

A possible mechanism for Mn release when soils are dried

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Chemical changes are known to occur when moist soils dry [1]. One of the most noticeable changes is the significant increase in exchangeable Mn in dried soils. In addition to this it has been observed that dried soils show a definite decrease in Cr oxidising capacity. It has been suggested that changes in the nature of humic substances may be responsible for these changes although how this occurs is unclear.

In the Mpumalanga Province of South Africa there are oxisols which are extremely enriched in Mn (up to 16 weight percent). Drying has a profound effect on the redox chemistry of these soils. To elucidate this drying effect we used a range of redox tests as well as surface-specific, attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. With ATR-FTIR we were able to investigate the chemical changes that occur on a drying surface. These changes included a marked drop in surface pH to below 1.6 as well as a change in the sorption of oxalate from a more outer-sphere to a more inner-sphere type of surface complex. From these results and the redox analyses we suggest a mechanism for drying-induced Mn release and suppression of Cr oxidising capacity in soils which involves the formation of Mn(III)-organic complexes through a reverse disproportionation reaction induced by the combination of low pH and the stabilising effect of an organic ligand.

Reference

- [1] Bartlett, R. J. & James, B. R. (1980) Studying, dried stored soil samples - some pitfalls, *Soil Science Society of America Journal*. 44, 721-724.

Kinetics of diamond oxidation at various oxygen fugacities

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Variations in the oxygen fugacities (fO_2) of kimberlite magmas from the Lac de Gras kimberlite field (N.W.T., Canada) show correlation with the dissolution features of diamonds recovered from these kimberlites and their diamond content. The goal of the present experimental study is to quantitatively constrain the effect of the fO_2 on the kinetics of diamond oxidation. We used diamonds with different colours, nitrogen content and other properties to test how the properties of the diamond might influence its oxidation rate in CO₂-CO gas mixtures. Oxidation was measured by weight loss, and diameter change of the diamond.

Diamond oxidation experiments in CO₂-CO gas mixtures at 100 kPa, temperatures 1000°, 1050° and 1100°C and various log fO_2 from the range -9.6 to -16.1 ±0.1 gave a logarithmic relationship between the rate of diamond oxidation and fO_2 :

$$\log V_{\text{oxidation}} = 0.264 \log fO_2 - \text{Temperature term}$$

This function allows us to calculate the change in diamond oxidation rate with fO_2 as follows:

$$V_1/V_2 = 10^{0.264(\log fO_2(1) - \log fO_2(2))}$$

The derived relationship between the rate of diamond oxidation and fO_2 shows that the difference in 1 log unit of fO_2 will result in almost twice as fast oxidation in CO-CO₂ gas mixture. At fO_2 of the Lac de Gras kimberlites (log fO_2 = -1 log units relative to iron-wustite buffer) and 1100°C diamond of 1 mg will be oxidized in 10 hours and 0.5 carat stone in 1.5 month. At these conditions we found no effect of diamond colour (degree of plastic deformation) on the oxidation rate. The fO_2 effect on diamond oxidation in melts at high pressure and the effect of variable nitrogen content in diamonds will be studied in the future experiments.