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**GRANT:** **DE-FG02-01ER15173**

**TITLE:** **Plants, Weathering, and the Evolution of Atmospheric Carbon Dioxide and Oxygen**

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## **FINAL REPORT**

Over the past six years we have completed several studies related to the proposed research. They can be divided into three sections: (1) Study of plants and weathering, (2) modeling the evolution of atmospheric CO<sub>2</sub> over Phanerozoic time (past 550 million years). (3) Modeling of atmospheric O<sub>2</sub> over Phanerozoic time. **References to papers published acknowledging this grant can be found at the end of this report and almost all are supplied in pdf form.**

### **(1) PLANTS AND WEATHERING**

The PhD thesis research of graduate student Megan Andrews is completed and presently is in the final stages of being written up for publication and for submission as a dissertation for the PhD degree from Yale University. Already two abstracts have been presented at national and international meetings (Andrews et al, 2006; 2007). Her research was conducted both in the field and in the laboratory. In the field she studied weathering beneath adjacent angiosperms and gymnosperms, both developed on the same rock type and under the same climate, in the Cascade Mountains of Washington State. She undertook bulk soil chemical analysis and the examination of the degree of mineral etching at the root-mineral interface. In the laboratory she analyzed the chemistry of soil water and that associated with litter decomposition, and the degree of etching of minerals attached to plant roots. Her results can be summarized as follows:

#### **Field study**

- Root density profiles are mirror images for angiosperms and gymnosperms at the study site: gymnosperms are most concentrated in top 10cm of soil, angiosperms in the bottom 10cm
- Several distinct soil element weathering patterns:
  1. Angiosperm leaching > gymnosperm leaching by 20-40% (Ca, Na, S)
  2. Gymnosperm leaching > angiosperm leaching by 20% (e.g. Mo, P, Be, La, Al, Ba, K, Ce, Zn, Cr,)
  3. Gymnosperm leaching >> angiosperm leaching by 30-40% (Li and Fe)
  4. Elements concentrated beneath angiosperms and leached beneath gymnosperms (V, Ni, Cu, Lu, Mn, Mg, Co, Cd,)
- Bulk chemistry of leaves/needles and twigs show different chemical vegetation compositions for angiosperms and gymnosperms, which supports different nutritional needs and physiologies
- Electron microprobe analysis of soil cores support the bulk element patterns for the major elements
- Soil textures, and presence or absence of clay, correlate with root density, as does intensity of mineral etching
- Minerals (e.g. plagioclase, feldspar, and biotite) are more highly etched near individual gymnosperm roots than angiosperm roots, but the integrated effect over the soil depth due to different root distributions explain the higher leaching of some elements beneath the angiosperms

### **Lab decomposition experiment**

- Conifer litter decomposition creates acidic soil (pH 5.5) and contains ~5x more dicarboxylic acids than neutral (pH 7.0) soil beneath maple litter decomposition
- Entire tree decomposition, maple or conifer, produces circumneutral soil pH and lower total organic acids concentrations; conifer tree soil has ~2x more dicarboxylic acids than the maple tree soil
- Conifer needles main source of decomposition acids for conifer tree; maple leaves are only a minor source of acids for the maple tree decomposition
- High levels of dicarboxylic acids and low pH account for mineral etching occurring beneath the conifer needles and not occurring beneath the maple litter

### **Lab tree growth experiment**

- Soil pH ~0.5 pH units lower beneath conifers compared to maples
- Organic acids in rhizosphere soils were ~2-10x more than in bulk soil from the same experiment
- Dicarboxylic acids were ~2-4 times greater in conifer soils than in maple soils
- Maple roots formed a fine, dense mat in the lower half of the soil while conifer roots were more spread out, penetrated less deeply, and had fewer fine networks
- Mineral etching of biotite was much greater beneath conifers
- Mineral etching of albite was much greater beneath the maples

- Lower pH and greater dicarboxylic acid concentrations beneath the conifers account for greater biotite etching, despite more scattered roots
- Dense root networks leading to greater mineral-root contact beneath the maples contributes to the overall greater etching of the plagioclase, despite lower concentrations of chelating organic acids

### **Implications for the effect of tree-induced weathering on the evolution of atmospheric CO<sub>2</sub>**

Carbon dioxide is removed from the atmosphere predominantly by the tree-accelerated weathering of Ca and Mg silicate minerals, and the evolution of trees over time, with the later introduction of angiosperms, may have had a major affect on the evolution of atmospheric CO<sub>2</sub>. In the temperate forests of this study, calcium and magnesium meet vastly different fates beneath the two types of trees. Calcium is leached beneath both groves of trees, but leached 20-40% more beneath the angiosperms. Magnesium is retained in the forest system beneath the angiosperms and leached from beneath the gymnosperms. Ca and Mg bearing minerals (particularly hornblende) were significantly etched beneath the gymnosperms and barely etched beneath the angiosperms. Thus, when considering the consumption of CO<sub>2</sub>, to form the dissolved bicarbonate in rivers that accompanies weathering-derived fluxes of Ca and Mg, it is critical to know which kinds of trees are present on which lithologies.

## **(2) MODELING OF PHANEROZOIC CO<sub>2</sub>**

At the very beginning of the grant a major paper was published (Berner and Kothavala, 2001) that summarized the latest GEOCARB calculations of CO<sub>2</sub> over Phanerozoic time (this was actually supported by the previous DOE grant). The paper to date has been cited over 200 times. Since then the modeling work has been further updated and extended to a number of problems. This includes application to the extinction and possible carbonate under-saturation that occurred at the Jurassic-Triassic boundary (Beerling and Berner, 2002, Berner and Beerling, 2007), compilation of new data on the role of plants in weathering (Berner et al, 2003), the relation between rates of global carbon burial, CO<sub>2</sub> and the formation of fossil fuels (Berner 2003a), application of CO<sub>2</sub> modeling to the weathering of Ca, Mg and S and the change in the concentration of these elements in seawater over time (Berner, 2004), the role of feedbacks in the co-evolution of plants and CO<sub>2</sub>, (Beerling and Berner, 2005) , the further expansion of the GEOCARB model to include both CO<sub>2</sub> and O<sub>2</sub> via a combined GEOCARBSULF model (Berner, 2006a), and the addition of the effects of basalt weathering as a major control on atmospheric CO<sub>2</sub> (Berner, 2006b).

Of special mention are two additional studies that address the problem of the role of CO<sub>2</sub> as a greenhouse gas in global warming (Royer et al, 2004; 2007). In the first paper we show that climate and CO<sub>2</sub>, based on both GEOCARB modeling and hundreds of independent proxies for paleo-CO<sub>2</sub>, correlate very well over the past 550 million years, and that an alternate theory of the control of climate by cosmic rays has many problems. In the latter 2007 paper we use this correlation to deduce the sensitivity of global mean

temperature to a doubling of atmospheric CO<sub>2</sub>, and results are in excellent agreement with the results of climatologists based on the historical record and on theoretical climate models (GCM's).

### **(3) MODELING OF ATMOSPHERIC O<sub>2</sub>**

During the past 6 years important new insights have been gathered on the evolution of atmospheric O<sub>2</sub> over the Phanerozoic and both its causes and its effects on biological evolution. Modeling of O<sub>2</sub> was updated and combined with the GEOCARB model for CO<sub>2</sub> by adding the sulfur cycle to the carbon cycle, resulting in the new model GEOCARBSULF (Berner, 2006). The results were then applied to evolutionary events, including the invasion of land by arthropods and vertebrates (Ward et al, 2006), the extinction at the end of the Permian period (Berner, 2005) and other major extinction and evolutionary events over the Phanerozoic (Berner et al, 2007). A large mid-Paleozoic rise in O<sub>2</sub> was ascribed to increased net global photosynthesis due to the rise of vascular land plants (Berner, 2003b)

Several satellite studies were done to improve O<sub>2</sub> modeling. This includes a multi-disciplinary study of the effect of O<sub>2</sub> levels on the burning of natural forest materials (Wildman et al, 2004). It was found that previous statements, that minimized allowable levels of O<sub>2</sub> for the preservation of past forests against global conflagration, were incorrect and that calculated past concentrations as high as 30% could have been attained. We also found, via field studies and theoretical modeling (Wildman et al 2004b, Bolton et al, 2006) that the rate limiting factor in the consumption of O<sub>2</sub>, by the weathering of organic matter and pyrite in shales, is the rate of uplift, erosion and exposure of fresh rock to weathering and not the level of O<sub>2</sub> in the atmosphere. This negates previous assumptions of a simple O<sub>2</sub>-weathering feedback.

We also examined other methods for deducing Phanerozoic levels of O<sub>2</sub>. A review of these methods is presented by Berner et al (2003). In this paper it is shown that O<sub>2</sub> levels much higher than at present were present during the Carboniferous and Permian periods based, on (1) the presence at that time of giant insects which could not fly under present-day O<sub>2</sub> levels. (2) increased fractionation of carbon isotopes during photosynthesis evidenced by the <sup>13</sup>C content of fossil plants (see also Beerling et al, 2002), (3) the anatomy of plants of this age which show special structures to resist burning and (4) burning experiments discussed above.

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