data for Santa Cruz marine terrace mean parent material is estimated from White et al. (2008). Chlorite in Chinese loess is calculated assuming a mean chlorite MgO concentration of 13.07 wt% and a mean carbonate-free loess MgO concentration of 2.05 – 2.44 wt% (Ji et al., 2006).

### **Mineral concentrations in selected British mudrock types**

Table 1 shows the data used to compare predicted and observed magnetic susceptibility for a limited subset of British rock types. The mineral magnetic and climate data are from the England and Wales data set described in the main text (Blundell et al., 2009). The parent material information is derived from the cited references.

### **Assumptions used in predicting the $\chi_{lf}$ values for the northern hemisphere sites of Maher and Thompson (1995).**

Only the MAP values are listed in Maher and Thompson (1995). Field capacity days were approximated using an empirical sigmoidal curve for England and Wales (unpublished) ( $365 * (1 - (1 / (1 + \text{EXP}(0.0025 * (\text{MAP} - 850))))$ ), where MAP is in mm/yr. MAT was set at 9 Celcius for all sites. Parent material chlorite concentration is unknown, so curves were generated for four different values.

## **References**

- Barrón, V., Torrent, J., and De Grave, E., 2003, Hydromaghemite, an intermediate in the hydrothermal transformation of 2-line ferrihydrite into hematite, *American Mineralogist*, v. 88, p. 1679–1688.
- Bonneville, S., van Cappellen, P. and Behrends, T., 2004, Microbial reduction of iron(III) oxyhydroxides: effects of mineral solubility and availability, *Chemical Geology*, v. 212, p. 255-268.
- Boyle, J.F., 2007, Simulating loss of primary silicate minerals from soil due to long-term weathering using Allogen: Comparison with soil chronosequence, lake sediment and river solute flux data, *Geomorphology*, v. 83, p. 121-135.
- Dearing, J.A., Bird, P.M., Dann, R.J.L., and Benjamin, S.F., 1997, Secondary ferrimagnetic minerals in Welsh soils: a comparison of mineral magnetic detection methods and implications for mineral formation, *Geophysical Journal International.*, v. 130, p. 727-736.

Evans, L.J. and Adams, W.A., 1975, Chlorite and illite in some Lower Palaeozoic mudstones of Mid Wales, *Clay Minerals*, v. 10, p. 387-397.

Hansel, C.M., Benner, S.G., and Fendorf, S., 2005, Competing Fe(II)-induced mineralization pathways of ferrihydrite, *Environmental Science and Technology*, v. 39, p. 7147-7153.

Heider, F., Zitelsberger, A. and Fabian, K., 1996, Magnetic susceptibility and remanent coercive force in grown magnetite crystals from 0.1 mm to 6 mm, *Physics of Earth and Planetary Interiors*, v. 93, p. 239-256.

Jeans, C.V., 2006a, Clay mineralogy of the Jurassic strata of the British Isles, *Clay Minerals*, v. 41, p. 187-307.

Jeans, C.V., 2006b, Clay mineralogy of the Cretaceous strata of the British Isles, *Clay Minerals*, v. 41, p. 47 - 150.

Ji, J., Zhao, L., Balsam, W., Chen, J., Wu, T. and Liu, L., 2006, Detecting chlorite in the Chinese loess sequence by diffuse reflectance spectroscopy, *Clays and Clay Minerals*, v. 54, p. 266-273.

Kirby, C.S., and Brady, J.A.E., 1998, Field determination of Fe<sup>2+</sup> oxidation rates in acid mine drainage using a continuously-stirred tank reactor, *Applied Geochemistry*, v. 13, p. 509-520.

Maher, B.A., 1988, Magnetic properties of some synthetic sub-micron magnetites, *Geophysical Journal*, v. 94, p. 83-96.

Maher, B.A. and Thompson, R., 1995, Paleorainfall reconstructions from pedogenic magnetic susceptibility variations in the Chinese loess and paleosols. *Quaternary Research* v. 37, p. 383-391.

Mottershead, D.N., 2000, Weathering of coastal defensive structures in southwest England: a 500 year stone durability trial, *Earth Surface Processes and Landforms*, v. 25, p. 1143-1159.

Schwertmann, U., Stanjek, H., and Becher, H. -H., 2004, Long-term in vitro transformation of 2-line ferrihydrite to goethite/hematite at 4, 10, 15 and 25°C, *Clay Minerals*, v. 39, p. 433-438.

Sverdrup, H., Warfvinge, P., 1988, Weathering of primary silicate minerals in the natural soil environment in relation to a chemical weathering model, *Water Air Soil Pollut.*, v. 38, p.387-408.

White, A.F., 2007, Quantitative approaches to characterizing natural chemical weathering rates, In, Brantley, S.L., Kubicki, J.D. and White, A.F. (eds). *Kinetics of Water-Rock Interaction*, Springer New York, Chapter 10, p. 469-543.

**Table DR1.** Mineral reactions incorporated into the model. All rates and quantities are expressed on a volumetric basis (mass or rate per unit volume of soil) and converted to soil water concentrations in the soil water for reaction rate calculations by dividing the flux of the species (moles per second per litre of soil) by the flux of water (litres per second per litre of soil).

Table DR1 - Mineral reactions incorporated into the model.

Boyle, Dearing, Blundell & Hannam

Process	Explanation
<p><b>Chemical weathering of Fe silicates</b></p> <p><b>Reaction</b>     <u>Primary Fe silicate</u> + 2H<sup>+</sup> → <u>Secondary silicate</u> + Fe<sup>2+</sup> + <u>other dissolved species</u></p> <p><b>Rate expression</b>     See Boyle, 2007</p>	<p>The ALLOGEN model (Boyle, 2007) is used to calculate the expected Fe release rate due to weathering. It uses experimentally determined mineral reaction kinetics applied in a soil hydrology framework.</p>
<p><b>Oxidation of dissolved Fe<sup>2+</sup> ions to HFO</b></p> <p><b>Reaction</b>     •            Fe<sup>2+</sup> → Fe<sup>3+</sup> + e<sup>-</sup></p> <p>                  •            Fe<sup>2+</sup> + 3OH<sup>-</sup> → Fe(OH)<sub>3</sub> (HFO)</p> <p><b>Rate expression</b>     Rate of HFO production (moles litre<sup>-1</sup> s<sup>-1</sup>) = k[Fe<sup>2+</sup>] where, k = 10<sup>-3.7</sup>, and [Fe<sup>2+</sup>] = is the concentration of dissolved Fe<sup>2+</sup> (moles litre<sup>-1</sup>)</p>	<p>Expression 2 is assumed to be the rate limiting step. The experimental data of Kirby and Brady (1998) have been used to quantify the oxidation rate of Fe<sup>2+</sup> under field conditions. The reaction rate is assumed to be first order with respect to [Fe<sup>2+</sup>], independent of pH within the typical range in temperate soils, and independent of [O<sub>2</sub>] under oxygenated conditions.</p>
<p><b>Reduction of HFO to Fe<sup>2+</sup> by dissimilatory iron reducing bacteria (DIRB) under reducing conditions</b></p> <p><b>Reaction</b>     Fe(OH)<sub>3</sub> + e<sup>-</sup> → Fe<sup>2+</sup> +            3OH<sup>-</sup></p> <p><b>Rate expression</b>     Rate of Fe<sup>2+</sup> production (moles litre<sup>-1</sup> s<sup>-1</sup>) = C<sub>f</sub>f[HFO] where, C = cell count (cell litre<sup>-1</sup>); and [HFO] = hydrous ferric oxide concentration (moles litre<sup>-1</sup>) Log<sub>10</sub>(f[HFO]) = 0.9 * (1 - e<sup>-(Log<sub>10</sub>[HFO] + 3.79))</sup>) - 20.5</p>	<p>Based on the experimental data of Bonneville et al. (2004) the cell-specific reduction rate is strongly, but non-linearly, dependent upon the HFO concentration.</p> <p>The cell-specific rate function, f[HFO], is approximated empirically based on the data of Bonneville et al. (2004).</p>
<p><b>Transformation of HFO to goethite and hematite</b></p> <p><b>Reaction</b>     •            Fe(OH)<sub>3</sub> → FeOOH (Goethite) + H<sub>2</sub>O</p> <p>                  •            2Fe(OH)<sub>3</sub> → Fe<sub>2</sub>O<sub>3</sub> (Hematite) + 3H<sub>2</sub>O</p> <p><b>Rate expression</b>     Combined rate (moles litre<sup>-1</sup> s<sup>-1</sup>) = k(pH,T)[HFO] where [HFO] = hydrous ferric oxide concentration (moles litre<sup>-1</sup>), and k(pH,T) = rate coefficient, which varies with both pH and temperature log(k(pH,T)) = 0.06258 * T + 0.0361pH<sup>2</sup> - 0.262pH - 8.51</p>	<p>Comprehensive experimental investigation of the low-temperature transformation of HFO to goethite and hematite has been undertaken by Schwertmann et al. (2004). The half-time data for transformation to goethite plus hematite are here expressed in the form of first order constants.</p> <p>log(k(pH,T)) varies as a linear function of temperature, with a regression constant that varies as a polynomial function of pH</p>
<p><b>Transformation of HFO to maghemite</b></p> <p><b>Reaction</b>     •            2Fe(OH)<sub>3</sub> → Fe<sub>2</sub>O<sub>3</sub> (Maghemite) + 3H<sub>2</sub>O</p> <p><b>Rate expression</b>     Rate of formation (moles litre<sup>-1</sup> s<sup>-1</sup>) = k[HFO], where, k = first order rate constant (s<sup>-1</sup>)</p>	<p>The experimental data of Barrón and Torrents (2003) for experimental aging of doped (citrate or phosphate) HFO have been fitted with a first order rate constants calculated using half-time estimates (k = ln(2)/t<sub>0.5</sub>). Extrapolating their experimental data to 10°C (a very long way) yields log(k) = -12.2 (s<sup>-1</sup>).</p>
<p><b>Reaction of HFO with Fe<sup>2+</sup> to form magnetite</b></p> <p><b>Reaction</b>     2Fe(OH)<sub>3</sub> + Fe<sup>2+</sup> + 2OH<sup>-</sup> → Fe<sub>3</sub>O<sub>4</sub> (Magnetite) + 4H<sub>2</sub>O</p> <p><b>Rate expression</b>     Rate of formation (moles litre<sup>-1</sup> s<sup>-1</sup>) = k<sub>(T,pH)</sub>[Fe<sup>2+</sup>][HFO] The value of K at 22°C and pH = 7 is 0.0006 (litre moles<sup>-1</sup> s<sup>-1</sup>). This is adjusted for temperature and pH using expressions below. k(T, pH) = k<sub>[22°C, pH 7]</sub> * (T-22)<sup>0.06258</sup> * e<sup>(pH-7)</sup> * 1.428</p>	<p>The data of Hansel et al. (2005) are consistent with the kinetic expression shown. The rate coefficient varies with pH, quantified for pH values of 7 and 8. It must also vary with temperature but this has not been studied. For compatibility with the goethite and hematite transformations, for which there are excellent temperature data, the same temperature dependence has been assumed (k ∝ 0.06258T). This is equivalent to assuming that there is no temperature impact on the relative rate of magnetite formation against the other oxides, consistent with field data (Blundell et al., 2009).</p>

**Table DR2. Mineralogy, climate, and magnetic susceptibility of mudrocks from England and Wales**

<b>Argillaceous rock age class</b>	<b>log mean N χ</b>	<b>MAP mm/yr</b>	<b>MAT °C</b>	<b>Oxic fract.</b>	<b>Chlorite wt%</b>	<b>Rock category</b>	
Cambrian	1.08	12	1530	8.7	0.24	26	Lower Palaeozoic mudstones, Wales (1)
Cretaceous	0.30	141	730	9.6	0.58	4	Clay dominated formations (< 2 μm) (2)
Devonian	1.86	156	1120	9.7	0.36	38	Slates and mudrocks, Devon (3)
Jurassic	0.39	542	640	9.3	0.63	10	Clay dominated formations (< 2 μm) (4)
Ordovician	0.75	84	1350	8.5	0.29	26	Lower Palaeozoic mudstones, Wales (1)
Silurian	0.81	121	1160	8.5	0.29	26	Lower Palaeozoic mudstones, Wales (1)

1. Evans and Adams (1975).
2. Jeans (2006a)
3. Mottershead (2000)
4. Jeans (2006b)