Here's a table of all the math alphabets defined in the unicode-math package showing the font and Unicode character that is used by default. In each case we try to typset the characters 'a á A α Δ '. As expected, the 'á' only shows up inside text fonts. Lowercase greek letters are affected where it makes sense, unlike the default behaviour when using traditional TFX fonts.

As per the documentation, most of the \sym macros map to the Mathematical Alphanumeric Symbols Unicode block in the designated "math" font (STIX Two Math in this case). Most of the \math macros are equivalent to the corresponding \sym macros, except for \mathbf, \mathit, \mathsf, and \mathtt, which map to "text" fonts, as shown. These can be configured to be equivalent to the corresponding \sym macros; the \mathtext macros always map to text fonts.

	\symXXX			\mathXXX			\mathtextXXX
rm	aΑαΔ	Math	U+0061	aáAα⊿			aáAαΔ
up	$aA\alpha\Delta$	Math	U+0061	aáAα⊿			
bbit	$aA\alpha\Delta$	Math	U+1D44E	$aA\alpha\Delta$			
bb	aA $lpha\Delta$	Math	U+1D552	aA $lpha\Delta$			
bfcal	$a\mathcal{A}\alpha\Delta$	Math	U+1D44E	$a\mathcal{A}\alpha\Delta$			
bffrak	a 21 $\alpha\Delta$	Math	U+1D586	a $\mathfrak{A} \alpha \Delta$			
bfit	$aA\alpha\Delta$	Math	U+1D482	$aA\alpha\Delta$			
bfscr	$\boldsymbol{a} \mathcal{A} \alpha \Delta$	Math	U+1D4EA	$\boldsymbol{a} \mathcal{A} \alpha \Delta$			
bfsfit	αΑαΔ	Math	U+1D656	αΑαΔ			
bfsfup	aΑαΔ	Math	U+1D5EE	aΑαΔ			
bfsf	aΑαΔ	Math	U+1D5EE	aΑαΔ			
bfup	$aA\alpha\Delta$	Math	U+1D41A	$aA\alpha\Delta$			
bf	$aA\alpha\Delta$	Math	U+1D41A	aáA?	Text	U+0061	aáA??
cal	$a\mathcal{A}\alpha\Delta$	Math	U+1D44E	$a\mathcal{A}\alpha\Delta$			
frak	$\mathfrak{a}\mathfrak{A}\alpha\Delta$	Math	U+1D51E	$\mathfrak{a}\mathfrak{A}\alpha\Delta$			
it	$aA\alpha\Delta$	Math	U+1D44E	aáA???	Text	U+0061	aáA???
normal	$aA\alpha\Delta$	Math	U+1D44E	$aA\alpha\Delta$			
scr	$a\mathcal{A}\alpha\Delta$	Math	U+1D4B6	$a\mathcal{A}\alpha\Delta$			
sfit	$aAlpha\Delta$	Math	U+1D622	$aAlpha\Delta$			
sfup	aA $lpha\Delta$	Math	U+1D5BA	aA $lpha\Delta$			
sf	aA $lpha\Delta$	Math	U+1D5BA	aA	cmss	U+0061	aA
tt	aA $lpha\Delta$	Math	U+1D68A	aA	cmtt	U+0061	aA

By default, \mathbf and \mathit use cmbx and cmit, respectively. For this document I've redefined them to use STIX Two Bold and STIX Two Italic. The important point is that they use the "text" encodings rather than the Mathematical Alphanumeric Symbols.

The fact that the two greek letters don't show up in \mathtextbf and \mathtextit is an artifact of the way these characters are implemented in Computer Modern; it's not immediately clear to me how easy it would be to fix that, but it's also not important.

Not shown: \symliteral , which I believe is functionally equivalent to \symrm but doesn't have a $\mbox{math partner}$.