

A new U/Pb-spike ($^{233-235}\text{U}/^{202-205}\text{Pb}$) for high precision zircon dating: First results of standard zircons, precision and accuracy

A. VON QUADT¹, S. GEORGIEV¹ AND I. PEYTICHEVA^{1,2}

¹ETH Zurich, IGMR, (georgiev@erdw.ethz.ch; vonquadt@erdw.ethz.ch)

²CLMK, BAS, Sofia 1000, (peytcheva@erdw.ethz.ch)

For high precision U/Pb zircon, xenotime and monazite analyses there is a new U/Pb spike ($^{233-235}\text{U}/^{202-205}\text{Pb}$) produced at ETH Zurich. The enrichment for the ^{205}Pb isotope is greater than 99.95 and for the ^{202}Pb isotope greater than 99.73. Important ratios of this new mixed double U/Pb spike are: $^{206}\text{Pb}/^{205}\text{Pb} - (0.001132)$, $^{204}\text{Pb}/^{202}\text{Pb} - (7.7351\text{E-}05)$, $^{206}\text{Pb}/^{204}\text{Pb} - (10.0025)$ and $^{233}\text{U}/^{235}\text{U} - (0.969945)$. The new U/Pb spike was calibrated against a highly pure metal solution based on NBS 982 and NBS 960. One of the aims to produce the new double lead and uranium spike ($^{233-235}\text{U}/^{202-205}\text{Pb}$) was to avoid the usage of external mass-fractionation, and to improve precision and accuracy of U-Pb measurements. In the past the instrumental mass-fractionation was estimated by repeated measurements of NBS 982 or NBS 981 material as well as of U 500 standard material.

The minimum amount of NBS Pb and U for the external fractionation correction is limited by Pb-blank, the temperature during the measurement and parameters of the ion counter system. Nevertheless, the measuring procedure needs more time for the measurement based on six Pb isotopes, three U isotopes and sometimes two additional isotope to correct interferences on the mass ^{202}Pb .

To demonstrate the advantage of the new ($^{233-235}\text{U}/^{202-205}\text{Pb}$) spike we have measured several zircon standards R33 (Black *et al.*, 2004), 91500 (Wiedenbeck *et al.*, 1995) and the PL zircon (Slama *et al.*, 2006) using a "common" $^{235}\text{U}/^{205}\text{Pb}$ and the new double U/Pb spike. First preliminary results show that the scattering of the $^{206}\text{Pb}/^{238}\text{U}$ ages and the mean error of the $^{206}\text{Pb}/^{238}\text{U}$ ages are much smaller compared to the use of the "conventional" $^{205}\text{Pb}/^{235}\text{U}$ spike.

References

- Black, L.P. *et al.* (2004). Improved $^{206}\text{Pb}/^{238}\text{U}$ microprobe geochronology by monitoring of a trace-element-related matrix effect; SHRIMP, ID-TIMS, ELA-ICPMS and oxygen isotope documentation for a series of zircon standards. *Chem. Geol.* **205**, 115-140
- Slama J., Kosler J., Schaltegger U., Tubrett M., Gutjahr M. (2006): New natural zircon standard for laser ablation ICP-MS U-Pb geochronology. Abstract WP05, 187-188, Winter Conference on Plasma Spectrochemistry, Tucson
- Wiedenbeck, M. *et al.* (1995). Three natural zircon standards for U-Th-Pb, Lu-Hf, trace element and REE analyses. *Geostand.-Newletters*, **19**,1,1-23

Identification of potential geochemical reactions in German subsurface storage sites of CO₂

HANS-DIETER VOSTEEN AND FRANZ MAY

Federal Institute for Geosciences and Natural Resources (BGR), Stilleweg 2, 30655 Hannover, Germany (Hans-Dieter.Vosteen@bgr.de)

Large scale CO₂ geological storage in Germany can be realized both in deep saline aquifers and in mature natural gas reservoirs. Some of the injected CO₂ will dissolve in the already highly mineralized Na-Ca-Cl brine to form CO₂ (aq) and carbonic acid. Such a change in brine composition can lead to dissolution or precipitation of minerals within the storage formation or the cap rock. Mineral dissolution will yield an increase in porosity. Depending on where it occurs, it can either increase the storage capacity or reduce the cap rock integrity. Mineral precipitation will either result in long term mineral storage of CO₂ or - if it occurs near to the well - it can yield technical problems during CO₂ injection. Numerical simulation of reactive transport processes and associated mineral reactions are generally used for predictions of such processes. But, reaction rates of silicates are very slow and reliable thermodynamic data obtained by experimental studies of mineral precipitation or dissolution is difficult to obtain. In many cases realistic thermodynamic data does not exist for all minerals within a rock formation. Data for lacking minerals such as mixed crystals has to be estimated. If we consider high-salinity brines, which are omnipresent in the North German Basin, the Pitzer formalism has to be used. Many simulation tools do not facilitate simulation of redox reactions or aluminosilicate reactions in combination with the Pitzer formalism. These limitations result in potentially unrealistic and therefore uncertain interpretations of geochemical simulation results. Another way to identify and quantify potential alteration reactions is to study natural analogues. For the case of CO₂ injection, natural analogues can be found in regions with CO₂-rich water, e.g. in active volcanic regions. Potential alteration reactions, identified by natural analogue studies can further be used as comparison and for qualitative calibration of numerical simulations. For the German storage formations Bunter Sandstone and Rotliegend sediments such natural analogue studies yield the dissolution of calcite and chlorite and precipitation of dolomite. Another slow alteration reaction is the dissolution of albite and the precipitation of kaolinite. By studying natural analogues of the Rhenish Massif, May (2005) found that the alteration of greywacke and shale rocks by CO₂-rich water led to the dissolution of chlorite and feldspar and to the precipitation of kaolinite, iron-bearing carbonates, quartz and bicarbonate water.

References

- May, F. (2005), Alteration of wall rocks by CO₂-rich water ascending in fault zones, *Oil & Gas Sciences and Technology* **60**,1: 19-32.