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Water stable isotope measurements of Antarctic samples by means of IRMS and WS-CRDS techniques

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In the last years in the scientific community there has been an increasing interest for the application of stable isotope techniques to several environmental problems such as drinking water safeguarding, groundwater management, climate change, soils and paleoclimate studies etc. For example, the water stable isotopes, being natural tracers of the hydrological cycle, have been extensively used as tools to characterize regional aquifers and to reconstruct past temperature changes from polar ice cores.
Here the need for improvements in analytical techniques: the high request for information calls for technologies that can offer a great quantity of analyses in short times and with low costs. Furthermore, sometimes it is difficult to obtain big amount of samples (as is the case for Antarctic ice cores or interstitial water) preventing the possibility to replicate the analyses.
Here, we present oxygen and hydrogen measurements performed on water samples covering a big range of isotopic values (from very negative antarctic precipitation to mid-latitude precipitation values) carried out with both the conventional Isotope Ratio Mass Spectrometry (IRMS) technique and with a new method based on laser absorption techniques, the Wavelenght Scanned Cavity Ringdown Spectroscopy (WS-CRDS). This study is focusing on improving the precision of the measurements carried out with WS-CRDS in order to extensively apply this method to Antarctic ice core paleoclimate studies.
The WS-CRDS is a variation of the CRDS developed in 1988 by O'Keef and Deacon. In CRDS a pulse of light goes through a box with high reflective inner surfaces; when there is no sample in the box the light beam doesn't find any obstacle in its path, but the reflectivity of the walls is not perfect so eventually there will be an absorption of the light beam; when the sample is injected in the box there is absorption and the difference between the time of absorption without and with sample is proportional to the quantity of the sample in the box. In the WS-CRDS the path of laser is longer, producing higher-sensitivity measurements. The instrument is paired with an autosampler and can be used without it and the vaporizer to analyze directly the isotopic composition of the water vapour in the atmosphere. In addition, the instrument can be moved from the laboratory and also used for outdoor measurements.
The more important improvements over traditional IRMS techniques are that WS-CRDS needs less sample in order to perform the analysis (<2 ul vs. 3/5 ml); that it doesn't need manipulation of the sample (like the gas/water equilibration techniques) and the analyses are faster. Coversely, memory effects may affect the measurements so there is the need to increase the number of injection to have a high precision measurement.
The laboratory of Isotope Geochemistry of the Department of Geosciences has recently acquired a WS-CRDS system from PICARRO. The isotopic data obtained with this new method have been compared with the ones obtained by means of IRMS methods. An HDO device coupled with a Thermo Finnigan Delta Plus Advantage mass spectrometer has been used, using the well know CO2 and H2/water equilibration technique. At the moment of the writing of the abstract the mean difference between the values obtained using PICARRO and using the traditional IRMS method is of the order of 0.1 per mil for the ratio 18O/16O and 1.00 per mil for the ratio D/H, but further measurements are currently underway.

O'Keef A., Deacon D.A.G., 1988. Cavity ring-down optical spectrometer for absorption measurements using pulsed laser sources, Rev. Sci. Instrum., 59, 2544.