Review of "On unifying carbonate rheology"

Submitted to EGUSphere
by J. Gilgannon and M. Herwegh

This manuscript presents an overview of the many papers published on high temperature flow laws for carbonates, to a great extent made up of natural and synthetic polycrystalline calcite, and the compiled results are used to evaluate a global flow law that is consistent with all of the experimental data. While earlier studies attributed changes in rheology to grain size or to composition (primarily X_{MgCO3}) alone, this re-evaluation of the entire dataset shows that polycrystalline calcite depends on both parameters, including deformation dominated by dislocation creep and diffusion creep. That is, deformation due to intracrystalline and inter-crystalline mechanisms depend on these parameters. This result is new and significant, particularly as increasing numbers of grain-size sensitive flow laws for geologically important lithologies (carbonates and silicates) are published and assumed to be due to grain boundary diffusion and sliding, and dislocation processes are typically thought to be independent of grain size (when internal climb and recover preclude increases in defect density) or depend on grain size when glide (Peierls law deformation) occurs with limited diffusion (and climb), giving rise to Hall-Petch strengthening by grain boundaries, not the weakening determined by this analysis.

One detail that might help the reader follow the development here is to state which carbonate minerals are included in the analysis. I find the inclusion of dolomite in this paper interesting, as some would not expect a single flow law to apply to both calcite aggregates/rocks (of varying but relatively low solid solution X_{MgCO3} values) and dolomite (at large $X_{MgCO3} = 0.5$). At the same time, I think this is an interesting perspective brought out by including both carbonate phases, calcite and dolomite, and attempting a fit to the entire dataset. At the outset, the different slip systems of these two carbonates would be expected to lead to different dislocation creep laws. However, without further information about the grain boundary structures and properties, I see the authors' point of including both fine-grained calcite and dolomite data that are dominated by grain-size-sensitive processes, including grain boundary diffusion and sliding. Why not compare these results normalizing by parameters of grain size and X_{MgCO3}? It is worth stating the beginning premise(s) of this analysis (and why you include dolomite data). Taking this further, it might be interesting to include magnesite deformation data (with X_{MgCO3} nearly equal to 1.0; Holyoke et al., 2014). Indeed, the mineral symmetry and structure of magnesite is essentially the same as calcite, while dolomite differs due to its ordered cation structure. Thus, any trends that go beyond creep of an individual carbonate phase might be more likely to hold for calcite and magnesite than for calcite and dolomite.

Of course, when applications are made to crustal rocks, the deformation behavior of calcite (of varying Mg content) and dolomite will be most useful. Thus, the ability to formulate a flow law that fits such a large dataset for crustal carbonates at varied conditions, grain sizes, and compositions is impressive and will serve as a reference in applications to natural deformations of carbonates. This contribution should therefore be of great interest to readers of EGUsphere, including geologists studying deformation in the laboratory, natural shear zones, and theoreticians evaluating physical processes of deformation.

This manuscript is well written and shouldn't take much revision for final publication. In the following, I offer some minor points that may improve the manuscript. However, I leave much of this to the authors' discretion.

Early in Section 3.4 (Normalization of data), it would be worth stating more explicitly that all mechanical data sets where calcite compositions have been reported and dolomite have been used in the normalization. Or I may have misunderstood how this was done. The dolomite data may throw off a best-fit to calcite aggregate data. In any case, please state exactly how this was done.

In Figure 11, it would be worth stating what the assumed tectonic setting is. These are classic lithosphere-dimensioned yield envelopes for carbonate deformation including frictional and plastic flow laws for an assumed, fixed strain rate, geothermal gradient and tectonic stress state (compressional, extensional, strike-slip/transform boundaries). Please include the assumed tectonic setting in the caption. Similarly, please include the assumed strain rate in figures 12b and 12c.

I find the comparisons of flow laws for non-zero-X_{MgCO3} calcite aggregates and dolomite very interesting, and I wonder if the authors might add some possible explanations of the differences in the discussion of this manuscript. At the outset, differences in crystal symmetry and structure of calcite and dolomite, and the different slip systems of these two minerals offer obvious reasons that their flow laws for coarse-grained aggregates associated with intracrystalline deformation cannot readily be combined into one simple relation. However, it is fair to wonder why this doesn't work well for grain-size-sensitive deformation and processes at grain boundaries (grain boundary diffusion and sliding). We know little about the atomic structures of grain boundaries, so a relationship that includes grain size and X_{MgCO3} might be expected to work for inter-crystalline creep mechanisms in relatively "unstructured" carbonate grain boundaries. It could be that mean jump distances or frequencies might differ for dolomite grain boundaries (where dolomite grains are ordered in Ca and Mg) from those at calcite grain boundaries. This might mean that grain boundary diffusion depends more strongly on X_{MgCO3} than captured by grain-size-sensitive calcite deformation results. Alternatively, nucleation (or reaction to add to one of the dolomite grains adjacent to a grain boundary) during diffusion creep and grain boundary sliding may differ at X_{MgCO3} values near 0.5. I don't think these potential differences can be evaluated without further data or information, but they are interesting possibilities. I wonder if grain-size-sensitive deformation of magnesite (at

X_{MgCO3} =1) with the same mineral structure as calcite might fit the universal carbonate deformation law presented here better than flow laws reported for dolomite.

Throughout, this manuscript is well written and I have only very minor editorial suggestions for rewording, which I will list below by line number:

Line 2 (abstract) – "… limestones and marbles. Such an"

Line 100 – Was this normalization done just for calcite samples? Or both calcite and dolomite samples? Please specify explicitly ("… of natural calcite samples… " or "… of natural calcite and synthetic (?) dolomite samples …")

Line 108 – again please specify if just calcite samples or both calcite and dolomite. The max X_{MgCO3} value of 0.17 certainly suggests that dolomite data were not included in the global fit.

Line 115 – "… sample data are transformed to:"

Line 117 – "and results for coarse grained …"

Line 120 – "… exponents to collapse data to a one-to-one curve …"

Line 128 – "… regimes that we think contribute to deformation and can be used in investigation and normalization. In our data there are two"

Line 129 – "… different deformation mechanisms are apparent: a low stress domain in which data have a slope of 1 in"

Line 130 – "… a high stress domain characterized by a slope of 7 …"

Line 147 – delete "then"

Line 155 – suggest deleting "that"

Line 156 – "… mechanisms; (2) XMgCO3 has two opposing effects …"

Line 157 – "… coarse grained natural samples is only half that of the compositional sensitivity of fine grained"

Line 160 – suggest replacing "visualized" by "illustrated"

Line 171 – "… and coarse grained samples in sections 5.2 and 5.3."

Line 174 – "The effect of magnesium on diffusion creep was first noted in the original work …"

Line 177 – "… magnesium can be separated empirically from grain size. Therefore,"

Lines 184-185 – "the observation of the same or broadly similar activation energies across Mg-carbonates (Herwegh et al., 2003). This observation suggests that mechanisms activated are thermodynamically equivalent, possibly the exact same mechanism for all chemistries."

Line 189 – "2008)) as reported for cation species self diffusion or diffusion creep of calcite (Herwegh …"

Line 190 – "… one should expect that local spatial gradient are reduced as XMgCO3 increases, and magnesium"

Line 191 – "… This is what we observe. …"

Line 192 – delete "which are derived from linearly spaced XMgCO3 values"

Lines 196-197 – "… (fig. 4a and c). Indeed, our results suggest that this compositional effect on flow law extended beyond synthetic Mg-carbonates …"

Line 198 – "strengthening by XMgCO3 may be due to solute-drag …"

Line 199 – "to the progress of linear defects. This second possibility is not expected if chemical diffusion is substantial as discussed earlier"

Line 235 – delete "the framing of"

Line 238 – "0.3). Notably the newly defined XMgCO3-sensitive diffusion creep law …"

Lines 245-246 – "… Lochseiten mylonite data. It is important to ask how well the equations fit carbonates …"

Line 248 – "Equations 5-6 were compared …"

Lines 251-253 – "… data appear to be fit well. In the case of diffusion creep of the Lochseiten mylonite, the data fit equation 5 at higher temperatures but not at lower temperatures (fig. 8c). Figure 8d shows that, as the second phase content rises to 10% and above, the observed rheologies depart from our model."

Line 255 – "The normalization of experimental results of coarse-grained natural sample results was limited to …"

Line 258 – "When compared to other coarse grained calcite experiments, the data fit the model relatively well (9a-c). However, they do"

Line 261 – "the spread of data points. …."

Line 262 – delete “will”

Line 263 – “there is a marked increase in strain. ‘the fit clearly overestimates …”

Line 264 – “… with in the range of Carrara marble experimental results. Regardless”

Line 269 – “… result of differences in sample …”

Line 271 – “… synthetic and natural for XMgCO3 values that”

Line 272 – “… Data plotted for SMgCO3 = 0.07 come from a fine grained …”

Line 275 – “While data plotted for XMgCO3 = 0.03 comes from a fine grained …

Line 277 – “… is not restricted to synthetic samples alone – it is not an artifact”

Lines 278-280 – “… there is a transition to a grain size sensitive dislocation creep field. We conclude from this that grain size sensitive and grain size insensitive dislocation creep fields are real.”

Line 292 – “a modified Hall-Petch relation has been proposed; the smaller the grain size, the stronger …”

Lines 294-296 – “in the dislocation field appears to be similar to the d^{-3} dependence of diffusion creep. Moreover, figure 10 implies that there is a transition as grain size increases to a grain size insensitive rheology.”

Line 298 – “To explain the ever diminishing …”

Line 300 – “… could transition from grain size strengthening to weakening and …”

Lines 301-302 – “deformation as grain size increased. In this model the grain size sensitivity of dislocation accommodated deformation changes according to the storage and recovery of dislocations, and the dependence of these processes on grain size. Breithaupt et al. (2023)”

Lines 305-309 – “… Breithaupt, 2022). Thus, the apparent results for diffusion creep and grain size sensitive deformation of polycrystalline calcite might be linked to the storage and recovery in grains, and how these change with size of grains. The model of Breithaupt et al. (2023) also explains the variation (hardening and weakening) in the effect of grain size for different calcite experiments. …”

Lines 312- 313 – “et al., 2002). This is most likely for lower temperature experiments of Sly et al. (2019). While the grain sizes of Renner et al. (2002) and Herwegh et al. (2003) seem to cover a similar range …”

Lines 315-316 – "… vs area-weighted); grain size values of Renner et al. (2002) might be half those measured by Herwegh et al. (2003; cf. table 5 in Berhger et al., 2011)."

Line 319 – "… sensitivity is needed. Short of adapting"

Lines 320-321 – "… the effect of XMgCO3, a pragmatic guide to modeling different rheologies based on grain size domains (Fig. 10)."

Line 323 – replace "if" by "for"

Line 325 – replace "if" by "for"

Line 326 – replace "if" by "for"

Line 328 – "… 1987), figure 11 illustrates this approach …"

Lines 329-331 – "it to a case for fine grained dislocation creep rheology that shows no grain size effect (dashed lines in fig. 11b), and the published flow laws for calcite (Schmid et al. 1980; Herwegh et al., 2003) fig. 11c). Regardless of which composite …"

Lines 333-336 – "when modelling crustal strength. Figure 11 also shows that the fine grained dislocation creep rheology predicts low strengths in the crust with depth."

Line 338 – "Using temperature and grain size measurements for mylonites …"

Line 339 – "… Figure 12 shows data from several thrusts of the Helvetic"

Lines 340-341 – "… Naxos (Herwegh et al., 2011) deformed at greenschist to amphibolite facies conditions. As before, the calcite-dolomite solvus …"

Line 353 – "… Using the same data as previously, figure …"

Line 355 – "… shear zones deform by a grain size sensitive …"

Line 359 – "… a shear zone would show more strength evolution …"

Line 367 – I'm a bit confused by the use of "grain size has a weakening effect". This would seem to state that larger grain sizes weaken the flow law, but I think you mean to state that fine-grain sizes (or larger grain boundary densities) weaken the flow law. Please revise. How about "grain boundaries have a weakening effect"?

Line 382 – "An. Important conclusion of this work is that …"

Line 385 – "If true, this calls into question the predictions of carbonate paleopiezometry for crustal strength. More importantly, these"

Lines 386-387 – "… also been shown that flow strength depends on iron concentration (Zhao et al., 2009-2018). …"

I look forward to seeing this paper in print,

Andreas Kronenberg