

## **Appendix 5: Detailed comparison of differences between FTIR data of Johnson and Rossman (2003, 2004) and this work**

In this appendix we provide details on differences between our new FTIR results and those of Johnson and Rossman (2003, 2004). The discrepancies can be attributed to one or more of the following reasons: 1) differences between spline-fit and linear baseline corrections; 2) user subjectivity associated with manually drawn spline-fit corrections; 3) use of different crystals that may have different H contents, and/or heterogeneity within single crystals; and 4) uncertainties in the method of using three random but mutually orthogonal polarized spectra, as opposed to collecting data in principal optical directions.

### ***Plagioclase and anorthoclase***

Application of spline-fit baseline corrections to plagioclase and anorthoclase spectra fit by Johnson and Rossman (2004) with linear baselines results in increased  $Abs_{tot}$  on the order of 3-5% (note that the discrepancy can be larger for other feldspars, for instance for adularia GRR1618 discussed below). This magnitude can largely account for discrepancies for two of the anorthoclase samples (GRR1554 and GRR1276a). For samples fit by Johnson and Rossman (2003) using curved baselines, we reproduced their  $Abs_{tot}$  to within 0.5% except in one case (GRR1280) in which it appears an error was made in the sense of curvature of their fit. A more significant issue appears to be heterogeneities in the samples – either due to different populations of grains from the same locality, or perhaps resulting from zoning in large crystals that were broken up prior to preparation. An example for which the first possibility might be relevant is GRR1968, which consists of anorthite phenocrysts in basalt that were prepared as individual

cuboids. GRR1389, on the other hand, is a fractured andesine megacryst several cm in dimensions that may exhibit mm-scale zoning that we have not systematically documented (zoning was not apparent in the slab we used, as noted above). This interpretation is consistent with our new FTIR spectra (Fig. 1a), showing 10-13% higher absorbance in all three optical directions (Table 1). A more extreme example of this kind of discrepancy is GRR1604 andesine, for which we measured ten times as much absorbance as in the original study; the newly measured  $Abs_{tot}$  is much more consistent with our SIMS measurements. Note that we did not find any evidence for "veiled" twin layers with fluid inclusions in the newly made section of GRR1604, as originally documented by Johnson and Rossman (2004).

The last possibility postulated in the introductory paragraph above to explain the discrepancies is the most difficult to assess. Whereas polarized spectra of anisotropic crystals taken in principal optical directions follow the Beer-Lambert law (i.e. absorbance scaling linearly with thickness), spectra taken in non-principal directions may not follow this relationship, with different absorbers having different relative intensities when measured at different thicknesses (Libowitzky and Rossman 1996; Asimow et al. 2006). However, Johnson and Rossman (2003) tested this possibility by measuring randomly oriented crystals and inferred that the technique of using three random but mutually orthogonal polarized spectra (taken from two orthogonal directions) yields the true  $Abs_{tot}$  to within  $\pm 5\%$  relative. This method was subsequently used to measure a very large number of feldspars in the survey study of Johnson and Rossman (2004), by other workers (e.g., Hamada et al. 2011, 2013; Yang 2012; Hui et al. 2013), and in this study. The fact that our SIMS and FTIR data are well correlated even though most of our

plagioclase and anorthoclase samples were not well oriented (whereas the crystals of GRR1280, GRR580, GRR1389 and GRR1968 that Johnson and Rossman originally studied were all well oriented) suggests that the method works reasonably well. It has an obvious advantage of convenience over the more rigorous method advocated by Libowitzky and Rossman (1996) that entails taking six spectra from three orthogonal sections. We performed new baseline corrections on the spectra taken by Johnson and Rossman (2003) on both the oriented cuboid and two randomly oriented cuboids of GRR1968 anorthite and the results are ambiguous (Table 1). Whereas  $Abs_{tot}$  of one of the randomly oriented cuboids is within 3% of the oriented sample, the other cuboid has 35% higher  $Abs_{tot}$  than the oriented sample, and this value is much closer to the absorbance measured on the newly prepared, randomly oriented cuboid of GRR1968 that was used for the SIMS measurements. Thus it is possible that the method is subject to larger than heretofore-assumed uncertainties, possibly increasing with increasing degrees of polarization; note the higher degree of band anisotropy for anorthite compared to other feldspars as shown in Fig. 1a of Johnson and Rossman (2003). Alternatively, there may be multiple populations of grains from this locality with different H contents, as postulated above.

### ***Sanidine***

Significant discrepancies between our FTIR results and those of Johnson and Rossman (2003, 2004) were also found for the three sanidines used in this study. We obtained new spectra on the originally prepared JV1 cuboid (a small section of which was used for SIMS) because we realized that the spectrum labeled "Elx" in Figure 5f in

Johnson and Rossman (2004) is in fact a redundant  $Z$  spectrum (taken via transmission along a different axis of the crystal than the labeled  $Z$  spectrum). Therefore we acquired a new  $X$  spectrum, which is characterized by lower absorbance; our newly estimated  $Abs_{tot}$  is higher however, due to the use of spline-fit baselines in this study. For GRR638, we measured virtually identical  $X$  and  $Z$  spectra as in Johnson and Rossman (2003), but a significantly different  $Y$  spectrum (18% lower absorbance). The cause of this discrepancy is unknown but could be related to the long path length (9.2 mm) that was previously used to measure this polarization, perhaps resulting in overestimation of absorbance due to divergence of the IR beam passing through the sample (even though the spectra were taken in the main compartment where such effects are minimal compared to the microscope, which has Cassegrainian optics). Unfortunately the original slab used to collect this spectrum was subsequently cut into smaller pieces, preventing us from verifying this possibility. Finally, our spectra for GRR2064 show consistently higher absorbance in all three polarizations, suggesting that there may be heterogeneity in crystals from this locality (again, no zoning was found in the particular cuboid we used for SIMS).

### ***Microcline and orthoclase***

Our newly measured mid-IR absorbance for GRR752 orthoclase diverges significantly from the original estimate of Johnson and Rossman (2004), and the discrepancy in this case is most likely due to heterogeneity within the sample. For adularia GRR1618, the difference between our new measurement of  $Abs_{tot}$  and the original estimate can be entirely attributed to differences between linear and spline fits

(the discrepancy is about 12%, larger in this case than for the anorthoclase samples discussed above). Discrepancies for the two microcline samples with higher H<sub>2</sub>O content are discussed in the main text.