Fully automated isotope analyses of non-exchangeable hydrogen of cellulose based on water vapour equilibration

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An improved method for determination of deuterium to hydrogen (D/H) ratios of nonexchangeable hydrogen in cellulose was developed. The method is based on the equilibration reaction of hydroxyl hydrogen of cellulose and water vapour of known isotopic composition. The equilibrated cellulose is pyrolysed and the total D/H ratio determined by subsequent online IRMS. By applying a mass balance the D/H ratio of nonexchangeable hydrogen is recalculated after an empirical calibration has been performed yielding a mean exchangeability of 0.239 and an equilibrium fractionation factor of 1.082 between hydroxyl hydrogen of cellulose and water hydrogen at 110°C. Equilibration takes 10min per sample. Results obtained by this online equilibration method agree very well with values obtained by nitration technique (R^2=0.995). The uncertainty of the equilibration method is ±4‰ resulting from a single standard deviation of ±2.8‰ for the equilibration determined by standard cellulose and 2.8‰ due to the variable exchangeability of hydroxyl hydrogen in cellulose due to crystalline areas. The latter uncertainty may be lowered by minimising crystallinity of the cellulose. Advantages of this new technique are (i) the considerably reduced sample amount required (as low as 0.2 mg, ideally 0.5 mg compared to 20 mg for the conventional nitration technique); (ii) an approximately 100-fold reduced process time and (iii) there is no need of hazardous chemicals as it is the case for the nitration technique.

Up to now the method was used to process several thousands of hydrogen measurements. Automation was hampered mainly due to sample delivery problems between the autosampler and equilibration chamber. A slight compaction of the sample containers significantly improved a proper sample admission to the equilibration chamber.

Hornblende cumulate recycling in the Torres del Paine (Chile): Evidence from field observations and petrology

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The Torres del Paine pluton (south Chile) has been emplaced at ~1kbar [1], about 12.5 Ma ago [2] and is formed of a western ‘feeder zone’, with vertical structures, and an eastern laccolith, showing horizontal contacts. It is a K-rich calc-alkaline intrusion, composed of a Mafic Complex (PMC) (~300m thick) and a younger granite (~1500m thick). The sheeted sill like PMC is constituted of an upper and a lower hornblende gabbro (up to 50% Hbl) and diorites, with ductile contacts.

The lower Hbl gabbro is shoshonitic, with anhedral kaersutite core (Mg#≈74), with Bt overgrowth. Millimetric apatite inclusions are frequent in Hbl cores, but Plg (An70) is rare. This is compatible with the absence of negative Eu anomalies in REE diagrams of Hbl cores analysed by LA-ICP-MS. The upper high-K Hbl gabbro displays poikilitic pargasite core (Mg#≈72) with euhedral Plg (An70-55) inclusions. Anhedral Ol (Mg#≈80-60) inclusions are found in the most primitive Hbl gabbros.

Matrix Mg-Hbl (Mg#≈65) is similar in both gabbroic types, and is in equilibrium with matrix Plg (An30), Bt, Tit and Ilm. Mg-Hbl have a higher Fe/Mg ratio, a lower Tschermaks and Edenite component, a lower Nb/Ta ratio and Eu negative anomalies. Fine grained diorite sills have mineral compositions similar to matrix of the Hbl gabbros.

Hbl-Plg thermometry [3] on matrix phases indicates emplacement temperature of 750°C. In contrast, calculations on pargasite-plagioclase pairs indicate cumulate formation at 950°C for the upper gabbro. Temperature of kaersutite-plagioclase pairs from the lower Hbl gabbro is estimated to be even higher. We propose that the lower Hbl gabbro had a longer residence time in a crustal magma chamber than the upper gabbro. Hbl texture indicates cumulate remobilisation and transport to shallow depth, where the magma crystallized as a sequence of sills to form the mafic part of the Torres del Paine laccolith.

[1] Putlitz *et al*. (2001) *XI Annual V.M. Goldschmidt Conference, Virginia, USA*.. [2] Michel *et al*. (2008) *Geology* **36/6**, 459-462. [3] Holland & Blundy (1994) *Contrib Min Pet* **116**, 433-447.