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Slow cooling of the lowermost oceanic crust at the fastspreading East Pacific Rise

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Model parameters and input conditions for the diffusion models

Ca-in-olivine

The Ca-in-olivine geospeedometer is based on the diffusive exchange of Ca between olivine and clinopyroxene during cooling, and cooling rates are determined from the measured Ca-concentration profiles in olivine. A detailed description of the Ca-in-olivine geospeedometer may be found in Coogan et al. (2002 and 2007), here we briefly summarize the modeling approach and the input parameters used, and review the inherent uncertainties. The method is based on Dodson's concept of closure temperature Tc (Dodson, 1973), which was extended by Dodson (1986) to the calculation of a closure profile (Tc-profile) to give:

$$Tc(x) = \frac{E}{R \ln\left(\frac{R Tc^2 D_0}{E s a^2}\right) + G(x)},$$
 Eq. (DR1)

at which *R*=ideal gas constant, *s*=cooling rate around the closure temperature *Tc*, and *a*=radius of the grain. The parameters *E* and D_0 refer to activation energy and the pre-exponential factor in the diffusion equation. Here, we used the diffusion data of Coogan et al. (2005) for diffusion along the c-axis and $fO_2=10^{-12}$ bar (*E*=207000 *J/mol* and $D_0=1*10^{-10}$). The closure function *G*(*x*) depends on the geometry of the cooling object and the position *x* within it. Here, we used the geometry of a sphere:

$$G(x) = 0.57721547 + 4 \sum_{n=1}^{z} \frac{(-1)^{n+1} \sin(n \pi x) \ln(n \pi)}{n \pi x}, \qquad \text{Eq. (DR2)}$$

with *z*=10.000.

As *Tc* appears on both sides of Eq. (DR1), the equation has to be solved iteratively.

The measured Ca-concentration profiles in olivine can be translated into closure temperatures using the thermometer of Köhler and Brey (1990):

$$Tc(x) = \frac{-42.5 P - 5792}{\ln\left(\frac{C_{Ca}^{Ol}(x)}{C_{Ca}^{Cpx}}\right) + 1.25} - 273,$$
 Eq. (DR3)

at which *P*=pressure (here, we assumed *P*=2kbar), C_{Ca}^{Ol} = measured concentration of Ca in olivine, C_{Ca}^{Cpx} =measured concentration of Ca in clinopyroxene (adjacent to the olivine grain).

The cooling rate *s* in Eq. (DR1) is iteratively changed until the best visual fit between the closure profile calculated from Eq. (DR1) and the closure profile calculated from Eq. (DR3) is attained.

Uncertainties inherent in the approach

Coogan et al. (2005) show that quantifiable systematic inaccuracies in cooling rates obtained from the Ca-in-olivine geospeedometer principally result from uncertainties in the partition coefficient for Ca between olivine and clinopyroxene ($K_{Ca}^{Ol/Cpx}$), and in the diffusion coefficient (D_0 and E) of Ca in olivine. They performed Monte Carlo simulations to evaluate the potential inaccuracies arising from uncertainties in these parameters. Cooling rates for a given measured Ca profile were calculated 2000 times allowing $K_{Ca}^{Ol/Cpx}$, E and D_0 to vary within given bounds. These bounds were taken from the experimental uncertainties in these parameters (Köhler and Brey, 1990 for $K_{Ca}^{Ol/Cpx}$ and Coogan et al., 2005 for D_0 and E). The predicted uncertainty (1 σ) in the cooling rate based on these simulations is a function of cooling rate, being 0.3 log units at a cooling rate of $3 \cdot 10^{-4}$ °Cyr⁻¹ to 0.2 log units at a cooling rate of 0.1° Cyr⁻¹.

We note that Shejwalkar and Coogan (2013) show that the Ca-content in olivine in equilibrium with clinopyroxene additionally depends on the forsterite content (*Fo*) of the olivine. However, their experimental calibration was carried out in a temperature range of 1170-1322°C, and cannot easily be extrapolated to the range of closure temperatures determined in olivine in the samples investigated here (Tc_{core} =860-770°C using the calibration of Köhler and Brey, 1990; Table DR2). Equation (13) in Shejwalkar and Coogan (2013) combines their results with the previous experiments by Köhler and Brey (1990) and was used to quantify the effect of the compositional dependence on the closure temperatures and cooling rates of the samples investigated here. It is found that Tc_{core} is increased by 30°C (for Fo=0.79; lowest Fo in investigated sample suite) and by 40°C (for Fo=0.84; highest Fo in investigated sample suite) when the compositional effect is accounted for. The resulting effect on the cooling rate depends on the length of the observed profile, but is below 0.5 orders of magnitude even for the longest profiles investigated here (and below a factor of two for the shortest profiles).

Fitting full profiles instead of using the highest Ca concentration measured in one olivine grain

VanTongeren et al. (2008) used the Ca-in-olivine geospeedometer to obtain cooling rates from the lower oceanic crust exposed in the Wadi Khafifah section of the Oman ophiolite. Instead of measuring and fitting full profiles (rim-core-rim) as recommended by Coogan et al. (2002), these authors only measured between 2-7 (on average 3) analyses per olivine grain and then used the highest measured Ca values from each crystal core for the calculation of closure temperature and cooling rate. We caution that this approach will overestimate the cooling rate and result in inaccurate results. Figure DR2 shows cooling rates obtained from a synthetic Ca-concentration profile in olivine. Fitting the full profile results in a cooling rate of 0.0005°Cyr⁻¹. Cases (i), (ii) and (iii) simulate data point affected by alteration (see Fig. DR 2 for details) Following the approach taken by VanTongeren et al. (2008) and using only the data points with highest Ca-concentrations overestimates the cooling rate of this crystal by up to 1.5 orders of magnitude (we note that given the limited number of analyses per grain carried out by VanTongeren et al., 2008, it would not be possible to identify these measurements as outliers from the actual profile shape).

To illustrate this point using natural samples, we show full concentration profiles of Ca in olivines from the Wadi Abyad in the Oman ophiolite from Coogan et al. (2002). Fitting these complete profiles with the approach outlined above results in cooling rates between 0.0035°Cyr⁻¹ to 0.00012°Cyr⁻¹, at which cooling rates are decreasing with decreasing sample depth above the Moho (Fig. DR3). Using the approach by VanTongeren et al. (2008) overestimates cooling rates by up to 2 orders of magnitude and shows no systematics of cooling rate with sample depth.

Mg-in-plagioclase

The Mg-in-plagioclase geospeedometer is based on the diffusive exchange of Mg between plagioclase and clinopyroxene during cooling (Faak et al., 2014). Partition and diffusion coefficients for Mg in plagioclase depend on the composition of the plagioclase (i.e., the anorthite-content), which has to be accounted for in the diffusion equation (Costa et al., 2003). Thus, it is not possible to use Dodson's analytical equation for the Mg-in-plagioclase system. Faak et al. (2014) presented a Mg-in-plagioclase geospeedometer based on a finite difference modeling approach using the diffusion equation of Costa et al. (2003) and applied this method to samples from the oceanic crust (Faak et al., 2014, 2015). A detailed description of the used diffusion model may be found in Faak et al. (2014), here we briefly summarize the modeling approach and the input parameters used.

Diffusion equation and diffusion coefficient

The diffusion of Mg in plagioclase is coupled with the anorthite content, X_{An} , in plagioclase, which needs to be accounted for in the diffusion equation (Eq. (7) in Costa et al., 2003) and the resulting diffusion equation to describe the flux of Mg has been presented by Costa et al. (2003):

$$\frac{\partial C_{Mg}}{\partial t} = \left(D_{Mg} \frac{\partial^2 C_{Mg}}{\partial x^2} + \frac{\partial C_{Mg}}{\partial x} \frac{\partial D_{Mg}}{\partial x} \right) - \frac{A}{RT} \left(D_{Mg} \frac{\partial C_{Mg}}{\partial x} \frac{\partial X_{An}}{\partial x} + C_{Mg} \frac{\partial D_{Mg}}{\partial x} \frac{\partial X_{An}}{\partial x} + D_{Mg} C_{Mg} \frac{\partial^2 X_{An}}{\partial x^2} \right)$$
(Eq. DR4)

where C_{Mg} =concentration of Mg in plagioclase, *t*=time, D_{Mg} =diffusion coefficient of Mg in plagioclase, *x*=distance and *A*=factor to describe the dependence of the partition coefficient on X_{An} .

We used the diffusion coefficient of Mg in plagioclase from Faak et al. (2013) that was determined experimentally in the compositional range of the lower oceanic crust:

(Eq. DR5)

$$D_{Mg}^{Pl} \ \left[\mathrm{m}^{2}\mathrm{s}^{-1}\right] = 1.25 \cdot 10^{-4} \ \left[\mathrm{m}^{2}\mathrm{s}^{-1}\right] \exp\left(\frac{-320924 \ \left[\mathrm{Jmol}^{-1}\right]}{RT}\right) \cdot \left(a_{SiO_{2}}\right)^{2.6}.$$

Initial and boundary conditions

The partition coefficient, $K_{Mg}^{Pl/Cpx}$, has been determined experimentally by Faak et al. (2013) and is given by the relationship:

$$\ln K_{Mg}^{Pl/C_{px}} = -9219 \ [K] \ \frac{1}{T} + 1.6 + \frac{16913 \ [Jmol^{-1}]}{RT} X_{An} + \ln a_{SiO_2}$$
(Eq. DR6)

This can be re-arranged to give the interface plagioclase composition as a function of the measured clinopyroxene composition, temperature and the silica activity in the system:

$$C_{Mg}^{Pl} = C_{Mg}^{Cpx} \exp\left[-9219 \left[K\right]\frac{1}{T} + 1.6 + \frac{16913 \left[Jmol^{-1}\right]}{RT}X_{An} + \ln a_{SiO_2}\right]$$
(Eq. DR7)

An initial profile is calculated based on Eq. (DR7) at temperatures around 1200°C (the exact starting temperature T_{start} depends on the grain size of the plagioclase and is given in Table DR1).

Silica activity

Solving equations (DR5-DR7) requires knowledge of the silica activity, a_{SiO_2} , as a function of temperature. Here, we assume a_{SiO_2} is constrained by the assemblage olivine+orthopyroxene as these are commonly observed phases in the samples studied. Faak et al. (2014 and 2015) show that in this case, the temperature dependent silica activity can be approximated with a polynomial of the form:

$$a_{SiO_2} = -4.86904 \cdot 10^{-7} T^2 + 1.51570 \cdot 10^{-3} T - 0.618707$$
 (Eq. DR8)

Uncertainties inherent in the approach

As discussed previously for the Ca-in-olivine geospeedometer, the main source of inaccuracy for cooling rates obtained from Mg-in-plagioclase geospeedometer results from uncertainties in the partition coefficient $K_{Mg}^{Pl/Cpx}$ and the diffusion coefficient D_{Mg}^{Pl} . Faat et al. (2014) estimated the effect of uncertainties in these parameters on the cooling rate by performing Monte Carlo simulations. Randomly distributed probability distributions of the parameters were used in 10.000 simulations, at which the parameters can vary within the bounds of the uncertainties in their calibration (Faak et al., 2013). The predicted uncertainty based on these simulations is 0.3 log units for a cooling rate of 0.1° Cyr⁻¹ and 0.3 log units for a cooling rate of 0.001° Cyr⁻¹. Faak et al. (2014) also discuss how the uncertainty of the cooling rate is affected if the chosen diffusion coefficient has a significant dependence on X_{An} or not (Costa et al., 2003; Faak et al., 2013; Van Orman et al., 2014). They show that the cooling rate obtained using the diffusion coefficient of Faak et al. (2013) is by a factor of 3 faster for a normally zoned plagioclase and by a factor of 4 slower for an inversely zoned plagioclase, if the diffusion coefficient depends on X_{An} (Van Orman et al., 2014).

Additionally, Faak et al. (2015) use the scatter in the data for one sample (i.e., the difference in the obtained cooling rates from multiple Mg-profiles in up to 5 plagioclase crystals in the same sample) as a measure for the precision of the cooling rate estimate for a single sample. Following this approach, they find the precision on the obtained cooling rate to be better than half an order of magnitude.

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Figure DR1. Direct comparison of 3 different Mg-profiles in plagioclase for samples from shallow gabbros from increasing depth (in meters below DGB) at the Hess Deep Rift (upper panel, data from Faak et al., 2015), and 3 different Mg-profiles in plagioclase for samples from the deeper plutonics drilled at IODP Site U1415 (lower panel).



Figure DR2. Cooling rates obtained from fitting a synthetic profile of Ca in olivine (solid line). Cases (i), (ii) and (iii) simulate the effect of secondary fluorescence on measurements of Ca in olivine at a distance of $60 \mu m$, $40 \mu m$ and $20 \mu m$ away from a CaCO3 vein with 40 wt% Ca (Dalton and Lane, 1996). We note that this is just one possibility of alteration that can be assed quantitatively. Higher values of measured Ca-concentrations in olivine may also result from other forms of alteration or inclusions. Grey dashed lines show profiles from fitting just the highest Ca concentrations and light grey numbers give the obtained cooling rates.



Figure DR3. Cooling rates obtained from fitting full concentration profiles of Ca in olivine in three samples from different depths in the Wadi Abyad (lower dT/dt) (Coogan et al., 2002; sample depth is given in m above the Moho) in comparison with cooling rates obtained from using only the highest Ca-concentrations measured near the core of the grain (upper dT/dt). Open symbols were excluded from the modeling approach (see Coogan et al., 2002 for details).

TABLE DR1. Summary of the cooling rates that were obtained from the *Mg-in-plagioclase*

Sample	Rock type ¹	Depth ² [m]	Crystal	Profile	Length [µm]	dT/dt [°C/yr]	log dT/dt	T-interval ³ [°C]
J10R1-49	troctolite	55.79	Plag1	P1	138	0.0030	-2.52	1000-810
J10R1-49	troctolite	55.79	Plag2	P1	105	0.0020	-2.70	980-800
J11R1-26	troctolite	65.26	Plag1	P1	165	0.0020	-2.70	1012-775
J11R1-26	troctolite	65.26	Plag2	P1	89	0.0010	-3.00	986-790
J11R1-26	troctolite	65.26	Plag3	P2	150	0.0015	-2.82	1005-800
J25G1-32	troctolite	104.12	Plag2	P1	260	0.0050	-2.30	1044-880
J25G1-32	troctolite	104.12	Plag2	P2	258	0.0040	-2.40	1044-870
P3R1-31	OI gabbro	12.81	Plag2	P1	470	0.0023	-2.64	1086-890
P4G1-5	OI gabbro	12.55	Plag4	P1	387	0.0030	-2.52	1073-920
P4G1-5	OI gabbro	12.55	Plag6	P1	694	0.0020	-2.70	1114-910
P4G1-10	OI gabbro	12.58	Plag1	P2	260	0.0010	-3.00	1044-930
P6R2-14	OI gabbro	24.14	Plag3	P1	128	0.0040	-2.40	994-840
P11R1-38	Ol gabbro	45.98	Plag1	P1	441	0.0001	-4.00	1082-805
P11R1-38	Ol gabbro	45.98	Plag2	P1	126	0.0012	-2.92	993-835
P11R1-38	Ol gabbro	45.98	Plag4	P1	165	0.0013	-2.89	1012-850

geospeedometer.

¹ Ol = olivine ² Depth is given in m below seafloor. ³ *T*-interval is the temperature range over which the diffusion process was modeled (see Faak et al., 2014 for details).

TABLE DR2. Summary of the cooling rates that were obtained from the *Ca-in-Olivine*

geospeedometer.

Sample	Rock type ¹	Depth ²	Crystal	Profile ³	Length	dT/dt	log dT/dt	Tc _{core} ⁴
	Olashbra	15.66	011	D1 f			2.20	[C]
J3R 1-00	Ol gabbio	15.00			900	0.0005	-3.30	010
J3R1-00	Ol gabbro	15.00		PZ N	015	0.0004	-3.40	830
J3R1-66	OI gabbro	15.66	OI2	PTT	690	0.0013	-2.89	830
J3R1-66	OI gabbro	15.66	OI2	P2 f	893	0.0005	-3.30	810
J3R1-66	OI gabbro	15.66	OI3	P1 f	968	0.0003	-3.52	790
J5R1-131	Ol gabbro	27.51	Ol2	P1 h	678	0.0002	-3.82	790
J5R1-131	Ol gabbro	27.51	Ol3	P1 h	931	0.0004	-3.46	855
J5R1-131	Ol gabbro	27.51	Ol3	P2 h	711	0.0003	-3.60	820
J8R2-79	Cpx oik ol gabbro	37.16	Ol1	P1 f	965	0.0003	-3.52	770
J8R2-79	Cpx oik ol gabbro	37.16	Ol2	P1 f	390	0.0009	-3.05	770
J8R2-79	Cpx oik ol gabbro	37.16	OI3	P1 f	435	0.0014	-2.85	790
J9R1-13	Cpx oik ol gabbro	45.33	Ol1	P1 f	663	0.0030	-2.52	840
J9R1-13	gabbro	45.33	Ol2	P2 h	427	0.0020	-2.70	860
J10R1-49	troctolite	55.79	Ol1	P1 h	262	0.0030	-2.52	840
J10R1-49	troctolite	55.79	Ol2	P1 f	261	0.0045	-2.35	820
J10R1-49	troctolite	55.79	Ol2	P2 f	287	0.0035	-2.46	820
J10R1-49	troctolite	55.79	Ol2	P3 h	198	0.0030	-2.52	820
J10R1-49	troctolite	55.79	OI3	P1 h	359	0.0010	-3.00	820
J10R1-49	troctolite	55.79	OI3	P2 h	320	0.0010	-3.00	810
J10R1-49	troctolite	55.79	Ol4	P1 h	325	0.0015	-2.82	830
J25G1-32	troctolite	104.12	Ol1	P1 f	428	0.0040	-2.40	840
J25G1-32	troctolite	104.12	Ol2	P1 h	328	0.0020	-2.70	840
J25G1-32	troctolite	104.12	OI3	P1 f	480	0.0025	-2.60	820
J25G1-32	troctolite	104.12	Ol3	P2 h	344	0.0012	-2.92	820
P3R1-31	Ol gabbro	12.81	Ol1	P1 h	361	0.0005	-3.30	790
P3R1-31	Ol gabbro	12.81	Ol1	P2 h	389	0.0005	-3.30	800
P3R1-31	Ol gabbro	12.81	Ol2	P1 f	641	0.0005	-3.30	780
P4G1-5	Ol gabbro	12.55	Ol1	P1 h	885	0.0004	-3.40	860
P4G1-5	Ol gabbro	12.55	Ol1	P2 h	791	0.0005	-3.30	860
P4G1-5	Ol gabbro	12.55	Ol2	P1 h	832	0.0004	-3.40	860

P4G1-5	Ol gabbro	12.55	OI2	P2 h	813	0.0003	-3.52	840
P4G1-5	Ol gabbro	12.55	OI3	P1 h	775	0.0004	-3.40	850
P11R1-38	Ol gabbro	45.98	OI1	P1 f	825	0.0010	-3.00	830
P11R1-38	Ol gabbro	45.98	OI1	P2 h	458	0.0010	-3.00	840
P11R1-38	Ol gabbro	45.98	Ol2	P1 f	647	0.0015	-2.82	830

¹ Ol = olivine; Cpx oik ol gabbro = clinopyroxene oikocryst-bearing olivine gabbro
² Depth is given in m below seafloor.
³ The letters f and h in the profile name refer to full profiles (core-rim-core) or half profiles (corerim). ⁴ $T_{c_{core}}$ refers to the obtained closure temperature at the core of the profile.