

# Cristobalite: The Hump

## New Data on Silica at Cone Ten

by Peter Sohngen

A wonderful machine, the dilatometer. You put a small sample of a material in it—your clay body, for instance—and it will heat it up, measure its expansion as the temperature increases, and record both temperature rise and expansion as these proceed. Such a device is, in the potter's frame of reference, a pretty fancy piece of technology, and awesomely expensive. Most of us have never heard of one, and, until recently, I had never known anyone who had access to one. But a few months ago I was introduced to a man who actually owns one: Ron Roy, a potter and ceramics consultant in Toronto, who very generously got interested in my questions and ran dilatometer tests for me at a very good rate. What I learned from these dilatometer tests is the subject of this article. It is about what happens when we add silica to a stoneware body, about the surprising appearance of cristobalite when we do so, and—perhaps more surprising—about why this may not be such a bad thing.

It has long been an assumption among stoneware potters that when you add fine ground quartz to your clay body you are adding—to the fired product—quartz rather than cristobalite. The argument, articulated most clearly in these pages by Jim Robinson in two landmark articles (*SP Vol.9, No.2 and Vol.16, No.2*), goes something like this:

When a typical body, comprised of clay, feldspar, and quartz, has been fired to cone 10 there will be three forms of silica in the product: quartz, cristobalite, and silica glass. There are three main sources of this silica: the ground quartz ingredient, the free silica that is a constituent of any clay, and, last but not least, the silica that appears when kaolinite breaks down into two new minerals, mullite and free silica.

An understanding of these processes is critical because they determine the thermal expansion of the clay body and thus the glaze fit and the body's resistance to thermal shock. (They affect strength, color, and absorption too, but it is thermal expansion that is my concern here.) Silica glass, which develops as the feldspar particles melt and incorporate silica from the surrounding material, has an extremely low thermal expansion, lower even than mullite; it is also a steady or "straight line" expansion, as might be expected from a non-crystalline (glass) material. The *crystalline* quartz, on the other hand, has a very high overall rate of thermal expansion. Furthermore, at 573°C this crystal structure expands (or contracts) abruptly. This "quartz inversion" occurs every time quartz is heated or cooled through 573°C.

Cristobalite, also a crystal, has an even higher overall rate of expansion, much higher than anything else that's likely to be in the body. And it has a pronounced inversion somewhere in the neighborhood of 200°C.

So, the argument continues, cristobalite is a bad thing. Its inversion temperature is well within the range of a kitchen oven, and therefore likely to be responsible for casserole failure; furthermore, it is clear that bodies high in cristobalite show dunting, shivering, and shattering. We put feldspar in our clay bodies to flux cristobalite; ideally we put enough in to flux all of it and eliminate it as a factor in the thermal expansion of the body. Having done this, we find that our glazes craze. We cure that problem by adding quartz. The particles of quartz sold as "200 mesh" or even "325" mesh are many thousands of times larger than the silica that results from mullitization, and much larger than the free silica in the clays as well; therefore, so the argument runs, it will not (for the most part) convert to cristobalite when fired to cone 10, but instead will remain quartz. Quartz inversion, which occurs at a temperature below the "set point" of stoneware glazes, will therefore put the glazes in some compression without, however, the hazards attendant upon the much lower inversion temperature of cristobalite.

Sound in reasoning though all this is – and I cannot imagine a better way to develop a good stoneware body than this – it involves a faulty premise. In a series of dilatometer tests, I believe I have ascertained that "325 mesh" quartz does in fact convert to cristobalite to a very significant extent at cone 10; and, furthermore, if it didn't it would not bring about the glaze fit that we are seeking when we add it to our stoneware bodies.

The first set of tests (Table 1) begins with clay constituents only, then feldspar is added; then, over the next five samples, 12% quartz is incorporated, the proportion remaining the same but the particle size decreasing from 80-100 mesh till "325 mesh" is reached.<sup>1</sup> As expected, the body comprised only of clay shows a terrific "cristobalite hump"<sup>2</sup> – the extremely steep part of the curve at lower left (Table 2). The rest of the curve is pretty steep too, and there is only a small quartz inversion indicated between 580°C and 600°C, suggesting that the greater part of the silica in this body converted to cristobalite when it was fired to cone 10. Potters know that this kind of body is a killer – that most glazes fired on it would shiver and shatter.

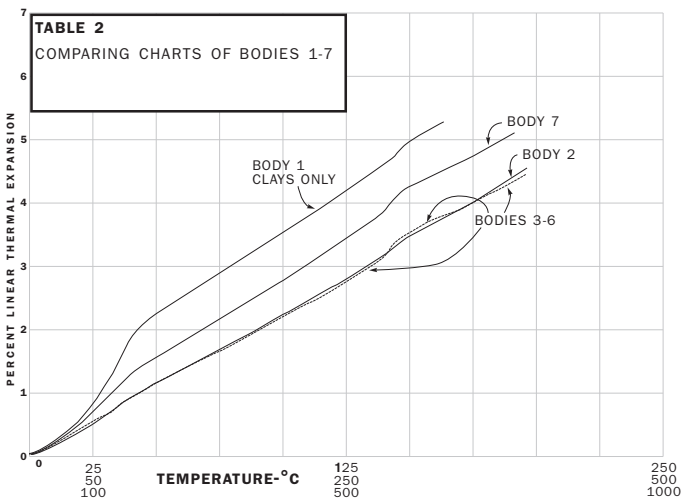
Body number 2, with the addition of 9.9% feldspar, also performs as expected on the dilatometer: the curve is tremendously flattened, the humps indicating inversions are almost wiped out, and the overall steepness of the curve is somewhat diminished. The melting feldspar has dissolved quite a bit of the silica, drawn it into the glass, where it has a much lower rate of expansion and does not go through inversion. Typical glazes will craze on such a body – mine do.



*Peter Sohngen, Icon.*

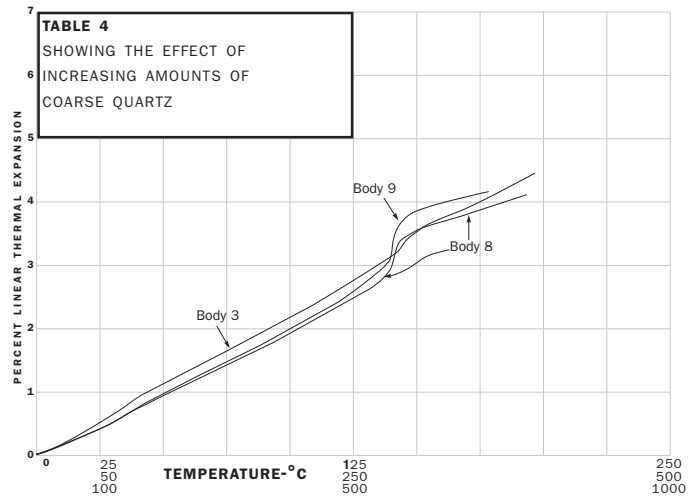
	1	2	3	4	5	6	7
HAWTHORNE BOND	75	67.6	59.5	59.5	59.5	59.5	59.5
OLD MINE #4	25	22.5	19.8	19.8	19.8	19.8	19.8
G 200 SPAR	0	9.9	8.7	8.7	8.7	8.7	8.7
80-100 MESH QUARTZ	0	0	11.9	0	0	0	0
100-150 MESH QUARTZ	0	0	0	11.9	0	0	0
150-200 MESH QUARTZ	0	0	0	0	11.9	0	0
200-270 MESH QUARTZ	0	0	0	0	0	11.9	0
"325 MESH" QUARTZ	0	0	0	0	0	0	11.9

From this point on, results were not so predictable. When 12% coarse quartz was included in the body (the proportions of the other ingredients remaining constant, of course), sized 80-100 mesh, there was a pronounced increase in the quartz inversion hump, and no change in the cristobalite. As the particle size of this quartz addition got smaller and smaller, there were no changes in this pattern, so there is only one line on Table 2 to represent bodies 3 through 6. Then suddenly in body 7, when the particle size gets down below 325 mesh – that is, when the quartz addition is the particle size potters might use – we see a sudden transformation. Cristobalite reappears dramatically – there is a 40% increase in the rate of expansion below 200°C, and the curve is steeper throughout as well, in keeping with the increase in cristobalite.



The dilatometer charts collated in Table 2, I believe, bear out the first half of my contention: that "325 mesh" quartz does convert to cristobalite to a large extent at cone 10. For the other half – the idea that we actually need a bit of this cristobalite for glaze fit – glazes were applied to the bodies in Table 1. Most typical was a celadon glaze I have used for many years on dinnerware. It shivered on body 1, as expected.

	3	8	9
HAWTHORNE	59.5	48.1	40.3
OM4	19.8	16.0	13.4
G 200 SPAR	8.7	7.1	5.9
80-100 MESH QUARTZ	11.9	28.8	40.3



On body 2 it crazed, also unsurprisingly. But on bodies 3 through 6, where there is a generous quartz inversion hump, the glaze continued to craze, and the density of the crazing remained undiminished from body 2 through 6. It is only on body 7 that the glaze fits.

But what if we go back to the coarse quartz, and increase it till we get enough quartz inversion to achieve glaze fit? The next set was designed to answer this question. The three bodies in Table 3 keep the clays and feldspar in a constant ratio to each other and increase the coarse quartz. Table 4 compares their dilatometer charts. As anticipated, the quartz inversion hump gets more and more pronounced. Nevertheless, *the glazes continue to craze*. The *density* of the crazing does drop off, especially between 8 and 9, indicating that this radical increase in the quartz inversion is having some effect; but we are now up to 40% quartz – not practical, I think.

The reason for this apparent anomaly becomes clear if we compare body 7, where glazes do fit, with body 9 (Table 5). Even though body 9 has such a large quartz hump, its overall contraction from some assumed set point of the glaze – say, 650°C – is much less than that of body 7.

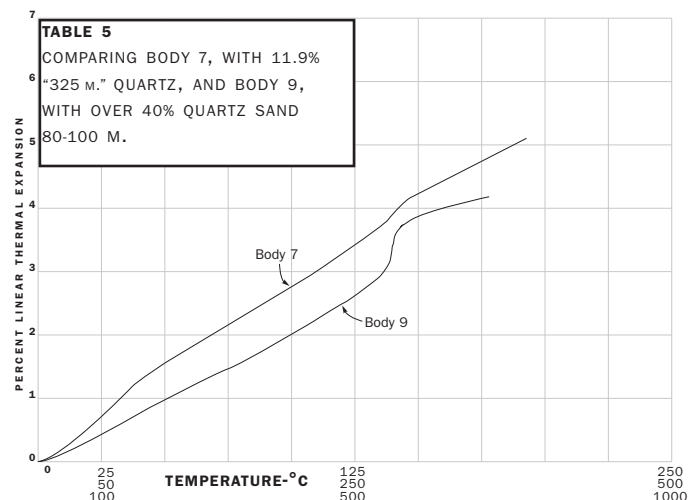
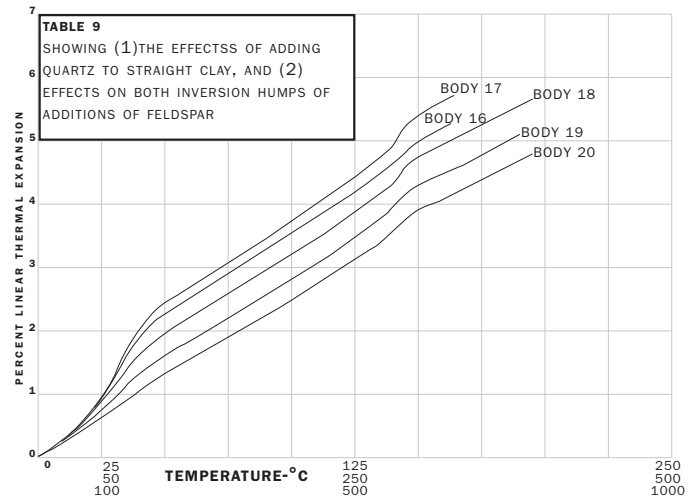


TABLE 6 STONEWARE BODIES WITH NO ADDED QUARTZ, WITH ADDITIONS OF FELDSPAR						
	10	11	12	13	14	15
HAWTHORNE	72.8	71.8	70.8	69.8	68.8	67.6
OM4	24.3	23.9	23.6	23.3	22.9	22.5
G-200 SPAR	2.9	4.3	5.7	7.0	8.3	9.9

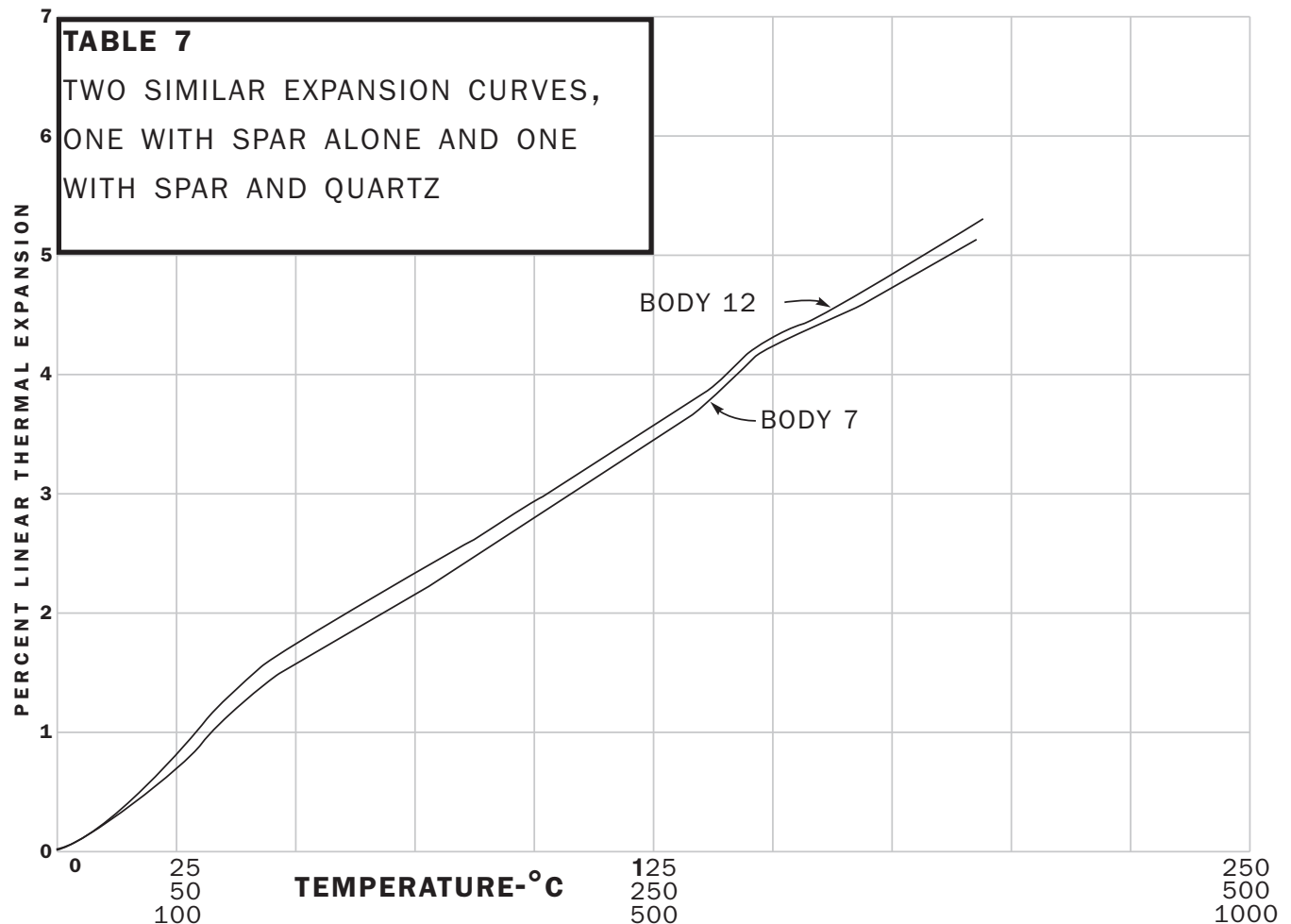
TABLE 8 CLAY ALONE, THEN CLAY PLUS QUARTZ, THEN THE LATTER WITH INCREMENTS OF FELDSPAR				
	16	17	18	20
HAWTHORNE	75	65.2	61.5	59.5
OM4	25	21.7	20.5	19.8
"325 MESH" QUARTZ	0	13	12.3	11.9
G-200 SPAR	0	0	5.7	8.7

Body 9 not only lacks the cristobalite inversion almost completely, its contraction rate above and below quartz inversion is much lower than that of body 7 – too low for most glazes to fit.

The question immediately arises, why add quartz at all? If we've been adding spar to eliminate cristobalite, and then getting cristobalite back when we add quartz to cure crazing, why not just cut back on the spar until crazing stops? The next set of tests was designed to answer that question. All the bodies in Table 6 were run on the dilatometer, and each chart was compared with the chart for body 7 to see which most closely matched. Body 12, with



5.7% spar and no added quartz, comes very close; the glazes fit it, and it would surely be a serviceable body. As Table 7 shows, however, it is not quite as good: for virtually the same overall contraction from 650°C down it depends somewhat more on cristobalite inversion, and less on quartz inversion or the gradient between the two – in other



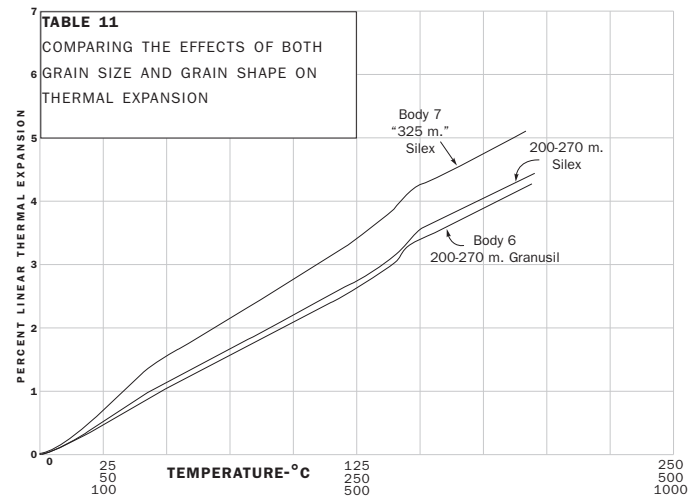
GRANUSIL 7020		NICKS NS-86 "200 MESH"	
3.5%	+50M		
11.5	+70		
40.6	+100		
34.9	+140	.3%	
8.5	+200	1.7	
1.0	+270	—	
	+325	12.0	
	-325	86.0	

words, glaze fit is achieved more by the sudden cristobalite squeeze at the very end of the cooling cycle and less by means of the more gradual contraction above it.

The similarity of the two dilatometer curves might suggest that one method of adjusting thermal expansion is as good as the other, and one might choose between them for reasons not related to thermal expansion. The choice to use feldspar alone to achieve glaze fit might be based on a need to have a smaller proportion of non-plastic material, the other has 20.6%, a difference that might well affect the throwing properties of a clay body. Lower spar might mean warmer color and even less warping. On the other hand, some potters need a body that is watertight when left unglazed, and in most cases 6% spar is not nearly enough for that. Others may simply opt for the marginally stronger and thermally more reliable body that spar and quartz together give.

The next set of tests (Table 8) was designed to answer two questions. I wanted to make sure that adding quartz to the clay body *before* the feldspar is put in results in the same increase in cristobalite – that is, make sure that the surprising appearance of cristobalite in body 7 is not the result of some interaction between feldspar and quartz. Secondly, once both cristobalite and quartz are present in a clay-quartz body I wanted to ascertain whether, when feldspar is added, it has more effect on cristobalite or on quartz. Table 9 shows the results. A comparison of bodies 16 and 17 clearly demonstrates once again that adding fine quartz results in a significant increase in cristobalite. Then when feldspar is added, roughly 6%, 9% and 11%, both the inversion humps are progressively flattened, and clearly cristobalite more so. This is welcome news. Does it suggest that, with further increases of both fine quartz and feldspar, we might get both less cristobalite and more quartz? Probably. Does it mean that we might get glazes to fit without any cristobalite? Perhaps not: note in Table 4 how the quartz increases enormously but the slope of the curve below quartz inversion hardly gets steeper at all. Cristobalite is needed, with it higher overall thermal expansion, to defeat crazing here.

To recapitulate: along with everyone else, I had long assumed that, when fine quartz was added to a cone 10 stoneware body, virtually none of it would convert to

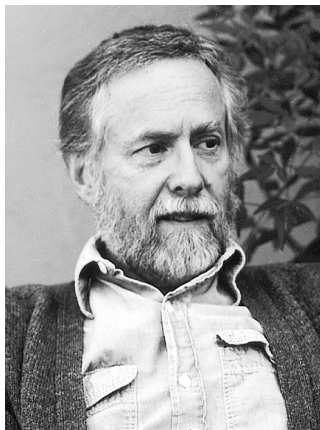


cristobalite. I was very surprised when the dilatometer tests showed that a significant proportion of it does, and even more surprised when glaze fit tests indicated that some of this cristobalite was necessary to prevent crazing, at least below reasonable levels of the spar and quartz addition.

Several other facts emerged from the dilatometer tests. First, coarser quartz – anything bigger than 270 mesh, which is almost impalpable between finger and thumb – seems *not* to convert to cristobalite, *does* contribute a generous quartz inversion, and (very important for glaze fit) does not increase the thermal expansion slope below quartz inversion. This is why adding quartz sand to a clay body doesn't cure crazing, even in very high amounts. Secondly, increases in feldspar seem to diminish cristobalite more than quartz, so that (presumably) both feldspar and quartz can be ratcheted up until glaze fit is attained with no appearance of cristobalite inversion. Ron Roy has sent me a dilatometer chart of his porcelain body, which of course has much larger amounts of spar and quartz in the recipe, and the chart shows no cristobalite and a generous quartz inversion hump, plus a sufficiently steep slope between for glaze fit. But proportions of spar and quartz like this – totaling something like 50% of the body – are clearly not practical for the stoneware potter.

What *is* practical is to consider a balance, not simply of spar and quartz, but of spar, fine quartz, and coarse quartz. The coarse material might be 40-80 mesh if texture and tooth are desired, or finer, perhaps actual 150-200 mesh (again, it must be emphasized, that what is commonly sold as "200 mesh silica" might be 75% or 85% finer than 325 mesh). Table 10 shows the particle size distribution of samples of two grades of quartz that my suppliers carry. I use both: Granusil 7020 in place of grog, because it works like grog and because it provides a little boost to quartz inversion, and "200 mesh" to complete glaze fit; I have already cut back the feldspar to about 6%. The result is a sound clay body with good glaze fit with only half the amount of non-plastic material the body formerly contained.

Dilatometers are not casseroles. The reliability of functional pots under thermal strain rests not only on the thermal expansion characteristics of the body but on many other factors as well: porosity, elasticity, the nature of the grog materials, the shape of the pot, and of course glaze fit. But the dilatometer can tell us a lot that we can't find out any other way. It can tell us not only how much expansion our pots are going through, but at what temperatures it occurs and what's making it occur. Relatively little is known about the effects on thermal expansion of a number of other possible clay body ingredients, and it would be fascinating and very practical to know, for instance, how the various grog materials compare in this regard: raw kyanite, calcined kyanite ("mullite"), pyrophyllite, brick grog, and some unusual things like zircon sand and molochite. Questions proliferate: What happens to thermal expansion when you add a little red earthenware clay to a cone 10 body? How



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does that compare to straight iron oxide? What if you substitute nepheline syenite for feldspar? What might a small addition of wollastonite do? Whether you are fine-tuning a casserole body or developing a really tough raku body, such questions—sometimes vital, always interesting—are just what the dilatometer was made for. This machine deserves to get a lot more use by potters in the future.<sup>3</sup>

#### FOOTNOTES

1. Please note: in samples 3 through 6 the particle size range of the quartz is as stated. Starting with Unimin's "Granusil 7010" I washed the material through the screens specified so that all of a stated size passed the larger screen and virtually none would pass the smaller. In sample 7, however, I used Unimin's "325 mesh Silex;" all I know about that is that 96.6% of it is said to be smaller than 325 mesh. Hence the quotation marks.

The alert reader will have wondered whether Granusil and Silex are, except for their sizes, the same. Mineralogically and chemically they are, for our purposes, identical: both are quartz; Granusil is 99.669% SiO<sub>2</sub>, Silex is 99.623%; the trace impurities tally very closely. Granusil is not ground, however, Silex is. In order to make sure that the different particle shape of the two kinds of quartz was not responsible for the change in thermal behavior between samples 6 and 7, I prepared a sample with 12% Silex which I had graded 200-270 mesh, by washing a coarser grind of Silex through screens. Comparing the charts for 200-270 mesh Silex (ground) and the same size Granusil (not ground) we do indeed find a difference (Table 11): the Silex example shows slightly larger humps for both quartz and cristobalite. Though very small, the differences are definitely there. When the 200-270 mesh Silex sample, however, is compared to the "325 mesh" Silex the difference is much greater. Something major takes place when the quartz is ground this fine: the cristobalite hump gets roughly 40% bigger, and the slope above cristobalite inversion gets significantly steeper.

2. Cristobalite inversion is thought to occur between 180°C and 260°C. The dilatometer charts presented here all show this inversion as completed by 200°C. This may be due to the complex mineral nature of a fired clay body, or the inherent bias of K-type thermocouples at low temperatures.

3. I am deeply grateful for a grant from the Memphis College of Art Faculty Enrichment Fund, which made this research possible.

I also owe a great deal of gratitude to Ron Roy and Frank Tucker of Tucker's Pottery Supplies in Toronto for their generosity with the dilatometer and with advice and encouragement. Ron can be reached at (416) 439-2621, e-mail at ronroy@total.net.

We all owe Jim Robinson of Phoenix, Oregon a tremendous debt for his clear thinking and inspiration. My effort here is merely a footnote to Jim's groundbreaking article in *STUDIO POTTER* ten years ago.