CA-U-Pb zircon dating obtained by the LA-ICP-MS system: Impact for their interpretations

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Laser ablation ICP-MS is a powerful method to determine the age of rocks by measuring U/Th/Pb isotopes. The method is fast, cheap and several applications present precise (< 1% $^{206}Pb/^{238}U$ age errors) and accurate results using corrections and reference materials [1]. For several years U-Pb zircon analyses by TIMS are using the CA [chemical abrasion] technique to avoid domains that have lost Pb parts [2,3]. In this work we apply the same CA technique for LA-ICPMS analyses, using the Excimer 193nm laser system with a constant geometry ablation cell connected to the quadrupole ICP-MS (PerkinElmer, Elan 6100). The selected target material are zircon grains of intrusive rocks with ages of 24 Ma (Miocene) and 80 Ma (Cretaceous) that show no inherited components.

The analyses we include TIMS and LA-ICPMS measurements of U/Pb ratios of CA- and non CA-treated zircons. All non CA-treated zircon measurements show a broader range of their $^{206}Pb/^{238}U$ ages including ratios which refer to recent lead loss or to small inherited Pb components. The CA-treated zircon measurements show a more homogenious age pattern due to the removal of domains with lead loss. In the case of not overlapping concordant ages the cluster with the youngiest ages should be interprated as time of magma crystallization, which is an important advantage of the techniques. Most publications [4] take the 2 sigma error into account for their calculation of $^{206}Pb/^{238}U$ ages; following this procedure we can demonstrate that the non CA-treated U/Pb ages are not overlapping with the CA-treated zircon grains measured by LA-ICP-MS and TIMS techniques. The standard error of this mean has even less geological significance if age variations are real [5]; note that the value of the standard error of the mean would decrease if greater numbers of zircons were measured.

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Souring control by six years of nitrate injection into a low temperature oil field

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Production of oil by water injection can result in souring by sulfate-reducing bacteria (SRB). Souring can be prevented or reversed by inclusion of nitrate in the injection water, which boosts the activity of nitrate-reducing bacteria (NRB). In the Medicine Hat Glauconitic C (MHGC) field, oil production through water injection was started in 2000. Souring, was noted in 2006. Field-wide injection of 2 mM nitrate was adopted as a souring control strategy in 2007. We have monitored the success of this strategy by monthy sampling of producing wells and analyzing the concentrations of sulfate, sulfide, nitrate and nitrite [1], as well as by determining mirobial community composition [2].

Field-wide nitrate injection decreased produced sulfide initially, but this was followed by recovery. Microbial zonation in which NRB grow close to the injection wellbore and SRB deeper in the reservoir was the suggested cause for this. Successful injection of nitrate pulses exceeding the nitrate reduction capacity of the NRB gave credit to this idea [1]. Constant nitrate injection over the past 6 years has given nitrate breakthrough at an increasing number of injection wells. This was associated with removal of sulfide, as well as with breakthrough of sulfate, nitrate and nitrite. Production of oil/water depleted of toluene and other alkylbenzenes and containing increased proportions of the toluene-utilizing NRB *Thauera* were also observed [2].

Long-term injection of nitrate and changes in water management strategy have caused a near complete reversal of souring in the MHGC field. Despite lack of success in the first two years persistence has since paid off.

[1] Voordouw *et al.* (2009) Environ. Sci.Technol. 43: 9512-9518. [2] Agrawal *et al.* (2012) Environ. Sci. Technol. 46: 1285-1292.

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