Supplementary Material (ESI) for Nanoscale

Carbonate-coordinated metal complexes preceed the formation of liquid amorphous mineral emulsions of divalent metal carbonates†

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Supporting Information

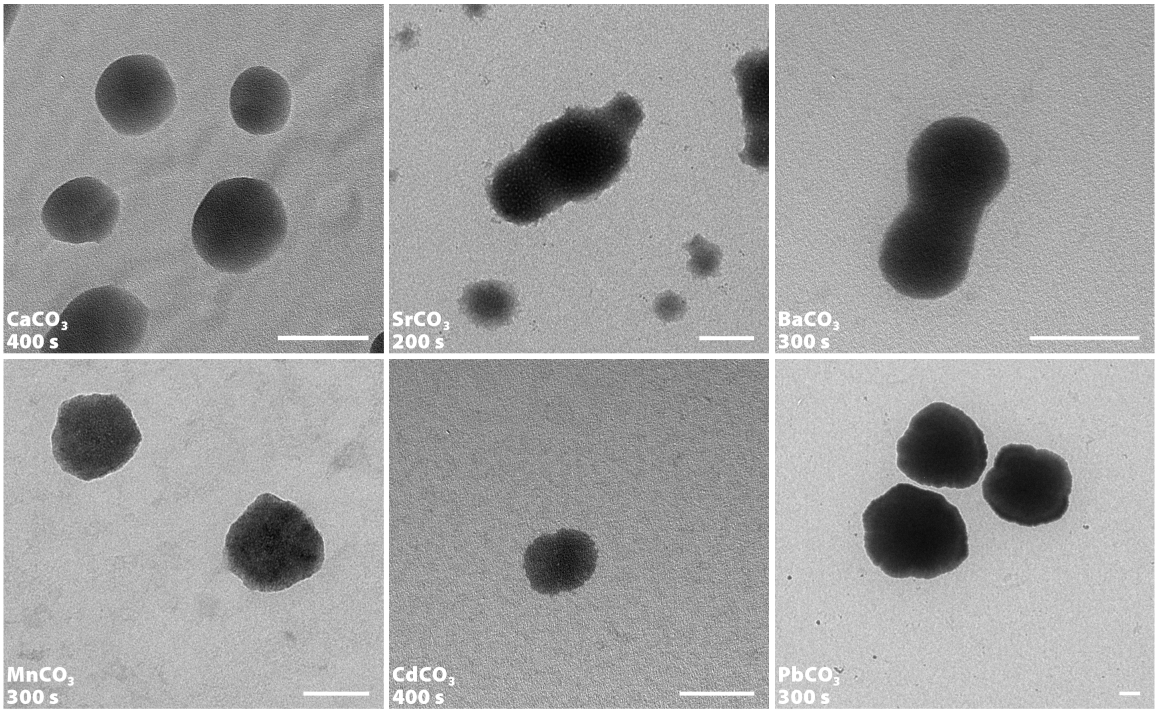


Fig. S1. Transmission electron micrographs of the liquid intermediate particles at higher resolution. The samples were taken at different times as indicated. As the electron beam is much more focused at higher magnifications, some of the samples already suffered from loss of water of hydration (Sr and Mn are most prominent). This drying process finally leads to crystallization. Scale bars: $CaCO_3$ 100 nm, $SrCO_3$ 100 nm, $BaCO_3$ 100 nm, $MnCO_3$ 100 nm, $CdCO_3$ 500 nm, $PbCO_3$ 500 nm.

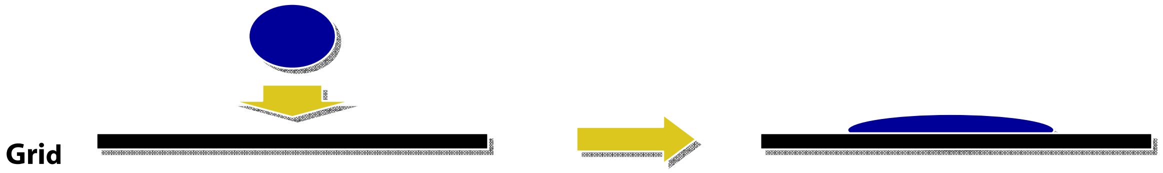


Fig. S2. Sketch of the spreading of a liquid particle on a TEM grid: the sample thickness is nearly constant whereas in case of a sphere. One can describe the situation in the latter case mathematically: the “chord length” l increases with decreasing distance b to the sphere’s center as given by Pythagorean theorem: $l=(r^2-b^2)1/2$.

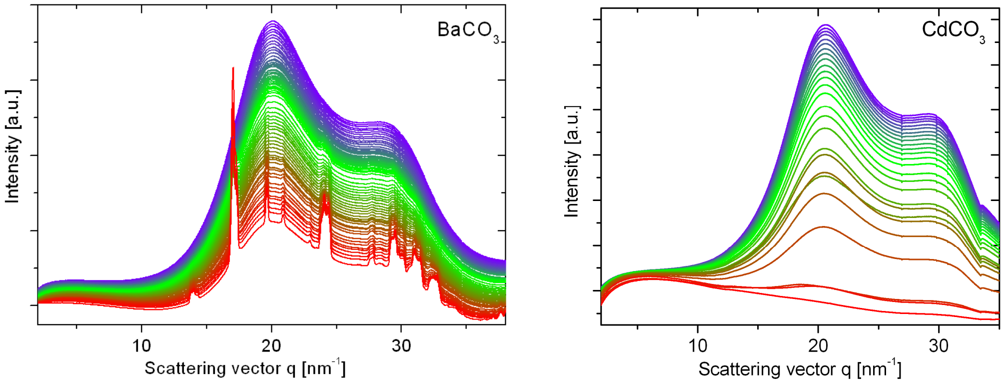


Fig. S3. Wide-angle scattering monitored during evaporation of a saturated divalent bicarbonate solution under levitated contact-free conditions, here barium carbonate and cadmium carbonate. The first scattering curves are colored in blue; the scattering during the last state of experiment is printed in red. Barium carbonate finally forms the mineral phase witherite, which is orthorhombic and isotypic with aragonite (high pressure phase of $CaCO_3$) and stable at ambient conditions. The evaporation of a cadmium bicarbonate solution does not end up in the crystalline material otavite, the cadmium carbonate remains in its amorphous phase.

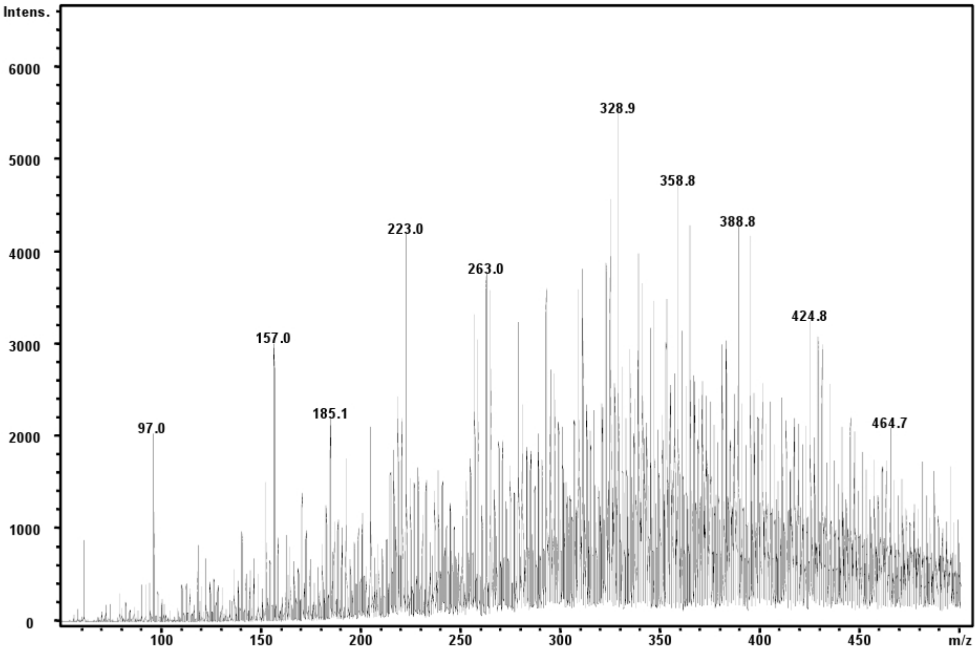


Fig. S4. Negative ESI mass spectrum of a saturated solution of carbon dioxide in water; the signal to noise ratio is very high. Some weak peaks are present; they can be assigned to clusters containing water and carbon dioxide, *e.g.* $[(H_2O)_9(HCO_3)]^-$ (223.0 Da) or $[(H_2O)_{19}(HCO_3)_2(H_2CO_3)]^{2-}$ (263.0 Da).

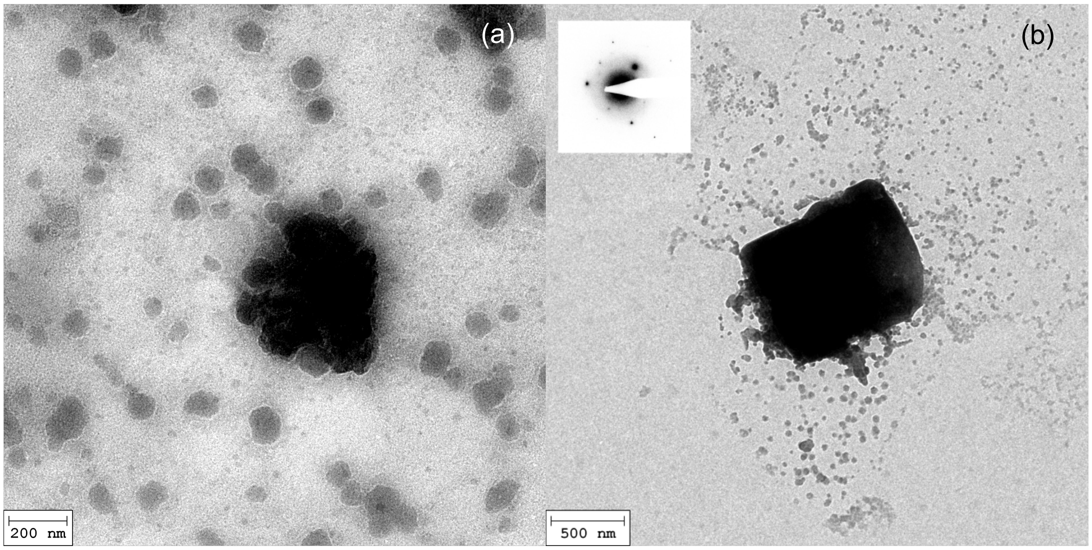
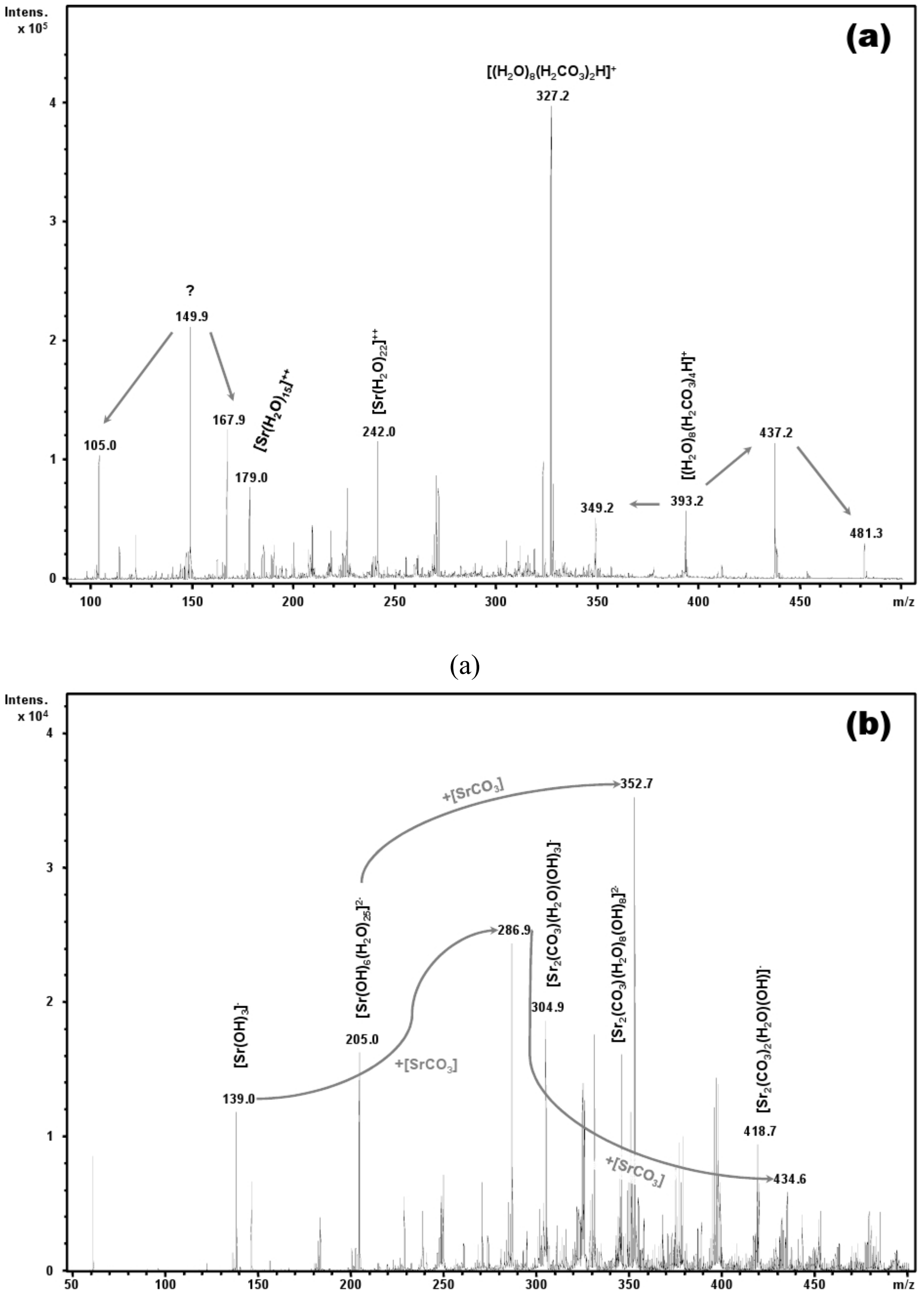


Fig. S5. (a) Particles formed after 400 s from a calcium carbonate solution at pH = $p\mathrm{K}_{\mathrm{A1}}$ = 10.3. (b) Particles formed after 200 s from a calcium carbonate solution at pH = 9.0



(a)

Fig. S6. Positive (a) and negative (b) ESI mass spectrum of a saturated solution of strontium bicarbonate.

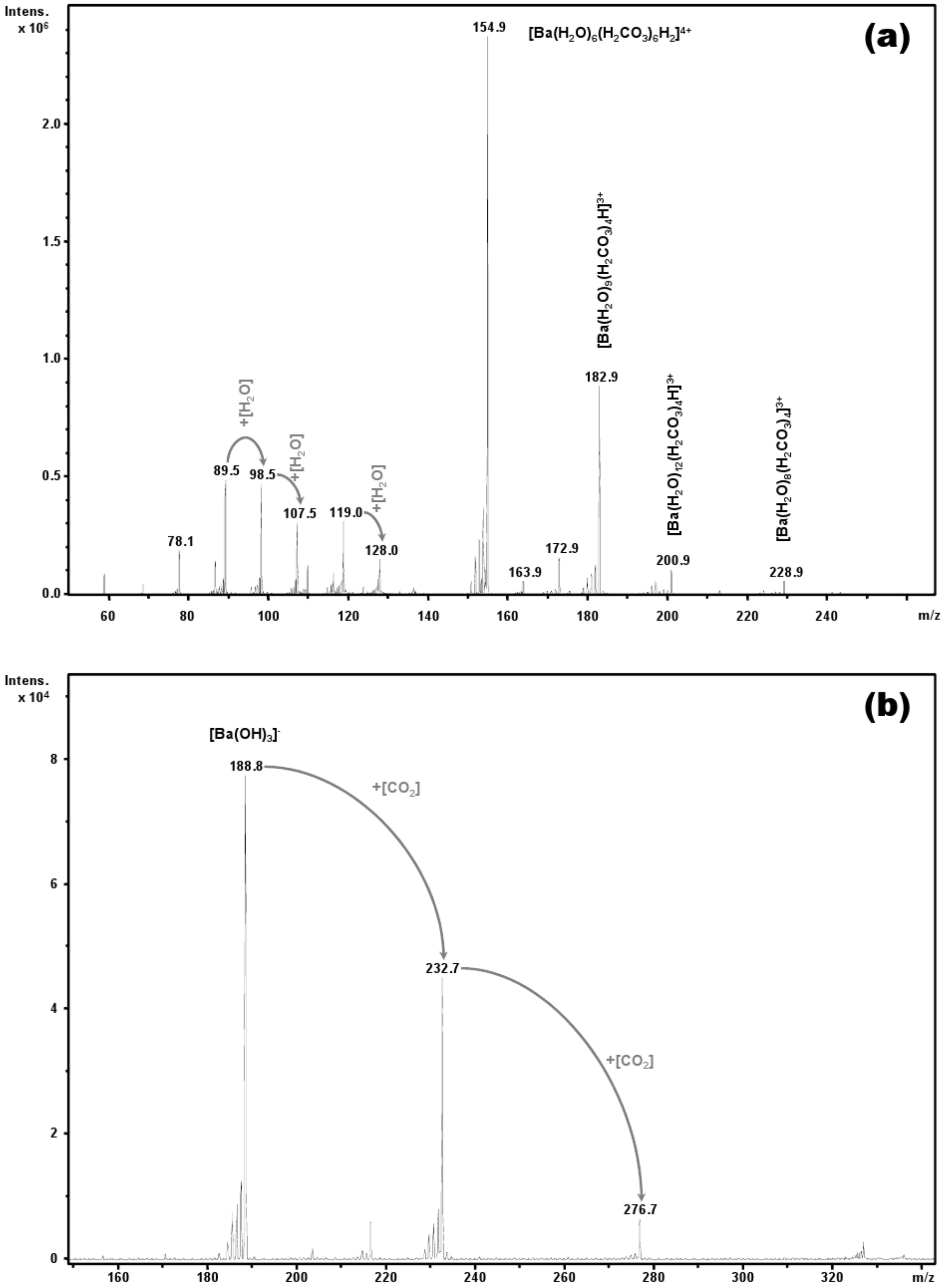


Fig. S7. Positive (a) and negative (b) ESI mass spectrum of a saturated solution of barium bicarbonate.

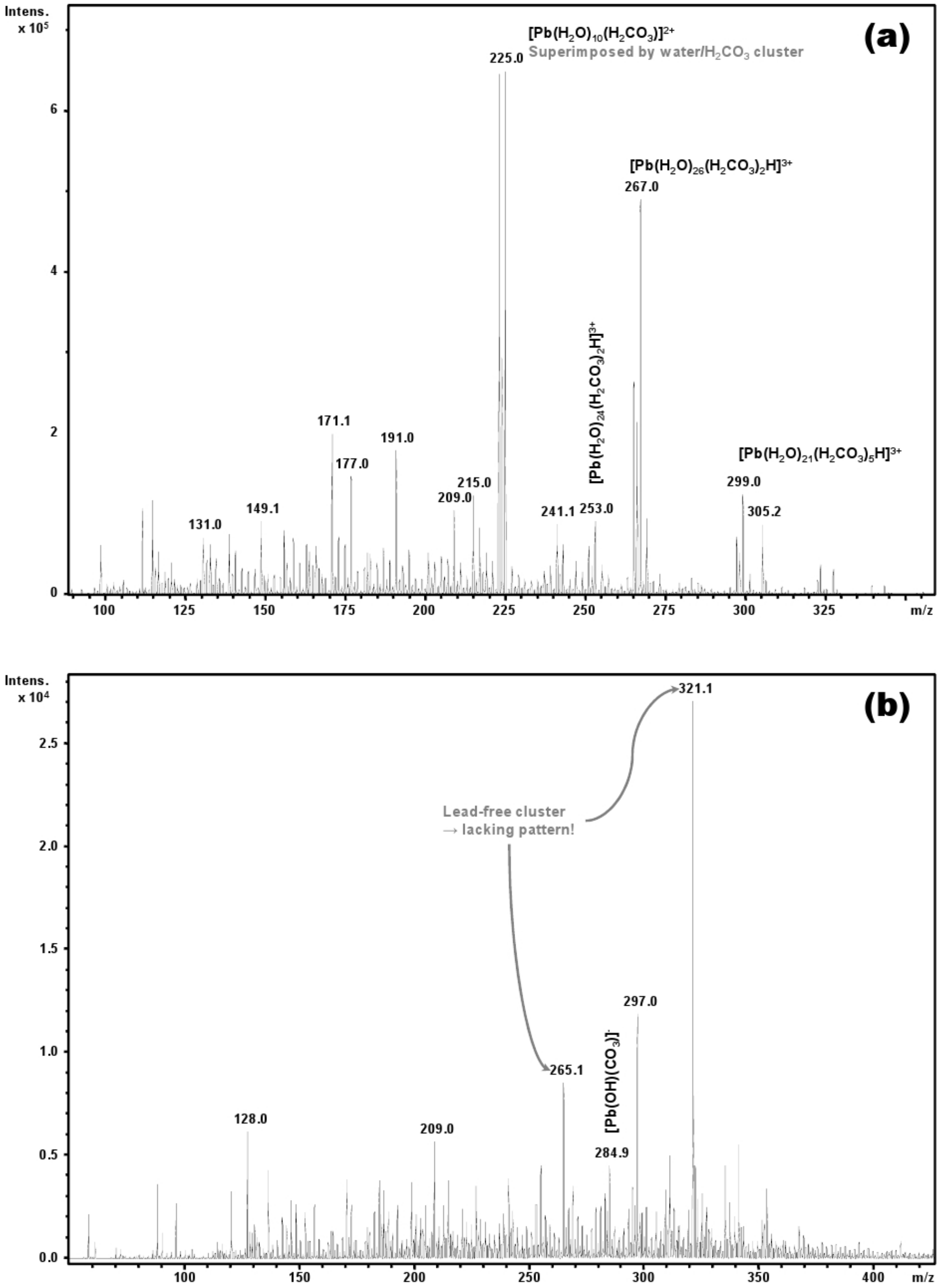


Fig. S8. Positive (a) and negative (b) ESI mass spectrum of a saturated solution of lead bicarbonate.

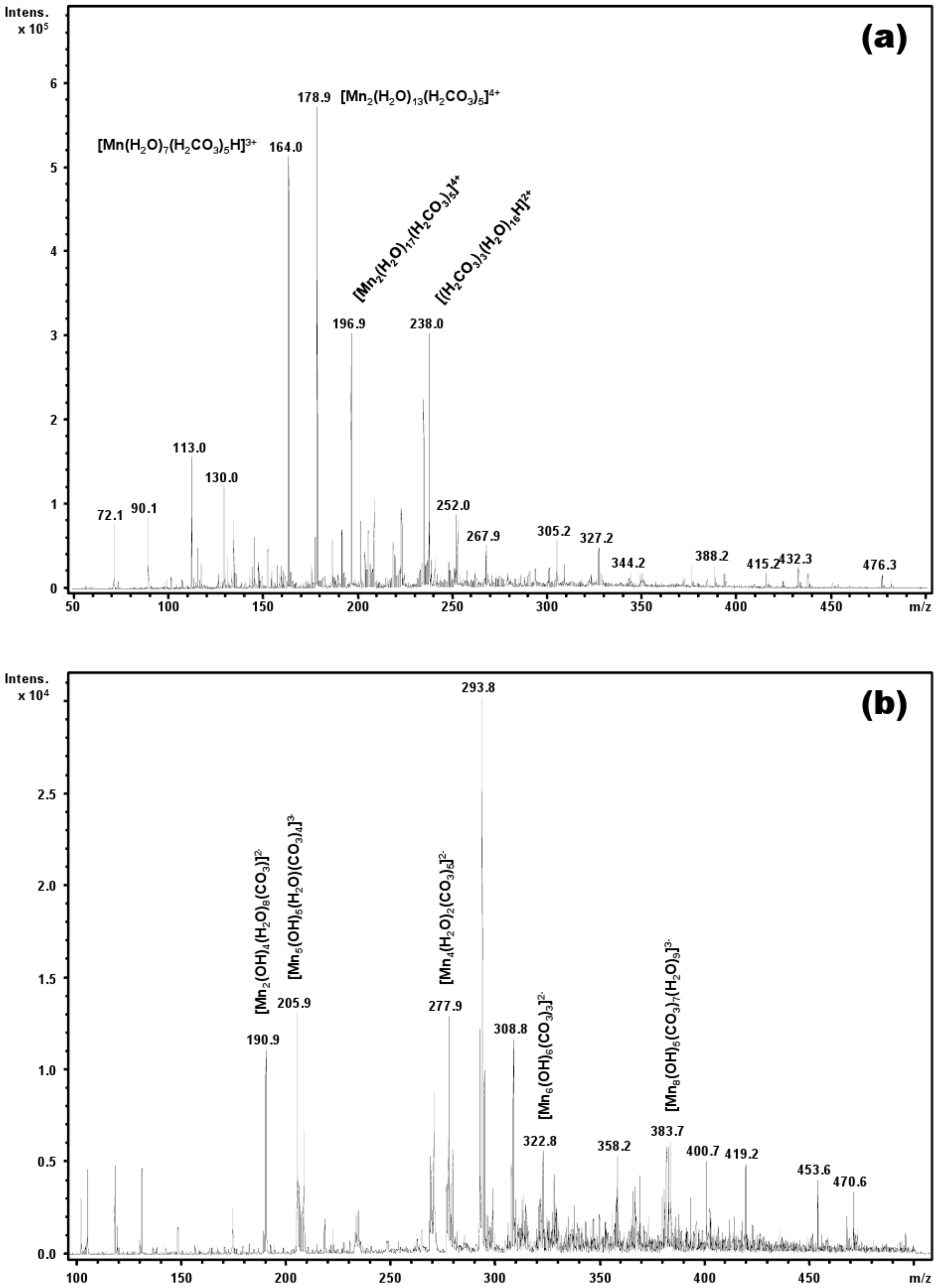


Fig. S9. Positive (a) and negative (b) ESI mass spectrum of a saturated solution of manganese bicarbonate.