

## Organo-mineral associations in density fractions of contrasting soils

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### Abstract

Organo-mineral interactions are important for the preservation of organic carbon (OC) in soils. To understand the role of soil minerals in carbon cycling, we used a sequential density fractionation procedure to isolate <math><1.6</math>, <math>1.6-1.8</math>, <math>1.8-2.0</math>, <math>2.0-2.2</math>, <math>2.2-2.6</math> and <math>>2.6</math> g cm<sup>-3</sup> density fractions in soils of contrasting mineralogies. We sampled 0-10 cm layer from four major Australian soil types - Chromosol, Ferrosol, Sodosol and Vertosol. Organic matter (OM) was found to be partitioned in four distinct pools: i) particulate organic matter <math><1.6</math> g cm<sup>-3</sup>; ii) phyllosilicate dominant <math>1.8-2.2</math> g cm<sup>-3</sup>; iii) quartz and feldspar dominant <math>>2.6</math> g cm<sup>-3</sup>; and iv) Fe oxides dominant <math>>2.0</math> g cm<sup>-3</sup>. X-ray photoelectron spectroscopy was used to investigate organic C and N bonding environments associated within the density fractions. The OC composition of all fractions was highly heterogeneous, representing a continuum of organic compounds. The mineral density fractions were enriched in distinct organic functional groups and we suggest that organo-mineral interactions improved the stability of organic carbon in soils. For example, the phyllosilicate dominant fractions were enriched with oxidised OC species (C-O, C=O, O-C=O) that support association of these species through ligand exchange with mineral edges and H-bonding. Protonated amide forms were also enriched in these fractions, especially in the smectite dominant fractions, which are able to adsorb to the mineral phase by direct electrostatic attraction. Phyllosilicate dominant fractions also displayed an increasing trend in  $\delta^{13}\text{C}$  values and decreasing C:N ratios with increasing density. Meanwhile, quartz and feldspar dominated fractions were enriched in aliphatic C, protonated amide forms and low C:N ratios. Relating bonding mechanisms to associated OM was made difficult in quartz and feldspar dominated fractions by inclusions of Fe oxides bearing minerals; however there is evidence to support H-bonding of lipids across surfaces and electrostatic attraction of proteinaceous substances with unsatisfied siloxane bonds, ligand bonding of O-C=O appears to be important when surfaces have Fe coatings. The Fe oxides dominant fractions had a greater proportion of oxidised C-O, C=O, O-C=O groups that suggest the presence of ligand exchange bonds with surface hydroxyl groups of the Fe oxides. The Fe oxides dominant fractions were also found to contain higher proportions of OC relative to the corresponding fractions in the other soils and displayed enrichment in  $\delta^{13}\text{C}$  with increasing fraction density, and decreases in the C:N ratios which were less pronounced. These results demonstrate the potential of mineral surfaces in influencing the chemical composition of OM bound in surfaces reactions and subsequently the stability of OM in organo-mineral associations.

**Notes**