

372 5. Discussion

373 5.1. Attainment of equilibrium in the Canary Islands rocks

374 The Canary Islands trace-element partition-coefficients presented here
375 were determined from euhedral, blade-shaped crystals free of melt inclu-
376 sions and chemical zonation. The corresponding quenched melt was in direct
377 contact with these crystals and shows no zonation in backscattered electron
378 images (Fig. 1). While equilibrium conditions are challenging to confirm for
379 a natural volcanic system, the euhedral forms, chemical homogeneity of crys-
380 tals, and congruency between samples from separate eruptions suggest that
381 the crystals grew in a stable environment, and were not subject to chemical
382 or physical perturbations during growth (Fig. 6).

383 5.2. Chemical heterogeneity and approach to equilibrium during the experi- 384 ments

385 During our experiments crystals of clinopyroxene were grown directly
386 from unseeded glasses and the run temperature was approached from su-
387 perliquidus. No attempts were made to reverse these experiments by re-
388 equilibrating crystals and liquids with deliberately mismatched trace-element
389 concentrations because of sluggish diffusion of most elements through the
390 clinopyroxene structure (Van Orman et al., 2001; Zhang et al., 2010). Some
391 consideration is therefore required before the proximity to chemical equilib-
392 rium can be established. Further information on the equilibration of these
393 experiments is in Section 9.

394 A necessary condition for equilibrium is chemical homogeneity within
395 all measured phases. Except for some sector and concentric zonation within

396 clinopyroxene, major- and trace-element concentrations are generally uniform
397 in both the quenched melt and the mineral phases. A variety of effects related
398 to crystal growth may have affected the proximity to which equilibrium was
399 approached during the experiments:

400 (a) During rapid crystallisation, disequilibrium kinetics may cause major-
401 and trace-elements to be incorporated into minerals at non-equilibrium con-
402 centrations (Lu et al., 1995). In the case of clinopyroxene-melt element
403 partitioning in alkali-silicate systems, experiments demonstrate that rapid
404 cooling rates (up to 50 °C / hr) result in depletions of Si, Ca and Mg in
405 the clinopyroxene that are compensated for by enrichments in Al, Na and
406 Ti (Mollo et al., 2013). Trace-element partitioning systematics determined
407 from these same experiments are consistent with slowly-cooled experiments
408 once crystal-chemical ($^{\text{IV}}\text{Al}$) systematics are accounted for (ibid. their Fig.
409 9). Deviations of the partition coefficient of several orders of magnitude can
410 occur only when small portions of a diffusive boundary layer become incor-
411 porated into the mineral phase as melt inclusions (Kennedy et al., 1993).

412 (b) Compositional zoning in mineral phases may occur when crystal
413 growth rates are high relative to diffusion within that crystal phase. In
414 concentrically-zoned minerals, compatible element concentrations are higher
415 than equilibrium values in the cores of crystals. Therefore preferential sam-
416 pling of the rims of concentrically-zoned minerals returns apparent parti-
417 tion coefficients that more closely approximate equilibrium conditions. At
418 low-degrees of crystallisation apparent partition coefficients for incompatible
419 elements are more subtly offset from equilibrium values than those for com-
420 patible elements because their concentration in the melt is more consistent

421 during crystallisation (Section 9).

422 Having recognised that equilibrium *sensu stricto* was not demonstrated
423 by our experimental charges, slow diffusion in the clinopyroxene emerges as
424 the primary cause of chemical heterogeneity, and thus the largest potential
425 source of bias to our derived partition coefficients. We quantify the departure
426 from chemical equilibrium with Ce-transects measured across some experi-
427 ment clinopyroxene via EPMA, with Ce as a proxy for the other compatible
428 elements (Supplement S1). Concentric growth-zoning has a smaller effect
429 on clinopyroxene Ce-concentration than sector zoning, the latter of which
430 was cancelled by averaging transects across several grains per experiment.
431 Apparent clinopyroxene–melt partition coefficients for compatible elements
432 (median Ce) are offset from equilibrium (rim Ce) to higher values by 4–8%
433 (Supplement S1). Large systematic errors outside of these figures are un-
434 likely because sets of trace-element partition-coefficients of common valence
435 define Ounma parabolae, discounting the presence of melt-inclusions within
436 the experiment clinopyroxene (see Fig. 8 below and Kennedy et al., 1993).

437 A 4–8% systematic positive bias in compatible element partition coeffi-
438 cients is small relative to the variation within our sample set, as well as within
439 literature values. Furthermore, many of our experimentally-derived partition
440 coefficients define trends with clinopyroxene major-element composition that
441 are continuous throughout a set of literature data (Fig. 7 below). For these
442 reasons, no correction factor has been applied to our data presented in the
443 figures below, or in Tables 4 and S1.