Numbers 11
Exodus 32
Numbers 25
Numbers 21
Numbers 14
Instead of a 1, 2, 3, 4, 5 order, Paul refers to these classes of sins in a 2, 1, 5, 4, 3 order.

Why does he do this? Is this simply a random list of sins? Or does Paul have some rationale, some purpose in referring to them in this way?

I would like to suggest that he follows a logical or idea-association order, rather than a simple random order. And I would further suggest that Paul employs a line of thought something like the following:
(1) The Israelites vividly remembered the appetizing foods in Egypt, and they longed to return to them.
(2) Having become dissatisfied with God's provision for their physical needs (i.e., the manna that God gave them), they turned to His provision for their spiritual or religious needs, and found it unsatisfying; thus they turned to worship of idols.
(3) Having turned to idolatry, thereby disobeying God's commandment in the first table of the Ten Commandments, they made idols of strange women and

