Comment

Comment on "Systematic variations of argon diffusion in feldspars and implications for thermochronometry" by Cassata and Renne

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Cassata and Renne (2013) is a data-rich paper potentially providing opportunities to systematically test long-standing models of argon diffusion behavior in feldspars and we congratulate them on a heroic achievement. That said, several of their interpretations are highly problematic due to misconceptions of both the nature of their sample and diffusion modeling.

(1) Evidence of grain-scale diffusion in an exsolved feldspar

The authors state that "*If exsolution lamellae defined the diffusion domain, each fragment, regardless of size, would yield the same D/a² value at a given temperature because they have the same lamellar microstructure. Therefore, our experiments corroborate the conclusion of Parsons et al. (1999) that strain-controlled, coherent microstructures do not provide fast-pathways for Ar diffusion, but rather define interfaces within complex domains.*"

The above claim cites a paper relevant to K-feldspar: but their pegmatite K-feldspar from Itrongay, Madagascar, is dominantly cryptoperthitic, and that the essentially ubiquitous linear array evident through the low temperature degassing is defined exclusively by the smallest diffusion domain. The authors did not undertake mineralogical characterization of their MADk K-feldspar but instead relied on published descriptions (Arnaud and Kelley, 1997; Wartho et al., 1999; Parsons and Lee, 2005). These and other papers (Hovis, 1988; Heinemann et al., 2001; Teng et al., 2001) describe this material as a homogeneous

feldspar, with Parsons and Lee (2005) noting sporadic albite lamellae with a maximum thickness of about 10 nm. These and other albite lamella would not behave as Ar diffusion boundaries as they are below the threshold size (Lee and Parsons, 1997) that lead to the formation of the misfit dislocations along even coherent boundaries and shown by Fitz Gerald et al. (2006) to be preserved during laboratory heating up to melting. Exsolution lamellae not separated by a planar system of misfit dislocations do not behave as porous boundaries that would define a diffusion domain in basement K-feldspars (Lovera et al., 1997, 2002). Thus degassing data for MADk K-feldspar cannot bear on the role of perthite boundaries in Ar diffusion in feldspar.

The second misconception is evidenced by Cassata and Renne's (2013) interpretation of the "kink" in Arrhenius plots of sized aliquots of MADk as reflecting structural modifications in response to lab heating rather than, as we have long held, due to the existence of multiple diffusion domains. They argue that the vertical displacements on Arrhenius plots between data of different sized aggregates "conclusively" proves the presence of a single diffusion domain and therefore any kinks cannot be due to the existence of multiple diffusion domains. However, their results are completely consistent with the predictions of the multi-domain model. Because both the Benson Mines and Madagascar samples are homogeneous K-feldspars, it is unsurprising that the largest diffusion domain (domain 2) coincides approximately with the size of the crystal while the much smaller domain (domain 1), documented in both materials by Lovera et al. (1997) and comprising only a small fraction of the sample, are surface related or distributed within the grain. Further evidence is provided by Flude et al. (2013) who used laser depth profiles to infer the existence of small, surface related domains. Thus the

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array observed during low-temperature degassing is the expected result of the simultaneous degassing of both domains with an effective diffusion radius (which is a volume weighted average of domain sizes) of

$$\rho_{eff} = \left(\frac{\phi_1}{\rho_1} + \frac{\phi_2}{\rho_2} \right)^{-1} = \rho_2 \left(\frac{\phi_1}{\rho_1/\rho_2} + \phi_2 \right)^{-1} \quad (1)$$

where ϕ and ρ are, respectively, the volume fraction and radius of the domain. While a reduction in the macroscopic grain size would not significantly alter either the size nor the volume fraction of the smallest domain, it would significantly reduce the effective size ρ_{eff} in almost identical proportion to the reduction of ρ_2 (i.e., the measured grain size).

To drive this point home, we show in Fig. 1a how the 145 and 100 μm grain size data of Cassata and Renne (2013) can be exactly modeled using two domain samples having the same smallest domain size and largest domains coinciding with their measured size. A negligibly larger volume concentration of the smallest domain (0.10 instead of 0.07) was used in the simulation of the 100 μm data to achieve the best fit to the observed extension of the linear array.
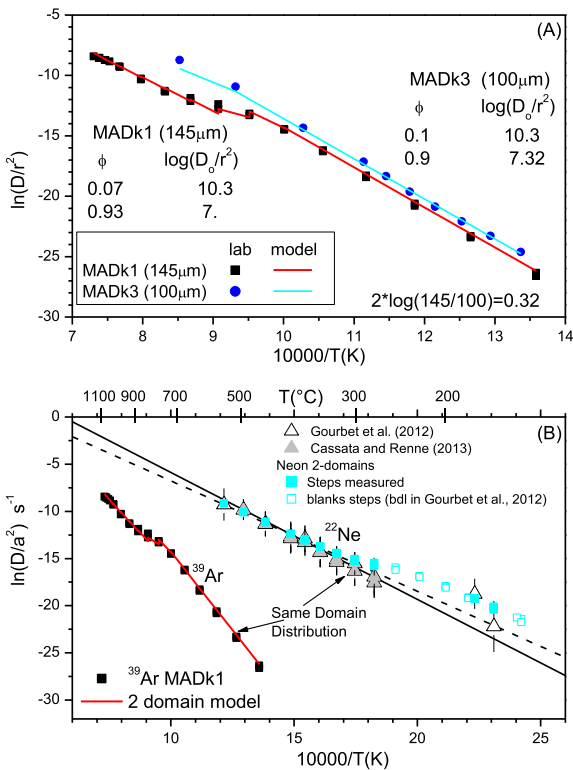

Fig. 1. (a) Shows a MDD model fit to the 100 and 145 μm data where the largest domain corresponds to the grain size. Note the excellent agreement between the data and the model. (b) Shows the same domain distribution modeled to both the Ar and Ne data. Note that the MDD fit describes the two low T data steps from Gourbet et al. (2012) while the single diffusion domain model does not.

The data for the two 100 μm sized fractions do not exhibit a kink in their Arrhenius plots (Fig. 3b and d of Cassata and Renne (2013)), seemingly inconsistent with their temperature induced phase change hypothesis, while the MDD model yields excellent agreement with the measured data (MAD3k model; Fig. 1a). Although they ascribe this anomaly to diffusion anisotropy, we note that because the 100, 145, and 175 μm aliquots share the same crystallographic orientation [0 0 1], their interpretation is problematic. The data of Cassata and Renne (2013) are not an unambiguous display of single domain behavior and thus deviations from linearity cannot be taken as evidence of a thermally-controlled phase change.

(2) Evidence that Arrhenius non-linearity reflects structural changes during heating

The authors state that "*The vertical displacements between arrays...require that smaller grains have smaller sub-grain domains and vice versa. Clearly this is illogical, as individual fragments of this compositionally homogeneous megacryst a priori differ only in size. Not surprisingly, all aliquots yield similar values of D_o when D_o/a^2 is multiplied by the square of the grain radius (Fig. 8b). Thus the 2 natural log unit displacement of the Arrhenius array must reflect an intrinsic change in the diffusive medium or diffusion mechanism(s).*"

Unfortunately, to arrive at this conclusion, the authors compounded the misunderstanding implicit in Eq. (1) (i.e., that the early linear array is defined solely by the smallest domain) with a misinterpretation of their Ne results. Specifically, they state that "*Because K and Na (and therefore ^{39}Ar and ^{22}Ne) are uniformly distributed in this sample, Ar and Ne a priori share the same domain distribution. The linearity of the Ne Arrhenius array (Fig. 9b) confirms that crystal fragments of this feldspar represent coherent, single diffusion domains...The curvature observed at high temperature on the Ar Arrhenius plot (Fig. 9a) therefore unambiguously reflects a crystallochemical change.*"

Even accepting that Ar and Ne are subject to the same diffusion barriers, the fact that Ne retention is more than 8 orders of magnitude lower than Ar, the smallest domain is already degassed by the first step shown by Cassata and Renne (2013) giving rise to the apparent linear array. Using all the Gourbet et al. (2012) Ne data (note: their first two steps were not shown by Cassata and Renne (2013)) and heating schedule, Fig. 1b shows the Ar and Ne Arrhenius plots for a sample having the same domain structure we document for the Madagascar K-feldspar in Fig. 1a. Clearly, the lack of curvature in the Ne array is not an indication of a "single diffusion domain" nor can it be used as an "unambiguous" probe to conclude that the observed curvature on the ^{39}Ar Arrhenius plot reflects a thermocrystallographic change. Additionally, the two lowest temperature data, shown as open triangles, are more consistent with the presence of two domains than one.

The observations we make above are not new. Cassata and Renne (2013) overlooked a set of experiments performed a generation ago (Harrison et al., 1991) specifically designed to test the mechanism responsible for the kink