Quantitative EPMA Mapping of Minor and Trace Elements in Zircons from Yellowstone Tuffs and Lavas

John H. Fournelle, Ilya Bindeman, John J. Donovan, John W. Valley

Application of electron microprobe analysis to accessory minerals requires concentrating the phases of interest. The resulting grains are commonly embedded in epoxy and polished. Epoxy is not a good companion to the electron microprobe. X-ray mapping of minor and trace elements in accessory phases is difficult, requiring very long count times at low currents, avoiding major epoxy damage. High beam current operation would be logical, but the grain outlines do not conform with the shape of the rastered electron beam, and instantaneous cratering of the epoxy can damage (coat) instrument parts, and break the specimen surface conductive coating. We report on here a mapping technique utilizing EPMA software that constrains the electron beam impact to only the mineral, allowing high beam currents and resulting low detection limits. Additionally, it is fully quantitative, yielding more information than qualitative dot or semi-quantitative counter-mode maps.

Assemblages of 300-500 grains ranging from 50-100 um length were mounted in Buehler Epoxide epoxy and finely polished. A Cameca SX51 was operated at 18 kV, 200 nA Faraday cup current, with a tight beam. In addition to Si, Zr and Hf, the following were analyzed: U Ma, Th Ma, P Ka, Y La (analysis of Yb, Er, Dy and Gd is also underway). Standards used were hafnon (Hancher), Th and U glasses (diopside glasses doped at 4 and 8 wt%), phosphates (Jarosewich and Boatner), zircon (USNM). Reconnaissance EPMA showed levels were sufficiently high so that 20-60 second counting times were used. Average detection limits for individual analyses were: U 340 ppm, Th 290 ppm, P 280 ppm, Y 170 ppm (Pb was below DL of 210 ppm and not mapped). The mapping software was the polygonal outline automation application of Probe for Windows (Advanced Microbeam Inc), where the boundary of the crystal is outlined and a grid of offset points is generated at a user-defined spacing interval (6 or 7 um). A full quantitative analysis was performed at each point on the grain. Total analysis time per spot was ~1 minute, so a map of a ~60 um grain took <2 hours to complete. The resulting compositional data was then plotted with Surfer (Golden Software.)

Zircons of Huckleberry Ridge Tuff (HRT, 2500 km3, 2 Ma), Lava Creek Tuff (LCT, 1000 km3, 0.6 Ma) and post-HRT and post-LCT lavas of Yellowstone Nat'l Park were separated and studied optically, and by BSE and CL prior to mapping. Igneous zircons with oscillatory and sector zoning and zircon with inherited cores were identified. X-ray
maps show that Y concentration correlates with CL intensity, and Y concentration doubles between different sector zones of the same crystal. Some individual zircons have 2-3 orders of magnitude variations in concentrations of U, Th, and Y from the detection limit up to 3 wt%. Mapping (100-150 analyses per single grain) shows complicated pictures of trace element distribution. Given that diffusion of 3+ and 4+ cations in zircon is negligible (Cherniak et al, 1996, 1997), this should either signify the original uneven trace element distribution, or reflect complicated and much faster dislocational diffusion. We also address the question of the role of solution-reprecipitation as an explanation of these features.

We are experimenting with high temperature epoxies (semi-conductor service; rated at degradation temp of up to 445 C), that may permit judicious use of micro-amp beam current levels, yielding significantly lower detection limits (10s of ppms) and/or more rapid maps.