The historian Thucydides —who had as much disdain for the mob as any other Greek intellectual — details many instances of the Assembly's irrationality during the war with Sparta. The most ruinous was the Sicilian expedition. In 416 b.c., the Assembly voted to conquer Sicily, perhaps to disrupt Spartan trade with the west, even though the Athenians had no idea of the size of the island or the scope of the operation. The general Nicias, who had opposed the invasion and only reluctantly agreed to it, was chosen to lead it. After arriving in Sicily, his co-general Alcibiades—who had promoted the expedition —got word of his impending prosecution in Athens for religious crimes. This was the so-called Profanation of the Mysteries in 415 b.c., when rumors swept Athens that Alcibiades and his friends had mocked the sacred Eleusinian mysteries. The religious nature of the allegations made it likely that the Assembly would usurp the courts and try him directly, a situation that could result in his swift execution. He fled rather than face the charges. According to Thucydides, when Nicias's military situation in Sicily became hopeless he refused to retreat, citing fear of retribution by the Assembly for cowardice.

As a victim of such conflict one could name the democratic leader Ephialtes, an associate of Pericles, who was assassinated. But his killing was an anomaly—the only political assassination of which we know from fifth-century Athens prior to the end of the Peloponnesian War.

Aristotle claims that Solon gave power to the demos.

In 429 b.c., the Athenian navy subdued Mytilene; the Assembly voted to kill all the men and sell the women and children into slavery. A ship was dispatched with the order —but the next day the Assembly repented and sent a ship to reverse the order. (The ship arrived in time).

In the end, the Athenians suffered perhaps the worst per-capita military defeat in history —and they blamed their leaders, "as if they had not voted for it themselves."

In his famous evaluation of political affairs after the death of Pericles in 429, Thucydides wrote that what was nominally a democracy was in fact the rule of one; Pericles had controlled the Assembly through sound leadership: "he led it rather than being led by it." Because Thucydides accepted the Greek idea that politics was primarily a matter of "who shall rule," he failed to see that if the limits to the actions of a political institution are found not in law but in a leader's ability to restrain that institution, then the government is not one of laws but of men. After Pericles died, he was followed by populists who took advantage of the Assembly's authority by appealing to the emotions of the crowd. The stage was set for the Assembly to disregard the limits of the law, and to demand the right to act as it desired because it desired to do so. One of the results was the defeat in Sicily.

In 411 b.c., an oligarchic faction, opposed to the excesses of the democracy, developed proposals to permanently reduce the power of the Assembly. To pass these measures, the oligarchs first had to limit participation to wealthy citizens, who would be amenable to the oligarchic proposals. The oligarchs convened the Assembly at Colonus, outside the walls of Athens. Sparta had a fort on Athenian soil, and the military danger limited participation in the Assembly to citizens able to afford armor. Meanwhile the Athenian navy, along with thousands of rowers, was at Samos in the Aegean Sea; this further weakened the democratic voices in Athens. The oligarchs proposed nothing less than to do away with the Assembly and to establish a Council of 400 as the ruling authority in Athens.