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Comment on 'Formation of fast-spreading lower oceanic crust as revealed by a new Mg-REE coupled geospeedometer' by Sun and Lissenberg

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Quantifying the cooling history of the lower oceanic crust, and other slowly cooled rock bodies, is fundamental for understanding heat transfer processes in the Earth and the formation of the Earth's crust from magmatic bodies. Geospeedometers offer a powerful tool to address this, but they need to be calibrated and applied carefully so that meaningful results can be obtained. Sun & Lissenberg (2018; hereafter S&L) present a new geospeedometer based on the different bulk closure temperatures of Mg and Rare Earth Elements (REEs) for diffusive exchange between plagioclase (pl) and clinopyroxene. They caution against the use of the existing experimentally calibrated Mg-in-pl thermometer of Faak et al (2013) and instead present a new thermometer. This Mg-thermometer is combined with an existing REE-thermometer, and cooling rates are derived from the different bulk closure temperatures for the two systems for samples from lower oceanic crust exposed at the Hess Deep Rift (HDR).

They criticize the results on cooling rates from the same locality of Faak et al. (2015) because "*in addition to the Dodson-type assumptions, results of Faak et al. (2015) are also likely subject to uncertainties from their Mg-exchange thermometer (Faak et al., 2013) and 1-D plane sheet approximation*." We find this statement surprising, as Faak et al. (2014, 2015) did not use Dodson-type equations, tested the assumption of clinopyroxene acting as an infinite reservoir, and specifically considered the role of diffusion in multiple dimensions. In the following we also show that the uncertainties in the Mg-exchange thermometer of Faak et al. (2013) are misrepresented.

We argue here that the approach of S&L is flawed on several counts and consequently, yields incorrect results. These include: (i) calibration and application without measurement of Mg content in plagioclase or REE in pyroxene, (ii) ignoring the role of silica activity ($aSiO_2$) in controlling the partitioning of Mg in plagioclase, (iii) use of an inappropriate diffusion model, (iv) inappropriately accounting for crystal shape in controlling diffusion distances, and (v) use of inappropriate concentration data for determination of cooling rates. We discuss each of these aspects in some detail below.

(i) Calibration and application without measurement of concentrations. Arguing that the directly experimentally calibrated model of Faak et al. (2013) is subject to uncertainties, S&L present a new geospeedometer that is based on their own Mg-in-pl thermometer. However, this is not derived from measured Mg-concentrations in coexisting plagioclase and clinopyroxene. Instead, the melt compositions from various experiments reported in the LEPR database are used to calculate Mg-concentrations in plagioclase based on the pl/melt partitioning model of Sun et al. (2017). The ratios of these calculated plagioclase Mg-concentrations and the reported Mg-concentrations in clinopyroxene are used to derive $K_{Mg}^{pl/cpx}$ through linear regression. Thus, their expression to describe Mg partitioning between plagioclase and clinopyroxene, and the resulting Mg-in-pl thermometer, are based on an idealized theoretical model rather than direct measurements. In contrast, Faak et al. (2013) based their calibration of $K_{Mg}^{pl/cpx}$ on direct experimental measurement of concentration profiles in coexisting plagioclase and clinopyroxene, where the Mg concentration data were collected specifically for this purpose.

Furthermore, in their application of the geospeedometer, concentrations of REEs were not analysed in 31 samples, but obtained from a linear correlation between REEs and X_{An} in 15 samples, where REEs were analysed. This means that 70% of the obtained cooling rates are based on trace element concentrations which were not measured. Such calibration and application of geospeedometers based on unmeasured concentrations are problematic, to say the least.

(ii) Ignoring the role of aSiO$_2$. The authors claim that results from the existing Mg-in-pl diffusion chronometer by Faak et al., (2014, 2015) are "*subject to uncertainties from their Mg-exchange thermometer", because this "thermometer has a strong dependence upon silica activities that can only be calculated using existing activity models*". Although S&L do not question the clearly demonstrated significant dependence of $K_{Mg}^{pl/cpx}$ on aSiO$_2$ shown by Faak et al.'s (2013) experimental study, they go on to suggest that the uncertainty in aSiO$_2$ is so large that the Faak et al. approach has 100-200°C uncertainties in closure temperature. A new geospeedometer is presented to "overcome the aforementioned limitations regarding … silica activities …" It is unclear, how ignoring a demonstrated dependence is supposed to reduce uncertainties. Further, their calibration strategy excludes *a priori* the possibility that a dependence on aSiO$_2$ may exist by calculating plagioclase MgO contents rather than measuring them. Hence any dependence of aSiO$_2$ on Mg partitioning cannot be tested for, although this is implied by the use of different symbols in their Fig. 3a. We contend that the S&L thermometer (and hence geospeedometer) is likely to have systematic errors related to variations in aSiO$_2$.

Further, the basis for their concern about uncertainties in aSiO$_2$ reflects a misunderstanding of the basic thermodynamics behind the calculation of aSiO$_2$. In their Fig. 1b, S&L show a purported difference between the aSiO$_2$ model applied by Faak et al. (2014, 2015) and Carmichael (2004). However this is misleading – aSiO$_2$ in all the calculations discussed in these studies are constrained by the equilibrium between olivine and orthopyroxene (i.e. ol + SiO$_2$ = opx), and are based on the MELTS thermodynamic dataset of Ghiorso & Sack (1995). Therefore, at any given *P-T* condition, it is not possible to get widely different $aSiO_2$ using different expressions. Figure 1b of S&L misrepresents the situation; i.e., the curves shown were not calculated for identical sets of relevant intensive thermodynamic variables. Notwithstanding all of these, it is unclear to us why the model of Carmichael (2004), developed for melts, should even be considered to constrain $aSiO_2$ using the bulk composition of a cumulate rock as done by S&L. For modelling subsolidus exchange of Mg between plagioclase and clinopyroxene in the lower oceanic crust, where olivine and orthopyroxene are generally present (the latter sometimes only as exsolution lamellae), using constraints from ol-opx stability as done by Faak et al. is clearly more appropriate.

As S&L demonstrate in their Fig. 1a, the effect of $aSiO_2$ on temperature can lead to changes in calculated temperature of 100-200°C. Ignoring this effect will lead to incorrect temperatures that can be off by 100-200°C, and according to S&L, this would lead to cooling rates that "*are about 0.3–2.4 orders of magnitude lower* ".

(iii) The diffusion model and use of averaged concentrations. Diffusion of trace elements in plagioclase occurs with a strong coupling to X_{An} (and therefore, the shape of anorthite zoning profiles) (see Costa et al., 2003). As a result, the diffusion equations governing atomic flux are different from those obtained using conventional diffusion equations, and result in very different evolution of concentration profile shapes. A very important consequence, for the present purposes, is that the calculated timescales are very different. Costa et al. (2003) showed that many observed shapes of Mg concentration gradients in natural plagioclase crystals can only be accounted for if such coupling is taken into account; the approach has been refined in later works (e.g. Dohmen et al. 2017) and used in numerous applications to geospeedometry.

S&L simply ignore this vast literature and use closure concepts based on conventional diffusion equations to calculate cooling rates. The importance of accounting for the coupling of trace element diffusion with X_{An} obviously increases with the extent of zoning of X_{An} and since plagioclase in the HDR plutonics "*is strongly and often complexly … zoned in major elements, with continuous, discontinuous, patchy and oscillatory zoning all occurring*" (Lissenberg et al., 2013) this is clearly important. Thus, the cooling rates obtained by S&L from plagioclase crystals that are strongly zoned in X_{An} must be incorrect (see discussions and illustrative examples in Costa et al.,2003; Faak et al. 2014; Dohmen et al. 2017, among others).

Another large uncertainty is introduced by S&L because they use averaged concentrations of X_{An} and Mg in plagioclase, and REE in pyroxene. The problem of this approach for Mg in plagioclase is obvious from the discussion above and the effect on cooling rates is addressed in (v). But S&L also use averaged REE concentrations despite Lissenberg et al. (2013) reporting "*strong trace element zoning in many (cpx) grains*" with substantial enrichment in REE in the rims of *both* clinopyroxenes and plagioclase crystals (e.g. La contents differing by up to an order of magnitude between core and rim, even at similar X_{An}). Such zoning cannot be produced by subsolidus diffusive equilibration between the phases, and instead it likely reflects partial preservation of magmatic zoning (e.g. Lissenberg et al., 2013); i.e. there is no reason to expect the bulk plagioclase and clinopyroxene compositions provide any information about the thermal history of the sample. In addition, the average of one analysis at the core and one at the rim in three grains from such crystals (as used by S&L for pyroxene) is clearly insufficient to accurately determine a bulk crystal composition.

(iv) Accounting for crystal shape. The modelling approach taken by S&L demands further simplifications. They treat the geometry of the plagioclase crystals as spheres. This is not correct for the natural crystals in this study that have aspect ratios around 1:3. Costa et al. (2008) showed using numerical calculations that 2D effects on diffusion lengths are important for elongate crystals. They demonstrated that "*ignoring the elongated shape of plagioclase tends to overestimate the time scales by more than one order of magnitude*". Faak et al. (2014) studied this for grain scale diffusion of Mg in plagioclase in 1D and 2D and demonstrated how using the long dimension in a plagioclase crystal with an aspect ratio of 1:3 can lead to an uncertainty in cooling rate of one order of magnitude. Thus, the approach of S&L of using the arithmetic means of average long and short dimensions as their average plagioclase grain size, and a spherical geometry, can lead to significant errors in the determined cooling rates.

(v) Inaccurate concentration data for determination of cooling rates. Finally, a problem with averaging measurements becomes very obvious, when S&L report Mg concentrations smaller than or similar to the given standard error, e.g. 0.14±0.16 wt% MgO in plagioclase for sample JC21-73R-13. Considering that the highest Mg concentrations in plagioclase phenocrysts from MOR basalts are typically ~0.3 wt% MgO, such numbers are meaningless, and in terms of cooling rates, this represents the difference between quenching (0.3 wt% MgO) and infinite slow cooling (0 wt% MgO). However, S&L still manage to obtain cooling rates from such data! Unfortunately, complete analysis of the problems with the data are not possible as the full dataset are not published.

Concluding comments

Any new model, and the simplifications that go into it, needs to be validated by comparison with benchmarks and/or other established results. To this end, Faak et al. (2015) and Faak and Gillis (2016) also obtained cooling rates for plutonic rocks from Hess Deep using Mg-in-pl geospeedometry and then compared these results with cooling rates obtained by the completely independent method of Ca-in-olivine geospeedometry. Both methods are based on grain-scale diffusion modelling, but rely on different diffusion equations (each appropriate for the system to be modelled), are based on independently calibrated diffusion coefficients, and independent experimentally calibrated thermometers. They found good agreement between the two methods, as well as consistency between samples and tight clustering of cooling rates from any given stratigraphic depth (Fig. 1), indicating good precision as well as accuracy of the determined cooling rates and their overall robustness. In comparison, the cooling rates determined by S&L scatter (by over two orders of magnitude at some depths) and are systematically faster from those determined by Faak et al. (2015) and Faak and Gillis (2016)(Fig. 1).

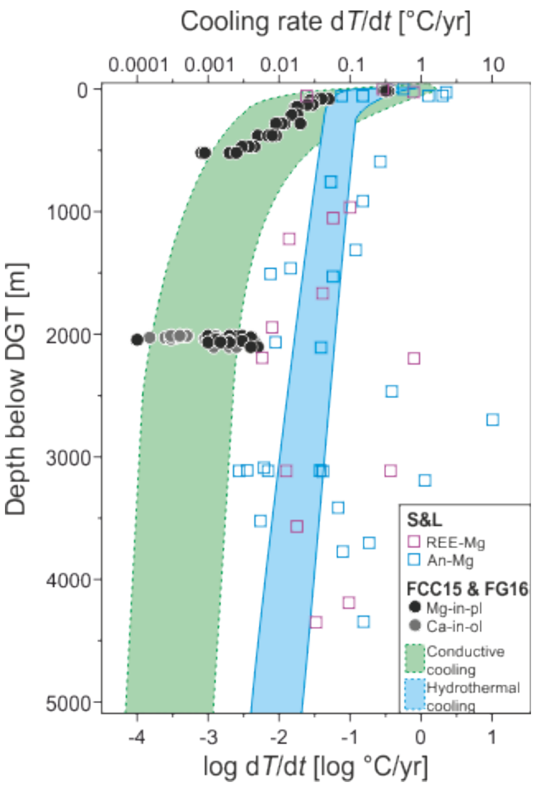

Fig. 1. Comparison of the cooling rates derived by S&L with those obtained by Faak et al., 2015 (FCC15) and Faak & Gillis, 2016 (FG16) from the same sample location. The green and blue envelopes show cooling rates predicted from thermal calculations for conductive and hydrothermal cooling models (see Faak et al., 2015 for a detailed

discussion).

Summarizing, S&L provide a “calibration” and application of a REE-Mg geospeedometer that is based largely on a dataset where REE (application) and Mg (calibration) concentrations in plagioclase were generally not measured, and the data were inappropriately averaged. They use a “simplified” partitioning model that ignores a demonstrated dependency on a key parameter (dependency on $aSiO_2$ of partition coefficients). This approach is combined with an incorrect diffusion equation to obtain cooling rates. The five points outlined above demonstrated that the very scattered, and very fast, cooling rates reported by S&L (Fig.1) are unlikely to reflect anything other than the problems in their methodology.

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