FROM RHIZOSPHERE TO ECOSYSTEM: HEAVY METALS AND PLANT DEFENSE

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Human use and manipulation of our natural resources, especially since the industrial revolution, has accelerated the introduction of HM's into soils resulting in a dramatic increase in their concentration in many soils of the United States (and beyond). Many of these HM's even at very low concentrations are toxic and reside in sites that are close to large and often socially downtrodden populations, and hence, pose a significant threat to both human health and the environment. Few remediation technologies have been effective at treating HM enriched soils *in-situ*. Phytoextraction, the use of specialized metal hyperaccumulating plants to remove metals from soils has been growing in popularity because it overcomes many of the limitations of conventional remediation methods. address the ecological implications that could arise from planting non-native plants capable of transferring metals from the soil to the shoots of the plant where they can then be introduced into the food chain, and/or have undesirable effects on ecosystem structure and function.

Elucidating how metals in specialized metal hyperaccumulating plant tissues influence plant physiology and insect feeding behavior is fundamental to understanding the evolution of this unique trait and the influence these plants may have on ecosystem structure and function. The elemental defense hypothesis (EDH) states that metals taken up and stored are effective at protecting plants from insect herbivores because of the inherent toxicity or unpalatability of the metals. A concomitant hypothesis, known as the trade-off hypothesis, states that plants will trade more physiologically costly chemical defenses (e.g. glucosinolates (GL's)) for less costly metal defenses. The objectives of this study were to investigate these hypotheses by examining the spatial and temporal relationship between Zn and GL concentration and speciation in leaves of the model Zn hyperaccumulator *Noccaea caerulescens* (formerly *Thlaspi caerulescense*) and assess how these patterns influence insect feeding behavior. A six week greenhouse study was conducted with *N. caerulescens* grown in soil receiving 250, 500 and 1000 uM Zn treatments. At the end of the experiment whole plant metal concentrations were determined in addition to the analysis of young, medium and old leaves for total metal content (ICP-MS), total GL's (as glucose) and GL species (HPLC). Metal distribution was also determined in young, medium and old leaves using synchrotron based x-ray fluorescence (SXRF) mapping and scanning electron microscopy (SEM-EDX), and the spatial distribution of specific GL's determined using matrix assisted laser desorption time of flight mass spectrometry (MALDI TOF/TOF MS) chemical mapping. The influence of these patterns on insect feeding behavior was assessed using the generalist herbivore *Trichoplusia ni* (Cabbage looper) in choice and no-choice feeding experiments. Preliminary results show that the concentration and distribution of Zn in young, medium and old leaves is inversely proportional to that of GL's with the younger leaves having a higher GL content than older leaves. Feeding patterns are alterned in response ot Zn concentrationa and distribution in the leaves providing evidence for the trade-off hypothesis.

Siqueiros Transform MORB; characteristics of a S-saturated suite

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Geochemically diverse mid-ocean ridge basalts, with a significant range of major and trace element contents in pillow-rim glasses, were recovered from the Siqueiros Transform Fault, in the East Pacific Ocean. All these glasses were S-saturated at eruption, on the basis of the presence of immiscible sulfide globules (Fig. 1A). Based on the compositions of silicate melt inclusions in early-crystallised olivine phenocrysts, previous workers [1] have interpreted the early Siqueiros liquids, which were less fractionated than the pillow-rim glasses, to be S-undersaturated. However, since we have observed numerous inclusions of immiscible sulfides in the same early olivine phenocrysts, we interpret that most of Siqueiros parental liquids were S-saturated early in their fractionation history. The compositions of these immiscible sulfide liquid inclusions in olivine are consistent with those from other MORB suites [2] and estimates of sulfide liquid compositions from mantle rocks (e.g., [3]). In the Siqueiros samples S-Saturation appears to be largely independent of liquid composition over a wide compositional range, and is only controlled by total Fe content (Fig. 1B).

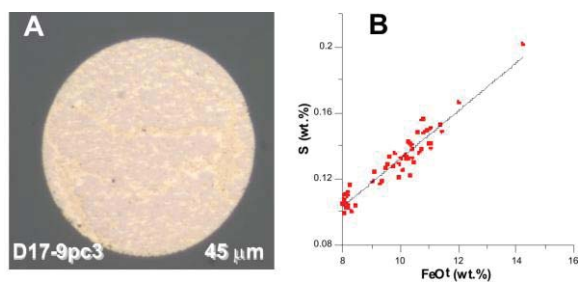

Figure 1: A; reflected light image of a 'quenched' immiscible sulfide globule in pillow-rim glass. B; relationship between FeO^t (all Fe as FeO) and S for Siqueiros Transform Fault pillow-rim glasses. The strong correlation indicates S-saturation (see [4]).

Laser Raman analyses, using the method of [5], of primitive and evolved pillow-rim glasses indicate that all S is present at S^{2-} and that the maximum fO_2 is therefore close to QFM. Mössbauer analyses are being completed to confirm the fO_2 of the pillow rim glasses.

Our data from the erupted basalts and inclusions provides a well constrained natural dataset that has been combined with experimental data to produce a new sulfur saturation model [6] and can be used to test the results of this and other models.

[1] Saal *et al.* (2002) *Nature* **419**, 451-455. [2] McNeill *et al.* (2009) *Proc. Xi'an Int. Ni-Cu Deposit Symposium.*, 4-5. [3] Luguet *et al.* (2003) *Geochim et Cosmochim acta* **67**, 1553-1570. [4] Wallace and Carmichael (1992) *Geochim et Cosmochim acta* **56**, 1863-1874. [5] Klimm *et al.* (submitted). [6] Bychkov *et al.* (2010) *13th IAGOD Symposium*, 304-305.