Calcite and gypsum solubility products in water-saturated salt-affected soil samples at 25°C and at least up to 14 dS m⁻¹

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Summary
Calcite and gypsum are salts of major ions characterized by poor solubility compared with other salts that may precipitate in soils. Knowledge of calcite and gypsum solubility products in water-saturated soil samples substantially contributes to a better assessment of processes involved in soil salinity. The new SALSOL-CHEMIS code for chemical equilibrium assessment was parameterized with published analytical data for aqueous synthetic calcite and gypsum-saturated solutions. Once parameterized, SALSOLCHEMIS was applied to calculations of the ionic activity products of calcium carbonate and calcium sulphate in 133 water-saturated soil samples from an irrigated salt-affected agricultural area in a semi-arid Mediterranean climate. During parameterization, sufficiently constant values for the ionic activity products of calcium carbonate and calcium sulphate were obtained only when the following were used in SALSOLCHEMIS: (i) the equations of Sposito & Traina for the free ion activity coefficient calculation, (ii) the assumption of the non-existence of the Ca(HCO₃)⁺ and CaCO₃⁻ ion pairs and (iii) a paradigm of total ion activity coefficients. The value of 4.62 can be assumed to be a reliable gypsum solubility product (pKs) in simple aqueous and soil solutions, while a value of 8.43 can only be assumed as a reliable calcite solubility product (pKs) in simple aqueous solutions. The saturated pastes and saturation extracts were found to be calcite over-saturated, with the former significantly being less so (pIAP = 8.29) than the latter (pIAP = 8.22). The calcite over-saturation of saturated pastes increased with the soil organic matter content. Nevertheless, the inhibition of calcite precipitation is caused by the soluble organic matter from a dissolved organic carbon threshold value that lies between 7 and 12 mM. The hypothesis of thermodynamic equilibrium is more adequate for the saturated pastes than for the saturation extracts.

Introduction
Calcite and gypsum are, respectively, the major calcium carbonate and calcium sulphate polymorphs in sediments and soils (Doner & Lynn, 1977). They can occur in soils as either primary or secondary minerals, and are particularly abundant in land under arid, semi-arid and dry sub-humid climates. However, calcite is less soluble than gypsum, and therefore less prone to leaching from soils. As a consequence, calcite is more abundant and more widely distributed in soils than gypsum: gypsum does not usually occur alone in soils, but together with calcite.

Calcite and gypsum, together or separately, have a substantial influence on soil properties, especially soil solution chemical properties. Where present, calcite buffers the soil solution pH, alkalinity and the concentration of calcium. Gypsum, on the other hand, also buffers the soil solution concentration of calcium as well as sulphate, and hence a relatively important part of soil solution salinity. If both calcite and gypsum are present, the buffer strength on pH, calcium, sulphate and alkalinity increases.

Calcite and gypsum are salts of major ions characterized by lower solubility compared with the other potentially precipitating salts in soils. Studies of mineral solubility start from the solubility product (Ks) determination, which is a thermodynamic property that, at usual pressures, depends only on temperature. The solubility product of a mineral is equal to the ionic activity product (IAP) of its component ions in the solution once equilibrium with the mineral has been attained. The solubility product determination of a mineral involves either the measurement or calculation of ion activities in the aqueous phase. Currently, the ion activity