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Dear Editor,

Potential limitation of cryogenic vacuum extractions and spiked experiments

Recent work has shown mineral mediated isotope fractionation of soil water.[1] That work speculated about the interactions between interlayer and hydroxyl water to explain the mineral water interaction and the poor performance of the cryogenic vacuum extraction method. Here we present new data that show clearly the relationship between temperature and the release of water from interlayer cations and organics, and from dihydroxylation during cryogenic extraction.

Recent discussions of soil water extraction methods for water isotope analysis have highlighted several concerns regarding cryogenic extraction for soils with elevated clay content[1] and large differences between cryogenic extraction and other extraction methodologies.[2] Gaj *et al*.[3] recently found mineral mediated isotope fractionation of soil water and speculated about the interactions between interlayer and hydroxyl water as a reason for the poor performance of the cryogenic vacuum extraction method. Here we present new data to test the hypothesis that the extraction temperature defines cryogenic performance. We then detail the mechanisms that appear to occur during dehydration.

A model 449 F3 Jupiter thermobalance equipped with a DSC/TG sample holder linked to a QMS 403 C Aeolus quadrupole mass spectrometer (both Netzsch, Selb, Germany) was used to measure the ions at *m/z* 18 and *m/z* 44 for water and carbon dioxide, respectively. Each of the eight powdered materials (100 mg) previously used in the study of Gaj *et al*.[3] was equilibrated at 53% relative humidity (RH). The material was heated from 20 to 1150°C at 10°C/min. The thermobalance is capable of measuring the weight loss with an accuracy of about 0.1 mass%. At the same time the energy required to attain the next temperature step is measured by comparing the sample with a reference (corundum) of known heat capacity. At certain temperatures, gases (e.g. water or CO_2) are released from the sample and transferred by a heated transfer line to the quadrupole mass spectrometer where they are detected.

Figure 1 shows the relationship between temperature and the ions at *m/z* 18 and *m/z* 44. The dotted lines indicate different extraction temperatures that were used in the original work of Gaj *et al*.[3] The first peak at ~100°C, seen for feldspar (S071), quartz (S044), illite/kaolinite (S181), and pure kaolinite (S117), is associated with the release of bound water.[4] This signal declines between 100 and 200°C. The other minerals have peaks that occur between 105 and 205°C. Smectite (B06) and the illite/smectite-mixed (S145) layer show a double peak. The first peak is related to the dehydration of mono- and divalent exchangeable cations whereas the second peak is attributed to the dehydration of bivalent exchangeable cations such as Ca or Mg. Dehydration of monovalent cations requires a temperature of about 200°C and bivalent cation dehydration occurs between 200 and 300°C. The double peak of the illite/smectite-mixed layer minerals is shifted towards a lower temperature window. However, hydratable bivalent interlayer cations are dehydrated between 100 and 200°C. A successful dehydration of goethite was only possible with a temperature of 205°C.

If organic compounds are oxidized, CO_2 is emitted when water is released. The presence of organics is, therefore, indicated by the presence of H_2O and CO_2 peaks between 300 and 500°C (i.e. goethite). Above 500°C, a phase transition from alpha to beta quartz occurs which is not related to any further water desorption. Carbonate decomposes between 600 and 900°C. This is observed in the chlorite sample and of course for the calcite. The recrystallization of silicates occurs at temperatures above 900°C.

Our new data show clearly why cryogenic soil water extraction performs well only on soils without clay minerals. Adding such minerals into the mix means that much higher temperatures are required for the different molecules to be released. Work needs to be done to relate these lab experiments to hydrological processes in the field. We know that interlayer and adsorbed water exchanges with water and water vapor within hours.[5,6] Hence this water is actively involved in the hydrological cycle. However, the standard protocol for cryogenic soil water extraction is not able to extract this type of water although the recovery efficiency is 94% (Table 1). The new data suggest that temperatures between 200 and 300°C should be used for soil water extractions. Higher temperatures could cause a release of water by oxidation of organics and dihydroxylation of hydroxide-containing minerals such as goethite.

This work supports the value of spiked experiments as discussed originally in Gaj *et al*.[3] These new data show clearly, however, that at temperatures lower than ~205°C, not all water will be released from mineral soils. As a result, water that remains after drying at ~100°C mixes with the spiked water. If water is extracted with methods that do not force a phase change (i.e. squeezing or centrifugation), the extracted water will be more enriched in the heavy isotopic species than the spiked water. How pronounced this effect will be depends on the mixing ratio where the effect will be stronger for extractions at low water contents. Alternatively, methods that force a phase change (such as cryogenic vacuum extraction) will cause depletion of the heavy isotopic species of the extracted water and enrichment of the heavy isotopic species in the remaining reservoir following an evaporation process.

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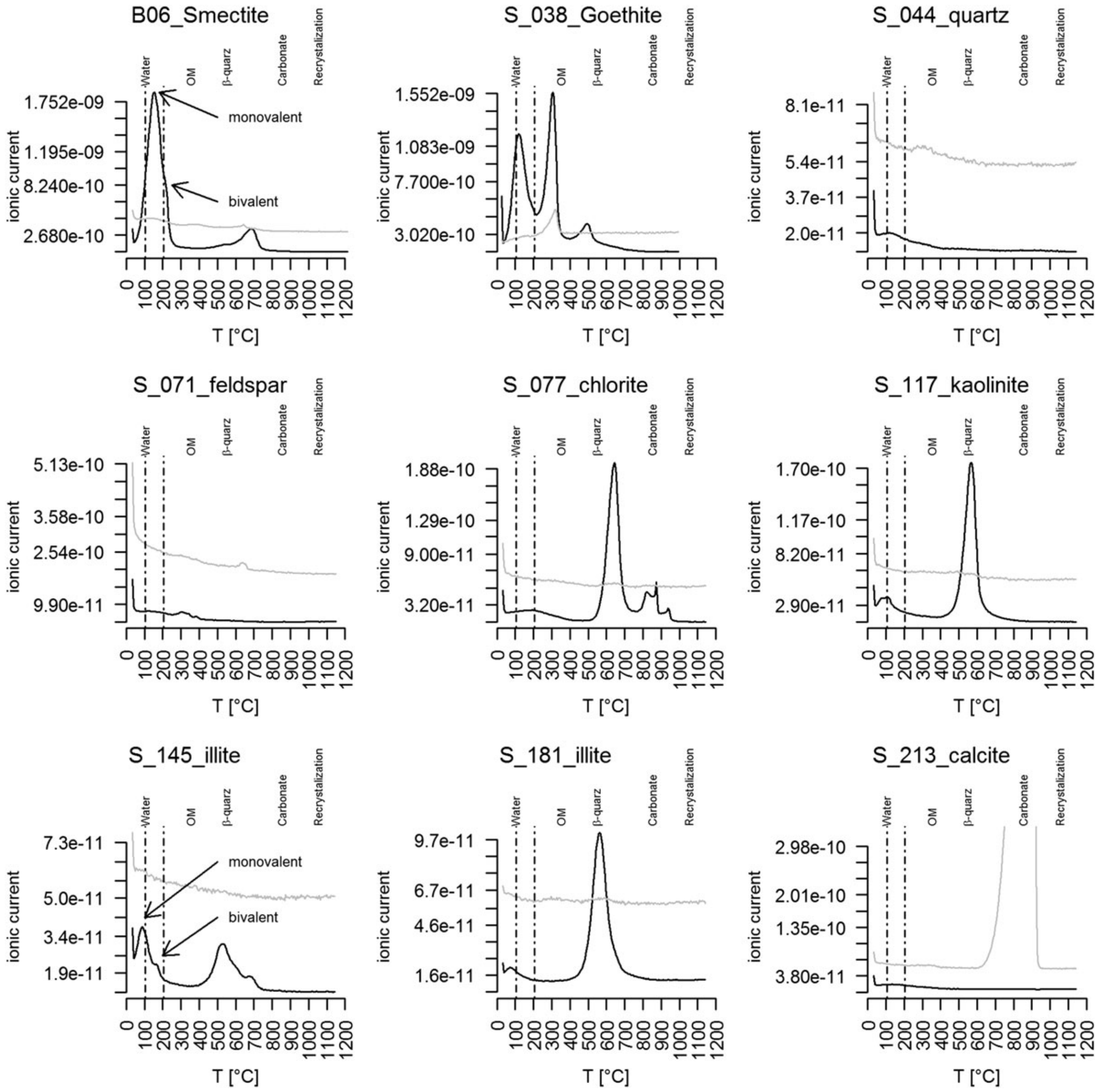

Figure 1. Release of water (black line) and CO_2 (grey lines) with increasing temperature during the DSC analysis. 105°C and 205° are indicated by dotted vertical lines. Dispersions of different compounds are indicated at the top of the graphs.

Table 1. Water recovery θ is calculated from the gravimetric difference between the spiked sample and the extracted sample. The standard deviation σ is calculated from $n = 5$ replicate samples. Difference between extracted and expected δ-values for extractions with 105°C and 205°C, $\delta^{18}O$ and $\delta^{2}H$ are shown (modified after Gaj *et al.*[3])

	B06	S038	S044	S077	S117	S145	S181	S213	S071
$\theta_{105^{\circ}C}$ [-]	0.97	0.94	1	0.99	0.97	0.99	0.99	1	1
$\sigma_{105^{\circ}C}$ [-]	0.01	0.08	0.02	0.02	0.02	0.01	0.01	0.01	0.01
$\theta_{205^{\circ}C}$ [-]	1.01	1.01	1.01	1	1.01	1.01	1.01	1.01	1.01
$\sigma_{205^{\circ}C}$ [-]	0.01	0.01	0	0.02	0	0.01	0.01	0.01	0
$\delta^{18}O_{105^{\circ}C}$ [‰]	−6.23	−6.31	−1.61	−5.66	−4.68	21.28	−2.6	−4.14	−4.05
$\delta^{2}H_{105^{\circ}C}$ [‰]	−29.2	−35.1	−9.5	−31	−26.7	−29.2	−14.9	−26.3	−15.9
$\delta^{18}O_{205^{\circ}C}$ [‰]	−1.94	−0.65	−0.21	−2.57	−1.76	−2.25	−0.02	−1.78	−1.27
$\delta^{2}H_{205^{\circ}C}$ [‰]	−16.7	−18.3	−0.9	−14.6	−11.8	−12.8	−1.8	−11.8	−7.1

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