Under the circumstances, we feel it is inadvisable to use $Na_2CO_3 \cdot CaCO_3$ as a standard for DTA, notwithstanding the excellent peaks obtained for the 1:1 compound.

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27 June 1972
M. Finch, R. M. McIntosh
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Dear Sir,

We certainly thank Finch and his co-workers for pointing out our error in describing sodium calcium carbonate ($Na_2CO_3 \cdot CaCO_3$) as a "previously unrecognized double carbonate"[1]. We took our inability to find earlier discussions of this compound as proof that they didn't exist. We apologize to our readers for any misconceptions caused by our failure to find this background information, which unfortunately is an extremely sparse collection for the 56-year span since Niggli[2] first reported the compound's existence.

In spite of the statement by Finch *et al.*, we feel that we made no other errors in our description of the thermal synthesis of sodium calcium carbonate and in our recommendation of it as a thermal analysis standard. The compound's decomposition temperature in CO_2 we stated only as "above 750°". At temperatures above this the sodium carbonates wreak havoc on sample holders. For purposes of our report we limited the temperatures investigated in detail to those significant to the solid-state formation of sodium calcium carbonate and to the detection and evaluation of its crystal transformations by DTA.

We neither neglected nor ignored the crystal transformations of Na_2CO_3 in studying the DTA-detected inversions of sodium calcium carbonate. Samples of Na_2CO_3 identical to the material we used to generate the double carbonate produce *no* DTA inversion responses from 390° to 450°, the temperature range where the double carbonate inversions occur. In addition, the Na_2CO_3 transformations appear to be at least an order of magnitude less energetic than those of the double carbonate.

The National Bureau of Standards DTA temperature standard materials were used to calibrate our reported temperatures. We may be wrong by 1°, but we certainly cannot be in error by 30° in reporting the temperatures of the double carbonate inversions. The Na_2CO_3 transformations definitely do not contribute to the four we report for the double carbonate.

The inability of Finch *et al.* to detect the four transformations "even on the most sensitive DTA setting" when heating the 1:1 molar Na_2CO_3–$CaCO_3$ mixture at 10° per minute merely points out that the double carbonate preparation is capable of serving as a DTA resolution standard. We also could detect only two inversions at this heating rate. Our apparatus resolved the two peaks into four at a heating rate of 5° per minute. Finch *et al.* are accepting their inability to resolve the four DTA peaks as proof that they don't exist.

In attempting to explain the source of the four DTA crystal inversion peaks we reported, Finch *et al.* call in a Na_2CO_3 peak which we have already shown should not be included, then credit two of the remaining DTA peaks to "incompletely reacted Na_2CO_3–$CaCO_3$ mixtures". We found that all four of the peaks we detected in such a mixture grew as the reaction progressed and appeared to remain in about the same size relationships. Because these peaks were completely reversible, appearing as exotherms on cooling and reappearing as endotherms on reheating, we concluded that these were four crystal transformations of sodium calcium carbonate. Our supposition appears more likely than theirs, but neither of us knows precisely what is occurring in the transformations. Because we were able to produce the DTA inversion signals routinely by heating the 1:1 molar mixture of Na_2CO_3 and $CaCO_3$, the DTA signals can still serve as standards, leaving the exact nature of the inversions for subsequent work.

Although Finch, McIntosh and Wilburn have objected to sodium calcium carbonate as a thermal analysis standard, their objections do not invalidate this use. We still recommend investigation of sodium calcium carbonate prepared by the solid-state reaction of the 1:1 molar mixture as a DTA standard both for temperature calibration and for testing resolution.

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