

## Comment and Reply on "Fluid-inclusion technique for determining maximum temperature in calcite and its comparison to the vitrinite reflectance geothermometer"

### COMMENT

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Barker and Goldstein (1990) proposed that homogenization temperatures ( $T_h$ ) of fluid inclusions in calcite provide a measure of the maximum temperature ( $T_{peak}$ ) and that  $T_h$  of inclusions in calcite can calibrate the relation between vitrinite reflectance ( $R_m$ ) and  $T_{peak}$ . They based these conclusions on the assumption that  $T_h$  "approaches"  $T_{peak}$  as a result of post-trapping reequilibration of the inclusions. Although we agree with the general conclusion reached by Barker and Goldstein (1990) that  $T_h$  of fluid inclusions from *some* geologic environments provides a reasonable approximation of  $T_{peak}$ , we question the choice of geologic environments used in their analysis. More than two-thirds of the data (53 out of 79  $T_h$ - $T_{peak}$  data pairs) used in their regression analysis is from terrestrial geothermal systems, yet they concluded that these data "demonstrate close agreement between  $T_h$  and present  $T_{peak}$  in sedimentary basins" (italics added). We believe the fact that most of their data are from geothermal systems strongly biases the relation between  $T_h$  and  $T_{peak}$ , making that relation in *sedimentary* carbonates more apparent than truly causal or "real." Furthermore, data and interpretations presented in Barker and Goldstein (1990) are not consistent with our current understanding of the reequilibration process.

Barker and Goldstein (1990) used data from two distinctly different geologic environments: terrestrial geothermal systems (and their fossil equivalents) and sedimentary basins. Inclusions in geothermal systems usually are trapped at temperatures not far removed from peak temperatures, as are inclusions in 35 out of 53 data sets listed in Barker and Goldstein (1990, Supplementary Data 9022) that are from geothermal systems. Additionally, numerous fluid-inclusion studies of geothermal systems have documented that inclusions are commonly trapped at or near the equilibrium vapor pressure—i.e., in a "boiling" system. Under these conditions, and *only* under these conditions, will the peak temperatures and homogenization temperatures of the inclusions be identical. Therefore,  $T_h$  of fluid inclusions from the geothermal environment is and should be equal to  $T_{peak}$ , and a regression analysis of these data should show a very good correlation between these two measurements, as Barker and Goldstein (1990) have shown.

If we remove the geothermal data from the regression analysis of Barker and Goldstein (1990), we can test the relation between  $T_h$  and  $T_{peak}$  in sedimentary basins. Data for sedimentary basins listed in Barker and Goldstein (1990, Supplementary Data 9022) for which  $T_{peak}$  and either  $T_{h\ mean}$  or  $T_{h\ mode}$  data are available are plotted in Figure 1 along with regression lines generated by simple linear regression of these data. In sedimentary basins, the relation between the mean homogenization temperature ( $T_{h\ mean}$ ) and the maximum temperature is given by  $T_{peak} = 24.7 + 0.868 T_{h\ mean}$  (sample size  $n = 23$ ; coefficient of correlation  $r = 0.717$ ). The similar relation between  $T_{h\ mode}$  and the maximum temperature is given by  $T_{peak} = 10.0 + 0.972 T_{h\ mode}$  (sample size  $n = 21$ ; coefficient of correlation  $r = 0.810$ ). The poorer correlation indicated by the correlation coefficients and by visual inspection of Figure 1 supports our assertion that the regression analyses of Barker and Goldstein (1990) are biased by the geothermal data. Our regression analyses, as well as plots

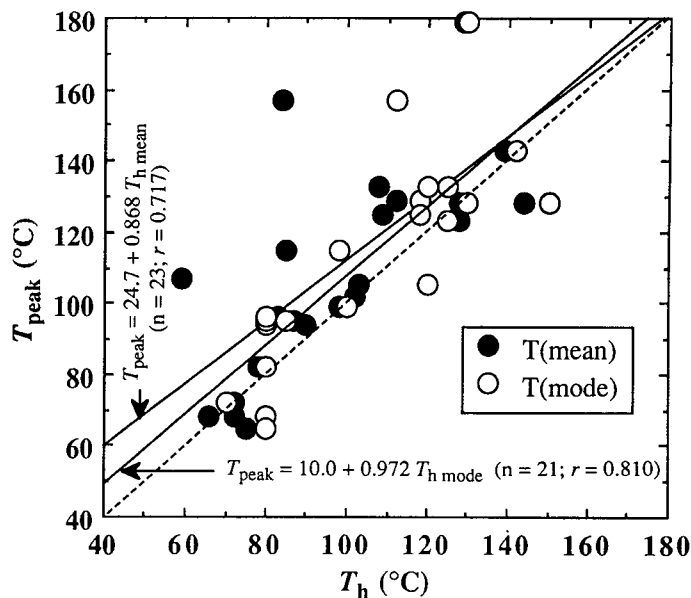


Figure 1. Relation between peak temperature and mean and modal homogenization temperatures of fluid inclusions from sedimentary basins. Dashed line represents perfect 1:1 correlation. Data are from Barker and Goldstein (1990, Supplementary Data 9022).

of  $T_{peak}$  vs.  $T_h$  (Fig. 1) clearly indicate that the agreement between these two parameters in *sedimentary basins* is much poorer than that suggested by Barker and Goldstein (1990).

Our second point concerns whether the data described by Barker and Goldstein (1990) represent inclusions that have reequilibrated at peak temperatures. Fluid inclusions in sediments reequilibrate when  $P_{int}$  exceeds  $P_{ext}$  during burial, as discussed by Burruss (1987). The reequilibration process will continue until  $P_{int}$  equals  $P_{ext}$  plus the strength of the mineral. Consider the homogenization temperatures of inclusions that have equilibrated to the extent that  $P_{int} = P_{ext}$ . If the confining pressure is greater than the equilibrium vapor pressure of the inclusion fluid (the inclusion is trapped in the one-phase fluid field), the homogenization temperature must be less than the reequilibration or peak temperature because of the positive slope of the fluid isochores in  $P$ - $T$  space. For a given fluid composition and temperature of reequilibration, the magnitude of the difference between  $T_h$  and  $T_{peak}$  will depend only on the amount by which the confining pressure exceeds the vapor pressure. However, if the confining pressure is the same as the equilibrium vapor pressure of the fluid in the inclusion, then the homogenization temperature and the reequilibration temperature will be identical. As discussed previously, this is, in fact, the case in most terrestrial geothermal systems and is the reason for the excellent correlation between  $T_h$  and  $T_{peak}$  in that environment.

If reequilibration occurs in the single-phase-fluid field,  $T_h$  can never be greater than  $T_{peak}$ . However, the maximum recorded homogenization temperature equals or exceeds  $T_{peak}$  in 20 out of 24 of the data sets from sedimentary basins listed in Barker and Goldstein (1990, Supplementary Data 9022; and see Barker and Goldstein, 1990, Fig. 2). Without having access to the individual samples and/or original data reported in Barker and Goldstein (1990, Supplementary Data 9022), we cannot explain why so many of the maximum homogenization temperatures exceed the peak

temperatures. It is obvious, however, that some significant part of the inclusion populations used to define the means and modes used by Barker and Goldstein (1990) cannot possibly represent reequilibration at peak temperatures. Specifically, homogenization temperatures of some part of the inclusions used to define the modes and means are known to be too high, and the means and modes calculated from these data must therefore be erroneously elevated. We conclude that the correlation between  $T_h$  and  $T_{peak}$  of carbonates from sedimentary basins is much poorer (Fig. 1) than that indicated by Barker and Goldstein (1990), and that reequilibration of the inclusions at peak temperatures and in a single-fluid-phase field cannot be invoked to explain any correlation that does exist between  $T_h$  and  $T_{peak}$ .

## REPLY

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We are pleased that the Comment by Bodnar and Burruss agrees with our general conclusions, but we are concerned that their statements may lead to misinterpretation of our 1990 paper.

Bodnar and Burruss suggest that sedimentary basins and geothermal systems should be treated differently. We discussed this in our paper and specifically suggested why the geothermal data could be expected to fit a 1:1 relation better than the lower temperature data from sedimentary basins. Additionally, their plot of our data from nongeothermal systems could be misinterpreted in relation to our work; it includes  $T_{h\text{ mean}}$  even though we proposed using  $T_{h\text{ mode}}$ . Their truncation of our  $T_{h\text{ mode}}$  data yielded the relation  $T_{peak} = 10.0 + 0.972 T_{h\text{ mode}}$  with a sample size of only 21; our full  $T_{h\text{ mode}}$  data set yielded  $T_{peak} = 12.1 + 0.965 T_{h\text{ mode}}$  with a sample size of 78. Thus, the high degree of similarity between the two relations clearly demonstrates the *absence* of the significant system-controlled bias that they suggest.

Bodnar and Burruss imply that we ascribed interpretive significance to the highest  $T_h$  data and that  $T_h$  data should not occur above  $T_{peak}$ . They do not allow for the known error in determining present  $T_{peak}$  (a factor we allowed for in our regression technique) and do not include the many factors that could result in a few erroneously high  $T_h$  data. Such problems are precisely why we attached no significance to the highest  $T_h$  measurements.

Bodnar and Burruss indicate that there is close agreement between the geothermal  $T_h$  data and  $T_{peak}$  because there is no need for a significant pressure correction for fluid inclusions trapped in boiling or near-boiling geothermal systems, and that large pressure corrections are needed in sedimentary basins. As we discussed (Barker and Goldstein, 1990), large amounts of methane and other gases can reduce the need for large pressure corrections for much sedimentary  $T_h$  data (Hanor, 1980), a factor Bodnar and Burruss do not include in their Comment. Thus, small pressure corrections may apply to sedimentary systems as well as the geothermal ones. Further, we did not use fluid-inclusion studies that had recorded evidence of boiling (Ellis and Mahon, 1977). Natural boiling may have occurred locally in these systems, but uniform vapor:liquid ratios and the characteristic homogenization to the liquid phase of these fluid inclusions do not suggest trapping during boiling (e.g., Browne, 1977; Freckman, 1978; Sterner, 1985). Moreover, most of our  $T_h$  mode data fall well below the boiling-point curve for fresh or hypersaline water (White, 1973; Fig. 1 here).

We cannot agree that our interpretations are not consistent with current understanding of fluid-inclusion reequilibration, or that we ever stated or implied that all  $T_h$  data resulted from reequilibration to  $T_{peak}$ . Many of the inclusion populations we reported have wide distributions or are polymodal over a wide range. This type of distribution is typical of

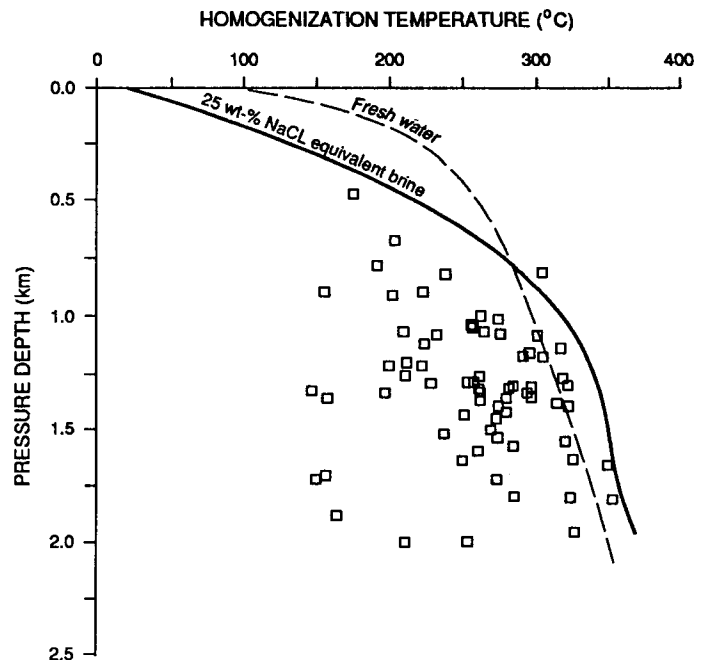


Figure 1. Plot of fluid-inclusion homogenization temperatures ( $T_{h\text{ mode}}$ ) measured in geothermal systems now at  $T_{peak}$  (Barker and Goldstein, 1990).

reequilibrated populations and populations entrapped over a range of temperatures. We noted many populations for which evidence pointed to initial fluid-inclusion entrapment well below  $T_{peak}$ , but in which the  $T_h$  upper mode closely matched the  $T_h$  of fluid inclusions formed at  $T_{peak}$  and closely approached  $T_{peak}$ . Therefore, we stand by our interpretation that *some* of the early fluid inclusions reequilibrate and *approach*  $T_{peak}$ .

In our paper, we showed that  $T_h$  mode *approaches*  $T_{peak}$ , and not that it is equal to it, as Bodnar and Burruss's Comment depicts. In spite of the excellent correlation in Barker and Goldstein (1990), we were careful to point out the weaknesses in estimating  $T_{peak}$  from  $T_h$  using such a statistical-empirical technique, and we reemphasize that careful studies integrating petrography and microthermometry should prove to be even more reliable.

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