Notice of AutoPeak

AutoPeak is an analysis process supported by Excel (Office 2010 suite and above), using a code developed in VBA (Visual Basic for Application). AutoPeak was created to analyse the temporal distribution the water concentration, δ18O and dD of a mix between a punctual water sample and a continuous-flow of a standard water. The acquisition of these signals is made by a line composed by a PICARRO analyser (a Cavity Ring-Down Spectrometer), a dry argon supply moisturised by standard water, a water injector (for direct water analyse) and a crusher (for fluid inclusion analysis). The line is heated in order to assure no condensation (and so isotopic fractionation in the line).

The output data from the PICARRO analyser are not a direct result, because they reflect the mix between the sample composition and the standard composition. The deconvolution between the signal and the baseline is simple, given by the following equations:

Equation 1 deconvolution of the δ18O signal

Equation 2 deconvolution of the δD signal

The challenge in these deconvolutions is to be able to properly frame the interval beginning by injecting water and ending with the return to the baseline, despite the noise and artefacts. The entire process, including the data management, is described in the following graph, where the subroutine names are in white rectangles.

Or

Figure 1 Organizational graph

The objective of the PeakDetermination subroutine is to try a full-automatic framing. This is a blind algorithm, in the sense that no input localizes the peaks to find; the primary objective of PeakDetermination is to determine all the potential peaks in the temporal distribution, artefacts as well as real peaks originated from injection or crush. After this listing, a unique framing method is applied, in order to limit observer bias. This treatment has two interests: first, it is necessary for the final isotopic calculus, and second it discriminate a great part of artefacts, for which the method cannot be achieved. These ones removed from the list, another and last discriminating process is implemented, three shape tests that ensure some peaks to be false. 1) the correlation must be sufficient between H2O and at least one of δ18O or δD; 2) the water distribution must be left hand asymmetric reported to normal distribution (skewness > 0); 3) the kurtosis of the left hand water distribution (in mirror) must be inferior to 1. Other tests are implemented but are not currently used by the algorithm. At the end of this, all the remaining peaks have to be the correct ones in order for the process to be completed. Two tests ensure that: first, the number of potential peaks is compared to the number of indicated ones, and second if they match the volume of the indicated standard injections is compared to the calculated volume for each potential peak of the set. The automatic framing is successful if the set passes these two tests. In this case, δ18O and δD are calculated in accordance with the determined interval of each defined peak. Else, the selection of the correct peaks is manual, in the range of the reduced list remaining after the shape tests. After the selection by the user, the CalculationAfterManualHandling subroutine does the formatting and calculus.

Concerning the method of framing, the beginning and the ending of the frame is different, because of the great asymmetry of a peak. The beginning of a peak consists in the instant when the H2O derivative (step 2s) which was inferior to ten become superior to ten for the next six points (step 2s) at least. Because the variation occurring by the extra-water supply is not in the same order that the noise variations (apart from artefacts linked to the crusher opening, which are discriminated during the process), this condition is sufficient for the left-hand framing. The problematic is different for the definition of the end of a peak, because the signal becomes slowly indistinct from the noise, with a threshold, which can significantly change the isotopic values. The approach is based on three conditions: 1) the peak must end before the next one, 2) from the maximum in water concentration, the decrease is longer that two hundred seconds, 3) at least two points in a range of nine consecutive ones have a positive derivative (step 2s). These conditions ensure that the decreasing signal is becoming insignificant before the noise.