METHOD COMPARISON FOR THE EXTRACTION OF LOW-MOLECULAR-WEIGHT ORGANIC ACIDS FROM CONSOLIDATED CLAY ROCK

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Low-molecular-weight organic acids (LMWOA) in the C₁ to C₅ range are ubiquitous, water-soluble components in the natural environment, and have been found in petroleum systems¹, soils², marine sediments³, and pore waters of rock formations⁴. In addition, for numerous anthropogenic activities in the subsurface, such as radioactive waste management programs, LMWOA’s are under investigation because of their influence on pore water geochemistry⁵ and their potential as complexing agents for radionuclides. Sampling of these compounds from aqueous systems (e.g. groundwater, pore water from soft sediments) has become a standard procedure. Nevertheless, extracting LMWOA’s from highly consolidated sediment or intact rock cores, with low water content, sometimes extremely low permeability, and active mineral surfaces interacting with the acids, is far from standardized. Published extraction methods include, for example, extractions of ground sample material by heated water extraction⁶, or pore water squeezing from drill cores⁷. The aim of this study is to test and to compare extraction methods for LMWOA’s from consolidated clay rock and rock cores for their individual organic acid yields.

Four different aqueous LMWOA extractions were investigated, using sample material from one drill core (Opalinus Clay, Mont Terri Rock Laboratory, Switzerland). In three tests, ground sample material was extracted by either ultra-sonication (5 min, <30 °C), accelerated solvent extraction (ASE; 3-cycle extraction, quartz chips—clay mixture, ≤3 h, 40 °C), or by mixing on a shaking table (150 min, 20 h, 30 °C), respectively. A solid-to-liquid ratio of 1:2 (1:1 in ASE) was chosen for the aqueous extractions. In a fourth approach, pore water from an intact rock core was obtained through a triaxial cell squeezing experiment (≥61 MPa, 1872 h, 30 °C). The core had a length of 200 mm, a diameter of 97 mm, and had an estimated water content of 5 to 9 wt.%. Aqueous samples were analyzed following a well-established HPLC protocol⁸.

All aqueous extractions and the pore water squeezing yielded LMWOA’s. The ultra-sonication method using high-energy input over a short period of time resulted in low amounts of methanoic acid (formate) and ethanoic acid (acetate). Three other species were found to be below the limit of quantification (LOQ = 5 µM). In contrast, the sequential, 3-cycle ASE extraction yielded also ethanedioic acid (oxalate). For ground sample material, the shaking table approach yielded the highest amount of acetate (20 µM), while formate was comparable to the ultra-sonication result (~8 µM). The most surprising finding from this method comparison were high amounts of LMWOA’s in pore water from the triaxial cell squeezing experiment. Formate and acetate concentrations were approximately 400 µM and 1200 µM, respectively. This molar 1:3 ratio was also reported for pore water of a different Opalinus Clay sample⁹. Logging of pressures and indirect volumetric measurements during the triaxial cell experiment indicated that up to 30 mL pore water were released from the rock core.

The results indicate method-dependent variabilities in the amount and molecular composition of LMWOA’s from Opalinus Clay sample material. Despite the drawback of very long operation time in the triaxial cell experiment, this method is a promising candidate for the extraction of LMWOA’s from consolidated sediment or rock. A slow increase of the confining...
pressure and later the axial load seem to be important to allow for pore water movement through connected pores.

Further testing of the performance of the ASE – even at elevated temperatures – and additional triaxial cell experiments are under way. Extractions of in-situ heated sample material from the Mont Terri Rock Laboratory (experiment HE-F) will depict how the temperature history has affected organic acid release into the pore water.

References