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Review of PhD thesis

Use and limitations of laser ablation ICPMS in geoscience applications

by Jitka Míková, supervised by Prof. Jan Košler

Dissertation is submitted as a set of three papers, two published in Journal of Analytical Atomic Spectrometry and one manuscript, which is currently under revision in the same journal. Although all papers are collaborative effort, except for the earliest contribution (Košler et al. 2005), in which candidate played a modest role (according to the statement provided by the supervisor on behalf of the co-authors), mgr Jitka Míková is the first author on the two remaining contributions (Míková 2007 and 2011), which indicates her key role. Most of the content of the dissertation already underwent very detailed and critical editorial revision and further evaluation of the scientific content I consider unnecessary. Also the third, submitted paper has been thoroughly checked by the two co-authors. Thus, in my further comments I focus on reviewing the provided material from point of view of its suitability for awarding the candidate a PhD degree. My judgment is based on the major achievements of work delivered in dissertation, on experience gained by the candidate over the course of the PhD studies and on her overall scientific activity (also external to PhD work).

All three papers that constitute the dissertation are thematically linked and their primary topic could be summarised as the studies of the causes of fractionation during laser ablation process. Fractionation and, so called, matrix effects have been long known to be the major obstacles affecting data accuracy and precision in LA ICPMS and as such are of fundamental interest to analytical geochemists. Fractionation may have numerous sources and their relative meaning and responsible mechanisms are far from obvious. Nevertheless, studies as the submitted dissertation, aiming at better understanding reasons behind the observations, are rare. Košler et al. (2005) and Míková et al. (2007) conducted a series of experiments on synthetic glasses and natural materials that involved detailed analyses of “ablation products” i.e. ejecta blankets, ablation pits and chemistry as well as mineralogy of aerosol particles. As a result Košler et al. (2005) were able to demonstrate that in addition to previously recognized effect of large particles, elimination of the fine and ultra fine particles also strongly influences fractionation. Chemical variations in particles correlate with their size and sampling of most representative fraction is necessary for increasing accuracy of measurements. Importantly, with detailed SIMS analyses the authors showed that thermally driven phase transitions accompanied by re-partitioning of elements between newly formed phases may be an important mechanism leading to the variations in Pb/U ratios, which has important implications for *in situ* U-Pb dating. Similarly Míková et al. (2007) explained observed variations among elemental ratios at the bottom and beneath the ablation pit (depth profiling) by thermally driven diffusion and size dependent

fractionation. The latter study also demonstrates relative ease of alkali elements as well as Ca and Si fractionation due to interaction of silicates with the laser. This has very important implications for performing ablation yield corrections, which commonly are based on Ca or Si. Both studies document strong correlation between the size of aerosol particles produced during ablation and composition of ablated material, which makes matrix matched external calibration crucial for precise and accurate LA ICPMS measurements. This is also the main conclusion of Chapter 4 dealing with matrix effects during laser ablation analysis of boron isotopes in tourmaline. It is demonstrated that due to uneasy treatment of boron during chemical preparation for analyses as solution, and common demand for high spatial resolution of boron isotopic composition, *in situ* LA MC ICPMS is a very promising alternative to wet and even SIMS techniques when appropriate matrix matching is available.

In addition to three papers submitted as dissertation the candidate is author or co-author on four more contributions published in *peer review* journals (European Journal of Mieralogy, Geochimica et Cosmochimica acta and Journal of Geosciences). All publications well document high analytical skills of the candidate and capability of applying her knowledge to solving geological problems. Moreover, her already broad analytical experience enables her to participate in a very broad range of research problems from methodological (Mikova and Denkova 2007) through classical geology (Košler et al. 2004, Janoušek et al. 2007) to paleo-environment (Novak et al. 2010). Over the course of her PhD studies, the candidate received extensive training in operating laser ablation systems coupled with two types of ICPMS instruments. Additionally, she had an opportunity to become acquainted with SIMS (Chapters 2 and 3) and TEM techniques (Chapter 2). Her education was broaden by participation in numerous courses and workshops dedicated to element and isotopic analysis with the use of the above mentioned techniques. Importantly, she also presented her results during four international conferences.

On the whole, I think that submitted dissertation and scientific career of mgr. Jitka Míková, fulfil all standards required for awarding her PhD degree.

Robert Anczkiewicz