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Evaluation of Perchloric versus Nitric Acid Digestion for Precise Determination of Trace and Ultra Trace Elements by ICP-MS

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In this study we present accurate determinations of LILE (Rb, Sr, Ba, Sc,U, Th, Pb), HFSE (Hf, Zr, Nb, Ta) and 14 REE's in ultramafic (Peridotites JP-1, PCC-1) and basalt (BCR-2, BIR-1) rock standards. Due to their low abundances, quantitative determinations of these element are difficult. It has been recently suggested that HNO_3/HF attack and evaporation gives lower recovery especially for REE in ICP-MS (Yokoyama et al., 1999). Yokoyama and co-workers have proposed an effective HF/$HClO_4$ digestion technique in order to avoid fluoride precipitation of REE. This study assessed the benefits of perchloric over nitric digestion techniques for ultramafic and mafic rock standards (Peridotites: JP1, PCC-1, basalts BCR-2, BIR-1, BHVO-2).

Three different digestions were tested. The first one involved double 4 ml HF:HNO_3 (1:1) attack and evaporation, followed by 10 ml HNO_3 (6N) digestion and evaporation to incipient dryness. The second technique involved 4 ml HF/ HNO_3 (1:1) attack, followed by a 2 ml HF/$HClO_4$ (1:1) attacks. Samples were then refluxed 2 times with decreasing amounts of $HClO_4$ at high temperature (up to 190ºC). After evaporation, 0.5 ml of 6N HCl was added and evaporated. This technique is a slight modification to that of Yokoyama et al. (1999). The third technique was developed by Ionov et al. (1992) and involves larger volumes of $HClO_4$. It consists of a primary attack using HF/$HClO_4$ (2:2.5) and a second HF/$HClO_4$ (1:1.5) digestion, followed by three consecutive attacks of 0.5, 0.25, 0.1 ml $HClO_4$ and evaporation at increasing temperatures (150º, 180º, 190°C respectively). All trace elements have been determined by ICP-MS using external calibration. Samples were taken up in 100 ml of 2% HNO_3 , achieving a dilution factor ca. 1000. We compared data obtained by various analytical techniques and data obtained by Laser ablation ICP-MS on quenched basaltic glasses BIR-1 and BCR-2.

The detection limits for most elements are in the range of 1 to 10 ppb. Our values for PCC-1, BCR-2, BIR-1 and BHVO-1 are comparable to those obtained by ID-SSMS (Jochum et al., 1989) and other ICPMS work (Govindaraju, 1989). The solution values obtained for BCR-2 and BIR-1 are in good agreement with LAM-ICP-MS values (this work and Norman et al., 1996). The LAM-ICP-MS values are free of dissolution and interference problems, thus suggesting that our solution values are accurate. The average of 22 analyses of JP-1 is within error of those published by Ionov et al. (1992). However systematic discrepancies with the Japanese Geological Survey's working values are observed. It is noted that HFSE/REE ratios (e.g. Hf/Sm, Nb/Ce) and HFSE ratios (e.g. Nb/Ta, Zr/Hf) vary widely for the ultramafic rocks depending on the digestion. This variability is also observed in literature thereby making it difficult to assess the true fractionation between HFSE and REE due to the various digestions.

Higher recovery of REE is obtained with $HClO_4$ digestion for ultramafic rocks compared with that for HNO_3 digestion. The benefits of the $HClO_4$ attack for basaltic rocks are less obvious with a recovery of only ~10-15% better than that for HNO_3 /HF digestion. On the other hand the use of $HClO_4$ significantly raises the acid blank due to the difficulty of safely and efficiently distilling $HClO_4$. The detection limits for most elements is at least 2 times worse with HF/$HClO_4$ than with HF/HNO_3. The small net gain in sensitivity from the use of $HClO_4$ must be weighed against the disadvantages (especially safety issues) involved in its use. Further work is continuing to further assess the advantages and drawbacks of the two types of acid digestions and further to characterize the ratio of HFSE relative to REE in these rock standards

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